

Graded-Index Polymer Optical Fiber with High Thermal Stability of Bandwidth

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The development of the perfluorinated (PF) polymer based graded-index polymer optical fiber (GI POF) for high-speed data communication is described. It was experimentally confirmed that gigabit data transmission for 500–1000 m at 1.3 μm wavelength was achieved by the low-loss PF polymer based GI POF. The thermal stability of poly (methyl methacrylate) PMMA based GI POF is discussed. We selected several kinds of dopants that can maintain a high glass transition temperature (T_g) of the GI POF core. By using the newly selected dopants, we succeeded in maintaining the parabolic refractive index profile of GI POF with no degradation even at 85 to 90°C for more than 5000 h.

KEYWORDS: graded-index polymer optical fiber, thermal stability, modal dispersion, material dispersion, bandwidth

1. Introduction

Recent progress in personal computer technology has enabled easy access to Internet from the home. In order to transmit large volumes of data bits such as those of moving pictures, a data rate of the order of megabit per second is required.¹⁾ However, current data transmission rate in the premises area is limited by the bandwidth of the physical layer to the order of kilobit per second (kb/s). With increasing demand for high-speed information transmission, recent interests are focused on gigabit-order data transmission such as gigabit Ethernet local-area network (LAN) system. Therefore, it is desirable to introduce the optical fiber networks even to the premises area in order to transmit more than 500–1000 Mbit data.

We have proposed a large-core, high-bandwidth graded-index (GI) polymer optical fiber (POF) as the physical layer of a short-distance high data rate network.²⁾ We confirmed that gigabit-order data transmission can be achieved in 100 m GI POF link. Furthermore, we also succeeded in preparing a low-loss GI POF even in the near infrared region by using perfluorinated polymer (PF polymer). Attenuation of the PF polymer based GI POF is 50 dB/km at 1.3 μm wavelength, which is widely utilized in a silica based optical fiber network in the trunk area.

2. Thermal Stability Test of PMMA based GI POF

2.1 Candidates for dopant

We previously proposed several kinds of dopant material for poly(methyl methacrylate) (PMMA) based GI POF.²⁾ To achieve good optical properties such as low loss and high bandwidth, these dopant materials had to satisfy the following conditions: good miscibility with PMMA, higher refractive index than PMMA, higher molecular weight than MMA molecule, and higher boiling point than the heat-drawing temperature (200°C). Poor miscibility between the dopant and PMMA leads to phase separation that causes large scattering loss.^{2,3)} Introduction of a benzene ring, and sulfur and halogen atoms except fluorine into the molecule is effective for increasing the refractive index. In this paper, we focused on the thermal stability and the long-term reliability as well as the optical properties of GI POF.

For the sake of achieving a thermally stable refractive index profile, diffusion and migration of the dopant material must be suppressed. The diffusion constant of the dopant material

is one of the important parameters by which the migration process of the dopant in GI POF can be investigated.

On the other hand, such dopant diffusion may depend on the mobility of the polymer matrix segments. The mobility of the polymer matrix segments dramatically changes near the glass transition temperature (T_g). Since T_g of the polymer is lowered by the dopant, differences in the plasticization effect among the used dopants can directly correspond to the mobility of the dopant in GI POF. The plasticization effect is the phenomenon which lowers the T_g of the polymer⁴⁾ by the addition of dopant material. Therefore, we selected the dopant material based on the plasticization effect of the dopant. The material having a poor plasticization effect can maintain a high T_g of the polymer when it is doped. Consequently, the use of such a material as the dopant of GI POF is effective for obtaining a thermally stable refractive index profile. Materials with high polar groups attached to aromatic rings (high polar aromatic groups) are the candidates for the dopant with low plasticization effect.⁵⁾

Several kinds of commercially available aromatic compounds in which two or three benzene rings or sulfur atoms are involved were adopted. The properties of the used dopants are listed in Table I together with their chemical structures. The plasticization effect was investigated by directly measuring T_g of the PMMA in which various concentrations (from 5 to 25 wt%) of the selected materials were doped.

2.2 Thermal stability test

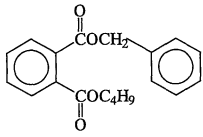
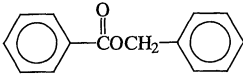
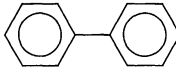
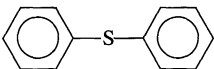
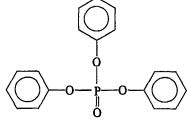
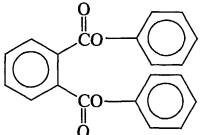
2.2.1 Refractive index distribution

The stability of the refractive index profile of GI POF directly affects the bandwidth characteristics. An investigation of the thermal stability of the refractive index profile could offer important information on the long-term reliability of GI POF. The process of the reliability test is described as follows: GI POF prepared by the interfacial-gel polymerization technique was oven-aged at 85°C or 90°C under room humidity. Thermal stability of POF and silica optical fiber is generally tested around 85°C, which is one of the thermal stability standards of cables such as glass optical fiber.⁶⁾ The refractive index distribution of GI POF after aging was measured using an Interphako interference microscope and was compared with the index profile of the original profile.

2.2.2 Bandwidth

Although the degree of degradation of the refractive index profile is too small to be detected by the index profile mea-

Table I. Used dopant materials and their physical properties.

Used monomer and dopant	Chemical Formula	Molecular Weight (g/mol)	Molecular Volume (\AA^3)	Solubility Parameter (cal/cm^3) ^{1/2}	Refractive index
Benzyl n-butyl phthalate (BBP)		312.4	467.5	9.504	1.540
Benzyl benzoate (BEN)		212.3	314.6	9.641	1.568
Diphenyl (DP)		154.21	258.2	8.796	1.587
Diphenyl sulfide (DPS)		186.3	277.8	9.431	1.633
Triphenyl phosphate (TPP)		326.3	449.2	9.42	1.563
Diphenyl phthalate (DPP)		318.3	336.4	13.26	—

surement, such a small degree of degradation would directly influence fiber bandwidth. Therefore, a bandwidth stability test was also performed. Bandwidth stability was measured by the time-domain measurement method. A narrow pulse-shaped input light signal from a pulse generator (Hamamatsu PLP-02) was injected into the 100-m long GI POF, and the output pulse was detected by the sampling head and analyzed by a sampling oscilloscope (Hamamatsu OOS-01). The output pulse shapes of the GI POF before and after oven aging at 85°C were compared.

3. Improvement in Thermal Stability

3.1 Thermal stability of the refractive index profile

Measured refractive index distributions of TPP-doped and DP-doped GI POFs are shown in Figs. 1 and 2, respectively. The dopant to MMA monomer ratio was 20 wt%. It is noted that the profile stability depends strongly on the dopant used. In the case of TPP-doped GI POF, no profile change was observed after aging for 5000 h at 85°C despite of the aged fiber was a naked fiber, i.e. it had no coating. On the other hand, in the case of DP-doped GI POF, the index profile degraded after aging only for 9 h at 85°C. The same thermal stability test was performed in other dopant system GI POFs. In the case of BBP-, DPS- and BEN-doped GI POFs, the same degradation phenomena as DP-doped GI POF were observed although the degradation rate was dependent on the kind of dopant. On the other hand, no degradation was observed in DPP-, newly selected dopant (dopant A)-, and TPP- doped GI POFs even after aging for 3000 h at 85°C.

T_g distribution in GI POF core was investigated. It is revealed that the T_g at the core center of DP doped GI POF is lowered to 74°C. This lowered T_g is considered to be the main reason for the refractive index profile degradation at 85°C. In

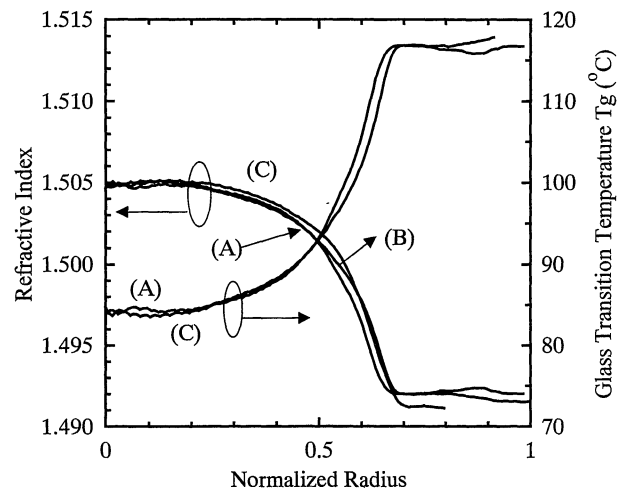


Fig. 1. Thermal stability of the refractive index profile of 20 wt% TPP-doped GI POF after aging at 85°C, compared to the glass transition temperature profile. (A) Original (B) after 3000 h (C) after 5200 h.

contrast, TPP-doped GI POF has a T_g value of 83°C at the central axis; thus it can maintain the same refractive index profile even after aging at 85°C for more than 5000 h.

Significant degradation of the index profile occurred in the area of $0 \leq \text{normalized radius} \leq 0.6$ having T_g less than 85°C as shown in Fig. 2 in the DP-doped GI POF. Therefore, from the results shown in Figs. 1 and 2, it is concluded that maintaining a high T_g in the core region is one of the important steps required for improving the thermal stability of the index profile of GI POF.

Thermal stability of the refractive index profile of BEN-doped GI POF compared to its T_g profile is shown in Fig. 3.

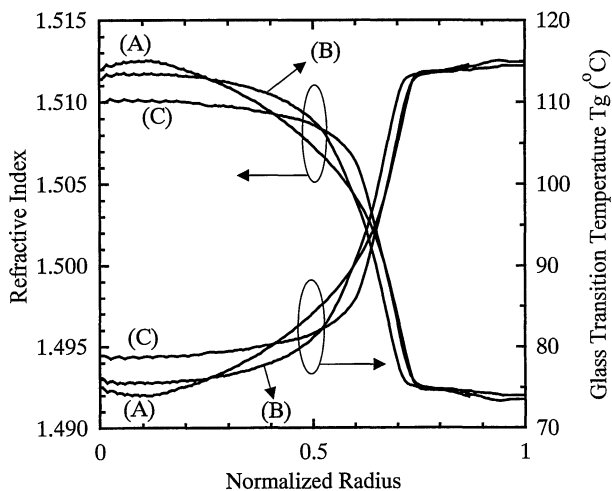


Fig. 2. Thermal stability of the refractive index profile of 20 wt% DP-doped GI POF after aging at 85°C, compared to the glass transition temperature profile. (A) Original (B) after 10 h (C) after 48 h.

In the case of 20 wt% BEN-doped GI POF, even though T_g at the core center is less than 70°C, which is lower than that of the 20 wt% DP-doped GI POF shown in Fig. 2, it was observed that the index profile was maintained for 240 h at 85°C. It degraded after aging for 500 h at 85°C. Although low T_g is one of the reasons why the index profile of DP-doped GI POF degrades at a fast rate, the diffusion phenomenon of the dopant has to be considered in order to explain the stability of BEN-doped GI POF shown in Fig. 2. Table I shows the molecular volumes and solubility parameters of the DP, DPS, BEN and TPP. A large molecular volume or strong interaction between dopant and polymer molecules affects the diffusion of the dopant into the polymer matrix. As shown in Table I, the molecular volume of BEN is larger than that of DP. Furthermore, the solubility parameter of BEN is closer to that (9.327) of PMMA than that of DP, which means that the miscibility of BEN and PMMA is higher than that of DP and PMMA. The difference in miscibility with the polymer matrix between BEN and DP may be attributed to the polarity of the materials because BEN and PMMA molecules have high polar carbonyl group, while DP has no such polar group. This difference corresponds to the difference in the diffusion constants of the dopants in PMMA. Therefore, not only high T_g but also large molecular volume and good miscibility are the required dopant properties in order to obtain a thermally stable graded index distribution.

3.2 Improvement in thermal stability of refractive index profile of GI POF

As shown in Figs. 1 and 2, differences in the refractive indices between the central axis and cladding (Δn) are 0.021 and 0.014 for DP- and TPP-doped GI POFs, respectively. These differences in Δn are translated to the numerical apertures (NAs) of 0.25 and 0.2, respectively, using the definition of NA given by eq. (1).

$$NA = n_1 \sqrt{\frac{2\Delta n}{n_1}} = \sqrt{2n_1 \cdot \Delta n} \quad (1)$$

here, n_1 denotes the refractive index of the central axis.

In the case of 20 wt% DPS-doped GI POF, a Δn value

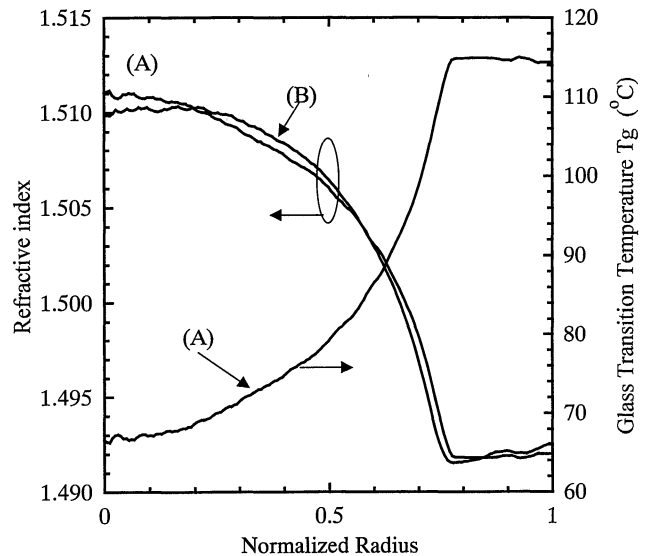


Fig. 3. Thermal stability of the refractive index profile of 20 wt% BEN-doped GI POF after 85°C aging compared to the glass transition temperature profile. (A) Original (B) after 240 h.

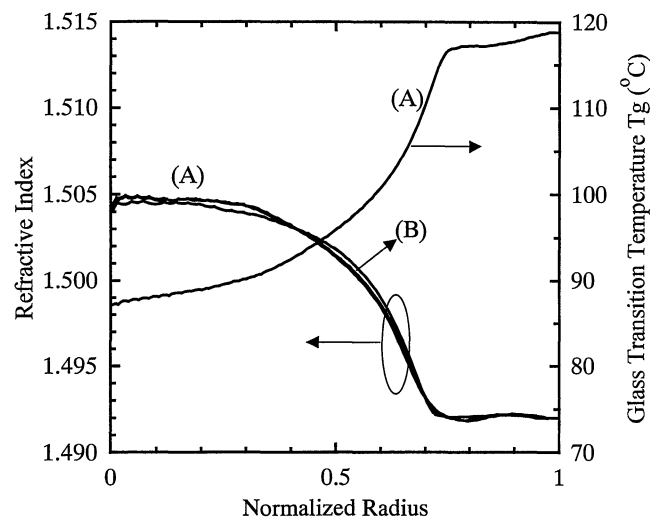


Fig. 4. Thermal stability of the refractive index profile of 11 wt% DPS-doped GI POF after aging at 90°C compared to the glass transition temperature profile. (A) Original (B) after 1000 h.

of 0.028 could be obtained which provides the low bending loss.⁶⁾ The differences in Δn among the GI POFs are due to the refractive indices of the dopants. Therefore, in order to obtain the same numerical aperture as TPP-doped GI POF, dopant concentration of DPS and DP should be lower than that of TPP. It is expected that low dopant concentration increases T_g of the core. For instance, the refractive index of DPS is as high as 1.633, so that the NA of 0.2 ($\Delta n = 0.014$) can be obtained with less than 15 wt% of dopant concentration.

The refractive index and glass transition temperature profile of 11 wt% DPS-doped GI POF and its thermal stability after oven-aging at 90°C are shown in Fig. 4. Δn is lowered to 0.014 because of low dopant concentration. However, it should be noted that T_g at the central axis is as high as 87°C and is markedly increased by decreasing the dopant concentration. It should be noted that the refractive index profile is

maintained even at 90 °C for 1000 h as shown in Fig. 4.

3.3 Bandwidth

The degradation of the refractive index profile of GI POF mentioned above directly influences its bandwidth characteristics. The pulse broadening phenomenon was investigated for 100 m GI POF before and after oven-aging at 85°C. The fibers used in this experiment were 20 wt% DP-doped GI POF and 11 wt% DPS-doped GI POF whose index profile stability at 85°C is shown in Figs. 2 and 4, respectively. The results of DP-doped and DPS-doped GI POFs are shown in Figs. 5 and 6, respectively. Significant output pulse broadening was observed for the DP-doped GI POF only after aging for 48 h, while no pulse width change was observed for the 11 wt% DPS-doped GI POF even after aging for 2000 h. In the case of the DP-doped GI POF, the output power intensity after aging for more than 48 h was so low that it could no longer be detected by the sampling head. On the other hand, it is also indicated from Fig. 6 that little attenuation increment is observed for the 11 wt% DPS-doped GI POF after aging for 2000 h because the output pulse detected even after aging for 2000 h aging maintained an almost the same power as the original one in Fig. 6.

High NA is one of the properties required for GI POF because it allows high coupling efficiency with lambertian light sources such as a light-emitting diode (LED) and low bending

loss. In order to increase the fiber NA, high dopant concentration is required, which can cause degradation of the refractive index profile. Dopant A is considered to be a suitable can-

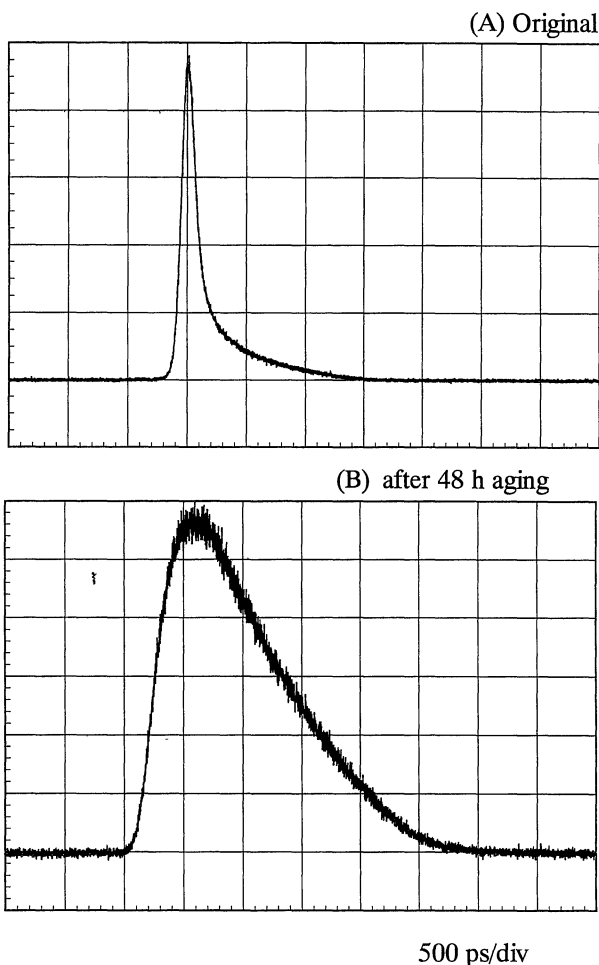


Fig. 5. Thermal stability of bandwidth of 20 wt% DP-doped 100 m GI POF after aging at 85°C. The bandwidth was measured at 650 nm wavelength.

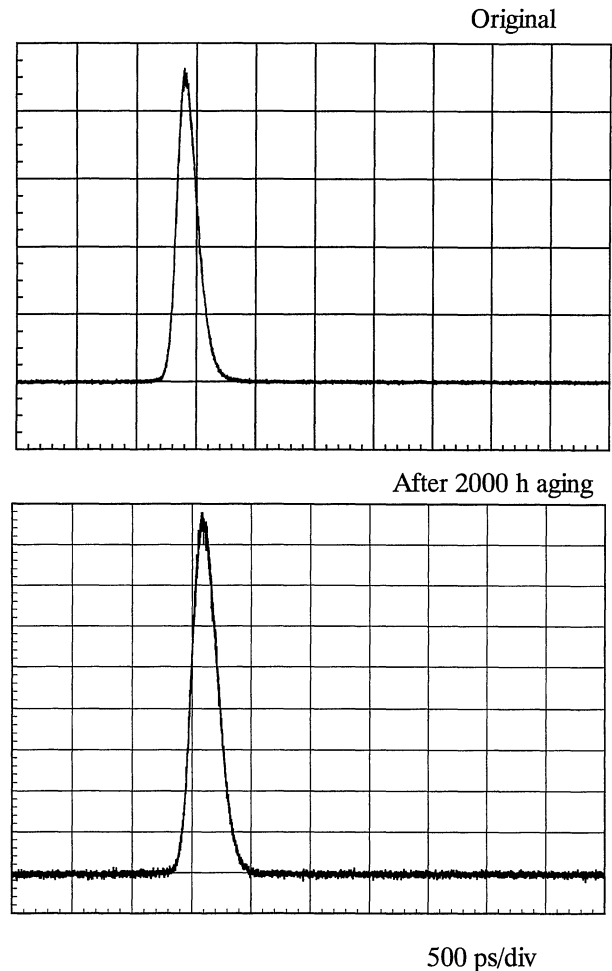


Fig. 6. Thermal stability of bandwidth of 11 wt% DPS-doped 100-m GI POF after aging at 85°C. The bandwidth was measured at 650 nm wavelength.

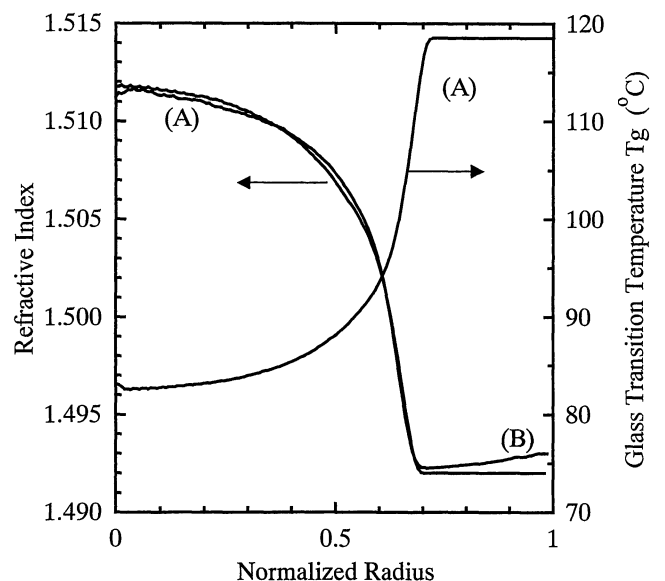


Fig. 7. Thermal stability of the refractive index profile of 16.7 wt% dopant A-doped GI POF after aging at 85°C compared to the glass transition temperature profile. (A) Original (B) after 500 h.

didate for a high NA GI POF with maintaining a thermally stable refractive index profile because of its high refractive index and poor plasticization effect. These two features are attributed to its chemical structure. The dopant A molecule has a sulfur atom that is responsible for its high refractive index and a sulfur-oxygen double bond that is responsible for its poor plasticization effect. The results of a profile stability test at 85°C in the case of 16.7 wt% dopant A doped GI POF are shown in Fig. 7, compared to corresponding T_g profiles. In spite of a high Δn of 0.02, T_g of the central axis is maintained at temperatures higher than 80°C. Consequently, no degradation of the index profile was observed.

However, all of these stability tests were performed only under room humidity atmosphere. It was confirmed that the stability of not only the bandwidth but also attenuation even at high temperature and high humidity was influenced by the molecular structure of the dopant. Thermal stability improvement under high humidity is under investigation, the details of which will be described elsewhere.

4. Development of PF polymer based GI POF

4.1 Low-loss transmission

We have previously reported^{3,7)} a 2.5 gigabit data transmission using the PMMA based GI POF. However, a high attenuation of 100 dB/km limits POF link length to approximately 100 m.

Therefore, the development of low-loss PF polymer based GI POF can expand the high-speed POF link application area to premises wiring in the access network. Figure 8 shows the experimentally measured attenuation spectrum of PF polymer based GI POF. The attenuation spectrum of conventional PMMA based GI POF is also shown for comparison. Large peaks observed in the spectrum of PMMA based GI POF are due to the intrinsic absorption loss caused by carbon-hydrogen stretching vibration. Therefore, the attenuation of PMMA based GI POF in the near-infrared region is more than 10000 dB/km, while less than 100 dB/km attenuation is constantly obtained for PF polymer based GI POF from the visible to the near-infrared region. The attenuation at 1.3 μm is 45 dB/km.

The theoretical attenuation limit of PF polymer base GI

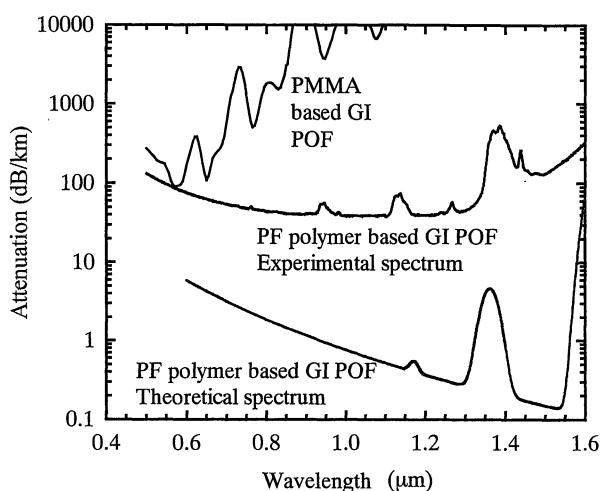


Fig. 8. Total attenuation spectra of PMMA based and PF polymer based GI POFs.

POF is an important issue in POF network design. We clarified the intrinsic attenuation factors of PF polymer based GI POF. In order to estimate intrinsic scattering and absorption losses, we adopted the thermally induced fluctuation theory and Morse potential energy theory, respectively.³⁾ The theoretical attenuation spectrum of PF polymer based GI POF is shown in Fig. 8. It should be noted that the theoretical attenuation limits at 1.3 μm and 1.5 μm wavelengths are 0.25 dB/km and 0.1 dB/km, respectively, which are comparable to that of silica fiber. These results suggest that the PF polymer based GI POF link is compatible with the silica based fiber network.

4.2 High speed transmission

Because a dramatic decrease in intrinsic absorption loss was achieved for PF polymer based GI POF, it is possible to utilize several kinds of transmitter and receiver devices. For instance, the conventional InGaAsP laser diode at 1.3 μm wavelength is one of the transmitter candidates. Therefore, we investigated the bandwidth performance of PF polymer based GI POF from the visible to the near-infrared region in order to adopt such optical devices for near-infrared use in the POF link. Figure 9 shows the experimental data of impulse response function measurement at 0.65 and 1.3 μm wavelengths, compared with the data from the conventional step-index type POF. An input pulse whose full width at half-maximum (FWHM) is 80 ps was coupled to 100-m-long POF via objective lens with 0.5 NA, which was larger than POF NA. The bandwidth of SI POF, which was estimated from the results in Fig. 9, was less than 100 MHz for a 100 m fiber because of large modal dispersion. On the other hand, in the case of PF polymer based GI POF, the bandwidth was approximately 2 GHz at 0.65 μm and 1.3 μm wavelengths.

Optimization of the refractive index profile of GI POF should be the key process in order to minimize modal dispersion. Figure 10 shows the relationship between bandwidth and refractive index profile of GI POF using the WKB method, taking into account both modal and material disper-

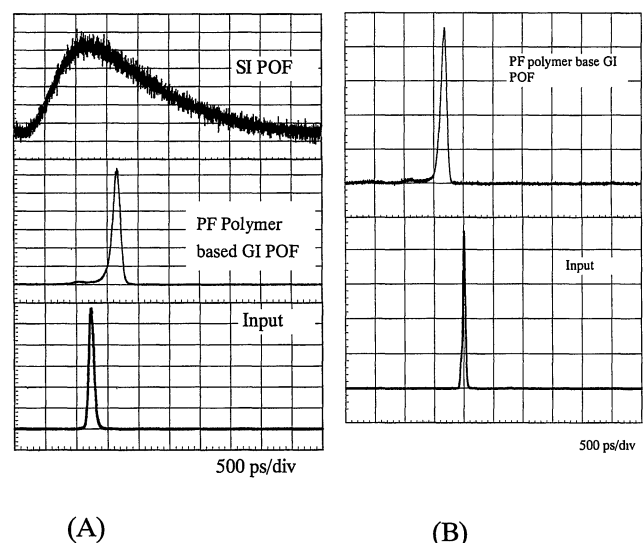


Fig. 9. Pulse distortion through the 100 m PF polymer based GI POF at 0.65 and 1.3 μm wavelengths, compared to that of conventional SI POF. (A) 0.65 μm wavelength (B) 1.3 μm wavelength.

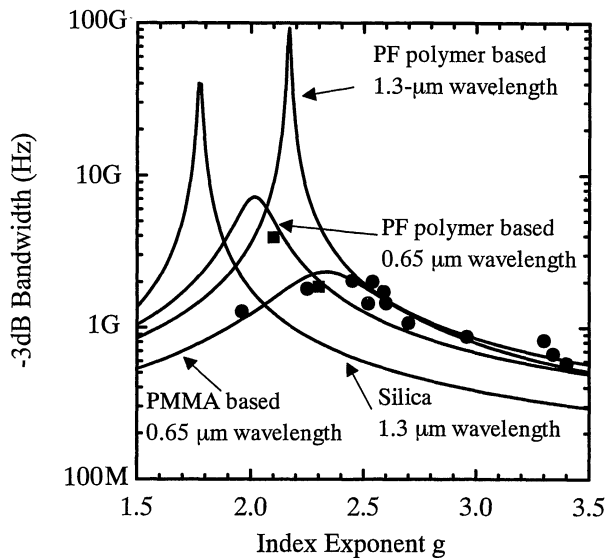


Fig. 10. Relationship between index exponent g and bandwidth of 100 m GI POF. Experimental values at $0.65 \mu\text{m}$ are shown by: \bullet : PMMA based GI POF \blacksquare : PF polymer based GI POF.

sions.^{8,9)} The parameter g in Fig. 10 is called the index exponent when the refractive index profile of GI POF is approximated by the power-law of the form.^{2,10)}

In the case of PMMA based GI POF, the maximum bandwidth of 100 m fiber at $0.65 \mu\text{m}$ wavelength is limited to approximately 3 GHz even when the refractive index profile is optimized, because of the large material dispersion of the PMMA. Plots in Fig. 10 represent the experimentally measured bandwidths. A good agreement between the theoretical and experimental values is observed for both PMMA and PF polymer based GI POFs, which indicates that bandwidth estimation by the WKB method is useful in designing the re-

fractive index profile of GI POF. As shown in Fig. 10, the bandwidth of PF polymer based GI POF is three times higher than that of PMMA based GI POF even at $0.65 \mu\text{m}$ wavelength, and 100 GHz can be obtained at $1.3 \mu\text{m}$ wavelength for 100 m transmission.

5. Conclusion

A high bandwidth in a wide wavelength range of the PF polymer based GI POF was theoretically and experimentally confirmed. The PF polymer based GI POF adopted not only the light source at $1.3 \mu\text{m}$ wavelength but also at 0.98 , 0.85 , 0.78 , or $0.65 \mu\text{m}$ wavelengths. High bandwidth stability at high temperature was experimentally confirmed. The glass transition temperature of the fiber core was maintained at a temperature as high as 85°C by using a new dopant, which enabled to cover the required thermal stability at 85°C in the Bellcore standard. These outstanding results indicate that GI POF with high thermal stability can be applied not only for indoor use but also for outdoor use in the premises network or drop line.

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