Polymer Optical Fiber for Near Infrared Use

YOSHITAKA TAKEZAWA and SHUICHI OHARA

Hitachi Research Laboratory, Hitachi, Ltd., 4026 Kuji-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan

SYNOPSIS

Using the empirical simulation that we developed to estimate loss spectra of amorphous polymers, we predicted the intrinsic loss spectrum of fluorine-containing polyarylate (FPAr) that should have a small attenuation loss in the near infrared region. Loss of FPAr is smaller than that of poly(methyl methacrylate), which is a typical optical polymer used as a core material in polymer optical fiber (POF), above 720 nm. FPAr was synthesized by phase transfer catalyzed polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane with isophthaloyl dichloride. Its glass-transition temperature (T_g) by DSC is 163°C. This indicates that FPAr has higher heat resistance than polycarbonate (PC) by about 10°C. A film of 100 μm thick has over 85% transmittance from 330 to 900 nm. Values from a tension test are similar to those of PC. As a result, FPAr is expected to be a good core polymer for POF, because of its high T_g, good transparency, and good flexibility. Next, the POF made of FPAr was fabricated by a melt-flow spinning method. It had larger attenuation loss than predicted. The difference from the simulation was extrinsic loss caused by the fabricating process. Therefore, when a more suitable fabricating process is developed, loss of FPAr-POF can be decreased, so that it will be applicable to optical communications in the near infrared region. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recently, there has been considerable interest in the development of polymer optical fiber (POF) such as graded-index type POF or single-mode type POF.[1] Most of the commercialized POF is step-index and multi-mode type, because of easier fabrication. Commercialized POF uses poly(methyl methacrylate) (PMMA) as its core generally, and bisphenol-A type polycarbonate (PC) is used for heat resistant applications.[2,3] These polymers have good transparency in the visible region and have an optical window near 660 nm, that is a low loss region. Thus POFs are used for optical communication with a red LED (typical wavelength = 660 nm) in the visible region and for many kinds of optical sensors.[4] It is, however, necessary for polymers to have transparency in the near infrared region, because silica optical fiber, which is typically employed for long distance optical communication, is used at longer wavelengths than for POF optical communication and there are a lot of superior laser diodes in the region above 780 nm.[5,6] There are a few reports on POFs for near infrared

optical communication.[5–8] The core polymers of these POFs are made of fluorinated or deuterated PMMA derivatives. These polymers have good transparency in this region, but their values of glass-transition temperature (T_g) are low. Therefore, we have studied a new transparent polymer that has heat resistance.

First, we developed the POF that had crosslinked fluoroalkyl methacrylate copolymer as its core.[8] After heating at 160°C in air for 1000 h, its attenuation loss increased less than 1 dB/m over the 780 nm wavelength region. Initially, attenuation loss of the POF at 780 nm is about 0.7 dB/m, and it is small enough to allow applications in short-distance optical local area networks (LANs) in automobiles, etc. However, the initial loss at 850 nm is about 2 dB/m, so large that it must be decreased for LAN applications.

In this paper, using the empirical simulation that we developed to estimate loss spectra of amorphous polymers,[9] we predicted the intrinsic loss spectrum of a new heat resistant fluorine-containing polyarylate (FPAr) from the chemical structures of the polymer repeating unit. Next, we synthesized the FPAr that has good transparency in the near infrared region and fabricated the POF made of FPAr.

EXPERIMENTAL

Polymerization of Fluorine-Containing Polyarylate

Figure 1 shows a scheme for phase transfer catalyzed polycondensation of fluorine-containing polyarylate (FPAr).[10] First, 0.05 mol of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (BPAF) was dissolved into 300 mL of 1 N NaOH aqueous solution, and 0.001 mol of tetra-n-butyl ammonium chloride (TBAC) as a phase transfer catalyst was added to this solution. Next, 0.05 mol of isophthaloyl dichloride (IPDC) was dissolved into 300 mL of dichloromethane. These two phases were stirred vigorously at room temperature for about 2 h. Then the water phase was removed. In the organic phase, the small amount of residual NaOH was removed by washing with pure water until the pH reached neutrality. After that, dichloromethane was vaporized by heating, and finally FPAr was obtained. The FPAr was dissolved into dichloromethane to eliminate impurities, and the solution was filtered through a Tefron membrane filter (pore size: 1.0 μm). By addition of a large amount of methanol to the filtrate, the FPAr was reprecipitated and dried under reduced pressure. Elemental analysis calc. for $C_{23}H_{12}O_4F_6$: C 59.2%, H 2.6%, O 13.7%, F 24.5%. Found: C 59.7%, H 2.9%, F 23.7%, Na 0.1%, Cl 0.3%.

Estimation of Intrinsic Loss Spectra of Amorphous Polymers

Figure 2 shows a flow diagram of the empirical simulation that we developed to estimate loss spectra of
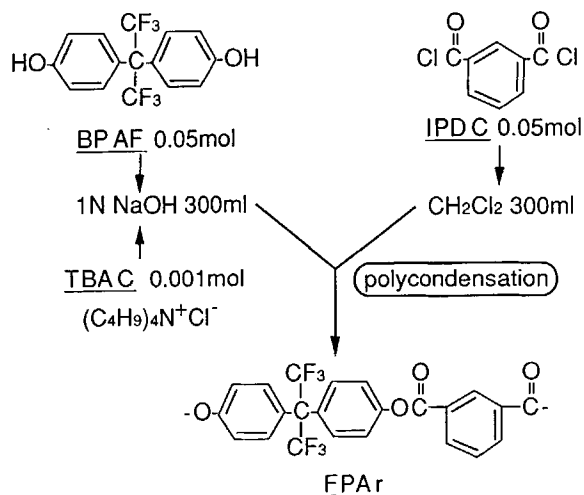

Figure 1 Scheme of phase transfer catalyzed polycondensation of FPAr.
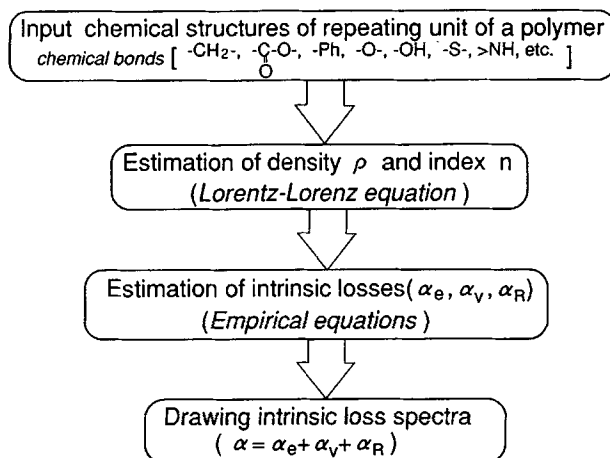

Figure 2 Flow diagram of the simulation to estimate the intrinsic loss spectra of amorphous polymers from the chemical structures of polymer repeating units.

amorphous polymers.[9] First, chemical structures of a polymer repeating unit are input into a computer from the keyboard. They include CH_2—, —$C(=O)O$—, —Ph—, —O—, —OH, —S—, > NH, etc. Then polymer density (ρ) and polymer index (n) are calculated using the Lorentz–Lorenz equation as shown below.[11]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi N\alpha' = \frac{[R]}{V} \equiv \phi \qquad (1)$$

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

Here, N is the number of molecules in a unit volume of a polymer, α' is polarization, $[R]$ is molar refraction (generally, the summation of atomic refraction), and V is molar volume. Applying reference values regarding atomic refractions of each atoms in a polymer repeating unit to eqs. (1) and (2), we can calculate refractive index of a polymer. Next, three intrinsic losses (α_e, α_v, α_R) at arbitrary wavelength are estimated from empirical equations.[9,12,13] Here, α_e, α_v, and α_R mean the electronic transition absorption loss, the absorption loss due to harmonics of the molecular vibration, and the Rayleigh scattering loss, respectively. Finally, the computer draws the loss spectrum using a plotter.

Empirical equations to estimate the three intrinsic losses are shown below.[9,12,13]

Electronic Transition Absorption Loss: α_e

$$\alpha_e = \exp\left(\frac{3.84 \times 10^3}{\lambda} - 3.19\right) \cdot \frac{\rho}{M}$$

$$\times (n_{CC} + n_{CO} + 3 \cdot n_{CS}) \qquad (3)$$

where α_e (dB/m) is the electronic transition absorption loss, λ (nm) is wavelength, ρ (g/cm^3) is polymer density, M (g/mol) is molecular weight of a polymer repeating unit, n_{CC}, n_{CO}, and n_{CS} mean the number of total benzene rings in a polymer repeating unit, the number of benzene rings neighboring a carbonyl group, and the number of benzene rings neighboring a sulphur atom, respectively.

Absorption Loss Caused by Harmonics of Molecular Vibration: α_V

$$\alpha_V(v) = 3.2 \times 10^5 \cdot n_{XH} \cdot \frac{\rho}{M}$$

$$\times \frac{v! v(K - 2v - 1)}{(K - 3) \cdot (K - 3) \cdots (K - v - 1)} \cdot r \quad (4)$$

$$\nu_V = \frac{\nu_1 v - \nu_1 X v(v + 1)}{1 - 2X} \quad (5)$$

where $\alpha_V(v)$ (dB/m) is the v-th harmonic peak absorption loss due to X — H (X — H = C — H, N — H, O — H) bonds, ν_V (cm^{-1}) is frequency of the v-th harmonic, n_{XH} means the number of X — H bonds in a polymer repeating unit, X is an anharmonicity constant, K is the reciprocal of X, ν_1 (cm^{-1}) is the fundamental frequency, v is the order of the harmonics, and $r = E_1^{XH}/E_1^{CH}$, E_1^{XH} is the absorption strength caused by the fundamental frequency of the X — H bond. Average values from experimental data in a lot of the model compounds are used as values of r and X of each X — H bond[12]; for a C — H bond, $r = 1$ and $X = 1.90 \times 10^{-2}$; for an N — H bond, $r = 0.91$ and $X = 2.10 \times 10^{-2}$; and for a O — H bond, $r = 2.3$ and $X = 1.84 \times 10^{-2}$. The band tail between two peaks is estimated using Gaussian approximation and the value of absorption loss due to combination tone, $\nu_V + \delta$, is estimated as 0.085 times the loss of the same order ν_V.

Rayleigh Scattering Loss: α_R

$$\alpha_R = \frac{1.0 \times 10^8}{\lambda^4} (n^2 - 1)^2 (n^2 + 2)^2$$

$$+ \frac{8.5 \times 10^9}{\lambda^4} (n^2 + 2)^2 \frac{\rho}{M} (5n_{CC}^2 + 0.3) \quad (6)$$

where α_R (dB/m) is the Rayleigh scattering loss, and n is the refractive index of the polymer.

Measurement of Attenuation Loss of POFs

The POF attenuation loss spectrum was measured by a cut-back method[5] using a halogen tungsten lamp and a grating monochrometer. One end of the POF was attached to an optical source, while the other end was attached to a detector for the maximum output power measurements. The output power I_1 of the sample POF with a length of L_1 (m) was measured in the 400–900 nm wavelength region. Then it was cut to the length L_2 (m), and the output power I_2 of the POF with a length of L_2 was measured. The attenuation loss α (dB/m) for the POF was calculated by using

$$\alpha(\text{dB/m}) = 10/(L_1 - L_2)\log(I_2/I_1). \quad (7)$$

RESULTS AND DISCUSSION

Design of Novel Transparent Polymer in the Near Infrared Region

In the near infrared region, there are a lot of superior laser diodes for optical transmission and optical communication systems using glass optical fiber. Therefore, transparent polymers in this region are needed for short-distance optical local area networks (LANs).[5,6] To decrease the optical loss of polymers in the near infrared region, the number of C — H bonds should be reduced in the polymer repeating unit.[5-8] Since the main cause of optical loss of organic polymers in this region is absorption loss due to harmonics of the C — H vibration, an overtone ν_V of the fundamental stretching vibration ν_1 and its combination tone, $\nu_V + \delta$, with a bending vibration δ. To reduce C — H content in the polymer, a fluorinated or deuterated polymer that has transparency in the near infrared region is used as a core polymer.[5-8] However, there are some problems for their polymers such as decreasing reactivity of monomers, increasing cost, and so on. Thus we have studied an effective method to decrease the optical loss of polymers in the near infrared region, and obtained a guide to molecular design that decreases the band tail of the absorption due to harmonics of C — H vibration from 780 to 850 nm when all aliphatic C — H bonds in the polymer repeating unit are exchanged by C — F bonds.[12] A large absorption peak of combination tone, $\nu_4 + \delta$, caused by aliphatic C — H bonds appears around 800 nm. The absorption peak of combination tone caused by aromatic C — H bonds is negligible compared with aliphatic C — H bonds. Based on this guide, we concluded that FPAr might have good transparency in the near infrared region, as well as heat resistance.

Estimation of Intrinsic Loss of FPAr

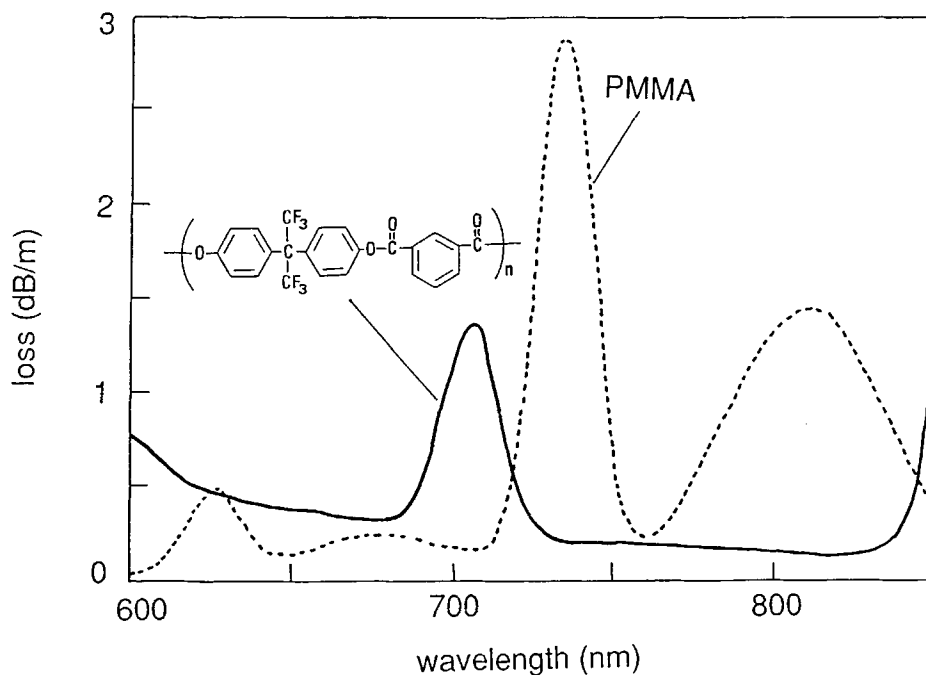The intrinsic loss spectrum of FPAr whose attenuation loss would be small was estimated. First,

Figure 3 Intrinsic loss spectra estimated from the simulation. The solid line is an intrinsic loss spectrum of FPAr, and the broken line is an intrinsic loss spectrum of PMMA.

chemical structures of FPAr were input into the computer, such as O—Ph, C, CF3, CF3, Ph—O, C=O, Ph, C=O. In this polymer repeating unit, there are twelve aromatic C—H bonds and no aliphatic C—H bonds, so n_{CH}(aromatic) = 12 and n_{CH}(aliphatic) = 0. Since there are no other X—H bonds, $n_{NH} = n_{OH}$ = 0. Similarly, there are three benzene rings in the repeating units, n_{CC} = 3, and the number of carbonyl groups neighboring benzene rings equals two, n_{CO} = 2. FPAr has no sulfur atoms, so n_{CS} = 0. Polymer density (ρ) and refractive index (n) were calculated using these parameters. In this case, we obtain ρ = 1.44, and n = 1.54. After these physical parameters were prepared, an intrinsic loss spectrum was drawn. Figure 3 shows the intrinsic loss spectrum of FPAr. The broken line is the intrinsic loss spectrum of PMMA that is a typical optical polymer used as a core material for POF. Loss of FPAr is smaller than that of PMMA above 720 nm, and the bottom of the loss is 0.12 dB/m at 820 nm. Generally speaking, aromatic polymers have large optical loss, but FPAr has good transparency, because it has no aliphatic C—H bonds. This indicates that FPAr would be applicable to the core polymer of a near infrared POF.

Fabrication of FPAr-POF

Table I lists physical properties of polymerized FPAr. Its T_g by DSC is 163°C. This indicates that

FPAr has higher heat resistance than PC by about 10°C. Molecular weight by GPC is $\overline{M_n}$ = 12,600 and $\overline{M_w}$ = 76,500. A film of 100 μm thickness has over 85% transmittance from 330 to 900 nm. The refractive index is about 1.55 with 1.54 being the calculated one. The results of a tension test are similar to those of PC. As a result, FPAr is expected to be a good core polymer for POF, because of its high T_g, good transparency, and good flexibility.

Next, we fabricated a FPAr-fiber by the melt-flow spinning method carried out at about 250°C. Its core diameter was about 1 mm. Figure 4 shows the attenuation loss of the FPAr fiber measured by

Table I Physical Properties of Synthesized Fluorine-Containing Polyarylate (FPAr)

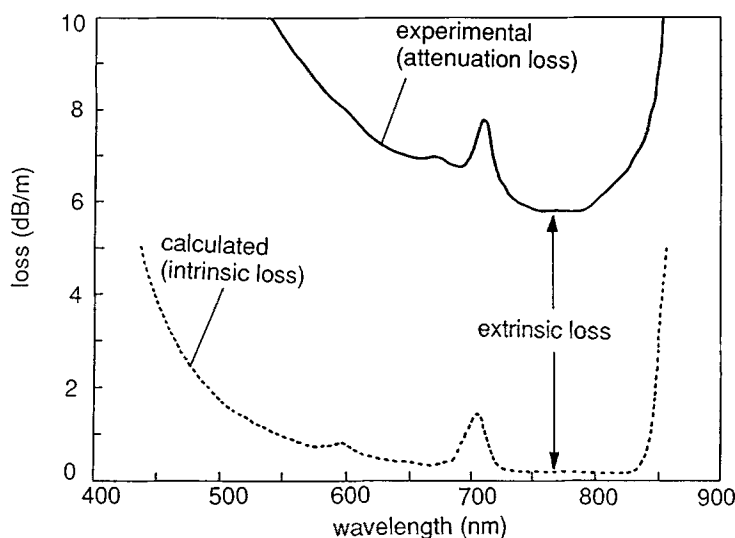|	
Structure	structure
T_g (°C)	163
Molecular Weight	
$\overline{M_n}$	12600
$\overline{M_w}$	76500
Transmittance (%) 330–900 nm; 100 μm film	> 85
Refractive index	1.55
Tensile strength (kg/mm²)	4.3–5.3
Elongation (%)	20–60
Elastic modulus (kg/mm²)	160–200

Figure 4 Loss spectra of POF made of FPAr. The solid line is an attenuation loss spectrum of FPAr-POF (experimental), and the broken line is an intrinsic loss spectrum of FPAr estimated from the simulation.

the cut back method. The broken line shows the estimated intrinsic loss spectrum from the simulation. We considered that the difference between the two spectra was extrinsic loss due to the fabricating process and contaminating dust, etc. After melt-flow spinning, the polymer became yellowish, so the absorbance of FPAr was measured before and after heating. According to the separating method of attenuation loss,[14] the change of color was caused by an increase of electronic transition absorption by a thermal oxidation reaction of the polymer, which caused approximately 55% of the extrinsic loss at 780 nm. Therefore, when a more suitable fabricating process is developed, the low-loss fiber in the near infrared region should be realized.

CONCLUSION

We predicted the intrinsic loss spectrum of FPAr whose attenuation loss would be small in the near infrared region using the simulation. Loss of FPAr is smaller than that of PMMA, which is a typical optical polymer used as a core material of POF, above 720 nm. FPAr was synthesized by phase transfer catalyzed polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane with isophthaloyl dichloride. FPAr is expected to be a good core polymer for POF, because of its high T_g, good transparency, and good flexibility. Next, an FPAr fiber was fabricated by the melt-flow spinning method. It had larger attenuation loss than predicted. The difference from the simulation was extrinsic loss caused by the fabricating process. Therefore, when a more suitable fabricating process is developed, loss of FPAr-POF can be decreased, and the FPAr should be applicable to optical communications in the near infrared region.

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