Plastic Optical Fibers with Fluoroalkyl Methacrylate Copolymer as Their Core

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SYNOPSIS

Novel plastic optical fibers having a core made of a crosslinking copolymer containing mainly fluoroalkyl methacrylate (FMA-POFs) were fabricated and their optical properties were analyzed. In the visible wavelength region, attenuation losses of as-manufactured FMA-POFs were low and their loss spectra were similar to that of the plastic optical fiber whose core was made of methyl methacrylate copolymer (MMA-POF). But after heating at 160°C in air, increases in attenuation losses of FMA-POFs were about 10 times smaller than that of the MMA-POF. FMA-POFs had an optical window at 780 nm. There was hardly any change in loss at 780 nm compared with the loss increase at 660 nm. This indicated that FMA-POFs would be applicable to optical communications at 780 nm in the near-IR region.

INTRODUCTION

Since plastic optical fibers (POFs) were developed by DuPont in 1964, attenuation losses of POFs have been decreasing considerably year after year due to results of investigations carried out by NTT research groups.[1-3] Kaino and co-workers[1] developed a low loss POF having a core made of poly(methyl methacrylate) (PMMA), which has an anattenuation loss of below 0.2 dB/m at 660 nm. This value nearly equals the loss limit of the intrinsic loss of PMMA at this wavelength. Still more, they have indicated that the ultimate loss limit of POFs would be about 0.006 dB/m at 660 nm, based on measurements using a trideutero, hexafluorobutyl pentadeuteromethacrylate polymer as its core.[3] But these POFs only have a thermal resistance temperature of about 80°C. As for heat resistance, POFs whose core consists of bisphenol-A type polycarbonate (PC) have a thermal resistance temperature of 125°C.[4] But an attenuation loss of PC-POF is about 1.2 dB/m at 660 nm which is considerably larger than that of PMMA-POF.

We have been investigating low loss POFs having high heat resistance by using crosslinked copolymer containing mainly methyl methacrylate (MMA) and a cladding made of poly(tetrafluoroethylene-co-hexafluoropropylene), so-called FEP.[5,6] The POFs have higher thermal resistance than PMMA-POFs, but when they are left at high temperature for a long time, their attenuation losses increase from the shorter wavelength region. We reported that the main cause of thermal degradation of our POFs was the increase of electronic transition absorption loss due to conjugated carbonyl double bonds formed by thermal oxidation of the core polymer.[7] In this paper, novel POFs whose core was made of a fluoroalkyl methacrylate copolymer, which could restrain the thermal oxidation reaction of the core and provide good transparency in the visible wavelength region, were fabricated and their optical properties were analyzed.

EXPERIMENTAL

Materials

2,2,2-Trifluoroethyl methacrylate (3FMA), 2,2,3,3-tetrafluoropropyl methacrylate (4FMA), and 2,2,-3,3,4,4,5,5-octafluoro pentylmethacrylate (8FMA)

Table I   Fluoroalkyl Methacrylate Monomers

Monomer	Structure	n_D (Polymer)	Electronic Density
Methyl methacrylate (MMA)	CH_3 $\vert$ $CH_2{=}C{-}C{-}O{-}CH_3$ $\parallel$ O	1.492	4.086
Trifluoroethyl methacrylate (3FMA)	CH_3 $\vert$ $CH_2{=}C{-}C{-}O{-}CH_2{-}CF_3$ $\parallel$ O	1.418	4.072
Tetrafluoropropyl methacrylate (4FMA)	CH_3 $\vert$ $CH_2{=}C{-}C{-}O{-}CH_2{-}CF_2{-}CF_2H$ $\parallel$ O	1.424	4.072
Octafluoropentyl methacrylate (8FMA)	CH_3 $\vert$ $CH_2{=}C{-}C{-}O{-}CH_2{-}(CF_2)_3{-}CF_2H$ $\parallel$ O	1.395	4.063

were used as fluoroalkyl methacrylate monomers. Table I shows structures of their monomers, the refractive indices of their polymers, and electronic densities of α-carbon on the polymer chain calculated by the MNDO method.[8] Lauroyl peroxide was used as initiator and ethyleneglycol dimethacrylate was used as crosslinking agent. These monomers were used after careful purification such as follows. First, polymerization inhibitors in the monomers were eliminated by rinsing with NaOH aqueous solution; then the slight amount of residual NaOH was removed by washing with pure water until the pH of the monomer reached neutrality. After drying by adding molecular sieves (3A1/8), the monomer was filtered through a 0.2 μm membrane filter made of polytetrafluoroethylene, and distilled under reduced pressure.

Fabrication of POFs

The POFs were fabricated as follows. Fluoroalkyl methacrylate (M_1) was used as the main monofunctional monomer and ethyleneglycol dimethacrylate (M_2) with a bifunctional monomer was used as crosslinking agent. These monomers were mixed at a suitable composition [M_1/M_2 = 19/1 to 4/1 (wt/wt)] and lauroyl peroxide (0.5 wt %) was added as polymerization initiator. The monomer mixture was poured into a cladding tube (inner diameter

= 1.0 mm, outer diameter = 1.8 mm) made of FEP. After the open end of this tube was sealed, it was heated at 100°C to polymerize the core monomer in the oil bath gradually from the one end to the other. The transfer speed of the tube was 5 cm/min. After that, the POF was after-cured at 120°C for 20 h in the oven.

Attenuation Loss Measurement

The POF attenuation loss spectrum was measured by a cut-back method[3] 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

$$\alpha \ (dB/m) = 10/(L_1 - L_2)\log(I_2/I_1) \quad (1)$$

Heating Test for POFs

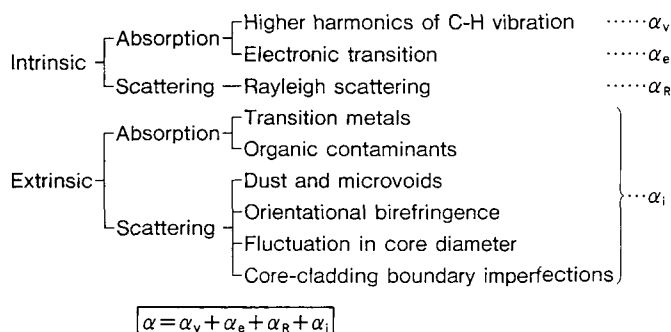Thermal properties of POFs were evaluated as follows. Sample POFs for the heating test were heated

Intrinsic — Absorption — Higher harmonics of C-H vibration $\cdots\cdots\alpha_v$
                         — Electronic transition $\cdots\cdots\alpha_e$
          — Scattering — Rayleigh scattering $\cdots\cdots\alpha_R$

Extrinsic — Absorption — Transition metals
                        — Organic contaminants
           — Scattering — Dust and microvoids
                        — Orientational birefringence $\cdots\alpha_i$
                        — Fluctuation in core diameter
                        — Core-cladding boundary imperfections

$$\alpha = \alpha_v + \alpha_e + \alpha_R + \alpha_i$$

Figure 1 Loss factors for POFs.

in an oven at 160°C in air. The lengths of sample POFs were 2 m each, and all cut out from the same POF source. One sample was taken out of the oven after heating every 100 h, and this sample was used for measurement of attenuation loss. A Hitachi 250-60 type spectrophotometer was used for measuring IR spectra by the KBr tablet method, of the core polymer before and after heating.

Contact Angle Measurement

Contact angles θ of the polymers were measured by the liquid drop technique[9] using several kinds of liquids whose critical surface tensions γ_c were known.

RESULTS AND DISCUSSION

Fluoroalkyl Methacrylate Polymer as Novel Core Polymer

The loss factors for POFs are given by eq. (2) and shown in Figure 1[7]:

$$\alpha = \alpha_e + \alpha_v + \alpha_R + \alpha_i \tag{2}$$

α_e is the intrinsic absorption loss due to electronic transition in core polymer, α_v is the intrinsic ab-

sorption loss due to higher harmonics of C—H molecular vibration in core polymer, α_R is the intrinsic scattering loss due to index fluctuation or density fluctuation present in the core polymer (i.e., Rayleigh scattering loss), and α_i is the extrinsic loss due to fabrication process, contaminating dust, etc.

We reported that the main cause of thermal degradation of the POFs was the increase of α_e due to conjugated carbonyl double bonds formed by thermal oxidation of the core polymer.[7] But the amount of reaction products was too small to be detected by IR, NMR spectra, and elemental analysis, etc. Thus thermal behavior of optical properties of the POFs must be discussed from a different viewpoint from that for conventional polymers. We thought that some intrinsic countermeasures were needed to restrain the thermal degradation of the POFs. So we searched for a novel core polymer, which had a high heat resistance and a good transparency, to restrain the thermal oxidation reaction. Methacrylate or acrylate polymers are suitable for the core of POFs because of their transparency in the visible wavelength region where POFs are used for the optical transmissions. Still more, these polymers have no aromatic group in the molecules so that their α_R values are very small. On the other hand, when halogens which have large electronegativities are
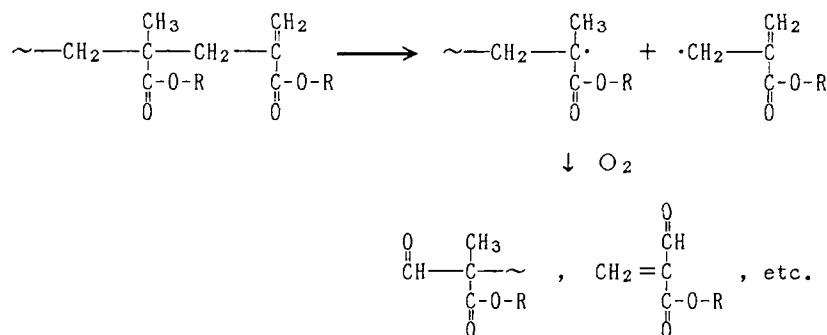
Figure 2 Scheme of thermal oxidation reaction of methacrylate polymer.
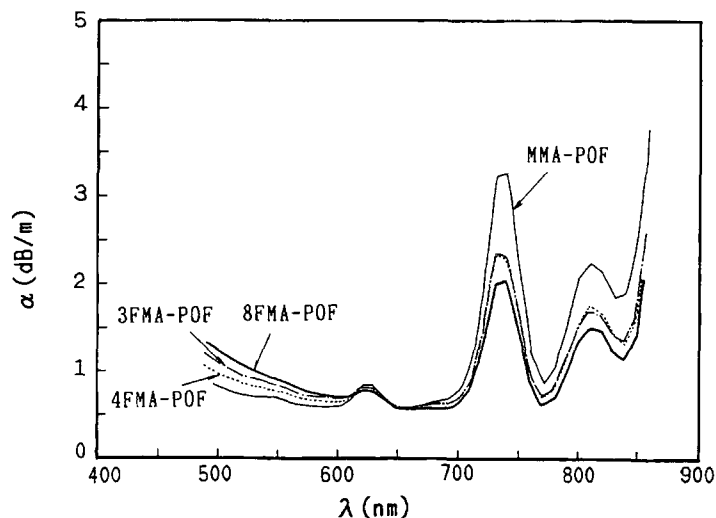
Figure 3 Attenuation loss of POFs before heating. Measurement: 10-9 m cut back. Crosslinking agent: Ethyleneglycol dimethacrylate.

introduced into the molecules, thermal oxidation reactions which are initiated by the formation of hydroperoxide as shown in Figure 2 would be restrained. Therefore, halogenated polymer would effectively reduce the formation of conjugated carbonyl double bonds by thermal oxidation of polymer. Based on this reasoning, we chose a fluoroalkyl methacrylate copolymer as core, which has a good transparency in the visible wavelength region and is easily polymerized. Table I shows electronic densities of α-carbon on the polymer chain calculated by the MNDO method.[8] We considered that the core polymer which has smaller electronic densities would

restrain thermal degradation of the POFs effectively. So, the order of heat resistance of the POF would be as below:

8FMA-POF > 4FMA-POF

= 3FMA-POF > MMA-POF

Attenuation Loss of the POFs before and after Heating

Figure 3 shows attenuation losses α (dB/m) of POFs before heating, where λ (nm) is wavelength. In the
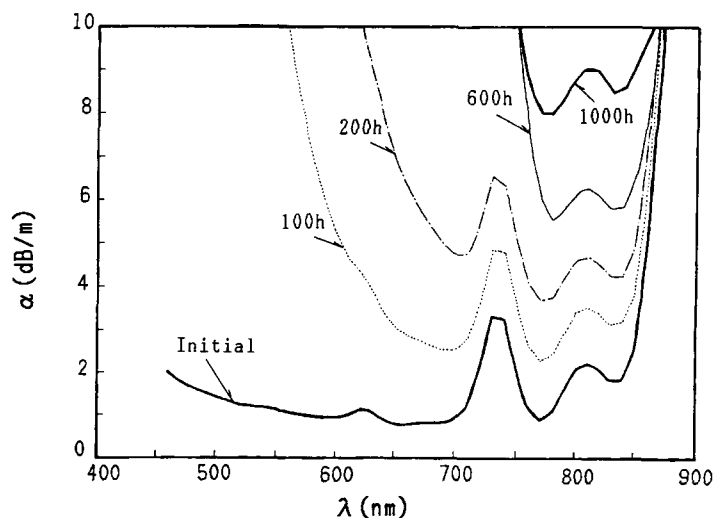

Figure 4 Time dependence of attenuation loss of MMA-POF on heating at 160°C in air. Measurement: 2-1 m cut back.
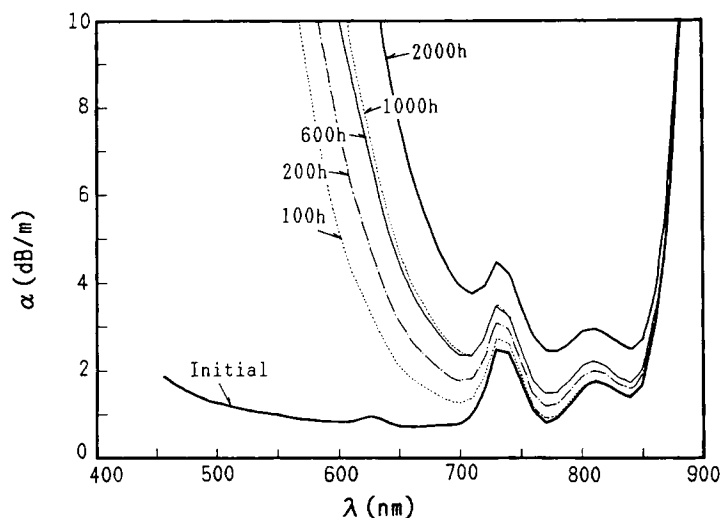
Figure 5 Time dependence of attenuation loss of 3FMA-POF on heating at 160°C in air. Measurement: 2-1 m cut back.

visible wavelength region, losses of FMA-POFs are low and their loss spectra are similar to that of MMA-POF. When a fluoropolymer is used as its core, concentration of C—H bonds in the molecules decreases, so that α_V values of FMA-POFs are smaller than MMA-POF in the near infrared region.[10] On the other hand, as indices of fluoropolymers are low, it is expected that α_R values of FMA-POFs would decrease because α_R is a function of index. But α_R values of FMA-POFs did not decrease compared with that of MMA-POF as far as Figure 3. The α_R values of fluoroalkyl methacrylate polymer (poly-FMA) species have been reported by Tanio

and co-workers.[11] They evaluated α_R values of several poly-FMAs and attributed the nearly equal α_R values of poly-FMAs and PMMA to increased isothermal compressibilities of poly-FMAs as α_R is a function of isothermal compressibility. Our results support their considerations, too.

Figures 4–7 shows the time dependence of attenuation losses of the POFs (MMA-POF, 3FMA-POF, 4FMA-POF, and 8FMA-POF) on heating at 160°C. All POFs are thermally degraded, and the attenuation loss increases from the short wavelength region. The increase of MMA-POF is especially remarkable. In a nitrogen atmosphere, the increase of
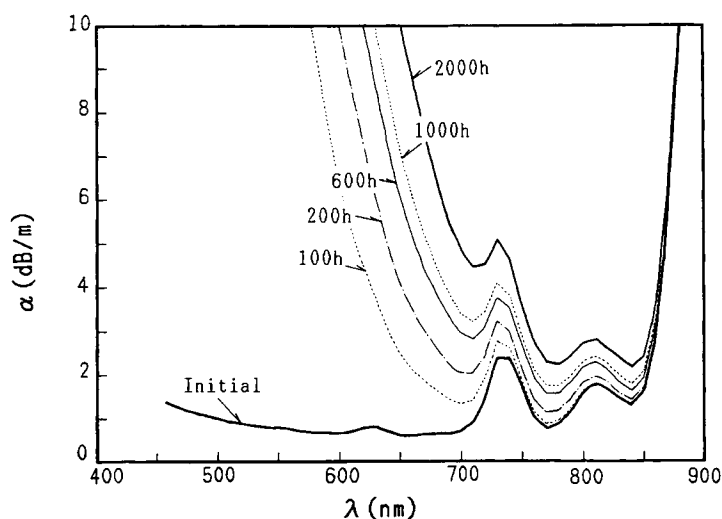

Figure 6 Time dependence of attenuation loss of 4FMA-POF on heating at 160°C in air. Measurement: 2-1 m cut back.
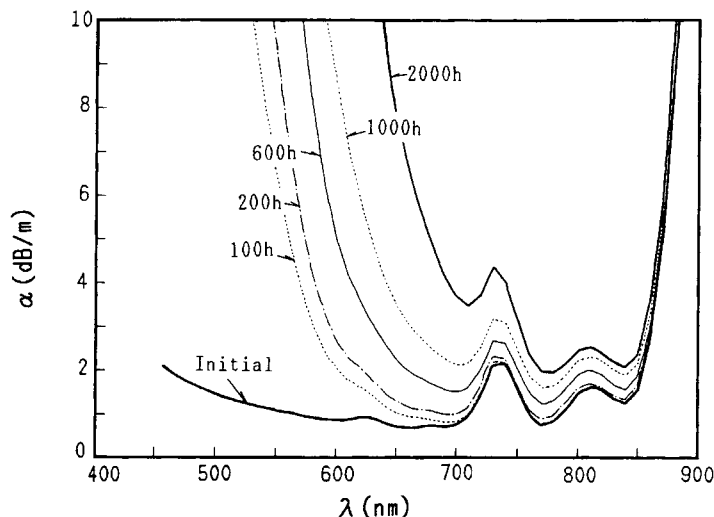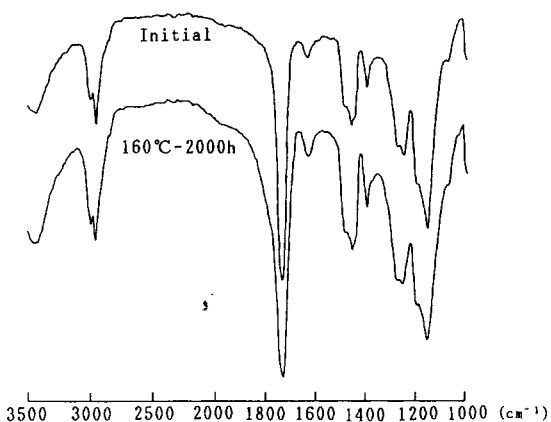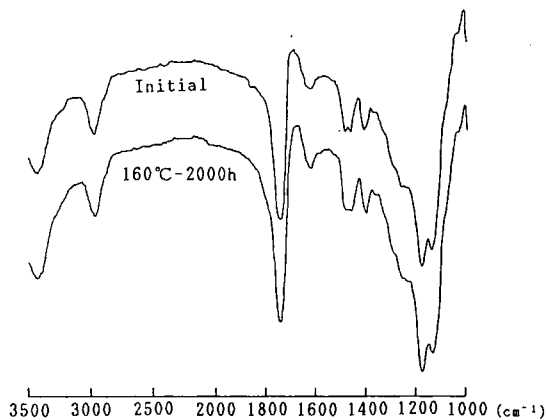
Figure 7 Time dependence of attenuation loss of 8FMA–POF on heating at 160°C in air. Measurement: 2–1 m cut back.

(a) Core polymer of MMA-POF.

(b) Core polymer of 8FMA-POF.

Figure 8 Infrared spectra of core polymers of POFs before and after heating at 160°C in air for 2000 h.

attenuation loss of those POFs was reported to be very small so that these increases were due to the conjugated carbonyl double bonds formed by thermal oxidation of core polymer.[7,12,13] But the amount of reaction products was very small. For example, Figure 8 shows IR spectra of core polymers of the POFs, (a) MMA–POF and (b) 8FMA–POF, respectively, before and after heating at 160°C for 2000 h in air. No matter how much the attenuation loss of the POFs increased after heating for 2000 h, hardly any chemical structures of the core polymers are changed.

Figure 9 shows attenuation loss spectra of thermally degraded POFs after heating at 160°C for 1000 h in air. The attenuation loss drops in the order MMA–POF, 4FMA–POF, 3FMA–POF, and 8FMA–POF. The order of 3FMA–POF and 4FMA–POF in this result is not the same order as the calculated values of electronic densities increase of α-carbon by the MNDO method. For the reason why the loss increase of 4FMA–POF is larger than that of 3FMA–POF, we attribute it to the difference in critical surface tensions of polymers. That is, the polymer which has lower critical surface tension adsorbs oxygen poorly,[14] so that oxidation reactions do not occur easily. Figure 10 shows Zisman plots of PMMA, P3FMA, P4FMA, and P8FMA. We can evaluate the critical surface tension γ_c of polymer by calculating the surface tension γ when cos $\theta = 1$ in Figure 10. The γ_c values of PMMA, P4FMA, P3FMA, and P8FMA are 41, 38, 29, and 25 dyn/cm, respectively. From these, it is considered that the reactivity for
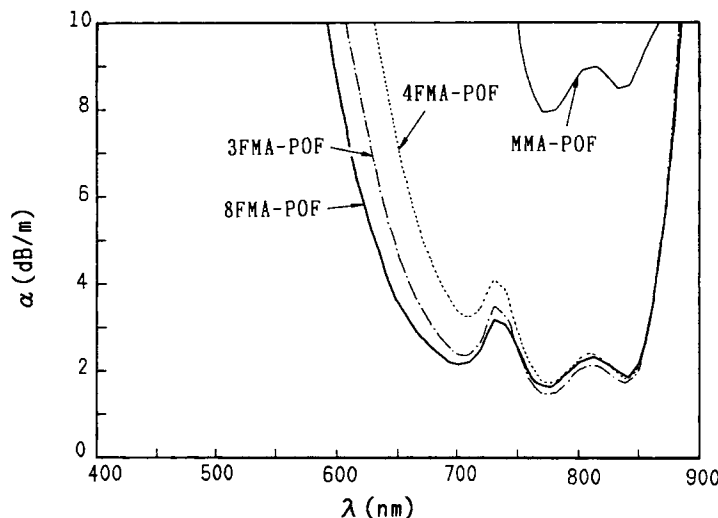
Figure 9 Attenuation loss of POFs after heating at 160°C in air for 1000 h. Measurement: 2–1 m cut back.

oxygen of P3FMA is smaller than that of P4FMA. Consequently, we consider that smaller electronic densities and smaller critical surface tensions of the polymers can restrain thermal oxidation reactions of the POFs effectively.

Figure 11 shows the time dependence of attenuation loss of the POFs on heating at 160°C, (a) at

Figure 10 Critical surface tensions of polymers: (●) PMMA; (■) P3FMA; (○) P4FMA; (×) P8FMA.

660 nm, (b) at 780 nm, and (c) at 850 nm, respectively. These wavelengths are suitable light sources for optical communications using POFs. The lowest optical window of the MMA–POF is near 660 nm, so that the light source at 660 nm is the most familiar. But the loss increase at 660 nm is the largest of the three wavelengths. For the FMA–POFs, attenuation losses at both 660 and 780 nm are as low as those of MMA–POF, but the loss at 850 nm is large, even initially, so that the use of FMA–POFs at 850 nm is unsuitable for optical transmissions. Attenuation loss increases of FMA–POFs are not large at 660 nm and besides very small at 780 and 850 nm compared with that of MMA–POF. Therefore, FMA–POFs are the most suited for optical communications at 780 nm.
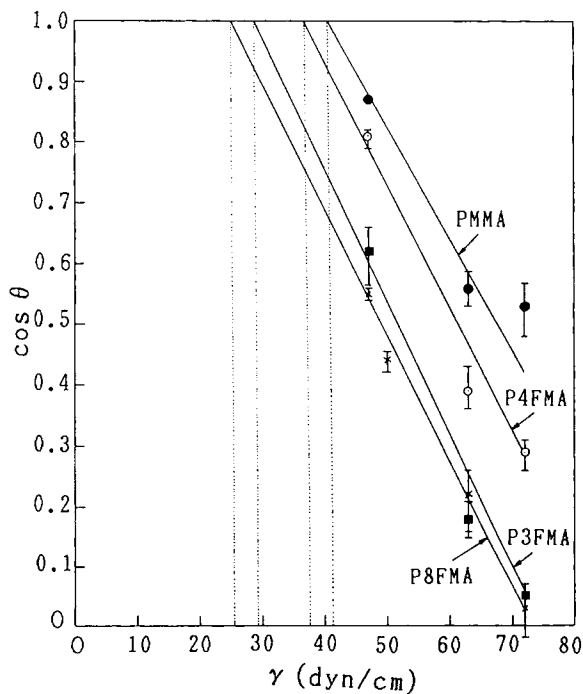
Further Consideration

We suggest that core polymers which have better thermal characterizations of optical properties than FMA copolymers would be α-fluoroacrylate copolymers. Table II shows the structures of these monomers and the electronic densities of their polymers calculated by the MNDO method. The electronic densities of these polymers are much smaller than those of PMMA and poly-FMAs, so that the POF having a core made of a α-fluoroacrylate copolymer will have better thermal characterizations of optical properties. It has been reported on the polymerization of α-fluoroacrylates.[15] We polymerized α-fluoroacrylates by the same conditions for radical polymerization as MMA. But we could not obtain POFs
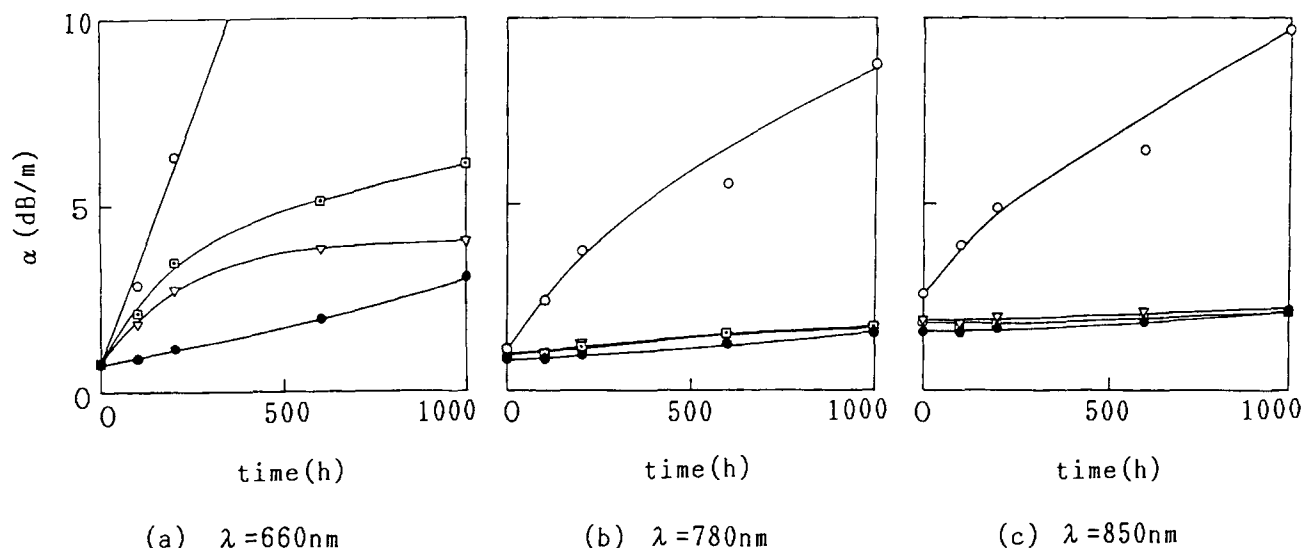
Figure 11 Time dependence of attenuation loss of the POFs on heating at 160°C in air: (○) MMA-POF; (▽) 3FMA-POF; (□) 4FMA-POF; (●) 8FMA-POF.

for which optical properties could be measured. Now, we are investigating the polymerization conditions of these monomers in order to fabricate the POFs.

CONCLUSIONS

We fabricated novel plastic optical fibers having a core made of fluoroalkyl methacrylate copolymer (FMA-POFs) and analyzed their optical properties. Loss increases of FMA-POFs were about 10 times

smaller than that of the POF having a methyl methacrylate copolymer as its core after heating at 160°C in air. We considered that electronic density and critical surface tension of polymers could be correlated to the thermal oxidation reaction of the POFs. An optical window of the FMA-POFs was at 780 nm. Hardly any loss change occurred at 780 nm, unlike the loss increase at 660 nm. This indicated that FMA-POFs would be applicable to optical communications at 780 nm in the near-IR region.

Table II α-Fluoroacrylate Monomers

Monomer	Structure	n_D (Polymer)	Electronic Density
Methyl α-fluoroacrylate (MFA)	$CH_2=C-C-O-CH_3$ with F above C, ∥O below	1.457	3.808
Trifluoroethyl α-fluoroacrylate (3FFA)	$CH_2=C-C-O-CH_2-CF_3$ with F above C, ∥O below	1.386	3.803
Pentafluoropropyl α-fluoroacrylate (5FFA)	$CH_2=C-C-O-CH_2-CF_2-CF_3$ with F above C, ∥O below	1.368	—

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