Design of Plastic Optical Fiber for Home Network

March 2010

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March 2010

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Engineering



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Acknowledgements

My heartfelt appreciation goes first and foremost to my advisor, Professor Yasuhiro Koike, for supporting my research in every way a student could want. His extensive experience of the field of photonics polymer has been a tremendous resource and made enormous contributions to this thesis. He is, moreover, an honorable man, and it has been a big pleasure and a privilege to work under his guidance. I hope that some day I may be able to create the future on the same stage with him.

I would like to acknowledge the counseling committee members for my Ph.D. thesis under Professors Kouichi Asakura, Naoaki Yamanaka, and Eisuke Nihei for their valuable comments, advices and taking time to review the dissertation.

I am especially indebted to Professor Yoshi Okamoto for encouraging me over the last five years. He provided me an opportunity to study in Polytechnic Institute of NYU and broadened my mind in polymer chemistry. I have learned from him a way of life as a researcher and how to make things enjoyable and exciting. Along with that, I have received much guidance from Dr. Frantisek Mikes for teaching me the basics and appeals of organic chemistry.

I am grateful to group leaders of Koike Photonics Polymer Project/JST, Dr. Akihiro Tagaya and Mr. Satoshi Takahashi who all have open door policies and always answered my questions.

I must express my gratitude to many graduate and undergraduate students, who have sharpened my comprehension of a copolymer of methyl methacrylate and pentafluorophenyl methacrylate; to Mr. Takahiro Kado for preparing and characterizing the copolymeric optical fiber; to Mr. Zen Satoh for studying the water absorption and birefringence; to Mr. Toshimitsu Araki for clarifying the intrinsic scattering loss. Without them, this dissertation surely would not have been possible. I take this opportunity to wish all members of Koike group continued good luck and good fortune in their careers.

Finally, I give deep thanks to my family for their constant moral and financial support during the last eight years.

March, 2010 Kotaro Koike This thesis is dedicated to the many wonderful graduate and undergraduate students who carried out research in Koike laboratory, and to the developers of plastic optical fiber across Japan and around the world.

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List of Symbols

BEN	benzyl benzoate
BHT	dibutylhydroxytoluene
BPO	benzoyl peroxide
BzMA	benzyl methacrylate
CDCl ₃	chloroform-d
CHCl ₃	chloroform
CH_2Cl_2	dichloromethane
СҮТОР	poly(perfluoro(butenyl vinyl ether))
DD	direct diffusion
DLS	dynamic light scattering
DPS	diphenyl sulfide
DSC	differential scanning calorimetry
FTTH	fiber to the home
FWMH	full width half maximum
Gbps	gigabit per second
GC	gas chromatography
GeO ₂	germanium oxide
GI	graded index
GOF	glass optical fiber
GPC	gel permeation chromatography
H_2SO_4	sulfuric acid
IR	infrared region
LAN	local area network
LD	leaser diode
LED	light emitting diode
MCA	methyl α -chloro acrylate
MeOH	methanol
$MgSO_4$	magnesium sulfate
MMA	methyl methacrylate
MMF	multimode fiber
MOST	media oriented system transport
NA	numerical aperture

NaOH	sodium hydroxide
<i>n</i> -BM	<i>n</i> -butyl mercaptan
NFP	near field pattern
<i>n</i> -LM	<i>n</i> -lauryl mercaptan
NMR	nuclear magnetic resonance
OFL	overfilled launch
PBD (TBPO)	di-tert-butyl peroxide
РВО	tert-butyl peroxy-2-ethylhexanoate
PC	poly(carbonate)
PF	perfluorinated
PFPh	pentafluorophenol
PFPMA	pentafluorophenyl methacrylate
PLC	power line communication
PMA	phenyl methacrylate
PMMA-d ₈	perdeuterated methyl methacrylate
POF	plastic optical fiber
PS	poly(styrene)
PTFE	polytetrafluoroethylen
RI	refractive index
RML	restricted mode launch
rpm	revolutions per minute
SEC	size-exclusion chromatography
SI	step index
SiO ₂	silica dioxide
SMF	single mode fiber
TCEMA	2,2,2-trichloroethyl methacrylate
TFEMA	2,2,2-trifluoroethyl methacrylate
TG	thermogravimetric
UTP	unshielded twisted pair
UV	ultra violet
VB	vinyl benzoate
VCSEL	vertical-cavity surface-emitting laser
VPAc	vinyl phenylacetate
WKB	Wentzel-Kramers-Brillouin

Chapter 1 Introduction

1.1 The Master of Light

Last year's (2009) Nobel Prize in Physics was awarded for two scientific achievements that have helped to shape the foundations of today's networked societies ^[1]. They have created many practical innovations for everyday life and provided new tools for scientific exploration.

In 1966, Charles K. Kao made a discovery that led to a breakthrough in fiber optics. He carefully calculated how to transmit light over long distances via optical glass fibers. With a fiber of purest glass it would be possible to transmit light signals over 100 kilometers, compared to only 20 meters for the fibers available in the 1960s. Kao's enthusiasm inspired other researchers to share his vision of the future potential of fiber optics. The first ultrapure fiber was successfully fabricated just four years later, in 1970^[2, 3].

Today optical fibers make up the circulatory system that nourishes our communication society. These low-loss glass fibers facilitate global broadband communication such as the Internet. Light flows in thin threads of glass, and it carries almost all of the telephony and data traffic in each and every direction. Text, music, images and video can be transferred around the globe in a split second. If we were to unravel all of the glass fibers that wind around the globe, we would get a single thread over one billion kilometers long—which is enough to encircle the globe more than 25,000 times—and is increasing by thousands of kilometers every hour.

1.2 Fundamentals of Fiber Optics1.2.1 Origin of Fiber Communications

The idea of communicating by light probably goes back to signal fires on prehistoric hilltops. The ancient Greeks relayed news of the fall of Troy by signal fires; Native Americans used smoke signals. Even the first "telegraph" was an optical one, invented by French engineer Glaude Chappe in 1790s. Operators relayed signals from one hilltop telegraph tower to the next by moving semaphore arms. Samuel Morse's electric telegraph put the optical telegraph out of business, but it left behind countless Telegraph Hills.

In 1880, a young scientist who had already earned an international reputation used beams of light to transmit voices in the first wireless telephone. Alexander Graham Bell had invented the telephone four years earlier, but he considered the photophone his greatest invention. It reproduced voices by detecting variations in the amount of sunlight or artificial light focused through the open air onto a receiver. Bell was elated to hear beams of light laugh and sing, but the Photophone never proved practical in cities, where too many things could get in the way of the light. Wires and radio waves proved more practical for communications.

A few people kept experimenting with optical communications. In the 1930s, an engineer named Norman R. French—who worked for the American Telephone & Telegraph Corp. built around Bell's telephone—patented the idea of communicating by sending light through pipes. But few people took optical communications seriously until Theodore Maiman demonstrated the first laser in 1960.

The laser generates a tightly focused beam of coherent light at a single pure wavelength. It's the optical equivalent of the pure carrier-frequency signal used by a radio or television station. That made it look very promising for communications, and many laboratories started experimenting. They first tried sending lased beams through air, but like Bell soon found that open air was not a very good transmission medium because fog, rain, snow, and haze could block signals. They tried sending light through more modern versions of Wheeler's light pipes and found other troubles.

Optical fibers were available, but they didn't look very promising. The fibers used in endoscopes are much clearer than window glass, but half the light that enters them is lost after 3 meters. That's fine for examining the stomach, but not for communications. Go through a mere 20 meters of such fiber, and only 1% of the light remains. Go another 20 meters, and only 1% of that light remains—0.01% of the input. Convinced that transparent solids inevitably absorbed too much light for optical communications, most engineers either gave up or tried to develop new versions of hollow light pipes or better ways to send light through the air.

Two young engineers at Standard Telecommunication Laboratories in England, Charles K. Kao

and George Hockham, took a different approach. Instead of asking how clear the best fiber was, Kao asked what the fundamental limit on loss in glass was. He and Hockham concluded that the loss was caused mostly by impurities, not by the glass itself. In 1966, they predicted that highly purified glass should be so clear that 10% of the light would remain after passing through at least 500 meters of fiber. Their prediction sounded fantastic to many people then, but it proved too conservative.

Publication of Kao and Hockham's paper set off a worldwide race to make better fibers. The first to beat the theoretical prediction were Robert Maurer, Donald Keck, and Peter Schultz at the Corning Glass Works (now Corning Inc.) in 1970. Others soon followed, and losses were pushed down to even lower levels. In today's best optical fibers, 10% of entering light remains after the light has passed through more than 50 kilometers of fiber. Losses are not quite that low in practical telecommunication systems, but impressive progress has been made. Because of that progress, fiber optics have become the backbone of long-distance telephone networks around the world.

1.2.2 Basic Fiber Concept

The two key elements of an optical fiber—from an optical standpoint—are its core and cladding. The core is the inner part of the fiber, which guides light. The cladding surrounds it completely. The refractive index of the core is higher than that of the cladding, so light in the core that strikes the boundary with the cladding at a glancing angle is confined in the core by total internal reflection, as shown in **Figure 1.1**.

The difference in refractive index between core and cladding need not be large. In practice, it is only about 1%. This still allows light guiding in fibers. For $n_1/n_0 = 0.99$, the critical angle θ_c is about 82°. Here, n_0 is the refractive index of the core and n_1 is the index of the cladding. Thus, light is confined in the core if it strikes the interface with the cladding at an angle of 8° or less to the surface. The upper limit can be considered the confinement angle in the fiber.



Figure 1.1 Light guiding in an optical fiber.

Another way to look at light guiding in a fiber is to measure the fiber's acceptance angle—the angle over which light rays entering the fiber will be guided along its core, shown in **Figure 1.2**. (Because the acceptance angle is measured in air outside the fiber, it differs from the confinement angle in the glass.) The acceptance angle normally is measured as numerical aperture (NA), which for light entering a fiber from air is approximately

$$NA = \sqrt{\left(n_0^2 - n_1^2\right)}.$$
 (1-1)

For a fiber with core index of 1.50 and cladding index of 1.485 (a 1% difference), NA = 0.21. An

alternative but equivalent definition is the sine of the half-angle over which the fiber can accept light rays, 12° in this example (θ in **Figure 1.2**). Another alternative definition is $NA = n_0 \sin \theta_c$, where θ_c is the confinement angle in the fiber core (8° in this example). These angles are measured from a line drawn through the center of the core, called the fiber axis.



Figure 1.2 Measuring the acceptance angle.

1.2.3 Classification of Optical Fibers

Optical fibers are not all alike. There are several different types, made for different applications, which guide light in subtly different ways. This section describes the basic concepts behind the various types of fibers. In the previous section, how the total internal reflection of light rays can guide light along optical fibers was described. This simple concept is a useful approximation of light guiding in many types of fiber, but it is not the whole story. The physics of light guiding is considerably more complex, because a fiber is really a waveguide and light is really an electromagnetic wave with frequency in the optical range.

Like other waveguides, an optical fiber guides waves in distinct patterns called modes, which describe the distribution of light energy across the waveguide. The precise patterns depend on the wavelength of light transmitted and on the variation in refractive index that shapes the core, which can be much more complex than the simple, single cores described in the above section. In essence, these variations in refractive index create boundary conditions that shape how electromagnetic waves travel through the waveguide, like the walls of a tunnel affect how sounds echo inside.

It's possible to calculate the nature of these transmission modes, but it takes a solid understanding of advanced calculus and differential equations, which is far beyond the scope of this dissertation. Instead, we'll look the characteristics of transmission modes, which are important in fiber-optic systems. By far the most important is the number of modes the fiber transmits. Fibers with small cores can transmit light in only a single mode. It can be hard to get the light into the fiber, but once it's inside, the light behaves very uniformly. It's easier to get light into fibers with larger cores that can support many modes, but light does not behave the same way in all the modes, which can complicate light transmission, as we will see later in this section.

Single-Mode Fiber

The basic requirement for single-mode fiber is that the core be small enough to restrict transmission to a single mode. This lowest-order mode can propagate in all fibers with smaller cores (as long as light can physically enter the fiber). Because single-mode transmission avoids modal dispersion, modal noise, and other effects that come with multimode transmission, single-mode fibers can carry signals at much higher speeds than multimode fibers. They are the standard choice for virtually all kinds of telecommunications that involve high data rates or span distances longer than a couple of kilometers, and are often used a slower speeds and shorter distances as well.

The simplest type of single-mode fiber, often called standard single mode, has a step-index

profile, with an abrupt boundary separating a high-index core and a lower-index cladding. The refractive index differential is 0.36% for a widely used fiber, and is well under 1% in other standard types. The simplest design is the matched-cladding fiber. The cladding is pure fused silica; germanium oxide (GeO₂) is added to the core to increase its refractive index.

Charles Kao recognized the advantages of single-mode fiber in the mid-1960s, but other early developers pointed to a trade-off that seemed inevitable. The smaller the core diameter, the harder it was to couple light into the fiber. Coupling light into single-mode fiber inevitably requires much tighter tolerances than coupling light into the larger cores of multimode fiber. However, those tighter tolerances have proved achievable, and single-mode fibers are widely used.

Step-Index Multimode Fiber

Step-index multimode fibers were the first fibers developed for imaging. While the basic structure is the same as a single-mode fiber, the core diameter is much larger. With the large diameter, it can collect power from the laser more efficiently than a smaller-core fiber. However, for communications, the large diameter is not necessarily unwelcome because of the narrow bandwidth property.

Modes are sometimes characterized by numbers. Single-mode fibers carry only the lowest-order mode, assigned the number 0. Multimode fibers also carry higher-order modes. The number of modes that can propagate in a fiber depends on the fiber's numerical aperture (or acceptance angle) as well as on its core diameter and the wavelength of the light. For a step-index multimode fiber, the number of such modes, N_m , is approximated by

Modes =
$$0.5 \left(\frac{\text{core diameter} \times NA \times \pi}{\text{wavelength}} \right)^2$$
 (1-2)

$$N_m = 0.5 \left(\frac{\pi D \times NA}{\lambda}\right)^2 \tag{1-3}$$

where λ is the wavelength and D is the core diameter. To plug in some representative numbers, a 100 µm core step-index fiber with NA = 0.29 would transmit thousands of modes at 850 nm. This formula is only an approximation and does not work for fibers carrying only a few modes.

Each mode has its own characteristic velocity through a step-index optical fiber, as if it were a

light ray entering the fiber at a distinct angle. This causes pulses to spread out as they travel along the fiber, in what is called modal dispersion. The more modes the fiber transmits, the more pulses spread out.

Although there are other kinds dispersion, modal dispersion is the largest in multimode step-index fibers. Precise calculations of how many modes cause how much dispersion are rarely meaningful. However, we can make useful approximations by using the ray model (which works for multimode step-index fibers) to calculate the difference between the travel times of light rays passing through a fiber and bouncing along at the confinement angle. For the typical confinement angle of 8° mentioned earlier, the difference in propagation time is about 1%. That means that an instantaneous pulse would stretch out to about 30 ns (30 billionths of a second) after passing through a kilometer of fiber.

That doesn't sound like much, but it becomes a serious restriction on transmission speed, because pulses that overlap can interfere with each other, making it impossible to receive the signal. The pulses have to be separated by more than 30 ns. We can estimate the maximum data rate for a given pulse spreading from the equation

Data rate =
$$\frac{0.7}{\text{pulse spreading}}$$
 (1-4)

Plug in a pulse spreading of 30 ns, and we find the maximum data rate is about 23 Mbit/s. In practice, the maximum data rate also depends on other factors.

Dispersions also depends on distance. The total modal dispersion is the product of the fiber's characteristic modal dispersion per unit length, D_0 , multiplied by the fiber length, L:

$$D = D_0 \times L \tag{1-5}$$

Thus a pulse that spreads to 30 ns over 1 km will spread to 60 ns over 2 km and 300 ns over 10 km. (For very accurate calculations, we should replace L with L^{γ} , where γ is a factor close to 1, which depends on the fiber type. However, γ normally is so close to 1 that it doesn't matter.)

Because total dispersion increases with transmission distance, the maximum transmission speed decreases. If the maximum data rate for a 1 km length of fiber is DR_0 , the maximum data rate for L kilometers is roughly

$$DR = \frac{DR_0}{L} \tag{1-6}$$

For now, the important thing to remember is that modal dispersion seriously limits transmission speed in step-index multimode fiber.

Graded-Index Multimode Fiber

As communication engineers began seriously investigating fiber optics in the early 1970s, they recognized modal dispersion limited the capacity of large-core step-index fiber. Single-mode fibers promised much more capacity, but many engineers doubted they could get enough light into the tiny cores. As an alternative, they developed multimode fiber in which the refractive index grades slowly from core into cladding. Careful control of the refractive-index gradient nearly eliminates modal dispersion in fibers with cores tens of micrometers in diameter, giving them much greater transmission capacity than step-index multimode fibers.

Optically, graded-index fibers guide light by refraction instead of total internal reflection. The fiber's refractive index decreases gradually away from its center, finally dropping to the same value as the cladding at the edge of the core, as shown in **Figure 1.3**. The change in refractive index causes refraction, bending light rays back toward the axis as they pass through layers with lower refractive indices. The refractive index does not change abruptly at the core-cladding boundary, so there is no total internal reflection.



Figure 1.3 The refractive-index gradient in a graded-index fiber bends light rays back toward the center of the fiber.

As in a step-index fiber, light rays follow different paths in a graded-index fiber. However, their speeds differ because the speed of light in the fiber core changes with its refractive index. Recall that the speed of light in a material, c_{mat} , is the velocity of light in a vaccum, c_{vaccum} , divided by refractive index:

$$c_{mat} = \frac{c_{vaccume}}{n_{mat}}$$
(1-7)

Thus the farther the light goes from the axis of the fiber, the faster its velocity. The difference isn't great, but it's enough to compensate for the longer paths followed by the light rays that go farthest from the axis of the fiber. Careful adjustment of the refractive index profile—the variation in refractive index with distance from the fiber axis—can greatly reduce modal dispersion by equalizing the transit times of different modes. Details about the theoretical bandwidth of graded-index multimode fibers will be described in Section 1.3.

Graded-index fibers were developed especially for communications. The long-time standard types have core diameters of 50 or 62.5 μ m and cladding diameters of 125 μ m; some have been made with 85 μ m cores and 125 μ m cladding diameter. The core diameters are large enough to

collect light efficiency from a variety of light sources. The cladding must be at least 20 μ m thick to keep light from leaking out.

The graded-index fiber is a compromise, which has much higher transmission capacity than large-core step-index fibers while retaining a core large enough to collect light easily. It was used for some telecommunications until the mid-1980s but gradually faded from use in telephone systems because single-mode fibers worked much better. Graded-index fibers remain in use, mostly for data communications and networks carrying signals moderate distances—typically no more than a couple of kilometers.

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1.3 Plastic Optical Fibers 1.3.1 Last Hundred Meters

Today, people are in the midst of a new revolution, with our perspective of the world shifted by the concept of 'networks'. Twenty years after the development of low-attenuation single-mode (SM) silica glass optical fiber (GOF) in the 1970s ^[2, 3], the United States launched the Information Superhighway project. The establishment of a global fiber-optic network has allowed the distribution of a wide range of media content, providing immediate access to new information. The world has become much smaller, eliminating physical constraints and endowing people with the ability to connect with anyone at anytime, living anywhere around the world. The internet has not only made our life more interesting and livable, but has created new industries, given rise to new cultures, and influenced politics. Indeed, it has changed our way of life.

However, there remains one final hurdle to achieving ubiquitous high-bandwidth connectivity; there is not yet a high-speed pipeline that connects users to the superhighway. In the 'last hundred meters' between the superhighway and users, especially in home and office local area networks (LANs), optical fibers must be bent at many points when laid down along walls. However, SM GOF is designed with a small core of just 5–10 µm so as to excite only one optical mode within the fiber, and is thus not capable of withstanding all the bends required in the last hundred meters. One solution that has been proposed was graded-index (GI) multimode (MM) GOF ^[4-6] as mentioned in Section 1.2.3. This fiber is designed based on the idea that excited modes will be refocused while propagating and modal dispersion will be reduced due to the lens-like function of the graded index profile in the core. Even then, an issue remained—the fiber diameter must be matched with extreme accuracy when connecting fibers. Although many connection devices are under intense investigation, they are generally expensive and are still not user friendly.

Currently, networks generally consist of SM GOF trunk lines and metal cables connecting the trunk lines to users. Light signals are converted to electric signals in this last node. This type of system does not require fiber alignment, and is thus easy to set up. However, the electrical signal intensity decreases with increasing signal frequency and transmission distance. Moreover, signals are easily affected by disturbances such as external electromagnetic interference and selfinduced electric fields. Hence, the maximum transmission rate for an electrical connection is no more than several hundred megabits per second. Considering that the transmission rate of SM GOF is more than several hundred terabits per second, about 10,000 times faster than metal cables, users cannot at present benefit fully from the advantages of optical connections. Due to this last hundred meters issue, users are still unable to experience the high-speed performance of the SM GOF superhighway.

The last hundred meters also cover more of the network than the trunk lines. When comparing
networks to the human body, the trunk lines function like arteries and veins, while the last hundred meters are represented by the capillaries. It is estimated that this last hundred meters would correspond to 95% of all optical networks ^[7]. It is clear that the expected market is huge, and researchers all over the world are competing to find a solution to this problem.

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1.3.2 The Birth of Plastic Optical Fibers

Plastic has gathered broad attention as an optimal candidate for a fiber material ^[8,9]. The first plastic optical fiber (POF), invented in 1966 by Du Pont, had a step-index (SI) profile in the core region. SI POF can be enlarged to about 980 μ m in diameter without losing its flexibility or ease of fiber alignment (**Figure 1.4**). SI POF is also advantageous in terms of mass production. Not only is SI POF inexpensive to fabricate, but it is also easy to mold and manufacture. Such fibers have high potential for realizing a complete high-speed optical network. The first commercialized SI POF was Eska, introduced by Mitsubishi Rayon in 1975, and Asahi Chemical and Toray also subsequently entered the market. Yet, the first fibers were not transparent enough to be used in the last hundred meters.

With research on transparency by Kaino and colleagues ^[10], a complete high-speed optical network has become realistic. Over the years, transparency has been enhanced to the theoretical limit ^[11-13]. Moreover, the thermal stability of POF, generally lower than that of silica, has been investigated from several perspectives. By these basic investigations, the thermal stability of SI POF has been enhanced sufficiently for use in the last hundred meters. Its bandwidth has also been improved ^[14-20]. However, despite innumerous developments, improvement of the bandwidth of SI POF has its limitations. Plastic run into exactly the same problem as that for silica. For transmission, it must excite several tens of thousands of modes, more modes than those found in MM GOF. The large core increases modal dispersion, drastically degrading its bandwidth to about several hundred megahertz over 100 m.



Figure 1.4 General constructions of optical fibers.

1.3.3 Development of Graded Index Plastic Optical Fibers

The modal dispersion can be reduced drastically by adopting an appropriate refractive index profile in the core region, as in MM GOF. In 1982, the first graded-index (GI) POF was developed as one approach to reducing modal dispersion. General refractive index profiles, as shown in **Figure 1.5**, generally can be approximated by the following power law:

$$n(r) = n_1 \left[1 - 2\Delta (r/R)^g \right]^{1/2}, \qquad 0 \le r \le R$$

= $n_1 (1 - 2\Delta)^{1/2}, \qquad R < r$ (1-8)

where n(r) is the refractive index n at radius r of the core, n_1 is the refractive index at the core center, n_2 is the refractive index of the cladding, R is the core radius, g is a refractive index profile coefficient, and Δ is the refractive index difference defined by



$$\Delta = \frac{n_1^2 - n_2^2}{2n_1^2} \cong \frac{n_1 - n_2}{n_1}$$
(1-9)

Figure 1.5 General refractive index profiles of GI POF.

The refractive index profile coefficient defines the refractive index profile in GI POF. The bandwidth properties of GI POF with refractive index profiles expressed by Eq. 1-8 have been analyzed by the Wentzel-Kramers-Brillouin (WKB) method ^[21-23]. Generally, the bandwidth of optical fiber that excites many modes, such as POF, is dominantly influenced by modal dispersion. However, once modal dispersion is reduced, as in GI POF, the influence of material dispersion on bandwidth can no longer be ignored. Material dispersion is caused by the dependence of refractive index on the wavelength of light. According to analysis by the WKB method, modal dispersion σ_{inter} , material dispersion σ_{intra} and total dispersion σ_{total} can be expressed as follows.

$$\sigma_{inter} = \frac{Ln\Delta}{2c} \frac{g}{g+1} \left(\frac{g+2}{3g+2}\right)^{1/2} \left[S_1^2 + \frac{4S_1S_2\Delta(g+1)}{2g+1} + \frac{4S_2^2\Delta^2(2g+2)^2}{(5g+2)(3g+2)}\right]^{1/2}$$
(1-10)

$$S_1 = \frac{g - 2 - \varepsilon}{g + 2}, \quad S_2 = \frac{3g - 2 - 2\varepsilon}{2(g + 2)}, \quad \varepsilon = \frac{-2n_1}{n} \frac{\lambda d\Delta}{\Delta d\lambda}, \quad n = n_1 - \lambda \frac{dn_1}{d\lambda}$$
(1-11)

$$\sigma_{intra} = \frac{L\sigma_s}{\lambda} \left[\left(-\lambda^2 \frac{d^2 n_1}{d\lambda^2} \right)^2 - 2\lambda^2 \frac{d^2 n_1}{d\lambda^2} (n\Delta) S_1 \left(\frac{2g}{2g+2} \right) + (n\Delta)^2 \left(\frac{g-2-\varepsilon}{g+2} \right)^2 \frac{2g}{3g+2} \right]^{1/2}$$
(1-12)

$$\sigma_{total} = \sqrt{\sigma_{inter}^2 + \sigma_{intra}^2}$$
(1-13)

Here, the spectral width σ_s is the wavelength dispersion of the input pulse, c is the light speed, λ is the wavelength of light and L is the transmission distance. As σ_{intra} is generally smaller than σ_{inter} , the bandwidth is mainly decided by σ_{inter} . However, when the bandwidth of the fiber is high enough, the influence of σ_{intra} on the bandwidth cannot be ignored. Indeed, it is calculated that σ_{inter} and σ_{total} reach absolute minima at g = 2.1 and g = 2.5, respectively ^[24], in the case of GI POF fabricated from poly(methyl methacrylate) (PMMA). The relationship between the theoretical bandwidth and g for PMMA-based GI POF at an operating wavelength of 650 nm is shown in **Figure 1.6**. The theoretical bandwidth was calculated using the wavelength dispersion of the light source at $\sigma_s = 1.0$ and 3.0 nm. As can be seen, the bandwidth of PMMA-based GI POF increases dramatically around the optimal refractive index profile coefficient, reaching a theoretical limit of about 3.0 GHz over 100 m. It can also be seen that the theoretical

bandwidth is much lower when g is not optimal. Therefore, it can be said that controlling the refractive index profile is critical for maximizing the bandwidth of GI POF.



Figure 1.6 Relationship between index profile coefficient g and calculated -3dB bandwidth for 100 m of PMMA-based GI POF at 650-nm wavelength when diphenyl sulfide (DPS) is utilized as the dopant.

1.4 Toward Gigabit Optical Home Network

As mentioned before, with rapidly increasing interest in fiber-to-the-home (FTTH) services and digital consumer electronics, the demand for high-speed home network connecting several devices such as PCs, high definition TVs, and other home electric appliances is increasing. Systems using a GI POF as the transmission medium and a vertical-cavity surface-emitting laser (VCSEL) ^[25] as the light source are expected to be the leading medium for realizing gigabit in-home communications. The VCSEL is a relatively new class of semiconductor laser that is monolithically fabricated. It is now considered to be a key device for the gigabit Ethernet, high speed LANs, computer links, and optical interconnects. A conceptual diagram of an optical home network system is shown in **Figure 1.7**.

Since the first GI POF was reported more than 20 years ago, a great deal of effort has been made on developing an enhanced GI POF with desired characteristics for the optical home network. However, there are still big problems that need to be solved and users are still unable to experience the high-speed performance of optical fibers. The problems can be divided into three categories; fiber attenuation, glass transition temperature, and heat decomposition temperature of the base material of GI POFs. In this section, these issues are summarized.



Figure 1.7 Conceptual diagram of optical home network systems using GI POF as the transmission medium.

1.4.1 Low Attenuation

Given the laying distance in a house (30–50 m), the POF attenuation needs to be less than 200 dB/km. For GI POF based on PMMA, which is the base material for most commercially available POFs, the wavelengths satisfying this requirement are limited to 570 and 650 nm because of C-H stretching vibrational absorption losses ^[26]. However, the emission wavelengths of long-life and inexpensive VCSEL are 670–680 nm. Thus, the development of novel base materials with low-loss characteristics is one of the most pressing issues.

Table 1.1 shows the history of POF attenuation. As the base material of the core region, PMMA has been mainly utilized and the attenuation have been tried to be reduced by removing impurities. However, we can see that perdeuterated PMMA (PMMA-d₈) ^[12, 13] and perfluorinated polymer (CYTOP[®]) ^[27-31] exhibited exceptionally low attenuations. As will be explained in Section 2.3, to decrease the C-H absorption losses, substituting hydrogen with heavier atoms such as deuterium or fluorine is an effective method.

There have been previous reports on low-loss POFs consisting of PMMA-d₈ and CYTOP[®]. Molecular structures and attenuation spectra of PMMA, PMMA-d₈, and CYTOP[®] -based GI POFs are shown in **Figure 1.8**. While PMMA-d₈ and CYTOP[®] have excellent low-loss characteristics, the synthesis procedures of monomers are complicated and hence the fibers are overpriced for general consumers when the core diameter is as large as several hundred micrometers. Actually, the GI POF based on CYTOP[®], which is called "Lucina[®]", was commercialized by AGC Co., Ltd. and was started to be laid down in office buildings, hospitals, condominium buildings and so on since 2001. However, the price is still a bottleneck and the fiber installation into houses is considered to be difficult. In addition, the high performance they provide is not necessary for the very short reach networks in houses, and less expensive materials with the required attenuations are desired.

Year	Organization	Туре	Core Material	Cladding Material	Lowest Attenuation (dB/km)	Wavelength (nm)
1968	Du Pont	SI	PMMA	Fluoro-polymer	500	650
1972	Toray	SI	PS	PMMA	1100	670
1977	Du Pont	SI	PMMA-d8		180	790
1978	Mitsubishi Rayon	SI	PMMA	Fluoro-polymer	300	650
1982	NTT	SI	PMMA	Fluoro-polymer	55	568
1982	NTT	SI	PMMA		114	670
1982	Keio University	GI	P(MMA-VPAc)	PMMA		670
1983	NTT	SI	PMMA-d8		20	650
1983	Mitsubishi Rayon	SI	PMMA	Fluoro-polymer	110	570
1985	Asahi Chemical	SI	PMMA	Fluoro-polymer	80	570
1986	Fujitsu	SI	PC	Polyorefin	450	770
1986	NTT	SI	P(5F3DSt)	Fluoro-polymer	178	850
1987	Keio University	GI	P(MMA-VPAc)	PMMA		596
1987	Hitachi	SI	Thermoset resin	Fluoro-polymer	600	650
1988	Keio University	GI	P(MMA-VPAc)	PMMA		660
1990	Keio University	GI	P(MMA-VB)	PMMA		652
1991	Hoechs Celanese	SI	PMMA	Fluoro-polymer	130	650
1992	Keio University	GI	PMMA-d8	PMMA-d8		688
1996	Keio University, KAST, AGC	GI	Perfluorinated Polymer	Perfluorinated Polymer		1300

Table 1.1History of POF attenuation



Figure 1.8 Chemical structures and attenuation spectra of PMMA-, PMMA- d_8 -, and CYTOP[®]-based GI POFs.

1.4.2 High Glass Transition Temperature

To utilize GI POFs in a house, both low-loss characteristics and adequate thermal stability are necessary. One important requirement is a high glass transition temperature (T_g) . The operating temperature limit required for a house is 70 °C. Since the temperature limit is generally $T_g - 20$ °C, the T_g for GI POF must be over 90 °C. Moreover, the difference in T_g between the base material and the actual core must be considered. The parabolic refractive index profile in the GI POF core region is formed by adding a low-molecular-weight dopant. **Figure 1.9** shows a typical relationship between refractive index and T_g of a GI POF which consists of PMMA and diphenyl sulfide (DPS) as the polymer matrix and dopant, respectively.



Figure 1.9 Relationship between refractive index and T_g of a GI POF which consists of PMMA and diphenyl sulfide (DPS) as the polymer matrix and dopant, respectively.

To obtain an enough NA (typical value is around 0.2), at least 5 mol % of DPS must be added to the core. In that case, the T_g of core polymer is decreased by 15–20 °C through the plasticization effect. Thus, the core base material should have a T_g of at least 110 °C, which is higher than that for PMMA. Details about the plasticization effect will be described in Section 2.4.

In previous studies, several polymers with high T_{gS} have been proposed especially as base materials of SI POF for automobile networks where much higher T_g is required ^[32-36]. Typical examples are polycarbonate and polyimide. Their chemical structures and T_{gS} are shown in **Figure 1.10**. While they have extremely high T_{gS} , their transparencies are poor. There are mainly two reasons for the high attenuation. One is a scattering loss. They have a lot of phenyl groups in main chains and it causes the partially crystalline structure. Since the most of polymer matrix is amorphous, the heterogeneity of refractive index (or density) leads to an extremely high scattering loss. Another one is an electronic transition absorption loss. As will be described in Section 2.3, the electronic transition absorption loss usually appears at shorter wavelength and does not influence the attenuation at the emission wavelength of the light source (VCSEL: 670-680 nm). However, when they have many conjugated systems, the tail of absorption peaks shift to near infrared wavelength region. A phenyl group itself has conjugated bonds and when the phenyl groups are directly connected, the π - π^* transition can be no longer ignored. After all, POFs based on polymers with such high T_gs and enough low loss characteristics have not been developed.



Polycarbonate (T_g ~145 °C)



Figure 1.10 Chemical structures and their T_g s of polycarbonate and polyimide.

1.4.3 High Heat Decomposition Temperature

Another parameter is a high decomposition temperature. So far, GI POFs have been conventionally prepared by batch processes; either the interfacial gel polymerization ^[37, 38] or direct diffusion (DD) methods. The interfacial gel polymerization technique is especially common in acrylic GI POF investigation and enables a precise control of an index profile that realizes high bandwidth. The commercialized GI POF "Lucina[®]" has been produced by the DD process. However, in both methods, a GI POF is prepared by heat drawing the "preform", which means the yield is totally dependent on the size of the preform. This is a great limitation factor in terms of the fabrication cost.

Thus, a new process for GI POF fabrication, called co-extrusion, is being studied ^[39-42]. The schematic representation of a co-extrusion instrument is shown in **Figure 1.11**. In this process, the core and cladding material are separately prepared. These two polymer bulks are then melted in respective extrusion parts and compounded in a die to fabricate a POF having a concentric circular core/cladding structure. At this point, the fiber does not have a graded refractive index distribution. By heating the fiber in the diffusion section, a radial concentration profile of low weight molecules is formed as a result of molecular diffusion. Finally, the GI POF is obtained by winding it onto a take-up reel. Previous studies have experimentally and theoretically clarified that high bandwidth GI POFs could be obtained by the co-extrusion process.

In this dissertation, we prepared GI POFs by batch processes to confirm that the proposed novel polymers are appropriate or not as the base material of GI POF satisfying all required characteristics. To produce inexpensive GI POFs, however, we will eventually have to continuously fabricate GI POFs using the co-extrusion process. In that case, the particular concern is a polymer degradation. Polymer bulks are melted at over 200 °C for several hours; polymers with low decomposition temperatures would degrade during the fabrication process. We have already clarified that GI POFs based on PMMA can be prepared without any thermal degradation by the co-extrusion process ^[41,42]. Thus, in this study, we used the 5% weight loss temperature (T_{d5}) of PMMA as an indication of the thermal degradation. The T_{d5} of PMMA is approximately 295 °C when the increasing temperature ratio is 10 °C/min under air.



Figure 1.11 Schematic diagram of a co-extrusion procedure.

1.5 Objective

Considering above requirements, we set on the purpose of this study. That is, designing a novel plastic optical fiber with following characteristics by using inexpensive materials and simple procedures for home network.

- \checkmark The attenuation at 670-680 nm is less than 200 dB/km.
- \checkmark The transmission speed is over 1 giga bit per second through 30 m length.
- ✓ The glass transition temperature of fiber is over 90 °C (base polymer > 110 °C).
- ✓ The 5% weight loss temperature is over 295 $^{\circ}$ C.

Here, the requirement for transmission speed is not severe for GI POF. Thus, in this thesis, a great deal of effort has been made on investigating other three properties.

1.6 Organization of This Thesis

The organization of this thesis is as follows; Chapter 1 reviewed the basic concept of fiber-optic communications, the history of GI POF, and current issues we have to conquer for realizing desired home networks. Chapter 2 summarizes background knowledge for POF base material especially optical and thermal properties. Chapter 3 describes the attenuation of fibers. Given the laying distance in a house, the attenuation of the fiber should be less than 200 dB/km. We focused on partially fluorinated and chlorinated methacrylates with few C-H bonds per unit volume. In both cases, GI POFs with attenuations of less than the required value at the emission wavelength of the light source (670-680 nm) were successfully obtained. Chapter 4 discusses thermal stabilities of a polymer with bulky side chain. The base polymer should have a glass transition temperature (T_g) and heat decomposition temperature (T_{d5}) of at least 110 °C and 295 °C, respectively. Poly(pentafluorophenyl methacrylate) (PFPMA) exhibited excellent thermal properties and an enough transmittance, whereas the bulky structure lowered the polymerization conversion, resulting much lower T_g and T_{d5} in bulk state. Chapter 5 describes a copolymerization. By copolymerizing PFPMA with methyl methacrylate (MMA), the residual PFPMA was drastically decreased due to the difference of monomer reactivity ratios. As the result, copolymer bulks with higher T_g and T_{d5} than required values were obtained when the PFPMA content was 0-60 mol%. Furthermore, the increment of isotropic scattering loss accompanied with general copolymerization was clarified to be negligibly small since the refractive index of poly(PFPMA) and PMMA are almost identical. Finally, we succeeded to prepare the copolymeric GI POF with the attenuation of 172-185 dB/km at 670-680 nm. The -3dB bandwidth was 1.34 GHz for 50-m length and the high capacity of 1.25 Gbps was demonstrated. Chapter 6 provides brief conclusions of this dissertation and suggests some directions for future works.

Chemical structures and their properties of polymers discussed in Chapters 3-5 are tabulated in **Table 1.2**. Red-letters mean that they are far away from the requirement. Regarding thermal properties, T_g and T_{d5} of bulk condition correspond to their values of POF.

Chapter	Polymer	C-H bond (%) ^a	Attenuation (dB/km) ^b	<i>T</i> _g (°C)		<i>T_{d5}</i> (°C)	
				Bulk ^C	Purified ^d	Bulk ^C	Purified ^d
	ΡΜΜΑ	100	295-323	110	115	293	295
3	Poly(TFEMA)	64	127-152	73	75	280	289
3	Poly(TCEMA)	51	104-136	123	130	258	271
4	Poly(PFPMA)	34	NA	105	130	223	317
5	MMA- <i>co</i> -PFPMA 65-35 (mol%)	68	172-185	118	126	298	305

 Table 1.2
 List of polymers and their properties discussed in Chapter 3-5

^a Percentage of C-H bonds per unit volume of polymer compared with that for PMMA.

^b Wavelength region is 670-680 nm.

^c Polymers obtained by polymerization in bulk.

^d Precipitated polymers by a traditional purification method.

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Chapter 2 Background Knowledge for POF Base Material

2.1 Preface

In chapter 2, we bring the background knowledge for designing base materials of POF and review relevant theories for this research. As mentioned in chapter 1, the purpose of this study is preparing a low loss and thermally stable GI POF which can be installed into houses as a transmission medium of gigabit home network. This chapter firstly summarizes the preparation method of ultrapure polymers. Intrinsic factors affecting the attenuation of POF are divided into three categories: molecular vibrational absorption, electronic transition absorption, and light scattering. We will discuss what kind of polymer structure gives high transparency from the point of above three factors. Regarding thermal stability, both glass transition temperature (T_g) and decomposition temperature (T_d) have to be considered. Phenomena of glass transition and heat decomposition of polymers will be described and we will discuss several parameters affecting these properties.

2.2 Polymerization Methods2.2.1 Reminders on Free Radical Reactions

Polymers for optical fibers must be ultimately transparent and should not have any impurities. Thus, the polymer is preferable to be prepared by a free radical polymerization which does not need metallic initiators, catalysts, and solvents. All polymers utilized in this dissertation were prepared by the free radical polymerization. In this section, the basic concept of free radical reaction is described.

Free radicals can be regarded as resulting from the hemolytic rupture of covalent bonds. They are generated by using either physical (thermal, radiative, etc.) excitation or chemical (oxydo-reduction, free radical addition, etc.) means. If they are not stabilized by particular substituent, their lifetime (about one second in normal polymerization conditions) is extremely short due to a very high reactivity. Their hybridization state is generally trigonal (sp₂) except for those carrying substituents of large size developing steric hindrance.

Free radicals can be involved in the following six reactions, all occurring in the polymerization processes:

Combination	$R^{\bullet} + {}^{\bullet}R' \to R - R'$
Disproportionation	$2 R - CH_2 - CH_2^{\bullet} \rightarrow R - CH_2 - CH_3 + R - CH = CH_2$
Abstraction/transfer	$R^{\bullet} + R'X \rightarrow RX + {}^{\bullet}R'$
Addition	$R^{\bullet} + H_2C = CR_1R_2 \rightarrow R - CH_2 - CR_1R_2$
Fragmentation	$RA^{\bullet} \rightarrow R^{\bullet} + A$
Rearrangement	$R''R'R \bullet A'R''R'R$

Free radicals can be stabilized by resonance and electron-withdrawing effects. When their stabilization is sufficient—in particular, due to the existence of many canonical forms—they can become persistent and be isolated, like the following free radicals:



Figure 2.1 Typical chemical structures with stabilized free radicals.

For TEMPO, the most suitable representation features a 3-electron N-O bond which explains why this free radical cannot dimerize by its nitrogen or oxygen atom. The free radicals of this family (known as "nitroxyl" radicals) are usually employed to reversively trap growing transient radicals and thus ensure a control of the propagation step.

Free radicals have thus a marked tendency to participate in chain reactions, more particularly in addition and abstraction reactions.

2.2.2 Processes Utilized for Radical Polymerization

Free radical polymerization is a versatile method of polymerization that is extensively utilized in industry for the preparation of a variety of polymeric materials; it can be applied to a large variety of vinyl and related monomers under various conditions and processes because of its compatibility with many functional groups and its tolerance of water and protic media. Five main techniques with their advantages and their drawbacks are commonly utilized: polymerization in bulk, solution polymerization, dispersion polymerization, suspension polymerization, and emulsion polymerization. A monomer that can be polymerized by radical means can be subjected to one or several of these techniques.

In these methods, polymerization in bulk—or polymerization of neat monomer melts—is a priori the most economical one because it requires neither solvent nor emulsifier and affords high-purity polymers. The feature of polymerization in bulk is absolutely imperative for polymers for optical fibers. Consequently, most polymers for base materials of optical fibers have been prepared by free radical polymerization in bulk. However, the gel effect, with its consequences (high viscosity, low diffusion rates, small heat conductivity) that will be described hereafter makes difficult its control and very few are the monomers that can be polymerized in bulk. The initiator must be soluble in the monomer melt, and organic peroxides are most commonly utilized.

The term of "polymerization in bulk" is utilized whenever the polymer formed is monomer-soluble; the latter plays the role of solvent for a reaction medium that witnesses a very strong viscosity buildup as the yield increases; the kinetics can then take an explosive mode, accelerated by the gel effect (or Trommsdorff effect). This phenomenon is actually a self-acceleration of the rate of polymerization (possibly until becoming explosive) followed by a strong deceleration of the process.

This self-acceleration can hardly be anticipated because it occurs simultaneously with a decrease of the monomer concentration; it has two causes that self-maintain the process:

- 1. The high viscosity of the reaction medium causes a pronounced decrease of the values of the rate constant of termination that are diffusion-controlled; this contributes to an increase in the concentration of polymeric free radicals and to a rise of the temperature in the reaction medium due to the exothermicity of the polymerization;
- 2. Because of the high value of the energy of activation of the dissociation step, this increase in temperature favors an even faster decomposition of the initiator, adding more free radicals into the medium.

However, the interfacial-gel polymerization technique, which is one of the batch methods of preparing GI POF and has been mainly utilized for forming graded index profiles, controls the gel effect and enables to design the profile precisely.

Followings are the summary of other popular polymerization techniques.

Solution

Monomer and initiator must be soluble in the liquid and the solvent must have the desired chain-transfer characteristics and boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). The presence of the solvent assists in heat removal and control (as it also does for suspension and emulsion polymerization systems). Polymer yield per reaction volume is lower than for bulk reactions. Also, solvent recovery and removal (from the polymer) is necessary. Many free radical and ionic polymerizations are carried out utilizing solution polymerization including water-soluble polymers prepared in aqueous solution (namely poly(acrylic acid), polyacrylamide, and poly(*N*-vinylpyrrolidinone)). Polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polybutadiene are prepared from organic solution polymerizations.

Suspension

A water insoluble monomer and initiator are used. Again, a chain-transfer agent may be used to control chain size. Stirring is usual. Droplets of monomer containing initiator and chain-transfer agent are formed. A protective colloidal agent, often poly(vinyl alcohol), is added to prevent coalescence of the droplets. Near the end, the particles become hard and are recovered by filtration. Because the liquid is water-based, solvent recovery and treatment in the polymerization process. Polymers produced by suspension polymerization include poly(vinyl chloride), polystyrene resins, and copolymers such as poly(styrene-coacrylonitrile), SAN, and poly(vinyl chloride-covinylidene chloride).

Emulsion

The system usually contains a water-soluble initiator (in contrast to the requirement that the initiator must not be water soluble in suspension polymerizations), chain-transfer agent, and a surfactant. The hydrophobic monomer forms large droplets that are stabilized by the surfactant. At a certain concentration, the surfactant molecules from micelles that contain 50-100 surfactant molecules. During polymerization, the monomer, that has a small but real water solubility, migrates from the monomer droplets through the water and into these micelles. Polymerization begins when the water-soluble initiator enters into the monomer-containing micelle. Because the

concentration of micelles (about 10^{21} /L) is high compared with the concentration of monomer droplets (about 10^{13} /L) the initiator is more likely to enter a micelle than a monomer droplet. As polymerization continues, monomer is transferred to the growing micelles. At about 50-80 % conversion the monomer droplets disappear and the micelles become large polymer-containing droplets. This suspension is called a latex. The latex is stable and can be used as is or the polymer recovered by coagulation. In inverse emulsion polymerization, the monomer, which is hydrophilic, is dispersed in an organic liquid. Here, the monomer is usually contained in an aqueous solution.

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2.3 Transparency (Attenuation)

The loss factors for POFs have been examined. It is apparent that various mechanisms contributing to losses for POFs are basically similar to those for glass optical fibers; but the relative magnitudes are different between the two fibers. **Figure 2.2** shows the loss factors for POFs. Absorption losses include higher harmonics of molecular vibration in the IR region and electronic transitional absorption in the UV region. Scattering losses include so-called Rayleigh scattering and loss due to imperfections in the waveguide structure.

The predicted loss factors for POF indicate the importance of clarifying factors that influence the attenuation loss in the visible wavelength region, where POFs transmit the most light ^[1]. It seems that, among intrinsic absorption loss values in the core materials, the most influential are high harmonics caused by vibrational absorption at the infrared region, due to carbon-hydrogen (CH) bonds ^[2, 3]. Rayleigh scattering loss is thought to be inversely proportional to the fourth power of the wavelength, as is the case in glass counterparts.

When extrinsic scattering loss is under consideration, the absorption due to impurities and the scattering due to migration of dust and microvoids can be reduced by designing appropriate fiber fabrication apparatus. Scattering losses caused by imperfections in the waveguide structure, such as fluctuations of core diameter and mismatching of the core-cladding boundary interface may be lowered by the development of a suitable fiber fabricating technique. Losses attributable to extrinsic factors such as scattering due to imperfections in the waveguide structure and to contaminants and microvoids should be neglected. After optimum process conditions in POF fabrication have been achieved, CH vibrational absorption may be a major loss factor. In this section, each intrinsic factors affecting POF attenuation will be described in detail.



Figure 2.2 Classification of intrinsic and extrinsic factors affecting the attenuation of POF.

2.3.1 Vibrational Absorption

Intrinsic absorption loss of POF is caused by electronic transition absorption and the molecular vibration absorption. As will be described later, electronic transition peaks appear in the ultraviolet wavelength region, and their absorption tails influence the transmission loss of POF. However, for aliphatic molecules like PMMA, this contribution is only important at wavelength below 600 nm, which is shorter than that for the optical light source. Thus, the absorption loss of aliphatic POF in near infrared region is mainly caused by the molecular vibration absorption due to the overtone vibration of bonds ^[2, 3]. Actual C-H overtone bands of polymers slightly deviate from the simple overtone estimation only within carbon and hydrogen because molecular vibrations are not perfectly harmonic. This is expressed in a nonsymmetric potential curve. From the Morse Potential approximation, we obtain the energy levels ($G(\upsilon)$) with a non-zero anharmonicity constant χ .

$$G(\upsilon) = v_0 \left(\upsilon + \frac{1}{2}\right) - v_0 \chi \left(\upsilon + \frac{1}{2}\right)^2 \qquad \upsilon = 0, \ 1, \ 2 \cdots$$
 (2-1)

The position of the fundamental vibration v_1 or an overtone v_v ($v=2, 3, 4\cdots$) is given by

$$v_{\upsilon} = G(\upsilon) - G(0) = \frac{v_1 \upsilon - v_1 \chi \upsilon(\upsilon + 1)}{1 - 2\chi} \qquad \upsilon = 2, 3, 4...$$
(2-2)

If the position of the fundamental vibration v_1 and the anharmonicity constant χ are known, the spectral positions of the overtones can be calculated by Eq. 2-2. From infrared spectroscopic data of compounds, one can determine the position of the fundamental absorption v_1 and the first overtone v_2 for all interesting vibrations, from which the χ -values can be calculated.

W. Groh came out with a very simple equation for the band strength (E_v) of an overtone normalized to the band strength (E_1) of its fundamental ^[2,3].

$$\frac{E_{\nu}}{E_{1}} = \frac{f(\chi)_{1}}{f(\chi)_{\nu}}$$
with $f(\chi)_{\nu} = \frac{1}{\nu(1/\chi - 2\nu - 1)} \cdot \begin{pmatrix} 1/\chi - 2\\ \nu \end{pmatrix}$
(2-3)

Any overtone band strength can be calculated if we know the anharmonicity constant χ and the fundamental band strength E_1 , both of which can be extracted from an infrared spectrum of an appropriate compound.

Values for the spectral position of the fundamental, the band strengths and the anharmonicity constants for the most important molecular vibrations in polymers are given in **Table 2.1**. The C-H absorption is most pronounced because of its large anharmonicity constant. In organic polymers, other vibrational absorptions mainly from C-C, C=C, and C-O bonds can occur. For C-C, C=C, and C-O vibrations, the fundamental vibrations are observed at longer wavelength in the IR region, and large overtone intensities are not expected in near infrared region. There is experimental evidence that the fourth overtones of the C-C, C=C and C-O groups, expected in the 1200-1500 nm range, are already undetectable.

Bond	v ₁ cm ⁻¹	$\frac{\lambda_{_1}}{nm}$	$\frac{E_1}{cm mol^{-1}}$	X
C-H	2950	3390	6.0×10 ⁵	1.9×10 ⁻²
C-D	2230	4484	2.4×10 ⁵	1.46×10 ⁻²
C=0	1846	5417	9.6×10 ⁶	6.5×10 ⁻³
C-F	1250	8000	2.4×10 ⁷	4×10 ⁻³

 Table 2.1
 Important molecular vibrations in organic polymers

Figure 2.3 shows the spectral overtone positions and normalized integral band strengths for different C-X vibrations. Each symbol represents the calculated spectral overtone positions and the corresponding band strengths. The results for C-D and C-F overtones are given. In the range from 600 to 900 nm wavelength, they are several orders of magnitude lower than that of the C-H overtones.



Figure 2.3 Calculated spectral overtone positions and normalized integral band strengths for different C-X vibration.

In order to obtain a quantitative absorption loss limits for amorphous polymers, W. Groh has proposed the relation between integral bandstrengths and absorption losses. For a bond C-X (here bond C-X denotes the bond of C-H, C-D, or C-F, etc.), the approximation relation is

$$\alpha_{\max}(v_{\nu}^{C-X}) = 3.2 \times 10^8 \frac{\rho}{M_0} n_C \left(\frac{E_{\nu}}{E_1^{CH}}\right)_{C-X}$$
(2-4)

where α_{max} (dB/km) is the loss for the band maximum, ρ (g/cm³) is density of polymer, M_0 (g/mol) is the molecular weight of a monomer unit, and n_c is the number of bond C-X in monomer unit. If we set $\rho = 1.19$ g/cm³, $M_0 = 100$ g/mol, and $n_c = 8$ as values for PMMA glass which has been used as a core material for polymer optical fiber, it follows from Eq. 2-4 that quotient $E_v / E_1^{CH} = 3.3 \times 10^{-8}$ refers to an absorption band of 1 dB/km as shown in **Figure 2.3**. From Eqs. 2-3 and 2-4, together with Table 2.1, the losses due to C-X overtone bands can be estimated.

Reduction of the loss of amorphous polymer is achieved by substituting the hydrogen atoms for heavier elements like deuterium or fluorine which have lower energy absorption bands.

2.3.2 Electronic Transition Absorption

Polymers, in common with all organic materials, absorb light in the ultraviolet region of the spectrum. The mechanism for this absorption depends on transitions between electronic energy levels of the bonds within the materials; the absorption of a photon causes an upward transition, leading to excitation of the electronic state of the solid.

Usually, electronic transition peaks appear in the ultraviolet wavelength region, and their absorption tails influence the transmission loss of POFs. Consequently, as a result of the relatively short wavelengths at which low loss windows are located in polymers, their contribution to the total attenuation of a fiber should be considered.

In the case of PMMA core POF, Kaino *et al.* found an $n-\pi^*$ transition due to an ester group in the MMA molecules, $n-\sigma^*$ of the chain transfer agent, and $\pi -\pi^*$ of an azo group, when azo compounds are used as a polymerization initiator ^[4]. The most significant absorption is caused by the transition of the $n-\pi^*$ orbital of the double bond within the ester group. In the case of poly(styrene), which is also a universal polymer for the POF, they found a $\pi -\pi^*$ transition of a phenyl group in the styrene molecule and an $n-\sigma^*$ transition of the SH bond in the chain transfer agents. It is the benzene ring that increase the electronic transition loss; the $\pi -\pi^*$ transition within the delocalized bonds of the phenyl ring produce an extremely intense absorption.

The effect of the electronic transition absorption on the attenuation at visible wavelength region obeys the Urbach's rule ^[5]. By adopting the measurement values to the rule, Kaino *et al.* proposed following equations which express electronic transitional losses for PMMA and PS core POFs ^[4].

$$\alpha_e(PMMA) = 1.58 \times 10^{12} \exp\left(\frac{1.15 \times 10^4}{\lambda}\right)$$
(2-5)

$$\alpha_e(PS) = 1.10 \times 10^5 \exp\left(\frac{8.0 \times 10^3}{\lambda}\right)$$
(2-6)

From these equations, α_e values of PS are calculated to be 98 dB/km and 9 dB/km at 500 nm and 600 nm, respectively. On the other hand, α_e for PMMA is less than 1 dB/km even at 500 nm. Polymers having phenyl groups generally have high electronic transition losses at a visible wavelength region, since the energy band gap between π and π^* level is small enough to be excited by a light with visible wavelength. As the length of the conjugated system becomes longer, the electronic transition absorption drastically shifts to the longer wavelength, and it can affect the

transmission loss of optical fibers.

2.3.3 Scattering

Using the Einstein's fluctuation theory ^[6], the intensity of the isotropic light scattering V_V^{iso} from thermally induced density fluctuations in a structureless liquid is expressed by

$$V_V^{iso} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 kT\beta$$
(2-7)

where λ_0 is the wavelength of light in vaccum, k is the Boltzmann constant, T is the absolute temperature, n is the refractive index, and β is the isothermal compressibility. The fluctuation theory for structureless liquids indicates that according to Eq. 2-7, the isotropic scattering loss decreases with the decrease in isothermal compressibility and refractive index. Previous studies have clarified that the value of V_V^{iso} calculated using the β at T_g according to a frozen model showed good agreement with the observed value for PMMA glass ^[7-9]. When the reported value of β at 100 °C (close to T_g) is used in Eq. 2-7, the calculated α^{iso} is 9.5 dB/km which is very close to observed value (9.7 dB/km) for PMMA glass polymerized above the T_g .

On the other hand, when the polymer has a large sized heterogeneity in its high ordered structure, it was reported that the intensity of isotropic scattering depends on the scattering angle. Some samples prepared in this thesis also strongly exhibited the forward excess isotropic scattering V_V , while anisotropic scattering H_V showed no angular dependence in its intensity. It should be noted that the large size heterogeneities causing the excess scattering are isotropic structures and are not due to anisotropic domains such as bundled or folded polymer chains.

To analyze polymers of which isotropic scattering strongly exhibits the angle dependency, Debye's light scattering method ^[10-12] can be applied. In structureless liquids or randomly oriented polymers, the isotropic part V_{V1}^{iso} of the V_V scattering is given by

$$V_{V1}^{iso} = V_{V1} - \frac{4}{3}H_V$$
(2-8)

Here, the observed V_V scattering intensity is separated into three terms as shown in **Figure** 2.4, namely

$$V_V = V_{V1}^{iso} + V_{V2}^{iso} + \frac{4}{3}H_V$$
(2-9)

where V_{V1}^{iso} denotes the isotropic background intensity which is independent of the scattering angle θ , and V_{V2}^{iso} is the isotropic scattering with the angular dependence due to large size heterogeneities.



Figure 2.4 Schematic diagram of V_V scattering for amorphous polymers.

 V_{V2}^{iso} is most important to investigate the structure giving the excess scattering discussed in this thesis. The angular dependence of the V_{V2}^{iso} intensity is caused by an interference effect due to the large size heterogeneities. When two close parallel beams with a wavelength λ are scattered at i and j points to the same direction, the phase difference of these beams is $v(\mathbf{r} \cdot \mathbf{s} - \mathbf{s}_0)$. Here $v = 2\pi/\lambda$, \mathbf{s}_0 and \mathbf{s} are the unit vectors having the directions of the incident and scattered beams, respectively, and (\mathbf{r}) is the vector connecting the two points i and j. Then a single secondary wave results, represented in complex form by $\exp[-iv(\mathbf{r} \cdot \mathbf{s} - \mathbf{s}_0)]$; the scattering intensity I_s then becomes

$$I_{s} = V \left\langle \eta^{2} \right\rangle \int_{V} \gamma(\mathbf{r}) \exp[-i v (\mathbf{r} \cdot \mathbf{s} - \mathbf{s}_{\theta})] d\mathbf{r}$$
(2-10)

where $\gamma(\mathbf{r})$ is the so-called correlation function introduced by Debye and Bueche and defined by
Eq. 2-11^[11].

$$\gamma(r) = \frac{\left\langle \eta(\boldsymbol{r}_i) \cdot \eta(\boldsymbol{r}_j) \right\rangle_r}{\left\langle \eta^2 \right\rangle}$$
(2-11)

Here $\eta(\mathbf{r}_i)$ and $\eta(\mathbf{r}_j)$ are the fluctuations of dielectric constants at the *i* and *j* positions which are a distance *r* apart, and $\langle \eta^2 \rangle$ denotes the mean-square average of the fluctuation of all dielectric constants.

In the isotropic media with no long range order, the average of $\exp[-iv(\mathbf{r}\cdot\mathbf{s}-\mathbf{s}_0)]$ in Eq. 2-10 becomes $\sin(vsr)/(vsr)$, $dV = 4\pi r^2 dr$, and $V_{V2}^{iso} = (\pi^2 I_s)/(\lambda_0^4 V)$. Thus, V_{V2}^{iso} was given by Debye and Bueche as

$$V_{V2}^{iso} = \frac{4\langle \eta^2 \rangle \pi^3}{\lambda_0^4} \int_0^\infty \frac{\sin(vsr)}{vsr} r^2 \gamma(r) dr \qquad (2-12)$$
$$s = |s - s_0| = 2\sin(\theta/2)$$
$$v = 2\pi/\lambda$$

where λ and λ_0 are wavelengths of light in a specimen and under vaccum, respectively ^[11]. In this thesis, the correlation function $\gamma(r)$ is assumed to be approximately by Eq. 2-13 as suggested by Debye *et al.*

$$\gamma(r) = \exp(-r/a) \tag{2-13}$$

where a is called the correlation length and is a measure of the size of the heterogeneities. Substituting Eq. 2-13 into Eq. 2-12 and integrating gives

$$V_{V2}^{iso} = \frac{8\pi^3 \langle \eta^2 \rangle a^3}{\lambda_0 (1 + \nu^2 s^2 a^2)^2}$$
(2-14)

The light scattering loss α is defined by

$$\alpha = -\frac{10}{y} \log\left(\frac{I}{I_0}\right)$$
(2-15)

where natural light with an intensity I_0 passes through a distance y and its intensity is decreased to I by only the light scattering. Differential of Eq. 2-15 gives

$$\alpha = (-10\log e) \left(\frac{1}{I} \frac{dI}{dy}\right)$$
(2-16)

Therefore, the scattering loss α corresponds to the decrease (dI) in light intensity (I) which is equal to the summation of light scattered in all directions after passing through a distance dy. When the scattered light I_s from a unit scattering volume is detected on the differential surface dS at a distance R from the scattering point $dS = 2\pi (R\sin\theta)(R \cdot d\theta)$, then $(I_s/I)R^2 = (1/2)(V_V + V_H + H_V + H_H)$ and

$$\frac{1}{I}\frac{dI}{dy} = -\int \frac{I_s}{I} dS = -\pi \int_0^\pi (V_v + V_H + H_v + H_H) \sin\theta \cdot d\theta$$
(2-17)

where the symbols V and H denote vertical and horizontal polarizations, respectively. Here the symbol A of the scattering component A_B is the direction of the polarizing phase of a scattered light and the subscript B is that of an incident light. θ is the scattering angle from the direction of the incident ray. In a randomly oriented polymer

$$H_V = V_H \tag{2-18}$$

$$H_{H} = V_{V} \cos^{2} \theta + H_{V} \sin^{2} \theta \tag{2-19}$$

The one obtains the scattering loss α expressed in terms of V_{V1}^{iso} , V_{V2}^{iso} , and H_V as follows:

$$\alpha = 10\log e\pi \int_0^{\pi} \left\{ \left(1 + \cos^2\theta\right) \left(V_{V_1}^{iso} + V_{V_2}^{iso}\right) + \frac{\left(13 + \cos^2\theta\right)}{3}H_V \right\} \sin\theta \ d\theta \qquad (2-20)$$

Now α is divided into three terms, α_1^{iso} , α_2^{iso} , and α^{aniso} .

$$\alpha = \alpha_1^{iso} + \alpha_2^{iso} + \alpha^{aniso}$$
(2-21)

where α_1^{iso} is the isotropic scattering loss from V_{V1}^{iso} with no angular dependence, α_2^{iso} is the isotropic scattering loss from V_{V2}^{iso} with angular dependence, and α^{aniso} is the anisotropic scattering loss from H_V . Since V_{V1}^{iso} and H_V have no angular dependence in there intensities, α_1^{iso} and α^{aniso} are simply calculated from Eq. 2-20 as follows:

$$\alpha_1^{iso} = 10\log e\pi \int_0^{\pi} (1 + \cos^2\theta) V_{V_1}^{iso} \sin\theta \, d\theta = \frac{80}{3}\log e\pi V_{V_1}^{iso}$$
(2-22)

$$\alpha^{aniso} = 10\log e\pi \int_0^{\pi} \frac{(13 + \cos^2 \theta)}{3} H_V \sin \theta \, d\theta = \frac{800}{9}\log e\pi H_V$$
(2-23)

In the case of α_2^{iso} , substitution of Eq.2-14 into Eq. 2-20 gives

$$\alpha_{2}^{iso} = 10\log e \pi \int_{0}^{\pi} (1 + \cos^{2} \theta) V_{V2}^{iso} \sin \theta \, d\theta$$

$$= \frac{320\log e a^{3} \langle \eta^{2} \rangle \pi^{4}}{\lambda_{0}^{4}} \left\{ \frac{(b+2)^{2}}{b^{2}(b+1)} - \frac{2(b+2)}{b^{3}} \ln(b+1) \right\}$$
(2-24)
$$b = 4v^{2}a^{2}$$

To determine the α_2^{iso} value, we first estimated the correlation length by the Debye plot^[12, 13] of experimental data of V_{V2}^{iso} and $\langle \eta^2 \rangle$ obtained by Eq. 2-14. Then these values were substituted in Eq. 2-24 to obtain α_2^{iso} .

2.4 Thermal Stability2.4.1 Glass Transition Temperature

The phenomenon

A completely amorphous polymer is rigid and breakable at $T < T_g$ and becomes viscous or elastomeric—depending upon its molar mass or the duration of the stress applied—at $T > T_g$. The origin of this phenomenon is still a matter of discussions, but the following points are beyond any controversy:

- The highly reversible extensibility (rubber elasticity) of polymer chains is related to their ability to coil and uncoil. The extension of an elastomer corresponds to a negative variation of its entropy. The examination of X-ray diffraction patterns of a stretched elastomer and of an unstretched one confirms this statement.
- The motion of a limited number of subchains is enough to impart a rubbery behavior to a
 polymer sample as observed in networks above their glass transition temperature. However,
 for very dense networks, the movement of chain segments is limited and the phenomenon is
 difficult to detect. Conversely, for polymers of short size, the motion of the whole chain can
 result in irreversible phenomena such as their creep and relaxation.
- In the glassy state $(T < T_g)$ the movement of subchains are not completely absent; they are only slowed down, especially in the absence of an external mechanical stress.
- For polymers of very high molar mass, the glass transition temperature is independent of their molar mass; thus, the glass transition temperature of vulcanized elastomers is close to that of the corresponding linear polymers.
- Finally, for compounds of intermediate molar mass, a second transition is observed at $T = T_{flui}$, which likely corresponds to the motion of the whole macromolecule and is generally identified with the glass transition temperature (at $T = T_g$) of polymers of low degree of polymerization.

From these factual observations, various theories were elaborated which, considered all together, can practically account for all aspects of the observed phenomena. Depending upon the experimental conditions, one or another among these theories may appear more suited to describe the behavior observed.

The Free Volume Theory

In spite of the fact that polymers are denser than homologs of low molar mass, the apparent volume they fill in the condensed state is not entirely occupied by their constitutive atoms. For instance, it is observed that the volume occupied by a solution of a polymer is lower than the sum of volumes of each component considered separately. This "unoccupied" volume in the condensed state is referred to as *free volume*; it results from the impossibility of molecular groups to take any position available in the vacant space due to restrictions imposed by valence angles. Whatever the temperature of the system and, in particular, for T = 0K, the following relation can be written

$$V_{T0} = V_0 + V_{f0} \tag{2-25}$$

where V_{T0} is the apparent volume of the sample, V_0 is the actually occupied volume, and V_{f0} is the free volume.

Raising the temperature of the system results in, a dilation that, strictly speaking, cannot be that of the constitutive atoms, but corresponds to their vibration due to thermal energy

$$V_T = V_0 + V_{f0} + (dV/dT)_g T$$
(2-26)

where $(dV/dT)_{g}$ is the volume expansion coefficient in the glassy state.

Whatever the temperature considered, the system is said to be in the glassy state when its free volume fraction is constant, a phenomenon observed for all polymers. **Figure 2.5**, which represents the variation of the volume of a completely amorphous polymer as a function of its temperature, illustrates this phenomenon.



Figure 2.5 Variation of the volume V of an amorphous polymer sample versus temperature.

The difference between experimental values of V = f(T) extrapolated to T = 0K corresponds to the "incompressible" free volume, namely:

$$V_{f0} = V_{T0g} - V_{T0 \, liq} \tag{2-27}$$

At the glass transition temperature, the free volume is large enough to allow the chains to move under a stress, and at this precise temperature the total volume can be expressed as

$$V_{T_g} = V_0 + V_{f0} + \left(\frac{dV}{dT}\right)_g T_g$$
(2-28)

Above the glass transition temperature ($T > T_g$), the volume expansion coefficient of a polymer is not that prevailing in the glassy state but that of the liquid or rubbery state, depending upon the range of molar masses considered:

$$V_T = V_{Tg} + \left(\frac{dV}{dT}\right)_{liq} \left(T - T_g\right)$$
(2-29)

This overall behavior is schematically represented in Figure 2.5.

According to the free-volume theory, at the glass transition temperature all polymers have practically the same fraction of free volume (f_{T_g}):

$$f_{Tg} = \left[V_{f0} + \left(\frac{dV}{dT} \right)_g T_g \right] / V_{Tg} = 0.025$$
(2-30)

and its value, which was obtained from measurements over a whole range of polymers different in nature and molar masses, is a quasi-universal constant. Above T_g , the fraction of free volume (f_T) can be written as

$$f_{T} = f_{Tg} + \left[\left(\frac{dV}{dT} \right)_{liq} - \left(\frac{dV}{dT} \right)_{g} \right] \left(T - T_{g} \right) = f_{Tg} + \left(\alpha_{liq} - \alpha_{g} \right) \left(T - T_{g} \right)$$
(2-31)

As compared to the "incompressible" volume, there exsists an excess of free volume which makes the motion of chains all the more easy as the free volume increases.

The difference between the volume expansion coefficients in the liquid and the glassy state for all polymers is approximately equal to

$$\Delta \alpha = \left(\alpha_{liq} - \alpha_{g}\right) \sim 5 \times 10^{-4} K^{-1}$$
(2-32)

In a study devoted to the viscosity of noncrystallizable *n*-alkanes, Doolittle established that the viscosity of these compounds varies with the temperature according to an Arrhenius-type law:

$$\eta_T = A \exp[BV_0 / (V_T - V_0)]$$
(2-33)

corresponding to

$$\ln \eta_T = \ln A + BV_0 / (V_T - V_0)$$
(2-34)

Since

$$V_0 / (V_T - V_0) \approx V_T / (V_T - V_0) = V_T / V_{free \ at \ T} \approx 1 / f_T$$
 (2-35)

one has

$$\ln \eta_T = \ln A + \frac{B}{f_T} \tag{2-36}$$

If the viscosity of amorphous polymers is measured at two different temperatures T and T_g , the above expression becomes

$$\ln(\eta_T / \eta_{T_g}) = -B(1/f_T - 1/f_{T_g})$$
(2-37)

which corresponds to

$$\ln(\eta_T/\eta_{T_g}) = \frac{-B\Delta\alpha(T-T_g)}{f_{T_g}[f_{T_g} + \Delta\alpha(T-T_g)]}$$
(2-38)

$$\ln(\eta_T/\eta_{T_g}) = \frac{-(B/f_{T_g})(T-T_g)}{f_{T_g}/\Delta\alpha + T - T_g}$$
(2-39)

If one poses

$$B/f_{T_g} = C_1$$
 and $f_{T_g}/\Delta\alpha = C_2$ (2-40)

one has

$$\ln(\eta_T / \eta_{T_g}) = \frac{-C_1 (T - T_g)}{C_2 + T - T_g}$$
(2-41)

This relationship is analogous to the empirical one established by Williams, Landel, and Ferry (WLF equation) which serves to relate the dielectric and mechanical relaxation times measure at a temperature T with those measured at the reference temperature (here T_g).

Introducing a_T , the shift factor, as the ratio of the relaxation time (τ_T) at T to that (τ_{T_g}) at T_g , the WLF equation can be written as

$$\ln a_T = \frac{-D_1 \left(T - T_g \right)}{D_2 + T - T_g}$$
(2-42)

The viscosity of a polymer in the liquid state can thus be related to its relaxation time:

$$a_T = \tau_T / \tau_{T_g} \approx \eta_T / \eta_{T_g} \tag{2-43}$$

From the measurement of the relaxation times determined at various temperatures, the values of D_1 and D_2 and hence the values of f_{Tg} and $\Delta \alpha$ can be deduced using the above expression.

Structual Parameters Affecting the Glass Transition Temperature

External factors affecting T_g , such as the cooling rate and the frequency of the mechanical stress, depend on the service conditions of the material considered. With respect to the structual or compositional parameters, they can be modified at will by the chemist or the formulator in order to adjust T_g and thus meet the requirements of a given applications.

In the preceeding paragraph the dimensionally was mentioned as affecting the value of T_g ; the effect is actually not very pronounced and is limited to highly cross-linked materials; this observation is logical since the glass transition phenomenon is related to the motion of relatively short sequences.

Effect of Molar Masses

The proportion of free volume introduced by chain ends decreases as the molar mass increases. Experimentally, it is thus logical to observe an increase of T_g with M. However, only empirical relationships could be established; for example, in the case of polystyrene, the generally used relationship is as follows ^[13]:

$$T_g = 373 \mathrm{K} - \frac{1.8 \times 10^5}{\overline{M}_n}$$
(2-44)

The variation of T_g with M thus becomes undetectable for molar masses higher than 10^5 g/mol.

Effect of the Polymer Molecular Structure

This effect is multiple since it can be related to the topology of the monomer unit or to the tacticity of the monomer sequences as well as to the extent of molecular interactions.

The cohesive properties thus play an important role in the glass transition phenomenon. Indeed, molecular interactions decrease the mobility of the chains which, according to the kinetic theory, must contribute to an increase of T_g and can be beneficial for certain applications. The comparison of the glass transition temperature of polypropylene –[CH₂-CH(CH₃)]_n-, whose T_g is -10 °C, with that of poly(vinyl alcohol) –[CH₂-CHOH]_n-, whose T_g is 70 °C, gives an ideal of the importance of interactions.

The effect of main chain substituents is more complex. The size of certain atoms or the geometry of some substituents may contribute to stiffen the chain backbone and cause an increase of T_g . For instance, the atomic radius of fluorine atoms in polytetrafluoroethylen (PTFE) imposes a

conformational structure that is mirrored in a higher glass transition temperature for this polymer $(T_{gPTFE} = 125 \text{ °C})$ than that of polyethylene $(T_{gPE} \sim -120 \text{ °C})$. Conversely, the grafting of side chains or branches of increasing size onto polymer backbones will distance one from another, which generates free volume and may in turn induce a decrease of T_g . Each additional brance indeed introduces a chain end that contributes to the free volume of the system. However, very long linear side chains can "consume" free volume by folding up regularly, which may stiffen the backbone and thus raise T_g . Table 2.2 gives the values of T_g for a series of polyacrylates, illustrating the effects due to the parameters previously discussed.

R	<i>T_g</i> (°C)	R	<i>T_g</i> (°C)
— CH ₃	+10	$CH_2 - CH - (CH_2)_3 - CH_3$	-50
CH ₂ $-$ CH ₃	-24	I CH₃	
	27	(CH ₂) ₁₁ CH ₃	-3
$-(CH_2)_2 - CH_3$	-37	(CH ₂) ₁₅ CH ₃	+35
$(CH_2)_3 - CH_3$	-54		+19
$-CH_2 - CH_3$ CH ₂ - CH CH ₃	-24		+6
(CH ₂) ₅ CH ₃	-57		+43
—(CH ₂) ₇ – CH ₃	-65		+147

Table 2.2 Glass transition temperature (T_g) for some atactic poly[alkyl (and other) acrylates] [14]

The effect of tacticity can be considerable for certain types of polymers. For instance, it has little impact on polyacrylates but is pronounced for polymethacrylates. Thus, for PMMA, $T_g^{\text{iso}} = 45 \text{ }^{\circ}\text{C}$ whereas $T_g^{\text{syndio}} = 150 \text{ }^{\circ}\text{C}$. It could indeed be established for 1,1-disubstituted ethylenic polymers that such a large difference in T_g s is due to a larger rotational energy of syndiotactic polymers compared to that of isotactic ones.

A similar behavior is observed for polymers carrying intrachain ethylenic unsaturations. The phenomenon is observed, in particular, for natural 1,4-polydienes: 1,4-*cis*-polyisoprene (natural rubber) exhibits a T_g equal to -72 °C, whereas that of 1,4-*trans*-polyisoprene (gutta-percha) is -58 °C. Such a difference originates from the configurations of the two polymers which can also be correlated with their corresponding stiffness.

One convenient means to manipulate the glass transition temperature of polymers is through copolymerization. Whatever the phenomenological interpretation given to this effect (additivity of free volumes or combined effects due to the chain stiffness and to molecular interactions), empirical relations can be used to evaluate the T_g of random copolymers. The relationship

$$1/T_{g1,2} = \left(w_1/T_{g1}\right) + \left(w_2/T_{g2}\right)$$
(2-45)

is sometimes used, where T_{g1} , T_{g2} , and $T_{g1,2}$ are the glass transition temperatures of the homopolymers and the copolymer respectively, with w_1 and w_2 being the mass fractions of the two types of monomeric units forming the copolymer; this relationship gives satisfactory results when T_{g1} and T_{g2} are not too different. In other cases, it is preferable to use the Gordon-Taylor relationship ^[15]

$$\left(T_{g1,2} - T_{g1}\right)w_1 = K\left(T_{g2} - T_{g1,2}\right)$$
(2-46)

where the constant K for a given pair of comonomers corresponds to

$$K = \left(\alpha_{liq,2} - \alpha_{g,2}\right) / \left(\alpha_{liq,1} - \alpha_{g,1}\right)$$
(2-47)

where the various α coefficients of this equation represent the coefficients of volume expansion of homopolymers 1 and 2 in the liquid and the glassy states.

Actually, this relationship is not completely an empirical one since it can also be established

using the free volume theory. A calculation based on this theory is presented below to evaluate the effect of external plasticization.

Effect of the Plasticizers

This phenomenon of plasticization results from the addition of a diluent (called plasticizer) to a polymer in which it is miscible in all proportions so as to lower its glass transition temperature. This diluent introduces free volume in the material and, like any solvent, promotes polymer—diluent interactions at the expense of polymer—polymer interactions. This phenomenon of plasticization results in the decrease of T_g . In the case of poly(vinyl chloride) (PVC), it is a process of great economic importance because most of the PVC annually produced and used its plasticized.

There are requirements to fulfill for a good plasticization, and it turns out that PVC is well-suited to these requirements. Among these, the following ones are essential: the polymer—plasticizer miscibility, which requires that the Flory-Huggins parameter (χ_{12}) be as low as possible (negative), a plasticizer of low vapor pressure (and then a rather high molar mass) to secure the polymer plasticization over a long period, and finally, all the toxicological, economic, etc, requirements determining the feasibility of the process.

Using the free volume theory, the value of T_g for the plasticized polymer can be calculated as a function on the composition of the blend. If one assumes, on the one hand, additivity of the polymer and the plasticizer (diluent: d) and, on the other, a common critical value (f) for the fraction of free volume for the two components and from their blend as well, then the fraction of free volume of a pure component at a given temperature T is equal to

$$f = f_g + \left(\alpha_{liq} - \alpha_g\right) \left(T - T_g\right)$$
(2-48)

The fraction of free volume introduced by the polymer in the blend at the glass transition temperature (T_{gm}) of the blend is expressed as

$$f_p = \left[f_{gp} + \left(\alpha_{liq} - \alpha_g \right) \left(T_{gm} - T_{gp} \right) \right] \mathcal{P}_p$$
(2-49)

where Φ_p is the volume fraction of polymer.

For the plasticizer, one has

$$f_d = \left[g_{gd} + \alpha_d \left(T_{gm} - T_{gd}\right)\right] \Phi_d$$
(2-50)

where Φ_d , the volume fraction of the plasticizer, is equal to $(1 - \Phi_p)$. It is thus possible to deduce the relationship

$$T_{gm} = \left\{ T_{gp} \left(\alpha_{liq} - \alpha_g \right) \Phi_p + T_{gd} \alpha_d \left(1 - \Phi_p \right) \right\} / \left\{ \Phi_p \left(\alpha_{liq} - \alpha_g \right) + \left(1 - \Phi_p \right) \alpha_d \right\}$$
(2-51)

A particularly well-known blend is that of poly(vinyl chloride) with dioctyl phthalate; the plasticizer extent can reach a value as high as 50 % and the T_g can be lowered by as much as 100 °C.

Flory proposed a constant value of $(\alpha_{liq} - \alpha_g)$, equal to 4.8×10^{-4} K⁻¹ for all polymers. Actually, this value is not universal; but, whatever the polymer considered, the measured ones generally fall in that range.

General Reference

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2.4.2 Heat Decomposition Temperature

The way in which a polymer degrades under the influence of thermal energy in an inert atmosphere is determined, on the one hand, by the chemical structure of the polymer itself, on the other hand by the presence of traces of unstable structures (impurities or additions). Thermal degradation does not occur until the temperature is so high that primary chemical bonds are separated. Pioneering work in this field was done by Madorsky and Straus ^[16], who found that some polymers (poly(methyl methacrylate)), poly(α -methyl styrene) and poly(tetrafluoroethylene)) mainly form back their monomers upon heating, while others (like polyethylene) yield a great many decomposition products. These two types of thermal polymer degradation are called chain depolymerization and random degradation.

Thermal Degradation

For many polymers thermal degradation is characterized by the breaking of the weakest bond and is consequently determined by a bond dissociation energy. Since the change in entropy is of the same order of magnitude in almost all dissociation reactions, it may be assumed that also the activation entropy will be approximately the same. This means that, in principle, the bond dissociation energy determines the phenomenon. So it may be expected that the temperature at which the same degree of conversion is reached will be virtually proportional to this bond dissociation energy. **Table 2.3** summarizes the most important data about the thermal degradation of polymers; these data are mainly taken from Madorsky and Strauss ^[16] and from Korshak *et al.*^[17] and Arnold ^[18].

	<i>T_{d,0}</i>	T _{d,1/2}	E _{act}	Monome	r k ₆₂₃	Char yield
polymer	(K)	(К)	(kJ/mol)	yield (%)	(%/min)	(%)
poly(methylene)	660	687	300	0	4.10 ⁻³	0
poly(ethylene)	653	677	264	0	8.10 ⁻³	0
poly(propylene)	593	660	243	0	7.10 ⁻²	0
poly(isobutylene)	-	621	205	20	2.7	0
poly(styrene)	600	637	230	~50	0.25	0
poly(m-methylstyrene)	-	631	234	45	0.90	0
poly(α -methyl styrene)	-	559	230	>95	228	0
poly(vinyl fluoride)	623	663	-	-	-	-
poly(vinyl chloride)	443	543	134	0	170	22
poly(trifluoro ethylene)	673	685	222	~1	2.10 ⁻²	-
poly(chloro-trifluoro ethylene)	-	653	239	27	4.10 ⁻²	-
poly(tetrafluoro ethylene)	-	782	339	>95	2.10 ⁻⁶	0
poly(vinyl cyclohexane)	-	642	205	0.1	0.45	0
poly(vinyl alcohol)	493	547	-	0	-	7
poly(vinyl acetate)	-	542	-	0	-	-
poly(acrylo-nitril)	563	723	-	-	-	15
poly(methyl acrylate)	-	601	-	0	10	0
poly(methyl methacrylate)	553	610	218	95	5.2	0
poly(butadiene)	553	680	260	2	2.10 ⁻²	0
poly(isoprene)	543	596	250	-	-	0
poly(p-phenylene)	>900	>925	-	0	-	85
poly(benzyl)	-	703	209	0	6.10 ⁻³	-
poly(p-xylylene)=	_	715	206	0	2 10 ⁻³	_
poly(p-phenyleneethylene)	-	/15	300	0	2.10	-
poly(ethylene oxide)	-	618	193	0	2.1	0
poly(propylene oxide)	-	586	147	1	5/20	0
poly(2,6-dimethyl	723	753	-	0	-	25
<u>p-phenylenoxide)</u>	725	, 33		0		
poly(ethylene terephtalate)	653	723	-	0	-	17
poly(dian terephtalate)	673	~750	-	0	-	20
poly(dian carbonate)	675	~750	117	0	-	30
poly(hexamethylene adipamide)	623	693	-	-	-	0
poly(ɛ-caproamide) (Nylon 6) poly(p-phenylene	623	703	180	-	-	0
terenttalamide)	~720	~800	-	-	-	~40
poly(pyromellitide) (Kapton)	723	~840	-	-	-	70
poly(m-phenylene		5.0				
2,5-oxadiazole)	683	~800	-	-	-	30
cellulose	500	600	210	-	-	7

 Table 2.3
 Thermal degradation of typical polymers
 [16-18]

In **Figure 2.6**, the dissociation energy of the weakest bond of the same polymers, supplemented with the data of a number of radical initiators (peroxides and azo compounds) is plotted against the most characteristic index of the heat resistance, viz. the temperature of "half decomposition" ($T_{d,1/2}$). The relationship is evident, though not sufficiently accurate for a reliable estimate of $T_{d,1/2}$.

The process of thermal decomposition or pyrolysis is characterized by a number of experimental indices:

a. The temperature of initial decomposition ($T_{d,0}$). This is the temperature at which the loss of weight during heating is just measurable (inclination point of the loss of weight/temperature curve).

b. The temperature of half decomposition $(T_{d,2/l})$. This is the temperature at which the loss of weight during pyrolysis (at a constant rate of temperature rise) reaches 50% of its final value.

c. The temperature of the maximum rate of decomposition ($T_{d,max}$), measured as the rate of loss of weight (at a standardized rate of temperature rise).

d. The average energy of activation ($E_{act,d}$), determined from the temperature dependence of the rate of loss of weight.

e. The amount of char residue at the end of the pyrolysis (at a standard temperature, normally 900 °C).



Figure 2.6 Correlation between temperatures of half decomposition and dissociation energy of weakest bond ^[14].

These indices, especially the characteristic temperatures, are dependent on the rate of heating (rise of temperature) applied during the pyrolysis (normally about 3K/min). At increasing rate of heating the characteristic temperature shifts to a higher value.

 Table 2.3 shows measured values of the main indices.
 They appear to be interrelated:

$$T_{d,0} \approx 0.9 T_{d,1/2}$$
 (2-52)

$$T_{d,\max} \approx T_{d,1/2} \tag{2-53}$$

$$E_{act,d} \approx T_{d,1/2} - 423$$
 (2-54)

As mentioned earlier, there are two types of thermal decomposition: chain depolymerization and random decomposition. Chain depolymerization is the successive release of monomer units from a chain end or at a weak link, which is essentially the reverse of chain polymerization; it is often called depropagaion or unzippering. This depolymerization begins at the ceiling temperature. Random degradation occurs by chain rupture at random points along the chain, giving a disperse mixture of fragments which are usually large compared with the monomer unit. The two types of thermal degradation may occur separately or in combination; the latter case is rather normal. Chain depolymerization is often the dominant degradation process in vinyl polymers, whereas the degradation of condensation polymer is mainly due to random chain rupture.

The overall mechanism of thermal decomposition of polymers has been studied by Wolfs *et al.* They used polymers in which the link between the structual units (CH₂-bridges) was radioactive, so that the course of decomposition could be traced by radioactivity measurements in gas and residue, together with chemical and elementary analysis.

The basic mechanism of pyrolysis is sketched in **Figure 2.7**. In the first stage of pyrolysis (<550 °C) a disproportionation takes place. Part of the decomposing material is enriched in hydrogen and evapolated as tar and primary gas, the rest forming the primary char. In the second phase (>550 °C) the primary char is further decomposed, i.e. mainly dehydrogenated, forming the secondary gas and final char. During the disproportionation reaction, hydrogen atoms of the aliphatic parts of the structual units are "shifted" to "saturate" part of the aromatic radicals, as is visualized by the simplified scheme:

$$(-(A)-CH_2-(A)-CH_2-)_n \rightarrow 2[\cdot (A)-CH_2 \cdot] \rightarrow H(A)CH_3 + -(A)-CH_2 - I_2 - I$$

where A is an aromatic nucleus.

The hydrogen shift during disproportionation is highly influenced by the nature of the structual groups. Groups which are capable of reacting with H atoms of the aromatic nucleus give rise to postcondensation (cross-linking); this occurs if the aromatic nucleus also contains -OH or =O groups. The char residue then is higher than in the case of non-substituted aromatic units. On the other hand, if the aromatic nucleus contains alkyl groups, the alkyl hydrogen may act as an extra source of hydrogen atoms; the formation of tar is enhanced in this case.



Figure 2.7 Basic mechanism of pyrolysis.

Kinetics of Thermal Degradation

Random thermal degradation can usually be described as a first-order reaction (loss of weight as a parameter) if the decomposition products are volatile. Chain depolymerization has been extensively studied by Simha and Wall^[19]. The two factors that are important for the course of the depolymerization are:

- (1) the reactivity of depropagating radical and
- (2) the availability of a reactive hydrogen atom for chain transfer.

All polymers containing α -hydrogens (such as polyacrylates, polyolefins, etc.) give poor yields of monomer; conversely, polymethacrylates and p- α -methylstyrenes five high yields of monomer, due to the blocking of chain transfer by the α -methyl group. Poly(tetrafluoroethylene) gives high yields of monomer because the strong C-F bonds are resistant to transfer reactions.

Also this type of degradation can be described by an overall quasi-first-order reaction, but the kinetic scheme may be complicated. Besides the rate constant two other parameters can be obtained by kinetic analysis:

the transfer constant =
$$k_{tr} = \frac{\text{probability of transfer}}{\text{probability of initiation}}$$
 (2-55)

the kinetic chain length =
$$\Lambda_{kin} = \frac{\text{probability of propagation}}{\text{probability of (termination + transfer)}}$$
 (2-56)

For polyethylene $\Lambda_{kin} \approx 0$ (no monomer produced); for poly(methyl methacrylate) $\Lambda_{kin} \approx 200$ (nearly 100 % monomer produced).

General Reference

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2.5 Conclusion

This chapter provided the background knowledge which is necessary for designing base materials of POF. Firstly, we reviewed the importance of radical polymerization in bulk. In this method, we can obtain highly pure polymers without any impurities and contaminants. From the overview of intrinsic three factors affecting attenuation of POF, especially from the Morse potential theory for absorption and the fluctuation theory for light scattering, we can say one of the effective ways to obtain polymers with high transparency is fluorination. Substituent with fluorine reduces the refractive index, thus leads to less scattering, and also reduces the vibrational absorption. To obtain a high T_g , cohesive properties of polymer molecular structure should be considered. Molecular interactions decrease the mobility of chains, according to the kinetic theory, which must contribute to an increase of T_g . The size of certain atoms or the geometry of some substituents may contribute to stiffen the chain backbone and cause an increase of T_g . However, it is still hard to theoretically predict T_g of polymers from chemical structures and the clear guideline for calculating or expecting T_g has not been established. Heat decomposition of polymers is divided into two types: depolymerization and random decomposition. Both degradations can be characterized by the breaking of the weakest bond and is consequently determined by a bond dissociation energy. While the mechanism of thermal degradation is too complicated to estimate accurately, the important thing we have to note is the bond dissociation energy.

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Chapter 3 Effect of Partial Halogenation on Fiber Attenuation -Poly(2,2,2-Trifluoro(chloro)ethyl Methacrylate)-

3.1 Preface

In chapter 2, basic knowledge for designing POF base materials were summarized and influential factors were described in detail. Previous studies have provided a clear guideline to decrease the attenuation of POF; substituent with fluorine reduces the refractive index, thus leads to less scattering, and also reduces the vibrational absorption, whereas the way of increasing thermal properties such as T_g and T_d has not become clear enough. Therefore, as the first approach to prepare a low-loss and thermally stable GI POF for home network, we started this work from the investigation of an effective method for obtaining polymers with low attenuation.

As mentioned in section 1.4, there have been previous reports on low-loss POFs consisting of perdeuterated PMMA^[1,2] and perfluorinated polymer (CYTOP[®])^[3-7]. They have no C-H bonds in its structures, which is the major factor of attenuation at the emission wavelength of the light source ^[8, 9], thus exhibit excellent low-loss characteristics. However, the synthesis procedures of monomers are complicated and hence the fibers are overpriced for general consumers. That was the biggest problem. On the other hand, surprisingly few studies have so far been made at partial substitution. Actually such a low attenuation property is not necessary for the very short reach networks in houses, and the attenuation of up to 200 dB/km is acceptable.

Compared to all hydrogen substituted polymers, a partial substitution can be obtained by simple procedures and is more cost effective. We believed that the critical factor for reducing attenuation should be not the per-substitution but the amount of C-H bonds per unit volume of polymers, that is, we expected that enough low-loss characteristics would be obtained by partial substitutions. To clarify the validity of this hypothesis, we investigated two kinds of methacrylates: poly(2,2,2-trifluoroethyl methacrylate) and poly(2,2,2-trichloroethyl methacrylate). Both

monomers are commercially available and less expensive and bone structures are very similar to that of MMA. Through the experiment, we also examined thermal properties of these polymers.

3.2 Materials

2,2,2-trifluoroethyl methacrylate (TFEMA) and 2,2,2-trichloroethyl methacrylate (TCEMA) were purchased from TOSOH F-TECH, Inc. and Oosaka Organic Chemical Industry Ltd. in Japan, respectively. Methyl methacrylate (MMA) was purchased from Mitsubishi gas chemical company, Inc. *Di-tert*-butyl peroxide (PERBUTYL[®] D: PBD), *tert*-butyl peroxi-2-ethylhexanoate (PERBUTYL[®] O: PBO) were brought from NOF Co. Benzoyl peroxide (BPO), *n-butyl* mercaptan (*n*-BM), *n-lauryl* mercaptan (*n*-LM), diphenyl sulfide (DPS), benzyl benzoate (BEN), methanol (MeOH), and dichloromethane (CH₂Cl₂) were purchased from Wako Pure Chemical Industries, Ltd. TFEMA and TCEMA were freshly distilled with traditional method at 56 °C / 110-115 mmHg and 67-68 °C / 10 mmHg, respectively, before use. The free radical initiator BPO was purified by recrystallization from methanol and all the other chemicals were used directly without further purification. Chemical structures are summarized in **Figure 3.1**.

<Monomer>





 $H_2C \xrightarrow{CH_3} 0$ $O \xrightarrow{CH_2 - CCI_3}$

methyl methacrylate (MMA) 2,2,2-trifluoroethyl methacrylate (TFEMA)

2,2,2-trichloroethyl methacrylate (TCEMA)

<Initiator>



Benzoyl peroxide (BPO)



Di-tert-butyl peroxide (PERBUTYL[®] D: PBD)



tert-butyl peroxi-2-ethylhexanoate (PERBUTYL® O: PBO)

<Chain transfer agent>

CH₃(CH₂)₃SH	<i>n-butyl</i> mercaptan (<i>n</i> -BM)

CH₃(CH₂)₁₁SH *n-lauryl* mercaptan (*n*-LM)

<Dopant>



Benzyl benzoate (BEN) n_D=1.568

Diphenyl sulfide (DPS) n_D=1.633

Figure 3.1 Chemical structures of monomers, initiators, chain transfer agents, and low-molecular-weight dopants used in chapter 3.

3.3 Preparation and Characterization of Polymers

For polymerization of TFEMA, the monomer mixtures, including PBO (0.3 mol%) as an initiator and *n*-BM (0.50 mol%) as a chain transfer agent were transferred into a glass ampule (ϕ 10 mm). The polymerization reactions were carried out at 70 °C in a water bath for 24 h. On the other hand, for polymerization of TCEMA, the monomer mixtures, including PBD (0.3 mol%) as an initiator and *n*-LM (0.50 mol%) as a chain transfer agent were transferred into a glass ampule. The polymerization reactions were carried out at 120 °C in an oil bath for 24 h. Preparation conditions are summarized in **Table 3.1**.

Obtained bulks were utilized for evaluating refractive indices, densities, and transmittances by a prism coupler and a density measurement kit, and an UV-VIS spectrophotometer, respectively. The amount of C-H bonds per unit volume compared with that for PMMA was calculated by

C - H bonds
$$\binom{\%}{=} \frac{n_2}{n_1} \cdot \frac{m_1}{m_2} \cdot \frac{d_2}{d_1} \times 100$$
 (3-1)

where d is density of sample, m is molecular weight, and n is number of C-H bond per unit monomer. The number of subscript 1 and 2 denote PMMA and others: poly(TFEMA) and poly(TCEMA). Bulks were solved into dichloromethane or chloroform then were poured into a large amount of methanol or ethanol with vigorous stirring to precipitate polymers. Purified polymer samples were died under vaccum at 90 °C for 24 h. The purified polymers obtained were used to measure glass transition temperatures and heat decomposition temperatures by using DSC and TG instrument, respectively. These basic properties are summarized in **Table 3.2**. Transmittance spectra and thermogravimetric curves are shown in **Figures 3.2** and **3.3**, respectively.

Polymer	Monomer	Initiator	Chain Transfer	Temperature	Time
poly(TFEMA)	TFEMA 8 g	PBO 0.3 mol%	n-BM 0.5 mol%	70 °C	24 h
poly(TCEMA)	TCEMA 8 g	PBD 0.3 mol%	n-LM 0.5 mol%	120 °C	24 h

 Table 3.1
 Preparation condition of poly(TFEMA) and poly(TCEMA)^{a, b}

^a The diameter of glass ampoule was 10 mm.

^b Ampoules were covered with stretched film (Dura[®] seal) without vacuumed.

Polymer	Refractive index ^{a, b}	Density ^a (g/cm ³)	C-H bond ^d (%)	$T_g (^{\circ}C)^{c}$	<i>T_{d5}</i> (°C) ^c
poly(TFEMA)	1.4182	1.41	64	75	289
poly(TCEMA)	1.5171	1.48	51	130	271

 Table 3.2
 Basic properties of poly(TFEMA) and poly(TCEMA)

^a Refractive indices and densities are the values of polymer bulks.

^b Refractive index were measured by the prism coupling method at 409.2, 650.3, 833.7, and 1546 nm. The value here is at D spectrum (589 nm) approximated by the Sellmeier equation using these four values.

^c T_g and T_{d5} (5% weight loss temperature) are the values of precipitated polymers.

^d The percentage means a ratio of amount of C-H bonds per unit volume compared with that for PMMA.



Figure 3.2 Transmittance spectra of PMMA, poly(TFEMA), and poly(TCEMA). Optical paths are 3.0-cm length.



Figure 3.3 Thermogravimetric curves of PMMA, poly(TFEMA), and poly(TCEMA).

The refractive index n of a material depends according to Lorentz-Lorenz relationship ^[10, 11], on the polarizability P of all the molecules residing in a uniform field:

$$\frac{n^{2}-1}{n^{2}-2} = \frac{4}{3}\pi P = \frac{4}{3}\pi N\alpha = \frac{4}{3}\pi N\frac{\mu}{E} \quad \left(\equiv \frac{[R]}{V} \equiv \phi\right)$$

$$n = \sqrt{\frac{2\phi+1}{\phi-1}}$$
(3-2)

The polarizability P is given by the number N of molecules per unit volume and the polarizability α of the isolated molecule. The polarizability α in turn, depends on the dipole moment μ induced by an electric field of strength E. Consequently, both α and n increase with increasing number and mobility of electrons in the molecule. Thus, carbon has a much higher polarizability than hydrogen. Since for this reason the hydrogen contribution to the polarizability can, to a first approximation, be ignored, most carbon-carbon chain polymers have about the same refractive index. Deviations from this "normal value" only occur when there are large side groups or if highly or lowly polar groups are present. **Table 3.2** shows that the refractive index of poly(TFEMA) is lower than that for PMMA (n_D=1.492) and the refractive index of poly(TCEMA) is in contrast higher. C-F and C-Cl bond has a lower and higher polarizability, respectively, fluorinated and chlorinated polymers generally exhibit relatively low and high refractive indices.

The percentages of C-H bond per unit volume in poly(PTFEMA) and poly(TCEMA) compared with that for PMMA were 64 % and 51 %, respectively. While they have the same born structure, chlorine atom occupies a larger volume than fluorine atom, thus the percentage of C-H bonds per unit volume in poly(TCEMA) is more effectively reduced. **Figure 3.2** shows the validity of the calculation. Peak intensities observed in poly(TCEMA) caused by the C-H vibrational absorption are actually smaller than that for poly(TFEMA). What is important here is that we can obtain highly transparent polymers by the partial substitution with both fluorine and chlorine.

Intrinsic glass transition temperature (T_g) of poly(TFEMA) was as low as 75 °C, whereas poly(TCEMA) showed a high T_g of 130 °C (the term of "intrinsic" means that the sample polymer has no plasticizer such as remaining monomer). The low T_g of poly(TFEMA) is not strongly related with fluorination but also with the long side chain. We confirmed that poly(ethyl methacrylate) also showed a similar low T_g . As shown in **Table 2.2**, polymers with long side chain, generally exhibit relatively low T_g since there are large amounts of free volume which increase the mobility against heat. On the other hand, while poly(TCEMA) should also have the large free

volume, the end group of side chain C-Cl₃ is much bulkier and heavier than those of C-H₃ and C-F₃ groups; the rotational movement is strictly hindranced and the mobility is considered to be reduced. We can see the similar effect in polymers shown in **Table 2.2**. For instance, the effect of introducing pentachlorophenyl groups for increasing T_g is much stronger than that of phenyl groups with no substituents.

Regarding heat decomposition temperature, 5% weight loss temperatures (T_{d5}) of poly(TFEMA) and poly(TCEMA) were 289 °C and 271 °C, respectively. **Figure 3.3** shows poly(TFEMA) has a high thermal stability which is compatible with that of PMMA, but on the other hand, poly(TCEMA) was found to start degrading at a lower temperature by around 20 °C. As mentioned in section 2.4, a heat decomposition of polymer normally depends on the weakest bond and is consequently characterized by a bond dissociation energy. Representative properties of hydrogen, fluorine, and chlorine are summarized in **Table 3.3**. The dissociation energy of C-Cl bond (78 kcal/mol) is smaller than those of C-H (99.5 kcal/mol) and C-F bond (116 kcal/mol) and this generally leads to low decomposition temperatures of chlorine compounds.

	Н	F	Cl
Outermost electron configuration	1s ¹	2s ² 2P ⁵	$3s^23P^53d^0$
Electronegativity (Pauling)	2.1	4.0	3.0
Ionization energy (kcal/g atom)	315.0	403.3	300.0
Electronic affinity (kcal/g atom)	17.8	83.5	87.3
C-X Bonding energy (kcal/mol)	99.5	116	78
C-X Bond length (angstrom)	1.091	1.317	1.766

 Table 3.3
 Comparison among hydrogen, fluorine, and chlorine atom

3.4 Fabrication of GI POF

Through the evaluation of transmittance using poly(TFEMA) and poly(TCEMA) bulks, we have clarified that the partial halogenation is effective method for reducing the C-H absorption losses which is the biggest cause of increasing the attenuation. Their advantages are the simple monomer synthesis and the polymerization requires no complicated procedures, that is, their low costs. For transmission media desired in short reach networks such as home network, these partial halogenated acrylates are believed to be promising candidates of POF base materials. However, the above experiment only shows that the small bulk with the length of 3.0 cm exhibit higher transmittance than that for PMMA. To confirm the potential of partial halogenation, it is necessary to demonstrate the low loss characteristic especially less than 200 dB/km at 670-680 nm wavelength by using fibers based on these polymers. In this section, the preparation methods of GI POFs based on each polymers are described in detail.

3.4.1 Poly(2,2,2-Trifluoroethyl Methacrylate) — Interfacial-Gel Polymerization Method

GI preforms based on poly(TFEMA) were prepared by the interfacial-gel polymerization technique ^[13, 14]. First, a glass tube charged with TFEMA monomer mixtures including PBO and n-BM as the initiator and chain transfer agent, respectively, is rotated on its axis at 3,000 rpm in an oven at 70 °C for 3-6 h. TFEMA monomer is placed on the inner wall of the glass tube due to centrifugal force, and gradually is polymerized. The schematic diagram is shown in **Figure 3.4**. After a heat treatment at 90 °C for 24 h, the polymer tube based on poly(TFEMA) is obtained as a cladding layer of a GI preform. Then the tube is filled with a core solution with PBO and *n*-BM. As a low-molecular-weight dopant, benzyl benzoate (BEN) is added to the core mixture. In the case of GI POF based on PMMA, diphenyl sulfide (DPS) has been typically utilized as the dopant for forming a GI profile in the core region. However, the solubility between TFEMA and DPS is poor and the obtained polymer exhibits hazy collar. From the explorer of several dopants, we found that BEN is the best dopant to be added into TFEMA. The tube filled with the mixture is heated in an oil bath at 80 °C for 48 h under nitrogen pressure of 0.2 MPa.

To add the pressure, we used an autoclave. This polymerization method in the autoclave with a certain pressure has been conventionally utilized for preparing GI preforms based on PMMA. Previous studies clarified that the amorphous polymer glasses such as PMMA polymerized at lower temperature than the glass transition temperature exhibit extremely high scattering losses because of density fluctuations ^[15-17]. Therefore, to obtain a low loss preform based on PMMA, the core solution had to be polymerized at as high as 120 °C, which is slightly higher than the T_g of PMMA. However, such a high temperature leads to numerous bubbles during the polymerization, since the boiling point of MMA is around 100 °C. In this way, the autoclave method was developed as the solution.

In the case of poly(TFEMA), it was not necessary to add the high pressure because the T_g of poly(TFEMA) is as low as 75 °C and the polymerization temperature of 80 °C which is much lower than the boiling point of TFEMA monomer was enough for eliminating the heterogeneous structure in the polymer matrix. However, TFEMA tends to degrade in an air atmosphere because of side reactions with oxygen, thus we adopted the autoclave method in which surrounding oxygen is removed by the nitrogen flow. The schematic representation of the core polymerization in the autoclave with nitrogen pressure is described in **Figure 3.5**.



Figure 3.4 Schematic representation of a polymer tube preparation.



Figure 3.5 Schematic representation of a core polymerization in an autoclave.
In this interfacial-gel polymerization process, the inner wall of the poly(TFEMA) tube becomes slightly swollen by the monomer-dopant mixture to form the polymer gel phase. The reaction rate of the polymerization is generally faster in the gel phase because of the "gel effect." Therefore, the polymer phase grows from the inner wall of the tube to the center. During this process, the TFEMA monomer can diffuse into the gel phase more easily than the dopant molecules because the molecular volume of dopant, which contains benzene rings, is larger than that of monomer. Thus, the dopant molecules are concentrated in the center region of the core to form an almost quadratic refractive index profile. The mechanism of the interfacial-gel polymerization technique is described in **Figure 3.6**.



Figure 3.6 Conceptual diagram of the interfacial-gel polymerization technique.

At that time, since we did not have any knowledge for preparing GI preforms based on other polymers except for PMMA, we firstly tried to prepare the GI preform based on poly(TFEMA) in the same manner of PMMA-based GI preform. During this polymerization process, however, the core solution dissolved the cladding layer and the cladding layer was crushed since the compatibility between poly(TFEMA) and TFEMA monomer is higher than that for the combination of PMMA and MMA. Thus, polymer tube was strengthened by increasing the weight-average molecular weight from 6.3×10^4 to 3.2×10^5 and the thickness from 40 % to 57 % (compared to the diameter of the

polymer tube). As the result, we could successfully obtain the preform without any cracks. **Figure 3.7** shows the improvement of design. The photographs indicate the upper part of preforms.



Figure 3.7 Improvement designs of GI preforms based on poly(TFEMA). Above photographs show the upper part of preforms. (a) Original one (b) Weight-average molecular weight is increased from 6.3×10^4 to 3.2×10^5 . (c) In addition to the effect of (b), thickness of cladding layer is increased from 40 % to 57 % (compared to the diameter of the polymer tube).

The GI POF with the diameter of 750 μ m was successfully prepared by heat-drawing of the obtained preform at 190-200 °C. The photograph of the heat drawing apparatus in our laboratory is shown in **Figure 3.8**. With all the high potential, the attenuation measured by the cut-back method was as high as 484 dB/km at 650 nm where the lowest loss window of the fiber. From the measurement of refractive index profile, it was clarified that the core region was highly shifted from the original boundary between the core solution and the tube to the cladding layer. As the result of dopant diffusion, the numerical aperture (NA) was as low as 0.15 and the thickness of cladding layer was only 10 % of the fiber diameter. Thus the incident light was not concentrated into the center core but the most light was lost soon. To solve the problem, we tried to shorten the polymerization time of the core solution by increasing the amount of initiator. **Figure 3.9** shows refractive index profiles of GI POFs based on poly(TFEMA) prepared with several amount of initiators. By increasing the amount of initiator, produced radicals per unit time are increased and the polymerization is completed in a shorter time. When the initiator of 0.054 mol% was added to the core solution, the optimum refractive index profile calculated by the modal and material dispersion of poly(TFEMA) was formed. Finally, a GI POF based on poly(TFEMA) with the low attenuation and high bandwidth was successfully obtained. The details will be described in section 3.5. Original and improved compositions of the cladding and core layers are summarized in Tables 3.4.



Figure 3.8 Photograph of the heat-drawing apparatus of preforms we utilized in this study.



Figure 3.9 Refractive index profiles of GI POFs based on poly(TFEMA) prepared with several amount of polymerization initiator. Open circles show the optimum index profile (index exponent: g=2.42) calculated by the modal and material dispersion.

	Cladding	Core
Original	TFEMA 208 g PBO 0.334 mol% <i>n</i> -BM 0.354 mol%	TFEMA 85 g PBO 0.011 mol% <i>n</i> -LM 0.199 mol% BEN 8.77 mol%
Improved	TFEMA 233 g PBO 0.334 mol% <i>n</i> -BM 0.093 mol%	TFEMA 85 g PBO 0.054 mol% <i>n</i> -LM 0.199 mol% BEN 8.77 mol%

 Table 3.4
 Cladding and core compositions of GI POFs based on poly(TFEMA)

3.4.2 Poly(2,2,2-Trichloroethyl Methacrylate) — Rod-in-Tube Method

In the similar way to poly(TFEMA), we firstly tried to prepare a GI preform based on poly(TCEMA) by the interfacial-gel polymerization technique. Both the core and cladding layers were prepared by using poly(TCEMA). However, the mechanical property of poly(TCEMA) was very weak and the preform was too brittle to make the fiber. The mechanical strength of polymer is related to the bond strength between molecular chains and the number density of molecular chain in unit area. In particular, the latter parameter strongly affects the brittleness. In 1972, Vincent reported a correlation between critical tensile strength and polymer cross-sectional area ^[18]. From his research through thirteen kinds of polymers, a good agreement between theses two factors was clarified; the tensile strength increased with decreasing the cross-sectional area. We calculated the intrinsic volume of MMA, TFEMA, and TCEMA unit in its polymer chain and compared their values. As the result, for MMA, TFEMA, and TCEMA, intrinsic volumes were 58, 81, and 98 (cm³/mol), respectively. Full details of the calculation are described in Appendix E. These results indicate that the brittleness of poly(TCEMA) might be due to the bulky structure of TCEMA and the corresponding small number density of molecular chain in unit area.

To prepare the fiber based on poly(TCEMA), we utilized a PMMA tube as the cladding layer (as mentioned in section 3.3, the refractive index of poly(TCEMA) is higher than that of PMMA). Before preparing the polymer tube, the round bottom of the glass tube has to be filled with polymers to obtain a tube without any holes. We investigated the best design of preform structures with considering the effect of bottom part. As the dopant for forming a parabolic refractive index profile, diphenyl sulfide (DPS) was added to the core solution. For the cladding, BPO and *n*-BM were used as the initiator and chain transfer agent, respectively. On the other hand, PBD and *n*-LM were used for the core. The core solution was polymerized in the autoclave at 120 $^{\circ}$ C for 48 h under nitrogen pressure of 0.6 MPa. Photographs of obtained preforms are shown in **Figure 3.10** with the schematic diagram of the structure.



Figure 3.10 Schematic diagrams and photos of preforms with different structures consisting with PMMA-claddings/bottoms and poly(TCEMA)-cores. The upper and lower pictures show the bottom parts and cross-sectional areas of preforms, respectively.

In the case of using PMMA as both the tube and bottom (left), the core region became hazy as a result of phase separation. During the core polymerization, TCEMA monomer dissolves the tube and bottom, then PMMA polymer coils are gradually diffused into the core solution. That is to say, the final polymer is kind of a blend polymer. The big difference of refractive index between PMMA and poly(TCEMA) causes the highly light scattering. To solve the problem, the structure with double cladding and double bottom (right) was investigated. While the scattering intensity was drastically reduced, you can see the boundary between the core and inner cladding is still hazy.

As the next solution, we tried to use a copolymer of MMA and TCEMA as the tube and bottom. To maintain the mechanical strength of the tube, the content of TCEMA was decided to be 17 mol%. Since the refractive index of the copolymer is 1.497, which is slightly higher than that of PMMA, the heterogeneous structure of refractive index was expected to be reduced. Schematic diagrams and photos of preforms with different structures consisting with copolymer-claddings/bottoms and poly(TCEMA)-cores are shown in **Figure 3.11**.



Figure 3.11 Schematic diagrams and photos of preforms with different structures consisting with copolymer (MMA/TCEMA=83/17 mol%)-claddings/bottoms and poly(TCEMA)-cores. The upper and lower pictures show the bottom parts and cross-sectional areas of preforms, respectively.

As we expected, the light scattering was reduced by adopting the copolymer double cladding and double bottom. The obtained preform could be heat drawn without any cracks and the GI POF was successfully obtained for the first time. However, the attenuation was much higher than 200 dB/km. From he result of transmittance measurement, the GI POF based on poly(TCEMA) should potentially have a lower attenuation than poly(TFEMA). There must be still extrinsic factors to increase the attenuation.

Therefore, we have investigated another preparation method for GI preforms: a rod-in-tube method ^[19]. In the rod-in-tube method, a core rod with a dopant and a cladding tube are prepared separately. Monomer mixtures with PBD as an initiator and *n*-LM as a chain transfer agent were transferred into a glass ampule and subjected to repeated freeze-pump-thaw cycles; this was followed by sealing under vacuum with flame. The polymerization reaction was carried out at 120 °C in an oil bath for 48 h. For the dopant, DPS of 5.3 mol% was added to the core solution. The cladding tube based on PMMA was prepared in the same manner as in the previous study. The core rod was inserted into the tube, and both ends were closed with Teflon[®] rods. The rod was then covered with a heat-shrinkable tube and heated in an vacuumed oven at 150 °C for 2 h. During the heat treatment, the core rod and cladding tube adhered to each other; the dopant diffused into the cladding layer, forming the GI profile. This way, the scattering loss for the core region did not

increase since both layers consisted of polymers. Moreover, the mechanism of the dopant diffusion obeys Fick's law ^[20-22] and is the same as for the co-extrusion process ^[23, 24]. The heat drawing for the GI preform was carried out at 220–240 °C, and the fiber diameter was controlled to be around 700 μ m. Finally, we succeeded in preparing a low loss GI POF based on poly(TCEMA). The schematic diagram of the rod-in-tube method is shown in **Figure 3.12**.

The interfacial-gel polymerization method has an advantage of being able to precisely control the refractive index profile ^[25-27], whereas the scattering loss of the core region tends to greatly increase when the core and cladding consist of different materials. To avoid the heterogeneous structure caused by the polymer blend, we had investigated the copolymeric double cladding as mentioned above, however the process was complicated and impurities such a dust in air could be included in the core region. On the other hand, in the rod-in-tube method, we can easily try several combination of core and cladding materials.



Figure 3.12 Schematic representation of the rod-in-tube method.

3.5 Characterization of GI POF 3.5.1 Attenuation

Attenuations of poly(TFEMA)-based and poly(TCEMA)-based GI POFs obtained in the previous section were measured by the cut-back method ^[28]. A tungsten lamp and a spectrum analyzer were used as a light source and a detector, respectively. A serious problem in the methacrylic-core POF such as PMMA-based GI POF is large attenuation at the emission wavelength of VCSEL (670-680 nm) due to the absorption loss by high-harmonic of C-H vibration (C-H overtone) in the polymer molecule. **Figure 3.13** shows the comparison of attenuation spectra among PMMA-, poly(TFEMA)-, and poly(TCEMA)-based GI POF. The magnification of around the emission wavelength is shown in **Figure 3.14**, and the attenuation values at several wavelengths are listed in **Table 3.5**.



Figure 3.13 Comparison of attenuation spectra among PMMA-, poly(TFEMA)-, and poly(TCEMA)-based GI POF. Wavelength region is from 500 nm to 800 nm.



Figure 3.14 Comparison of attenuation spectra among PMMA-, poly(TFEMA)-, and poly(TCEMA)-based GI POF. Wavelength region is from 600 nm to 700 nm.

Table 3.5	Attenuation	values of	of PMMA-,	poly(TFEMA)-,	and poly(TCEMA)-based	GI POFs
-----------	-------------	-----------	-----------	---------------	-----------	--------------	---------

	Wavelength			
	650 nm	670 nm	680 nm	
PMMA ^a	194 (dB/km)	295	323	
poly(TFEMA) ^{a,b}	71	127	152	
poly(TCEMA) ^c	61	104	136	

^a Preform was prepared by the interfacial-gel polymerization technique.

^b Both the core and cladding consist of poly(TFEMA).

^c Preform was prepared by the rod-in-tube method and the core and cladding consist of poly(TCEMA) and PMMA, respectively.

As shown in **Figure 3.13**, C-H peaks of poly(TFEMA)- and poly(TCEMA)-based GI POFs were much smaller than those of PMMA-based GI POF. We have already confirmed that the percentage of C-H bonds per unit volume in poly(TFEMA) and poly(TCEMA) are 64% and 51%, respectively, compared to that for PMMA. Measured attenuation spectra seem to be fitted well to the estimation. The emission wavelength of VCSEL (670-680 nm) are located in between the fifth and sixth harmonic C-H vibrational absorptions, so that the reduction of these peaks directly affect to the attenuation at the wavelength region. While the attenuation at wavelengths of 670–680 nm for the PMMA-based GI POF was as high as 295–323 dB/km due to the strong C-H absorption losses, the poly(TFEMA)- and poly(TCEMA)-based GI POF had much smaller attenuations of 127–152 dB/km and 104–136 dB/km, which satisfy the required attenuation for the proposed optical home network systems. These results obtained so far prove clearly that the partial halogenation is an effective way to reduce the attenuation of POF.

To keep using the fiber as a transmission medium for home networks, low attenuation should be maintained for a long time such as 20-30 years. The biggest cause of attenuation degradation is water absorption. For the wavelength region of 670-680 nm, the 4th O-H stretching vibration and O-H bending vibration combine. Kaino reported that the attenuation of a POF based on PMMA considerably increased in a humid environment ^[29, 30]. On the other hand, it is known that fluorinated polymers generally have high humid stability. Thus, the GI POF based on poly(TFEMA) is expected to have a higher stability than the GI POF based on PMMA. However, this characteristic depend on not only the core polymer but also the kind of dopant within the core region ^[31, 32]. To confirm the potential of humid stability of poly(TFEMA), a poly(TFEMA) bulk and a PMMA bulk samples were prepared to have exactly the same volume (ϕ 12×300 mm) and water absorptions of polymer bulks were measured by immersing the samples in water at 60 °C. The time series variation is shown in Figure 3.15. The saturated water absorption of poly(TFEMA) was as small as 0.13 wt% and was less than 10% of the absorption for PMMA. This is due to fluorine and the smaller amount of carbonyl groups per unit volume, which tend to produce hydrogen bonds with water molecules. In this thesis, we could not experimentally compare the humid stability using GI POFs, but this result indicates that the partial fluorination potentially contributes not only to the improvement of the attenuation but also the stability of the low attenuation.



Figure 3.15 Amount of absorbed water into PMMA and poly(TFEMA) bulk samples. Time series variation was measured by immersing samples into water at 60 $^{\circ}$ C.

3.5.2 Bandwidth

As described in section 1.3, the bandwidth of GI POF strongly depends on the refractive index profile, and not only the modal dispersion but also the material dispersion must be considered. The material dispersion is induced by the wavelength dependence of the refractive index of the polymer and the finite spectral width of the light source. To compare the difference of bandwidth due to the difference of material dispersions, the same light source (InGaAsP LD) with the wavelength of 650 nm and the spectral width was 2.8 nm was utilized in all bandwidth measurements. The material dispersion can be calculated by the wavelength dependence of the refractive index. The calculation method was described in section 1.3. Wavelength dependences of the refractive index and the material dispersion of PMMA, poly(TFEMA), and poly(TCEMA) are shown in **Figures 3.16**, and **3.17**, respectively. Refractive indices of these polymer bulks were measured by the prism coupling method at the wavelength of 409.2, 650.3, 833.7, and 1546 nm. Obtained these four plots were approximated by the Sellmeier equation and the wavelength dependence of the refractive index was obtained.

Figure 3.17 indicates that the material dispersion of poly(TFEMA) is the smallest among three polymers. Perfluorinated polymer also has been clarified to have a smaller material dispersion than even silica particularly in the visible to near infrared region, and the effect has been considered to be caused by the fluorine substitution. The small material dispersion means that the fiber potentially has a high bandwidth. Thus, we firstly investigated the bandwidth of the GI POF based on poly(TFEMA). To maximize the bandwidth, it is necessary to form an optimum refractive index profile in the core region and we have to know the optimum index exponent for the polymer. Since the core consist of poly(TFEMA) and dopant, a poly(TFEMA) bulk with BEN was prepared and the wavelength dependence of refractive index were measured in the same manner as described above. Using data of poly(TFEMA) and poly(TFEMA) with BEN, the optimum index exponent was calculated as follows^[33]

$$g_{opt} = 2 - \frac{2n_1}{N_1}P - \Delta \frac{\left(4 - \frac{2n_1}{N_1}P\right)\left(3 - \frac{2n_1}{N_1}P\right)}{5 - \frac{4n_1}{N_1}P}$$

$$N_1 = n_1 - \lambda \frac{dn_1}{d\lambda}$$
(3-1)

where g_{opt} signifies the optimum index exponent, and P that is called as a profile dispersion is written as follows

$$P = \frac{\lambda}{\Delta} \frac{d\Delta}{d\lambda} = \frac{\lambda}{\Delta} \frac{n_2^2}{n_1^2} \left(\frac{1}{n_1} \frac{dn_1}{d\lambda} - \frac{1}{n_2} \frac{dn_2}{d\lambda} \right)$$
(3-2)

where n_1 is the refractive index at the core center, n_2 is the refractive index of the cladding, λ is the wavelength of light, Δ is the relative index difference given by Eq. 1-9. In this way, the optimum index exponent g of a GI POF based on poly(TFEMA) with BEN was calculated to be 2.42. As mentioned above, we have already succeeded in preparing the GI POF with the optimum refractive index profile by controlling the amount of initiator (see Figure 3.9).



Figure 3.16 Comparison of refractive indices among PMMA, poly(TFEMA), and poly(TCEMA).



Figure 3.17 Comparison of material dispersions among PMMA, poly(TFEMA), and poly(TCEMA).

To confirm the difference between poly(TFEMA) and PMMA, a GI POF based on PMMA with the optimum refractive index profile was also prepared. The optimum index exponent of a PMMA-DPS system has been reported to be 2.49^[33]. The refractive index profile of the GI POF measured by using a Interphako is shown in **Figure 3.18**.



Figure 3.18 Refractive index profile of PMMA-based GI POF with the ideal graded index. Solid line and open circles indicate the experimental data and the calculated profile by the power-law form with the index exponent of 2.49, respectively.

The -3dB bandwidths of PMMA- and poly(TFEMA)-based GI POF were measured by the time domain method ^[28]. When the fiber is practically used as the transmission medium of home networks, the fiber is supposed to be directly connected with the light source and launched with smaller NA and spot size than those of the core: restricted mode launch condition as shown in **Figure B.6**. Thus a 1-m silica GI MMF with the core diameter of 50 μ m was utilized as the probe fiber. Output waveforms through the PMMA- and poly(TFEMA)-based GI POF is shown in **Figure 3.19**. The fiber lengths were 50 m. As the reference (input pulse in **Figure 3.19**), the output pulse through a probe fiber was used.



Figure 3.19 Measured output pulse waveforms of PMMA-and poly(TFEMA)-based GI POF for 50 m length. Both fibers have their optimum refractive index profiles. The -3dB bandwidths of PMMA- and poly(TFEMA)-based GI POF were 3.41 and 4.86 GHz, respectively.

The output pulse through the poly(TFEMA)-based GI POF was narrower than that of the PMMA-based. Since both fibers have their optimum refractive index profiles in their core regions, output pulses were not so broaden through the fiber, but we can see the slight difference between PMMA and poly(TFEMA) caused by the difference of material dispersions. Calculated -3dB bandwidths of PMMA- and poly(TFEMA)-based GI POF were 3.41 and 4.86 GHz, respectively, and the high potential of poly(TFEMA) with fluorine substitutions was experimentally demonstrated.

On the other hand, the -3dB bandwidth of obtained GI POF based on poly(TCEMA) was as narrow as 869 MHz for 50-m length. The narrow bandwidth was estimated to be caused by the nonideal refractive index profile. In the case of poly(TCEMA)-based GI POF with PMMA-cladding, the refractive index profile was hard to be measured accurately by the transverse interferometric technique using Interphako, since there was the sharp wall of refractive index on the boundary between the core and cladding. Thus, the profile was evaluated by the near field pattern (NFP) method ^[28]. The light intensity profile through the fiber can be related with the refractive index profile by Eq. B-1. **Figure 3.20** shows the output power through the 50-m fiber launched by a SI POF with the core diameter of 980 µm, that is, in the OFL condition.



Figure 3.20 Normalized power distribution in radial direction through the GI POF based on poly(TCEMA). The test fiber was launched by a SI POF with the core diameter of $980 \,\mu\text{m}$.

As shown in Figure 3.20, the refractive index profile of the fiber based on poly(TCEMA) was found to be an almost step-index like. In the rod-in-tube method, the core and cladding polymer was adhered each other in a vacuumed oven at 150 °C for 2h. We expected that the dopant diffused into the cladding layer, forming the GI profile, during the heat treatment,. However, from the power distribution of Figure 3.20, we can see the dopant diffusion was not enough in the short Thus, the preform was prepared again in the condition of 150 °C for 6 h and the fiber was period. obtained by heat drawing the preform. As the result, the -3dB bandwidth was improved from 869 MHz to 1.32 GHz for 50-m length. The original and improved output pulse waveforms are shown in Figure 3.21. At the same time, however, other problem occurred. The attenuation of the improved fiber was drastically increased particularly in the wavelength region of shorter than 700 As mentioned in section 3.3, poly(TCEMA) has a low decomposition temperature due to the nm. While we have further investigated the way to solve the problem, a weak C-Cl bonds. poly(TCEMA)-based GI POF which simultaneously exhibits a low loss and high bandwidth characteristic has not been obtained so far.



Figure 3.21 Measured output pulse waveforms of poly(TCEMA)-based GI POF for 50 m length. The solid line and broken line indicate the fiber prepared from preforms heated in a vacuumed oven at 150 °C for 2h and 6 h, respectively.



Figure 3.22 Attenuation spectra of GI POFs based on poly(TCEMA). The solid line and broken line indicate the fiber prepared from preforms heated in a vacuumed oven at 150 °C for 2h and 6 h, respectively.

3.5.3 Eye-Pattern

From the bandwidth investigation, the GI POF based on poly(TFEMA) has been clarified to have as high as 4.86 GHz for 50-m length. The performance of the fiber system was confirmed by the eye-pattern method^[28]. Full details of the eye-pattern method will be described in section B.5, but an outline of the technique is explained here. A 1.25 Gbps data transmission through the poly(TFEMA)-based GI POF with the length of 50 m was demonstrated. Random data patterns at 1.25 Gbps from pulse pattern generator (MP1758A, Anritsu Ltd.) were converted to optical signals at 670 nm by a optical Gigabit Ethernet transceiver (EDL1000G, Firecomms Ltd.). The optical signals were coupled into the poly(TFEMA)-based GI POF and were reconverted to electric signals by the transceiver and detected by sampling oscilloscope (86100 A, Agilent Inc.). An eye diagram was measured and a mask regulated as Gigabit Ethernet by TTC standard (JT-957) was covered. As shown in **Figure 3.23**, a good eye opening without any error is obtained and it is confirmed that this fiber sufficiently ensures the 1.25 Gbps transmission through 50-m length.



Figure 3.23 Eye diagram of 1.25 Gbps data transmission after a 50-m poly(TFEMA) –based GI POF with the ideal index profile.

3.6 Conclusion

In this chapter, two kinds of partially halogenated methacrylate with a similar structure to PMMA have been investigated. DSC and TG measurements have revealed the difference of thermal properties between the fluorinated and chlorinated methacrylates. Fluorination does not strongly affect the glass transition temperature, whereas chlorination attributes to reduce the mobility against heat and leads to the high T_g . On the other hand, the chlorinated polymer started to decompose at lower temperature because of carbon-chlorine bonds with the smaller dissociation energy. Poly(TFEMA) and poly(TCEMA) have smaller amount of C-H bonds per unit volume compared with PMMA, and exhibited higher transmittances. We succeeded in preparing GI POFs based on poly(TFEMA) and poly(TCEMA) by the interfacial-gel polymerization technique and the rod-in-tube method, respectively, for the first time. Attenuations at the emission wavelength of the light source (670-680 nm) were less than the required value in home network (200 dB/km). In previous studies, low-loss POFs consisting of perdeuterated PMMA and perfluorinated polymer (CYTOP®) were reported. Compared with these polymers, both TFEMA and TCEMA are commercially available and less expensive. Furthermore, no complicated polymerizations and fabrication procedures of GI POFs are necessary. The critical factor for reducing attenuation was clarified to be an amount of C-H bonds per unit volume, and partial substitution with fluorine or chlorine is enough for POFs to be used in very short reach networks.

This chapter also allowed us to understand what kind of polymer is suitable for the base material of desired GI POFs. Firstly, partial fluorination is better than chlorination. Although the effect of increasing T_g seems to be attractive, the low decomposition temperature of chlorinated polymer is the intrinsic issue. In addition, the high refractive index means that a large amount of dopant have to be added to the core, which results in lowering T_g of the fiber. Secondly, introducing a bulky structure to the side chain particularly close to the main chain will be effective for improving T_g .

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Chapter 4 Thermal Stability of Polymer with Bulky Side Chain -Poly(Pentafluorophenyl Methacrylate)-

4.1 Preface

In the previous chapter, we have got some ideas how to design polymers with low attenuation and high thermal properties for GI POF to be used in home networks. Based on the concept given in the conclusion of chapter 3, poly(pentafluorophenyl methacrylate) (poly(PFPMA)) has been investigated. First of all, we focused on the bone structure of poly(phenyl methacrylate) (poly(PMA)). The T_g of poly(PMA) was known to be as high as 129 °C because of the bulky structure in the side chain. Here, we should notice that the T_g of poly(benzyl methacrylate) is 64 °C; it strongly depends on the length of side chain. Poly(PMA) has ten C-H bonds per monomer unit, and which bonding should be replaced by C-F bond must be considered. In the case of poly(PMA), the C-H bond can be divided into aliphatic and aromatic bonds and each vibrational peak occurs at different wavelengths. From the transmittance measurement of PMA monomer, we found aromatic C-H peaks more strongly affect the attenuation at the emission wavelength of the light source. Thus, we selected poly(PFPMA) with no aromatic C-H bonds. As described in chapter 3, partial fluorination effectively reduces the attenuation of POFs, and does not strongly affect the T_g ; the high T_g of poly(PMA) will be maintained.

4.2 Materials

Pentafluorophenyl methacrylate (PFPMA) and methyl methacrylate (MMA) were purchased from SynQuest Laboratories, Inc. and Mitsubishi gas chemical company, Inc., respectively. *Di-tert*-butyl peroxide (PERBUTYL[®] D: PBD) was brought from NOF Co. Pentafluorophenol (PFP_h), *n-butyl* mercaptan (*n*-BM), benzoyl peroxide (BPO), diphenyl sulfide (DPS), methanol (MeOH), dichloromethane (CH₂Cl₂), dibutylhydroxytoluene (BHT), potassium carbonate (K₂CO₃), and calcium hydride (CaH₂) were brought from Wako Pure Chemical Industries, Ltd. PFPMA and MMA were freshly distilled with traditional method at 38-40 °C / 5 mmHg and 50-52 °C / 100 mmHg, respectively, before use. Other chemicals were used directly without further purification. Structures of main substances are summarized in **Figure 4.1**.



Figure 4.1 Chemical structures of PFPMA, PFPh, and BHT.

4.3 Preparation and Characterization of Polymer

For polymerization of PFPMA, the monomer mixture, including PBD (0.86 mol%) as an initiator and *n*-BM (0.28 mol%) as a chain transfer agent were transferred into a glass ampule (ϕ 10 mm). The polymerization reaction was carried out at 110 °C in an oil bath for 24 h. The composition is shown in **Table 4.1**. The obtained bulk were used for evaluation of refractive index, density, and transmittance. The amount of C-H bonds per unit volume compared with that for PMMA was calculated by Eq. 3-1. Then the bulk was solved into dichloromethane and poured into a large amount of methanol with vigorous stirring to precipitate the polymer. After drying at 90 °C for 24 h under vacuumed, we measured the glass transition temperature and heat decomposition temperature. These basic properties are summarized in **Table 4.2**. Transmittance spectrum and thermogravimetric curve are compared with those of PMMA in **Figures 4.2** and **4.3**, respectively.

 T_g and T_{d5} of poly(PFPMA) were 130 °C and 317 °C, respectively, and both values were higher than required values in home networks. As we expected, the T_g was almost the same as that for poly(PMA). The percentage of C-H bonds per unit volume calculated from the density was as small as 34 % compared to PMMA, and the excellent transmittance was actually confirmed. In chapter 3, we have revealed that attenuations at 670-680 nm wavelengths of poly(TFEMA)- and poly(TCEMA)-based GI POFs were 127-152 dB/km and 104-136 dB/km, respectively. The small amount of C-H bonds in poly(PFPMA) is the almost half ratio of above polymers, and suggests a possibility of the GI POF with much lower attenuation.

Polymer	Monomer	Initiator	Chain Transfer	Temperature	Time
poly(PFPMA)	PFPMA 7 g	PBD 0.86 mol% (0.50 wt%)	n-BM 0.28 mol% (0.1 wt%)	110 °C	24 h

 Table 4.1
 Preparation condition of poly(PFPMA)^{a, b}

^a The diameter of glass ampoule was 10 mm.

^b Ampoules were covered with stretched film (Dura[®] seal) without vacuumed.

Table 4.2	Basic proper	ties of poly(PFPMA)
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Polymer	Refractive index ^{a, b}	Density ^a (g/cm ³)	C-H bond ^d (%)	$T_g (^{\circ}C)^{c}$	<i>T_{d5}</i> (°C) ^c
poly(PFPMA)	1.4873	1.60	34	130	317

^a Refractive indices and densities are the values of polymer bulks.

^b Refractive index were measured by the prism coupling method at 409.2, 650.3, 833.7, and 1546 nm. The value here is at D spectrum (589 nm) approximated by the Sellmeier equation using these four values.

^c T_g and T_{d5} (5% weight loss temperature) are the values of precipitated polymers.

^d The percentage means a ratio of amount of C-H bonds per unit volume compared with that for PMMA.



Figure 4.2 Transmittance spectra of PMMA and poly(PFPMA). Optical paths are 3.0-cm length.



Figure 4.3 Thermogravimetric curves of PMMA and poly(PFPMA).

4.4 Fabrication of GI POF

A GI preform based on poly(PFPMA) was prepared by the interfacial-gel polymerization technique ^[1, 2]. First, a glass tube charged with PFPMA monomer mixtures including BPO and *n*-BM as the initiator and chain transfer agent, respectively, was rotated on its axis at 3,000 rpm in an oven at 70 °C for 3-6 h. PFPMA monomer was placed on the inner wall of the glass tube due to centrifugal force, and gradually was polymerized. After a heat treatment at 90 °C for 24 h, the polymer tube based on poly(PFPMA) was obtained as a cladding layer of the GI preform. Secondly, the tube was filled with a core solution with PBD and *n*-BM. As a low-molecular-weight dopant, diphenyl sulfide (DPS) was added to the core mixture. The tube filled with the mixture was heated in an autoclave at 120 °C for 48 h under nitrogen pressure of 0.6 MPa. While a GI profile was confirmed by the preform analyzer (Index Profiler IP-5500, Seiko EG&G Co., Ltd.) (**Figure 4.4**), the preform was highly-deformed and could not successfully heat drawn to the fiber.

If the cladding layer consists of poly(PFPMA) had a T_g of 130 °C as measured in the previous section, the preform should not have changed the shape at 120 °C which is lower than the T_g . As the result of DSC measurement, the T_g of cladding layer was found to be as low as 95 °C.



Figure 4.4 Refractive index profile of the GI preform based on poly(PFPMA)-DPS system.

4.5 Glass Transition Temperature of Polymer Bulk 4.5.1 Polymerization Temperature

For plastic optical fibers, T_g of polymer bulk is practically important rather than that of intrinsic one even if the polymer potentially had a high T_g . To obtain the GI POF with the high T_g , the reason for the low T_g has been investigated. First of all, we focused on the effect of polymerization temperature on T_g . The relationship between T_g of poly(PFPMA) bulks and polymerization temperatures is shown in **Figure 4.5**. Other parameters were the same as **Table 4.1**. **Figures 4.6** and **4.7** represent the effect of polymerization time and temperature on T_g , respectively. Temperatures in polymerization tubes measured with a thermocouple were almost the same as heating temperatures.

In Figure 4.5, we can see the linear relationship between T_g of bulks and the polymerization temperature; T_g s are almost equal to the polymerization temperature. Figure 4.6 indicates that the relationship is not influenced by the polymerization time. On the other hand, from the result of Figure 4.7, it is clear that the T_g is totally controlled by the temperature surrounding the polymer bulk. This phenomenon can be explained as follows; As the polymerization progresses and the conversion increases, the T_g also gradually increases to the surrounding temperature. Accordingly, polymer chains with small mobility trap unreacted monomers and radical initiators.



Figure 4.5 Relationship between T_g of poly(PFPMA) bulk and polymerization temperature (85-100 °C).



Figure 4.6 Relationship between T_g of poly(PFPMA) bulk and polymerization temperature. Polymerization time was 24 h (\circ) and 48 h (\bullet).



Figure 4.7 Relationship between T_g of poly(PFPMA) bulk and polymerization temperature. (\odot): polymerization was carried out at each temperature for 24 h, (\times): further heat treated at 100 °C for 24 h.

Based on above results, to obtain poly(PFPMA) bulk with the maximum T_g of 130 °C, PFPMA monomer is necessary to be polymerized at over 130 °C. Thus, we investigated the relationship between the T_g and the polymerization temperature in the region from 105 °C to 130 °C. The result is shown in **Figure 4.8** with the value of **Figure 4.5**.



Figure 4.8 Relationship between T_g of poly(PFPMA) bulk and polymerization temperature (85-130 °C).

Contrary to our expectation, in the temperature region over 100 °C, T_g sharply decreased as the polymerization temperature increased. As mentioned in section 2.4, structural parameters affecting T_g can be classified into two categories: polymer itself and others. In the condition of high polymerization temperature, dissociation of initiator is accelerated and the high concentration of free radicals produces polymers with low molecular weight ^[3]. Furthermore, the ratio of isotactic configuration which generally exhibits lower T_g than syndio tactic increases ^[4]. For other reasons, presence of plasticizers is possible ^[5]. This diluent introduces free volume in the material and, like any solvent, results in the decrease of T_g . Firstly, we precipitated all polymer bulks and measured T_g s of purified polymers. Then the amount of remaining monomer in bulks were quantitatively analyzed by a gas chromatography. Each result is presented in **Figures 4.9** and **4.10**.



Figure 4.9 Comparison of T_g between bulk and precipitated polymers. (\circ): Bulk, (\bullet): precipitated poly(PFPMA).



Figure 4.10 Relationship among polymerization temperature, T_g of poly(PFPMA) bulk, and the amount of remaining monomer in bulk. (\circ): T_g of bulk, (\times): amount of remaining PFPMA.

All purified poly(PFPMA) samples showed a high T_g of 130 °C and it was clarified that there was no relation between the polymer T_g and polymerization temperature. On the other hand, the amount of remaining PFPMA in bulk strongly depends on the polymerization temperature. **Figure 4.11** shows the relationship between T_g of bulk and the amount of remaining monomer. There was a good linear relationship. Accordingly, it seems reasonable to suppose that the low T_g of bulk is due to the plasticization effect of residual monomers.



Figure 4.11 Relationship between T_g of poly(PFPMA) bulk and the amount of remaining monomer in bulk.

4.5.2 Origin of Low Polymerization Conversion

In this section, the reason why a large amount of remaining monomer occurred in the polymerization at high temperature will be discussed. Some possibilities have been investigated one by one.

Initiator

As the thermal polymerization initiator, we have utilized *di-tert*-butyl peroxide (PERBUTYL[®] D: PBD). Each initiator has a adequate polymerization temperature related with the rate of disappearance. At a high temperature, there is in general a possibility that initiator is totally consumed before the polymerization completes. To confirm the amount of remaining PBD in bulks, we adopted the gas chromatography. The result is presented in **Figure 4.12**. As shown in **Table 4.1**, initial concentration of PBD is 0.50 wt%. When the polymerization temperature is in the region from 85 °C to 120 °C, almost of all initiator added in the monomer was found to be remained in the bulk. On the contrary, the initiator was dissociated and was utilized for initiating polymerization reaction at over 120 °C. This result seems to be quite suitable to the reported 10-hour half-life temperature of 123.7 °C, and tells us the initiator sufficiently worked at higher temperatures.


Figure 4.12 Amount of remaining initiator (PBD) in poly(PFPMA) bulks polymerized at transverse temperature for 24 h.

Inhibitor

Since the PFPMA monomer was utilized after careful distillation, we can say with fair certainty that an inhibitor added by the supplier had been already removed. However, it is possible that other substances worked as an inhibitor or a retarder. **Figure 4.13** shows a comparison of gas chromatograms between PFPMA monomer and a supernatant of dissolved polymer bulk polymerized at 130 $^{\circ}$ C for 24 h.



Figure 4.13 Comparison of gas chromatograms between distilled PFPMA monomer and a supernatant of dissolved polymer bulk polymerized at $130 \,^{\circ}$ C for 24 h.

Here, CH_2Cl_2 and MeOH were utilized for dissolving and precipitating the polymer, respectively. BHT was used as a standard sample. To compare them in the same condition, PFPMA monomer was also evaluated with CH_2Cl_2 , MeOH, and BHT. Mainly four strong peaks due to byproducts were confirmed in both distilled monomer and bulk. These peaks were analyzed by a mass spectrometry and were found to be A: 2.5-dimethyl-2-cycropentenon, B: NA, C: pentafluorophenol (PFPh), and D: tetrafluorophenyl methacrylate. Among these, the C peak of pentafluorophenol exceptionally increased after polymerized at 130 °C. Thus, the polymerization

temperature dependency of the amount of PFPh was examined. The result is shown in **Figure 4.14**. With increasing the polymerization temperature, the amount of PFPh linearly increased. The concentration of PFPh in the bulk polymerized at 130 $^{\circ}$ C for 24 h was 0.85 wt% and was twice of the initial content in PFPMA monomer (0.43 wt%).



Figure 4.14 Temperature dependency of the amount of PFPh in poly(PFPMA) bulks. Broken line indicates the initial concentration of PFPh in distilled PFPMA monomer.

The small amount of PFPh in monomer is the residue accompanied with the monomer synthesis procedure (PFPMA monomer is prepared by PFPh and methacryloyl chloride). The increment of PFPh during polymerization is estimated to be caused by the hydrolysis of PFPMA monomer or polymer. Although the behavior of PFPh in polymerization has not been clear enough, it is possible that the PFPh or radicals occurred with the breakdown reaction disturb the ordinary polymerization. Thus, we tired to remove the PFPh in monomer and prevent the hydrolysis by adding potassium carbonate and calcium hydride to the monomer, respectively. The monomer was filtered and freshly distilled again before use. As the result, the initial concentration of PFPh in monomer was also as small as 0.17 wt%. The relationship between T_g of bulk and polymerization temperature

was investigated again by using the monomer without PFPh. The result is presented in **Figure 4.15** with the data of **Figure 4.8**. Compared with the original data, we can see a slight difference after removing PFPh. However, the tendency is quite similar and the maximum T_g of poly(PFPMA) bulk is still around 105 °C, which is lower than the intrinsic value by 25 °C.



Figure 4.15 Relationship between T_g of poly(PFPMA) bulk and polymerization temperature. (\odot) and (\bullet) represent T_g plots of poly(PFPMA) bulks prepared from PFPMA monomer with PFPh of 0.43 wt% and 0.03 wt%, respectively.

Ceiling Temperature

From investigations so far, the low T_g of poly(PFPMA) bulk is believed to be derived by not extrinsic factors but intrinsic one. We focused on a parameter of ceiling temperature. For most chain polymerizations there is some temperature at which the reaction becomes a reversible one, that is, the propagation step should be written as an equilibrium reaction.

$$M_n \bullet + M \xrightarrow[k_{dp}]{k_{dp}} M_{n+1} \bullet$$
 (4-1)

where k_p and k_{dp} are rate constants for propagation and depropagation reactions, respectively. The overall effect of temperature on polymerization is complex, due to the presence of this propagation-depropagation equilibrium. When the temperature is initially increased for the polymerization of a monomer, the polymerization rate increases as k_p increases. However, at higher temperatures the depropagation rate constant k_{dp} , which was initially zero, increases and becomes significant with increasing temperature. Finally, a temperature—the ceiling temperature T_c —is reached at which the propagation and depropagation rates are equal. At the ceiling temperature the net rate of polymer production is zero. For an equilibrium situation the difference in free energy is given by the following equation.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT\ln K$$
(4-2)

The ΔG° , ΔH° , and ΔS° for a polymerization are the differences in free energy, enthalpy, and entropy, respectively, between 1 mol of monomer and 1 mol of repeating units in the polymer product in the appropriate standard states. The standard state for monomer is often taken as the pure monomer or a 1 *M* solution. The standard state for the polymer is usually the solid amorphous or slightly crystalline polymer or a solution that is 1 *M* in the repeat unit of the polymer. *R*, *T*, and *K* indicates gas constant, absolute temperature, and equilibrium constant, respectively. The equilibrium constant is defined by k_p/k_{dp} or more conveniently by

$$K = \frac{\left[M_{n+1}\cdot\right]}{\left[M_{n}\cdot\right]\left[M\right]} = \frac{1}{\left[M\right]}$$
(4-3)

Combination of Eqs. 4-2 and 4-3 yields

$$T_c = \frac{\Delta H^{\circ}}{\Delta S^{\circ} + R \ln[M]_c}$$
(4-4)

or

$$\ln[M]_{c} = \frac{\Delta H^{\circ}}{RT_{c}} - \frac{\Delta S^{\circ}}{R}$$
(4-5)

Eq. 4-5 shows the equilibrium monomer concentration $|M|_{c}$ as a function of the reaction or ceiling temperature T_c . (Note that ΔH° in Eqs. 4-4 and 4-5 can be replaced by ΔH because the enthalpy change is independent of [M]. This is not the case for ΔS since the entropy change is dependent on |M|.) Since ΔH° is a negative quantity, the monomer concentration in equilibrium with polymer increases with increasing temperature, that is, a plot of $[M]_{-}$ versus 1/T is linear with a negative slope of $\Delta H^{\circ}/R$ and intercept of $-\Delta S^{\circ}/R$. This means that there is a series of ceiling temperatures corresponding to different equilibrium monomer concentrations. For any monomer solution of concentration $[M]_c$, there is a temperature T_c at which polymerization does not occur. Stated another way, the polymerization of a particular monomer solution at a particular temperature proceeds until equilibrium is established, that is, until the monomer concentration decreases to the $[M]_c$ value corresponding to that T_c temperature. There is an upper temperature limit above which polymer cannot be obtained even from pure monomer. The reader is cautioned to note that the literature often appears to refer only to a singular T_c values—"the ceiling temperature." It is clear from the discussion above that each monomer concentration has its T_c value. The apparent designation of a singular T_c value usually refers to the T_c for the pure monomer or in some cases to that for the monomer at unit molar.

Figure 4.16 shows T_g of poly(PFPMA) bulks firstly polymerized at 100 °C for 24 h then further heated at transverse temperatures for 24 h. **Figure 4.17** is the amount of residual monomer in the bulk. Solid lines denote the T_g and the amount of remaining monomer of the bulk polymerized at 100 °C for 24 h. When the bulk was further polymerized at below 110 °C, the remaining monomer was decreased and T_g was increased. However, at over 115 °C, just the opposite occurred. These results indicate that the optimum temperature to maximize the polymerization conversion is about 105 °C. In other words, the ceiling temperature corresponding to the minimum monomer concentration exists in the temperature region. As mentioned earlier, the intrinsic T_g of poly(PFPMA) is 130 °C and the higher polymerization temperature is necessary to prepare the bulk with the T_g of 130 °C. However, with considering the result of **Figures 4.16** and **4.17**, we have to conclude that such bulk can not be obtained.



Figure 4.16 T_g of poly(PFPMA) bulks firstly polymerized at 100 °C for 24 h then further heated at transverse temperatures for 24 h.



Figure 4.17 Amount of remaining monomer in poly(PFPMA) bulks firstly polymerized at 100 °C for 24 h then further heated at transverse temperatures for 24 h.

Why is the ceiling temperature of PFPMA low? In the case of PMMA, the bulk polymerized at 100-130 °C exhibits almost the same T_g and we can know the ceiling temperature is much higher. Otsu *et al.* reported ceiling temperatures of phenyl methacrylate and 2,6-dimethylphenyl methacrylate, and proved that the bulkiness of benzene ring with two methyl groups remarkably reduced the reactivity of carbon-carbon double bond ^[6]. Furthermore, correlations of ceiling temperature and reactivity with bulkiness of ortho-substitutent in radical polymerization of phenyl methacrylate also have been investigated ^[7]. While it is debatable whether pentafluorophenyl group in PFPMA unit has a strong effect on disturbing the propagation reaction, at this time, it seems reasonable to suppose that the low ceiling temperature of PFPMA is caused by the steric hindrance.

4.6 Heat Decomposition Temperature of Polymer Bulk

As given in **Table 4.2**, T_{d5} of purified poly(PFPMA) was as high as 317 °C. However, poly(PFPMA) has a large amount of remaining monomer in bulk state as discussed in the previous section. Here, the influence of the remaining monomer on the polymer degradation was examined. The thermogravimetric curve of poly(PFPMA) bulk polymerized at 110 °C having the smallest amount of unreacted PFPMA was measured by a TG instrument. For comparison, PMMA bulks was prepared in the same manner. The result is shown in **Figure 4.18**.



Figure 4.18 Thermogravimetric curves of poly(PFPMA) and PMMA bulk. Polymerizations were carried out at 110 °C.

Even in the bulk state, PMMA maintains the high T_{d5} of 293 °C, which is almost the same as that of precipitated one. In the adequate polymerization condition, the conversion of PMMA is in general 99 % or more, and the quite small amount of remaining MMA does not affect the polymer degradation. On the other hand, as shown in **Figure 4.10**, the poly(PFPMA) bulk has a much larger amount of unreacted monomer. Consequently, the weight of polymer bulk starts to decrease at around 190 °C accompanied with the volatilization of monomer, which follows numerous bubbles during the POF fabrication.

4.7 Conclusion

In chapter 4, optical and thermal properties of poly(PFPMA) have been studied. It was confirmed that the polymer exhibited a higher transmittance than PMMA at a broad wavelength region. The amount of C-H bonds per unit volume which is the main factor for determining the attenuation of POFs was only 34 %. This value suggests that the attenuation of GI POF based on poly(PFPMA) will be much lower than those of poly(TFEMA) and poly(TCEMA). Furthermore, poly(TFEMA) and poly(TCEMA) has crucial disadvantages in the glass transition temperature and heat decomposition temperature, respectively, whereas poly(PFPMA) was revealed to have excellent thermal stabilities satisfying the requirement in home network. However, probably due to the steric hindrance of bulky structure, the polymer bulk with high conversion could not be obtained, resulted in the low T_g and low T_d .

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Chapter 5 Low-Loss and Thermally Stable Copolymeric Optical Fiber -Methyl Methacrylate-*co*-Pentafluorophenyl Methacrylate-

5.1 Preface

In this chapter, we report on a novel GI POF based on a partially fluorinated copolymer with lower loss and higher thermal stabilities than those for PMMA. For the core material, a copolymer of MMA and pentafluorophenyl methacrylate (PFPMA) was utilized. As described in the previous chapter, the Tg and Td5 of purified poly(PFPMA) are 130 °C and 317 °C, respectively, which are much higher than those for PMMA. One of the notable features of poly(PFPMA) was that its polymerization proceeds to a low conversion due to the steric hindrance. The residual monomer lowers the T_g and leads to numerous bubbles that increase the attenuation of the fiber especially in the co-extrusion process. Thus, we have tried to reduce the amount of remaining monomer by utilizing the difference of monomer reactivity ratios. There were two main reasons for choosing MMA as a comonomer of PFPMA. The first was the monomer reactivity ratios. When PFPMA is M1 and MMA is M2, r12 and r21 are 1.30 and 0.56, respectively. This indicates that PFPMA preferentially polymerizes; therefore, we believed that the amount of unreacted PFPMA would be reduced by copolymerizing with MMA. The second was their refractive indices. In general, a copolymer tends to have extremely high scattering losses due to the large inherent heterogeneous structure of refractive indices. Consequently, copolymers have not been the leading candidate for POF base materials. However, in this copolymeric system, the increment in scattering loss is negligibly small since the refractive indices of both homopolymers are almost the same (PMMA: n_D = 1.4914, poly(PFPMA): $n_D = 1.4873$). Moreover, the percentage of C-H bonds per unit volume of poly(PFPMA) compared with that of PMMA is only 34%, so smaller absorption losses and lower attenuation can be expected.

5.2 Kinetics of Copolymerization

The term "copolymerization" is used when the starting material consists of at least two different reaction partners, and copolymers can be produced in very different ways from homopolymers. In this section, basic principles of copolymerization which helps us to understand several phenomena of MMA-*co*-PFPMA will be described.

5.2.1 The Copolymeric Equation

In 1936 Dostal made the first attack on the mechanism of copolymerization by assuming that the rate of addition of monomer to a growing free radical depends only on the nature of the end group on the radical chain. Thus monomers M_1 and M_2 lead to radicals of types M_1 and M_2 . There are four possible ways in which monomer can add:

The kinetics of copolymerization was more fully elucidated in 1944 by Alfrey, Mayo, Simha, and Wall. To Dostal's reaction scheme they added the assumption of the steady state applied to each radical type separately, that is, the concentrations of M_1 and M_2 must each remain constant. It follows that the rate of conversion of M_1 to M_2 must equal that of conversion of M_2 to M_1 .

$$k_{21}[M_2 \cdot][M_1] = k_{12}[M_1 \cdot][M_2]$$
(5-2)

The rates of disappearance of the two types of monomer are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1 \cdot][M_1] + k_{21}[M_2 \cdot][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1 \cdot][M_2] + k_{22}[M_2 \cdot][M_2]$$
(5-3)

By defining $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and combining Eqs. 5-2 and 5-3, it can be shown that the composition of copolymer being formed at any instant is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$
(5-4)

This is known as the copolymer equation; it has been verified by many experimental investigations of copolymer composition.

5.2.2 Monomer Reactivity Ratios

The monomer reactivity ratios r_1 and r_2 are the ratios of the rate of constant for a given radical adding its own monomer to the rate constant for its adding the other monomer. Thus $r_1 > 1$ means that the radical M_1 . prefers to add M_1 ; $r_1 < 1$ means that it prefers to add M_2 . In the system styrene (M_1) -methyl methacrylate (M_2) , for example, $r_1 = 0.52$ and $r_2 = 0.46$; each radical add the other monomer about twice as fast as its own.

Since the rate constants for initiation and termination do not appear in Eq. 5-4, the composition of the copolymer is independent of overall reaction rate and initiator concentration. The reactivity ratios are unaffected in most cases by the presence of inhibitors, chain transfer agents, or solvents. Even in heterogeneous systems they remain unchanged, unless the availability of the monomers is altered by there distribution between phases. A change from a free radical to an ionic mechanism, however, changes r_1 and r_2 markedly.

A few typical values of monomer reactivity ratios are given in **Table 5.1**. An extensive compilation is given by Young.

Monomer	Monomer	r_1	r ₂	T (°C)
Acrylonitrile	1,3-Butadiene	0.02	0.3	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.03	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.01	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
-	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

 Table 5.1
 Typical monomer reactivity ratios ^[1]

5.2.3 Types of Copolymerization

Ideal

A copolymer system is said to be ideal when the two radicals show the same preference for adding one of the monomers over the other: $k_{11}/k_{12} = k_{21}/k_{22}$, or $r_1 = 1/r_2$, or $r_1r_2 = 1$. In this case, the end group on the growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. The copolymer equation reduces to $d[M_1]/d[M_2] = r_1[M_1]/[M_2]$.

Alternating

Here each radical prefers to react exclusively with the other monomer: $r_1 = r_2 = 0$. The monomers alternate regularly along the chain, regardless of the composition of the monomer feed. The copolymer equation simplifies to $d[M_1]/d[M_2]=1$. Most actual cases lie between the ideal and the alternating systems: $0 < r_1r_2 < 1$. A third possibility, with both r_1 and r_2 greater than unity, corresponds to the tendency to form block copolymers.

5.2.4 Instantaneous Composition of Feed and Polymer

Let F_1 and F_2 be the mole fractions of monomers 1 and 2 in the polymer being formed at any instant:

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d([M_1] + [M_2])}$$
(5-5)

If f_1 and f_2 similarly represent mole fractions in the monomer feed,

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$
(5-6)

the copolymer equation can be written as

$$F_{1} = \frac{r_{1}f_{1}^{2} + f_{1}f_{2}}{r_{1}f_{1}^{2} + 2f_{1}f_{2} + r_{2}f_{2}^{2}}$$
(5-7)

It is apparent that in general F_1 does not equal f_1 , and both f_1 and F_1 change as the polymerization proceeds. The polymer obtained over a finite range of conversion consists of a continuous distribution of varying composition.

Eq. 5-7 may be used to calculate curves of feed versus instantaneous polymer composition for various monomer reactivity ratios. Such curves for a series of ideal copolymerizations ($r_1r_2 = 1$) are shown in **Figure 5.1**. Except for pairs of monomers having very similar reactivities, only a small range of feeds gives copolymers containing appreciable amounts of both components.

Several curves for nonideal cases are shown in **Figure 5.2**. These curves show the effect of increasing tendency toward alternation. As alternation increases, more and more feeds yield a copolymer containing a good deal of each component. This tendency makes practical the preparation of many important copolymers.

If one of the monomers is very much more reactive than the other, the first polymer formed contains mostly the more reactive monomer. Later in the polymerization this monomer is largely used up, and the last polymer formed consists mainly of the less reactive monomer. A copolymer of styrene and vinyl acetate is prepared from such a system.



Figure 5.1 Instantaneous composition of copolymer (mole fraction F_1) as a function of monomer composition (mole fraction f_1) for ideal copolymers with the values of $r_1 = 1/r_2$ indicated.



Figure 5.2 Instantaneous composition of copolymer F_1 as a function of monomer composition f_1 for the values of reactivity ratios r_1/r_2 indicated.

For cases in which both r_1 and r_2 are less (or greater) than unity, the curves of **Figure 5.2** cross the line representing $F_1 = f_1$. At the point of intersection polymerization proceeds without a change in the composition of feed or polymer. This is known as azeotropic copolymerization. Solution of Eq. 5-4 with $d[M_1]/d[M_2] = [M_1]/[M_2]$ gives the critical composition for the azeotrope:

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1} \tag{5-8}$$

or, from Eq. 5-7,

$$(f_1)_{critical} = \frac{1 - r_2}{2 - r_1 - r_2}$$
 (5-9)

5.2.5 Experimental Determination of Copolymerization Parameters

The copolymerization equation describes the relative change in the monomer concentrations as a function of the instantaneous monomer concentrations. These changes are not directly experimentally accessible. There are several ways of determining the copolymerization parameters as follows:

- a. Direct curve fitting on polymer-monomer composition plots. This is a poor method, since the composition curve is rather insensitive to small changes in r_1 and r_2 .
- b. The copolymer equation may be solved for one of the reactivity ratios:

$$r_{2} = \frac{[M_{1}]}{[M_{2}]} \left[\frac{d[M_{2}]}{d[M_{1}]} \left(1 + \frac{[M_{1}]}{[M_{2}]} r_{1} \right) - 1 \right]$$
(5-10)

Each experiment with a given feed gives a straight line; the intersection of several of these allows the evaluation of r_1 and r_2 . If the experimental errors are high, the lines may not intersect in a single point; the region within which the intersections occur gives information about the precision of the experimental results.

c. Eq. 5-7 can be rearranged to

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}r_1$$
(5-11)

This is the equation of a straight line with slope r_1 and intercept r_2 . Each experiment gives one point on the line. The least-squares treatment of a series of such points gives the best values of r_1 and r_2 in a straightforward way. By defining the variables G and H to

$$G = \frac{f_1(2F_1 - 1)}{(1 - f_1)F_1} = x \left(1 - \frac{1}{y}\right)$$
(5-12)

$$H = \frac{f_1^2 (1 - F_1)}{(1 - f_1)^2 F_1} = \frac{x^2}{y}$$
(5-13)

Eq. 5-11 can be expressed as

$$G = Hr_1 - r_2 \tag{5-14}$$

$$\frac{G}{H} = r_1 - \frac{r_2}{H} \tag{5-15}$$

where $x = [M_1]/[M_2]$, and $y = d[M_1]/d[M_2]$, where $[M_1]$ and $[M_2]$ are the molar concentrations in the monomer feed and $d[M_1]$ and $d[M_2]$ in the final polymer. *G* is then plotted against *H*, or *G*/*H* against 1/H, in the Fineman-Ross equations ^[2] (Eqs. 5-14 and 5-15).

d. A new assistance variable α is introduced in the Kelen-Tudos procedure ^[3] and this variable is calculated from the largest and smallest values of H:

$$\alpha = \sqrt{H_m \cdot H_M} \tag{5-16}$$

and then, $G/(\alpha + H)$ is plotted against $H/(\alpha + H)$.

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{5-17}$$

where $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$. By plotting η versus ξ according to the linear Eq. 5-17, r_1 and r_2 are directly obtained from the intercepts at $\xi = 1$ and $\xi = 0$, respectively (see Figure 5.3).



Figure 5.3 Kelen-Tudos diagram for the determination of the reactivity ratios.

Copolymerization parameters are determined by carrying out copolymerization experiments with differing initial monomers compositions. The copolymerizations are followed to small yields and then, either the copolymer composition or (more rarely) the unconverted monomer composition is determined. Confirmation that copolymer is actually formed is required in all cases, and this can be done by solubility determinations, ultracentrifugation in a density gradient, or by cloud point titration. The initial monomer concentrations are used for the relative monomer ratios in Eqs. 5-12 and 5-13, and the relative copolymer compositions in these equations given by the compositions determined for small yields (or exactly, at yield zero). In such cases, the Fineman-Ross method is not accurate for a wide range of concentrations and the method described by Kelen and Tudos is often preferred. Thus, in this dissertation, the Kelen-Tudos method was utilized for determining reactivity ratios.

5.2.6 Variation of Copolymer Composition with Conversion

The copolymer equation (Eq. 5-4) predicts the average composition of the polymer formed at any instant in the polymerization. Not only may statistical fluctuations of composition about this average occur, but also polymer formed during a finite interval may contain a range of compositions resulting from variation of feed composition. In this case, the overall polymer composition can be calculated by integrating the copolymer equation ^[4, 5].

The direct integration of the copolymer equation gives a result that is not convenient for calculations. The most convenient method for calculating copolymer composition and distribution involves the use of Eq. 5-7. For a system in which $F_1 > f_1$, when dM moles of monomer have polymerized, the polymer contains $F_1 dM$ moles of monomer 1, and the feed contains $(f_1 - df_1)(M - dM)$ moles of monomer 1. For a material balance,

$$Mf_{1} - (M - dM)(f_{1} - df_{1}) = F_{1}dM$$
(5-18)

Combining this with Eq. 5-7 gives

$$\frac{dM}{M} = \frac{df_1}{F_1 - f_1}$$
(5-19)

Which can easily integrated by numerical or graphic means to give the desired composition of polymer as a function of conversion. One convenient closed-form result of this integration is

$$\log\left(\frac{M}{M_{0}}\right) = \frac{r_{2}}{1 - r_{2}}\log\left(\frac{f_{1}}{(f_{1})_{0}}\right) + \frac{r_{1}}{1 - r_{1}}\log\left(\frac{f_{2}}{(f_{2})_{0}}\right) + \frac{1 - r_{1}r_{2}}{(1 - r_{1})(1 - r_{2})}\log\left(\frac{(f_{1})_{0} - \varepsilon}{f_{1} - \varepsilon}\right)$$
(5-20)

where $\varepsilon = (1 - r_2)/(2 - r_1 + r_2).$

General References

C. E. Carraher Jr., Polymer Chemistry, 6th ed., chapter 6, New York and Basel: Marcel Dekker, Inc. (2003).

F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., chapter 5, New York: John Wiley & Sons (1984).

5.3 Materials

Pentafluorophenyl methacrylate (PFPMA), methyl methacrylate (MMA), and 2,2,2-trifluoroethyl methacrylate (TFEMA) were purchased from SynQuest Laboratories, Inc., Mitsubishi gas chemical company, Inc., and TOSOH F-TECH, Inc., respectively. *Di-tert*-butyl peroxide (PERBUTYL[®] D: PBD) was brought from NOF Co. *n-butyl* mercaptan (*n*-BM), *n-lauryl* mercaptan, benzoyl peroxide (BPO), diphenyl sulfide (DPS), methanol (MeOH), chloroform (CHCl₃), dibutylhydroxytoluene (BHT), chloroform-d (CDCl₃), and tetrahydrofuran (THF) were brought from Wako Pure Chemical Industries, Ltd. Monomers were freshly distilled with traditional method before use and other chemicals were used directly without further purification.

5.4 Polymer Preparation

The monomer mixtures, including weighed amounts of comonomers, PBD (0.35 mol%) as an initiator and *n*-LM (0.10 mol%) as a chain transfer agent were transferred into a glass ampule. The tube was subjected to repeated freeze-pump-thaw cycles and sealed under vacuum. The polymerization reactions were carried out at 80 $^{\circ}$ C in a water bath. After the reaction mixture reached proper viscosity, the glass tube was opened and the contents were poured into a large amount of methanol with vigorous stirring to precipitate the polymer. The purified polymer samples were dried under vacuum at 90 $^{\circ}$ C for 24 h. The conversions of the copolymerization reactions were in the range of 7-15 %. The purified polymers obtained were used to measure the monomer reactivity ratio.

For other measurements, bulk and purified copolymers were prepared as follows. Monomer mixtures with PBD (0.01 mol%) as an initiator and *n*-LM (0.125 mol%) as a chain transfer agent were transferred into glass ampules and subjected to repeated freeze-pump-thaw cycles; this was followed by sealing under vacuum with flame. The polymerization reactions were carried out at 100-130 °C in oil baths for 48 h. Obtained bulks were dissolved in chloroform and precipitated from a large amount of methanol with vigorous stirring. The purified polymer samples were dried under vacuum at 50 and 90 °C for 24 h at each temperature to allow the solvents evaporating. The reaction scheme of MMA-*co*-PFPMA is presented in **Figure 5.4**.



Figure 5.4 Reaction scheme of a copolymer of methyl methacrylate and pentafluorophenyl methacrylate.

5.5 Determination of Monomer Reactivity Ratios

Monomer reactivity ratios were determined by the Kelen-Tudos method. Detail procedures are described in section 5.2. The molar fraction of PFPMA unit in the feed $[M_1]$ and in the final copolymer $d[M_1]$, polymerization conversion, and parameters in K-T method are listed in **Table 5.2**. Values of $d[M_1]$ were determined by H¹-NMR spectra. The corresponding η versus ξ plot is shown in **Figure 5.5**. From the slope and the intercept of the approximated expression (see Eq. 5-17), the r_{12} (PFPMA) and r_{21} (MMA) were calculated to be 1.30 and 0.56, respectively. Here, α was 0.3363. These values are compatible with reported monomer reactivity ratios: r_{12} = 1.20 and $r_{21} = 0.51$ ^[6]. **Figure 5.6** is a plot of molar fraction of PFPMA in the copolymer $d[M_1]$ versus the molar fraction of PFPMA in the feed $[M_1]$ and the curve calculated from the copolymer equation (Eq. 5-4).

Sample	[M ₁] ^C (mol%)	d[M ₁] ^C (mol%)	Conv. (wt%)	x	у	Н	G	η	ξ
P1	0	0	-	-	-	-	-	-	-
P2	9.99	15.56	13.5	0.11	0.18	0.07	-0.49	0.17	-1.22
Р3	20.02	30.19	12.6	0.25	0.43	0.14	-0.33	0.30	-0.68
P4	30.00	40.47	7.90	0.43	0.68	0.27	-0.20	0.45	-0.33
Р5	39.98	48.79	14.8	0.67	0.95	0.47	-0.03	0.58	-0.04
P6	50.00	61.00	-	1.00	1.56	0.64	0.36	0.66	0.37
Ρ7	70.00	76.29	14.7	2.33	3.22	1.69	1.61	0.83	0.79
P8	100	100	-	-	-	-	-	-	-

 Table 5.2
 Results of copolymerization reaction of PFPMA and MMA^{a,b}, and Kelen-Tudos parameters

^a Reaction was run with PBD (0.35 mol%) and *n*-LM (0.10 mol%) as an initiator and a chain transfer agent, respectively.

 $^{\rm b}$ The polymerization reaction was carried out at 80 $^{\circ}$ C for about 1 h.

^c $[M_1]$ and $d[M_1]$ are the molar concentration of PFPMA in the monomer feed and in the final polymer, respectively.



Figure 5.5 The η versus ξ plot with the approximated line from the data in Table 5.2.



Figure 5.6 The $[M_1]$ versus $d[M_1]$ plot from the data in **Table 5.2**. The solid line and broken line represent theoretical curves calculated from Eq. 5-4 using $r_1 = 1.30$ and $r_2 = 0.56$ and $r_1 = r_2 = 1$, respectively.

5.6 Thermal Properties5.6.1 Glass Transition Temperature

The relationship between the T_g of MMA-*co*-PFPMA bulk and PFPMA content in the monomer feed was examined. Studies in chapter 5 has suggested that poly(PFPMA) has a low ceiling temperature and the polymerization temperature strongly affects the conversion—i.e., the T_g of the bulk. Thus, the copolymerizations were carried out at 100, 110, 120, and 130 °C, and all copolymer bulks were analyzed by a DSC. The preparation conditions and results are presented in **Table 5.3** and **Figures 5.7** and **5.8**, respectively. The numbers in figures denote the polymerization temperature.

Table 5.3 Preparation condition for copolymer bulks^{a, b}

Initiator	Chain Transfer	Temperature	Time
PBD 0.01 mol%	n-LM 0.125 mol%	100-130 °C	48h

^a The diameter of glass ampoule was 10 mm.

^b Monomer mixtures were subjected to repeated freeze-pump-thaw cycles, which were followed by sealing under vacuum with flame.



Figure 5.7 T_g plots of MMA-*co*-PFPMA bulks polymerized at 100 °C (upper) and 110 °C (lower) for 48 h against the PFPMA content in the monomer feed.



Figure 5.8 T_g plots of MMA-*co*-PFPMA bulks polymerized at 120 °C (upper) and 130 °C (lower) for 48 h against the PFPMA content in the monomer feed.

 T_g for copolymers can generally be described by the Gordon-Taylor equation^[7] and changes linearly with the weight fractions of the monomer content. For this copolymeric system, however, it was interesting to observe that the T_g plots exhibited positive deviations at all polymerization temperatures. While the abscissa axes of Figures 5.7 and 5.8 are the molar fraction of PFPMA in the monomer feed, the results are similar even if it is converted to the weight fraction. $T_{\rm g}$ for PMMA is in the range of 109-114 °C and the influence of the polymerization temperature is small. On the other hand, for poly(PFPMA), T_g is 91–96 °C when the polymerization temperature is 100-120 °C, but it drastically decreases to 74 °C when polymerized at 130 °C. To discuss the results shown in Figures 5.7 and 5.8 in detail, the amount of remaining monomers in the bulks polymerized at 110 °C—which provided the highest T_g —was determined by a gas chromatography. Additionally, T_g for the purified polymers was also analyzed. The purification was carried out by a traditional method. Obtained bulks were solved into chloroform then poured into methanol with vigorous stirring to precipitate polymers. Precipitated polymers were dried under vaccum at 90 °C for 24 h. Although there seemed to be no big difference in T_g for the polymerization temperatures of 110 °C and 120 °C, the bulks polymerized at 120-130 °C tended to have some voids caused by the volume contraction. Thus, the polymerization temperature was fixed to 110 $^{\circ}$ C in this study. Results are shown in Figures 5.9 and 5.10.



Figure 5.9 T_g plots of MMA-*co*-PFPMA bulks polymerized at 110 °C for 48°)h and the amount of remaining MMA (\diamond) and PFPMA (\diamond) monomer in the bulks against the PFPMA content in the monomer feed.



Figure 5.10 Comparison of T_g between bulks (\circ) and purified copolymers (\bullet).

The amount of remaining MMA in all bulks except for poly(PFPMA) was about 1 wt%, whereas the remaining PFPMA underwent many changes. While approximately 7 wt% of unreacted PFPMA remained in the poly(PFPMA) bulk, the amount of PFPMA drastically decreased after copolymerizing with MMA. This may be derived from the monomer reactivity ratios. **Figure 5.11** shows the change in copolymer composition with the polymerization conversion calculated by integrating the copolymer equation. Here, r_{12} and r_{21} (M_1 : PFPMA, M_2 : MMA) are 1.30 and 0.56, respectively, and the initial monomer content in the feed is 50/50 mol%.



Figure 5.11 Change in accumulated copolymer composition with polymerization conversion when the initial MMA and PFPMA contents in the monomer feed are 50 mol%.

Given ideal polymerization, PFPMA polymerizes preferentially; the polymer consisted of 60 mol% PFPMA units in the initial stage. As a result, the PFPMA conversion was improved with the presence of MMA. On the other hand, **Figure 5.10** indicates that the T_g of purified copolymer with no remaining monomers linearly increased as the PFPMA content in the monomer feed increased due to the high T_g of poly(PFPMA). Figures 5.9 and 5.10 show that the T_g of the copolymer bulk increased with increasing PFPMA content when the bulk had a small amount of remaining monomers, while it decreased when the bulk has a lot of remaining monomers due to the

plasticization effect. This is why the T_g plots for the copolymer bulks exhibited positive deviations. The most important point about these experiments is that the copolymer bulks had higher T_g than PMMA when the PFPMA content in the monomer feed was 0–60 mol%.

5.6.2 Heat Decomposition temperature

Next, we have investigated the heat decomposition property of MMA-*co*-PFPMA. Thermogravimetric curves of bulk and purified polymers are shown in **Figures 5.12** and **5.13**, respectively. These polymers correspond to the sample examined in **Figure 5.10**. **Figure 5.14** is a comparison of T_{d5} between bulk and purified polymers. For purified polymers, the thermogravimetric curves shifted to higher temperature with increasing PFPMA content since the T_{d5} of poly(PFPMA) was as high as 317 °C. On the other hand, the weight of poly(PFPMA) bulk began to decrease at 190 °C due to the vaporization of the remaining 7 wt% of the monomer. This issue has already discussed in section 4.6. However, the curve of the copolymer bulk was almost the same as the purified one due to the small amount of remaining monomers in the bulk. Figure 5.14 indicates that the copolymer bulks had higher decomposition temperatures than PMMA when the PFPMA content in the monomer feed was 0–60 mol%.


Figure 5.12 Thermogravimetric curves of PMMA, MMA-*co*-PFPMA (65/35 mol%), and poly(PFPMA) bulks measured under an air stream at a scanning rate of 10 °C/min.



Figure 5.13 Thermogravimetric curves of purified PMMA, MMA-*co*-PFPMA (65/35 mol%), and poly(PFPMA) measured under an air stream at a scanning rate of 10 °C/min.



Figure 5.14 Change of 5% weight loss temperatures for MMA-*co*-PFPMA bulk (\circ) and purified polymers (\bullet) against PFPMA content in the monomer feed.

5.7 Optimization of Polymerization Conditions

In the previous section, we have clarified that the copolymer of MMA and PFPMA has higher T_g and Td than those for PMMA and satisfies the requirement of home networks when the PFPMA content in the monomer feed is 0–60 mol%. In this section, the optimum preparation condition that provides the highest T_g is discussed by focusing on the amount of initiator. As shown in **Figure 5.10**, we confirmed that the copolymer has the highest T_g at 117 °C when the PFPMA content and amount of PBD are 23 and 0.01 mol%, respectively. From the data, the maximum T_g should be obtained when the PFPMA content is at 23–50 mol% by increasing the amount of added PBD. **Figure 5.15** shows the T_g plots of the copolymer bulks with PFPMA contents of 23, 35, and 50 mol% versus the amount of added PBD.



Figure 5.15 Relationship between the amount of PBD and T_g of the copolymer bulks. PFPMA contents in the monomer feed were 23 (•), 35 (\Diamond), and 50 (×) mol%.

The copolymer bulk was found to have the highest T_g of 118 °C when the PFPMA content and amount of added PBD were 35 and 0.1 mol%, respectively. Interestingly, increasing the PBD to more than 0.1 mol% lowered the T_g of the bulks. There are two possible hypotheses for this phenomenon: either T_g of the polymer itself decreased with the reduction in molecular weight ^[8], or T_g was decreased by the increment in low-molecular weight compounds which plasticized the bulk. The T_g of purified copolymer with a PFPMA content of 35 mol%, the weight-average molecular weight (**Figure 5.16**), and the amount of unreacted monomers and PBD (**Figure 5.17**) were measured.

The molecular weight decreased from 460,000 to 150,000 as the amount of added PBD was increased from 0.01 to 1.5 mol%, while the T_g of the purified copolymers were almost the same. On the other hand, while the amount of remaining MMA was 0.8–0.9 wt% in all cases, the remaining PFPMA decreased from 0.6 to 0.07 wt% when the added PBD increased from 0.01 to 0.1 mol%. In addition, the amount of unreacted PBD increased against the amount of added PBD in the feed. **Figure 5.18** shows the relationship between the ΔT_g (purified–bulk) and the total amount of remaining components in the bulk.

The approximated line by the least-square method goes through near the zero point; this means that the plasticization effect from the remaining monomers and unreacted PBD decreased the T_g of the copolymer bulks. Therefore, the copolymer bulk had the highest T_g when the amount of added PBD was 0.1 mol% and produced the fewest remaining components, as shown in **Figure 5.17**. The optimum preparation conditions for T_g are summarized in **Table 5.4**. In the following investigation, the copolymer bulks prepared with these conditions except for the monomer concentration were utilized.



Figure 5.16 Relationship between the amount of PBD in the monomer feed, T_g of purified polymers (\Box), and weight-average molecular weight (\bullet).



Figure 5.17 Amount of residual MMA (\diamond), PFPMA (\blacklozenge), and PBD (\triangle) in copolymer bulks against the amount of PBD in the monomer feed. The PFPMA content in the monomer feed was 35 mol%.



Figure 5.18 Relationship between the total amount of remaining monomers and PBD in copolymer bulks and ΔT_g (purified–bulk). The PFPMA content in the monomer feed was 35 mol%.

Table 5.4 Optimum preparation conditions for copolymer b	ulks
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MMA	PFPMA	Initiator	Chain Transfer	Temperature	Time
35 mol%	65 mol%	PBD 0.1 mol%	n-LM 0.125 mol%	110 °C	48h

5.8 Optical Properties 5.8.1 Absorption Loss

In this section, absorption losses of MMA-*co*-PFPMA bulks are discussed. The preparation conditions are given in Table 5.4. Since the wavelengths of the high-speed light source (670–680 nm) are located in the tail of the 5th overtone of C-H stretching vibrational absorption ^[9], reducing the C-H bonds per unit volume of polymers is the most effective way for lowering the attenuation. The C-H bonds per unit volume can be estimated by the density of the bulk and is calculated from Eq. 5-21 for this copolymeric system.

$$n = \left(\frac{8w_1}{m_1} + \frac{5w_2}{m_2}\right) dN_A$$
 (5-21)

where d is the density of the bulk, w_1 and w_2 are weight fractions of MMA and PFPMA, m_1 and m_2 are molecular weights of MMA and PFPMA, and N_A is Avogadro's number. Figure 5.19 shows the data from the density measurement of copolymer bulks and the percentages of C-H bonds per unit volume compared to PMMA.

While the number of C-H bonds per PFPMA monomer unit is five, which is smaller than that for MMA by only three, the amount per unit volume of poly(PFPMA) is as small as 34% of that for PMMA due to the bulky structure. Accordingly, the percentage of C-H bonds per unit volume of the copolymer decreased linearly as the PFPMA content in the monomer feed increased. The transmittance of the copolymer bulk with a PFPMA content of 35 mol% was measured and compared with those for PMMA and poly(PFPMA). To evaluate the data precisely, the measured transmittance was corrected to take the light reflection at end faces of the bulk into account. The reflectance ratio can be obtained by refractive index values. The refractive indices of copolymer bulks were measured by the prism coupling method, and the data are summarized in **Table 5.5**. The revised transmittance spectra are shown in **Figure 5.20**.



Figure 5.19 Density (\blacklozenge) and percentage of C-H bonds per unit volume compared with that for PMMA of copolymer bulks (\diamondsuit) against the PFPMA content in the monomer feed.

_						
			Refractive index			
	MMA ^c (mol%)	PFPMA ^c (mol%)	409.2 (nm)	650.3 (nm)	833.7 (nm)	1546 (nm)
_	100	0	1.5054	1.4886	1.4851	1.4794
	65	35	1.5005	1.4807	1.4760	1.4699
	0	100	1.5076	1.4838	1.4786	1.4717

Table 5.5Refractive indices of PMMA, MMA-co-PFPMA (65/35 mol%), poly(PFPMA) bulks^{a, b}

^a The polymerization reactions were performed at 110 °C for 48 h with PBD (0.1 mol%) and *n*-LM (0.125 mol%).

^b Monomer conversions were 93–99 wt%.

^c Molar concentration in the monomer feed.



Figure 5.20 Transmittance spectra of PMMA, MMA-*co*-PFPMA (65/35 mol%), and poly(PFPMA) bulks. The optical path was 3.0 cm.

The strong peaks at 720 and 900 nm correspond to the 4th and 5th overtones of C-H vibration, respectively ^[9]. The copolymer had 68% C-H bonds per unit volume compared to PMMA, as shown in Figure 5.19; this resulted in a smaller C-H absorption intensity for the transmittance spectrum. The electronic transitional absorption loss of the copolymer was confirmed to be small enough and we can see it does not influence the transmittance at the emission wavelength of the light source. Moreover, a conspicuous increment in the scattering loss, which is one of the specific characteristics of copolymers, was not observed. In general, when both monomer reactivity ratios are not equal to unity, large heterogeneous structures of refractive index are formed and the copolymers tend to have extremely high scattering losses. However, since PMMA and poly(PFPMA) had almost identical refractive indices, as shown in Table 5.5, the increment in scattering loss was negligibly small and the effect on reducing C-H absorption was enhanced in this As for light scattering property of MMA-co-PFPMA, we will copolymeric system. circumstantially discuss in the next section. The copolymer bulk was clarified as having a higher transmittance at broad wavelengths than PMMA.

To keep using the copolymeric fiber as a transmission medium for home networks, the low attenuation should be maintained for a long time. As mentioned in section 3.5, the biggest cause of attenuation degradation is water absorption ^[10, 11]. For the wavelength region of 670–680 nm, the 4^{th} O-H stretching vibration and O-H bending vibration combine. The water absorption of the polymer bulks was measured by immersing the samples in water at 75 °C and is shown in **Figure 5.21**. The saturated water absorption of poly(PFPMA) is as small as 0.04 wt% and is 1/50 of the absorption for PMMA. This is due to fluorine and the smaller amount of carbonyl groups per unit volume, which tend to produce hydrogen bonds with water molecules. The saturated water absorptions of the copolymers with PFPMA contents of 6, 23, and 50 mol% were 1.4, 0.68, and 0.25 wt%, respectively. Based on these results, GI POFs based on the copolymer are expected to have good humid stabilities.



Figure 5.21 Time series variation of water absorption measured with water at 75 °C. The sample volumes were $\phi 10 \times 10$ mm. The PFPMA contents in the monomer feed were 0 (\circ), 6 (Δ), 23 (\diamond), 50 (\Box), and 100 (\times) mol%.

5.8.2 Scattering Loss

In the previous section, the copolymer of MMA and PFPMA was revealed to have a higher transmittance than that for PMMA at broad wavelengths because of having a smaller amount of C-H bonds per unit volume. From the result of **Figure 5.20**, the scattering loss of the copolymer also seems to be small enough, but the accurate intensity of scattering loss can not be determined by the transmittance measurement. In this section, the scattering loss of the copolymer is discussed in detail.

As mentioned before, copolymers generally have extremely high scattering losses due to the heterogeneous structure of refractive index and have not been the leading candidate for POF base materials. For instance, in the case of MMA-*co*-PFPMA system, the final copolymer has a broad content distribution because of the difference of monomer reactivity ratios: r_{12} (PFPMA) = 1.30, r_{21} (MMA) = 0.56. Figure 5.22 shows the content distribution of the final copolymer calculated by integrating the copolymer equation (Eq. 5-4). The initial monomer content of MMA and PFPMA is 50/50 mol%. The calculation method was described in section 5.2.



Figure 5.22 Distribution of MMA-*co*-PFPMA composition after 100% polymerization when MMA/PFPMA=50/50 mol% in feed.

As shown in **Figure 5.22**, except for the special condition of $r_{12} = r_{21} = 1$, each polymer chain usually consists of two kinds of monomer unit with different composition, resulting the fluctuation of refractive index and the corresponding light scattering. Using the fluctuation theory ^[12], the intensity of the isotropic light scattering V_V^{iso} from thermally induced density fluctuations in a structureless liquid is expressed by

$$V_V^{iso} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 kT\beta$$
(5-22)

However, when the polymer has such a large sized heterogeneity in its high ordered structure, it is known that the intensity of isotropic scattering depends on the scattering angle as shown in **Figure 2.4**. The part of isotropic scattering with angular dependence is given by ^[13, 14]

$$V_{V2}^{iso} = \frac{8\pi^3 \langle \eta^2 \rangle a^3}{\lambda_0 (1 + \nu^2 s^2 a^2)^2}$$
(5-23)

Full details and explanations of each parameter have already been described in section 2.3, but the point we wish to emphasize here is the $\langle \eta^2 \rangle$ which denotes the mean-square average of the fluctuation of all dielectric constants. In the copolymeric system of MMA and PFPMA, the refractive indices of PMMA ($n_D = 1.4914$) and poly(PFPMA) ($n_D = 1.4873$) are almost identical. In other words, even if the copolymer has a broad content distribution, the dielectric fluctuation must be much smaller compared with those for general copolymers. Thus we expected that the increment of scattering loss accompanied with the copolymerization would be negligibly small. To clarify the validity of the hypothesis and determine the intrinsic scattering loss of the copolymer, we did following experiments.

Firstly, we prepared three kinds of polymers: PMMA, MMA-*co*-PFPMA (50/50 mol%), and poly(PFPMA). Monomer mixtures with PBD (0.10 mol%) as an initiator and *n*-LM (0.125 mol%) as a chain transfer agent were transferred into glass ampules with the diameter of 10 mm and subjected to repeated freeze-pump-thaw cycles; this was followed by sealing under vacuum with flame. The polymerization reactions were carried out at 90, 110, 130, and 150 °C in oil baths for 48 h.

Light scattering intensities V_V and H_V were measured by using a super dynamic light

scattering spectrophotometer (Otsuka Electronics Co. Ltd., DLS-7000). The symbol A of the scattering component A_B is the direction of the polarizing phase of a scattered light and the subscript B is that of an incident light, where the symbols V and H denote vertical and horizontal polarizations, respectively. Details of measurement method are written in section A.7. The correlation length a which is a measure of the size of the heterogeneities and the mean-square average of dielectric fluctuation $\langle \eta^2 \rangle$ were calculated based on the theory given in section 2.3. The total scattering loss α_t is composed by three parts: α_1^{iso} , α_2^{iso} , and α^{aniso} . α_1^{iso} is the isotropic scattering loss from V_{V1}^{iso} with no angular dependence, α_2^{iso} is the isotropic scattering loss from H_V . Each scattering loss was obtained by Eqs. 2-22, 2-23, and 2-24. As typical data, molecular weight, glass transition temperature, amount of residual monomer, and refractive index were also measured by GPC, DSC, GC, and prism coupling, respectively. Relationships between the light scattering intensity and scattering angle for three kind polymers are shown in Figures. 5.23-5.28. Scattering data and all physical properties are summarized in Tables 5.6, and 5.7, respectively.



Figure 5.23 V_V scattering of PMMA bulks polymerized at 90 °C (\diamond), 110 °C (\Box), and 130 °C (\triangle) for 48 h.



Figure 5.24 H_V scattering of PMMA bulks polymerized at 90 °C (\Diamond), 110 °C (\Box), and 130 °C (\triangle) for 48 h.



Figure 5.25 V_V scattering of MMA-*co*-PFPMA (50/50 mol%) bulks polymerized at 90 °C (\diamond), 110 °C (\Box), 130 °C (\triangle), and 150 °C (\circ) for 48 h.



Figure 5.26 H_V scattering of MMA-*co*-PFPMA (50/50 mol%) bulks polymerized at 90 °C (\diamond), 110 °C (\Box), 130 °C (\triangle), and 150 °C (\circ) for 48 h.



Figure 5.27 V_V scattering of poly(PFPMA) bulks polymerized at 90 °C (\diamond), 110 °C (\Box), and 130 °C (\triangle) for 48 h.



Figure 5.28 H_V scattering of poly(PFPMA) bulks polymerized at 90 °C (\diamond), 110 °C (\Box), and 130 °C (\triangle) for 48 h.

	P.T. (°C)	a (nm)	⟨η²⟩ (×10 ⁻⁹)	α ^{iso} (dBkm ⁻¹)	α2 ^{iso} (dBkm ⁻¹)	α ^{aniso} (dBkm ⁻¹)	α _t (dBkm⁻¹)
РММА	90 110 130 150 ^b	148.0 106.7 -	3.53 0.30 0 -	78.9 9.1 10.5 -	41.0 2.2 0	4.1 2.9 2.5	124.1 14.2 13.1
MMA- <i>co</i> -PFPMA 50/50 (mol%)	90 110 130 150	132.7 79.3 73.8	1.63 3.45 0 2.95	5.5 4.0 5.2 5.8	16.6 17.2 0 13.2	52.2 38.1 41.1 44.3	74.2 59.3 46.3 63.3
poly(PFPMA)	90 110 130 150 ^c	172.2 200.3 -	28.9 0 23.2	7.6 9.1 5.1	4.1 0 4.0	71.9 73.7 76.5	83.6 82.7 85.6

Table 5.6 Scattering parameters of PMMA, MMA-*co*-PFPMA (50/50 mol%), and poly(PFPMA) polymerized at 90, 110, 130, and 150 $^{\circ}$ C ^a

^a Polymerization reactions were carried out with PBD (0.1 mol%) and n-LM (0.125 mol%).

^b Numerous bubbles were produced during the polymerization.

^c Solid bulk could not be obtained due to the low conversion.

	P.T.	Mw		T _a	Residue	b	
	(°C)	(×10 ⁵)	ww/wn	(°Č)	MMA	PFPMA	n ₆₃₃
	90	1.3	1.8	102	3.0	0	1.4890
	110	1.2	1.7	113	0.7	0	1.4886
FIVIIVIA	130	1.0	1.6	107	1.0	0	1.4891
	150 ິ	-	-	-	-	-	-
	90	2.8	2.8	98	2.1	3.5	1.4809
MMA- <i>co</i> -PFPMA	110	2.3	2.3	113	0.5	1.6	1.4800
50/50 (mol%)	130	1.7	1.7	101	0.8	3.2	1.4811
	150	1.4	1.4	66	1.9	10.8	1.4817
	90	3.3	2.4	90	0	7.8	1.4855
poly(PFPMA)	110	2.3	2.2	99	0	5.2	1.4849
	ر 130	1.6	1.8	77	0	10.9	1.4858
	150 [°]	-	-	-	-	-	-

Table 5.7 Physical properties of PMMA, MMA-co-PFPMA (50/50 mol%), and poly(PFPMA) polymerized at 90, 110, 130, and 150 $^{\rm o}$ C $^{\rm a}$

^a Polymerization reactions were carried out with PBD (0.1 mol%) and n-LM (0.125 mol%).

^b Refractive index at 633 nm wavelength.

^c Numerous bubbles were produced during the polymerization.

^d Solid bulk could not be obtained due to the low conversion.

First of all, we will discuss isotropic scattering with angular dependency V_{V2}^{iso} . For PMMA, polymer bulks polymerized at 90 and 110 °C exhibited forward isotropic scatterings, whereas the bulk polymerized at 130 °C showed no angular dependency. Koike *et al.* reported that the origin of the excess light scattering observed in PMMA bulks as follows ^[15-17]. The large-size heterogeneities causing the excess scattering of several hundred dB/km are the isotropic structures with a correlation length of several hundred angstroms and are not due to extrinsic impurities, high molecular weight, formation of cross-links, specific tacticities, or aging. The excess scattering is mainly due to voids caused by the volume shrinkage accompanying polymerization of the remaining monomer trapped inside the polymer glass. In addition, he mentioned that the heterogeneous structure is generated during the polymerization below T_g at high conversion but disappears after a long enough heat treatment above T_g . The result of Figure 5.23 agrees well with his report. Poly(PFPMA) bulks also showed similar tendency. In this case, however, we can see the polymer bulk showed no angular dependency when polymerized at 110 °C, not 130 °C. As discussed in chapter 4, for poly(PFPMA), the polymerization conversion drastically decreases with increasing the polymerization temperature above 110 °C because of the steric hindrance or the low ceiling temperature. Actually, the amount of remaining monomer in the poly(PFPMA) bulk polymerized at 130 °C was measured to be 10.9 wt%, and the remaining monomer is believed to form the large-size heterogeneity. Kaino et al. also reported the effect of a large amount of residual monomer to the light scattering property by using PMMA and poly(styrene)^[18]. Similarly to these homopolymers, in the copolymer of MMA and PFPMA, it was interestingly observed that the isotropic scattering with angular dependence disappears when polymerized at above T_g . We may, therefore, reasonably conclude that the heterogeneous structure causing the high scattering loss can be eliminated by reducing the dielectric fluctuation.

Next, we will see the intrinsic isotropic scattering with no angular dependency V_{V1}^{iso} . Here, we deal with PMMA, MMA-*co*-PFPMA, and poly(PFPMA) bulks polymerized at 130, 130, and 110 °C, respectively, which showed no angular dependences. For PMMA, isotropic scattering loss α_1^{iso} calculated from V_{V1}^{iso} was 10.5 dB/km and was compatible with reported values ^[15-17]. As mentioned before, V_{V1}^{iso} is expressed by Eq. 5-22 and can be directly related to refractive index and isothermal compressibility. To compare the observed V_{V1}^{iso} with the value calculated from Eq. 5-22, we estimated the isothermal compressibility from its chemical structure ^[19, 20]. Full details of the estimation method are described in Appendix E. **Table 5.8** is the comparison of V_{V1}^{iso} and α_1^{iso} between observed and calculated values. This calculation method can be applied to amorphous homopolymers but it is debatable whether the method is suitable for copolymers. Thus, we listed here only calculated values for PMMA and poly(PFPMA).

	eta at \mathcal{T}_g (cal.)	Vv1 ^{iso} (×10 ⁻¹⁰ m ² N ⁻¹)		${lpha_1}^{\sf iso}$ (dBkm ⁻¹)	
	(×10 ⁻¹⁰ m ² N ⁻¹)	cal.	obs.	cal.	obs.
PMMA	3.7	2.7	2.9	9.8	10.5
MMA- <i>co</i> -PFPMA 50/50 (mol%)	-	-	1.4	-	5.2
poly(PFPMA)	4.1	3.0	2.5	10.8	9.1
PMMA MMA- <i>co</i> -PFPMA 50/50 (mol%) poly(PFPMA)	(×10 ⁻¹⁰ m ² N ⁻¹) 3.7 - 4.1	2.7 - 3.0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	 cal. 	0 1

 Table 5.8
 Isotropic light scattering loss at 633 nm calculated from their molecular structures in comparison with observed values

Calculated V_{V1}^{iso} of both PMMA and poly(PFPMA) agreed well with their observed values, and it was confirmed that the intensity of isotropic scatterings of PMMA and poly(PFPMA) are intrinsically very close. On the other hand, the V_{V1}^{iso} of MMA-*co*-PFPMA was much smaller than those of PMMA and poly(PFPMA). As mentioned above, V_{V1}^{iso} is affected by refractive index and isothermal compressibility. However, as listed in **Table 5.7**, the refractive indices of these three polymers are almost the same and the slight difference can not be the reason for causing the big difference of V_{V1}^{iso} . Moreover, it is also hard to believe that only the isothermal compressibility of the copolymer is exceptionally small. Accordingly, it is not to be denied that the observed values included some errors. One possibility is a birefringence. The basic concept of this phenomenon is described in Appendix D. If the polymer bulk has a relatively large birefringence which can affect the polarization of incident light and scattered light, the detected V_V and H_V would be slightly distorted. There is room for argument on this point.

From the measurement of H_V scattering, it was found that the H_V increases with increasing the PFPMA content. The anisotropic scattering can be theoretically expressed by

$$H_{V} = \frac{16\pi^{4} (n^{2} + 2)^{2} N \langle \eta^{2} \rangle}{135\lambda_{0}^{4}}$$
(5-24)

where *n* is the refractive index, λ_0 is the wavelength in vacuum, *N* is the number of scattering

units per cm³, and $\langle \eta^2 \rangle$ is the mean square of the anisotropic parameter of polarizability per scattering unit. As shown in this equation, H_V strongly depends on the polarizability. Thus the copolymer and poly(PFPMA) having phenyl groups are believed to exhibit larger H_V than PMMA. Similar result was reported for poly(benzyl methacrylate) ^[21], poly(styrene) ^[21], and poly(carbonate) ^[23, 24].

These results lead to the conclusion that the total scattering loss of the copolymer is slightly higher than that for PMMA by about 30 dB/km when the copolymer consists of MMA and PFPMA with the same concentration. However, it is not due to the copolymerization but also the anisotropy of PFPMA having phenyl groups.

5.9 Fabrication of GI POF— Rod-in-Tube Method

From section 5.6 to 5.8, we have clarified that the copolymer of MMA and PFPMA has higher thermal stabilities and a higher transmittance than those for PMMA. Regarding thermal properties, T_g and T_{d5} already satisfied the target values for home networks when the PFPMA content in the monomer feed is 0-60 mol%. The last one is the attenuation. To confirm the attenuation of the fiber based on the copolymer, we have investigated the preparation of the copolymeric GI POF.

As a dopant that forms a parabolic refractive index profile in the core region of the GI POF, diphenyl sulfide (DPS) was selected. DPS is a common dopant for GI POFs based on PMMA and shows a good solubility with MMA-*co*-PFPMA. Copolymer bulks with several amounts of DPS were prepared under the conditions given in **Table 5.4**, and the T_g and refractive index were measured. For comparison, the same experiments were carried out with PMMA. The results are shown in **Figures 5.29**, **5.30** and **5.31**. x and y in linear approximate equations correspond to the horizontal and vertical axes, respectively.

Note that the refractive index of the copolymer was slightly lower than that for PMMA. The data summarized in **Table 5.5** indicates that the copolymer had a lower refractive index than both PMMA and poly(PFPMA). This is because the copolymer had a larger free volume since the unit size of MMA and PFPMA are quite different. Thus, the copolymer with DPS had a lower T_g than PMMA by approximately 15 °C when they had the same refractive index.



Figure 5.29 Relationship between the amount of doped DPS and T_g of MMA-*co*-PFPMA (65/35 mol%) (\circ) and PMMA (\bullet) bulks.



Figure 5.30 Relationship between the amount of doped DPS and refractive index of MMA-*co*-PFPMA ($65/35 \mod$) (\circ) and PMMA (\bullet) bulks.



Figure 5.31 Relationship between the T_g and refractive index of MMA-*co*-PFPMA (65/35 mol%) (\circ) and PMMA (\bullet) bulks.

An important parameter that indicates the appropriate amount of dopant is the numerical aperture (NA), which is expressed as follows (same as Eq. 1-1):

$$NA = \sqrt{n_1^2 - n_2^2}$$
(5-25)

where n_1 and n_2 are the refractive indices of the core center and cladding layer, respectively. To confine the light into the core region, a NA of over 0.2 is desired. In other words, the necessary amount of dopant depends on the kind of cladding material. For instance, if we use a copolymer with the same composition as the core, the refractive index of the core must be over 1.4971 to obtain a NA of 0.2 from the following equation:

$$n_1 = \sqrt{NA^2 + n_2^2} = \sqrt{0.2^2 + 1.4837^2} = 1.4971$$
(5-26)

where 1.4837 is the refractive index of the copolymer with a PFPMA content of 35 mol%. When

the refractive index of the copolymer core is 1.4971, the T_g is calculated as 93 °C from approximated line in **Figure 5.31**, which satisfies the required value of home networks (> 90 °C).

$$T_g = -1726.8 \times 1.4971 + 2678.2 = 93 \tag{5-24}$$

However, the mechanical properties of this copolymer are somewhat inferior to PMMA, and thus the copolymer cladding system is not suitable. On the other hand, when using PMMA as the cladding material, the necessary refractive index of the core is calculated as 1.5048, which results in a low T_g of 80 °C.

Therefore, to reduce the refractive index of the cladding, a copolymer of MMA and 2,2,2-trifluoroethyl methacrylate (TFEMA) was investigated as the cladding material. Although the T_g of poly(TFEMA) is as low as 75 °C, the refractive index is also as small as 1.4182. We have already shown these basic data of poly(TFEMA) in **Table 3.2**.

In a previous study, the relationship among the T_g , refractive index, and TFEMA content in the monomer feed has been reported ^[25]. When the TFEMA content is 20 mol%, a copolymer with a low refractive index of approximately 1.47 that maintains a T_g of over 100 °C can be obtained. Moreover, GI POFs with the copolymer cladding have been revealed to have good humid stabilities since the saturated water absorption of the copolymer is much lower than that of PMMA. Based on the theory of light propagation, a small part of the propagating light goes through the cladding layer. Thus, the cladding material should also have a high transparency. The percentage of C-H bonds per unit volume of poly(TFEMA) is 64% of that for PMMA, and the copolymer has smaller absorption losses. In addition, the scattering loss of the copolymer is small enough because both monomer reactivity ratios are close to unity. When MMA is M1 and TFEMA is M2, the reactivity ratios are $r_{12} = 0.83$ and $r_{21} = 0.86$. PMMA and poly(TFEMA) have quite different refractive indices, and it must be noted that the mechanism for reducing the heterogeneity of the refractive indices is completely different from MMA-co-PFPMA. In this thesis, a cladding with 20 mol% TFEMA was utilized. The T_g and refractive index were 100 °C and 1.4703, respectively. To maintain the T_g of the core over 90 °C, the amount of added DPS must be less than 5.7 mol%, according to the approximated equation in Figure 5.29. Thus, MMA-co-PFPMA (65/35 mol%) with 5 mol% DPS was prepared as the core. T_g was 92 °C and the NA was 0.28.

Firstly, we tried to prepare the preform with a GI profile by the interfacial-gel polymerization technique ^[26, 27], however, the boundary between the core and cladding layer became hazy because the core and cladding consisted of different materials. Thus, as we investigated for preparing the GI preform based on poly(TCEMA) in section 3.4, we adopted the rod-in-tube method ^[28].

In the rod-in-tube method, a core rod with a dopant and a cladding tube are separately prepared. The core rod was prepared in the same manner without purification as given in Table 5.4. For the dopant, 5 mol% DPS ($n_D = 1.633$) was added to the core solution. The cladding tube based on MMA-co-TFEMA (20/80 mol%) was prepared as follows. A glass tube containing monomer mixtures -0.20 mol% BPO as the initiator, and 0.28 mol% nBM as the chain transfer agent-was rotated on its axis at 3,000 rpm in an oven at 70 °C for 3 h. The monomer mixtures were placed on the inner wall of the glass tube through centrifugal force and polymerized. After heat treatment at 90 °C for 24 h, a polymer tube was obtained as a cladding layer for a GI preform. The core rod was inserted into the tube, and both ends were closed with Teflon rods. The rod was then covered with a heat-shrinkable tube and heated in an oven at 150 °C for 24 h. During the heat treatment, the core rod and cladding tube adhered to each other; the dopant diffused into the cladding layer, forming the GI profile. This way, the scattering loss for the core region did not increase since both layers consisted of similar polymers. Actually we could prepare a GI preform having the MMA-co-PFPMA core without any hazy part. The heat drawing for the GI preform was carried out at 220-240 °C, and the fiber diameter was controlled to be 600 µm. The final compositions of cladding and core layers are summarized in Table 5.9.

Table 5.9 Final cladding and core compositions of GI POFs based on MMA-co-PFPMA

Cladding	Core
MMA 80 mol%	MMA 65 mol%
TFEMA 20 mol%	PFPMA 35 mol%
BPO 0.20 mol%	PBD 0.10 mol%
<i>n</i> -BM 0.28 mol%	<i>n</i> -LM 0.125 mol%
	DPS 5.0 mol%

5.10 Characterization of GI POF Based on MMA-*co*-PFPMA 5.10.1 Attenuation

The attenuation spectrum of the GI POF is shown in **Figures 5.32** and **5.33**. The broken line is a spectrum of a typical GI POF based on PMMA for comparison. The attenuation spectra were measured by the cut-back method ^[29]. The emission wavelength (670–680 nm) of VCSEL is located in between the 5th and 6th overtones of C-H stretching vibrational absorptions. While the attenuation at wavelengths of 670–680 nm for the PMMA-based GI POF was as high as 295–323 dB/km due to the strong C-H absorption losses, the copolymeric GI POF had much smaller peaks and the attenuations were 172–185 dB/km, which satisfies the required attenuation for the proposed optical home network systems. Attenuation values are summarized in **Table 5.10**. As discussed in section 5.8, the light scattering of MMA-*co*-PFPMA is slightly higher than that of PMMA due to the anisotropy of phenyl groups. However, this figure clearly indicates that the effect of fluoro substitution for reducing the C-H bonds per unit volume was much larger than the slight increment of scattering loss.



Figure 5.32 Attenuation spectra of GI POFs based on MMA-*co*-PFPMA (65/35 mol%) (solid line) and PMMA (broken line).



Figure 5.33 Magnification of Figure 5.32. Attenuation spectra of GI POFs based on MMA-*co*-PFPMA (65/35 mol%) (solid line) and PMMA (broken line).

Table 5.10 Attenuation values of MMA-co-PFPMA (65/35 mol%), and PMMA-based GI POFs

	Wavelength				
	650 nm	670 nm	680 nm		
PMMA ^a	194 (dB/km)	295	323		
MMA- <i>co</i> -PFPMA ^b 65/35 mol%	130	172	185		

^a Preform was prepared by the interfacial-gel polymerization technique.

^b Preform was prepared by the rod-in-tube method and the core and cladding consist of MMA-*co*-PFPMA (65 / 35 mol%) and MMA-*co*-TFEMA (80 / 20 mol%), respectively.

5.10.2 Bandwidth

The -3dB bandwidth ^[29] of the GI POF—measured by launching via SMF with the core of 5 μ m—was as high as 1.34 GHz. The length of the test fiber was 50 m, which is expected to be the maximum laying distance in a house, and the launching method was almost identical to the exciting condition supposed in practical use. The high bandwidth ensures that there is enough capacity to transmit data at a high-speed rate of Gbit/s. This is attributed to the GI profile in the core region. The refractive index profile was difficult to be measured precisely by the transverse interferometric technique using Interphako, since there was the sharp wall of refractive index on the boundary between the MMA-*co*-PFPMA core (n_D=1.4837) and MMA-*co*-TFEMA cladding (n_D=1.4703). Thus, the profile was evaluated by the near field pattern (NFP) method ^[29]. **Figure 5.34** represents the cross-sectional NFP image and light intensity profile of the GI POF, which directly relate to the refractive index profile in the core region. The DPS added in the core diffused into the cladding layer and formed the quadratic profile, leading to high-speed data transmission. However, with considering the material dispersion of MMA-*co*-PFPMA, which is similar to that of PMMA, this copolymeric fiber should have potentially a much higher bandwidth. The optimization of the heating process for obtaining the optimum refractive index profile has to be further investigated.



Figure 5.34 Observed cross-sectional NFP image (left) and intensity profile (right) for the GI POF based on MMA-*co*-PFPMA (65/35 mol%) through 50 m and launched via a SI POF with the core diameter of 400 μ m.

5.10.3 Eye-Pattern

The performance of the fiber system was confirmed by the eye-pattern method ^[29]. Full details of the eye-pattern method will be described in section B.5, but an outline of the technique is explained here. A 1.25 Gbps data transmission through the copolymeric GI POF with the length of 30 m was demonstrated. Random data patterns at 1.25 Gbps from pulse pattern generator (MP1758A, Anritsu Ltd.) were converted to optical signals at 670 nm by a optical Gigabit Ethernet transceiver (EDL1000G, Firecomms Ltd.). The optical signals were coupled into the copolymeric GI POF and were reconverted to electric signals by the transceiver and detected by sampling oscilloscope (86100 A, Agilent Inc.). An eye diagram was measured and a mask regulated as Gigabit Ethernet by TTC standard (JT-957) was covered. As shown in **Figure 5.35**, a good eye opening without any error is obtained and it is confirmed that this fiber sufficiently ensures the 1.25 Gbps transmission through 30-m length.



Figure 5.35 Eye diagram of 1.25 Gbps data transmission after the 30-m GI POF based on MMA-*co*-PFPMA (65/35 mol%).

5.11 Conclusion

As a novel base material for GI POF to be used in gigabit in-home communications, MMA and PFPMA copolymers were prepared, and its thermal and optical properties were characterized. In chapter 4, we have mentioned that poly(PFPMA) bulk has much lower T_g and T_d than those for precipitated one because of having a large amount of remaining monomer. In this chapter, the problem was successfully solved by using the difference of monomer reactivity ratios. When the PFPMA content in the monomer feed was 0–60 mol%, both the T_g and T_d were shown to be higher than desired values for home networks. Furthermore, the optimum preparation condition was investigated, and the highest T_g of 118 °C was obtained when the PFPMA content and amount of added initiator were 35 and 0.1 mol%, respectively. In general, copolymers show extremely high scattering loss accompanied with copolymerization was not observed. As the result, the copolymer with few C-H bonds exhibited a higher transmittance than that for PMMA.

A low-loss GI POF based on the copolymer with an attenuation of 172–185 dB/km at wavelengths of 670–680 nm was successfully obtained. The -3dB bandwidth was as high as 1.34 GHz for 50 m and the 1.25 Gbps data transmission was demonstrated. Both the core and cladding layer were designed to have good humid stability, and the minimum T_g was controlled to be over 90 °C, ensuring long-term operation in a house environment.

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Chapter 6 Conclusion and Future Work

The world is definitely turning digital. Aside regular telephone and web browsing, content-rich services such as music, images and video have now a tremendous impact on communications, hence telecommunication infrastructure. To back such accelerated capacity demand in worldwide exchanges, data rates kept on increasing and optical fiber, which is the most versatile media that can be used to convey information, is conquering more and more footprint in operator's networks. Optical fibers can now be encountered anywhere in network such as submarine links, long distance terrestrial networks, metropolitan and access loops, and Fiber-to-the-Home (FTTH) drop architectures, but not inside building and houses. The trunk line is connected to metal cables and light signals are still converted to electric signals in last nodes. In reality, FTTH subscribers do not experience the high performance of the optical information highway.

A graded index plastic optical fiber (GI POF) has been the leading candidate to directly connect the trunk line with users since it was developed in 1982. However, at the present moment, we have only a Lucina[®] which is based on a perfluorinated polymer (CYTOP[®]) as the solution. This is clearly overpriced for general consumers because of the high material cost. In this study, we focused on home network with the maximum length of 30-50 m and set a definite goal as follows; the fiber attenuation is less than 200 dB/km at 670-680 nm wavelengths, the transmission speed is over 1 Gbps, the glass transition temperature of the fiber is over 90 °C, and the 5% weight loss temperature of the base material is over 295 °C (for a mass production using the co-extrusion process). Furthermore, all materials used for the fiber must be commercially available.

In chapter 3, we firstly investigated the effect of partial halogenation on the fiber attenuation. We succeeded in preparing GI POFs based on poly(TFEMA) and poly(TCEMA) by the interfacial-gel polymerization technique and the rod-in-tube method, respectively. Attenuations of the poly(TFEMA)- and poly(TCEMA)-based GI POFs were 127–152 and 104–136 dB/km at 670-680 nm, respectively. These results allowed us to understand that the partial substitution with fluorine or chlorine is enough for POFs to be used in home network. In addition, thermal analyses carried out in chapter 3 gave us some ideas to design polymer materials with high thermal stabilities; to obtain both high glass transition temperature and high decomposition temperature, bulky structures with fluorine are preferred to be introduced into the side chain.

In chapter 4, optical and thermal properties of poly(PFPMA) have been studied. Poly(PFPMA) is a methacrylate having perfluorophenyl groups in the side chain. As expected, the polymer showed excellent high transmittance and high T_g (130 °C) and T_{d5} (317 °C). However, the bulky side chain lowered its polymerization conversion, leading to the degradation of thermal properties due to the large amount of residual monomer.

To solve the problem, in chapter 5, we investigated a copolymeric system of MMA and PFPMA. We believed that the conversion of PFPMA would increase by copolymerizing with MMA because PFPMA is more reactive than MMA. As the result, when the PFPMA content in the monomer feed was 0–60 mol%, the amount of remaining monomers were small enough and both T_g and T_{d5} were shown to be higher than required values of home network. Furthermore, we clarified that the scattering loss accompanied with general copolymerizations was negligibly small. A GI POF based on the copolymer was successfully obtained by the rod-in-tube method, and the attenuation was as low as 172–185 dB/km at 670–680 nm wavelengths because of having few C-H bonds. The -3dB bandwidth was 1.34 GHz for 50 m and the 1.25 Gbps data transmission was demonstrated. Both the core and cladding layer were designed to have good humid stabilities, and the minimum T_g was controlled to be over 90 °C, ensuring a long-term operation in a house environment. More noteworthy is that all materials used for the GI POF are commercially available, and no complicated synthesis, purification, or polymerization technique is necessary.

At the present moment, there are several competing technologies as the transmission media for home network. In particular, wireless local area network (LAN), unshielded twisted pair (UTP) cable, and power line communication (PLC) are considered to be leading candidates. We compared them in perspective of the transmission speed, reliability, easy handling, safeness, and cost. **Table 6.1** shows the comparative chart. You can see only the copolymeric fiber we proposed satisfies all the required level.
		High speed ^a	Reliability	Easy handling	Safeness	Low cost
Wireless LAN		×	×	0	×	0
UTP cable		\bigtriangleup	\bigtriangleup	\bigtriangleup	0	0
PLC		×	\bigtriangleup	0	\bigtriangleup	0
GI POF	CYTOP®	0	0	\bigtriangleup	0	×
	РММА	imes ^b	0	0	0	0
	Copolymer	0	\bigcirc	\bigcirc	0	0

 Table 6.1
 Comparative chart of several competing technologies for home network

^a At least a bit rate of 1 Gbps is necessary in distance of 30 m length.

^b Adequate high speed light sources have not been developed.

Following lists are some of the points that the author still considers to be insufficiently investigated or improvable.

Chapter 5

- ✓ Measurement of accurate light scattering by removing the birefringence effect.
- \checkmark Optimization of the refractive index profile in the core region.
- ✓ Exploring other dopants for higher T_g .
- ✓ Confirmation of the fiber stability under a heat and humid environment.
- ✓ Measurement of bending loss.
- \checkmark Fabrication and optimization of the copolymeric GI POF by the co-extrusion process.

We believe the fiber is a promising candidate for home network and this research makes some contribution for future development of plastic optical fibers.

Appendix A Experimental Methodology of Polymers

A.1 Glass Transition Temperature

Glass transition temperature (T_g) is one of the most important parameter which tells us the operating temperature limit of optical fibers. The glass transition temperature of polymer can be analyzed by a differential scanning calorimetry (DSC). In contrast to earlier use of a large, expensive adiabatic calorimeter for measurements of specific heat and enthalpies of transition, these measurements are now usually carried out on quite small samples in a DSC. The term is applied to two different modes of analysis, of which the one more closely related to traditional calorimetry is described here.

In DSC an average-temperature circuit measures and controls the temperature of sample and reference holders to conform to a predetermined time—temperature program. This temperature is plotted on one axis of an x—y recorder. At the same time, a temperature-difference circuit compares the temperatures of the sample and reference holders and proportions power to the heater in each holder so that the temperatures remain equal. When the sample undergoes a thermal transition, the power to the two heaters is adjusted to maintain their temperatures, and a signal proportional to the power difference is plotted on the second axis o the recorder. The area under the resulting curve is a direct measure of the heat of transition. Although the DSC is less accurate than a good adiabatic calorimeter (1-2 % versus 0.1 %), its accuracy is adequate for most uses and its advantages of speed and low cost make it the outstanding instrument of choice for most modern calorimetry.

In this dissertation, T_g measurements were performed on DSC-60 (Shimadzu Co.). All polymer samples were heated under an air atmosphere from room temperature to around 150 °C (it depends on the kind of polymer), then cooled to 0 °C and reheated to 150 °C at a scanning rate of 10 °C/min. T_g was measured during the second heating scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

A.2 Heat Decomposition Temperature

To compare heat decomposition temperatures of several polymers, we defined a 5 % weight loss temperature, that is, a temperature at which the weight of the polymer sample decreases to 95 %. That value can be obtained by measuring the m vs. T curve (TG); this is called the thermogravimetric (TG) curve.

Thermogravimetry is one of the basic method in thermal analysis. The instrument is built around a furnance where the sample is mechanically connected to an analytical balance; hence the name thermobarance for a TG instrument. The three essentially parts of a modern TG instrument are the balance, the furnance, and the instrument control/data handling system. A sensitive and reliable analytical balance is a central part of a TG instrument and it is therefore understandable that many of the TG instrument companies are former or present balance manufactures. Sensitivities typically in the order of 1 μ g and maximum loads of 1 g are required for the balance. In most cases the actual samples in a TG experiment weigh from 10 to 50 mg. Several types of balances, but a null-point weighing mechanism is favored because then the sample always remains in the same heating zone of the furnance.

There are basically three ways to place the sample relative to the balance and furnance; horizontal, top-loading, and suspended, each of which have their own advantages and disadvantages. In all cases, it is important that the sample is within the uniform temperature zone of the furnance and that the balance mechanism is protected from radiant heat and corrosive gases either evolving from the sample or used as reactive atmosphere. While all commercial thermobalances offer the use of an inert (nitrogen or argon) or oxidative (air or oxgen) atmosphere, only very few are designed to be used with corrosive and reactive atmosphere, e.g., chlorine and sulfur dioxide.

In this study, a model of TG/DTA-6200 (SII Nanotechnology Inc.) was utilized for the thermogravimetric analysis. The basic diagram is described in **Figure A.1**. TG analyses were carried out in an air stream at a scanning rate of 10 °C/min from room temperature to 450-500 °C. For polymers to be used as the base material of optical fibers, the data under an air atmosphere is more important than that for nitrogen pressure, since the polymer bulk is supposed to be melted under air in the co-extrusion process. Although a new type co-extrusion equipment using nitrogen pressure for extruding melted polymers is under investigation, it would be difficult to remove oxygen completely even in the gas co-extrusion procedure.



Figure A.1 Schematic representation of a thermogravimetric analysis.

A.3 Molecular Weight

Molecular weight of polymer can be measured by size-exclusion chromatography (SEC), which is a particular form of liquid chromatography. It is based on the separation of molecules due to their different size. All molecules over a particular size are excluded from porous silica gel or polymer beads with a defined pore size, while molecules with molecular masses below the exclusion limit of the packing material are retained. In contrast to all the liquid chromatography methods, SEC is not based on any chemical interactions with the stationary phase. The eluents can be either aqueous or organic solvents. Depending on the solvent, the technique is often referred to as gel filtration (aqueous eluents) or gel permeation (non-polar organic eluents). SEC is used mainly for the separation of large molecules. The stationary phase particles have pores of different sizes. Two extremes can be differentiated in the interaction of the molecules with the porous stationary phase. Those molecules that are too large to diffuse into any of the pores are not retained at all and are thus excluded from the stationary phase; they are eluted with the mobile phase as the first-eluted constituents (total exclusion). The smallest analytes, on the other hand, can diffuse into all the pores, and these are retained most strongly (total permeation). Analytes of medium size can permeate into only some of the pores, and thus elute in between the largest and smallest analytes (see Figure A.2).

In this study, the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of polymers was estimated by a gel-permeation chromatography (GPC-LC20AD, Shimadzu Co.) using THF as the eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained using polystyrene standards.



Figure A.2 Schematic representation of a size-exclusion chromatography.

A.4 Amount of Remaining Monomer

In this dissertation, the analysis of determining the amount of remaining monomers in polymer bulks plays a very important role. To investigate the best polymerization condition for obtaining polymer bulks with its highest T_g , the quantitative estimation of unreacted monomers which lowers T_g of bulks is absolutely imperative. The amount of remaining monomers was measured by a gas chromatography. The basic concept is described below:

Gas chromatography has a history going back to about 1940. That such a technique might be possible was suggested by Martin who did so much to establish chromatography as a valuable tool for the analyst. Like all chromatographic techniques, gas chromatography separates mixtures by taking advantage of their components differential distribution between two phases—one stationary and the other moving past it. The distinctive feature of gas chromatography is the use of a gas as the moving, or mobile, phase. A sample of the mixture to be separated is introduced into this gas stream just before it encounters the stationary phase; the components are separated by elution and detected as they emerge in the gas at the other end of the column. They are distinguished by the different times which take to pass through the column—the retention times.

The retention time of a substance is dictated by the position of its distribution equilibrium between the two phases; separation of a mixture, therefore, depends on its components having significantly different distribution equilibria. Because there is little interaction between molecules in the gas phase, the gaseous mobile phase plays a mainly passive role in the separation, serving merely to carry the components through the system. The distribution equilibria are effectively controlled by the components vapour pressures and their sorption by the stationary phase. Accordingly, the separation has to be carried out at a temperature at which the components vapour pressures are high enough to allow a realistically short analysis time, but at which the differences between their vapour pressures is proportionately high.

We used a model of GC-2010 (Shimadzu Co.) for measurements. The main components are shown in **Figure A.3**. All gas chromatograph must have a supply of gas to act as mobile phase and some means of controlling and measuring its flow rate. They must have a column, which is normally contained within a thermostatted oven. There will be some means of introducing the sample into the gas stream, usually called an injection system, and some means of detecting the separated components as they emerge from the column. The detector will have ancillary equipment associated with it to provide a permanent record of the analysis and to manipulate the data.



Figure A.3 Block diagram of gas chromatograph.

The analytical procedure is as follows: A polymer bulk is dissolved with some solvents such as chloroform and dichloromethane, then butylated hydroxytoluene (BHT) is added to the polymer solution as the standard specimen. The polymer is precipitated by adding a poor solvent such as methanol and ethanol. The supernatant liquid including monomers and BHT is injected to the equipment. The area of each peak can be calculated by the attached software. From the calibration curve which shows the relationship between area ratio and weight ratio of the monomer and BHT, the amount of remaining monomer in the polymer bulk can be obtained.

A.5 Refractive Index

Refractive index of polymer was measured by the prism coupling method using a prism coupler (Model 2010, Metricon co.). The principal components of the Model 2010 are illustrated in **Figure A.4**. A laser beam strikes the base of a high refractive index prism and is reflected onto a photodetector. The polymer sample to be measured is attached into contact with the prism base by means of a pneumatically-operated coupling head. The angle of incidence θ of the laser beam can be varied by means of a rotary table upon which the prism, polymer sample, coupling head and photodetector are mounted. At a certain values of θ , called mode angles, photons violate the total internal reflection criterion, and tunnel from the base of the prism into the polymer sample and enter into optical propagation modes, causing a sharp drop in the intensity of light striking the photodetector. From the critical angle and the refractive index of prism at a measured wavelength, the refractive index of polymer sample can be calculated by Snell's law,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \tag{A-1}$$

The measurements were carried out at the wavelengths of 409.2, 650.3, 833.7, and 1546 nm. By adopting the obtained values of refractive index at each wavelength into trinomial Sellmeier equation, which is expressed as Eq. A-2, the wavelength dependency of refractive index can be calculated.

$$n = \sqrt{\frac{a}{1 - b/\lambda^2} + \frac{c}{1 - d/\lambda^2} + \frac{f}{1 - e/\lambda^2} + 1}$$
(A-2)



Figure A.4 Optical system of prism coupler Model 2010.

A.6 Transmittance

The transmittance and its spectrum were measured by using a UV-VIS spectrophotometer (U-2800A type, Hitachi Co.). The most flexible, general-purpose spectrophotometers are double-beam, automatically recording types. The double-beam design provides tow equivalent paths for radiation, both originating with the same source. One of these beams traverses the sample, while the other passes through an identical cuvet containing reference material. The two beams are measured separately, either by duplicate detectors or by the rapidly alternating use of the same detector.

Figure A.5 shows the optical schematic of the U-2800A spectrophotometer. This instrument makes double use of its one monochromator, sending the beam of radiation through it twice. Radiation from a deuterium lamp or Iodine tungsten lamp is focused by the combination of a curved mirror M1 and a grating onto the entrance slit S2. The concave mirror of M2 collimates the beam. The beam next encounters the half mirror HM, then passes alternately via the mirror M4 to the lens L2, through the reference cuvet, to the detector D2, or the mirror M3 to the lens L1 and the sample cuvet, to the detector D1.

To evaluate the data precisely, the measured transmittance X was corrected as below to take the light reflections at the end faces of the bulks into account.

$$T = X / (1 - R)^2 \tag{A-3}$$

where T is the actual transmittance and R is the reflectance ratio. When the light enters the surface vertically, the reflectance ratio can be described by the following expression.

$$R = \left[(n_1 - n_2) / (n_1 + n_2) \right]^2 \tag{A-4}$$

where n_1 and n_2 are the refractive indices of polymer bulk and air, respectively. The refractive indices of the bulks were measured by the prism coupling method as described in the section of A.5. n_1 for each wavelength was calculated by the Sellmeier equation, and n_2 was approximated as 1.0003.



Figure A.5 The optical schematic of the U-2800A type spectrophotometer: WI Lamp; Iodine tungsten lamp (VIS), D2 Lamp; Deuterium lamp (UV), M1; Concave spherical reflector, S1; Slit, G; Diffraction grating, S2; Slit, F; Filter, M2; Mirror, HM; Half mirror, M3 M4; Flat mirror, L1 L2; Lens, D1 D2; Detector.

A.7 Scattering

The light scattering intensity was measured by using a super dynamic light scattering spectrophotometer (Otsuka Electronics Co. Ltd., DLS-7000). The measurement system is shown in **Figure A.6**. The light source is a 10-mW polarized He-Ne laser with the wavelength of 633 nm which is set up to obtain vertical polarization. The laser beam is divided into two by a half mirror. One is directly monitored by a photomultiplier tube (PMT) to compensate for the fluctuation of the laser intensity. The other beam passes through a light chopper and a polarizer (Glan Tompson prism) and then enters the sample from the side.



Figure A.6 Schematic diagram of a light scattering measurement system.

The sample is placed in the center of the cylindrical glass cell. The gap between the sample and the inner wall of the glass cell is filled with immersion oil whose index of refraction was 1.5. The glass cell is perpendicularly located on the center of the goniometer. The scattered light from the sample passes through pinhole A (1 mm diameter)-analyzer (Glan Tompson prism)-converging lens-pinhole B (0.1 mm diameter) and is detected by a PMT. Since pinhole B is located just on the focal point of the converging lens, only nearly parallel rays scattered from the center of the sample are detected. Considering the parallel incident beam and the parallel scattered beam, the scattering volume viewed from the PMT is inversely proportional to $\sin \theta$. Here θ is the scattering angle defined between the incident and scattering beams. Therefore, the observed intensity is multiplied by $\sin \theta$ to obtain normalized V_V (polarized) and H_V (depolarized) scatterings.

The setting of the scattering angle and the measurement of the scattering intensity are all operated by a computer. At a fixed scattering angle, the scattering intensities are measured 200 times, and this average is employed for data analysis. With a light chopper-lock-in amplifier system, the S/N ratio of the signal even for weak scattering light is sufficiently improved.

In this thesis, V_V and H_V intensities were measured. To estimate the absolute intensities of these, pure benzene which was purified in the same manner as the monomer mixture mentioned above was used as a standard for calibration. Since the V_V intensity of pure benzene is known to be 9.22×10^{-6} (cm⁻¹) at 633 nm wavelength, observed V_V and H_V intensities of samples were corrected as follows:

$$V_{V}(or H_{V})(cm^{-1}) = \frac{I_{s}/I_{0}}{I_{s(benzene)}} \times 9.22 \times 10^{-6} (cm^{-1})$$
(A-5)

where $I_{s(benzene)}$ and $I_{0(benzene)}$ are averages of scattered and incident light intensity of pure benzene in the range of θ =30-130 ° where benzene had no angular dependence. To confirm the accuracy of the setup, the light intensity of purified carbon tetrachloride was measured and the V_V was calculated by Eq. A-5. The value was about 5.8×10^{-6} (cm⁻¹) and was very close to the reported value of 5.9×10^{-6} (cm⁻¹).

A.8 Density

The density of polymer bulk was measured by using a density measuring kit (A&D Co., Ltd.). This method is based on the Alchimedes principle which states that the buoyant force on a submerged object is equal to the weight of the fluid that is displaced by the object. The density of solid sample can be calculated by the following equation.

$$\rho = \frac{A}{A-B} \times \left(\rho_0 - d\right) + d \tag{A-6}$$

where ρ is density of sample, A is weight in air, B is weight in water, ρ_0 is density of water, and d is density of air (0.001 g/cm³). A and B was measured by the way of the left and right description in **Figure A.7**, and ρ_0 was determined by **Table A.1**.



Figure A.7 The schematic diagram of the density measuring kit.

Temp.	0	1	2	3	4	5	6	7	8	9
	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0	99984	99990	99994	99996	99997	99996	99994	99990	99985	99978
10	99970	99961	99949	99938	99924	99910	99894	99877	99860	99841
20	99820	99799	99777	99754	99730	99704	99678	99651	99623	99594
30	99565	99534	99503	99470	99437	99403	99368	99333	99297	99259

 Table A.1
 Relationship between temperature and density of water

A.9 Copolymer Composition

In order to determine monomer reactivity ratios experimentally, we need to know the copolymer composition. Among several ways to examine the composition, the nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful tool. In this dissertation, purified polymer samples were dissolved into chloroform-d and were analyzed by using ¹H-NMR (AC 300 spectrometer, Bruker Co., Ltd.). The basic principle is described below.

Atomic nuclei with uneven numbers of protons posses a magnetic moment and therefore precess about a magnetic field from an oscillating radio frequency. If the oscillating frequency of the electromagnetic field equals the precession frequency of the atomic nuclei, a resonance signal is observed whose frequency depends on the ratio of the nuclear magnetic field to the rotational torque on the nucleus and on the strength of the external, steady, magnetic field. High-resolution nuclear magnetic resonance detects the shielding from neighboring protons in the same molecule. Such high-resolution spectroscopy methods can be used to elucidate the configuration and constitution of molecules.

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Appendix B Experimental Methodology of Optical Fibers

B.1 Refractive Index Profile

Refractive index profiles of plastic optical fibers were measured by using Interphako (Carl Zeiss aus Jena Co., Ltd.). Schematic representation of the Interphako interference microscopy is shown in **Figure B.1**. The light from (Lt) enters into a sample (S) in a glass cell (G) which is placed on stage (St) via slit (Sl) and a condenser lens (CL). The sample is immersed in the matching oil in a glass cell (G). Transparent liquid, which does not penetrate into the sample (complex of Nikon immersion oil and Junsei liquid parafin), was used as the matching oil. The light beam traversing the sample is divided into two beams by prism (Pr-1). One beam is displaced at a distance Δy_p perpendicular to the light axis by rotary wedge (RW) (Shearing device) and then recombined with the other beams by prism (Pr-2).

When shearing distance Δy_p is longer than diameter $2r_p$ of the sample, the two individual images of the specimen are completely separated, and an ordinary Mach-Zehnder interference pattern (Total splitting) is obtained as shown in **Figure B.2**. When the sample images are slightly sheared ($\Delta y_p \ll 2r_p$), an overlapped image pattern is observed as shown in **Figure B.2**(A) (Partial splitting). In **Figure B.2**, the circles denote the boundary of the sample and immersion oil, and straight lines are the interference fringes. The fringe on the center of the sample is called "standard interference fringe". The distance D between consecutive interference fringes in the surrounding medium corresponds to one wavelength of incident ray. In the case of the partial splitting method, the fringe is produced by the interference of two beams passed the sample at two positions which are distance Δy_p apart.

In this dissertation, the transverse interferometric technique is employed for the fiber measurement. The theory of he transverse interferometric technique was described in detail in references.



Figure B.1 Diagram of the primary elements for the shearing method of the Interphako interference microscopy:

Lt; light source, Sl; slit, CL; condenser lens, St; stage, G; glass cell, S; sample, OL; objective lens, RW; rotary wedge, EP; eye price, Pr-1; beam splitting prism, Pr-2; beam combining prism, Δy_p ; shearing distance



Figure B.2 Schematic representation of interference patterns by the Interphako interference microscopy.

B.2 Near Field Pattern

Near field pattern is one of the methods for estimating the refractive index profile. While the light intensity profile propagating through a SI fiber is uniformity, the output power of a GI fiber exhibits a parabolic intensity profile related to the refractive index profile of the fiber. The relationship between the refractive index and the intensity profile is

$$\frac{n(r) - n_2}{n(0) - n_2} \cong \frac{n^2(r) - n_2^2}{n^2(0) - n_2^2} = \frac{P(r)}{P(0)}$$
(B-1)

where n_2 is the refractive index of the cladding, and n(0) and P(0) are the refractive index and the power intensity of the center of the core region, respectively.

In the case that we could not measure the refractive index profile of the fiber accurately by the Interphako interference microscopy, it was evaluated by the intensity profile of NFP image. The optical system and the measurement system are described in **Figures B.3** and **B.4**, respectively. As the NFP optical system, a model of A6501 (Hamamatsu photonics, Co.) was utilized.



Figure B.3 Optical system of a Near Field Pattern.



Figure B.4 Schematic representation of a NFP measurement system.

B.3 Attenuation

Attenuation of optical power in a fiber waveguide is a result of absorption processes, scattering mechanisms, and waveguide effects. The manufacturer is generally interested in the magnitudes of the individual contributions to attenuation, whereas the system engineer who uses the fiber is more concerned with the total transmission loss of a fiber. Here we shall treat only measurement techniques for total transmission loss.

One of two basic methods is normally used for determining attenuation in multimode fibers. The earliest and most common approach involves measuring the optical power transmitted through a long and a short length of the same fiber by using identical input couplings. This method is known as the cutback technique. The other technique involves the use of an optical time domain reflectometer (OTDR). In this dissertation, we utilized the cutback method.

The cutback technique, which is a destructive method requiring access to both ends of the fiber is illustrated in **Figure B.5**. To find the transmission loss, the optical power is first measured at the output (or far end) of the fiber. Then without disturbing the input condition, the fiber is cut off a few meters from the source, and the output power at this near end is measured. If P_F and P_N represent the output powers of the far and near ends of the fiber, respectively, the average loss α in decibels per kilometer is given by

$$a = \frac{10}{L} \log \frac{P_N}{P_F} \tag{B-2}$$

where L (in kilometers) is the separation of the two measurement points. By using the cutback method the optical power emerging from the short fiber length is basically the input power to the fiber of length L, provided certain precautions are takes. These include index-matching the fiber output end to the detector surface, avoiding any instabilities in the optical source, and illuminating the same spot on the detector surface.

In carrying out this measuring technique, special attention must be paid to how optical power is launched into the fiber. This is because different launch conditions can yield different loss values. The effects on modal distributions in the fiber resulting from changes in the numerical aperture and spot size on the launch end of the fiber are shown in **Figure B.6**. If the spot size is small and its NA is less than that of the fiber core, the optical power in the fiber is concentrated in the center of the core. In this case, the attenuation contribution arising from higher-order-mode power loss is negligible. In **Figure B.6** (b) the spot size is larger than the fiber core and the spot NA is larger than that of the fiber. For this overfilled condition, those parts of the incident light beam that fall

outside the fiber core and outside the fiber NA are lost. In addition, there is a large contribution to the attenuation arising from higher-mode power loss. The difference of launch condition is also important for the bandwidth measurement, which will be described in section B.4.

In general, accurate loss data which can be extrapolated to arbitrary fiber lengths are only achievable under a steady-state equilibrium-mode distribution. An equilibrium-mode distribution occurs when the far-end and near-end radiation patterns are identical. Steady-state equilibrium-mode distributions can be achieved either by matched-beam or mandrel-wrap excitation methods. In the matched-beam method both the source NA and the spot size are well controlled so that a definite modal pattern is launched. In the mandrel-wrap excitation technique, excess higher-order modes launched by initially overexciting the fiber are filtered out by wrapping several turns of fiver around a mandrel which is about 1.0 to 1.5 cm in diameter.

In this study, a tungsten lamp (AQ-4303B, Ando Electric Co., Ltd.) and a spectrum analyzer (AQ-6315R, Ando Electric Co., Ltd.) were utilized as the light source and the detector, respectively, and the mandrel-wrap method was adopted. This launch condition is corresponded to **Figure B.6** (b).



Figure B.5 Schematic experimental setup for determining fiber attenuation by the cutback technique. The optical power is first measured at the far end, the fiber is then cut at the near end, and the power output there is measured.

(a) Restricted mode launch (RML) condition



Figure B.6 The effects of launch numerical aperture and spot size on the modal distribution. Underfilling the fiber excites only lower-order modes; an overfilled fiber has excess attenuation from higher-order mode loss.

B.4 Bandwidth

-3dB bandwidth of POF was measured by the time domain method. An experimental set up is schematically shown in **Figure B.7**. As the light source, an InGaAsP laser diode (LD) whose emission peak is located around 650 nm is used and a short light pulse with the full width half maximum (FWMH) of from 50 to 100 ps is produced by a picosecond light pulser (C8898, Hamamatsu Photonics Co.). The light emitted from the LD is coupled into the fiber via a probe fiber. A smooth surface of the fiber end is achieved by a hot plate. For a detector, a sampling oscilloscope (C8188, Hamamatsu Photonics Co.) with a computer for calculating Fast Fourier Transfer (FFT) is used to record the output pulse and to estimate the bandwidth.

The bandwidth of the POF can be measured by the pulse broadening. The principle of the time domain measurement is described below. The input and output waveform of light pulse is assumed to be x(t) and y(t), and h(t) are

$$y(t) = \int_0^t h(t-\tau) x(\tau) d\tau = h(t) \otimes x(t)$$
(B-3)

where \otimes denotes the convolution. In the measurement system mentioned above, the input and output pulses are detected. Therefore, in order to obtain the impulse response function h(t) from the relationship in Eq. B-3, fourier transform is usually operated. Fourier transform of x(t), y(t), and h(t) are assumed to be $X(\omega)$, $Y(\omega)$, and $H(\omega)$, respectively. Then these relations are given by

$$Y(\omega) = H(\omega) \cdot X(\omega) \tag{B-4}$$

Therefore,

$$h(t) = \mathfrak{I}^{-1}[H(\omega)] = \mathfrak{I}^{-1}\left[\frac{Y(\omega)}{X(\omega)}\right]$$
(B-5)

where \mathfrak{I}^{-1} is the inverse Fourier transform. The bandwidth of POF is determined at the 3 dB level of the transmission function $H(\omega)$.



Figure B.7 Schematic representation of the impulse response function measurement system.

The input waveform is obtained by using a 1-m single mode glass optical fiber which does not broaden the pulse as the test fiber. On the other hand, the output waveform through a POF is usually evaluated in two ways, that is, a restricted mode launch (RML) condition and an overfilled mode launch (OFL) condition. The concept has been already shown in **Figure B.6**. The value of -3dB bandwidth strongly depends on the launch condition. For RML condition, a graded index multimode glass optical fiber with the core diameter of 50 μ m and a single mode glass optical fiber with the core diameter of 50 μ m and a single mode glass optical fiber with the core diameter of 50 μ m and a single mode glass optical fiber with the core diameter of 50 μ m was used as the probe fiber in chapter 3 and chapter 5, respectively. Both probes have smaller NA than that of a test fiber. For OFL condition, a SI POF which has a larger core diameter and a larger numerical aperture were utilized.

B.5 Eye-Pattern

The eye-pattern technique is a simple but powerful experimental method for assessing the data-handling ability of a digital transmission system. This method has been used extensively for evaluating the performance of wire systems and can also be applied to optical fiber data links. The eye-pattern measurements are made in the time domain and allow the effects of waveform distortion to be shown immediately on an oscilloscope.

An eye-pattern measurement can be made with the basic equipment shown in **Figure B.8**. The output from a pseudorandom data pattern generator is applied to the vertical input of an oscilloscope and the data rate is used to trigger the horizontal sweep. This results in the type of pattern shown in **Figure B.9**, which is called the eye pattern because the display shape resembles a human eye. To see how the display pattern is formed, consider the eight possible 3-bit-long non return to zero (NRZ) combinations shown **Figure B.10**. When these eight combinations are superimposed simultaneously, an eye pattern as shown in **Figure B.9** is formed.

To measure system performance with the eye-pattern method, a variety of word patterns should be provided. A convenient approach is to generate a random data signal, because this is the characteristic of data streams found in practice. This type of signal generates one and zeros at a uniform rate bit in a random manner. A variety of pseudorandom pattern generators are available for this purpose. The word pseudorandom means that the generated combination or sequence of ones and zeros will eventually repeat but that it is sufficiently random for test purposes. A pseudorandom bit sequence comprises four different 2-bit-long combinations, eight different 3-bit-long combinations, sixteen different 4-bit-long combinations, and so on (that is, sequences of 2^{N} different N-bit-long combinations) up to a limit set by the instrument. After this limit has been generated, the data sequence will repeat.

In this dissertation, random data patterns at 1.25 Gbps from a pulse pattern generator (MP1758A, Anritsu Ltd.), were converted to optical signals at 665 nm by an optical Gigabit Ethernet transceiver (EDL1000G, Firecomms Ltd.). The optical signals were coupled into the test fiber and were reconverted to electric signals by the transceiver and detected by sampling oscilloscope (86100 A, Agilent Inc.). Obtained eye diagrams were evaluated by covering a mask which is regulated as the Gigabit Ethernet of TTC standard (JT-957).



Trigger line

Figure B.8 Basic equipment used for eye-pattern generation.



Figure B.9 Eye-pattern diagram.



Figure B.10 Eight possible 3-bit-long NRZ combinations.

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Appendix C Another Copolymeric System -Methyl α-chloro Acrylate-*co*-2,2,2-Trichloroethyl Methacrylate-

C.1 Preface

In this thesis, we have discussed several polymers as base materials of a novel GI POF for realizing high-speed optical home networks. As a future-oriented study, however, we have simultaneously investigated another polymer system for high speed automobile networks with the capacity over gigabit per second. The biggest difference between home networks and automobile networks is the operating temperature environment. For home networks, as mentioned in section 1.4, T_g of fibers should be at least over 90 °C, whereas for automobile networks, much higher T_g s are required to the fiber.

C.2 Review of POF in Automotive Sectors

In recent years there has been a significant increase in the complexity of electrical systems within the vehicle. Earlier, stand-alone electrical systems dominated, but today complex, in-vehicle networked electronic/computer systems are commonplace. The increasing complexity of in-vehicle electronic systems, with the associated rapid growth in the number of sensors, actuators and electrical control units, gives rise to complex control networking requirements. The cumulative customer requirements, for greater connectivity and interoperability of consumer devices, places higher demands on data communication systems. Today it is not uncommon to find 10 or 20 consumer electronic device units hooked up within a car, including: main units, DVD players, navigation systems, telephones, Bluetooth interfaces, voice recognition systems, high-end amplifiers and TV tuners. To meet all necessary requirements for data transfer between such devices, POF has been a great solution.

POF has for many years been extensively used in industrial field buses such as PROFIBUS, SERCOS and INTERBUS-S for controlling process equipment in rugged manufacturing environments. POF is attractive to the automotive industry because it reduces the weight of the wiring harness and because it provides a very good price-to-performance ratio for multimedia applications due to the availability of low cost connectors and transceivers. In addition, one more big advantage of optical fibers is that there is no emission of electromagnetic fields, and the fiber can not be affected by them.

In 1988 the domestic digital bus (D2B)^[1] was introduced in Daimler-Benz cars as the first optical data bus for an infotainment system. The D2B bus is based on a ring-bus topology with 1-mm POF and red light-emitting diodes (LEDs) around 650 nm. The system data rate at 5.6 Mbps is capable of transmitting speech, audio, and control data for phones, sound systems and speech-recognition systems. In 2001 the byteflight POF bus ^[2] was introduced by BMW into the 7 Series for an airbag sensor and deployment network capable of operating at 10 Mbps. Byteflight is a star net configuration and communication is bidirectional on a single POF. The optical components are composed of a red LED and photodiode integrated into the optical connector. Another milestone for POF based automotive network also occurred in 2001 with the first use of the Media Oriented System Transport (MOST)^[3, 4] also in the BMW 7 Series. The MOST bus is based largely on the same physical layer as the D2B network but with a raw data rate of 44.2 Mbps which allows the transmission of compressed video data. The MOST bus has now been introduced in more than 55 series car models. Now in development is a POF multimedia automotive bus, IDB-1394, based on the consumer IEEE 1394.b standard. This bus is being designed to carry 250 Mbps of data over POF and leverages the IEEE 1394.b bus both in terms of cost and also the availability of PHY and LINK Layer silicon ICs and the future deployment of consumer IEEE 1394 POF products and applications. **Figure C.1** shows the summary of several standards for automobile networks.



Figure C.1 Category of automotive networks. Yellow and orange collars indicate optical and electrical transmission system, respectively.

C.3 Motivation and Strategy

The use of an optical physical layer in the automotive area makes high demands on the deployed components in regard to the temperature range. From a temperature range viewpoint, the vehicle can be divided into three category groups: passenger area (-40 °C to +85 °C), roof module and trunk (-40 °C to +105 °C), and engine compartment (-40 °C to +125 °C) ^[5].

Typically, car manufactures actually use SI POF based on PMMA for interconnecting MOST components, which offers an attenuation of about 150 dB/km at a wavelength of 650 nm. The fiber consists of a 1.0 mm core and two claddings. There is a black PA12 cladding inside, which is inseparably connected to the core. This cladding needs to be black for laser welding of the ferrule contact. The second PA12 cladding outside is modified with elastomer for better elasticity. The outside diameter of the whole POF is 2.3 mm and the complete fiber is flame-retardant.

As mentioned above, the consumer world has a significant influence on the automotive sector. The employments of hard disk drivers, DVD players, multimedia servers etc., in the vehicle, are no longer dreams of the future. Such emerging new use cases demand an amount of bandwidth that the current infotainment systems are no longer able to provide. We believe the combination of GI POF ^[6] and VCSEL ^[7] is also a potentially interesting solution for the physical layer use in vehicle networks, not only for the infotainment networking but also for safety-critical networks. However, to introduce GI POF into all automotive networking systems, a novel base material with high T_g of over 145 °C (because the operating temperature is generally considered to be lower than the T_g by 20 °C) is absolutely imperative. For home networking, we mentioned that the attenuation of GI POF must be less than 200 dB/km at the emission wavelength of VCSEL (670-680 nm), while for automotive, even the twice attenuation 400 dB/km is acceptable since the maximum laying distance in cars is as short as 18-m length.

In this chapter, we propose a copolymer of methyl α -chloro acrylate (MCA) and 2,2,2-trichloroethyl methacrylate (TCEMA) as the candidate of a novel base material with high T_g . The chemical structure of the copolymer is shown in **Figure C. 2**. Both monomers can be easily synthesized and no complicated polymerization procedure is necessary. As described in chapter 3, halogenation reduces the amount of C-H bonds per unit volume and also the attenuation at the communication wavelength since halogen atoms possess a large volume. At the same time, the mobility of polymer main chain is reduced because of the bulky and heavy side chain. Among many partially halogenated acrylic polymers, we firstly focused on PMCA. Compared to PMMA, the percentage of C-H bonds per unit volume is 65 %, and the T_g is as high as 147 °C which satisfies the required T_g for even engine compartments. However, it was clarified that PMCA has a crucial disadvantage for the fiber fabrication process. In order to draw PMCA fiber, the polymer rod has to
be heated above 270 °C because of the extremely strong viscoelasticity, but the polymer rod started to decompose at lower temperature and this produced numerous bubbles.

As a result of further investigation, we found that the refractive index is almost the same as that for PTCEMA which was studied in chapter 3. The refractive indices of PMCA and PTCEMA are 1.5173 and 1.5144 (at 650.3 nm), respectively. Generally, copolymers with large size heterogeneous domain of refractive index have extremely high scattering loss can not be used as a core material of POF. In chapter 5, however, we have already clarified that the scattering loss is negligibly small when the dielectric fluctuation of refractive index is small enough. Since the decomposition temperature of PTCEMA is higher than that of PMCA, we expected that numerous bubbles produced during the fiber fabrication would be reduced. As described in chapter 3, we know even the decomposition temperature of PTCEMA is not enough for the co-extrusion process. However, as future-oriented first trial, several copolymers of MCA and TCEMA with different compositions were prepared and the thermal, mechanical and optical characteristics have been investigated in detail.



Figure C.2 Reaction scheme of a copolymer of methyl a-chloro acrylate and 2,2,2-trichloroethyl methacrylate.

C.4 Materials

Methyl acrylate, dimethylformamide, chlorine, sulfuric acid (H₂SO₄), methanol (MeOH), chloroform (CHCl₃), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), anhydrous magnesium sulfate (MgSO₄), chloroform-d (CDCl₃), *di-tert*-butyl peroxide (TBPO), and *n-butyl* mercaptan (*n*-BM) were purchased from Aldrich. Diphenyl sulfide (DPS) and TCEMA monomer were bought from Kanto Chemical Co., Inc. and Osaka Organic Chemical Industry Ltd. in Japan, respectively. TCEMA monomer was freshly distilled before use and all the other chemicals were used directly without further purification.

C.5 Monomer Synthesis

MCA was prepared by the modified method reported in the literature using dehydrochlorination of α , β -dichloropropionate ^[8]. The best yield of methyl α , β -dichloropropionate was obtained using following procedure. Methyl acrylate (1500 mL, 1434 g, 16.7 mol) and dimethylformamide (43 g, 3 wt% on methyl acrylate) were charged in a 3000 ml three neck round bottom flask equipped with a thermometer and a deward type condenser. The chlorination was carried out at 25-30 °C and was completed during 6-7 hrs after absorption of the theoretical amount of chlorine (1178 g). Crude methyl α , β -dichloropropionate was fractionally distilled. The fraction boiling at 67-68 °C/8 mmHg (2430 g) was pure product in 93 % yield. Dehydrochlorination was carried out as follows; a round bottom flask was charged with methyl α , β -dichloropropionate (300 g) and sulfuric acid (100 g). The solution was heated in a simple distillation setup with no column. Distillation boiling at 80-150 °C was collected. The distillation has to be performed without substantial reflux. Crude product was washed with an aqueous solution of sodium carbonate (1M), water, dried with anhydrous magnesium sulfate, and fractionally distilled at 71 °C/ 8.5 mmHg.

C.6 Polymer Preparation

The monomer mixtures, including weighed amounts of comonomers, TBPO (0.05 mol%) as an initiator and *n*-BM (0.45 mol%) as a chain transfer agent were transferred into a glass ampule. The tube was subjected to repeated freeze-pump-thaw cycles and sealed under vacuum. The polymerization reactions were carried out at 80 °C in a water bath. After the reaction mixture reached proper viscosity, the glass tube was opened and the contents were poured into a large amount of methanol with vigorous stirring to precipitate the polymer. The purified polymer samples were dried under vacuum at 50 °C for 24 h. The conversions of the copolymerization reactions were in the range of 7-17 %. The purified polymers obtained were used to measure the monomer reactivity ratio, $T_{\rm g}$, thermal and mechanical properties, and molecular weight.

To evaluate the mechanical properties, thin films were prepared using the purified polymers. The polymer in chloroform solution was cast onto a glass plate and spread to a uniform thickness of approximately 30 μ m using a knife coater. After the polymer film was peeled from the glass plate, the film was dried under vacuum at 90 °C for 48 h. The film was stamped out with a dumbbell-shaped die defined by ISO 527-3 for measuring the tensile strength.

For measurements of refractive index and transmittance, copolymer bulks were prepared. The polymerization reactions were conducted at programmed temperatures of 75 °C, 90 °C, 105 °C, and 120 °C. The polymerization time was 12 h for each temperature. The conversions of the copolymerization reactions were in the range of 96-97 %.

C.7 Determination of Monomer Reactivity Ratios

Monomer reactivity ratios were determined by the Kelen-Tudos method ^[9]. Details were described in section 5.2. The molar fraction of MCA unit in the feed $[M_1]$ and in the final copolymer $d[M_1]$, polymerization conversion, and parameters in K-T method are summarized in **Table C.1**. The corresponding η versus ξ plot is shown in **Figure C.3**. From the slope and the intercept of the approximated expression (see Eq. 5-17), the r_{12} (MCA) and r_{21} (TCEMA) were calculated to be 2.06 and 0.40, respectively. Here, α was 0.3044. The r_{12} and r_{21} were previously reported as $r_{12} = 0.50$ and $r_{21} = 0.82$ by Chien et al ^[10]. We have repeatedly analyzed the compositions of MCA and TCEMA copolymers by NMR measurement and elementary analysis and then confirmed these reactivity ratios. **Figure C.4** is a plot of molar fraction of MCA in the copolymer $d[M_1]$ versus the molar fraction of MCA in the feed $[M_1]$ and the curve calculated from the copolymer equation (Eq. 5-4).

In the case of bulk polymerization, a few unreacted monomer may remain in the resulting polymer and they often cause bubbles during heat drawing so that the remaining monomer is desired to have high boiling point. Since MCA is more reactive than TCEMA, the unreacted monomers in the resulted polymer may consist of mostly TCEMA. TCEMA has a high b.p. of 70 °C under 15 mmHg and may hardly diffuse out during the fiber drawing and helps to prevent bubbling. This is also one of the advantage of this copolymer system for fiber fabrication.

Sample	[M ₁] ^C (mol%)	d[M ₁] ^c (mol%)	Conv. (wt%)	x	У	Η	G	η	ξ
P1	0	0	-	-	-	-	-	-	-
P2	10.59	22.01	17.5	0.12	0.28	0.05	-0.30	0.14	-0.85
Р3	19.83	36.68 ^d	13.0	0.25	0.58	0.11	-0.18	0.26	-0.44
P4	30.01	49.34	13.2	0.43	0.97	0.19	-0.01	0.38	-0.02
P5	39.91	59.82 ^d	9.4	0.66	1.49	0.30	0.22	0.49	0.36
P6	49.65	68.08	8.2	0.99	2.13	0.46	0.52	0.60	0.69
Ρ7	59.85	76.17 ^d	15.8	1.49	3.20	0.70	1.02	0.70	1.02
P8	69.74	83.06	7.3	2.30	4.90	1.08	1.83	0.78	1.32
Р9	79.77	89.29 ^d	9.7	3.94	8.34	1.86	3.47	0.86	1.60
P10	89.74	95.69	8.1	8.75	22.19	3.45	8.36	0.92	2.23
P11	100	100	-	-	-	-	-	-	-

 Table C.1
 Results of copolymerization reaction of MCA and TCEMA^{a,b}, and Kelen-Tudos parameters

^a Reaction was run with TBPO (0.05 mol%) and *n*-BuSH (0.45 mol%) as an initiator and a chain transfer agent, respectively.

^b The polymerization reaction was carried out at 80 °C for about 30 min.

 $^{\rm c}$ $[M_1]$ and $d[M_1]$ are the molar concentration of MCA in the monomer feed and in the final polymer, respectively.

^d The compositions of P3, P5, P7 and P9 were also determined by elementary analysis and found to be 36.02, 61.61, 73.74 and 90.15, respectively.



Figure C.3 The η versus ξ plot from the data in **Table C.1**.



Figure C.4 The $[M_1]$ versus $d[M_1]$ plot from the data in **Table C.1**. The solid line and broken line represent theoretical curves calculated from Eq. 5-4 using $r_1 = 2.06$ and $r_2 = 0.40$ and $r_1 = r_2 = 1$, respectively.

C.8 Polymer Characterization C.8.1 Thermal Property

 T_g and thermogravimetric curve of copolymers in **Table C.1** were measured and the results are summarized in **Table C.2**. As typical data, the number average and weight average molecular weight, and the polydispersity are also shown in **Table C.2**. Figure C.5 shows a plot of the copolymer T_g versus the composition of MCA in the copolymer. T_g of copolymer can be generally described by the Gordon-Taylor equation ^[11];

$$T_{g} = \left(w_{1}T_{g1} + kw_{2}T_{g2}\right) / \left(w_{1} + kw_{2}\right)$$
(C-1)

where w_1 and w_2 are weight fractions of the two monomeric units in the copolymer, T_{g1} and T_{g2} are T_{gs} of related homopolymers, and k is a fitting constant. As shown in **Figure C.5**, when k = 1, there is no any strong interaction between the two monomers and the T_g should be linearly related to the weight fraction of monomers. However, when there are dipole-dipole attractions between monomer moieties, the T_g positively deviates from the Gordon-Taylor equation accompanied by a decrease in the segmental mobility of the polymer chain.

In the case of the copolymer system of MCA and TCEMA, a plot of T_g versus the weight fraction of MCA was interestingly deviated negatively from the linear relationship of the Gordon-Taylor equation. This result suggests that there is some repulsion between MCA and TCEMA moieties due to the electronegative chlorine atom substituents in both monomers as shown in **Figure C.6**. As the result, the T_g of the copolymer decreases, but the values are higher than 130 °C at any composition, which is about 30 °C higher than that of PMMA.

Sample	<i>T</i> _g (°C)	<i>T_{d5}</i> (°C)	<i>T_{d10}</i> (°C)	M _w (*10 ⁴)	M _n (*10 ⁴)	M _w /M _n
P1	132.5	276.6	282.3	8.03	3.11	2.58
P2	132.4	267.5	275.9	14.71	7.53	1.95
Р3	132.3	263.3	272.9	20.04	10.10	1.99
P4	133.5	264.0	274.6	17.76	8.26	2.15
P5	134.4	259.8	272.2	22.75	11.81	1.93
P6	136.0	257.4	269.5	17.75	8.65	2.05
P7	137.3	247.7	259.3	26.51	14.66	1.81
P8	140.6	247.9	260.2	23.00	10.63	2.16
Р9	142.9	248.2	259.3	32.96	16.32	2.02
P10	145.8	244.8	256.2	24.90	11.34	2.20
P11	147.3	241.5	252.4	29.08	9.03	3.22

Table C.2 T_g , 5 % and 10 w% weight loss temperature, the number and weight average molecularweight and the dispersity of Sample P 1 - P 11 in Table C.1



Figure C.5 Composition dependence of T_g s of MCA-TCEMA copolymers (\circ) and T_g values calculated from Gordon-Taylor equation when k = 1 (×).



Figure C.6 The dipole-dipole repulsion between MCA and TCEMA moieties.

Figure C.7 shows thermogravimetric curves of copolymers with different compositions. The homopolymer of MCA (P11) starts to decompose at a lower temperature than PTCEMA (P1) by about 70 °C. Decomposition temperatures of thermogravimetric curves are shifted to higher temperature as the composition of TCEMA in the copolymer increases, and it was found that the low temperature decomposition of PMCA could be improved by copolymerizing with TCEMA.



Figure C.7 Thermogravimetric analysis in air stream with a heating ratio of 10 °C/min; each sample number is corresponded to **Tables C.1** and **C.2**.

C.8.2 Mechanical Property

In chapter 3, we showed that the GI POF with the core of PTCEMA and the cladding of PMMA could be successfully prepared by the rod-in-tube method. PTCEMA is actually very brittle and was hard to be heat drawn without any cracks when the cladding also consists of PTCEMA. As one of the conclusion of chapter 3, we clarified that the mechanical property of core material is not so important for the fiber strength if the cladding material had an enough mechanical property and the core was covered well by the cladding. However, before we adopted the rod-in-tube method, that is, the preform was prepared by the interfacial-gel polymerization method, we had to use PTCEMA as not only the core but also the cladding to avoid the incompatibility between the core and cladding. Thus the mechanical property of core polymer was considered to be important. Characterizations here are based on such concepts.

The mechanical properties were evaluated by measuring the strain-stress curve of copolymer films. The film was elongated by using a universal tensile testing machine (TENSILON RTC-1210A, A&D Co., Ltd.). While copolymer films of P1-P11 in **Table C.1** were attempted to prepare, due to the weak mechanical strength of PTCEMA, only P6-P11 films could be obtained. The stress and strain were calculated as follows;

$$\sigma = \frac{F}{A} \tag{C-2}$$

$$\varepsilon = \frac{\Delta L_0}{L_0} \times 100 \tag{C-3}$$

where σ is tensile stress (MPa), F is force (N), A is initial cross-section area of film (mm²), ε is strain (%), L_0 is initial distance (mm), and ΔL_0 is increment distance (mm). The tensile strengths of the film were evaluated by continuously measuring the force as the film is elongated at a constant ratio of extension. To evaluate the mechanical strength of copolymer, the films were elongated at room temperature with an elongation speed of 0.1 mm/min. The stress-strain curve is shown in **Figure C.8**. The breaking strain of P6 (MCA: 68.08 mol% in copolymer) and P11 (MCA: 100 mol% in copolymer) were approximately 0.2 % and 1 %, respectively. These results indicate that the brittleness of PTCEMA can be improved by copolymerizing with MCA.

On the other hand, the viscoelasticity of copolymer was evaluated by the elongation test at 160 $^{\circ}$ C over the T_g of copolymers with elongation speed of 10 mm/min. As mentioned in section C.3, problems of PMCA were the low decomposition temperature and the strong viscoelasticity which

cause numerous bubbles during the heat drawing procedure of POF. From the result of **Figure C.7**, the decomposition temperature has been slightly improved by copolymerizing with TCEMA. One more important parameter to be solved is the viscoelasticity. **Figure C.9** shows that the viscoelasticity of PMCA were lowered by copolymerizing with TCEMA. Regarding T_g of the copolymer, we discussed that there is some repulsion between MCA and TCEMA moieties due to the electronegative chlorine atom substituents in both monomers as shown in **Figure C.6**. As the result, T_g plots against the weight fraction of MCA were deviated negatively from the linear relationship of the Gordon-Taylor equation. The result of Figure C.9 is believed to be caused by the similar effect.



Figure C.8 Strain-Stress curves at room temperature with a drawing rate of 0.1 mm/min; each sample number is corresponded to **Tables C.1** and **C.2**.



Figure C.9 Strain-Stress curves at 160 °C with a drawing rate of 10 mm/min; each sample number is corresponded to **Tables C.1** and **C.2**.

C.8.3 Optical Property

Copolymer bulks in different compositions were prepared and the refractive indices were measured. The result is summarized in **Table C.3** and **Figure C.10**. In general, the copolymer systems even a random copolymerization, the transmitting light into the fiber is scattered due to heterogeneous distribution of the monomers having different refractive index. In the present case, however, the increment of scattering loss can be negligible since both homopolymers have almost the same refractive index. The transmittances of homo and copolymer bulks were measured and the result is shown in **Figure C.11**. The sample lengths were 3.0 cm and the obtained transmittances were corrected for removing the refraction loss at both end faces. The calculation method was described in section A.6.

In the case of acrylic polymers, the predominant factor of attenuation from the visible to near-infrared region is C-H stretching vibrational absorption. The strong peaks at 720 nm and 900 nm in **Figure C.11** correspond to the 4th and 5th over-tones of the C-H vibration. The desired communication wavelength for acrylic-based polymer is 670-680 nm, however, the attenuation of PMMA is too high to be utilized even within short distant home networks due to the absorption peaks as mentioned before. On the other hand, the percentage of C-H bonds in partially chlorinated PMCA and PTCEMA calculated by their densities were 65 % and 51 %, respectively. Accordingly, as shown in **Figure C.11**, the peak intensities of PMCA and PTCEMA are reduced by half compared with that of PMMA, and not only the transmittance at these regions but also at broad wavelength is higher. The transmittance of MCA/TCEMA=80/20 (mol%) copolymer bulk was similar to those of PMCA and PTCEMA homopolymers and much higher than that of PMMA.

Sample	$[M_1]^d$	Refractive index					
Jumpic	(mol%)	409.2 (nm)	650.3 (nm)	833.7 (nm)	1546 (nm)		
B1	0	1.5345	1.5144	1.5094	1.5038		
B2	50	1.5334	1.5144	1.5100	1.5041		
B3	70	1.5354	1.5157	1.5112	1.5055		
B4	80	1.5370	1.5169	1.5126	1.5067		
B5	90	1.5363	1.5172	1.5127	1.5069		
B6	100	1.5365	1.5173	1.5125	1.5070		

 Table C.3
 Composition of MCA unit in feed and refractive indices of copolymer bulks ^{a, b, c}

^a Reaction was run with TBPO (0.05 mol%) and *n*-BuSH (0.45 mol%) as an initiator and a chain transfer agent, respectively.

^b The polymerization reactions were carried out at 75 °C, 90 °C, 105 °C, 120 ° for 12 hrs for each temperature.

^c Monomer conversions were 96-97 wt%.

 d [M₁] is the molar concentration of MCA in the monomer feed.



Figure C.10 Refractive indices of MCA-TCEMA copolymers at wavelengths of 409.2 nm (\Box), 650.3 nm (\diamondsuit), 833.7 nm (\bigcirc), and 1546 nm (\bigtriangleup).



Figure C.11 Transmittance spectra of B 1. MCA/TCEMA = 0/100 (mol%), B 4. MCA/TCEMA = 80/20 (mol%), B 6. MCA/TCEMA = 100/0 (mol%), and PMMA bulk.

C.9 Fabrication of GI POF

A GI POF based on the copolymer of MCA and TCEMA was prepared. MCA in the feed was 80 mol%, which corresponded to B4 in **Table C.3** and **Figure C.11**, for both cladding and core, DPS of 7 mol% was added into the core solution as a dopant for forming a graded refractive index profile. The preform was prepared by the interfacial-gel polymerization technique ^[12, 13]. When the GI preform was made of PMCA homopolymer, it never could be heat drawn even at temperature over 270 °C and numerous bubbles occurred from low temperature decomposition. In the case of using PTCEMA for core and cladding, the preform could be heat drawn, but the fiber was too brittle to be rolled up. However, the GI preform based on the copolymer could be heat drawn at as low as 210 °C and a 30-m length GI POF was successfully obtained without any bubbles and cracks as shown in **Figure C.12**. This result shows that the strong viscoelasticity and the low temperature decomposition of PMCA, and the brittleness of PTCEMA were all improved by copolymerizing with each other.



Figure C.12 Photograph of GI POF (30 m length) based on MCA/TCEMA = 80/20 (mol%) copolymer.

C.10 Conclusion

In this chapter, we investigated a copolymer of MCA and TCEMA as the base material of a novel GI POF for high speed automobile networks. The homopolymer of MCA has high viscosity and tends to decompose at the heat drawing temperature and the homopolymer of TCEMA is brittle. However, these disadvantages of both homopolymers could be improved by copolymerizing MCA and TCEMA. T_g s of copolymers were in the range of 133-147 °C and were much higher than that for PMMA. Since the refractive indices of PMCA and PTCEMA are almost the same, excess light scattering through the copolymer did not occur and the transmittance of copolymer bulk was found to be much higher than that of PMMA. Thus, the GI POF prepared by the copolymer may be applied as a transmission medium which requires low attenuation at 670-680 nm wavelength and high thermal stability.

In this dissertation, regarding thermal properties, we only investigated the intrinsic T_g s and decomposition temperatures of precipitated copolymers. Further study including the analysis of copolymer bulks with remaining monomer will necessary to evaluate the copolymeric system as the transmission medium of automobile networks. Although the UV-vis spectrum of the copolymer exhibited a higher transmittance, the light scattering analysis is also important to expect the accurate attenuation of the fiber.

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Appendix D Birefringence

If a substrate is anisotropic, which means that it has different properties in different directions, it will be doubly refracting or birefringent (when transparent). Birefringence is evidenced by the ability of a material to rotate the plane of polarized light. It is defined as the difference in refractive indices in the directions parallel and perpendicular to the direction of orientation:

$$\Delta n = n_{\parallel} - n_{\perp} \tag{D-1}$$

Birefringence may be a natural property or artificially induced by means of force fields. Natural birefringence is mainly found in crystalline substances; artificial birefringence is normally based on mechanical orientation, either in the solid or in the liquid state: stretch and flow orientation respectively. Melts and solutions may show birefringence, caused by

- a) mechanical orientation: flow birefringence
- b) electrical fields: the Kerr effect
- c) magnetic fields: the Cotton-Mouton effect

Related to birefringence is the optical activity or –rotation (of the plane of polarization of the light). This also may be a natural or an artificially aroused effect. Natural optical activity is based on the structure of the molecules (optically active center). Artificial optical rotation is found in magnetic fields: the Faraday-Verdet effect. Orientation in polymers is normally effected by stretching. One therefore observes the phenomenon of birefringence in polymer melts under forced flow (shear stress) or under tension, and in solid polymers after stretch orientation; the oriented polymer is cooled to below its glass transition temperature before the molecules have had a chance to relax to their random coiled configuration.

Birefringence is not restricted to visible light. Some of the infrared absorption bands of

oriented polymers show infrared dichroism; they absorb different amounts of polarized infrared radiation in different directions (parallel or perpendicular to the direction of orientation). Dyed oriented polymers often show dichroism to visible light due to orientation of the dye molecules (together with the polymer molecules).

For rubber-elastic materials (i.e. polymers above their T_g), theory predicts that the retractive stress is directly proportional to the degree of orientation, which in turn is directly proportional to the birefringence. Thus, for uniaxial tension, the birefringence and the retractive are related by the simple equation:

$$n_{\parallel} - n_{\perp} = C\sigma \tag{D-2}$$

C is called the stress optical coefficient. The value of C depends on the chemical structure of the polymer and is somewhat temperature-dependent. The theory of rubber elasticity leads to the following expression:

$$C = \frac{2\pi \left(\alpha_{\parallel} - \alpha_{\perp}\right) \left(\overline{n^2 + 2}\right)^2}{45 \overline{nkT}}$$
(D-3)

where $\alpha_{\parallel} - \alpha_{\perp}$ is the difference in polarizability of a polymer segment parallel and perpendicular to the direction of the chain. n is the average refractive index (n equals n of the unoriented polymer). C is normally expressed in 10⁻¹²m²/N which are called brewsters. According to theory, C is independent of the degree of cross-linking. During stress relaxation the birefringence decreases with the stress, so that their ratio remains constant. The same is true during creep.

Rigid amorphous polymers also become birefringent when a stress is applied to them. A much greater stress is required, however, to produce a given value of birefringence in a rigid polymer than in a rubber: the stress optical coefficient is much lower. It usually changes rapidly with temperature in the neighborhood of the glass-rubber transition. For some polymers it even changes sign at T_g .

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Appendix E Estimation Method of Isothermal Compressibility

The intensity of the isotropic light scattering V_V^{iso} from thermally induced density fluctuations in a structureless liquid is expressed by Eq. 2-7 and is proportional to the refractive index and the isothermal compressibility β . To estimate the β , Tanio *et al.* clarified following correlations between physical properties for amorphous polymers.

- (1) Relation between the intrinsic molecular volume V_{int} and actual molecular volume V (Correlation 1).
- (2) Relation between actual molecular volume V and molecular weight between chain entanglements M_c (Correlation 2).
- (3) Relation between the number of chain atoms between physical entanglements N_c and the cross-sectional area per polymer chain A (Correlation 3).
- (4) Relation between the cross-sectional area per polymer chain A and the isothermal compressibility at a liquid-liquid transition temperature β at T_{ll} (Correlation 4).

The intrinsic molecular volume V_{int} of monomer unit for amorphous polymer can be calculated from the atomic radius and bond length of the constituent atoms based on the method developed by Slonimskii *et al*^[1]. When an atom **B** (atomic radius R) is bound to atom **B**_i (atomic radius R_i) with bond length d_i , the atomic volume $\Delta V(\mathbf{B})$ of atom **B** is given by

$$\Delta V(\mathbf{B}) = (4/3)\pi R^3 - \sum_i (1/3)\pi h_i^2 (3R - h_i)$$

$$h_i = R - \left(R^2 + d_i^2 - R_i^2\right) / 2d_i$$
(E-1)

If the molecule consists of atoms $\mathbf{B}_1 - \mathbf{B}_i$, the intrinsic molecular volume V_{int} is given by

$$V_{\rm int} = N_A \sum_j \Delta V(\mathbf{B}_j) \tag{E-2}$$

where N_A is Avogadro's number. The actual molecular volume V of the monomer unit is obtained from the value of density ρ of polymer using

$$V = \frac{M_0}{\rho} \tag{E-3}$$

The actual molecular volume V is expressed as

$$V = \frac{V_{\text{int}}}{K} \tag{E-4}$$

where K is the packing coefficient of the molecule. From the experiment using several amorphous polymers (polyethylene (PE), polyvinyl alcohol (PVA), poly (vinyl acetate) (PVAc), PMMA, PS, and poly(*n*-butyl methacrylate) (PnBMA)), the $V - V_{int}$ plots were found to be linear and K values for typical amorphous polymers were clarified to be about 0.68.

Hoffman ^[2] found a linear correlation between the molecular weight between chain entanglements M_c and the square of the actual molecular volume of the monomer unit. He obtained the correlation $M_c \propto V^{1.67}$. In order to confirm the correlation between M_c and Vfor amorphous polymers, Tanio *et al.* collected data on the M_c of the amorphous polymers (PE, PVA, PVAc, PMMA, PS, and PnBMA). As the result, the $M_c - V^{1.67}$ plot for the amorphous polymers were

$$M_c = 18.3V^{1.67}$$
(E-5)

Boyer and Miller ^[3] discussed a correlation involving N_c the number of chain atoms between physical entanglements and the cross-sectional area A, per polymer chain. This correlation is expressed as

$$\log N_c = k_1 + k_2 (\log A - 2)$$
 (E-6)

where k_1 and k_2 are constants ($k_1=2.929$, $k_2=0.614$). Tanio *et al.* use $N_c = M_c/m$, where m is the molecular weight per chain atom ($m = M_0/Z$, where M_0 is the molecular weight of a monomer unit and Z is the number of chain atoms in the monomer unit). The plot of the N_c against A for the amorphous polymers (PE, PVA, PVAc, PMMA, PS, and PnBMA) fitted the approximated line given by Eq. E-6 quite well.

Boyer and Miller ^[3, 4] reported the correlation between isothermal compressibility β at a liquid-liquid transition temperature (T_{ll}) and the cross-sectional area per polymer chain from lattice parameters as

$$\log(10^{11}\beta_{atT_u}) = -0.21 + 0.55\log A \tag{E-7}$$

The liquid-liquid transition temperature appears to be a useful liquid-state reference temperature and is usually found by a variety of dynamic, thermodynamic methods. The concept of a T_{ll} was vigorously studied by Boyer ^[5]. He found that T_{ll} is near 1.2 T_g for most polymers. Lobanov and Frenkel ^[6] have estimated T_{ll} for a variety of polymers from dielectric loss data and proposed an empirical relation between T_g and T_{ll} .

$$T_{ll} = T_g + 76 \,(K)$$
 (E-8)

For T_{ll} from 250 K to 500 K, the numerical difference between the two empirical rules is slight.

By combining the above relationship, the isothermal compressibility β at T_{ll} can be calculated from the intrinsic molecular volume V_{int} . However, the value of isothermal compressibility at T_g of polymers is necessary to estimate the light scattering loss in glassy state. The isothermal compressibility β of polymers increases linearly with T from T_g to T_{ll} . Thus we should know the slope $d\beta/dT$ in the range between T_g and T_{ll} in order to estimate isothermal compressibility at T_g . It is interesting that the values of $(1/\beta_{at T_{ll}})(d\beta/dT)$ in the range between T_g and T_{ll} for several amorphous polymers are almost the same (average value is 4.8×10^{-3} K⁻¹). When we use this value $((1/\beta_{at T_{ll}})(d\beta/dT) = 4.8 \times 10^{-3}$ K⁻¹ at $T_g < T < T_{ll}$) and the empirical relationship between T_{ll} and T_g $(T_{ll}=T_g+76$ K), we can estimate the isothermal compressibility at T_g from the value of β at T_{ll} .

To determine the isotropic scattering loss by Eq. 2-7, we need not only the isothermal compressibility at T_g but also the refractive index of the polymer. In our case, we could directly measure refractive indices of polymer samples. But in the case that it would be difficult to obtain the refractive index of a desired polymer, we can also estimate the refractive index by the chemical structure.

The refractive index of a compound can be calculated from its molar refraction and molecular volume using the Lorents-Lorenz equation,

$$n = \sqrt{\left(2\frac{[R]}{V} + 1\right) / \left(1 - \frac{[R]}{V}\right)}$$
(E-9)

where [R] is molar refraction and V is the molecular volume. The molar refraction [R] is taken as the sum of atomic refractions. Thus, we can estimate the refractive index of a polymer from molar refraction and molecular volume.

The procedure for estimating the isotropic light scattering loss of amorphous polymers from its molecular structure proposed by Tanio *et al.* is summarized in **Figure E.1**.



Figure E.1 Estimating method of the isotropic light scattering loss for amorphous polymer glass from its molecular structure.

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Appendix F Vertical Cavity Semiconductor Lasers

An alternative design for semiconductor lasers is to have resonator mirrors above and below the active layer. This is called a vertical-cavity surface-emitting laser (VCSEL) because the light resonates vertically in the wafer, perpendicular to the junction, and emerges from the surface, as shown in **Figure F.1**.

The mirrors in VCSELs are formed by depositing a series of layers with alternating compositions, so they selectively reflect a narrow range of wavelengths, depending on their thickness and refractive indices. This multilayer reflector uses an effect similar to a fiber grating, but the concept of selective reflection by a stack of many thin-film layers coated on optics came before either fiber gratings or VCSELs. A VCSEL emits from a round spot on the surface of the wafer that is larger than the core of a single-mode fiber, but small enough to fit into a graded-index multimode core. Because the emitting area is circular and larger than an edge-emitting laser, a VCSEL beam is circular and does not spread out as rapidly (the differences arise from diffraction effects).

VCSELs have a number of attractions. They have low threshold currents and are quite efficient in converting electrical input into light. This means they consume little power and have to dissipate less heat than edge-emitting lasers, giving them a longer lifetime than edge-emitting diode lasers. They are easy to manufacture and package. Like other semiconductor lasers, they can be directly modulated at high speeds—so they can generate signals well over 1 Gbit/s.

Most VCSELs are made from GaAs semiconductor materials, which meet the requirements for making multilayer mirrors much better than InP-based compounds. The present strength of single VCSELs is an inexpensive light sources at wavelengths of red to near IR, where they offer better lifetimes and lower costs than edge-emitting GaAs lasers and serious competition for LED sources. A crucial advantage of VCSELs is their ability to generate higher-speed signals than LEDs. This makes present VCSELs quite attractive for gigabit networks that transmit signals up to a few kilometers.

Unlike other diode lasers, VCSELs can be fabricated in tow-dimensional arrays covering the surface of a wafer, which can generate separately modulated outputs that emerge from the chip surface. Such arrays of independent emitters are attractive for optical switching and signal processing, with beams going through free space as well as through fibers.



Figure F.1 Schematic diagram of a vertical-cavity surface-emitting laser.

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