Physical Aging and Light Scattering of Low-Loss Poly(methyl methacrylate) Glass

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(Received June 26, 1997)

ABSTRACT: Isothermal aging has been carried out on low-loss poly(methyl methacrylate) (PMMA) glass at 18°C below the glass transition temperature (T_g). The effect of enthalpy relaxation on light scattering loss of PMMA glass which had no excess scattering was investigated by the use of differential scanning calorimeter (DSC) and light scattering measurement. The light scattering intensity of PMMA glass did not increase with increasing aging time. It is seen that the light scattering loss of glassy PMMA is not affected inherently by physical aging as a result of its approach to thermodynamic equilibrium at a temperature 18°C below its T_g .

KEY WORDS Physical Aging / Light Scattering Loss / Poly(methyl methacrylate) / Glass Transition Temperature / Enthalpy Relaxation / Amorphous Polymer / Polymer Glass /

Polymer glasses are essentially thermodynamic non-equilibrium states. Physical aging¹ is the term used to describe the time dependence of changes in the behavior of a polymer glass held at temperatures below the glass transition; such changes are normally the result of continuous slow relaxation of the glass from its initial non-equilibrium state towards its final thermodynamic equilibrium state. The thermodynamical properties such as volume^{2,3} or enthalpy^{4,5} have been mainly considered for the study of this phenomenon. After a quench into the glassy state, the polymer shows a continuous decrease of the specific volume with time, which leads to a decrease in free volume and thus of mobility of the polymer molecules. This change of mobility of the molecular segments is assumed to be the origin of the change in dynamic mechanical properties during aging.⁶ Many other properties of amorphous polymer glasses can be affected by aging. However, the effect of isothermal aging, and the resulting densification, on the optical properties of amorphous polymer glasses has not been studied well.

Poly(methyl methacrylate) (PMMA) glass is a common optical amorphous polymer and has been already used as a core material of polymer optical fiber (POF). The two important intrinsic loss factors in POF are C–H overtone absorption and Rayleigh scattering due to density fluctuations. Recently, we demonstrated that the light scattering loss of PMMA glasses, even in using contaminant-free monomer varied widely with polymerization and heat-treatment conditions.^{7–11} PMMA glasses polymerized below the glass transition temperature (T_g) had excess scattering loss (hundreds dB km⁻¹) due to large-size (several hundreds Å) heterogeneous structure with the order of 10⁻⁵–10⁻⁴ of refractive-index difference. On the other hand, with sufficient heat-treatment above the T_g , this size heterogeneity

almost completely disappeared and the isotropic light scattering loss was reduced to 9.7 dB km⁻¹ (633 nm) which is close to the value (9.5 dB km⁻¹) predicted from the thermally induced fluctuation theory.¹² The glass transition temperature is the critical temperature for determining the excess light scattering of PMMA glasses.

In this study, isothermal aging has been carried out on low-loss PMMA glass at 18°C below T_g . The effect of enthalpy relaxation on light scattering loss of PMMA glass which had no excess scattering was investigated as it approached equilibrium by the use of differential scanning calorimeter (DSC) and light scattering measurement.

EXPERIMENTAL

Preparation of PMMA Bulk

After an ordinary purification procedure of methyl methacrylate (MMA) monomer with a distillation (bp 46–47°C/100 mmHg) and 0.2 µm membrane filter, a rigorous purification was carried out as follows: Ampoule A with the distilled monomer was connected with two ampoules B and C carefully purified. Here, di-*tert*-butyl peroxide (DBPO) as an initiator and *n*-butyl mercaptan (*n*BM) as a chain transfer agent were placed in ampoule B and ampoule C was empty. Ampoules A and B were frozen with liquid nitrogen, evacuated, and substituted by nitrogen. Then the monomers, DBPO, and *n*BM were degassed by several freeze-thaw cycles, and slowly distilled into the ampoule C under vacuum by cooling ampoule C with liquid nitrogen. Ampoule C was sealed under vacuum and immersed in silicone oil for polymerization. After polymerization, the resulting cylindrical polymer sample with a 20 mm diameter was removed from ampoule C for measurement.

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Light Scattering Measurement

Light scattering measurements were made with light scattering spectrophotometer (Otsuka Electronics, DLS-7000). The details of theory and analytical procedure of light scattering were described elsewhere.⁷ 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. In this paper, polarized (V_V) and depolarized (H_V) scattered intensities were measured at room temperature. Here the letters H and V (or v) denote horizontal and vertical polarization, respectively, and the upper case letter and the subscript denote the scattered and the incident beam, respectively. 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 measurement error of the scattering intensity (V_V or H_V) was less than 2%.

In order to analyze the local structure, we separated V_V into the two terms of eq 1.

$$V_V = V_{V1} + V_{V2} \quad (1)$$

where V_{V1} denotes the background intensity independent of the scattering angle, and V_{V2} denotes the 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 V_{V1} is given by eq 2.

$$V_{V1}^{\text{iso}} = V_{V1} - (4/3)H_V \quad (2)$$

Here, the H_V intensity for our sample examined in this paper had no angular dependence (see ref 7).

Scattering loss was estimated by integrating the scattering intensities in all directions. 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} . Here α_1^{iso} is the loss due to the isotropic 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 .

$$\alpha_1^{\text{iso}} (\text{dB km}^{-1}) = 1.16 \times 10^6 \pi V_{V1}^{\text{iso}} \quad (3)$$

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

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

$$\alpha^{\text{aniso}} (\text{dB km}^{-1}) = 3.86 \times 10^6 \pi H_V \quad (5)$$

Equation 4 is obtained using Debye's theory.^{13,14} Here symbol a ($\text{\AA}$) is called the correlation length and is a measure of the size of the heterogeneous structure inside the bulk. Symbol $\langle \eta^2 \rangle$ 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.

Enthalpy Relaxation Measurement

The enthalpy relaxation of polymer glasses was measured by means of DSC (Shimadzu Co., DSC-50). The following standard thermal history was employed for the low-loss PMMA sample:

1) In order to eliminate the effects of previous thermal history after polymerization, the PMMA sample was annealed at 110°C for 3 h.

2) The PMMA sample was annealed for an aging time of t_a at the chosen aging temperature T_a (in this study, $T_a = 90^\circ\text{C}$).

3) The PMMA sample was quenched down to the room temperature.

4) Then DSC measurements were carried out on increasing temperature from room temperature to 170°C at a heating rate of $10^\circ\text{C min}^{-1}$.

Other Measurement

The molecular weight was measured by a gel permeation chromatography (GPC) (Tosoh Co., HLC-8120GPC) with tetrahydrofuran (THF) as a carrier. The densities were compared by preparing aqueous solutions of calcium nitrate and determining whether test specimens sank or floated in these standard solutions.¹⁵

RESULTS AND DISCUSSION

The total light scattering loss of PMMA glasses varies widely with polymerization conditions from *ca.* 13 dB km^{-1} to *ca.* 800 dB km^{-1} at $\lambda_0 = 633$ nm.⁷⁻¹¹ With polymerization above the T_g , the isotropic light scattering loss was reduced to 9.7 dB km^{-1} (633 nm) which is close to the value (9.5 dB km^{-1}) predicted from the thermally induced fluctuation theory.¹² The intensity of the isotropic light scattering (V_{V1}^{iso}) from thermally induced density fluctuations in a structureless liquid is written as,¹²

$$V_{V1}^{\text{iso}} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 k T \beta \quad (6)$$

where λ_0 is the wavelength of light in vacuum, k is the Boltzmann constant, T is the absolute temperature, n is the refractive index, and β is the isothermal compressibility. The fluctuation theory for structureless liquids indicates that according to eq 6, the isotropic scattering loss decreases with the decrease in isothermal compressibility and refractive index. The value of V_{V1}^{iso} calculated using the value of β at T_g according to a frozen model was good agreement with the observed value for PMMA glass.⁸ In this study, the low-loss PMMA glass with no excess scattering (its isotropic light scattering loss at 633 nm is 9.7 dB km^{-1}) was used for calorimetric and light scattering measurement. This PMMA sample ($M_w = 7.0 \times 10^4$, $M_w/M_n = 2.1$) was polymerized at 130°C for 96 h and the weight percentages of DBPO and *n*BM were each 0.20 wt%.

The heat capacity of a polymer glass undergoes a step change in the glass transition region. We have defined the glass transition temperature, T_g , as the temperature at which the change of heat capacity associated with glass transition is $\Delta C_p/2$, where ΔC_p is the specific heat

Figure 1. DSC curves of PMMA glasses aged at 90°C.

Figure 2. Enthalpy relaxation (ΔH) plotted as a function of aging time for PMMA glass at 90°C.

increment between the liquid and glass states at glass transition region. The value of T_g for unaged low-loss PMMA glass was 108°C.

Physical aging is the phenomenon which is known to be time- and temperature-dependent.¹⁶ Most of the studies on physical aging for amorphous polymers have been performed at temperatures close to T_g . We measured the enthalpy relaxation for low-loss PMMA glass at temperatures, $T_g - 28^\circ\text{C}$, $T_g - 18^\circ\text{C}$, and $T_g - 8^\circ\text{C}$. The amounts of enthalpy relaxation was 3.3, 3.8, and 1.8 J g^{-1} , respectively. The maximum value of enthalpy relaxation was found at $T_g - 18^\circ\text{C}$. Therefore, in this work, we have studied isothermal aging effects occurring at 18°C below T_g . DSC studies of the enthalpy relaxation process for low-loss PMMA glasses of different aging times at 90°C ($= T_g - 18^\circ\text{C}$) are illustrated in Figure 1. Aging at 90°C produces an endothermic peak at the glass transition temperature. When aging times increase, the endothermic peak increases. From these thermograms, enthalpy relaxation ΔH can be determined by taking the difference between the curve corresponding to the quenched state and the curves corresponding to different aged states. Figure 2 presents the evolution of ΔH as a

Figure 3. Density plotted as a function of aging time for PMMA glass at 90°C.

Figure 4. V_V scattering by PMMA glasses aged at 90°C.

Table I. Light scattering losses of PMMA glasses aged at 90°C

Aging time, t_a	ΔH	α_1^{iso}	α_2^{iso}	α^{aniso}	α_t
days	J g^{-1}	dB km^{-1}	dB km^{-1}	dB km^{-1}	dB km^{-1}
0	0	9.7	0	2.8	12.6
7	-2.5	8.7	0	2.6	11.3
28	-3.1	9.3	0	2.6	12.0
70	-3.8	9.6	0	2.7	12.3

function of aging time for an aging temperature of 90°C.

The density measurements for low-loss PMMA glass were performed with isothermal aging at 90°C. The result is shown in Figure 3. Before aging, the value of density was 1.191. With increasing time, the density increased, and reached to 1.193 at 70 days. This increase is caused by the densification due to the aging effect below T_g , which was recognized by a large enthalpy relaxation peak just after the T_g in Figure 1 when increasing the temperature.

In order to rigorously confirm the effect of the densification on the excess scattering, polarized (V_V) and depolarized (H_V) scattering intensities were measured for aged PMMA samples. Figure 4 shows V_V scattering for unaged and aged PMMA glasses. Before aging, the isotropic V_V scattering had no angular dependence and isotropic light scattering loss, α_1^{iso} value was 9.7 dB km^{-1} as shown in Table I. With increasing aging time, the isotropic light scattering V_V did not increase, and α_1^{iso} value at 70 days was 9.6 dB km^{-1} . Figure 5 shows H_V

Figure 5. H_V scattering by PMMA glasses aged at 90°C.

scattering for unaged and aged PMMA glasses. The H_V scattering was also independent of both aging time and scattering angle, and anisotropic light scattering loss α^{aniso} was about 2.7 dB km^{-1} at any aging time. This result means that the densification during aging below T_g does not generate the large-size isotropic or anisotropic heterogeneities and occurs homogeneously. It is seen that light scattering loss of PMMA glass is not affected inherently by physical aging.

PMMA glasses polymerized below T_g had excess scattering loss (hundreds dB km^{-1}) due to large-size (several hundreds Å) heterogeneous structure with the order of 10^{-5} – 10^{-4} of refractive-index difference. It was experimentally and theoretically clarified that this fluctuation would not be caused by a small amount of remaining monomers or additives, the molecular weight of polymers, the stereoregularity due to the specific tacticity of PMMA, nor crosslinking as the result of the gel effect.⁷

We investigated the effect of the heat treatment below and above T_g on the V_V intensity.⁷ It is quite interesting to point out that when PMMA glass polymerized below T_g was continuously heated below T_g , the V_V intensity gradually increased, decreasing the remaining monomer. However, when PMMA glass polymerized below T_g was heat treated above T_g , the V_V intensity remarkably decreased to the value predicted by the thermally induced fluctuation theory. Thus we can say that the T_g is the critical temperature for determining the excess scattering. Furthermore, the temperature dependence of the V_V intensity around T_g was investigated.⁸ As for low-loss PMMA glass with no excess scattering, the V_V versus temperature was quite consistent with the fluctuation theory. On the other hand, in the case of PMMA glass with excess scattering, an abrupt decrease in V_V scattering around T_g was observed with increasing temperature.

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 to several hundreds dB km^{-1} . In the case of PMMA, the volume contraction in the polymerization process is about 20%. The excess scattering is, we believe, mainly due to voids caused by the volume shrinkage accompanying polymerization of the remaining monomer trapped inside the polymer glass. We proposed an excess scattering model¹¹ at high conversion from the assumption that the heterogeneous structure consists of two phases due to the localization of the monomer, initiator, and voids caused by shrinkage during polymerization. This excess scattering model proposed shows that if a slight amount of monomer trapped inside the PMMA glass is polymerized *in situ*, generating slightly localized voids due to the aggregation of the unreacted initiator, a 1 wt% rise in the conversion around $P=95 \text{ wt\%}$ increases the scattering loss by several hundreds dB km^{-1} .

CONCLUSION

Isothermal aging has been carried out on low-loss PMMA glass at 18°C below T_g as the polymer approaches equilibrium. The effect of enthalpy relaxation on light scattering loss of PMMA glass which had no excess scattering was investigated by differential scanning calorimetry, density and light scattering measurements. The light scattering intensity of PMMA glass did not increase with increasing aging time. It is seen that light scattering loss of PMMA glass is not affected by physical aging under the above conditions.

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