High Temperature Resistant Graded-Index Polymer Optical Fiber

Masataka Sato, Miki Hirai, Takaaki Ishigure, and Yasuhiro Koike

***Abstract*—The dopant system graded-index polymer optical fiber (GI POF) for high temperature stability both in bandwidth and attenuation is reported for the first time. We confirmed that the Numerical Aperture (NA) of the GI POF strongly influences the high temperature stability of the GI POF in the attenuation. It was confirmed in this paper that the attenuation increment was mainly induced by the bending loss, since the GI POF drawn by high tension tended to show its length shrinkage, resulting in irregular bending due to the orientation relaxation of polymer chain. We clarified the optimum drawing tension which maintains high mechanical property and minimizes the length shrinkage of the GI POF at high temperature, and the optimum fabrication conditions of the GI POF for high temperature stability both in bandwidth and attenuation.**

***Index Terms*—Attenuation, dopant molecules, glass transition temperature, graded index polymer optical fiber, heat-drawing tension, high temperature stability, length shrinkage, numerical aperture.**

I. Introduction

With increasing demand of high-speed data transmission even in the access area, polymer optical fiber (POF) is expected to be a high data transmission medium. We have proposed the low loss, high bandwidth poly methyl methacrylate (PMMA)-dopant system Graded-Index (GI) polymer optical fiber (POF) [1], [2]. To realize high-speed data communication by utilizing PMMA base GI POF, high temperature stability both in bandwidth and attenuation becomes important issue. The quadratic refractive index profile of the GI POF is formed by the concentration distribution of the dopant which is generally the aromatic compound having higher refractive index than that of PMMA. So, if the dopant molecules diffuse in the polymer matrix, the index profile degrades. Therefore, high temperature stability of the GI POF in the bandwidth has been of concern because the index profile degradation seriously affects the bandwidth. We have already reported high temperature resistant GI POF in bandwidth [3]. It was confirmed in our previous paper [3] that maintaining high Tg at the core of the GI POF by designing appropriate dopant structure is one of the remedies for the high temperature stability of the GI POF in bandwidth. On the other hand, it was observed that maintaining high Tg at the core of the GI POF also improves the high temperature stability of the GI POF in the attenuation as shown in Fig. 1. The Tg at the core of the 20 wt.% tricrezyl phosphate (TCP)-doped GI POF (curve A) and the 11 wt.% diphenyl sulfoxide (DPSO)-doped GI POF (curve B) were 80 °C and 92 °C, respectively. The fiber drawing tension of these GI POFs were almost the same (200 gf). It should be noted that larger length shrinkage of the GI POF was observed during the temperature resistance test of 20 wt.% TCP-doped GI POF rather than that of 11 wt.% DPSO-doped GI POF. Therefore, it was suggested that largely shrunk fiber showed high attenuation increment. Since the GI POF was obtained by heat drawing process, the polymer chain would be oriented during fiber drawing process. The length shrinkage of the GI POF at high temperature is induced by the orientation relaxation of polymer chain. In this paper, we investigated the main origin of the attenuation increment at high temperature. Particularly, we focused on the relation between orientation relaxation of polymer and attenuation increment of the GI POF.

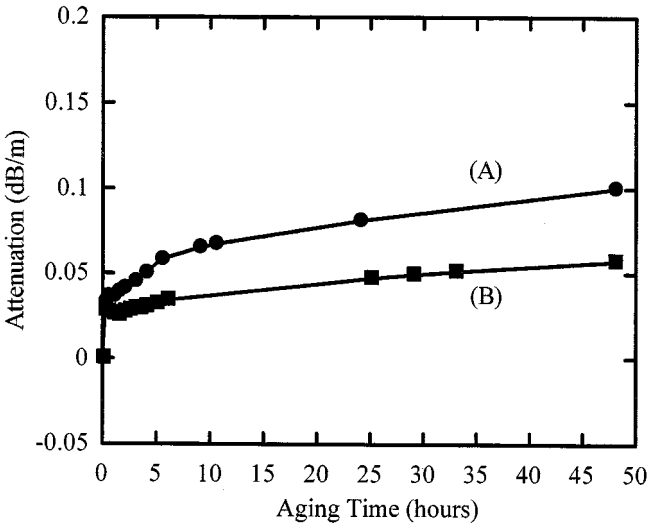


Fig. 1. High temperature stability of the attenuation of the GI POF through the aging at 70 °C: (A) 20 wt.% TCP-doped GI POF and (B) 11 wt.% DPSO-doped GI POF.

II. Experiments

A. Formation of GI POF

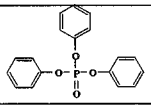
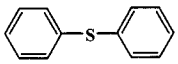
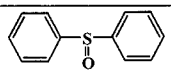
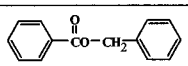
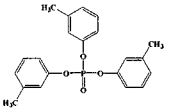
The Graded-Index (GI) polymer optical fiber (POF) was obtained by the heat drawing of the GI preform. The GI perform was prepared by the interfacial-gel polymerization technique which we have already reported [2]. Its process is summarized as follows: First, a pure PMMA tube was prepared, where the outer diameter was 18 to 50 mm and the inner diameter was 60% of the outer diameter. Next, the PMMA tube filled with MMA monomer and dopant mixture containing initiator and

Manuscript received June 20, 2000; revised August 25, 2000. This work was supported by the research fund of Plastic Optical Fiber Project from Telecommunications Advancement Organization (TAO) of Japan.

The authors are with the Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan.

Publisher Item Identifier S 0733-8724(00)10542-0.

TABLE I
CHEMICAL STRUCTURES AND PROPERTIES OF DOPANTS USED

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
Tricresyl Phosphate (TCP)		368.37	520.8	8.244	1.557

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 grows from the inner wall of the tube to the center. During this process, the MMA monomer can easily diffuse into the 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 monomer. Thus, the dopant molecules form the concentration distribution in the core, which corresponds to the refractive index profile.

B. Candidates of Dopant

We previously proposed several kinds of dopant material for PMMA base GI POF [2], [3]. Dopant for GI POF should satisfy the following properties in order to obtain low-loss, high bandwidth, and high temperature resistant GI POF:

1) Good miscibility with PMMA.
2) Higher refractive index than PMMA.
3) Higher boiling point than heat-drawing temperature (240 °C).
4) Larger molecular volume than MMA monomer.
5) Maintenance of high Tg at core center.

Maintaining high Tg at the core center is important for GI POF to have high temperature stability in the bandwidth [3]. Although Tg of the core of GI POF is lowered by doping, Tg can be close to that of PMMA homopolymer by decreasing feed concentration of the dopant, or selecting suitable dopant which has a low plasticization effect. Since the materials with sulfur or benzene ring in these structures can have much higher refractive index than that of PMMA, feed concentration of the dopant can be decreased to obtain the sufficient refractive index difference between the core and cladding of the GI POF. Plasticization effect generally depends on the chemical structure of the dopant because they are affected by the polarity and mobility of the dopant [4]. We selected the dopant with low plasticization effect and high refractive index by introducing bulky substituents such as aromatic ring. It is considered that higher numerical aperture (NA) of the fiber than 0.2 is required to achieve the high coupling efficiency between the light source and fiber and to decrease the bending loss of the POF. Consequently, high Tg at the core of the GI POF can be maintained by using such a dopant with high refractive index. Therefore, in this paper, several kinds of commercially available aromatic compounds were adopted. The properties of dopants used in this paper are listed in Table I together with their chemical structures.

C. High Temperature Stability Test of the Attenuation of the GI POF

High temperature stability of the attenuation of the GI POFs in which several kinds and concentrations of dopant were used was investigated. Measurement setup is schematically shown in Fig. 2. As the light source, an InGaAsP laser diode whose emitting wavelength is 655 nm was used and the optical power meter detected the optical output power from 12-m length GI POF. Here, 10-m length GI POF is placed in the constant temperature chamber, and the both 1-meter length ends of POF were placed outside of chamber. On the other hand, a tungsten lump was also used when the wavelength dependence of the attenuation change was measured through the aging, and the optical output power was detected with using the optical spectrum analyzer. High temperature stability of the attenuation was investigated by continuously measuring the output power change from the GI POF through the aging, where the connection between the light source and the fiber, and between the fiber and the detector were fixed. Since the output power from the GI POF is very sensitive to the coupling conditions between the light source and fiber and between the fiber and detector, both coupling conditions were fixed through the aging. The length shrinkage of the GI POF was also measured in order to investigate the relation between the amount of shrinkage and the attenuation increment of the GI POF. For the measurement of the absolute amount of shrinkage, the 1-m fibers were placed in a constant temperature

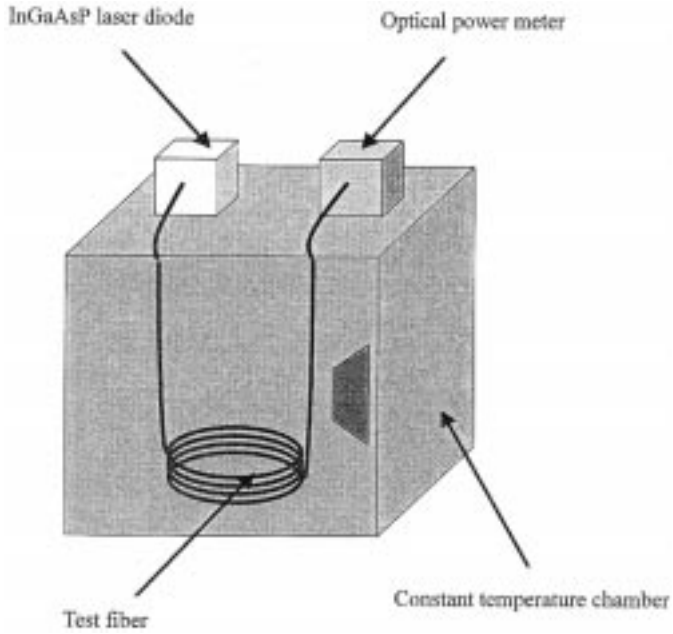


Fig. 2. Schematic representation of test method of high temperature stability in the attenuation of the GI POF.

chamber at 70 °C and fiber length change was directly measured through the aging.

Mechanical property of the GI POF was also measured in order to clarify the relation between the drawing tension (orientation of polymer chain) and mechanical strength of the GI POF. The apparatus used for mechanical property measurement was RTC1210-A (ORIENTIC. Co., Ltd). A 10-cm length fiber was held between air chucks. The drawing speed was 100 mm/min. The stress-strain curve was obtained by measuring continuously the force developed as the sample was elongated at constant rate of extension.

The influence of water molecules absorbed in polymer matrix should be investigated when the high temperature and high humidity stability of the GI POF is considered, because it has been reported that PMMA, the polymer matrix of the GI POF, can absorb 2 wt.% of water at maximum when the PMMA bulk is placed in hot water at 60 °C. We have already obtained many experimental data on this issue and found that the attenuation was not simply influenced by the amount of absorbed water [5]. An important factor causing large attenuation increment is the excess scattering loss due to some large sized aggregation of water molecules, which depends on the affinity of water with polymer matrix. Details about the aggregation of absorbed water molecule be described in another paper.

III. Results and Discussions

A. Effect of Length Shrinkage of GI POF on the Attenuation

The GI POF is prepared by heat drawing from the GI perform. Fig. 3 shows the relation between the core center Tg of the GI POF and the length shrinkage of the GI POF after 48 hours of aging at 70 °C. The core center Tg of the GI POF was estimated from the measured refractive index distributions [3]. Since the dopant concentration distribution corresponds to the refractive index profile of the GI POF, the GI POF has a Tg profile in

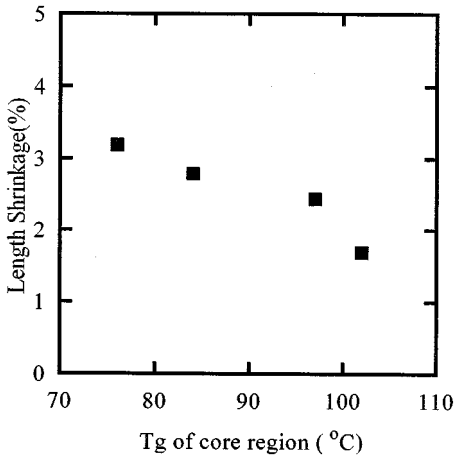


Fig. 3. Relation between the Tg at core center of the GI POF and length shrinkage of the GI POF after 48 hours aging at 70 °C. Fiber drawing tension: 200 gf.

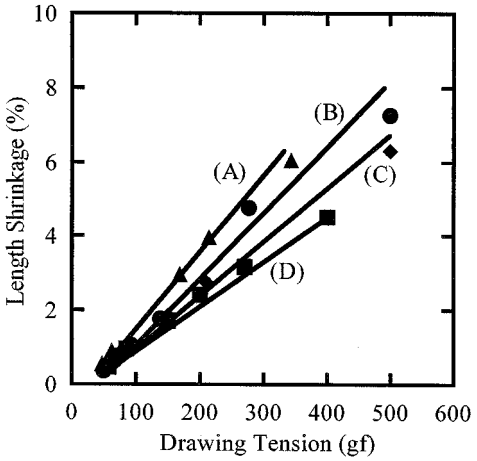


Fig. 4. Relation between the drawing tension and the length shrinkage of the GI POF after 48 hours of aging at 70 °C. (A) 20 wt.% BEN-doped GI POF; (B) 11 wt.% DPS-doped GI POF; (C) 20 wt.% TPP-doped GI POF; and (D) 11 wt.% DPSO-doped GI POF.

the core region. The accurate Tg profile was obtained from two measurements. First, the relation between dopant concentration and refractive index of PMMA including dopant was measured. Second, the relation between dopant concentration and Tg of the polymer was measured. From these two relations, another relation between the refractive index of doped PMMA and its Tg could be calculated. Therefore, the Tg distribution in the core of the GI POF was obtained by the refractive index profile and this relation. The NAs of all GI POFs shown in Fig. 3 are almost the same as 0.2 and the drawing tensions of the GI POFs are also the same (200 gt). Since the mobility of the polymer segment is dramatically changes around Tg, the GI POF having low Tg at the core region tends to show large length shrinkage as shown in Fig. 3. On the other hand, the degree of the orientation of polymer chain is dominated by the heat drawing tension from the GI perform. Fig. 4 shows the relation between the length shrinkage of the GI POFs after 48 hours of aging at 70 °C and the fiber drawing tension from the GI preforms. The GI POFs shown in Fig. 4 have almost the same NA (0.2). As the drawing tension is directly related to the orientation degree of polymer

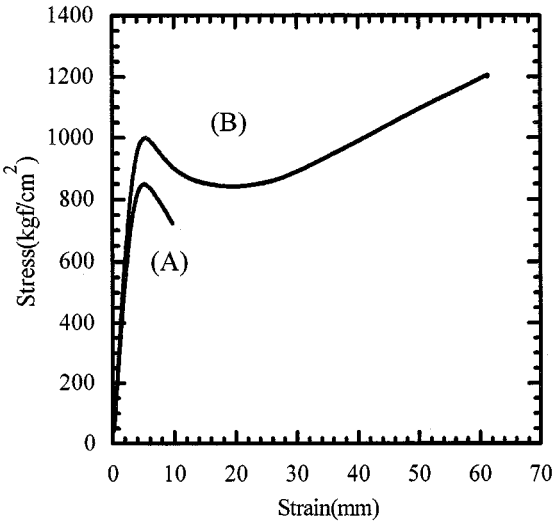


Fig. 5. Stress-strain curve of 11 wt.% DPS-doped GI POF: (A) drawing tension 50 gf and (B) drawing tension 92 gf.

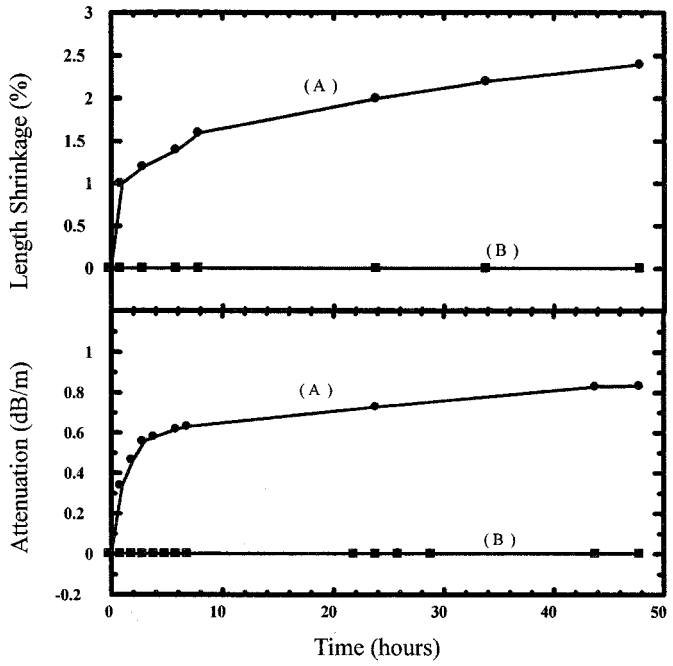


Fig. 6. Change of the attenuation and length shrinkage of 11 wt.% DPS-doped GI POF during the aging at 70 °C: (A) drawing tension 280 gf and (B) drawing tension 50 gf.

chains, the GI POF drawn by high tension tends to show large length shrinkage at high temperature due to the relaxation of the orientation of polymer chain. Dopant kind dependency of the length shrinkage of the GI POF was also observed, as shown in Fig. 4. It is suggested that these results shown in Fig. 4 are also originated in the difference of the Tg of the core of the GI POF.

From the result of Fig. 4, drawing tension should be decreased if it is required to eliminate the length shrinkage of the fiber. However, when the orientation of the polymer chains is reduced by drawing with low tension, the mechanical property is dramatically degraded. Fig. 5 shows the stress-strain curves of the GI POFs drawn with 50 gf and 92 gf tensions. It is concluded from Figs. 4 and 5 that optimum drawing tension exists, by

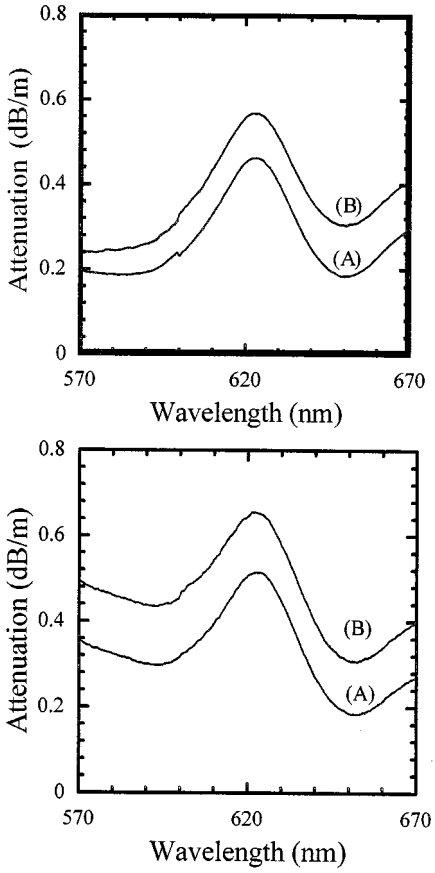


Fig. 7. Attenuation spectrum of the GI POF. Top: Through the aging at 70 °C: (A) before aging and (B) after 48 hours of aging. Bottom: When the fiber is bent: (A) original and (B) bending radius 25 mm, bending angle 90 ° × 1time.

which both mechanical strength and heat-shrinking problems are solved. Further more, length shrinkage of the GI POF at high temperature should be eliminated even if the optical property such as the attenuation is stable.

B. High Temperature Stability of the GI POF in the Attenuation

High temperature stability of the attenuation of GI POF was investigated. Fig. 6 shows the relation between the attenuation increment and length shrinkage of 11 wt.% diphenyl sulfide (DPS)-doped GI POF through the aging at 70 °C. With increasing the amount of length shrinkage, the attenuation increases. It is obvious that the length shrinkage correlates to the attenuation increment of the GI POF through the aging at 70 °C. On the other hand, change of the attenuation spectrum of the GI POF before and after aging at 70 °C was measured. The results are shown in Fig. 7 (top). It should be noted that the increment of the attenuation is almost independent of the wavelength. Three reasons of such a wavelength independent attenuation increment should be considered: excess scattering loss by large heterogeneous structures, imperfection of the waveguide structure, and bending loss. We previously confirmed and reported that no scattering loss increment was observed from the PMMA homopolymer and from the PMMA doped with all kinds of dopant used in this paper through the aging even at 85 °C for 70 days [6]. Therefore, this result suggests that no large size heterogeneous structure was formed

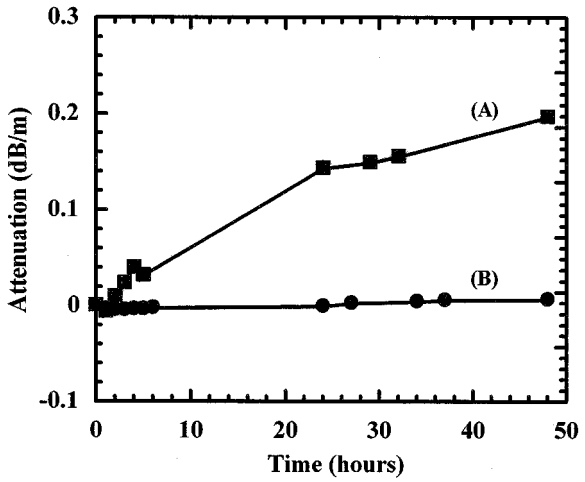


Fig. 8. NA dependence of high temperature stability in the attenuation through the aging at 70 °C: (A) NA of fiber = 0.12, drawing tension = 85 gf (11 wt.% TCP-doped GI POF) and (B) NA of fiber = 0.24, drawing tension = 275 gf (20 wt.% DPS-doped GI POF).

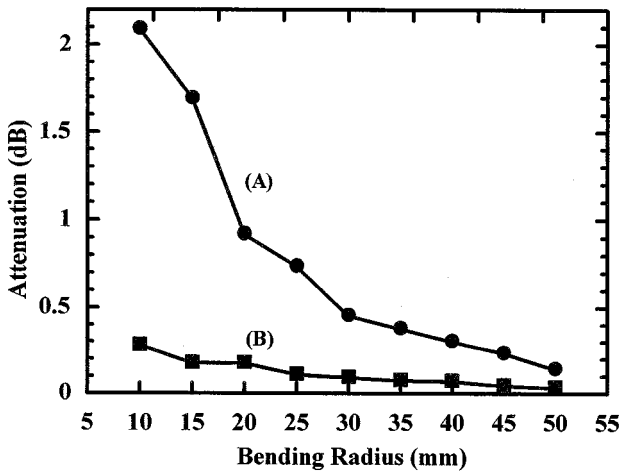


Fig. 9. Relation between attenuation increment and bending radius of GI POF: (A) NA of fiber = 0.12 (11 wt.% TCP-doped GI POF) and (B) NA of fiber = 0.24 (20 wt.% DPS-doped GI POF) bending angle: 90 °.

in the GI POF through the aging. On the other hand, when the GI POF was statically bent, the attenuation increment was observed as shown in Fig. 7 (bottom). Similar wavelength independent attenuation increment shown in Fig. 7 (top) is observed. If the attenuation increase is caused by the random bending originated in the fiber shrinking process, the NA of the GI POF can significantly influence the high temperature stability in the attenuation of the GI POF. Therefore, the fiber NA dependence of the high temperature stability in the attenuation of the GI POF was investigated.

C. Numerical Aperture Dependence of Temperature Stability in the Attenuation of the GI POF

As described in Section III-B, we confirmed that the attenuation increment of the GI POF under high temperature atmosphere could be eliminated by decreasing the length shrinkage of the GI POF. However, Fig. 8 indicates that decreasing the drawing tension to eliminate the length shrinkage is not a necessarily the best solution of temperature stability problem in the attenuation of the GI POF. The sample shown by curve A was drawn by 85-gf tension, and the sample shown by curve B was drawn by 275-gf tension. Fig. 8 shows the high temperature stability in the attenuation of the GI POFs having different NA through the aging at 70 °C. As in the case of 11 wt.% tricresyl phosphate (TCP)-doped GI POF, attenuation increment is observed although the length shrinkage is sufficiently small because the fiber was drawn with low tension. Furthermore, since only 11 wt.% of TCP was doped in the GI POF (A), high Tg as 90 °C is maintained at the core region. Fiber (A) satisfies two important factors: high Tg and small length shrinkage. However, NA is as low as 0.12 because the refractive index of TCP (1.557) is lowest in all the dopant molecules listed in Table I and the feed concentration of TCP should be low in order to decrease the length shrinkage of the fiber through the aging.

On the other hand, it is noteworthy that no attenuation increment is observed in the 20 wt.% DPS-doped GI POF in spite of large shrinkage. One should note that the NA of DPS-doped

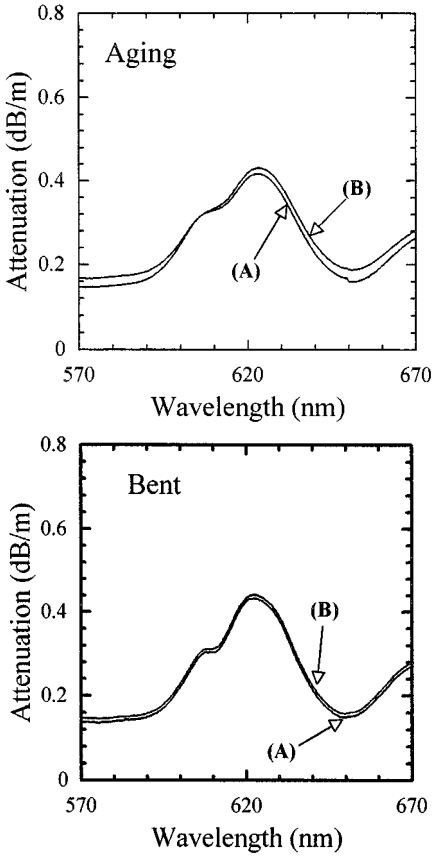


Fig. 10. Attenuation spectrum of 20 wt.% DPS-doped GI POF. Top: Through the aging at 70 °C: (A) before aging and (B) After 48 hours of aging. Bottom: When the fiber is bent: (A) original and (B) bending radius = 25 mm, bending angle = 90 ° × 1time.

fiber is twice as large as that of 11 wt.% TCP-doped GI POF. Since DPS has much higher refractive index than other dopant molecules listed in this paper, high NA GI POF can be easily obtained. Therefore, it was clarified that high NA is effective to maintain the low attenuation of the GI POF at high temperature. It is obvious that the fiber NA also affects the bending loss

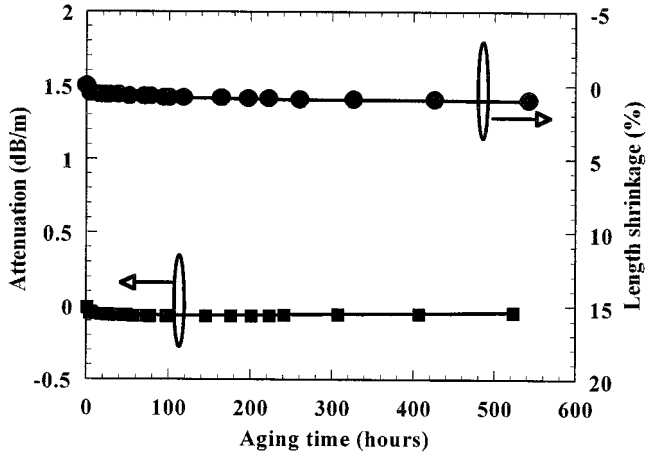


Fig. 11. High temperature stability and length shrinkage of 20 wt.% DPSO-doped GI POF through the aging at 70 °C.

of the fiber [7]. Therefore, it can be suggested that the irregular bending that is caused through the shrinking process of the fiber mainly induces the attenuation increment observed in the GI POF at 70 °C. The relation between the bending loss of the GI POFs and their NAs is shown in Fig. 9 Bending angle was 90 °. Bending loss of the GI POF dramatically decreases with increasing fiber NA because guided mode is effectively confined in the GI POF Fig. 10 (top) shows the attenuation change of high NA (0.25) GI POF before and after 48 hours aging at 70 °C. In the case of high NA GI POF, little attenuation increment is observed through the aging at 70 °C. Furthermore, when the high NA GI POF is statically bent, little attenuation increment is also observed as shown in Fig. 10 (bottom).

Therefore, from Figs. 6–10, it was experimentally concluded that the attenuation increment of the GI POF under high temperature was mainly caused by random kink, which was made in the fiber shrinking process. As described in Section III-B, optimizing the drawing tension and increasing the fiber NA enable to obtain the high temperature resistant GI POF in the attenuation. In order to obtain the high NA GI POF (small length shrinkage at high temperature), the suitable dopant having high refractive index and low plasticization should be selected.

Finally, the result of high temperature stability test in the attenuation of the GI POF is shown in Fig. 11. The dopant used was DPSO and the drawing tension of the GI POF was 80 gf. We have successfully obtained the GI POF in which no attenuation increment was observed after more than 500 hours of aging at 70 °C. As DPSO has much higher refractive index and has bulky substituents, it has a great advantage in obtaining the GI POF with high temperature stability.

IV. Conclusion

High temperature stability in the attenuation of PMMA base GI POF was investigated. It was confirmed that the drawing tension and NA of the GI POF are important factors because the attenuation increment at high temperature is mainly induced by the random kink of the fiber which is caused by the orientation relaxation of polymer chain. Although decreasing the drawing tension of the GI POF reduces the length shrinkage of the fiber, good mechanical properties of the GI POF should be maintained by controlling the drawing tension. It was experimentally verified that the GI POF fabricated under the optimum conditions [high NA (>0.25) and optimum drawing tension (around 100 gf)] represented sufficiently high stability through the aging at 70 °C for 500 h.

References

[1] T. Ishigure, E. Nihei, and Y. Koike, "Graded-index polymer optical fiber for high speed data communication," *Appl. Opt.*, vol. 33, no. 19, pp. 4261–4266, 1994.

[2] Y. Koike, T. Ishigure, and E. Nihei, "High-bandwidth graded index polymer optical fiber," *J. Lightwave Technol.*, vol. 37, no. 7, pp. 1475–1489, 1995.

[3] T. Ishigure, M. Sato, E. Nihei, and Y. Koike, "Graded-index polymer optical fiber with high thermal stability," *Jpn. Appl. Phys.*, vol. 37, pp. 3986–3991, 1998.

[4] J. Stepek and H. Daoust, *Additive for Plastics*. Berlin: Springer-Verlag, 1975, ch. 1.

[5] M. Sato, T. Ishigure, E. Nihei, and Y. Koike, "Thermal and humidity resistant GI POF," in *Proc. 7th Int. Plastic Optical Fibers Conf.*, 1998, pp. 108–109.

[6] N. Tanio, H. Kato, Y. Koike, H. E. Bair, S. Matuoka, and L. L. Blyler Jr., "Physical aging and light scattering of low-loss poly(methyl methacrylate) glass," *Polym. J.*, vol. 30, no. 1, pp. 56–59, 1998.

[7] D. Kalymnios, I. W. Rogers, and S. Thushyanthan, "Bend losses in plastic optical fibers," in *Proc. POF Conf.*, 1997, pp. 35–36.

Masataka Sato was born in Akita, Japan, on November 30, 1973. He received the B.S. degree in applied chemistry, and the M.S. degree in material science from Keio University, Yokohama, Japan, in 1996, 1998, respectively. He is currently working towards the Ph.D. degree at Keio University, Japan.

His current research interest is in optical and temperature properties of photonics polymer.

Miki Hirai was born in Saitama, Japan, on April 30, 1976. She received the B.S. degree in applied chemistry from Keio University, Yokohama, Japan, in 1999. She is currently working towards the M.S. degree at Keio University, Japan.

Her current research interest is in mechanical properties of the graded-index polymer optical fiber.

Takaaki Ishigure was born in Gifu, Japan, on July 30, 1968. He received the B.S. degree in applied chemistry, and the M.S. and Ph.D. degrees in material science from Keio University, Yokohama, Japan, in 1991, 1993, and 1996, respectively.

He is currently with Keio University, Japan, as an Instructor. His current research interest is in fabrication and system application of the graded-index polymer optical fiber.

Yasuhiro Koike was born in Nagano, Japan, on April 7, 1954. He received the B.S., M.S., and Ph.D. degrees in applied chemistry from Keio University, Yokohama, Japan, in 1977, 1979, and 1982, respectively.

He has been a Professor of Keio University and developed the high-bandwidth GI polymer optical fiber. He has been concurrently the leader of "Plastic Optical Fiber" project of Telecommunications Advancement Organization (TAO) of JAPAN, and "photonics Polymer" Project of ERATO of Japan since 1998 and 2000, respectively. He stayed as a Visiting rResearcher at AT&T Bell Laboratories from 1989 through 1990.

Dr. Koike received the International Engineering and Technology Award of the Society of Plastics Engineers in 1994.