

Temperature Dependence of Light Scattering by Low-Loss Poly(methyl methacrylate) Glasses

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ABSTRACT: A poly(methyl methacrylate) glass with the lowest light scattering loss (13 dB km^{-1} at 633 nm wavelength) among data reported so far and with no angular dependence in its scattering intensity was prepared by radical polymerization above the glass transition temperature (T_g) (Sample A). The temperature dependence of the light scattering intensity for this PMMA glass was investigated, in comparison with the PMMA glass polymerized below T_g and having excess scattering loss (hundreds dB km^{-1}) due to large-size heterogeneous structures (Sample B). In the sample A, the polarized scattering intensity (V_v) slightly changed below T_g and increased smoothly with increasing temperature above T_g in accordance with the fluctuation theory for structureless liquids. On the other hand, in the sample B, an abrupt decrease in V_v scattering around T_g was observed with increasing temperature. On the basis also of our previous study, it is suggested that the different trend of temperature dependences of light scattering and of excess scattering even in highly purified PMMA glasses depends on whether the strain inhomogeneities generated during the polymerization process are already relaxed above T_g or retained below T_g , and that the scattering behavior is not directly affected by first order structures such as molecular weight, tacticity, and remaining monomers.

KEY WORDS Light Scattering / Poly(methyl methacrylate) / Temperature Dependence / Glass Transition Temperature / Heterogeneous Structure / Glassy Polymer / Optical Polymer /

Recently, the possibility of lowering the light scattering loss in poly(methyl methacrylate) (PMMA) glass used as the core materials of a plastic optical fiber has been discussed.¹⁻⁶ The light scattering loss of the PMMA glasses prepared from contaminant-free monomer depended on the conditions of polymerization and heat-treatment.^{1,2} We succeeded in preparing the PMMA glass^{1,2} with a light scattering loss of 13 dB km^{-1} (633 nm) which is the lowest value among reported data so far, and is close to the value predicted from the fluctuation theory⁷ for structureless liquids. As for the PMMA glass with excess scattering, the angular dependence of scattered light intensity suggests the existence of heterogeneous regions (several hundreds Å) with the order of

10^{-5} — 10^{-4} of refractive-index differences. It was experimentally and theoretically clarified that this fluctuation would not be caused by the inhomogeneity in the molecular weight, inherent tacticity, nor contamination of monomer.^{1,2}

Two-types of temperature dependences of the light scattering were reported for PMMA glasses. In one type, an abrupt decrease in the polarized scattered light intensity (V_v) occurred around glass transition temperature (T_g) on heating.⁸ In the other type, the V_v intensity slightly increased below T_g , and smoothly increased above T_g with rising temperature.^{5,9} In those papers, the relation between the temperature dependence of the V_v and heterogeneous structures was not discussed. There-

fore, the origin of the temperature dependence of light scattering in PMMA glasses is still obscure.

In this study, we prepared two different PMMA glasses from carefully purified monomer, which perhaps correspond to the above two-types samples reported so far. One was polymerized below T_g , and had excess scattering (hundreds dB km^{-1}) due to the large-size heterogeneity. The other was polymerized above T_g , which had no excess scattering, and the total scattering loss was 13 dB km^{-1} (633 nm). The difference in the temperature dependence of V_v intensity between two samples is quantitatively discussed, considering the local structures inside the PMMA glasses.

EXPERIMENTAL

Preparation of PMMA Bulk

In order to eliminate the effects of unknown impurities on light scattering, a PMMA sample was prepared by carefully purifying the monomer as follows: First, inhibitors in the MMA monomer were removed by washing with 0.5 N NaOH aqueous solution, followed by washing out a slight amount of NaOH with pure water. The monomer was dried over Na_2SO_4 , filtered through a $0.2 \mu\text{m}$ membrane filter, and distilled under reduced pressure (bp $46\text{--}47^\circ\text{C}/100 \text{ mmHg}$) into a cleaned ampul A.

Further, rigorous purification was carried out as follows: The ampul A containing the distilled monomer was connected with two ampuls B and C carefully cleaned. Here, di-tert-butyl peroxide (DBPO) as an initiator and *n*-butyl mercaptan (nBM) as a chain transfer agent were placed in the ampul B, and the ampul C was empty. Ampuls A and B were frozen with liquid nitrogen, evacuated, and then substituted by nitrogen. Then MMA, DBPO, and nBM were degassed by several freezethaw cycles, and slowly distilled into the ampul C under vacuum by cooling the ampul C with liquid nitrogen. Finally, the ampul C was sealed under vacuum, and immersed in

silicone oil for polymerization. After polymerization under various conditions, the resulting cylindrical PMMA sample with a 20 mm diameter was taken out of the ampul C for measurement of light scattering.

Light Scattering Measurement

A scattered light intensity was measured by apparatus described in detail elsewhere.^{1,2} Polarized (V_v) and depolarized (H_v) scattered light intensities were measured using the incident beam of wavelength $\lambda_0 = 633 \text{ nm}$. To estimate the absolute intensity, pure benzene purified in the same manner as the monomer mixture mentioned above was used as a standard for calibration. The observed depolarization factor ρ was 0.42 and close to the published value of 0.43 (633 nm wavelength).¹⁰ Measurements could be made over the range of scattering angle θ from 30° to 120° . In this paper, the measuring temperature was from room temperature to 150°C .

The turbidity of polymer bulk is written as,

$$\tau = \pi \int_0^\pi \left\{ (1 + \cos^2 \theta)(V_{v1} + V_{v2}) + (2 + \sin^2 \theta)H_v \right\} \sin \theta d\theta \quad (1)$$

where V_{v1} denotes the background component contained in V_v , which is independent of the scattering angle, and V_{v2} is the excess scattering with the angular dependence. The isotropic part (V_{v1}^{iso}) of V_{v1} is given by Eq. (2).

$$V_{v1}^{\text{iso}} = V_{v1} - \frac{4}{3} H_v \quad (2)$$

When there is no angular dependence in H_v , the angular dependence of the V_v is attributed to the isotropic scattering V_{v2}^{iso} due to the large size of heterogeneities. Therefore,

$$\tau = \pi \int_0^\pi \left\{ (1 + \cos^2 \theta)(V_{v1}^{\text{iso}} + V_{v2}^{\text{iso}}) + \frac{(13 + \cos^2 \theta)}{3} H_v \right\} \sin \theta d\theta \quad (3)$$

Each turbidity for $V_{V_1}^{\text{iso}}$, $V_{V_2}^{\text{iso}}$, and H_V were independently calculated in eq 3, and converted to scattering loss (dB km^{-1}) as follows: The total light scattering loss α_t (dB km^{-1}) is composed of three terms, *i.e.* α_1^{iso} , α_2^{iso} , and α^{aniso} , where α_1^{iso} is the scattering loss coming from the $V_{V_1}^{\text{iso}}$, α_2^{iso} from the $V_{V_2}^{\text{iso}}$, and α^{aniso} from the anisotropic scattering, H_V . Since V_{V_1} and H_V are independent of the scattering angle, α^{aniso} and α_1^{iso} are given by eq. 4 and 5, details of which are described elsewhere.^{1,2}

$$\alpha^{\text{aniso}}(\text{dB km}^{-1}) = 1.21 \times 10^7 H_V \quad (4)$$

$$\alpha_1^{\text{iso}}(\text{dB km}^{-1}) = (3.64 V_{V_1} - 4.85 H_V) \times 10^6 \quad (5)$$

Here, H_V and V_{V_1} have a unit of cm^{-1} .

By Debye's thermal fluctuation theory^{11,12}, α_2^{iso} is given as,

$$\alpha_2^{\text{iso}}(\text{dB km}^{-1}) = \frac{1.35 \times 10^{16} a^3 \langle \eta^2 \rangle}{n^4 \lambda^4} \times \left\{ \frac{(b+2)^2}{b^2(b+1)} - \frac{2(b+2)}{b^3} \ln(b+1) \right\} \\ b = \frac{16\pi^2 a^2}{\lambda^2} \quad (6)$$

Here, symbol a (nm) 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 the medium, and λ (nm) the wavelength of light in the medium.

Other Measurements

The molecular weight (\bar{M}_w) was measured by a 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 temperatures (T_g) of polymers were 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 concentration in the supernatant solution was determined by gas chromatography. Then, the weight percentage of the monomer was calculated.

RESULTS AND DISCUSSION

Figure 1 shows the effect of polymerization time on V_V scattering intensity, where the samples were polymerized at 70°C . The weight percentages of DBPO and nBM were each 0.20 wt% (unless otherwise noted, the concentrations of DBPO and nBM were each 0.20 wt% in this paper). With increase in polymerization time, the V_V intensity increased. The scattering parameters and properties of these PMMA samples are summarized in Table I. With the polymerization time from 4 days to 10 days, the total scattering loss α_t remarkably increased from 62 dB km^{-1} to 734 dB km^{-1} , while the anisotropic scattering loss α^{aniso} slightly increased from 4 to 7 dB km^{-1} . The correlation length slightly increased, but, $\langle \eta^2 \rangle$ remarkably increased from 10.5×10^{-9} to 113.2×10^{-9} . It is suggested that the isotropic inhomogeneities with the order of several hundreds Å are formed during polymerization. Here, it was noted that the remaining monomer decreased from 5.5 wt% to 4.0 wt% as shown in Table I. However, in other samples polymerized at 130°C for 96 h, 150°C for 24 h, and 180°C for 24 h, the V_V intensity

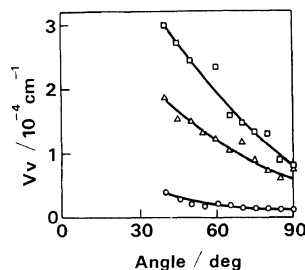


Figure 1. V_V scattering by PMMA glasses polymerized at 70°C for 4 days (○), 9 days (△), and 10 days (□).

Table I. Properties of PMMA glasses polymerized at 70°C for 4 days, 9 days, and 10 days

Polymerization time	a	$\langle \eta^2 \rangle$	α_1^{iso}	α_2^{iso}	α^{aniso}	α_1	T_g	Remaining monomer
day	Å	$\times 10^{-9}$	dB km^{-1}	dB km^{-1}	dB km^{-1}	dB km^{-1}	°C	wt%
4	676	10.5	16.8	40.8	4.4	62.0	79.5	5.5
9	856	43.2	79.7	238.9	6.3	324.9	85.7	4.7
10	868	113.2	87.9	638.0	7.6	733.5	96.9	4.0

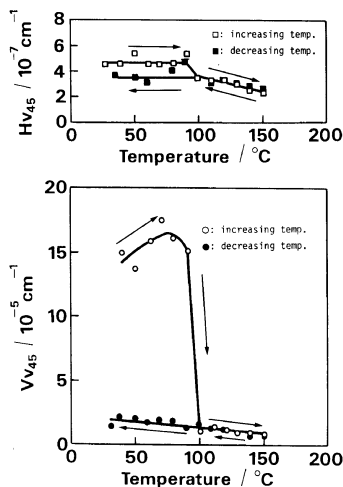


Figure 2. Temperature dependence of V_{v45} and H_{v45} components for PMMA glass polymerized at 70°C for 216 h. □, ○, increasing temp; ■, ●, decreasing temp.

did not increase even in the long heat-treatment at 70°C for 6 days, and the amount of remaining monomer (3.6 wt%) was almost unchanged; the details for this will be published soon. From these results, we believe that the large size heterogeneity at 70°C is formed by the isotropic strain brought about from this slight decrease in the remaining monomer from 5.5 to 4.0 wt%.

Figure 2 shows the temperature dependence of V_V scattering at 45° (V_{v45}) and H_V scattering at 45° (H_{v45}) for PMMA glass with excess scattering on both heating and cooling. This PMMA sample was polymerized at 70°C for 216 h (9 days) ($\bar{M}_w = 1.1 \times 10^5$, remaining monomer = 4.7 wt%). With increasing temperature, an abrupt decrease in V_{v45} around

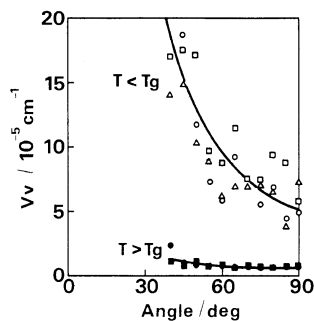


Figure 3. V_V scattering by PMMA glass polymerized at 70°C for 216 h. Measured at 30°C (○), 40°C (△), 70°C (□), 100°C (●), and 130°C (■) (increasing the temperature).

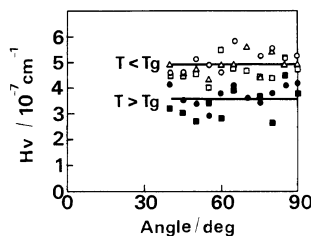


Figure 4. H_V scattering by PMMA glass polymerized at 70°C for 216 h. Measured at 30°C (○), 40°C (△), 70°C (□), 100°C (●), and 130°C (■) (increasing the temperature).

$T_g = 85.7^\circ\text{C}$ (by DSC) was observed. Figures 3 and 4 show the temperature dependences of V_V and H_V intensities from $\theta = 40^\circ$ to 90° for this sample on heating, respectively. The scattering parameters are listed in Table II.

In the case of increasing temperature, when the measured temperature T was lower than T_g , all V_V intensities had angular dependence and were almost the same in the range of 30–70°C. On the other hand, when $T > T_g$,

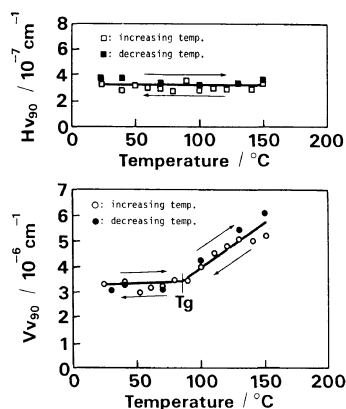
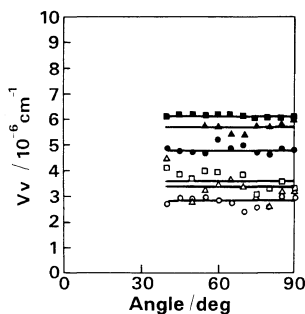
Table II. Temperature dependence of scattering parameters of PMMA glass polymerized at 70°C for 216 h (increasing the temperature)

Measuring temperature °C	a Å	$\langle \eta^2 \rangle$ $\times 10^{-9}$	α_1^{iso} dB km $^{-1}$	α_2^{iso} dB km $^{-1}$	α^{aniso} dB km $^{-1}$	α_t dB km $^{-1}$
30	856	43.2	79.7	238.9	6.3	324.9
40	738	40.4	97.3	178.9	5.9	282.2
70	735	53.8	129.8	236.5	5.7	372.0
100	512	2.4	15.4	5.9	4.5	25.8
130	522	3.3	14.5	8.3	4.2	26.9

the V_V intensity abruptly decreased to *ca.* $6 \times 10^{-6} \text{ cm}^{-1}$ with little angular dependence. If PMMA samples have large size heterogeneities, the V_V scattering at low angle increases. Figure 3 and Table II indicate that these heterogeneous structures with dielectric fluctuations $\langle \eta^2 \rangle \simeq 50 \times 10^{-9}$ almost vanished above T_g . In the case of decreasing temperature from 150°C to 24°C, no abrupt changes in V_V and H_V around T_g were observed. It is suggested that the isotropic strain inhomogeneities generated during polymerization below T_g is relaxed when measured above T_g .

As for anisotropic change with increasing temperature, the anisotropic scattering loss α^{aniso} slightly decreased from 6.3 dB km $^{-1}$ to 4.2 dB km $^{-1}$. Probably the apparent excess anisotropic loss, *ca.* 2 dB km $^{-1}$, was caused by radial-birefringence² which occurred irregularly by adhesion between the sample and inner wall of the glass tube during volume contraction when polymerizing or cooling the sample.

Figure 5 shows the temperature dependence of V_V scattering at 90° (V_{V90}) and H_V scattering at 90° (H_{V90}) for the PMMA glass with no excess scattering and no angular dependence. These PMMA samples were polymerized at 130°C for 96 h, 150°C for 24 h, and 180°C for 24 h ($\bar{M}_w = 5.9 \times 10^4$, $T_g = 85.1^\circ\text{C}$, remaining monomer = 3.6 wt%). The V_{V90} intensity slightly increased from 24°C to 90°C near T_g , and smoothly increased with temperature from 90°C to 150°C. Here, as shown in Figure 6, the


Figure 5. Temperature dependence of V_{V90} and H_{V90} components for PMMA glass polymerized at 130—150—180°C cycle. □, ○, increasing temp.; ■, ●, decreasing temp.

Figure 6. V_V scattering by PMMA glass polymerized at 130—150—160—180°C cycle. Measured at 30°C (○), 40°C (△), 70°C (□), 100°C (●), 130°C (▲), and 150°C (■) (increasing the temperature).

V_V scattering had no angular dependence at any temperature. This temperature dependence of the V_V was reversible for increasing and de-

Table III. Temperature dependence of scattering parameters of PMMA glass polymerized at 130°C for 96 h–150°C for 24 h–180°C for 24 h (increasing the temperature)

Measuring temperature °C	a Å	$\langle \eta^2 \rangle$ $\times 10^{-9}$	α_1^{iso} dB km $^{-1}$	α_2^{iso} dB km $^{-1}$	α^{aniso} dB km $^{-1}$	α_1 dB km $^{-1}$
24	—	—	9.5	0	4.1	13.7
40	—	—	10.2	0	4.0	14.2
70	—	—	10.8	0	3.7	14.5
100	—	—	12.6	0	3.4	16.0
130	—	—	17.2	0	3.7	20.9
150	—	—	19.8	0	3.9	23.7

creasing temperature. The H_V scattering was also independent of both temperature and scattering angle. Table III shows scattering parameters at various temperatures.

The isotropic part V_V^{iso} of the V_V is given by eq. 7.

$$V_V^{\text{iso}} = V_V - \frac{4}{3} H_V \quad (7)$$

The intensity of the isotropic V_V^{iso} scattering from thermally induced density fluctuations in a structureless liquid is written as,⁷

$$V_V^{\text{iso}} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 k T \beta \quad (8)$$

where λ_0 is the wavelength of light in vacuum, k the Boltzmann constant, T the absolute temperature, and β the isothermal compressibility.

The observed and calculated V_V^{iso} values below and above T_g are shown in Figure 7. The observed V_V^{iso} value was obtained from Figure 5 with eq 2. The calculated V_V^{iso} was obtained from eq 8 as follows: At $T < T_g$, the V_V^{iso} was calculated using the values of refractive index n and T at each temperature and the value¹³ of β at 100°C (near to T_g) according to a frozen model^{4,8}, while at $T > T_g$, the values of n , T , and β at corresponding temperatures were used. The observed V_V^{iso} are in good agreement with calculated ones throughout the entire temperature range investigated. Crist reported⁴ that the scattering loss limit of PMMA glasses was 14 dB km $^{-1}$ at 633 nm wavelength

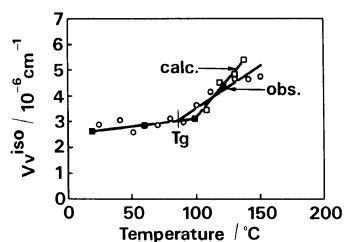


Figure 7. Temperature dependence of observed (○) and calculated (□, ■) V_V^{iso} components for PMMA glass polymerized at 130–150–180°C cycle. □, β at each temperature; ■, β at 100°C.

using the reported β value at 120°C. However, the T_g for our PMMA glass with low loss exists around 85–100°C. When the β value at 100°C is used in eq 8, the calculated α_1^{iso} at 24°C is 9.7 dB km $^{-1}$ which is close to our experimental α_1^{iso} value (9.5 dB km $^{-1}$) at 24°C in Table III. Therefore, it becomes clear in this paper that the fluctuation theory expressed by eq 8 is quantitatively applicable to PMMA glasses with no large size of heterogeneities.

Recently, the temperature dependence of light scattering by PMMA glasses has been reported. With regard to the V_V scattering, the results reported by Patterson⁹ and Fujiki *et al.*⁵ were qualitatively similar to our results for low loss PMMA glass. As for the temperature dependence of the H_V scattering, the result reported by Patterson⁹ was similar to our results, although the absolute value was not presented.

Dettenmair and Fischer⁸ who studied the

V_V scattering for commercial PMMA glasses reported the abrupt decrease in V_V around T_g . This result is similar to our result of PMMA glass (polymerized below T_g) with excess scattering and angular dependence in V_V . Probably, the strain inhomogeneities in this PMMA glass are relaxed when increasing temperature around T_g .

We believe that the different trend of temperature dependences of light scattering around T_g in these two types may occur according to whether the isotropic strain inhomogeneities formed during polymerization are already relaxed or not. The first order structures such as molecular weight, tacticity, and remaining monomers would not be directly related to this temperature dependence as described elsewhere.^{1,2}

CONCLUSION

The temperature dependence of light scattering by two-types PMMA glasses was investigated. As for PMMA glass with excess scattering, an abrupt decrease in V_V scattering around T_g due to relaxation was observed with increasing temperature. In the case of low loss PMMA glass with no excess scattering, the V_V intensity underwent a small change below T_g , and increased smoothly with temperature above T_g , according to the fluctuation theory for

structureless liquids. A slight amount of decrease in the remaining monomer at high conversion polymerization below T_g brought about extreme increase in the light scattering loss from 13 dB km^{-1} to several hundreds dB km^{-1} , possibly due to the occurrence of isotropic inhomogeneous strain.

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