

# Empirical Estimation Method of Intrinsic Loss Spectra in Transparent Amorphous Polymers for Plastic Optical Fibers

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## SYNOPSIS

We have developed a novel simulation to estimate the intrinsic loss spectrum of a plastic optical fiber (POF) having a transparent amorphous polymer as its core. Loss for POF is divided into four elements, that is,  $\alpha_e$ ,  $\alpha_v$ ,  $\alpha_R$ , and  $\alpha_i$ . Here,  $\alpha_e$  means the electronic transition absorption loss,  $\alpha_v$  the absorption loss due to harmonics of molecular vibrations, and  $\alpha_R$  Rayleigh scattering loss. These three losses cause attenuation loss intrinsically and determine the lower limit of loss in the POF. The  $\alpha_i$  is the extrinsic loss due to fabrication process and contaminating dust, etc., and as such can be decreased to a negligible amount. We clarified the relationship between the chemical structure of polymer repeating unit and the three intrinsic losses and derived empirical equations to estimate the losses. The spectra estimated by this simulation agreed well with experimental ones. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(methyl methacrylate) (PMMA), polystyrene (PSt), and bisphenol-A type polycarbonate (PC) are used as core materials for plastic optical fibers (POFs).<sup>1-3</sup> These polymers have good transparency in the visible region and have optical windows, that is, a low loss region, near 660 nm. Thus POFs are used for optical communication with a red LED (typical wavelength = 660 nm) in the visible region. It is, however, necessary for polymers to have transparency in the near-infrared (IR) region because silica optical fiber, which is typically employed for long-distance optical communication, is used at longer wavelengths than for POF optical communication. There are a few reports on a POF for near-IR optical communication.<sup>1,2,4,5</sup> The cores of these POFs are made of fluorinated or deuterated PMMA derivatives. For optical polymers, it is necessary to clarify the optical properties over a wide wavelength region from visible to near IR. Therefore, a simple evaluating method for optical transmittance is needed.

To consider optical properties of transparent optical organic materials, we need to prepare a very purified sample containing little contaminant to evaluate its optical transmission loss. Even a small amount of contaminants in the core polymer of a POF causes large attenuation loss because the optical path length of the POF is so long that the loss due to contaminant becomes integrated. Thus it is impossible to measure optical loss accurately. In the case of the solution state, we can provide the highly purified material easily, but it is difficult with solid polymers to get a sufficiently purified sample, which has no contaminant. Therefore, we have studied methods to estimate the optical loss empirically from the chemical structure of a polymer repeating unit.

Attenuation loss of POFs is divided into four parts,<sup>1</sup> that is,  $\alpha_e$ ,  $\alpha_v$ ,  $\alpha_R$ , and  $\alpha_i$ . Here,  $\alpha_e$  means electronic transition absorption loss,  $\alpha_v$  absorption loss due to harmonics of molecular vibrations, and  $\alpha_R$  Rayleigh scattering loss. These three losses cause its attenuation loss intrinsically and determine the lower limit of loss in the POF. Besides these intrinsic losses,  $\alpha_i$  is the extrinsic loss due to the fabrication process and contaminating dust, and so on. It is significantly reduced by using a purified monomer and closed polymerization system, so that it is important to clarify the relationship between the three intrinsic

losses and the chemical structure of a polymer. We have already derived empirical equations to estimate two of the intrinsic losses,  $\alpha_v$  and  $\alpha_R$ .<sup>6,7</sup> In this work we derive an equation to estimate  $\alpha_e$  and propose a new simulation method to estimate intrinsic loss spectra from the chemical structures of the polymer repeating units.

## EXPERIMENTAL

### Materials

Table I shows several amorphous polymers used to measure the absorbance for the electronic transition absorption loss. To eliminate the effect of unknown impurities, we needed to purify these polymers before measurements. They were purified as follows: First, the polymers were dissolved in dichloromethane separately, and then filtered through a Teflon

membrane filter (pore size 0.2  $\mu\text{m}$ ). By addition of a large amount of methanol to the filtrate, the polymers were reprecipitated and were then dried under reduced pressure.

### Estimation of the Electronic Transition Absorption Loss

Absorbance was measured using a spectrophotometer (Hitachi, Ltd. 330 type) for the 200–2500 nm wavelength region. As absorbance  $A$  by a unit optical path length (1 cm) is given by eq. (1), the electronic transition absorption loss  $\alpha_e$  (dB/m) is obtained from eq. (2):

$$A = \epsilon c \quad (1)$$

$$\alpha_e = 10^3 A = 10^3 \epsilon c \quad (2)$$

Here  $\epsilon$  (1/mol cm) is molar extinction coefficient,

**Table I Amorphous Polymers**

Polymer	Structure	M (g/mol)	$\rho$ (g/cm <sup>3</sup> )
PMMA		100	1.19
PSt		104	1.07
PC		254	1.20
PAr		358	1.21
PSF		442	1.22
PES		232	1.37

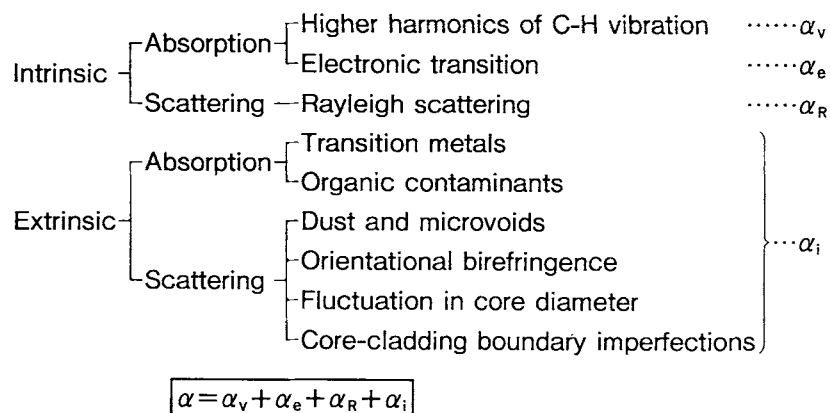


Figure 1 Loss factors for POFs.

and  $c$  (mol/l) is solution concentration. Isopropyl alcohol and dichloromethane were used as the measurement solvents because they did not absorb light in the measurement wavelength region.

### Measurement of Attenuation Loss of POFs

The POF attenuation loss spectrum was measured by a cut-back method<sup>1</sup> 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  $\alpha$  (dB/m) for the POF was calculated by using

$$\alpha \text{ (dB/m)} = 10 / (L_1 - L_2) \log(I_2 / I_1) \quad (3)$$

## RESULTS AND DISCUSSION

### Estimation of Intrinsic Losses of Plastic Optical Fibers

Attenuation loss  $\alpha$  of POFs is divided into four parts ( $\alpha_e$ ,  $\alpha_v$ ,  $\alpha_R$ ,  $\alpha_i$ ) as shown in eq. (4) and Figure 1.

$$\alpha = \alpha_e + \alpha_v + \alpha_R + \alpha_i \quad (4)$$

Figure 2 shows the separated intrinsic loss spectra of PMMA, according to this separation.<sup>8</sup> There is a difficulty in separating attenuation loss into individual loss factors like this example for many other polymers because of their partial crystallization, insolubility in solvent for spectral measurements, and

so on. PMMA represents a fortuitous case. Therefore, we have studied a simple method to estimate intrinsic losses of transparent amorphous polymers empirically from the chemical structure of the polymer repeating unit and have already derived empirical equations to estimate two of the intrinsic losses,  $\alpha_v$  and  $\alpha_R$ .<sup>6,7</sup> Those equations are shown below. In the present work, we present a new empirical equation to estimate  $\alpha_e$ , the remaining intrinsic loss.

### Absorption Loss Due to Harmonics of Molecular Vibrations<sup>4,6</sup>: $\alpha_v$

The  $\alpha_v$  is caused by the  $v$ th higher harmonic (overtone)  $\nu_v$  of the fundamental stretching vibration  $\nu_1$  and its combination tone  $\nu_v + \delta$  with bending vibration  $\delta$ . As is shown in Figure 2,  $\alpha_v$  decreases exponentially as the wavelength becomes shorter. For most chemical bonds, such as C—C, C—O, C=O, and so on,  $\nu_1$  is observed at longer wavelength in the IR region, so that  $\alpha_v$  due to these chemical bonds in the visible region is negligible compared with that due to the X—H (X—H=C—H, N—H, or O—H) bonds. Thus we derived Eqs. (5) and (6) to estimate the  $v$ th harmonic peak absorption loss  $\alpha_v(v)$  (dB/m) due to X—H bonds, which cause attenuation loss mainly from the visible to near-IR regions.<sup>6</sup>

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

$$\alpha_v(v) = 3.2 \times 10^5 n_{\text{XH}} \times \frac{\rho}{M} \frac{v! v (K - 2v - 1)}{(K - 3)(K - 3) \cdots (K - v - 1)} r \quad (6)$$

where  $\rho$  (cm<sup>3</sup>) is polymer density,  $M$  (g/mol) is molecular weight of a polymer repeating unit,  $n_{\text{XH}}$  means the number of C—H, N—H, or O—H

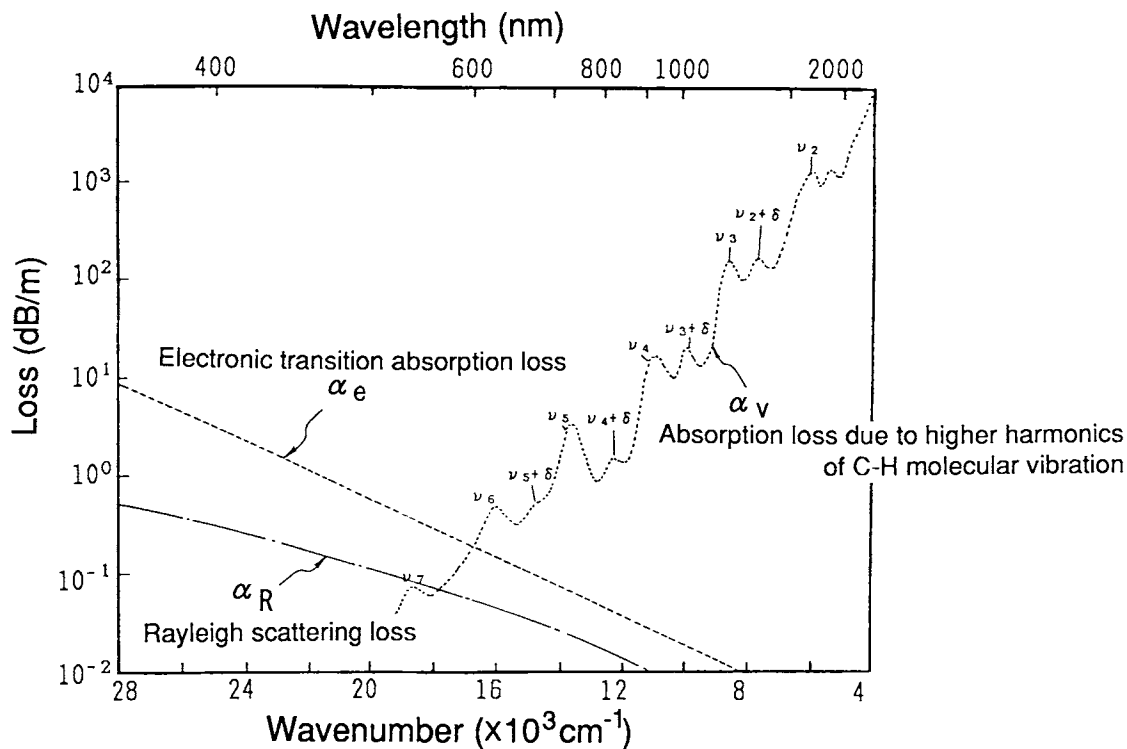


Figure 2 Intrinsic loss spectra of PMMA.

bonds in a polymer repeating unit,  $\chi$  is an anharmonicity constant,  $\nu_1$  ( $\text{cm}^{-1}$ ) is the fundamental frequency,  $K$  is the reciprocal of  $\chi$ ,  $\nu$  is the order of the higher harmonics, and  $r = E_1^{\text{XH}}/E_1^{\text{CH}}$ ,  $E_1^{\text{XH}}$  is the absorption strength due to the fundamental frequency of the X—H bond. Average values from experimental data in many of the model compounds are used as values of  $r$  and  $\chi$  of each X—H bond;<sup>6</sup> for a C—H bond,  $r = 1$  and  $\chi = 1.90 \times 10^{-2}$ ; for a N—H bond,  $r = 0.91$  and  $\chi = 2.10 \times 10^{-2}$ ; and for a O—H bond,  $r = 2.3$  and  $\chi = 1.84 \times 10^{-2}$ . The band tail between two peaks is estimated using a probability function.

#### Rayleigh Scattering Loss<sup>7</sup>: $\alpha_R$

Rayleigh scattering loss  $\alpha_R$  is caused by fluctuations of the density and refractive index in a polymer. The  $\alpha_R$  is divided into two losses.<sup>9-11</sup> One is isotropic scattering loss  $\alpha^{\text{iso}}$  and the other is anisotropic scattering loss  $\alpha^{\text{aniso}}$ . We derived an empirical equation to estimate  $\alpha_R$  (dB/m) as shown below:<sup>7</sup>

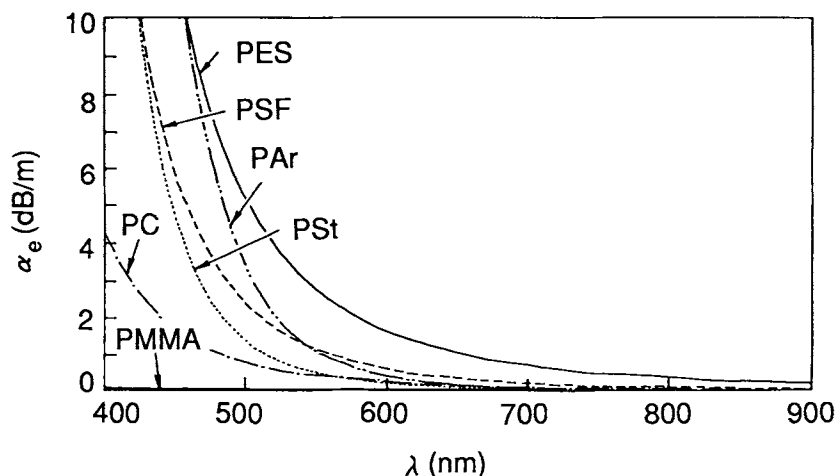
$$\begin{aligned} \alpha_R &= \alpha^{\text{iso}} + \alpha^{\text{aniso}} \\ &= \frac{1.0 \times 10^8}{\lambda^4} (n^2 - 1)^2 (n^2 + 2)^2 \\ &\quad + \frac{8.5 \times 10^9}{\lambda^4} (n^2 + 2)^2 \frac{\rho}{M} (5n_{\text{CC}}^2 + 0.3) \quad (7) \end{aligned}$$

where  $\lambda$  (nm) is wavelength,  $n$  is refractive index of a polymer,  $\rho$  ( $\text{cm}^3$ ) is polymer density,  $M$  (g/mol) is molecular weight of a polymer repeating unit, and  $n_{\text{CC}}$  is the number of benzene rings in the polymer repeating unit. In this equation we made two significant assumptions:<sup>7,9</sup> (i)  $H_V$  scattering, which is depolarized scattering intensity, is independent of the scattering angle and no large anisotropic order exists in a solid polymer. (ii) Excess light scattering  $V_{v2}$  equals zero, in other words,  $V_v$  scattering, which is polarized scattering intensity, means intensity of Rayleigh scattering, which has no angular dependence.

#### Electronic Transition Absorption Loss: $\alpha_e$

Absorption loss due to electronic transition in the visible region for organic compounds is caused by the existence of double bonds. That is, there are two kinds of electronic transition absorptions, those due to the  $\pi \rightarrow \pi^*$  transition of the carbon-carbon double bond ( $\text{>C=C<}$ ), and those due to the  $n \rightarrow \pi^*$  transition of the carbonyl group ( $\text{>C=O}$ ). The band tail of the electronic transition is related to the Urbach rule,<sup>12</sup> given by eq. (8):

$$\alpha_e = A_0 \exp\left(\frac{B_0}{\lambda}\right) \quad (8)$$



**Figure 3** Electronic transition absorption loss of amorphous polymers.

where  $A_0$  and  $B_0$  are material constants and  $\lambda$  (nm) is wavelength. The relationship between  $\alpha_e$  (dB/m) and absorbance  $A$  is given by eq. (2). From eqs. (2) and (8), we can estimate  $A_0$  and  $B_0$ . The  $\alpha_e$  with arbitrary wavelength  $\lambda$  is obtained using eq. (8). Using  $c = 10^3 \rho / M$  as concentration of a solid polymer, we calculate the  $\alpha_e$  of polymers.

Figure 3 shows the  $\alpha_e$  spectra of PMMA, PSt, PC, polyarylate (PAr), polysulfone (PSF), and polyethersulfone (PES) calculated from eq. (8) based on measured data from the polymer solution. From these spectra, we propose an empirical equation:

$$\alpha_e = \exp\left(\frac{3.84 \times 10^3}{\lambda} - 3.19\right) \frac{\rho}{M} \times (n_{CC} + n_{CO} + 3n_{CS}) \quad (9)$$

where  $\rho$  (g/cm<sup>3</sup>) 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 sulfur atom, respectively.

Table II lists the  $\alpha_e$  values of PMMA, PSt, PC, PAr, PSF, and PES estimated by eq. (9). Here, values in parentheses are the observed ones.  $D_e$  is defined as specific concentration of benzene rings in a polymer. These estimated values are nearly equal to the observed ones, so this indicates that our proposed empirical equation can estimate the  $\alpha_e$  of amorphous polymers, especially in aromatic polymers.

**Table II** Electronic Transition Absorption Loss of Amorphous Polymers

Polymers	$\frac{\rho}{M}$ (mol/cm <sup>3</sup> )	$n_{CC}$	$n_{CO}$	$n_{CS}$	$D_e$ (mol/cm <sup>3</sup> )	$\alpha_e$ (dB/m) <sup>a</sup>		
						$\lambda = 600$ nm	$\lambda = 700$ nm	$\lambda = 800$ nm
PES	$5.91 \times 10^{-3}$	2	0	2	$4.73 \times 10^{-2}$	1.18 (1.61)	0.47 (0.70)	0.24 (0.37)
PSF	$2.76 \times 10^{-3}$	4	0	2	$2.76 \times 10^{-2}$	0.69 (0.63)	0.28 (0.24)	0.14 (0.12)
PAr	$3.38 \times 10^{-3}$	3	2	0	$1.69 \times 10^{-2}$	0.42 (0.43)	0.17 (0.10)	0.08 (0.03)
PC	$4.72 \times 10^{-3}$	2	0	0	$9.44 \times 10^{-3}$	0.24 (0.25)	0.10 (0.11)	0.05 (0.06)
PSt	$1.03 \times 10^{-2}$	1	0	0	$1.03 \times 10^{-2}$	0.26 (0.21)	0.10 (0.06)	0.05 (0.02)
PMMA	$1.19 \times 10^{-2}$	0	0	0	0	0 (0.00)	0 (0.00)	0 (0.00)

<sup>a</sup> Values in parentheses are the observed ones.

### Estimation of Loss Spectrum

In the previous section we derived empirical equations to estimate three intrinsic losses from the chemical structure of a polymer repeating unit. When we know both density and refractive index of a polymer, we can estimate the intrinsic loss spectrum using these equations. It is, however, impossible for polymers, whose density and refractive index are not known, to predict intrinsic optical loss spectra. Thus we calculated polymer density  $\rho$  and refractive index  $n$  according to reported methods<sup>13,14</sup> and developed a new simulation.

### Calculation of Polymer Density<sup>13,14</sup>

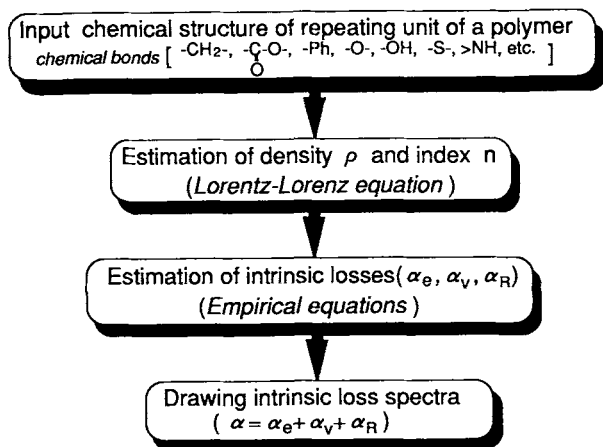
Density  $\rho$  of amorphous polymers can be calculated with the values of van der Waals radius, bonding distance, and bonding type. When an atom  $A_i$  (whose van der Waals radius is  $R_i$ ) connects with an atom  $A$ , occupied volume  $V_A$  of the atom  $A$  is defined as eq. (10):

$$V_A = 4\pi R^3/3 - \sum_i \pi h_i^2 (3R - h_i)/3 \quad (10)$$

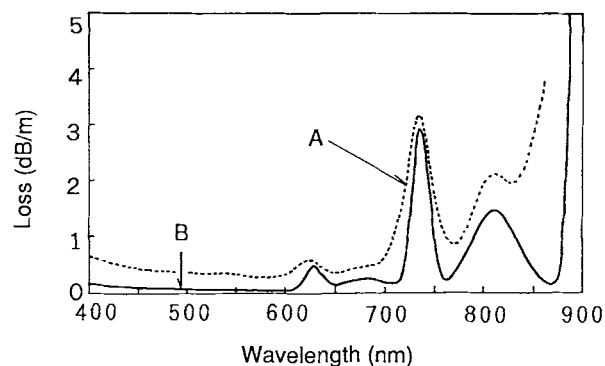
Here,  $h_i = R - (R^2 + d_i^2 - R_i^2)/(2d_i)$ . When the polymer repeating unit contains atoms from  $A_1$  to  $A_j$ , its molar volume is given by eq. (11):

$$V_{\text{int}} = N_A \sum_j V_{A,j} \quad (11)$$

where  $N_A$  is Avogadro constant. As molar volume  $V$  ( $= M/\rho$ ;  $M$  is molecular weight of a repeating unit) per unit volume is proportional to  $V_{\text{int}}$  and its packing constant  $K_p$  is 0.681, its density  $\rho$  is calculated by eq. (12):



**Figure 4** Estimation method of intrinsic loss spectra.



**Figure 5** Loss spectra of PMMA. (A) Attenuation loss of PMMA core POF (experimental), (B) estimated intrinsic loss from our empirical equations.

$$\rho = K_p M / V_{\text{int}} \quad (12)$$

Applying reference values regarding van der Waals radius of each atom to eq. (12), we can calculate polymer densities.

### Calculation of Refractive Index of Polymers<sup>14</sup>

We used a Lorentz-Lorenz equation to calculate refractive index  $n$  of polymers as shown in eq. (13):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi N \alpha' = \frac{[R]}{V} \equiv \phi \quad (13)$$

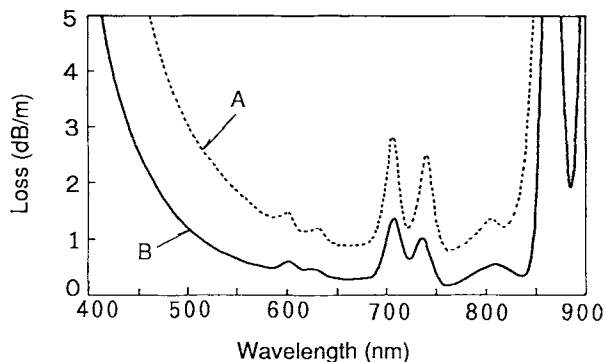
$$n = \sqrt{\frac{2\phi + 1}{1 - \phi}} \quad (14)$$

Here  $N$  is the number of molecules in a unit volume of a polymer,  $\alpha'$  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 atom in a polymer repeating unit to eqs. (13) and (14), we can calculate refractive index of a polymer.

### Simulation of Intrinsic Loss Spectra

Figure 4 shows a flow diagram for estimating intrinsic loss spectra of amorphous polymers empirically. We developed a computer program to predict the loss spectra of amorphous polymers from the chemical structures of polymer repeating units. The simulation is explained using two examples.

First, this simulation was applied to PMMA. We input the chemical structures of PMMA into the computer, such as CH<sub>2</sub>, C, CH<sub>3</sub>, C(=O)O, CH<sub>3</sub>, in order. In its polymer repeating unit, there are eight aliphatic C—H bonds, then  $n_{\text{CH}}$  (aliphatic)



**Figure 6** Loss spectra of PC. (A) Attenuation loss of PC core POF (experimental), (B) estimated intrinsic loss from our empirical equations.

equals eight. Since there are no other X—H bonds,  $n_{\text{NH}} = n_{\text{OH}} = 0$ . Similarly, there are no benzene rings in its repeating units, then  $n_{\text{CC}} = n_{\text{CO}} = n_{\text{CS}} = 0$ . Polymer density  $\rho$  and refractive index  $n$  were calculated using those parameters. In this case we obtained  $\rho = 1.17$  (1.19), and  $n = 1.49$  (1.49). Here, values in parentheses are the observed data. After these physical parameters were prepared, an intrinsic loss spectrum was drawn. Figure 5 shows an attenuation loss spectrum (curve A: experimental) of PMMA core POF and an intrinsic loss spectrum (curve B) estimated from our empirical equations. We considered that the difference between these spectra was due to the extrinsic loss  $\alpha_i$ . The shape of the predicted spectrum was similar to the experimental one.

Next, this simulation was applied to bisphenol-A type PC. We input the chemical structures of PC into the computer, such as O—Ph (Ph: phenyl  $\text{C}_6\text{H}_4$ ), C,  $\text{CH}_3$ ,  $\text{CH}_3$ , Ph—O,  $\text{C}=\text{O}$ , in order. In its polymer repeat unit, there are six aliphatic CH bonds and eight aromatic CH bonds, then  $n_{\text{CH}}$  (aliphatic) = 6,  $n_{\text{CH}}$  (aromatic) = 8. There are no other X—H bonds, so  $n_{\text{NH}} = n_{\text{OH}} = 0$ . However, there are two benzene rings in its repeating unit, then  $n_{\text{CC}} = 2$ . Though there is one carbonyl group, it does not neighbor a benzene ring, then  $n_{\text{CO}} = n_{\text{CS}} = 0$ . In this case we obtained  $\rho = 1.20$  (1.20), and  $n = 1.59$  (1.59). Values in parentheses are the observed data. Figure 6 shows spectra of PC. Curve A is an experimental one, that is, an attenuation loss spectrum of PC core POF, and curve B is an intrinsic loss spectrum estimated from our empirical equations. As shown in both Figures 5 and 6, shapes of predicted spectra were similar to the experimental ones.

Consequently, we confirmed that the empirical eqs. (6), (7), and (9) were applicable to estimation of intrinsic loss spectra of transparent amorphous polymers.

## CONCLUSION

We have clarified the relationship between the chemical structure of polymer repeating units and three intrinsic losses due to the polymer itself. Then we developed empirical equations to simulate the intrinsic loss spectra from the chemical structures of the polymer repeating units. The spectra obtained from the simulation agreed well with the experimental ones.

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