Thermally Stable High-Bandwidth Graded-Index Polymer Optical Fiber

Masataka Sato, Takaaki Ishigure, and Yasuhiro Koike

***Abstract*—High-bandwidth poly (methyl methacrylate) PMMA base graded-index polymer optical fiber (GI POF) with high thermal stability is proposed. No distortion of bandwidth was observed even after more than 10 000 hours aging at 85 °C by selecting the large sized aromatic dopant which has the stable secondary interaction with PMMA matrix and maintains the high glass transition temperature (Tg) of the core of GI POF. The relationship between the heat-drawing condition from the GI preform to the fiber and the thermal stability in the attenuation was investigated. It was clarified that the length shrinkage of the fiber during the aging at high temperature caused large attenuation increase. On the other hand, the degree of shrinkage could be tightly controlled by changing the heat-drawing tension. It was confirmed that the GI POF drawn with optimized heat-drawing tension had no shrinkage of the fiber during aging at 70 °C and no attenuation increase was observed.**

***Index Terms*—Attenuation, bandwidth, dopant molecules, glass transition temperature, graded index polymer optical fiber (GI POF), heat-drawing tension, thermal stability.**

I. Introduction

RECENTLY, high-speed data communication systems such as digital home network and high-speed local area network (LAN) has been rapidly developed even in the access area. In these advances, the development of optical fiber network, which is the most important infrastructure for high-speed data communication, has been required.

We have proposed the interfacial-gel polymerization technique as a fabrication process of the large-core, high-bandwidth graded-index (GI) polymer optical fiber (POF) [1], [2]. Furthermore, recent development of the perfluorinated polymer base GI POF is considered to enable a high-speed data communication in premise area [3]. In order to realize the GI POF link in the premises network, the thermal stability and the long-term reliability become key issues. In the interfacial-gel polymerization technique, the refractive index distribution of the GI POF is formed by the concentration distribution of the unreactive dopant having higher refractive index than that of the polymer matrix.

In this paper, it was confirmed that the dopant kind and concentration strongly influenced the thermal stability of GI POF, especially the degradation of the refractive index profile of the GI POF by the migration of dopant molecules. The relationship between the glass transition temperature (Tg) of the dopant added polymer and the thermal stability of the GI POF was quantitatively analyzed. Finally, we succeeded in fabricating the thermally stable PMMA base GI POF at high temperature (70–90 °C) by adopting specified dopant based on the above concept.

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II. Experiment

A. Formation of GI POF

The GI POF was obtained by the heat drawing of the GI preform. The GI preform was prepared by the interfacial-gel polymerization technique, which we have already reported [2]. The fabrication process is summarized as follows: First, a pure poly methyl methacrylate (PMMA) tube whose outer diameter was 18–50 mm and inner diameter was 60% of the outer diameter was prepared. Next, the PMMA tube filled with MMA monomer and dopant mixture containing initiator and chain transfer agent was placed in an oil bath at 90 °C. Here, inner wall of PMMA tube was 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 due to "gel effect." Therefore, the polymer phase gradually grows from the inner wall of the tube to the center axis of the tube during polymerization. In this process, the MMA monomer can more easily diffuse into the polymer gel phase compared to the dopant molecules, because the molecular volume of the dopant, which has benzene rings in it, is larger than that of the monomer. Therefore, the dopant molecules have been gradually concentrated in the center region of the core during the polymerization process. After the complete polymerization up to the center of the core region, the radial distribution of the dopant concentration is formed. Since the refractive index of the dopant is higher than that of the PMMA matrix, the radial refractive index distribution is successfully formed in the GI preform.

B. Dopant Characteristics

We have proposed several kinds of dopant materials for the PMMA base GI POF [2] according to following aspects. The dopant should satisfy the following properties in order to obtain low-loss, high-bandwidth GI POF by the interfacial-gel polymerization technique:

1) good miscibility with PMMA;
2) higher refractive index than that of PMMA;
3) higher boiling point than heat-drawing temperature (200 °C);

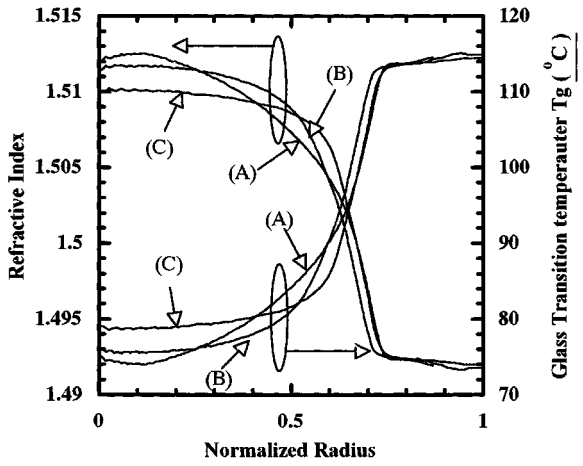


Fig. 1. Thermal stability of the refractive index profile of 20 wt.% DP-doped GI POF after aging at 85 °C, compared to the glass transition temperature profile. (A) Original, (B) after 10 h, and (C) after 24 h.

4) larger molecular volume than that of MMA monomer;
5) secondary interaction with PMMA matrix.

Although it is possible to prepare the low-loss and high-bandwidth GI POF by selecting the dopant satisfying the above items of 1)–4) [1], the thermal stability of the GI POF strongly depends on the chemical structure of the dopant and secondary interaction between dopant molecules and polymer matrix as listed in the item 5). Fig. 1 shows the thermal stability of the refractive index profile of 20 wt.% diphenyl-doped GI POF after aging at 85 °C, along with the glass transition temperature profile. It is noted that the degradation of the index profile of the GI POF was observed only after 10 h of aging at 85 °C as shown in Fig. 1.

For the sake of thermally stable refractive index profile, the diffusion and migration of the dopant material have to be inhibited. The molecular volume of the dopant is important factor for the diffusion constant of the dopant. On the other hand, it is also supposed that such dopant diffusion could depend on the mobility of segments of the polymer matrix. The mobility of the segment of polymer dramatically changes around the glass transition temperature (Tg). By adding the dopant materials, the Tg of the polymer is lowered because the dopant works as plasticizer [4]. Thus, designing the dopant offering low plasticization effect is one solution for maintaining the high Tg of the center of the core.

On the other hand, the Tg of the center of the core can be close to that of the PMMA homopolymer by decreasing the feed concentration of the dopant. In this case, the dopant, which has a much higher refractive index than that of the PMMA, is required. Plasticization effect is dependent on the chemical structure of dopants because they are affected by the polarity and flexibility of dopant molecules [4]. Therefore, it can be said that the dopant whose flexibility is reduced by bulky substituents has low plasticization effect. Furthermore, since the materials with sulfur or benzene ring in these structures have much higher refractive index than that of the PMMA, the feed concentration of the dopant can be decreased.

Several kinds of commercially available aromatic compounds were adopted. The properties of dopants used are listed in Table I together with their chemical structures.

C. Thermal Stability Test

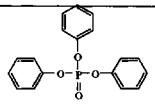
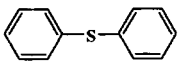
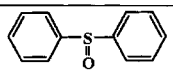
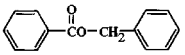
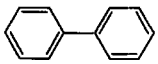
1) Glass Transition Temperature: The plasticization effect was investigated by measuring the Tg of the dopant added PMMA in which the concentration of the dopant was from 5 to 15 wt.%. Since the dopant concentration distribution corresponds to the refractive index profile of the GI POF, the GI POF has a Tg profile in the core region. In order to obtain the accurate Tg profile from the measured refractive index profile of the GI POF, the relation between the glass transition temperature and the refractive index of dopant added PMMA was measured. The glass transition temperature of the dopant added PMMA was measured by using Shimazu differential scanning calorimeter (DSC-50). The heating rate for the DSC was 20 °C/min. The refractive index of the polymer was measured by using a Metricon PC-2000 prism coupler by which a plate like sample could be adopted for the measurement.

2) Refractive Index Distribution: Thermal stability of the refractive index profile of the GI POF directly affects the bandwidth stability. Investigation of the thermal stability of the refractive index profile could offer important information about the thermal stability of the GI POF in the bandwidth. The process of the stability test is described as follows: the GI POF prepared by the interfacial-gel polymerization technique was aged at 85 °C or 90 °C. Thermal stability of the POF is generally tested around 85 °C because this condition is one of the thermal stability standards of many cables including glass optical fiber. The refractive index distribution of the GI POF after aging was measured by Interphako interference microscopy [5] and was compared with the index profile of the original one.

3) Bandwidth: Even if the degradation of the index profile is small enough to be detected by the index profile measurement, only slight amount of the degradation of the refractive index profile might decrease the fiber bandwidth of long fiber. Therefore, the bandwidth stability test was also performed. The bandwidth stability was measured by a time-domain measurement method. A narrow input pulse signal generated by a pulse generator (Hamamatsu PLP-02) was injected to the various length (30–100 m) GI POF, and the output pulse was detected by the sampling head and analyzed by a sampling oscilloscope (Hamamatsu OOS-1). The output pulse waveforms from the GI POF before and after aging at 85 °C were compared.

4) Attenuation: The long-term stability in the attenuation of the GI POF was tested. We investigated the thermal stability of the attenuation of the GI POF at high temperature. The stability test of the attenuation spectrum was measured with using 5-m length GI POF's. The influence of water molecules absorbed in polymer matrix should be investigated, because it has been reported that PMMA, the polymer matrix of the GI POF, absorbs 2 wt.% of water when the PMMA bulk is placed in hot water at 60 °C. We have already got many experimental data on this issue and found that the attenuation was not simply influenced by the amount of absorbed water. An important factor causing large attenuation is the scattering loss due to some large sized

TABLE I

Used dopant	Chemical structure	Molecular Weight (g/mol)	Molecular Volume (Å^3)	Solubility parameter (cal/cm^3)$^{1/2}$	Refractive index
Triphenyl Phosphate (TPP)		326.3	449.2	9.42	1.563
Diphenyl Sulfide (DPS)		186.3	277.8	9.431	1.633
Diphenyl Sulfoxide (DPSO)		202.3	286.9	11.95	1.606
Benzyl Benzoate (BEN)		212.3	314.6	9.641	1.568
Dipenyl (DP)		154.21	258.2	8.796	1.587

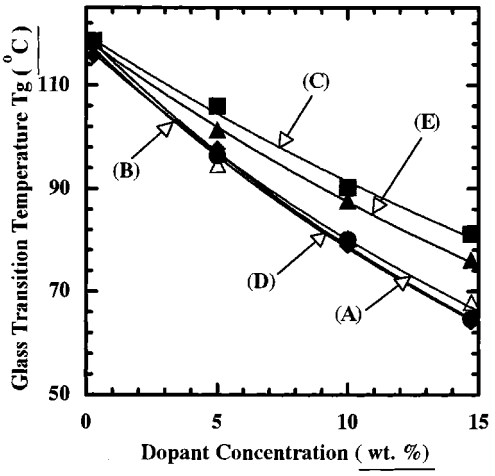


Fig. 2. Relationship between dopant concentration and Tg of dopant added PMMA specimen. (A) BEN, (B) DP, (C) TPP, (D) DPS, and (E) DPSO.

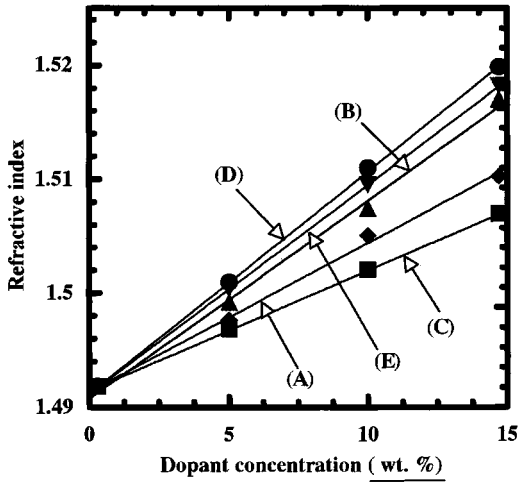


Fig. 3. Relationship between dopant concentration and refractive index of dopant added PMMA specimen. (A) BEN, (B) DP, (C) TPP, (D) DPS, and (E) DPSO.

aggregation of water molecules, which depends on the affinity of water with polymer matrix. Details about the aggregation of absorbed water molecules will be described in another paper.

III. Results and Discussion

A. Glass Transition Temperature

The dopant concentration versus the Tg of the dopant added PMMA specimen is shown in Fig. 2, and the relation between the dopant concentration and the refractive index of the dopant added PMMA is shown in Fig. 3. Here, benzyl benzoate (BEN), diphenyl (DP), triphenyl phosphate (TPP), diphenyl sulfide (DPS), and diphenyl sulfoxide (DPSO) were used. As shown in Fig. 2, decrease of the glass transition temperature is dependent on the kind of dopant used at the same dopant concentration. These dopant kind dependencies of the Tg could be understood as the difference of plasticization effect. On the other hand, it can be said from Fig. 3 that the feed concentration of the dopant can be decreased by selecting the dopant such as DPS and DPSO, which have higher refractive index than that of other dopant molecules adopted in this paper if the GI

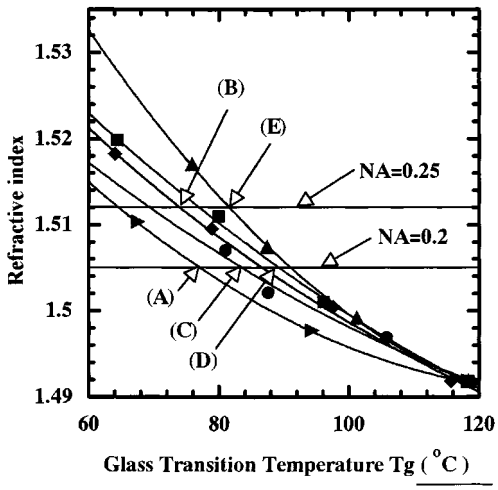


Fig. 4. Relationship between Tg and refractive index of dopant added PMMA specimen. (A) BEN, (B) DP, (C) TPP, (D) DPS, (E) DPSO.

POF's with the same NA are prepared by using these dopant molecules. A relation between the Tg and the refractive index

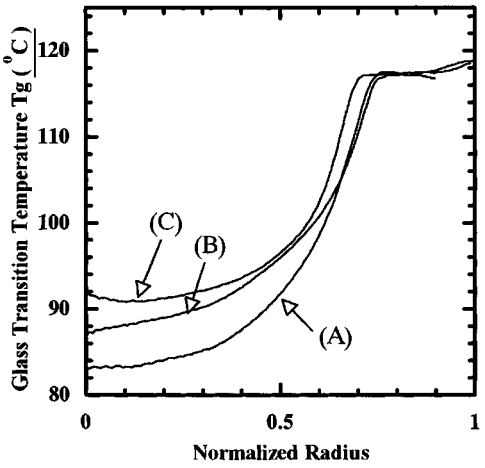


Fig. 5. Tg profile of PMMA base GI POF. (A) 20 wt.% TPP-doped GI POF. (B) 11 wt.% DPS- doped GI POF. (C) 12.5 wt.% DPSO-doped GI POF.

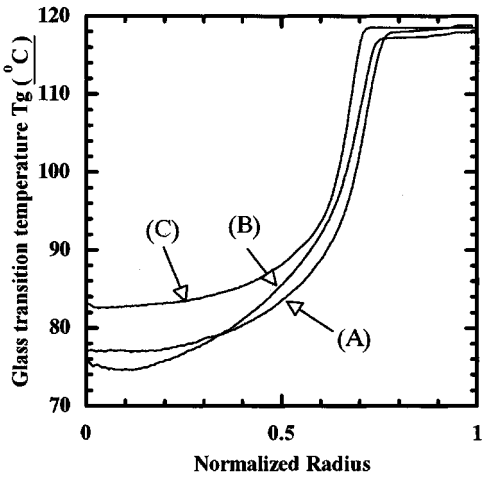


Fig. 6. Tg profile of PMMA base GI POF. (A) 20 wt.% DPS-doped GI POF. (B) 17.5 wt.% DP- doped GI POF. (C) 17.5 wt.% DPSO-doped GI POF.

of the dopant added PMMA is shown in Fig. 4. It is revealed that TPP, DPS and DPSO are candidates of dopant to prepare the GI POF having a high Tg as 85–95 °C at the core center with maintaining 0.2 of NA. Furthermore, in order to achieve a high coupling efficiency between a light source and the POF, higher NA is required. Therefore, it is concluded from Fig. 4 that DPSO is the suitable dopant for obtaining a high NA as 0.25, maintaining the high Tg at the core center of the GI POF.

B. Thermal Stability of Bandwidth.

The radial distribution of the Tg in the GI POF's having the same NA of 0.2 was estimated from the measured refractive index distributions. The results for TPP doped, DPS doped, and DPSO doped GI POF's are shown in Fig. 5. In order to obtain GI POF's with the same NA (0.2), the concentration of TPP, DPS and DPSO added to MMA monomer was 20 wt.%, 11 wt.%, and 12.5 wt.%, respectively. In these samples, the Tg at the core center was higher than 80 °C. It is clarified from Figs. 3 and 5 that low dopant concentration is effective to maintain the high Tg as in the case of DPS doped GI POF. Particularly, in the case of DPSO doped GI POF, the Tg at the core center was the highest (90 °C) among samples. Higher refractive index than that of other dopant molecules and low plasticization effect of DPSO is the main reason of maintaining the high Tg.

As described in the Section III-A, the high NA is one of the important properties of POF. Fig. 6 shows the Tg distributions of DP doped, DPS doped, and DPSO doped GI POF's whose NA were 0.25. The dopant concentration was 20 wt.%, 17.5 wt.%, and 17.5 wt.%, respectively. The dopant concentration must be higher to achieve 0.25 of NA compared to 0.2 of NA. In the case of DP doped and DPS doped GI POF's, the Tg at the core center is lowered to 75 °C due to the plasticization effect. On the contrary, the Tg at the core center maintained as high as 85 °C in the case of DPSO doped GI POF. The thermal stability of the index profile of DPSO doped (17.5 wt.%) GI POF at 85 °C is shown in Fig. 7. No degradation of the index profile was observed even after 1000 h aging. Therefore, it is concluded that both low plasticization and much higher refractive index than that of the PMMA are required properties for the dopant in order

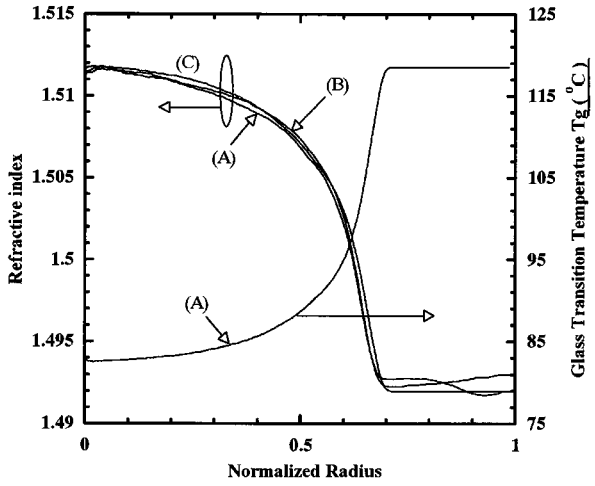


Fig. 7. Thermal stability of the refractive index profile of 17.5 wt.% DPSO-doped GI POF after aging at 85 °C, compared to the glass transition temperature profile. (A) Original, (B) after 600 h, (C) after 1000 h

to achieve high NA GI POF with maintaining the thermal stability of the index profile.

The degradation of the refractive index profile of the GI POF directly influences the bandwidth characteristics of the GI POF. Therefore, the bandwidth characteristics of the GI POF were investigated with using 30 m GI POF's before and after oven aging at 85 °C by the time domain method. The output pulse broadening of 20 wt.% DP doped GI POF before and after oven aging at 85 °C is shown in Fig. 8. The output pulse significantly distorted only after 24 h aging. It is considered that the distortion of the output pulse was caused by the degradation of the refractive index profile, i.e., the migration of the dopant. The pulse broadening of DPS-doped GI POF in which higher Tg than 85 °C is maintained at the core center as shown in Fig. 5, is shown in Fig. 9 before and after oven aged at 85 °C. No pulse distortion was observed even after 12 000 h aging at 85 °C.

On the other hand, Fig. 10(1) and (b) show the thermal stabilities of the index profile of 17.5 wt.% DPS doped and 20 wt.% BEN-doped GI POF's through oven aging at 85 °C, respectively. The Tg distributions of these samples were also shown

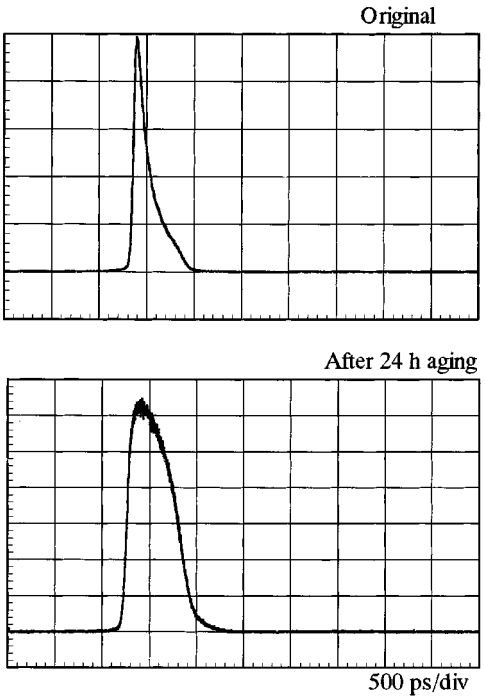


Fig. 8. Thermal stability of 20 wt.% DP-doped 30m GI POF after aging at 85 °C. The bandwidth was measured at 650 nm wavelength.

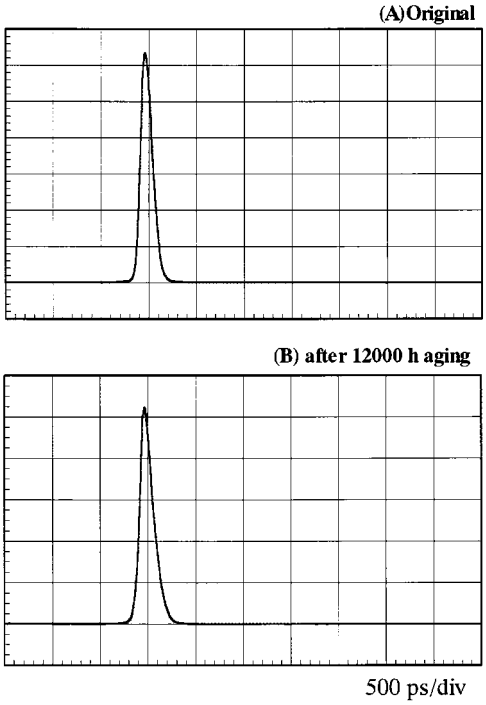


Fig. 9. Thermal stability of 11 wt.% DPS-doped 30 m GI POF after aging at 85 °C. The bandwidth was measured at 650 nm wavelength.

in Fig. 10. The migration process was rather different although both the Tgs at the core center were lower than the aging temperature. Although the high Tg is one of the reasons why the index profile maintains effectively, other factor has to be considered in order to explain the high stability of BEN-doped GI POF shown in Fig. 10(a). As shown in Table I, BEN has a larger molecular volume than DPS. The large molecular volume could prohibit

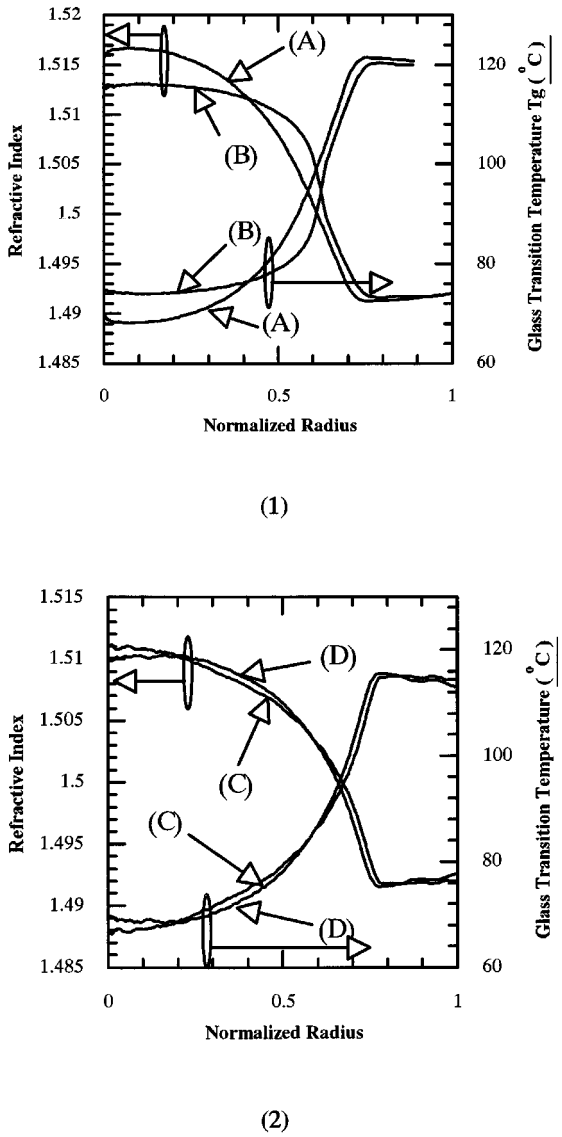


Fig. 10. Thermal stability of the refractive index of GI POF after aging at 85 °C, compared to the glass transition temperature. (1) 17.5 wt.% DPS-doped GI POF (A) Original (B): after 24 h (2) 20 wt.% BEN-doped GI POF (C) Original (D) after 48 h.

the diffusion of the dopant molecules. Furthermore, both BEN and MMA have carbonyl group ($-C=O$) and this segment produces the strong interaction between the polymer chain and the dopant molecules. On the other hand, as DPS has no such groups in it, the dopant molecules can easily diffuse to degrade the index profile of the GI POF. However, the index profile can be maintained after 2000 h aging at 90°C when the feed concentration of DPS was decreased to 11 wt.% and the Tg at the core center was maintained as high as 90 °C as shown in Fig. 11. Thus, it is concluded that the Tg at the core center is one of the important issues to achieve the thermally stable GI POF in the bandwidth.

C. Thermal Stability of Attenuation

The attenuation spectra of DPS-doped (11 wt.%) GI POF before and after aging at 70 °C for 1 day are shown in Fig. 12. It should be noted that only wavelength independent attenuation

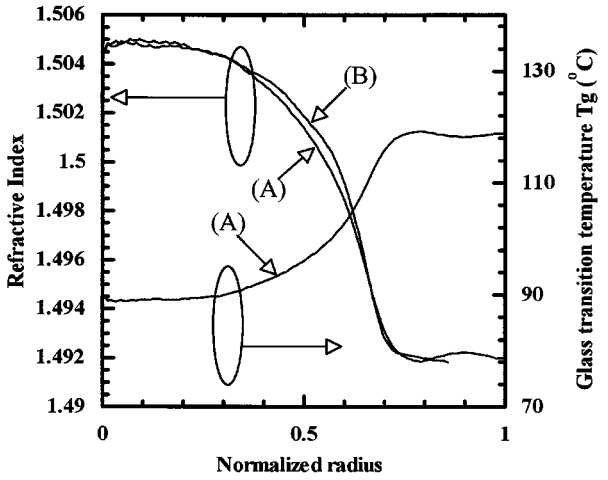


Fig. 11. Thermal stability of the refractive index of 11 wt.% DPS-doped GI POF after aging at 90 °C, compared to the glass transition temperature. (A) Original and (B) after 2000 h.

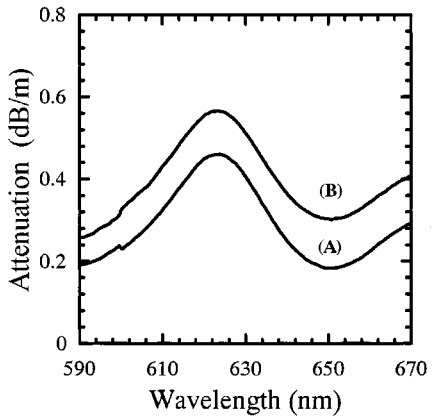


Fig. 12. Wavelength dependency of the total attenuation of 11 wt.% DPS-doped GI POF at 70 °C. Drawing tension 280 gf: (A) original and (B) aged at 70 °C for 1 day.

increment was observed. It is considered that such wavelength independent excess attenuation is due to an excess scattering loss by large heterogeneous structures, imperfection of waveguide structure, or bending loss. We previously confirmed and reported that no scattering loss increase from the PMMA homopolymer and the dopant added PMMA was observed through oven aging even at 85 °C for 70 days [6]. Therefore, this result suggests that no large size heterogeneous structure may be formed in the GI POF through the aging. On the other hand, when the GI POF was statically bent, the attenuation increase was observed. The results when the bending radius is 20 mm and 5 mm are shown in Fig. 13. Similar wavelength independent attenuation increase as shown in Fig. 12 is observed.

Fig. 14 shows the length shrinkage of the GI POF through aging at 70 °C. As indicated in Fig. 14, with increasing the heat drawing tension, the length shrinkage becomes large. Furthermore, the relation between the length shrinkage and the attenuation increase is also shown in Fig. 14. Large shrinkage causes high attenuation increase. From the results shown in Figs. 12–14, it is considered that the attenuation increment of

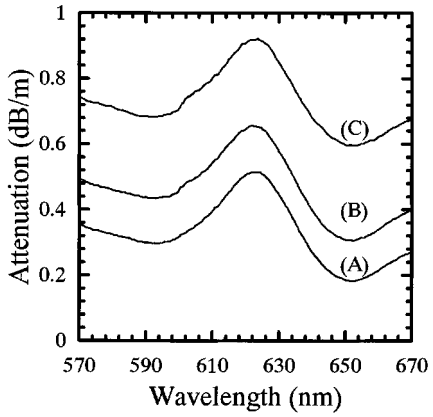


Fig. 13. Wavelength dependency of the bending loss of 11 wt.% DPS-doped GI POF. (A) Original. (B) Bending radius 20 mm. (C) Bending radius 5 mm.

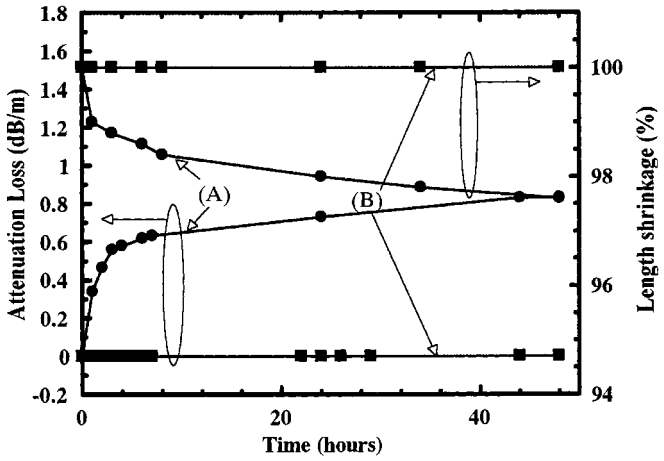


Fig. 14. Drawing tension effect on the fiber shrinkage and attenuation at 70 °C. (A) Drawing tension 280 gf. (B) Drawing tension 50 gf.

the GI POF is mainly caused by the bending loss, which is induced by the random shrinkage through the aging. Therefore, no attenuation increase is observed in the GI POF with no length shrinkage through the aging at 70 °C as shown in Fig. 14.

IV. Conclusion

The dopant design for PMMA base GI POF to improve the thermal stability was discussed. The new dopant molecules were designed to maintain the high Tg at the core center, based on the aspect of molecular volume, chemical structure, secondary interaction with PMMA matrix, and refractive index. And the GI POF with high thermal stability was successfully obtained. It was found that no degradation in the refractive index profile and bandwidth was observed after 10 000 h aging at 85 °C. Thermal stability of the attenuation of the GI POF was also discussed. We clarified that the thermal stability of the attenuation of the GI POF depends on the heat drawing tension. By investigating the thermal stability in both the attenuation and the bandwidth, it is considered that DPSO, which is newly selected dopant, is a promising candidate on the dopant of thermally stable PMMA base GI POF.

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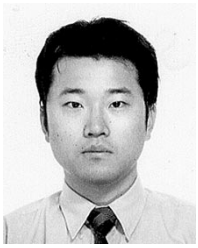

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