

Analysis of Thermal Degradation for Plastic Optical Fibers

YOSHITAKA TAKEZAWA,¹ SEIKICHI TANNO,¹ NORIAKI TAKETANI,¹ SHUICHI OHARA,¹ and HIDEKI ASANO²

¹Hitachi Research Laboratory, Hitachi, Ltd., 4026 Kuji-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan, and ²Cable Research Laboratory, Hitachi Cable, Ltd., 5-1-1 Hitaka-cho, Hitachi-shi, Ibaraki-ken, 319-14 Japan

SYNOPSIS

Attenuation loss of plastic optical fibers (POFs) gradually increases with long use at high temperature. We separated attenuation loss of the POFs before and after heating at 150°C in air into four loss factors, and identified the main factor for attenuation loss increase as electronic transition absorption loss (α_e). The increase of α_e was caused by a thermal oxidation reaction of the core polymer in the POF. But, according to NMR and FT-IR spectra, elementary analysis, etc., hardly any reaction products were detected. We assume that the reaction products were only a small amount of the conjugated carbonyl groups. So we fabricated POFs containing model compounds with conjugated carbonyl groups, and measured their attenuation loss. The attenuation loss spectra of these POFs were similar to those of thermally degraded POFs. Consequently, a very small amount of conjugated carbonyl groups were formed by the thermal oxidation reaction of core polymer so that α_e increased to an unacceptable level.

INTRODUCTION

Attenuation loss of commercial plastic optical fibers (POFs) is about four orders larger than that of glass optical fibers with the lowest loss grade.^{1,2} But POFs have good flexibility and applicability due to their large core diameter and high numerical aperture. Therefore, they are expected to be applied as a short distant optical communication medium, for example, computer-to-terminal data links in office automation systems.³ However, since the core of conventional POFs is made of poly(methyl methacrylate) (PMMA), which has a low glass transition temperature, they cannot be used for computer-to-sensor data transmission medium in care engine chambers or in closed places near heating units, because of their poor thermal resistance.

We have been studying heat resistant POFs with a crosslinked PMMA as core.^{4,5} Our POFs can be used up to 200°C for a few days. But if they are used at temperatures of 150°C for a few thousand hours, their attenuation loss increases in the shorter wavelength region. In the case of POFs, the light transmits in a long optical path, so that even very small

chemical and physical changes due to thermal degradation greatly influence the attenuation loss. Therefore, it is important to determine these small changes and to investigate the causes of thermal degradation of the POFs so that heat resistance of the POFs can be improved.

Optical properties of a few core polymers have been studied⁶⁻⁹ regarding light scattering and light absorption; but their thermal characterizations have not been reported, nor has a chemical and physical analysis of thermal degradation for the optical polymers been made yet.

In this paper, we separated attenuation loss of the POFs before and after heating at 150°C in air into four loss factors, and identified the main factor of increased attenuation loss by thermal degradation. Then we discussed why the main factor for the degraded POFs was increased by thermal degradation.

EXPERIMENTAL

Fabrication of POFs

The POFs were fabricated as follows: Methyl methacrylate (MMA) was used as the main monofunctional monomer, and ethyleneglycol dimethacrylate

which was a bifunctional monomer was used as crosslinking agent. These monomers were mixed at a suitable composition 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 tetrafluoroethylene-hexafluoropropylene copolymer (FEP). After one end of this tube was sealed, it was heated at 100°C to polymerize the core monomer from the sealed end to another end of it. After that, the POF was after-cured at 120°C for 20 h.

Attenuation Loss Measurement

The POF attenuation loss spectrum was measured by a cutback method using a halogen tungsten lamp and a grating monochromator. 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 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 output power measured again. From the sample POF output power I_1 and the cut POF output power I_2 , the attenuation loss α (dB/m) for the POF was calculated using

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

Loss Factors Measurement

Loss factors for POFs are given by

$$\alpha = \alpha_e + \alpha_v + \alpha_R + \alpha_i \quad (2)$$

Here, α_e is electronic transition absorption loss, α_v is the higher harmonic absorption loss of the C—H molecular vibration, α_R is the Rayleigh scattering loss, and α_i is scattering loss due to imperfections in the POF structure.

Each loss factor of the POFs was estimated as follows using the method of Kaino.^{6,7} The α_e and α_v are estimated from the absorbance of a 1.5-mm-thick polymer plate with the same composition as the core using a spectrophotometer (Hitachi, Ltd., 330 type) in the 200–2600 nm wavelength region. The α_e , whose peak is located in the ultraviolet (UV) region and has a tail extending into the visible wavelength region, obeys the so-called Urbach rule.¹⁰ Then the α_e value at an arbitrary wavelength λ is shown as

$$\alpha_e = A_0 \cdot \exp(B_0/\lambda) \quad (3)$$

Here, A_0 and B_0 , which are material constants, are determined from the absorbance spectra. The α_v , whose normal vibration is located in the infrared (IR) region, declines with shorter wavelength. The relation between the logarithm of $\alpha_v(n)$, which is loss of the n th higher harmonics, and quantum number n of the molecular vibration can be approximated to the first degree as shown by

$$\log[\alpha_v(n)] = p \cdot n + q \quad (4)$$

Here, p and q , which are material constants, are determined from the absorbance spectra. The α_R is estimated from turbidity τ at 633 nm using a light scattering instrument (Ohtsuka Denshi, Ltd., DLS-700 type). The α_R at arbitrary wavelength λ is calculated according to the $1/\lambda^4$ rule. The relation between α_R (dB/m) and τ (cm^{-1}) is shown as

$$\alpha_R = 4.342 \cdot 10^2 \cdot \tau \quad (5)$$

The α_i is calculated using eq. (2).

RESULTS AND DISCUSSION

Separation of Loss Factors for POFs before and after Heating

Changes in attenuation loss of the POF before and after heating at 150°C in air are shown in Figure 1. Initially, the attenuation loss is low in the visible wavelength region. With longer heating, the attenuation loss gradually increases for the near UV region and the core polymer of the heated POF becomes yellowish in color. This behavior has been observed in almost all POFs, e.g., polycarbonate- or polystyrene-core POFs. To identify the causes of this increased attenuation loss, we tried to divide the attenuation loss of the POFs before and after heating at 150°C in air into four loss factors.

Loss factors for POFs are divided as shown in Figure 2 and total attenuation loss α is written as eq. (2). The α_e is loss due to electronic transition absorption of chemical bonds in the core polymer. The α_e in the visible wavelength region is due to the tail of this electronic transition absorption which has an absorption maximum in the UV region. The α_v is loss due to the higher harmonic absorption of the C—H molecular vibration which has a normal vibration in the IR region. Since the normal vibrations of chemical bonds, C—C, C—O, and C=O, are observed at longer wavelengths in the IR region, the higher harmonic absorptions of these chemical

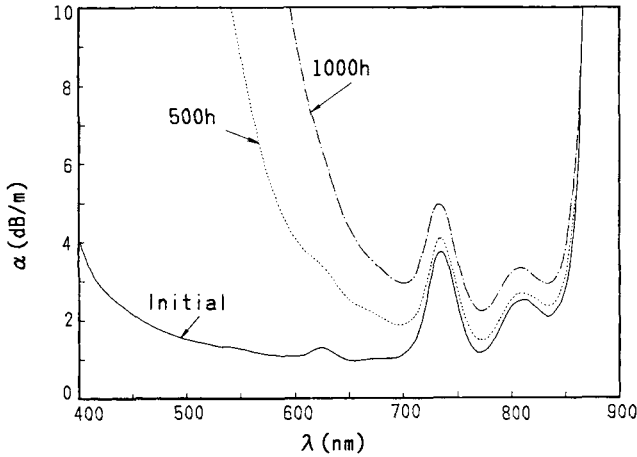


Figure 1 Loss of POFs after heating at 150°C.

bonds in the visible wavelength region are much smaller than that of the C—H bond.^{11,12} The α_R is Rayleigh scattering loss due to fluctuations of the density and the refractive index in the core polymer. These three loss factors are intrinsic ones. The α_i is an extrinsic loss due to the POF fabricating process and any impurities. For this extrinsic loss α_i , the loss factor from impurity absorptions and scattering due to dust and microvoids can be significantly reduced by using a carefully purified monomer and a closed polymerization system. Further as our studied POFs were not fabricated by a spinning method but by a casting method, orientational birefringence scattering can be ignored. Therefore, the main factors in the POFs for extrinsic loss α_i are scattering loss due to fluctuation in core diameter and core-cladding boundary imperfections, i.e., scattering loss due to imperfections in the POF structure. Consequently, total attenuation loss α for the POFs can be divided into four factors shown as eq. (2).

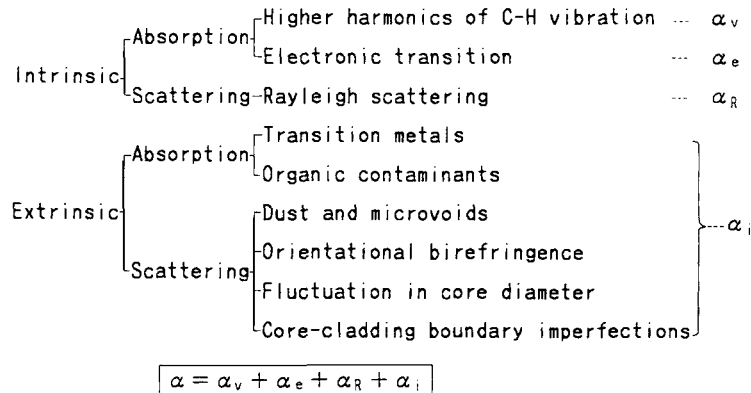


Figure 2 Loss factors for POFs.

Table I shows the change of α_e for core polymer plate before and after heating at 150°C in air for 500 h. Equations (6) and (7) show relationships between α_e and λ , which are determined from each absorbance spectra:

$$\alpha_e (\text{initial}) = 5.25 \cdot 10^{-4} \cdot \exp(3.48 \cdot 10^3 / \lambda) \quad (6)$$

$$\begin{aligned} \alpha_e (150^\circ\text{C}, 500 \text{ h}) \\ = 7.76 \cdot 10^{-4} \cdot \exp(5.11 \cdot 10^3 / \lambda) \quad (7) \end{aligned}$$

The α_e after heating for 500 h increases too much. In Table I, the bottom row lists change of attenuation loss α for the POF before and after heating. The value of α below 500 nm is too large to be measured, but the change of α_e before and after heating nearly equals the change of α . This indicates that the main factor for attenuation loss increase should be α_e .

Table II shows change of α_v for core polymer plate before and after heating at 150°C in air for 500 h. Here, ν_n means the n th higher harmonics of the C—H molecular stretching vibration, and $\nu_n + \delta$ means the combination tone between ν_n and the normal C—H molecular bending vibration δ . Equations (8) and (9) show the relationship between $\alpha_v(n)$ and n , which is determined from each absorbance spectra:

$$\begin{aligned} \text{initial, } \nu_n: \log[\alpha_v(n)] &= -0.815 \cdot n + 4.55 \\ \nu_n + \delta: \log[\alpha_v(n)] &= -0.795 \cdot n + 3.40 \end{aligned} \quad (8)$$

$$\begin{aligned} 150^\circ\text{C}, 500 \text{ h, } \nu_n: \log[\alpha_v(n)] &= -0.836 \cdot n + 4.59 \\ \nu_n + \delta: \log[\alpha_v(n)] \\ &= -0.827 \cdot n + 3.43 \end{aligned} \quad (9)$$

Table I Electronic Transition Absorption Loss (α_e : dB/m)

Wavelength (nm)	400	450	500	550	600	660	700	800	900
α_e (initial)	3.13	1.19	0.55	0.29	0.17	0.10	0.07	0.04	0.02
α_e (150°C, 500 h)	276	66.8	21.4	8.46	3.90	1.80	1.15	0.46	0.23
Change of α_e	273	65.6	20.9	8.17	3.73	1.70	1.08	0.42	0.21
Change of α for POF	—	—	—	8.23	3.64	1.83	0.92	0.17	—

Table II Higher Harmonic Absorption Loss of C—H Molecular Vibration (α_v : dB/m)

Higher Harmonics (λ , nm)	ν_4 (900)	$\nu_4 + \delta$ (810)	ν_5 (740)	$\nu_5 + \delta$ (680)	ν_6 (630)	ν_7 (550)
α_v (initial)	19.50	1.66	2.99	0.27	0.46	0.07
α_v (150°C, 500 h)	17.74	1.33	2.59	0.20	0.38	0.06

The α_v after heating decreases a little, but this change is much smaller than the change of α_e . Table III shows the change of α_R for the core polymer rod before and after heating at 150°C in air for 500 h. The α_R is very small compared with other loss factors and its increase is also small.

Figure 3 shows results of individual loss for the as-manufactured POF. Before heating, its attenuation loss α is low in the visible wavelength region. In the near UV region, α_e is the main factor for α . And in the near IR region, α_v is the main factor. The peaks at the wavelengths 630, 740, 810, and 900 nm in the spectrum are higher harmonics (overtones and combination tones) of the C—H molecular vibration. Figure 4 shows results of individual loss for the POF after heating at 150°C in air for 500 h. The α_e has the biggest increase, and the other losses have only a small change compared with the change of α_e . Therefore, α_e is the main factor for attenuation loss increase of the POFs by heating.

Causes of Thermal Degradation for POFs

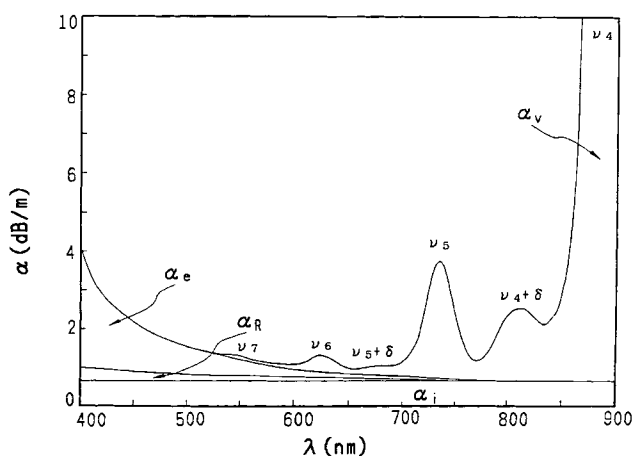
The electronic absorption loss α_e in the visible wavelength region is caused by the existence of double bonds. That is, there are two kinds of electronic transition absorptions, due to the $\pi \rightarrow \pi^*$ transition of the carbon-carbon double bond ($>C=C<$) and

Table III Rayleigh Scattering Loss (α_R) (Sample: 10 mm ϕ Rod; Wavelength: 633 nm)

	Initial	100 h	500 h
α_R (dB/m)	5.3×10^{-2}	6.0×10^{-2}	8.8×10^{-2}

the $n \rightarrow \pi^*$ transition of the carbonyl group ($>C=O$). Therefore, we considered that the main cause of α_e increase was the regeneration of monomer, which had a $>C=C<$ double bond, by depolymerization of core polymer or the increase of the carbonyl group by thermal oxidation of the core polymer. But, according to NMR and FT-IR spectra, elementary analysis, etc., these reactions hardly occurred. Figure 5 shows the IR spectra of the core polymer of the POF before and after heating at 150°C in air for 500 h. No clear change is observed. Figure 6 shows the calculated attenuation loss of the POF when it contains MMA monomer at 10 wt % content. The increased α_e of MMA (10 wt %) is calculated on the basis of

$$\alpha_e (\text{MMA, 10 wt \%}) = 9.35 \cdot 10^{-11} \cdot \exp(9.21 \cdot 10^3 / \lambda) \quad (10)$$

**Figure 3** Loss of POF before heating.

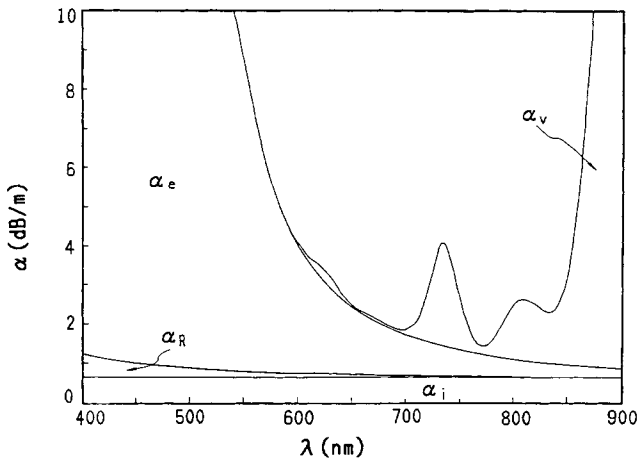


Figure 4 Loss of POF after heating at 150°C for 500 h.

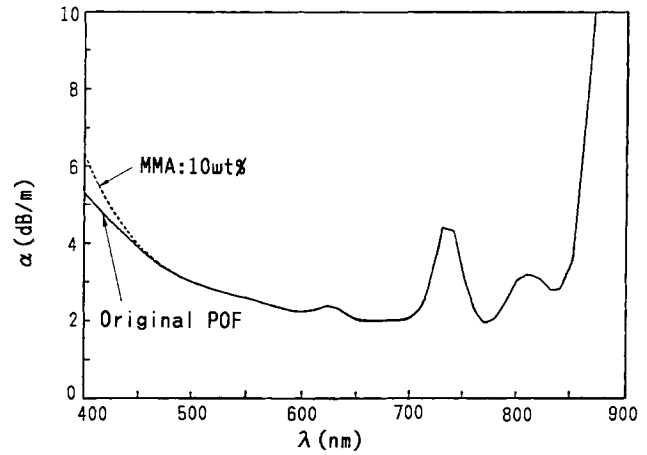


Figure 6 Calculated loss of POF containing MMA monomer.

The calculated α_e of MMA monomer is so small in the visible region that the effect of the depolymerized monomer can be neglected if a small amount of MMA is formed by depolymerization. On the other hand, the increase in attenuation loss of the POF was small even after heating at 150°C for 1000 h in a nitrogen atmosphere. The extent of increase was about 1/8 of that of the POF heating at 150°C for 1000 h in air. So we think the oxidation reaction must be closely related to the thermal degradation of the POF.

The absorption peak is reported to shift to a longer wavelength region if carbonyl groups, which are produced by thermal oxidation, conjugate with other carbonyl groups or double bonds. As a result of conjugation, α_e of carbonyl groups in the visible region should increase too much so as to be no longer negligible. Thus we assumed that only a small

amount of conjugated carbonyl groups, which were produced under the lower detectable limits of the instrumental analyses used, were formed in the core polymer by thermal oxidation of the POFs so that α_e in the visible wavelength region increased to the remarkable extent seen in Figure 4.

So we fabricated POFs containing model compounds with various carbonyl groups which might be formed by thermal oxidation reactions of core polymer, and measured their attenuation loss. Table IV shows the model compounds used for discussing the cause of the electronic transition absorption loss increase. Here, 2,5-hexanedione (25HD) has no conjugated carbonyl group, 3,4-hexanedione (34HD) has conjugated carbonyl groups, and *p*-benzoquinone (BQ) has conjugated carbonyl groups and $>C=C<$ double bonds. Figure 7 shows attenuation loss of POFs containing 25HD. Since it lacks con-

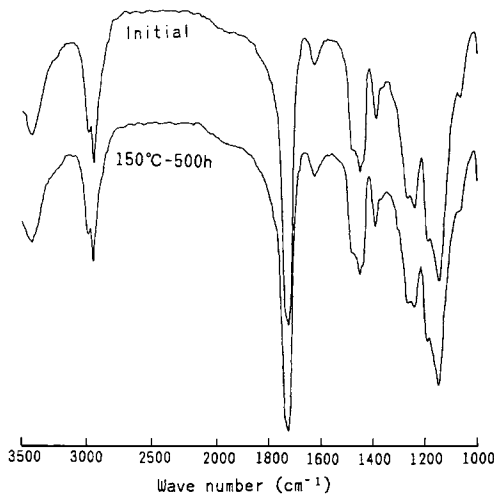


Figure 5 Infrared spectra of core polymer of POF.

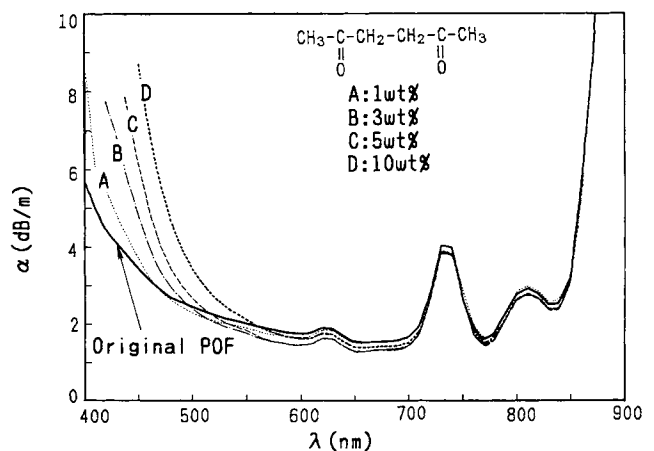

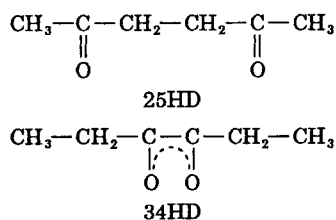


Figure 7 Loss of POFs containing 2,5-hexanedione.

Table IV Model Compounds for Electronic Transition Absorption Loss

Compounds	Structure	λ_{\max} (nm)	ϵ_{\max} ($\text{cm}^{-1} \text{mol}^{-1} \text{L}$)
2,5-Hexanedione (25HD)	$\begin{array}{c} \text{CH}_3\text{CCH}_2\text{CH}_2\text{CCH}_3 \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$	268	49.3
3,4-Hexanedione (34HD)	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CCCH}_2\text{CH}_3 \\ \parallel \\ \text{OO} \end{array}$	260	225
<i>p</i> -Benzoquinone (BQ)		241	1.80×10^4

jugated carbonyl groups, the increase of attenuation loss in the visible wavelength region, even for 10 wt % of 25HD, is much smaller than that of thermally degraded POF. Figure 8 shows attenuation loss of POFs containing 34HD. 34HD has adjacent carbonyl groups and these groups are conjugated with each other as indicated below:



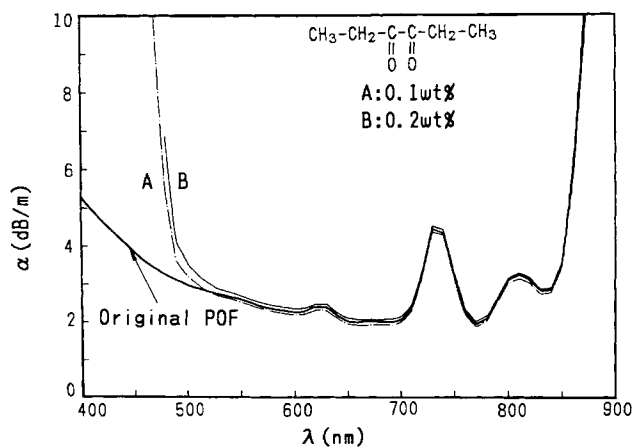
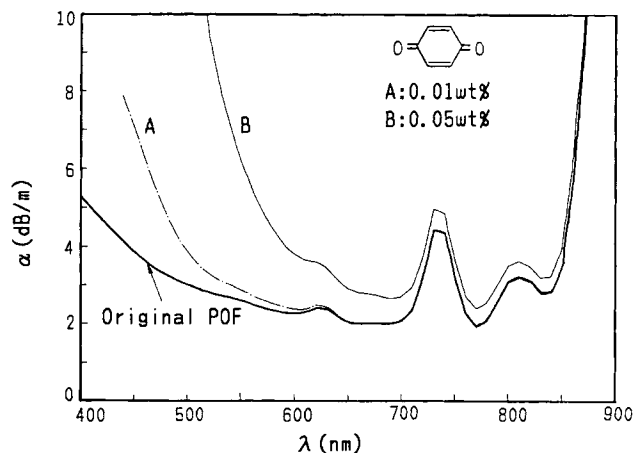
Therefore, attenuation loss of the POF containing 34HD with only 0.1 wt % content nearly equals that of POF containing 25HD with 10 wt % content. Figure 9 shows attenuation loss of POFs containing BQ. Loss spectrum of the POF containing BQ at

only 0.05 wt % content is similar to that of thermally degraded POF (Fig. 1).

Consequently, it is considered that the main cause of α_e increases of the POFs is formation of only a small amount of conjugated carbonyl groups and $>\text{C}=\text{C}<$ double bonds by thermal oxidation of core polymer.

CONCLUSION

The attenuation loss of plastic optical fiber (POF) was separated into four factors before and after heating at 150°C in air. A main factor for increase of attenuation loss of the POF by heating was electronic transition absorption loss. The increase of electronic absorption loss was caused by a thermal oxidation reaction of core polymer of the POF, but hardly any reaction products could be detected. It was considered that only a small amount of conjugated carbonyl groups was formed in the core poly-

**Figure 8** Loss of POFs containing 3,4-hexanedione.**Figure 9** Loss of POFs containing benzoquinone.

mer by thermal oxidation reactions so that electronic transition absorption loss increased to an unacceptable level.

The authors wish to thank Dr. S. Numata and Dr. A. Mukoh for their invaluable contributions to techniques and discussions.

REFERENCES

1. T. Miya, Y. Terunuma, T. Hosaka, and T. Miyashita, *Electron. Lett.*, **15**, 106 (1979).
2. T. Miyashita and T. Manabe, *IEEE J. Quantum Electron.*, **QE-18**, 1432 (1982).
3. D. E. Willauer, *Electro. Conf. Rec.*, 27.4.1 (1982).
4. N. Taketani, S. Tanno, S. Ohara, H. Asano, and T. Abe, *Kobunshi Ronbunshu*, to appear.
5. M. Shimura, N. Taketani, S. Tanno, H. Asano, and T. Abe, *OFC'89*, **WE3**, 64 (1989).
6. T. Kaino, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 37 (1987).
7. T. Kaino, *Kobunshi Ronbunshu*, **42**, 257 (1985).
8. Y. Koike, N. Tanio, and Y. Ohtsuka, *Macromolecules*, **22**, 1367 (1989).
9. A. Tanaka, H. Sawada, and N. Wakatsuki, *Fujitsu Sci. Tech. J.*, **23**, 166 (1987).
10. F. Urbach, *Phys. Rev.*, **92**, 1324 (1953).
11. O. H. Wheeler, *Chem. Rev.*, **59**, 629 (1959).
12. W. Groh, *Makromol. Chem.*, **189**, 2861 (1988).

Received January 2, 1990

Accepted September 6, 1990