NOTE

Effect of Tacticity on Relaxation Process with Sub- T_g Annealing in Poly(methyl methacrylate)

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Polymer glasses are essentially thermodynamic nonequilibrium states. Structural and property changes that occur in polymer glasses with annealing below glass transition temperature (T_g) can be described as the kinetic approach to equilibrium of certain extensive thermodynamic properties following a rapid change in thermodynamic conditions. The nonequilibrium state of polymer glass can be defined by thermodynamic conditions (temperature, T ; pressure, P) and the extensive properties (entropy, S ; enthalpy, H ; volume, V ; etc.)

Microscopically, the structural relaxation of polymer glass is generally thought to arise from a kinetic adjustment of a material structure to new equilibrium conditions. It is worth while to investigate the effect of tacticity on the rate of enthalpy and volume relaxation so as to estimate the

molecular mechanism of the relaxation process in polymer glasses at temperatures below T_g .

The samples used throughout the experiments are listed in Table I. Atactic PMMA was obtained by the bulk-polymerization at 60°C with azobisisobutyronitrile as initiator. Isotactic and syndiotactic PMMA were obtained by anionic polymerization at 0°C with *n*-butyllithium in toluene and tetrahydrofuran, respectively. All samples were fractionated by fractional precipitation. Tacticity was determined by NMR and molecular weight (M_n) and molecular weight distribution (M_w/M_n) were obtained by GPC. These data along with those for thermal analysis we also listed in Table I.

In order to describe the annealing effect at temperature below T_g , it is convenient to measure thermodynamic quantities such as enthalpy and volume. The heat capacity (C_p) measurement by a

Table I. Sample characterization and thermal properties

Sample	NMR triad			M_n^a $\times 10^5$	M_w/M_n^a	T_g^b °C	ΔC_p^c J g ⁻¹
	[I]	[S]	[H]				
Atactic	0.13	0.43	0.44	1.5	1.5	103	0.285
Isotactic	0.93	0.03	0.04	1.6	1.2	44	0.287
Syndiotactic	0.20	0.60	0.20	2.0	1.7	109	0.285

^a Molecular weight (M_n) and molecular weight distribution (M_w/M_n) were obtained by GPC.

^b Glass transition temperature (T_g) was determined by DSC (Perkin-Elmer DSC II) at a heating rate of 10°C min⁻¹.

^c Heat capacity difference between liquid and glassy states (ΔC_p) was obtained by DSC at a heating rate of 10°C min⁻¹.

differential scanning calorimeter (DSC) is a good method¹ for analyzing the relaxation process with annealing below T_g , and has the advantage of requiring only a small amount of sample (about 20 mg in this study). In order to compensate for the inadequacy of a DSC measurement as pointed out by Richardson and Savill,² the C_p measurements for the annealed and unannealed samples were carried out over a wide temperature range throughout T_g . By integrating DSC curves for each sample from the annealing temperature (T_a) to ($T_g + 30^\circ\text{C}$), the excess enthalpy (ΔH_i) of annealed glass was obtained. The measurement of C_p and the calculation of ΔH_i were reported previously.³

Doing on the assumption of a single relaxation time response, the enthalpy relaxation process with annealing below T_g may be described as follows.⁴

$$\Delta H_i = \Delta H_0 \exp(-t/\tau) \quad (1)$$

ΔH_0 is the excess enthalpy of an unannealed sample and τ is the enthalpy relaxation process was satisfactorily described by a single relaxation process. However, the increase in relaxation time with annealing time was pointed out by Uchidoi *et al.*⁵ Therefore, we used the relaxation time when $\Delta H_i/\Delta H_0$ was equal to 0.5 as the apparent relaxation time $\tau_{1/2}$. The apparent relaxation time, $\tau_{1/2}$, was plotted against $T_g - T_a$ in Figure 1. At the same value of ($T_g - T_a$), isotactic PMMA shows a longer relaxation time than syndiotactic and atactic PMMA. The enthalpy relaxation of isotactic PMMA hardly occurs in comparison with syndiotactic and atactic PMMA. The syndiotactic sample showed a similar value and temperature dependence of the relaxation time of atactic sample. Since the syndiotactic sample used in this study had stereoregularity, it was difficult to conclude whether the tacticity effect on the rate of relaxation between the syndiotactic and atactic samples actually existed or not.

From an Arrhenius temperature dependence of the relaxation time, enthalpy relaxation rates can be expressed empirically in terms of temperature as follows.

$$\tau^{-1} = \exp(-E^*/RT) \quad (2)$$

From eq 2, the apparent activation energy of enthalpy relaxation, E^* , was obtained. The apparent activation energy was 330 kJ mol⁻¹ for atactic, 337

Figure 1. Apparent relaxation time, $\tau_{1/2}$, plots against $T_g - T_a$ for atactic (○), syndiotactic (◐) and isotactic PMMA (●). T_g and T_a are glass transition temperature and annealing temperature, respectively.

kJ mol⁻¹ for syndiotactic and 432 kJ mol⁻¹ for isotactic PMMA. We studied the effect of chemical structure,⁶ molecular weight⁷ and hydrogen bond formation⁸ on the rate of enthalpy relaxation, and estimated that the enthalpy relaxation process was due to the segmental motion of the main chain whose length was comprised of a few repeating units. For isotactic PMMA, the internal rotation of the main chain in a glassy state was considered to be restricted by steric hindrance. Therefore, it is probable that the segmental motion of main chain related to the enthalpy relaxation hardly occurs and the rate of enthalpy relaxation may be slower than that of atactic and syndiotactic PMMA.

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