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Physical aging in poly(methyl methacrylate) glass: densification via density fluctuation

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Abstract

The physical aging in poly(methyl methacrylate) during annealing just below T_g was investigated by light scattering and oscillating-DSC in which a sinusoidal temperature rise was imposed over the conventional linear temperature rise. Light scattering intensity decreased monotonously with increasing scattering angle. The intensity was found to increase rapidly and then to decrease gradually with annealing time t_a. The correlation length and the mean-square density fluctuations by Debye–Bueche plot increased at an early stage and then decreased with t_a. The width of the glass transition, obtained by the Fourier transform treatment of the oscillated DSC heat flow, increased with t_a at an early stage and then decreased. The endothermic peak, given by the non-reversing part of the oscillating DSC heat flow, appeared even at an early stage of the aging. These results suggest that: (1) as-quenched PMMA glass is partially densified to yield an inhomogeneity in density with a correlation length about 200 nm; (2) by the annealing, the density fluctuations grow at first by a decrease in density at the low density regions and an expansion of the low density regions to increase the correlation length; and (3) the densification then proceeds at the low density regions to reduce the correlation length and to get higher density as a whole, by approaching a rather homogeneous glassy state.

Keywords: Density fluctuation ; Light scattering; Oscillating DSC

1. Introduction

When amorphous polymers are rapidly cooled below the glass transition temperature T_g, the thermodynamic quantity such as enthalpy is frozen-in at around the T_g. Hence, glassy polymers usually exist at a nonequilibrium state. Annealing of glassy polymers below the T_g results in a relaxation of the thermodynamic quantity toward an equilibrium state. This process is referred to as physical aging [1,2]. The relaxation of the enthalpy can be monitored by differential scanning calorimetry (DSC). An endothermic peak appears in the DSC thermogram when the aged polymer is reheated around the glass transition region. The peak increases in magnitude and shifts to higher temperatures with increasing aging time [3–8]. Associated with the enthalpy relaxation, the glassy polymer is densified [1–3] and the free volume decreases [9,10].

In poly(methyl methacrylate) (PMMA), excess light scattering having a strong scattering angle dependence was found and a long-range density fluctuation with a correlation length about 200 nm was suggested [11,12]. The excess scattering was also demonstrated in organic and inorganic glasses such as *o*-terphenyl, poly(methyl-*p*-tolysiloxane) [13–15], and B_2O_3 [16–18]. Thus the density fluctuation seems to be general for glassy materials.

In this paper, to understand the nature of the density fluctuation in the glassy materials, we investigate the time variation of the density fluctuation during the physical aging in PMMA glass by light scattering and oscillating-DSC in which one can separate the glass transition and the endothermic peak [19–26].

2. Experimental section

The polymer specimen used in this study is commercial PMMA, supplied by Mitsubishi Rayon Co. Ltd; MD001, $M_w = 75\,000$, $M_w/M_n = 1.9$.

The specimen was compression-molded at 170°C for 5 min into a thick film about 2 mm thick and was then quenched in an ice-water bath. The thick film thus prepared was used for the light scattering study. A thin film about 0.2 mm thick was also prepared in the same way as above. The thin specimen was for the oscillating-DSC study. The

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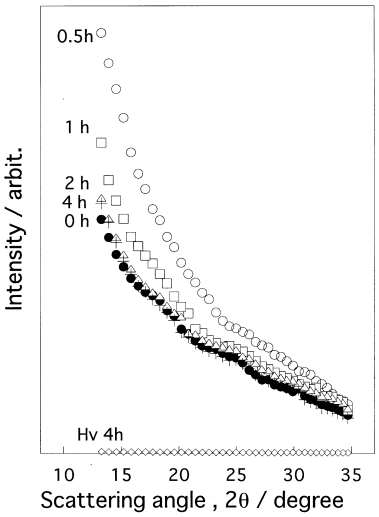

Fig. 1. The change in Vv light scattering profiles of PMMA at 80°C with aging time: ●,0 h; ○,0.5 h; □,1 h; △,2 h; + ,4 h, and Hv light scattering profile at aging time of 4 h: ◇.

thin film of 10 mg was placed in an aluminum pan and annealed at 170°C for 5 min to eliminate the effect of previous thermal and mechanical histories. After the specimen was rapidly quenched to room temperature, it was annealed at 80°C for various aging times and then cooled rapidly to room temperature.

A 633 nm He–Ne laser (5 mW; LHR-151, Melles Griot Co. Ltd) was used as a light source. After passing through a Glan–Tompson polarizer and a light chopper, vertically-polarized incident light was passed through the specimen, placed in a hot chamber set at a desired temperature. The scattered light from the sample passed through a Glan–Tompson analyzer and a narrow bandpass filter (3 nm half width at 633 nm) to isolate the Rayleigh scattering. We employed two optical geometries; one was the Vv geometry in which the optical axis of analyzer was set parallel to that of polarizer, and the other was the Hv geometry with a perpendicular set of the two axis. The scattered light was detected by a photomultiplier (R268, Hamamatsu Photonics Co. Ltd) mounted on a goniometer. The photocurrent was converted to EMF and measured with a single-phase lock-in amplifier (5600, NF Electronic Instrument Co., Ltd). The angular distribution of scattering intensity $I(\theta)$ was obtained after applying the correction for the scattering volume [27].

The oscillating-DSC thermogram was measured by a Seiko Instruments Exster 6200 calibrated with standard Indium. The data were stored in a Hewlett Packard 712/100 Work Station. A sinusoidal temperature rise was imposed over the conventional linear temperature rise: [19–26]

$$T = T_0 + Bt - A_T \sin(\omega t) \quad (1)$$

where T_0 is the starting temperature of the scanning experiment, B is the linear heating rate, t is the time, A_T is the amplitude of the temperature oscillation, and ω is the oscillating frequency given by $2\pi/p$, p being the oscillating period. T_0 was 20°C, B was 5°C min^{-1}, A_T was 2°C, and p was 50 s throughout this study. The total heat flow curve, which is indistinguishable by the conventional DSC, was evaluated by taking sliding averages over full cycles of oscillation for the oscillated heat flow. The reversing part of the heat flow was calculated by the Fourier-transform treatment of the oscillated heat flow. The non-reversing part of the heat flow was obtained as the difference between the total heat flow and the reversing part [19–26].

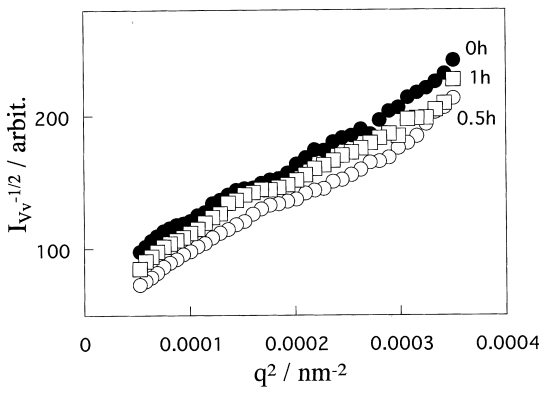

Fig. 2. Debye–Bueche plot for Vv light scattering profile of PMMA at 80°C: ●,0 h; ○,0.5 h; □,1 h.

3. Results and discussion

Fig. 1 shows the Vv light scattering profiles $I_{VV}(\theta)$ of PMMA glass at 80°C (T_g − 17 K) for various aging times. The scattering intensity decreases monotonously with the scattering angle. The angular dependence of the intensity could be ascribed to the long-range density fluctuation [11–15]. The interesting result here is that the intensity increases rapidly and then decreases gradually with aging time.

The Vv scattering intensity I_{VV} is given by:[12]

$$I_{VV} = I_{VV1} + I_{VV2} + \frac{4}{3} I_{HV} \quad (2)$$

where I_{VV1} is the isotropic light scattering intensity from the thermally induced short-range density fluctuation which is independent of the scattering angle, I_{VV2} is the excess scattering due to the long-range density fluctuation having an angular dependence with scattering angle, and I_{HV} is the Hv scattering intensity which is ascribed to the optical anisotropy. The I_{HV} is also shown in Fig. 1. The I_{VV} is much larger than the I_{HV}; i.e. the I_{VV} is about 100 times larger than the I_{HV}, suggesting that the I_{HV} contributed to the I_{VV} is negligible. On the other hand, the I_{VV1} is given by

$$I_{VV1} = \frac{\pi^2}{9\lambda_0^4} (n^2 - 1)^2 (n^2 + 2)^2 \, kT\beta \quad (3)$$

where λ_0 is the wavelength of light in vacuum, n is the refractive index which is described by the density by

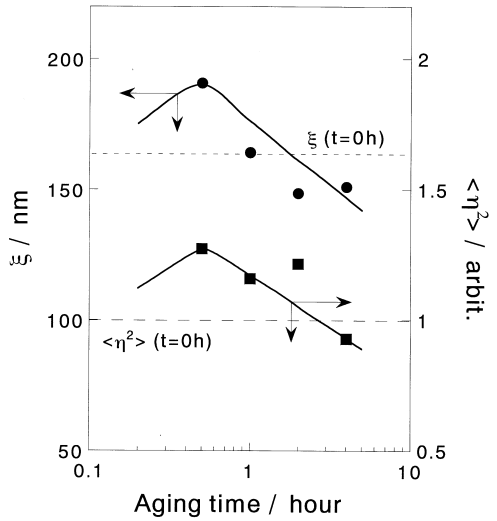

Fig. 3. Changes of the correlation length ξ and the mean-square density fluctuation $\langle\eta^2\rangle$ of PMMA with aging time at 80°C.

Lorentz–Lorenz equation, k is the Boltzman constant, T is the absolute temperature, and β is the isothermal compressibility. Since (1) the extrapolated small angle X-ray scattering intensity is related to the density and the β [28], and (2) the light scattering which is independent of the scattering angle is ascribed to the short-range density fluctuation below the length of several nm, the I_{VV1} can be discussed using the small angle X-ray scattering intensity. As demonstrated by Wendorff [29], no change of the small angle X-ray scattering intensity was seen with aging, suggesting no change of the I_{VV1} with aging. Hence, the change of the I_{VV} with aging is not ascribed to the I_{VV1} but to the change of the I_{VV2}, and the density fluctuation can be discussed by the I_{VV}. The angular dependence of the I_{VV} is described by Debye–Bueche type scattering function: [11–13]

$$I_{VV}^{-1/2} = \frac{1}{A} + \frac{\xi^2}{A} q^2 \tag{4}$$

$$A = \frac{8\pi^3 \langle\eta^2\rangle \xi^3}{\lambda^4} \tag{5}$$

where ξ is the correlation length, q is the scattering vector; $q = 4\pi/\lambda\sin(\theta/2)$, λ being the wavelength of light in specimen, and $\langle\eta^2\rangle$ is the mean-square average of the density fluctuations. As shown in Fig. 2, the plot of $I_{VV}^{-1/2}$ vs q^2 yielded straight lines as expected from the Debye–Bueche form.

The correlation length ξ and the mean-square density fluctuation $\langle\eta^2\rangle$ can be obtained from the slope and the intercept in the plots of $I_{VV}^{-1/2}$ vs q^2. The result is shown in Fig. 3 as a function of aging time t_a. The as-quenched PMMA has a long-range density fluctuation having a correlation length about 200 nm. By aging, the correlation length and the mean-square density fluctuation increase simultaneously at first ($t_a \leq 0.5$ h) and then they decrease with time ($t_a > 0.5$ h). This result suggests that the density fluctuation in the as-quenched PMMA glass grows further at first and then it decays to get a rather homogeneous glass during the physical aging. The evolution of the density fluctuation may explain the anomalous increase of the light scattering intensity of inorganic glasses at around the glass transition temperature during the heating process [16–18].

Fig. 4a shows the total heat flow of PMMA glass for various aging times at 80°C obtained by oscillating-DSC. A single glass transition is seen in the as-quenched specimen. When the quenched specimen is aged, a shoulder appears below the pre-existing glass transition at first ($0.5 \leq t_a \leq 2$ h). The shoulder shifted to a higher temperature with aging time and then an endothermic peak appears ($t_a = 8$ h). The peak shifts to a higher temperature and it increases in magnitude with aging time.

Such a shoulder was also observed in the conventional DSC thermograms of glassy polymers aged for short period [3–5]. It would be very characteristic to the physical aging. However, there is no adequate interpretation so far because there are two possibilities to interpret the shoulder: one is the appearance of two glass transitions and the other is the superposition of the glass transition curve and the endothermic peak. One could analyze the oscillating-DSC data as follows.

The oscillated heat flow can be separated into the glass transition as the reversing part and the endothermic peak of the enthalpy relaxation as the non-reversing part, since the reversing part is attributed to the thermodynamic heat capacity and the non-reversing part is attributed to the kinetic event [19–26]. In the curve of the reversing part of the heat flow, a single glass transition is seen [Fig. 4(b)]. The glass transition is wide in the aging period at which the shoulder is observed in the total heat flow ($0.17 \leq t_a \leq 2$ h). In this period, a broad and small endothermic peak appears in the curve of the non-reversing part of the heat flow [Fig. 4(c)]. The peak shifts to a higher temperature and it increases in magnitude with aging time, as expected by Tool–Narayanaswamy–Moynihan type model [4,6]. Then, the appearance of the shoulder is ascribed to the superposition of the broad glass transition curve and the small endothermic peak.

As shown in Fig. 4(b), the width of the glass transition increases at first ($t_a \leq 0.5$ h) and then it decreases with aging time ($0.5\text{ h} < t_a$).[1] The decrease of the width may correspond to the sharpening of the α relaxation peak by dynamic mechanical spectroscopy [31] and dielectric spectroscopy [32]. Note that the width of the glass transition increases when the density fluctuation by light scattering increases, while it decreases when the density fluctuation decreases. Thus the change of the width could be ascribed to the change of the density fluctuation.

The increase of the width at $t_a \leq 0.5$ h is caused by the

[1] A small distortion is seen in the heat flow curve for the aged specimen at $t_a = 385$ h. This may be caused by the nonlinearity between a sinusoidal input and the resulting output which increases as the magnitude of the exothermic peak increases [30].

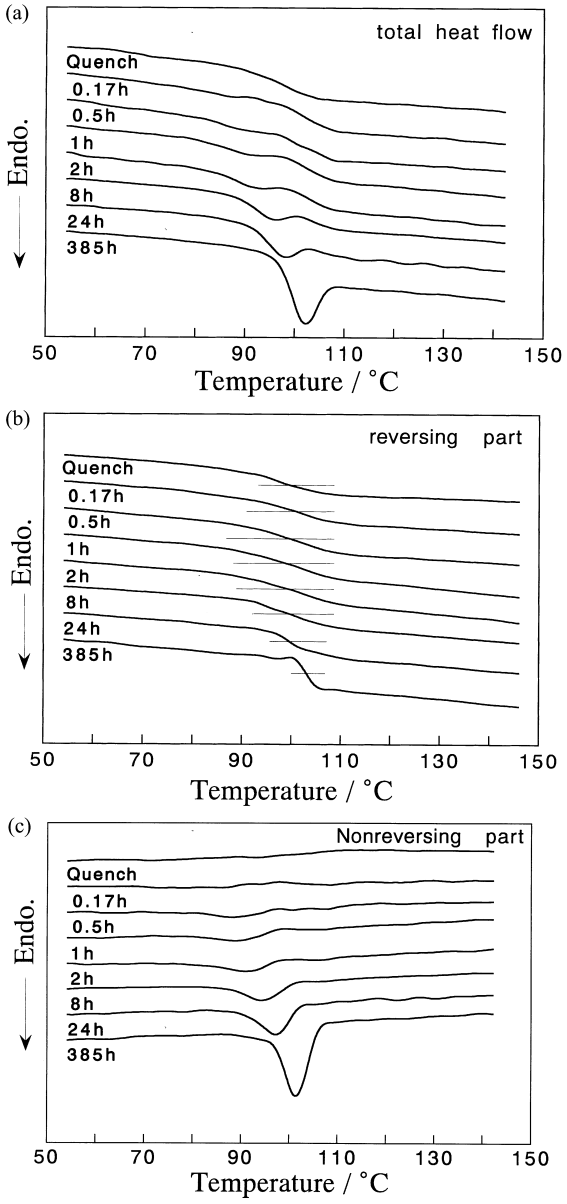

Fig. 4. The oscillated DSC curve of PMMA aged at 80°C for various times: (a) total heat flow; (b) reversing part of heat flow; and (c) non-reversing part of heat flow. The width of the glass transition is indicated by thin line in (b).

depression of the onset temperature of the glass transition. It may suggest that the density in low density regions decreases with aging [as shown by the open arrow in Fig. 5(a)]. As shown in Fig. 4(c), the endothermic peak appears in this period, suggesting that the PMMA glass densifies even at early stage of the aging. Thus, during the decrease in density in the low density regions, a densification proceeds in high density regions[2] [as shown by the solid arrow

[2] The N_2 gas permeability coefficient P decreases by aging in PMMA; Log P at 25°C and 1 cmHg for the as-quenched specimen is -10.4 ml(STP) cm^{-3} s^{-1} and that for aged specimen ($t_a = 100$ h at 80°C) is -10.7 ml(STP) cm^{-3} s^{-1} [33]. This may support the densification of the aged specimen.

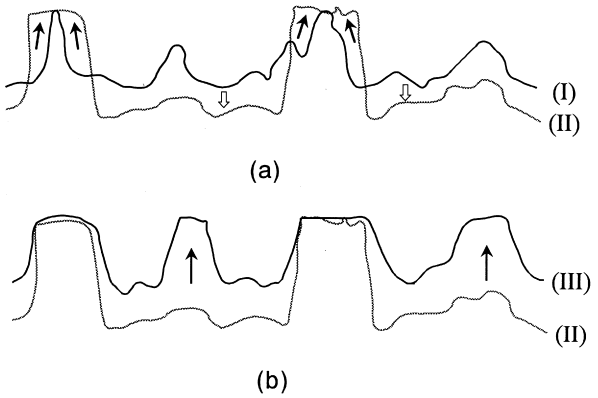

Fig. 5. A schematic representation of change in the density profile during the physical aging: (a) early stage, (b) late stage.

in Fig. 5(b)]. Such development of the density fluctuation may be induced by the dissipative process in a non-equilibrium state demonstrated by Lindenmeyer [34] and by the existence of local nematic ordering suggested by Monte Carlo simulations [35]. The less-densification in low density regions and the densification in high density regions should lead to the increase in $\langle\eta^2\rangle$ and ξ (Fig. 3).

On the other hand, the decrease of the width at late stage ($0.5\ \text{h} < t_a$) is caused by the elevation of the onset temperature of the glass transition, suggesting a densification at low density regions [see arrow in Fig. 5(b)]. The densification may reduce both ξ and $\langle\eta^2\rangle$ (Fig. 3).

Thus, from the light scattering and oscillating-DSC studies, one may describe the change in density profile with the physical aging as follows. The as-quenched PMMA glass is partially densified to render an inhomogeneity with a correlation length of ca. 200 nm (profile I in Fig.5). The density fluctuation grows further for a while at early stage of aging (from profile I to II). Then the fluctuation decays by evolution of high density domains in low density regions to reduce the correlation length (from profile II to III). By the latter process, the system eventually would attain a rather homogeneous glassy state with high density.

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