

# Empirical Prediction Method of Intrinsic Light Scattering Loss of Transparent Amorphous Polymers

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## SYNOPSIS

We studied simple empirical equations to estimate the values of intrinsic light scattering loss  $\alpha_R$  of various polymers applicable for plastic optical fibers, especially for aromatic amorphous polymers. The  $\alpha_R$  is divided into two losses, that is,  $\alpha^{\text{iso}}$  and  $\alpha^{\text{aniso}}$ . Here,  $\alpha^{\text{iso}}$  means the isotropic scattering loss;  $\alpha^{\text{aniso}}$ , the anisotropic scattering loss. The  $\alpha^{\text{iso}}$  is mainly a function of refractive index, and the  $\alpha^{\text{aniso}}$  is a function of refractive index, density, and the number of benzene rings in the polymer repeating unit. Therefore, when the polymer density and the structure of its repeating unit are known, the values of  $\alpha_R$  can be estimated. We derived new empirical equations for predicting the values of each intrinsic light scattering loss,  $\alpha^{\text{iso}}$  and  $\alpha^{\text{aniso}}$ . The estimated values were approximately equal to the experimental ones. The values of  $\alpha_R$  of aromatic amorphous polymers were not so large inherently, and they were a few hundred decibels per kilometer at the highest. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

As transparent aromatic amorphous polymers are highly heat resistant, their use for core materials of plastic optical fibers (POFs), optical waveguides, etc., which can be used in automobile engine chambers, is expected. Their intrinsic light scattering losses are considered to be much larger than those of aliphatic polymers, like poly(methyl methacrylate) (PMMA), however, because the chemical structures of their repeating units include benzene rings which have a very large optical anisotropy.<sup>1-7</sup> Therefore these aromatic polymers have not been used as core materials of POFs. Regarding polycarbonate (PC), its optical properties have been reported,<sup>6,7</sup> and a POF with a PC core has been developed commercially as a high heat-resistant POF. Other aromatic amorphous polymers have not been examined, and there might be some transparent ones among them. To study of intrinsic light scattering of polymers, it is necessary to purify them sufficiently to eliminate the effect of unknown impurities. But deriving a suitable purification procedure

for all aromatic polymers is difficult. Thus some simple prediction methods of intrinsic light scattering loss of the polymers are needed.

In this work we measured the intrinsic light scattering losses of several aromatic polymers and predicted those losses empirically from the chemical structures of their repeating units.

## EXPERIMENTAL

### Materials

Table I lists the amorphous polymers used to measure intrinsic light scattering losses in this study. To eliminate the effect of unknown impurities, the purification method for these polymers is shown below. Polycondensation type polymers, i.e., PC, polyarylate (PAr), polysulfone (PSF), and polyethersulfone (PES), were dissolved in dichloromethane and then filtered through a Teflon membrane filter (pore size: 0.2  $\mu\text{m}$ ). By adding a large amount of methanol to the filtrate, the polymers were reprecipitated and then dried under reduced pressure. Addition polymerization type polymers, i.e., PMMA and polystyrene (PSt), were polymerized using their purified monomers. Their monomers were purified carefully by an ordinary procedure, rinsing the

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**Table I Amorphous Polymers**

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

monomers with aqueous NaOH solution, and distilling them under reduced pressure. Rodlike samples, having a diameter of 10 mm $\phi$  was obtained by a press-casting method at a temperature above its glass transition temperature ( $T_g$ ).

#### Measurement of Light Scattering Loss

The light scattering loss ( $\alpha_R$ ) of the polymer was measured by the literature method.<sup>3</sup> Figure 1 gives a block diagram of the measurement apparatus for light scattering intensity. The light source was a He-Ne laser (wavelength, 633 nm), which was set up to obtain a vertical polarization. The laser beam was divided into two beams by a half-mirror. One was directly monitored by a photomultiplier tube to compensate for fluctuation of the laser intensity.

The other beam passed through a light chopper and polarizer and then entered the rodlike sample from the side. The gap between the sample and the inner wall of the glass cell was filled with immersion oil (refractive index: 1.5). This glass cell was perpendicularly located on the center of the goniometer. The scattered light intensity ( $V_v, H_v$ ) from the sample was detected by a photomultiplier [ $V_v$  ( $\text{cm}^{-1}$ ): polarized scattering intensity;  $H_v$  ( $\text{cm}^{-1}$ ): depolarized scattering intensity]. From Eq. (1) the intensity  $V_v^{\text{iso}}$  of the isotropic scattering is obtained. The isotropic turbidity  $\tau^{\text{iso}}$  ( $\text{cm}^{-1}$ ) and the isotropic scattering loss  $\alpha^{\text{iso}}$  (dB/m) due to  $V_v$  are estimated from Eq. (2), and the anisotropic turbidity  $\tau^{\text{aniso}}$  ( $\text{cm}^{-1}$ ) and the anisotropic scattering loss  $\alpha^{\text{aniso}}$  (dB/m) due to  $H_v$  are calculated from Eq. (3). The  $\alpha_R$  is given by Eq. (4).

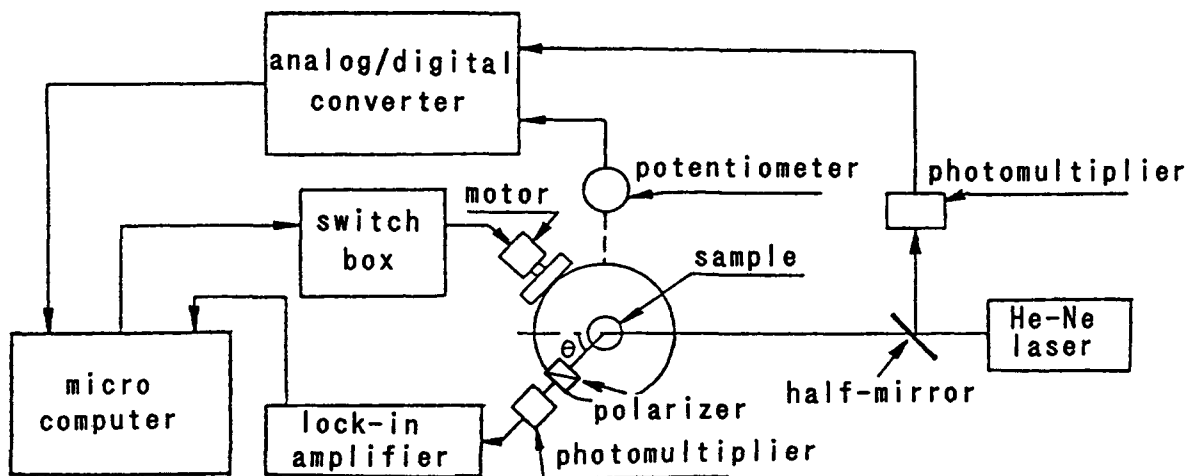


Figure 1 Diagram of light scattering measurement apparatus.

$$V_v^{\text{iso}} = V_v - \frac{4}{3} H_v \quad (1)$$

$$\alpha^{\text{iso}} = 4.342 \times 10^2 \times \tau^{\text{iso}}$$

$$= 4.342 \times 10^2 \frac{8}{3} \pi V_v^{\text{iso}} \quad (2)$$

$$\alpha^{\text{aniso}} = 4.342 \times 10^2 \times \tau^{\text{aniso}}$$

$$= 4.342 \times 10^2 \frac{80}{9} \pi H_v \quad (3)$$

$$\alpha_R = \alpha^{\text{iso}} + \alpha^{\text{aniso}} \quad (4)$$

## RESULTS AND DISCUSSION

### Prediction of Isotropic Scattering Loss

The  $\alpha_R$  is divided into two losses as shown in Eq. (4). The isotropic scattering loss  $\alpha^{\text{iso}}$  is further divided into two components, one is  $\alpha_1^{\text{iso}}$ , which has no angular dependence, and the other is  $\alpha_2^{\text{iso}}$ , which has an angular dependence due to heterogeneities existing in a polymer, i.e., fluctuation of density or refractive index of the polymer. We can decrease  $\alpha_2^{\text{iso}}$  to a negligible magnitude by annealing, so that we used the approximation  $\alpha_2^{\text{iso}} = 0$  in this study. We confirmed that the measured  $\alpha^{\text{iso}}$  curves of all polymers in Table I had no angular dependence. Thus we have defined  $\alpha_R$  as the ultimate loss limit of a polymer, that is, intrinsic light scattering loss.

The intensity  $V_v^{\text{iso}}$  of the isotropic scattering from thermally induced density fluctuations in a structureless liquid is given by Eq. (5),<sup>3</sup>

$$V_v^{\text{iso}} = \frac{\pi^2}{9\lambda^4} (n^2 - 1)^2 (n^2 + 2)^2 kT\beta \quad (5)$$

where  $\lambda$  (cm) is the wavelength under vacuum,  $n$  is the refractive index,  $k$  ( $=1.381 \times 10^{-16}$  erg/K) is the Boltzmann constant,  $T$  is the absolute temperature, and  $\beta$  ( $\text{cm}^2/\text{dyn}$ ) is the isothermal compressibility at the glass transition temperature  $T_g$ . Thus  $\alpha^{\text{iso}}$  (dB/m) is given by Eq. (6).

$$\alpha^{\text{iso}} = 4.342 \times 10^2 \times \tau^{\text{iso}} = \frac{5.50 \times 10^{-13}}{\lambda^4} (n^2 - 1)^2 (n^2 + 2)^2 T\beta \quad (6)$$

The  $\alpha^{\text{iso}}$  is a function of the refractive index ( $n$ ) and the isothermal compressibility ( $\beta$ ) of its polymer. Then if both values were known,  $\alpha^{\text{iso}}$  could be calculated accurately. However, we could not easily obtain  $\beta$  values of all other polymers, so that it is difficult to calculate  $\alpha^{\text{iso}}$  of all amorphous polymers from Eq. (6).

Table II lists values of  $n$  and  $\beta$  at the temperature over  $T_g$  of PMMA, PSt, PC, PAr, PSF, and PES from Refs. 1–9 and our experimental one. As shown in Table II, values of  $\beta$  at the temperature over  $T_g$  for these polymers are the same order, from  $5 \times 10^{-11}$  to  $8 \times 10^{-11}$ . As for the other many amorphous polymers, their  $\beta$  values are within the extent.<sup>8</sup> Thus we assumed that  $\beta$  at  $T_g$  was independent of the kind of polymers, that is,  $\beta = 6.3 \times 10^{-11}$   $\text{cm}^2/\text{dyn}$ , and proposed the following equation to estimate  $\alpha^{\text{iso}}$  (dB/m) empirically from the chemical structure of the polymer repeating unit:

$$\alpha^{\text{iso}} \approx \frac{1.0 \times 10^{-20}}{\lambda^4} (n^2 - 1)^2 (n^2 + 2)^2 \quad (7)$$

**Table II Physical Constants Concerning  $\alpha^{\text{iso}}$** 

Polymers	$n$	$(n^2 - 1)^2 (n^2 + 2)^2$	$T_g$ (°C)	$\beta$ (cm <sup>2</sup> /dyn)
PES	1.65	66.2	230	—
PSF	1.63	59.5	189	$5.6 \times 10^{-11}$ (220°C) <sup>a</sup>
PAr	1.60	50.6	193	$7.0 \times 10^{-11}$ (250°C)
PC	1.59	47.9	150	$8.0 \times 10^{-11}$ (250°C)
PSt	1.59	47.9	100	$5.8 \times 10^{-11}$ (100°C)
PMMA	1.49	26.5	120	$5.2 \times 10^{-11}$ (120°C)

<sup>a</sup> Values in parentheses are measured temperatures.

### Prediction of Anisotropic Scattering Loss

Next, the intensity  $H_v$  of the anisotropic scattering is given by Eq. (8):

$$H_v = \frac{16\pi^2}{135\lambda^4} (n^2 + 2)^2 N \delta^2 \quad (8)$$

where  $N$  ( $= N_0 \times \rho / M$ ) is the number of repeating units in 1 cm<sup>3</sup> of a polymer,  $N_0$  ( $= 6.02 \times 10^{23}$ ) is the Avogadro number,  $\rho$  (g/cm<sup>3</sup>) is the density of a polymer,  $M$  (g/mol) is the molecular weight of repeating units, and  $\delta^2$  ( $10^{-50}$  cm<sup>6</sup>) is the mean-square polarizability anisotropy of scattering centers. Therefore,  $\alpha^{\text{aniso}}$  (dB/m) is given by Eq. (9).

$$\begin{aligned} \alpha^{\text{aniso}} &= 4.342 \times 10^2 \times \tau^{\text{aniso}} \\ &= \frac{1.42 \times 10^4}{\lambda^4} (n^2 + 2)^2 N \delta^2 \quad (9) \end{aligned}$$

It is a function of the refractive index ( $n$ ),  $N$ , and  $\delta^2$ . However, we could not easily obtain  $\delta^2$  values of all other polymers, so that it is difficult to calculate  $\alpha^{\text{aniso}}$  of all amorphous polymers from Eq. (9). Therefore, if the value of  $\delta^2$  were known by an empirical procedure, we could estimate  $\alpha^{\text{aniso}}$  from the chemical structure of its repeating unit of a polymer.

Table III shows values of  $n$ ,  $N$ , and  $\delta^2$  of PMMA, PSt, and PC from Ref. 6. Here, we assumed that  $\delta^2$

was a function of the number ( $p$ ) of benzene rings in the polymer repeating unit. As shown in Fig. 2,  $\delta^2$  was proportional to  $p^2$ , and  $10^{-3} \times \delta^2 = 5p^2 + 0.3$ .

Thus we derived the following equation to estimate  $\alpha^{\text{aniso}}$  (dB/m) empirically from the chemical structure of the polymer repeating unit:

$$\alpha^{\text{aniso}} = \frac{8.5 \times 10^{-19}}{\lambda^4} (n^2 + 2)^2 \frac{\rho}{M} (5p^2 + 0.3) \quad (10)$$

### Estimation of Light Scattering Loss by Empirical Equations

The values of  $\alpha^{\text{iso}}$  and  $\alpha^{\text{aniso}}$  estimated from Eqs. (7) and (10) concerning PMMA, PSt, PC, PAr, PSF, and PES are shown in Table IV. The values estimated from Eqs. (7) and (10) agreed well with the values that were calculated from Eqs. (6) and (9) or observed with our samples. This indicates the validity of Eqs. (7) and (10). We could not obtain reasonable values of  $\alpha_R$  concerning PSF and PES because it was difficult to fabricate rodlike samples having no microvoids. Thus their values were very large, though their light scattering intensity had no angular dependence. Furthermore, the  $\alpha_R$  of aromatic amorphous polymers was not so large inherently, and it was only a few hundred decibels per kilometer, at the highest.

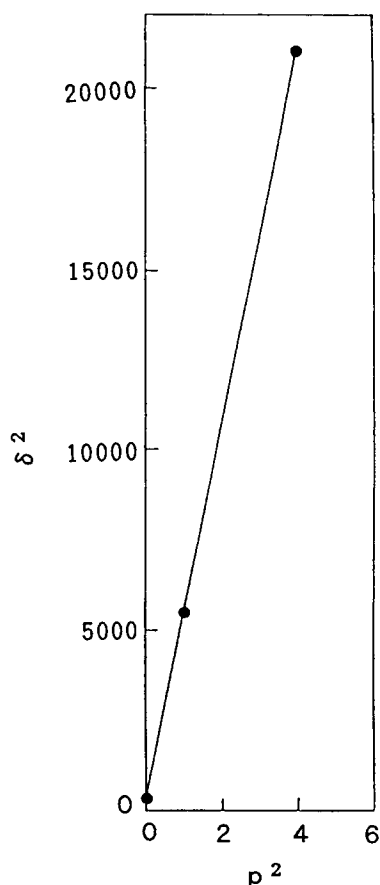
**Table III Physical Constants Concerning  $\alpha^{\text{aniso}}$** 

Polymers	$n$	$(n^2 + 2)^2$	$N = \frac{\rho}{M} N_0$ (cm <sup>-3</sup> )	$\delta^2$ ( $10^{-50}$ cm <sup>6</sup> )	$(n^2 + 2)^2 N \delta^2$
PC	1.59	20.5	$2.8 \times 10^{21}$	21000	$1.2 \times 10^{-23}$
PSt	1.59	20.5	$6.2 \times 10^{21}$	5506	$7.0 \times 10^{-24}$
PMMA	1.49	17.8	$7.2 \times 10^{21}$	326	$4.2 \times 10^{-25}$

**Table IV** Estimation of Light Scattering Losses of Amorphous Polymers (at  $\lambda = 633$  nm)

Polymers	$\rho/M$ (mol/cm <sup>3</sup> )	$n$	$p$	$\alpha^{\text{iso}}$ (db/m)			$\alpha^{\text{aniso}}$ (db/m)		
				Cal.		Obs.	Cal.		Obs.
				Eq. (6)	Eq. (7)		Eq. (9)	Eq. (10)	
PES	$5.91 \times 10^{-3}$	1.65	2	—	0.041	—	—	0.142	—
PSF	$2.76 \times 10^{-3}$	1.63	4	0.032	0.037	—	—	0.262	—
PAr	$3.38 \times 10^{-3}$	1.60	3	0.037	0.032	0.065	—	0.169	0.189
PC	$4.72 \times 10^{-3}$	1.59	2	0.037	0.030	0.060	0.104	0.104	0.106
PSt	$1.03 \times 10^{-2}$	1.59	1	0.028	0.030	0.021	0.060	0.059	0.060
PMMA	$1.19 \times 10^{-2}$	1.49	0	0.014	0.017	0.012	0.002	0.003	0.005

Consequently, if the polymer density and the structure of its repeating unit are known, we can estimate the intrinsic light scattering losses using those equations without any experimental measurements.



**Figure 2** Relation between the square number ( $p^2$ ) of benzene rings in the repeating unit of polymer and the mean-square polarizability anisotropy of scattering centers ( $\delta^2$ ).

## CONCLUSIONS

We derived new empirical equations for predicting intrinsic light scattering losses of transparent amorphous polymers. When the polymer density and the structure of its repeating unit were known, we could estimate the intrinsic light scattering losses using those equations. The intrinsic light scattering losses of aromatic amorphous polymers were not so large inherently, and they were a few hundred decibels per kilometer, at the highest.

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## REFERENCES

1. T. Kaino, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 37 (1987).
2. M. Fujiki, T. Kaino, and S. Oikawa, *Polym. J.*, **15**, 693 (1983).
3. Y. Koike, N. Tanio, and Y. Ohtsuka, *Macromolecules*, **22**, 1367 (1989).
4. N. Tanio, Y. Koike, and Y. Ohtsuka, *Polym. J.*, **21**, 259 (1989).
5. R. E. Judd and B. Crist, *J. Polym. Sci. Polym. Lett.*, **18**, 717 (1980).
6. M. Dettenmaier and E. W. Fischer, *Makromol. Chem.*, **177**, 1185 (1987).
7. A. Tanaka, H. Sawada, and N. Wakatsuki, *Fujitsu Sci. Tech. J.*, **23**, 166 (1987).
8. The Society of Polymer Science, Japan; *Polymer Data Handbook*, Baifukan, Tokyo, p. 575, 1986.
9. P. Zoller, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1453 (1982).

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