

Inherent Light Scattering Losses by Amorphous Optical Polymer Glasses

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ABSTRACT: Inherent light scattering losses by several methacrylic ester polymers were investigated. The intensities of polarized scattering (V_V) from poly(methyl methacrylate) (PMMA) reported so far were in the order of 10^{-5} cm^{-1} even in a sample polymerized with rigorous purification, and had angular dependence in its V_V intensity, which implied the existence of large size heterogeneities of several hundreds Å. In this paper, alkyl (ethyl and isobutyl) and fluoroalkyl (trifluoroethyl and trihydroperfluoropropyl) methacrylate glasses as well as PMMA, in which the V_V intensities were in the order of 10^{-6} cm^{-1} and no large size of heterogeneities were recognized, were prepared for the first time. Considering that our data are quite near the value predicted by the thermally induced fluctuation theory, and on the basis of our previous study, it is suggested that the scattering data presented in this paper show an inherent limited loss for these methacrylic ester polymer glasses in the atmosphere.

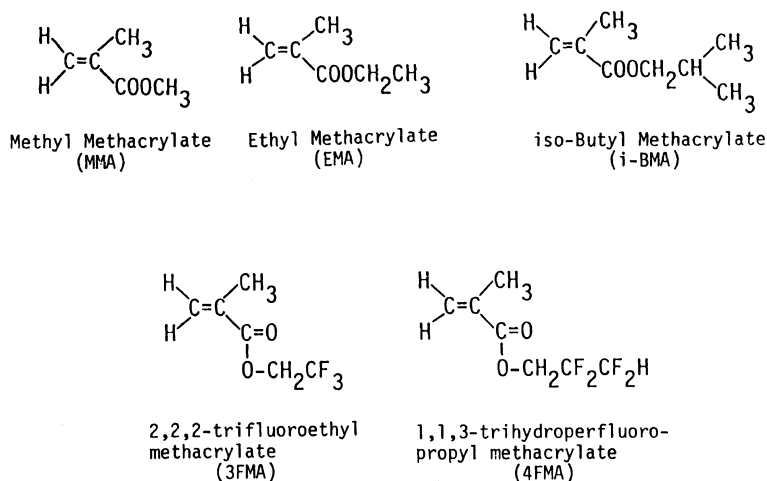
KEY WORDS Light Scattering / Methacrylic Ester Polymers / Heterogeneous Structure / Optical Polymer / Compressibility / Poly(methyl methacrylate) / Glass Transition Temperature /

Transparent amorphous polymer bulks have been expected as materials of polymer optical fibers^{1,2} and other new optical waveguides.³ In using them, a very slight amount of heterogeneity causes a large light scattering loss. Poly(methyl methacrylate) (PMMA) glass has been considered the most transparent among common optical polymer materials and is already used as a core material of polymer optical fiber. Even in highly purified PMMA bulks in which no nodular structure is observable by neutron or X-ray scatterings, large size heterogeneities of several hundreds Å have been invariably observed by the angular dependence of polarized light scattering (V_V) for all PMMA glasses reported so far.⁴⁻⁶ The light scattering intensities of these samples were much larger than the values predicted by a thermally induced fluctuation theory⁷ for structureless liquids, eq 1.

$$V_V^{\text{iso}} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 kT\beta \quad (1)$$

were V_V^{iso} is the isotropic part of V_V , n the refractive index of the polymer, k the Boltzmann's constant, T the absolute temperature, β the isothermal compressibility, and λ_0 the wavelength of light in vacuum.

Recently, we demonstrated^{8,9} that in spite of polymerization from contaminant-free monomer, the total light scattering loss of PMMA varied widely with polymerization conditions from *ca.* 13 dB km⁻¹ to *ca.* 800 dB km⁻¹ at $\lambda_0 = 633 \text{ nm}$. Here the anisotropic scattering loss coming from depolarized scattering (H_V) was almost unchanged in the range of 4—6 dB km⁻¹. In the PMMA sample with 13 dB km⁻¹, the isotropic scattering loss was *ca.* 9 dB km⁻¹ which was quite near the value predicted from eq 1, 9.5 dB km⁻¹, and no angular dependence in the V_V intensity was



Scheme 1.

observed.

It should be strongly emphasized that although PMMA samples prepared with different polymerization conditions or different thermal histories had isotropic scattering losses from 9 dB km^{-1} to *ca.* 800 dB km^{-1} with angular dependences in V_V , the scattering losses of all these samples were reduced to a constant loss *ca.* 9 dB km^{-1} with no angular dependence in V_V by sufficient heat treatment around 180°C . The value, 9 dB km^{-1} , is one order smaller than the data reported so far in contaminant-free PMMA glasses.

It is important to confirm if the thermally induced fluctuation theory is applicable to estimate inherent scattering loss in general methacrylic ester polymers with different structures, molecular weights, and tacticities, and if the PMMA is the most transparent among them as expected. In this paper, the inherent scattering losses for several methacrylic ester polymers suitable as material for polymer optical fibers or other optical devices were investigated, and compared with the value predicted by eq 1, on the basis of the previous study in PMMA glasses.⁹ The following methacrylic ester monomers were used in this paper:

EXPERIMENTAL

Preparation of Polymer Bulk

After an ordinary purification procedure of monomer with a distillation and $0.2 \mu\text{m}$ membrane filter, rigorous purification was carried out as follows: Ampul A with the distilled monomer was connected with two ampuls B and C carefully purified. Here, di-*tert*-butyl peroxide (DBPO) as an initiator and *n*-butyl mercaptan (nBM) as a chain transfer agent were placed in ampul B, and ampul C was empty. Ampuls A and B were frozen with liquid nitrogen, evacuated, and substituted by nitrogen. Then the monomers, DBPO, and nBM were degassed by several freeze-thaw cycles, and slowly distilled into the ampul C under vacuum by cooling ampul C with liquid nitrogen.

When glittering due to impurities in the monomer mixture was noted using a He-Ne laser beam, the monomer mixture in ampul C was tipped back into ampul A, and redistilled under vacuum into ampul C. This process was repeated until no glittering was detected in the distilled monomer mixture. Finally, ampul C was sealed under vacuum and immersed in silicone oil for polymerization. After polymerization under various conditions, the resulting

cylindrical polymer sample with a 20 mm diameter was taken out of ampul C for measurement.

Light Scattering Measurement

Light scattering measurements were made with our apparatus, the details of which are described elsewhere.⁹ The sample was placed in the center of the cylindrical glass cell. The gap between the sample and inner wall of the glass cell was filled with immersion oil with a refractive index of 1.5. This glass cell was perpendicularly located at the center of the goniometer, and a parallel beam of vertically polarized He-Ne laser (wavelength $\lambda_0 = 633$ nm) was injected from the side. The setting of the scattering angle (θ) and measurement of the scattering intensity were all conducted by a micro-computer, and the average scattering intensity for 200 times at a fixed scattering angle was employed for data analysis.

Polarized (V_V) and depolarized (H_V) scattered intensities were measured. Here, the letter H and V denote horizontal and vertical polarizations, respectively, and the upper case letter and subscript denote the scattered and incident beam, respectively. The measurement error of the scattering intensity (V_V or H_V) in the order of 10^{-8} cm^{-1} was less than 2%.

Other Measurements

Molecular weight was measured by gel permeation chromatography (GPC) (column; Showa Denko Co., Shodex AC-80M, RI; Showa Denko Co., Shodex RI SE-11) with chloroform as a carrier. The glass transition temperature (T_g) of polymers was measured by a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-1B), at a heating rate of $32^\circ\text{C min}^{-1}$.

The weight percentage of the remaining monomer in the PMMA bulk was measured as follows: The polymer sample was dissolved in a small amount of acetone, followed by adding methanol to precipitate the polymer. The

monomer content in the supernatant solution was measured by gas chromatography.

Refractive indices of polymers were measured by an Abbe refractometer (ATAGO Model 3).

Densities were determined by a floating method in a series of calcium nitrate aqueous solutions.¹⁰

ANALYTICAL PROCEDURE

In Figure 1 is shown a typical angular dependence in the V_V intensity due to large size heterogeneities inside polymer bulk. In order to analyze the local structure, we separated V_V into the two terms of eq 2.

$$V_V = V_{V1} + V_{V2} \quad (2)$$

where V_{V1} denotes the background intensity independent of the scattering angle, and V_{V2} , excess scattering with angular dependence due to large size heterogeneities. In a structureless liquid or randomly oriented polymer bulk, the isotropic part V_{V1}^{iso} of the V_{V1} is given by eq 3.

$$V_{V1}^{\text{iso}} = V_{V1} - (4/3)H_V \quad (3)$$

Here, the H_V intensity for all samples examined in this paper had no angular dependence.

Scattering loss was estimated by integrating the scattering intensities in all directions. Here the total light scattering loss α_t (dB km^{-1}) contains three terms, *i.e.*, α_1^{iso} , α_2^{iso} , and α^{aniso} .

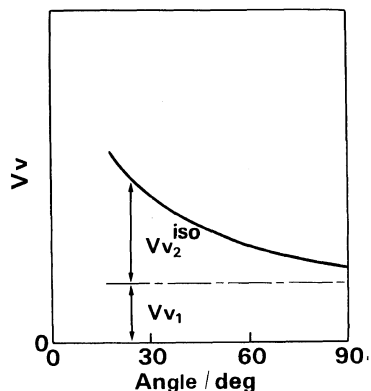


Figure 1. V_V scattering by polymer glass.

Here α_1^{iso} is the loss due to the V_{V1}^{iso} scattering without angular dependence, α_2^{iso} is due to the isotropic V_{V2} scattering with angular dependence, and α^{aniso} is due to anisotropic scattering (H_V).

$$\alpha_1^{\text{iso}}(\text{dB km}^{-1}) = 1.16 \times 10^6 \pi V_{V1}^{\text{iso}} \quad (4)$$

$$\alpha_2^{\text{iso}}(\text{dB km}^{-1}) = \frac{1.35 \times 10^9 a^3 \langle \eta^2 \rangle}{n^4 \lambda^4} \times \left\{ \frac{(b+2)^2}{b^2(b+1)} - \frac{2(b+2)}{b^3} \ln(b+1) \right\} \quad (5)$$

$$b = \frac{16\pi^2 a^2}{\lambda^2}$$

$$\alpha^{\text{aniso}}(\text{dB km}^{-1}) = 3.86 \times 10^6 \pi H_V \quad (6)$$

Equation 5 is obtained using Debye's theory.^{11,12} Here a (Å) is called the correlation length and is a measure of the size of the heterogeneous structure inside the bulk. $\langle \eta^2 \rangle$ denotes the mean-square average of the fluctuation of all dielectric constants, n is the refractive index of medium, and λ is the wavelength of light in a medium.

These scattering losses in our treatment are based on the following two assumptions:

(1) The H_V is independent of the scattering angle.

(2) The V_{V2} scattering having angular dependence is superimposed on the constant background V_{V1} .

RESULTS AND DISCUSSION

First, we have to confirm the validity of the above two assumptions in our data analysis. For the assumption (1), no samples prepared in this paper had angular dependence in the H_V intensities which were in the order of 10^{-7} cm^{-1} , which implies that no anisotropic order exists inside the samples. Therefore, assumption (1) seems reasonable in our experiment. For assumption (2), it is difficult to experimentally discriminate the V_{V2} com-

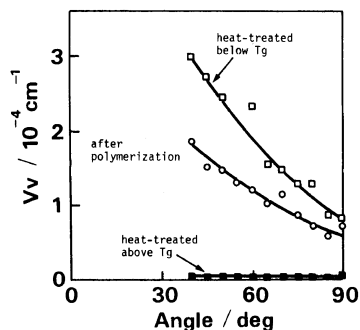


Figure 2. V_V scattering by PMMA glass polymerized at 70°C for 216 h (○). □, heat-treated at 70°C for 24 h; ■, sufficiently heat-treated at 180°C.

ponent from the observed V_V . In Debye's theory,¹² $V_{V2}^{-1/2}$ vs. $\sin^2(\theta/2)$ gives a linear relation (Debye plot). Therefore, by changing the V_{V2} value between 0 and the observed V_V little by little, V_{V2} where the Debye plot became closest to a straight line was obtained by a least square technique in a computer, and was used.

Figure 2 shows the effect of heat treatment above and below T_g on V_V vs. the scattering-angle curve in the PMMA glass polymerized at 70°C for 216 h. While the V_V intensity increased by heat-treatment at 70°C below T_g , the V_V intensity dramatically decreased by enough heat-treatment at 180°C at which the angular dependence in the V_V intensity completely disappeared. The scattering parameters and physical properties of these samples are listed in Table I. After the polymerization, a heterogeneous structure of *ca.* 860 (Å) was observed, where the dielectric fluctuation with $\langle \eta^2 \rangle = 43 \times 10^{-9}$ existed inside the bulk, causing a scattering loss of $\alpha_2^{\text{iso}} = 239 \text{ dB km}^{-1}$. The total scattering loss α_1 was 325 dB km^{-1} , this being much larger than the value predicted from the fluctuation theory. On the other hand, at sufficient heat-treatment at 180°C, this size heterogeneity almost completely disappeared and the total loss was reduced to 13 dB km^{-1} . It is noteworthy that the α_1^{iso} of 8.9 dB km^{-1} is quite near the value, 9.5 dB km^{-1} , as predicted by eq 1 using the

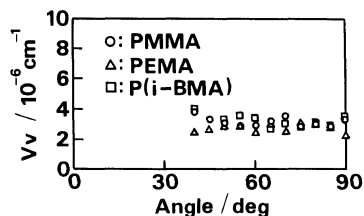
Table I. Properties of PMMA glass polymerized at 70°C for 216 h

	a	$\langle \eta^2 \rangle$	α_1^{iso}	α_2^{iso}	α^{aniso}	α_1	T_g	Remaining monomer
	Å	$\times 10^{-9}$	dB km ⁻¹	dB km ⁻¹	dB km ⁻¹	dB km ⁻¹	°C	wt%
After polymerization	856	43.2	79.7	238.9	6.3	324.9	86	4.7
Heat-treated at 70°C for 24 h	868	113.2	87.9	638.0	7.6	733.5	97	4.0
Sufficiently heat-treated at 180°C	—	—	8.9	0	4.0	12.9	102	1.7

published β^{13} for PMMA glass.

Although with heat treatment at 180°C the T_g increased from 86°C to 102°C due to the reduction of remaining monomer from 4.7 wt% to 1.7 wt%, it was confirmed in ref 9 that the remaining monomer up to *ca.* 5 wt% did not significantly increase the excess scattering. We can say that the reduction of remaining monomer in Table I is not related to the remarkable decrease in scattering loss. It was confirmed in ref 9 that the large excess scattering in the PMMA is not caused by the molecular weight of polymers in the range of $M_w = 4 \times 10^4 - 1.2 \times 10^5$, the stereoregularity due to the specific tacticity of PMMA, nor crosslinking as a result of the gel effect.

Possibly, the strain inhomogeneities caused by the volume contraction during polymerization are relaxed by heat treatment above T_g . Considering that volume contraction from monomer to polymer in the bulk polymerization of PMMA is about 20%, it is reasonably considered that this would cause some strain inhomogeneity composed of dense and sparse domains in polymerization below T_g . This would have a dominant effect on the excess scattering of the PMMA glass reported so far, although many origins of the excess scattering in PMMA were proposed. The anisotropic scattering loss, α^{aniso} in Table I was almost unchanged compared with other isotropic scattering losses. Therefore, the strain inhomogeneity with the correlation length a (Å) in Table I would be mainly composed of

**Figure 3.** V_v scattering by PMMA, poly(EMA), and poly(i-BMA) glasses polymerized at 130°C for 96 h.

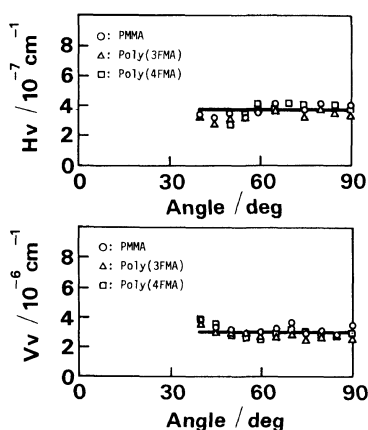
isotropic heterogeneous structures with dense and sparse domains.

In order to investigate the inherent scattering loss for methacrylic ester polymers, polymerization or heat treatment above T_g was carried out. Figure 3 shows the V_v scattering intensities of PMMA ($T_g = 111^\circ\text{C}$), Poly(ethyl methacrylate) (PEMA) ($T_g = 60^\circ\text{C}$), and Poly(isobutyl methacrylate) (P(i-BMA)) ($T_g = 54^\circ\text{C}$) glasses polymerized at 130°C for 96 h. The V_v scattering intensities of PEMA and P(i-BMA) which had more bulky side chains than PMMA were independent on the scattering angle and no large size heterogeneities were recognized. It is noteworthy that the scattering losses for these methacrylic ester polymer bulks are almost the same as the PMMA bulk. The V_v scattering with angular dependence in these polymers prepared by other different conditions were all reduced to the values quite near V_v in Figure 3.

Fluoroalkyl methacrylate polymers are expected to serve as new optical materials because of their high resistance to water-

Table II. Properties of PMMA, poly(3FMA), and poly(4FMA) glasses polymerized at 130°C for 96 h

Sample	Refractive index	α_1^{iso}	α_2^{iso}	α^{aniso}	α_t	T_g
	n	dB km ⁻¹	dB km ⁻¹	dB km ⁻¹	dB km ⁻¹	(°C)
PMMA	1.487	9.7	0	4.7	14.4	111
Poly(3FMA)	1.419	8.2	0	4.1	12.3	95
Poly(4FMA)	1.421	8.4	0	4.6	13.0	97

**Figure 4.** V_V and H_V scattering by PMMA, poly(3FMA), and poly(4FMA) glasses polymerized at 130°C for 96 h.

absorption and its lower refractive indices. Some fluoroalkyl methacrylates have been already used as clad material for plastic optical fibers. However, the inherent scattering loss and local structure for these fluoroalkyl methacrylate polymers have not been clarified. The V_V and H_V scatterings of poly(2,2,2-trifluoroethyl methacrylate, 3FMA), poly-(1,1,3-trihydroperfluoropropyl methacrylate, 4FMA) glasses are shown in Figure 4 with those of PMMA. It is interesting that the light scattering losses of their fluoroalkyl methacrylate glasses were almost the same as that of PMMA, and that no angular dependence in the V_V and H_V intensities was recognized. As in the same in other polymers, the V_V and H_V of these fluoroalkyl methacrylate polymers prepared with different polymerization conditions resulted in almost

the same values in Figure 4 by sufficient heat treatment above T_g .

The scattering parameters, refractive index, and T_g for these fluoroalkyl polymers are summarized in Table II. The fluctuation theory for structureless liquids indicates that according to eq 1, scattering loss decreases with decrease in refractive index. Since fluorine-containing polymers have lower refractive indices, these polymers have been expected as transparent optical materials for plastic optical fibers or other optical waveguides. For instance, assuming only the effect of refractive index, if the refractive index of polymer is reduced from 1.5 to 1.4, the scattering loss predicted by eq 1 becomes about one half. If it is assumed that the isothermal compressibilities β in eq 1 for poly(3FMA) and poly(4FMA) are the same as that of PMMA, α_1^{iso} calculated by eq 1 should be 5.9 dB km⁻¹ and 6.0 dB km⁻¹, respectively. However, the experimental α_1^{iso} values for these polymers in Table II are larger than these values, being 8.2 dB km⁻¹ and 8.4 dB km⁻¹, respectively.

In order to investigate the inherent scattering loss for these polymer glasses, we should consider the isothermal compressibility β in eq 1. However, the β for these polymers has not been measured precisely by the mechanical procedure. Boyer and Miller¹⁴ calculated the β at a liquid-liquid transition temperature¹⁵ (T_{ll}) universally from the cross-sectional area (A) per polymer chain. The area A was calculated from a molecular weight (M_c) between chain entanglements.¹⁶ On the other hand,

Hoffmann¹⁷ found a linear correlation between M_c and the square of the volume of monomer unit in the chain ($V_g(\text{cm}^3 \text{mol}^{-1})$). Therefore, combining the above relations, the compressibility β is calculated by obtaining the volume $V_g = M_0/d$ where M_0 is the molecular weight of a monomer unit and d is the density of the polymer. The M_c values calculated from the V_g for alkyl methacrylate polymers were quite consistent with the values experimentally obtained by a viscoelasticity measurement.

The compressibilities β at T_{11} for PMMA, poly(3FMA), and poly(4FMA) calculated from the V_g were 6.0×10^{-11} , 6.7×10^{-11} , and $7.4 \times 10^{-11} \text{cm}^2 \text{dyn}^{-1}$ respectively. Although we could not obtain the compressibility at T_g , the relation of $T_{11} = T_g + ca. 75(\text{K})$ has been proposed for most polymers.¹⁴ The temperature dependence of the compressibility (*i.e.*, the slope of the β vs. temperature curve) in the range between T_g and T_{11} slightly decreased on increasing the volume of the side chain of methacrylic ester polymers.¹⁸ Therefore, the difference of the compressibility β at T_g among PMMA, poly(3FMA), and poly(4FMA) may be slightly enlarged compared with the difference at T_{11} . As described above, the calculated β of poly(3FMA) and poly(4FMA) are 1.1 and 1.2 times the β of PMMA at T_{11} , respectively. Using these β , the predicted α_1^{iso} values from eq 1 should be slightly larger than 6.6 and 7.4dB km^{-1} for poly(3FMA) and poly(4FMA), respectively, which approach the α_1^{iso} values of 8.2 and 8.4dB km^{-1} in Table II.

Considering these opposite effects between β and the refractive index on the isotropic scattering loss, the values of α_1^{iso} of fluorine-containing polymers in Table II may be quite near the values predicted by the fluctuation theory, eq 1. It is concluded that the scattering losses in this paper for methacrylic ester polymer glasses are essentially inherent losses that occur in the atmosphere. In the above discussion, the polymer having a small side chain generally has a lower compressibility β .

Therefore, in order to prepare more transparent polymer materials, amorphous fluorine-containing monomers with lower polarizability and with no bulky side chains should be used.

CONCLUSIONS

The inherent light scattering losses for several methacrylic ester polymers, candidates for the polymeric optical materials, were investigated. It is noteworthy that the light scattering losses of some alkyl and fluoroalkyl methacrylate glasses were one order smaller than the value of the PMMA reported so far, and no large size heterogeneities were recognized. The isotropic losses for these polymers presented in this paper are near the values predicted by the thermally induced fluctuation theory, and seem essentially inherent limited loss for these methacrylic ester polymer glasses in the atmosphere.

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