High-bandwidth, graded-index polymer optical fiber for near-infrared use

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We describe graded-index polymer optical fibers with high bandwidth (5.12 GHz for 100-m transmission) and low loss in the near-infrared region (56 and 115 dB/km at wavelengths of 688 and 773 nm, respectively) that we successfully obtained with a new interfacial-gel polymerization technique using an all-deuterated methyl methacrylate monomer and a partially fluorinated acrylate monomer. The necessity for both low attenuation and high bandwidth for a polymer optical fiber is described for its use as a physical media in a high-speed multimedia network. © 1996 Optical Society of America

Key words: Graded index, polymer optical fiber, high bandwidth, low absorption loss.

1. Introduction

Growing demands for information processing and transmission have led to an increased use of optical fibers for high-speed communication. In a long-haul transmission system, a single-mode glass optical fiber is the most suitable medium because of its high bandwidth and transparency. On the other hand, a polymer optical fiber (POF) can offer several advantages compared with glass optical fibers such as a large core with good flexibility, easy processing and handling, and low cost. Interests also focused on short-range high-speed communication within the home, and building has grown in recent years because of multimedia networks. High bandwidth and low attenuation are required characteristics for the POF to be applied in short-range communication systems. All commercially available POF's have been of the step-index (SI) type with a bandwidth of only 50 MHz achieved in 100-m transmissions as a result of large modal dispersion.¹ To solve this modal dispersion problem, we proposed a high-bandwidth graded-index (GI) POF.^{2,3} The bandwidth of the GI POF was 5-20 GHz with a 100-m fiber that was more than 100 times larger than that of a conventional, commercially available SI POF.

Attenuation of the POF is approximately 100 dB/km in the visible region and, at 1.3 or 1.55 μm , which are the wavelength standards used in glass optical fiber systems, attenuation of the POF becomes higher than 100,000 dB/km. Such attenuation is induced by the intrinsic overtone absorption of a carbon-hydrogen bond. It has been reported that one can eliminate this absorption loss by substituting the hydrogen atoms in the polymer molecule for heavier atoms.^{4,5} If the absorption loss decreases with the substitution of hydrogen for deuterium or halogen atoms, the possible distance for signal transmission is limited by dispersion in the case of a SI POF link. High bandwidth is necessary for such low-loss POF. We describe a low-loss, highbandwidth POF for use in the visible and nearinfrared regions, which represents our initial success in this area. The fabrication process and its optical properties are explained.

2. Preparation of the Graded-Index Fiber

The GI POF was obtained by heat-drawing the GI preform with a diameter of 10 mm. The preform rod in which the refractive index gradually decreases from the center axis to the periphery was prepared by the interfacial-gel polymerization technique. We have previously described the high-bandwidth GI POF prepared with poly(methyl methacrylate) (PMMA) as the matrix polymer.^{2,3} As the attenuation of the PMMA-based GI POF in the near-infrared to infrared region is dominated by the intrinsic absorption of the carbon-hydrogen stretching vibration mentioned above, perdeuterated MMA (MMA-d8), in

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Fig. 1. Comparison of the refractive-index profile between PMMA-based and PMMA-d8-based GI preforms: (A) MMA-d8-BB-d5 system, (B) MMA-BB system.

which all the hydrogen atoms in the MMA are substituted for deuterium atoms, and a partially fluorinated acrylate monomer (hexafluoroisopropyl 2-fluoroacrylate: HFIP 2-FA) were used.

Both MMA-d8-based and partially fluorinated acrylate-based GI preforms were prepared by the interfacial-gel polymerization technique we described elsewhere.^{2,3}

A. Perdeuterated Methyl Methacrylate

The polymer tube, filled with a mixture of purified MMA-d8 and perdeuterated bromobenzene (BB-d5) with a specified amount of initiator and chain transfer agent, was heated to 95 °C. After 20 h of polymerization, the preform was heat-treated at 110 °C for 24 h to complete the polymerization. The refractive-index distribution was formed by heterogeneous polymerization from the inner wall of the polymer tube based on the interfacial-gel polymerization technique.²

The GI POF was obtained by heat-drawing the preform to 180-200 °C. By controlling the velocity of fiber take-up, it was possible to obtain a GI POF with the desired diameter, which in our case was 0.5 mm.

B. Fluorinated Acrylate

When one polymerizes a fluorinated acrylate (HFIP 2-FA) polymer in an oxygen atmosphere it tends to have a yellow color, which can be prevented when polymerization is performed under vacuum. The fabrication process was almost the same as that for a MMA-d8-based GI preform mentioned above. Dibutyl phthalate (DBP) was used as the dopant to form the radial index profile.

3. Results and Discussion

A. Refractive-Index Distribution of the Graded-Index Preform and Fiber

The refractive-index distributions of the preform and fiber were measured by the longitudinal and transverse interferometric technique, respectively. Figure 1 is a comparison of the refractive-index profile between the MMA–BB system and MMA-d8–



Fig. 2. Refractive-index distribution of a poly-HFIP 2-FA-based GI POF.

BB-d5 system preforms, where n_0 , and n are the refractive indices at the center axis, at a distance r from the center axis, respectively, and Rp denotes the diameter of the preform. The PMMA-d8-based preform has an almost quadratic refractive-index profile that is nearly the same as that formed from its hydrogenated counterpart. The index profile is maintained through the heat-drawing process. Figure 2 shows the refractive-index distribution of the HFIP 2-FA-based GI POF. It is noteworthy that, even in the case of a partially fluorinated polymer, the interfacial-gel polymerization technique can be successfully adopted to form the index gradient in the preform.

B. Attenuation of Light Transmission

The total attenuation spectrum of light transmission through the GI POF was measured by using a spectrum analyzer (ADVANTEST Co. Model TQ8345). We used a white-light source and adopted the cutback method. The results for the MMA-d8-based and HFIP 2-FA-based GI POF's are shown in Fig. 3 compared with the attenuation spectrum of the PMMA-based GI POF previously reported.² The minimum attenuations of the MMA-d8-based and HFIP 2-FA-based GI POF are 56 dB/km at 688-nm wavelength and 115 dB/km at 773-nm wavelength, respectively. Details are summarized in Table 1. It should be noted that the several peaks caused by the overtone of the carbon-hydrogen stretching vibration absorption in the MMA-based GI POF were



Fig. 3. Comparison of the total attenuation spectra of (A) PMMAbased, (B) poly-HFIP 2-FA-based, (C) PMMA-d8 based GI POF's.

Table 1. Comparison of Light Transmission Attenuation-POF's

	Attenuation (dB/km)		
Wavelength (nm)	MMA– BB	MMA-d8– BB-d5	HFIP 2-FA–DBP
570	90	128	_
650	107.5	65	286.7
780	785	94	158
850	2982.5	192	493.3
Minimum at	90	56	115
Wavelength	570 nm	688 nm	773 nm

eliminated in the MMA-d8-based GI POF at wavelengths longer than 600 nm. The absorption peak around 730-nm wavelength with an attenuation of 3000 dB/km in the MMA-based GI POF decreased to a small peak around 750 nm in the spectrum of MMA-d8-based GI POF. This absorption is considered to be caused by the seventh harmonic generation of the carbon-deuterium stretching vibration and by the fourth harmonic generation of the oxygenhydrogen vibration, which belongs to water molecules that are slightly absorbed into the polymer. The attenuation of MMA-d8-based GI POF at 780-nm wavelength decreased to 94 dB/km, which was approximately one eighth of the attenuation of the PMMA-based POF (approximately 800–900 dB/km). On the other hand, in the case of HFIP 2-FA-based GI POF, the absorption peak that is due to the fifth harmonic generation of the carbon-hydrogen bonding still exists because three carbon-hydrogen bonds remain in the monomer unit.

We made a quantitative estimation of the vibrational absorption loss by using the Morse Potential theory described as follows.⁴ The energy level G(v)that belongs to the vibrational absorption between two atoms can be written as

$$G(v) = v_0(v + 1/2) - v_0\chi(v + 1/2)^2, \tag{1}$$

where v = 1, 2, 3... is the quantum number, χ is the anharmonicity constant, and ν_0 is the original vibration between only two atoms ($\chi = 0$). The position of the fundamental vibration in a real polymer ν_1 or an overtone ν_v (v = 2, 3, 4, ...) is now given by

$$\nu_v = G(v) - G(0) = \nu_v - \chi \nu_0 \nu(v+1).$$
(2)

Therefore,

$$v_v = [v_1 v - \chi v_1 v (v+1)]/(1-2\chi).$$
(3)

From infrared spectroscopic data, one can find ν_1 and ν_2 for all vibrations such as C–H, C–D, and C–F from which the χ value can be calculated. The position of all higher overtones can be calculated by Eq. (3). Furthermore, any overtone band strength (absorption energy) can be calculated if we know the anharmonicity constant χ and the fundamental band strength $E(\nu_1)$.

These calculations for C–H, C–D, and C–F vibrations have already been performed by Groh.⁴ From the absorption band strength estimation, the absorption loss in the polymer that is due to the overtone intensity was approximated by

$$D_{\max}(\nu_{v}^{C-X}) = 3.2 \times 10^{8} \left(\frac{\rho}{M_{G}}\right) N_{c} \left(\frac{E_{v}}{E_{1}^{C-H}}\right)_{C-X},$$
 (4)

where $D_{\text{max}}(v_v^{\text{C-X}})$ is the attenuation in decibels per kilometer of the *v*th overtone of the C–X bond, ρ is the density of absorbing species in grams per cubic centimeter, M_G is the molecular weight of a repeating unit in grams per mole, N_c is the number of the bonds of interest in the repeating unit, and the ratio $(E_v/E_1^{\text{C-H}})$ is the normalized overtone intensity of the C–X bond dominated by the C–H fundamental. The estimated results are shown in Fig. 4.

For C–H, C–D, and C–F vibrations, χ is 1.9 × 10⁻², 1.5×10^{-2} , and 4.0×10^{-3} , respectively. From the literature,⁴ the fundamental vibrations ν_1 of C–H, C–D, and C–F bonds in polymers exist at $v_1 = 2950$, 2230, and 1250 cm^{-1} , respectively. Deuterium and halogen atoms can be considered as promising alternatives for shifting the wavelength of the fundamental vibration to a wavelength longer than that of the carbon-hydrogen bond. In the Morse Potential calculation for the C-H bond in PMMA, the sixth harmonic vibration appears at 627-nm wavelength, which corresponds to an absorption loss of 427 dB/km. On the other hand, the eighth harmonic absorption loss of the C–D bond at the same wavelength (626 nm) for deuterated PMMA is approximately 0.82 dB/km, which is approximately 520 times smaller than that of the sixth harmonic C-H absorption. However, when the wavelength is longer than 1000 nm, the absorption loss for the C-D bond becomes serious. For example, the calculated loss that is due to the fourth harmonic vibration of a C-D bond at 1174-nm wavelength is as large as 3670 dB/km. It has also been recognized that⁵ all-deuterated PMMA-



Fig. 4. Spectral overtone positions versus absorption loss of different C-X vibrations in conventional acrylate polymers: \bullet , carbon-hydrogen bond; \blacksquare , carbon-deuterium bond; \blacktriangle , carbon-fluorine bond.

based POF had the absorption peak of an O–H bond because of absorption of water in the polymer.

On the other hand, it is well known that a fluoropolymer has low water absorption. Furthermore, the wavelength of the fundamental vibration of a C–F bond is longer than that of a C–D bond, the absorption loss at 1171-nm wavelength that is due to the seventh harmonic C–F vibration for an imaginary fluorinated PMMA is still as low as 0.12 dB/km. The fluoropolymer is one of the suitable materials for fabrication of low-loss polymer optical fiber in the near-IR and IR regions.

Since the absorption strength should be proportional to the concentration of the C–H bond per unit volume, the absorption loss through the HFIP 2-FA-based GI POF can also be estimated by that of the PMMA-based POF. The concentration of C–H bonds in the HFIP 2-FA polymer is 2.12×10^{-2} mol/cm³, which is approximately one fourth of the value in PMMA (9.52 $\times 10^{-2}$ mol/cm³). The calculated absorption loss at 735 nm for the HFIP 2-FA-based GI POF was 618 dB/km. This is slightly less than that of the measured value (813 dB/km) in Fig. 2, because the C–H bond belonging to the dopant is not considered to be in the core of the GI POF.

C. Bandwidth

The bandwidth measurement of the GI and SI POF's was performed by determining the impulse response function of the fiber. The experimental setup of the impulse response function measurement system is shown in Fig. 5. A pulse of 10 MHz from an In-GaAlP laser diode (660-nm wavelength) was injected (0.3 NA) into the POF. The output pulse was detected by a sampling head (Model OOS-01, Hamamatsu Photonics Co.). The transfer function of the fiber was calculated by a fast Fourier transform of the input and output pulses. The pulse broadenings of the MMA-d8-based and HFIP 2-FA-based GI POF are shown in Figs. 6 and 7, respectively, compared with that of a SI POF with the same fiber length. It has been already shown that the output pulse of MMA-based GI POF has little distortion compared with the SI POF.² In the case of MMA-d8based and HFIP 2-FA-based GI POF's, little pulse broadening was observed. The bandwidth of the SI POF estimated at the 3-dB level in the transfer function is 5 MHz km, whereas the bandwidth of the MMA-d8-based GI POF in Fig. 5 was 512 MHz km and that of HFIP 2-FA-based GI POF was 600 MHz km, which are approximately 100 times larger than that of the SI POF.

It is well known that the bandwidth can be maximized by optimizing the shape of the GI distribution of the fiber core. The index distribution is expressed by a power law of the form

$$n(r) = n_0 [1 - (r/R_p)^g \Delta], \tag{5}$$

where Δ is a parameter that can be used to measure the relative refractive-index difference, $\Delta = (n_0 - n_c)/n_0$, n_0 and n_c are the refractive-index values at



Fig. 5. Schematic representation of the impulse response function measurement.

the core center and in the fiber cladding, respectively, Rp is the radius of the core, and parameter g is the exponent of the power law.

Olshansky and Keck derived⁶ the optimum index profile as a function of g, which is expressed as follows:

$$g_{\text{opt}} = 2 + \varepsilon - \Delta \frac{(4 + \varepsilon)(3 + \varepsilon)}{5 + 2\varepsilon}.$$
 (6)

Here ε is the parameter of material dispersion. Therefore, without material dispersion, we have simply

$$g_{\rm opt} = 2 + \frac{12}{5}\Delta. \tag{7}$$

Since $\Delta = 0.01-0.03$ for the GI POF fabricated by the interfacial-gel polymerization technique, the maximum bandwidth is achieved when *g* is approximately 2.

By using the MMA-d8 and the partially fluorinated acrylate polymer (HFIP 2-FA), the optical window shifts to a longer wavelength than that (650-nm wavelength) of the MMA-based GI POF. Therefore, the bandwidth should be maximized at the wavelength at which the lowest attenuation of each fiber can be obtained.

Low absorption loss is one of the advantages of the fluorinated polymer for POF as mentioned above. Furthermore, the low material dispersion is considered to be another of its advantages. The material dispersion caused by the refractive-index dependence on the wavelengths was estimated by measuring the refractive indices of the PMMA and poly-HFIP 2-FA at several wavelengths. The material dispersion



Fig. 6. Pulse broadening through PMMA-d8based GI and PMMA-based SI POF's. Fiber length is 38 m.

can be shown as

$$D_{\rm mat} = -\frac{\lambda}{c} \frac{d^2 n}{d\lambda^2}, \qquad (8)$$

where *c* and λ denote the velocity of light in vacuum and wavelength, respectively. Figure 8 shows the calculated material dispersion of the PMMA and poly-HFIP 2-FA. The refractive-index dependence on the wavelength was approximated by the Sellmeier equation.⁷ It should be noted that, even at a wavelength of 650 nm, the material dispersion $D_{\rm mat}$ of poly-HFIP 2-FA is 0.136 (ns/nm km), which was less than half of that of PMMA [0.305 (ns/nm km)]. The calculated material dispersion of the PMMA is almost the same as that in Ref. 8, [0.39 (ns/nm km)]. Because the material dispersion decreases as the wavelength becomes longer, the use of the near-IR region for communication is advantageous for POF's. The calculated material dispersion of the poly-HFIP 2-FA at a wavelength of 780 nm is 0.078 (ns/nm km).



500ps/div.

Fig. 7. Pulse broadening through poly-HFIP 2-FA-based GI and PMMA-based SI POF's. Fiber length is 24 m.

4. Conclusion

High-bandwidth (greater than 500 MHz km) with low attenuation in the near-infrared region has been successfully fabricated with the interfacial-gel polymerization technique with perdeuterated MMA and partially fluorinated acrylate (HFIP 2-FA) monomers. The attenuations of MMA-d8-based and HFIP 2-FA-based GI POF's are 56 dB/km at 688 nm and 115 dB/km at 773-nm wavelength. At a wavelength of 780 nm, which is the emission peak wavelength of a conventional inexpensive compact disc laser diode, the attenuations are 94 and 150 dB/km, respectively, which is approximately one eighth of the attenuation of a PMMA-based GI POF at the same wavelength. Substitution of the hydrogen atoms for deuterium or fluorine dramatically decreases the absorption loss of the POF. However, the absorption of water in the POF continues to be a problem because of the overtone absorption of the oxygen hydrogen bond in the water molecule in the near-infrared region. It was theoretically and experimentally confirmed that the fluorinated polymer is a suitable candidate for low-loss POF's.



Fig. 8. Material dispersion of (A) PMMA and (B) poly-HFIP 2-FA.

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