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Characteristics of glass transition in propylene/ethylene copolymers and polyethylene

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Abstract

For propylene/ethylene random copolymers, the relationship between T_g and the composition has been investigated. At a constant composition, T_g is variable depending on the cohesive state of ethylene units in the glass. For polyethylene, the reference values of $T_g = 130$, 134, 135, 153, and 237 K correspond to the cohesive enthalpies of 3.08, 3.19, 3.23 (=6.46/2), 3.77, and 6.46 kJ per molar ethylene unit in the glasses, respectively. The heat capacity jump at the glass transition for these polymers was simulated using the scheme of melting of ordered parts followed by recrystallization. At the mole fractions of propylene (meso) units of 0.3 and 0.4, a distinct peak is apparent in the heat capacity jump curve.

Keywords: Heat capacity; Glass transition; Melting; Polyethylene; Propylene/ethylene copolymer

1. Introduction

The relationships between the glass transition temperature, T_g, and the composition for binary random copolymers are grouped into three classes of concave, convex, and monotonous incremental (or decremental) curves [1–3]. Here, T_g is the onset temperature of the heat capacity jump at the glass transition [4,5]. For propylene/ethylene (P/E) random copolymers, it should show the monotonous decremental curve [6,7], because T_g for polyethylene (PE) is over 20 K smaller than T_g (270 K) [8] for isotactic polypropylene (iPP). According to the glass transition studies for PE [8–13], the experimental values of T_g are in the range of 130–250 K. In this study, attempting to clarify why T_g of PE is varied as above, the relationship between T_g and the composition for P/E random copolymers was investigated together with the jump profiles of heat capacity, C_p, at the glass transition, which is simulated using the scheme of melting of ordered parts followed by recrystallization [14].

2. Theoretical treatments and discussion

For binary random copolymers, T_g is given by [3,14–17]

$$T_g = \frac{T_g(1)(h^{\text{int}} + h^{\text{conf}}(X_A))}{h^{\text{int}}(1) + h^{\text{conf}}(1) - T_g(1)(s^{\text{conf}}(1) - s^{\text{conf}}(X_A))} \tag{1}$$

with

$$h^{\text{int}} = h^{\text{int}}(1) - (h^{\text{int}}(1) - h^{\text{int}}(0))(1 - X_A)$$

where X_A is the mole fraction of A units, $T_g(1)$ is the T_g value for a homopolymer with $X_A = 1$, $h^{\text{int}}(1)$, and

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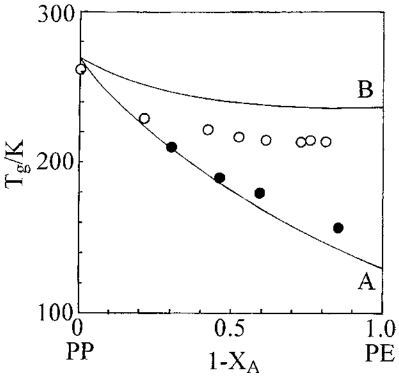

Fig. 1. Relationship between T_g and $1 - X_A$ for P/E random copolymers. Curve A: T_g and h^{int} for PE are 130 K and 3.08 kJ per molar ethylene unit and curve B: T_g and h^{int} for PE are 237 K and 6.46 kJ per molar ethylene unit. ●: from [6], and ○: from [7].

$h^{conf}(1)$, and $s^{conf}(1)$ are the intermolecular cohesive enthalpy per molar structural unit, the conformational enthalpy and entropy per molar structural unit for a homopolymer composed of A units ($X_A = 1$), $h^{conf}(X_A)$ and $s^{conf}(X_A)$ are the conformational enthalpy and entropy per molar structural unit for a copolymer with X_A, and $h^{int}(0)$ is the intermolecular cohesive enthalpy per molar structural unit for a homopolymer composed of B units ($X_A = 0$).

Fig. 1 shows the relationship between T_g and $1 - X_A$ calculated from Eq. (1) for P/E random copolymers, together with experimental values previously reported [6,7]. In the calculation, the rotational isomeric state (RIS) model [3,18–20] of the degree of polymerization $x = 100$ with a random configuration of meso units (of iPP) and ethylene units was used. Both T_g's of curves A and B, T_g^A and T_g^B, were calculated using $h^{int}(0) = 3.08$ kJ per molar ethylene unit for curve A with $T_g = 130$ K [13] at $X_A = 0$ and $h^{int}(0) = 6.46$ kJ per molar ethylene unit for curve B with $T_g = 237$ K [8] at $X_A = 0$, respectively. The value of $h^{int}(0)$ for PE was found by trial and error calculations of Eq. (1) in order to set T_g for PE at 130 or 237 K. Setting of other $T_g = 134$ K [21], 135 K, or 153 K [9] for PE led $h^{int}(0) = 3.19$, 3.23 (=6.46/2), or 3.77 kJ per molar ethylene unit, respectively. For iPP, $T_g = 270$ K [8] and $h^{int}(1) = 5.69$ kJ mol^{-1} (the cohesive energy for methyl residue of meso unit [22]) were used. The value for $h^{conf}(X_A)$ may be approximated by $[\{h_1^{conf}(X_A) - h_2^{conf}(X_A)\}X_A + h_2^{conf}(X_A)]$, where $h_1^{conf}(X_A)$ is $h^{conf}(X_A)$ at 270 K and $h_2^{conf}(X_A)$ is $h^{conf}(X_A)$ at 130 or 237 K. Fig. 1 suggests that the experimental values of T_g for P/E random copolymers should be distributed between curves A and B as a function of the molar cohesive enthalpy of ethylene units.

In the next stage, the C_p jump profiles at the glass transition were predicted for P/E random copolymers.

First, the following scheme of a glass transition was hypothesized. In the cooling process from the melt, the ordered parts are generated near T_g^A and then confined in the glass below T_g^A. The relaxation process below T_g^A transforms the glass into an aggregation of glassy clusters with different T_g. In the heating process, the glassy states of clusters are released at each T_g and then the melting of ordered parts confined in each cluster continues up to the end temperature, T_e, of C_p jump at each glass transition. T_g^A and T_g^B should be the minimum and the maximum of T_g for glassy clusters, respectively. The glass transition enthalpy per molar structural unit, h_g, is given by [5,23–25]:

$$h_g\left(\approx \frac{RT_g^2}{c_2}\right) = h_g^{conf} + h_g^{int} \tag{2}$$

where c_2 is the constant in the WLF equation [26], R is the gas constant, h_g^{conf} is the conformational enthalpy per molar structural unit at T_g, and h_g^{int} is the intermolecular cohesive enthalpy per molar structural unit at T_g. Whereas the transition enthalpy per molar structural unit for ordered parts in the glass, h_x, is given by [5,23–25]:

$$h_x \approx h_g + \Delta h \tag{3}$$

with

$$\Delta h \approx \int_{T_g}^{T_e} \Delta C_p(T)\,dT$$

and

$$\frac{RT_g \ln(Z_g/Z_0)}{x} \le \Delta h \le \frac{T_g(xs_g^{conf} - R\ln Z_0)}{x}$$

where Δh is the heat change per molar structural unit due to the melting of ordered parts at the glass transition, $\Delta C_p(T)$ is the difference in the observed C_p and the hypothesized superheated glass C_p at the glass transition, Z_g is the conformational partition function for a chain at T_g, Z_0 is the component conformational partition function regardless of the temperature for a chain, and s_g^{conf} is the conformational entropy per molar structural unit at T_g. Approximating Δh $(= h_x - h_g)$ as $\Delta C_p^0(T_e - T_g)/2$, the minimum and the maximum of T_e for ordered parts in clusters, T_e^A and T_e^B, are given as

$$T_e^A \approx T_g^A + \frac{2T_g^A\{R\ln(Z_g^A/Z_0)\}}{(x\Delta C_p^0)} \tag{4}$$

$$T_e^B \approx T_g^B + \frac{2T_g^B(xs_g^{\mathrm{conf}A} - R\ln Z_0)}{(x\Delta C_p^0)} \tag{5}$$

with

$$\Delta C_p^0 = \Delta C_A^0 + (1 - X_A)(\Delta C_A^0 - \Delta C_A^0)$$

where Z_g^A is Z at T_g^A, $s_g^{\mathrm{conf}A}$ is s^{conf} at T_g^A, ΔC_p^0 is the difference in the liquid C_p and the glass C_p at the half way of C_p jump, ΔC_A^0 is ΔC_p^0 (=19.2 J K^{-1} mol^{-1}) [8] for iPP, and ΔC_B^0 is ΔC_p^0 (=21.0 J K^{-1} mol^{-1}) [8] for PE. In Eq. (5), the approximate equality $(T_e^A - T_g^A)/T_g^A \approx (T_e^B - T_g^B)/T_g^B$ is suggested. It corresponds to $\Delta h \approx$ constant.

Second, the relationships among T_g, T_e, and the melting temperature, T_m, are discussed. T_m for binary random copolymers is represented by the modified Flory equation [27–32]:

$$T_m = -\left\{\left(\frac{aR}{h_u}\right)\ln X - \frac{1}{T_m^0}\right\}^{-1} \tag{6}$$

with

$$a \approx \frac{2h_u}{2h_u - h_x}$$

where X (=X_A or $1 - X_A$) is the mole fraction of major component, T_m^0 is the melting temperature for a homopolymer ($X = 1$), and h_u is the heat of fusion per molar structural unit for a homopolymer ($X = 1$). For P/E random copolymers with $1 - X_A \approx 0.30$–0.75, T_m is the melting temperature of ordered parts which do not satisfy at least one of the structural conditions of a crystal cell. Fig. 2 shows the plots of T_g^A, T_g^B, and T_m versus $1 - X_A$ for P/E random copolymers. Among T_g^A, T_e^B, and T_m, the relationships of $T_m \geq T_e^B > T_g^A$ for $1 - X_A \leq 0.33$ and $T_e^B > T_m > T_g^A$ for $1 - X_A > 0.33$ were found. However T_e^B over T_m of the latter could not be recognized. So demanding $T_e^B = T_m > T_g^A$ for $1 - X_A > 0.33$, the C_p jump curve should be expanded upward, because Δh is almost constant at a constant composition. The elevation of T_g by annealing for the glasses should expand upward the C_p jump curve as well [14].

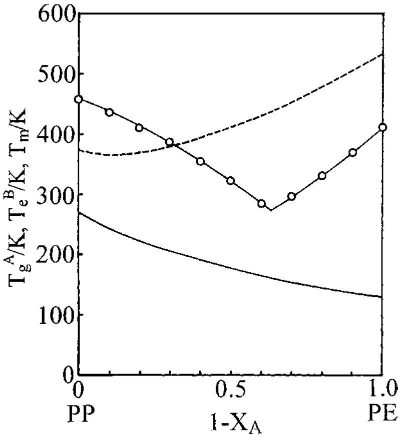

Fig. 2. Plots of T_g^A (—), T_e^B (- - -), and T_m (○) against $1 - X_A$ for P/E random copolymers.

Third, in order to simulate these phenomena, the division of $\Delta C_p(T)$ at the glass transition is suggested as [14]:

$$\Delta C_p(T) = \Delta C_p^a(T) + \Delta C_p^b(T) \tag{7}$$

with

$$\int_{T_g}^{T_e} \Delta C_p(T)\,\mathrm{d}T = \int_{T_g}^{T_e} \Delta C_p^a(T)\,\mathrm{d}T \quad \text{and}$$

$$\int_{T_g}^{T_e} \Delta C_p^b(T)\,\mathrm{d}T = 0$$

where $\Delta C_p^a(T)$ is the C_p change with an endothermic peak due to the melting of ordered parts and $\Delta C_p^b(T)$ is the C_p change due to the recrystallization followed by melting. The annealing for glasses should lead the elevation of T_g and the enhancement of $\Delta C_p^a(T)$.

Figs. 3 and 4 show the schematic plots of $\Delta C_p(T)$, $\Delta C_p^a(T)$ and $\Delta C_p^b(T)$ in the C_p jump at the glass transition for P/E random copolymers with T_g^A and T_e^B, where $\Delta C_p(T)$ and $\Delta C_p^a(T)$ may be approximated as [33]:

$$\Delta C_p(T) = -0.1\sin 2\pi y + \Delta C_p^0 y \tag{8}$$

with

$$y = \frac{T - T_g}{T_e - T_g},$$

$$\Delta C_p^a(T) \approx \frac{10\Delta h}{(T_e - T_g)}\frac{\{\phi(t) - \phi(\pm 2.5)\}}{\sum_t\{\phi(t) - \phi(\pm 2.5)\}} \tag{9}$$

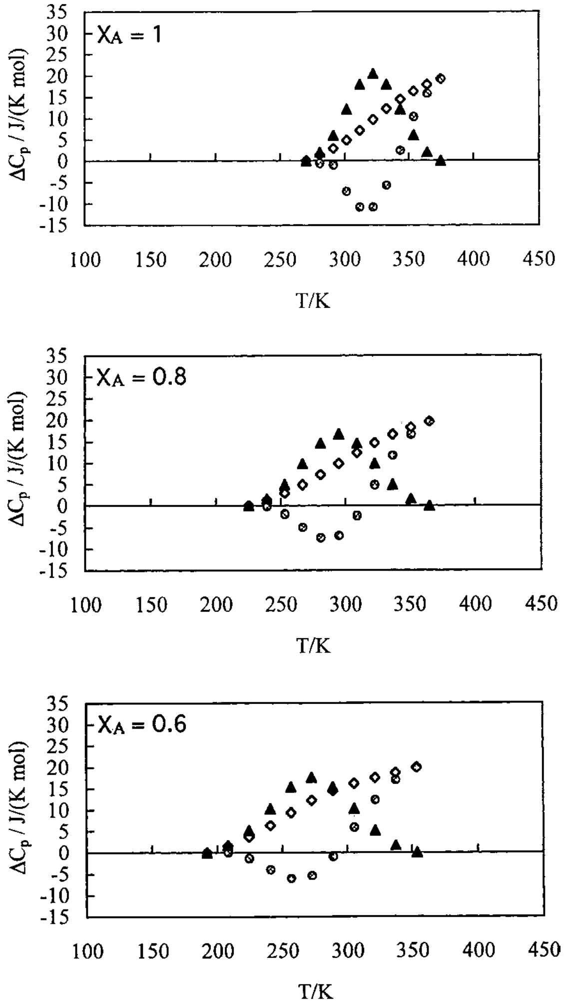

Fig. 3. Schematic plots of $\Delta C_p(T)$ (◇); $\Delta C_p^a(T)$ (▲), and $\Delta C_p^b(T)$ (○) in C_p jump at the glass transition for P/E random copolymers. From top, $X_A = 1$, 0.8, and 0.6.

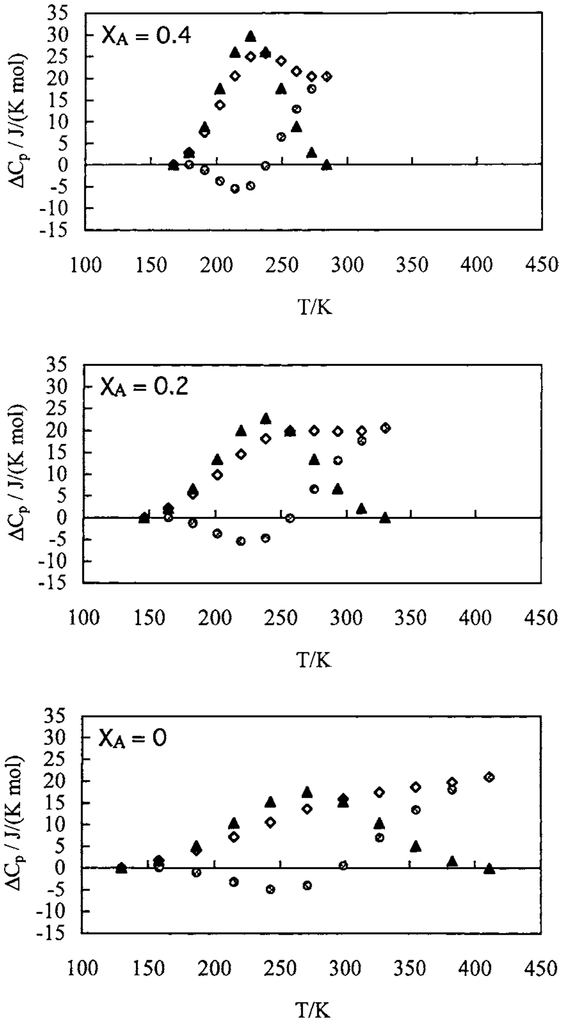

Fig. 4. Schematic plots of $\Delta C_p(T)$ (◇); $\Delta C_p^a(T)$ (▲) and $\Delta C_p^b(T)$ (○) in C_p jump at the glass transition for P/E random copolymers. From top, $X_A = 0.4$, 0.2, and 0.

with

$$\phi(t) = \left\{\frac{1}{\{(2\pi)^{1/2}\mu\}}\right\}\exp\left(-\frac{t^2}{2\mu^2}\right),$$

$$\Delta h = \frac{T_g(xs_g^{\mathrm{conf}A} - R\ln \mathrm{Z}_0)}{x}$$

and

$$t = \frac{\{T - (T_g^A + T_e^{\mathrm{B}})/2\}/2}{(T_e^{\mathrm{B}} - T_g^A)/10}$$

(here $t = \pm 2.5, \pm 2.0, \pm 1.5, \pm 1.0, \pm 0.5, 0$), where $\phi(t)$ is the Gaussian distribution function and μ is the standard deviation (here $\mu = 1$). $\Delta C_p^b(T)$ can be derived from Eq. (7). T_g used is T_g^A in Fig. 1. As T_e, T_e^B for $1 - X_A \leq 0.33$ and the value of T_m for $1 - X_A > 0.33$ were used.

Fig. 5 shows the profiles of C_p jump at the glass transition for P/E random copolymers. For P/E random copolymers with $X_A = 0.3$ and 0.4, the clear peak was generated on the C_p jump curve. C_p jump curves with a peak are observed actually

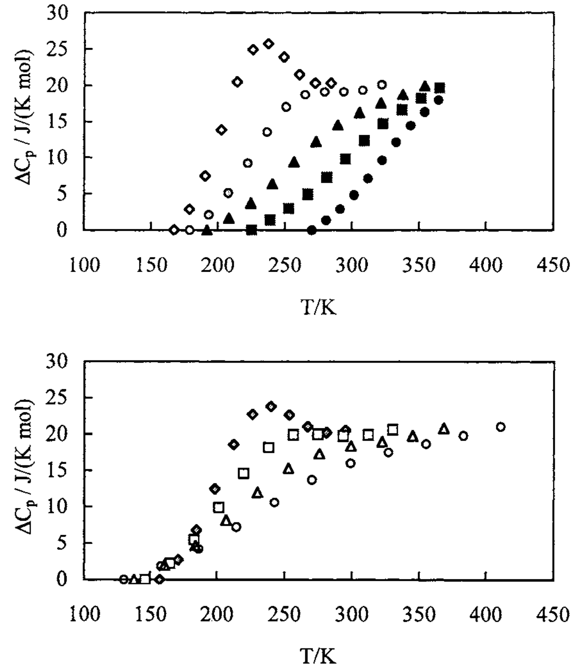

Fig. 5. C_p jump profiles for P/E random copolymers. Top: (●) $X_A = 1$; (■) $X_A = 0.8$; (▲) $X_A = 0.6$; (○) $X_A = 0.5$; (◇) $X_A = 0.4$. Bottom: (◇) $X_A = 0.3$; (□) $X_A = 0.2$; (△) $X_A = 0.1$; (○) $X_A = 0$.

for P/E random copolymers with $X_A = 0.22$ and 0.30 [6].

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