Conformational effects on the composition dependence of T_g in binary copolymers

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An equation is proposed for the glass transition temperature (T_g) of binary copolymers, using the criterion that $\Delta F = 0$. The equation is used in an investigation of the composition dependence of T_g for rotational isomeric state models of S/MMA, VDC/MA, ET/EA and E/P copolymers, and of a-PP. A comparison is made of calculated and experimental T_g values, the coincidence of which supports the conclusion that the composition dependence of T_g for these copolymers and for a-PP may be governed by the first and second order interaction energies about a skeletal bond of an isolated chain molecule.

INTRODUCTION

Theoretical attempts to investigate the composition dependence of T_g for random copolymers have been made by Gordon and Taylor[1], Gibbs and Dimarzio[2] etc, involving proposed empirical equations for T_g. However, a statistical mechanical treatment of T_g using the rotational isomeric state (RIS) model[3] has not been made except for studies of the composition dependence of T_g in copolymers by Tonelli[4–6], and of the conformational effects on T_g and relaxation phenomena in polymers by the author[7]. Tonelli reported that T_g may be related to the intramolecular equilibrium flexibility of a copolymer as manifested by its conformational entropy. In a previous paper[7], the author proposed two conditions for the criterion for T_g,

(1) the free energy difference ΔF per molar structural unit between the frozen solid and the fluid, still melted at a given temperature in the vicinity of T_g, is nearly zero;

(2) T_g should be taken as the temperature at which segmental motions of molecular chains are frozen in the glassy state or overcome intermolecular attractions.

In the present paper an equation for the composition dependence of T_g will be proposed on the basis of the above criterion and will be calculated for the RIS models of styrene/(methyl methacrylate)(S/MMA), (vinylidene chloride)/(methyl acrylate) (VDC/MA), ethylene/propylene (E/P) copolymers and atactic polypropylene (a-PP). Comparison of the calculated values of T_g with experimental results will be made to investigate the correctness of the first and second-order parameters expressing the statistical weights of the RIS, together with the equation for T_g.

THEORY

According to the criterion for T_g, the free energy ΔF per molar structural unit of a random copolymer composed of components A and B is almost zero at T_g, i.e.

$$\Delta F = h_x - T_g(X_A)s_x \approx 0 \qquad (1)$$

where h_x and s_x are the transition enthalpy and entropy per molar structural unit of a copolymer, X_A is the mole fraction of component A, and $T_g(X_A)$ is the glass transition temperature at X_A.

$T_g(X_A)$ in equation (1) can be rewritten as:

$$T_g(X_A) = \frac{T_g(1)(h^v + h^c(X_A))}{h^v + h^c(1) - T_g(1)(s^c(1) - s^c(X_A))} \qquad (2)$$

where $T_g(1)$, h^v, $h^c(1)$ and $s^c(1)$ are the glass transition temperature, intermolecular cohesive energy, conformational enthalpy and entropy per molar structural unit of a homopolymer ($X_A = 1$) respectively, and $h^c(X_A)$ and $s^c(X_A)$ are the conformational enthalpy and entropy per molar structural unit at X_A. Data from Reference 8 was used for the value of h^v in equation (2). Values of $h^c(X_A)$ and $s^c(X_A)$ were calculated for the RIS model of each copolymer generated using random numbers.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between T_g and X_A for an RIS model of the S/MMA copolymer. $h^c(X_A)$ and $s^c(X_A)$ in equation (2) were calculated using the conformation parameters of i-PS[9] and i-PMMA[10]. For i-PS and i-PMMA, values of $T_g = 378$ K and $T_g = 386$ K were used, respectively[11,12] Taking the second-order relative interaction energy E''_ω between phenyl groups in i-PS to be 2 000 cal mol^{-1}, two almost similar concave curves are obtained, depending on whether unit A is S or MMA. The experimental result by Hirooka *et al.*[11], which produced a concave curve, lies near the two calculated curves. For the case of $E''_\omega = 2\,200$ cal mol^{-1}, two concave curves are obtained that are entirely in disagreement, depending on whether unit A is S or MMA. Flory took 2 000 ~ 2 600 cal mol^{-1} as the value of E''_ω. According to the above result, $E''_\omega = 2\,000$ cal mol^{-1} appears to be adequate.

In *Figure 2*, T_g for an RIS model of VDC/MA copolymer is plotted as a function of the MA mole fraction. Calculations of $h^c(X_A)$ and $s^c(X_A)$ were made using the conformational parameters of PVDC[13] and i-PMA[14]. For PVDC and i-PMA, the values $T_g = 256$ K and $T_g = 276$ K were adopted[12], respectively.

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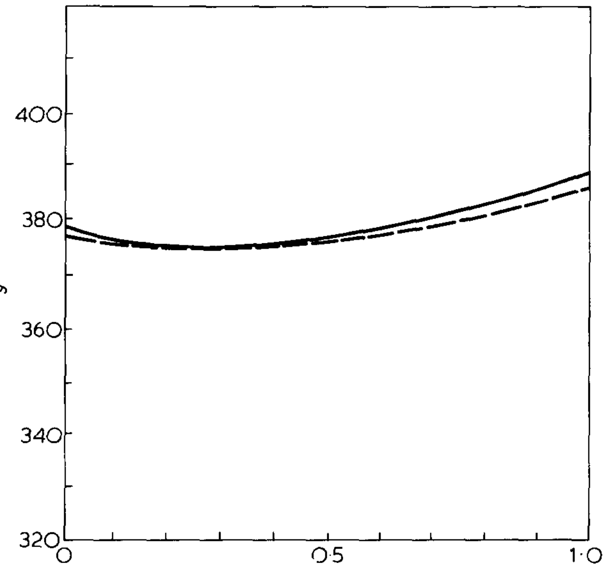

Figure 1 Relation between T_g and MMA mole fraction for S/MMA copolymer with unit A of S(solid curve) or MMA (dashed curve) for the case: E''_ω = 2 000 cal mol^{-1}

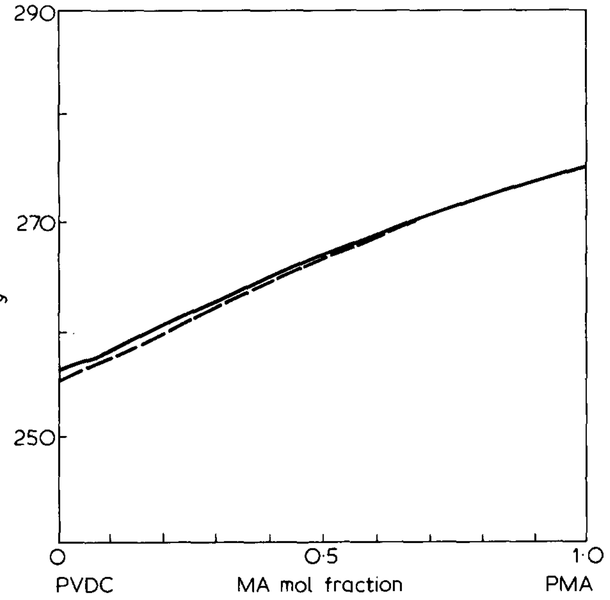

Figure 2 Relation between T_g and MA mole fraction for VDC/MA copolymer with unit A of VDC (solid curve) or MA (dashed curve)

If the relative interaction energies E_η and E''_ω related to the statistical weight η for the first-order interaction of the transition state, and the second-order statistical weight ω'' for the interacting pair $COOCH_3$–$COOCH_3$ in i-PMA, are taken as -200 cal mol^{-1} and 500 cal mol^{-1}, respectively, and taking the second-order statistical weight ψ for the gauche|$\overline{\text{gauche}}$ and $\overline{\text{gauche}}$|gauche states in PVDC as 0.1, then two concave curves are obtained, depending whether unit A is VDC or MA. These two curves were much the same. The value of T_g at X_A (VDC mole fraction) = 0 is equal to T_g of i-PMA. The value of T_g at X_A (MA mole fraction) = 0 is 2 ~ 3° less than T_g of PVDC.

Figure 3 shows the relationship between T_g and X_A for an RIS model of ET/EA copolymer, together with the experimental results obtained by Edgar[15]. $h^c(X_A)$ and $s^c(X_A)$ were calculated using the conformational parameters of PET and PEA[3]. For PET and PEA, T_g was taken to be 342 K and 205 K[15], respectively. If ET is selected as component A, then the calculated values of $T_g(X_A)$ are almost in agreement with the experimental result of Edgar[15]. Taking EA as component A and the value of h^ν as 2 900 cal mol^{-1} (molar cohesive energy of –CO–O–), the T_g difference between the calculated and experimental values increases with decreasing X_A. However, taking h^ν as 3 400 cal mol^{-1}, the calculated values of T_g are almost in agreement with the experimental result and lie near the T_g *versus* X_A (ET mole fraction) curve. h^ν = 3400 cal mol^{-1} is nearly equal to the sum of the molar cohesive energies of –CO–O–- and $-CH_2-$, i.e. 2 900 cal mol^{-1} and 680 cal mol^{-1}, respectively.

Figure 4 shows the relationship between T_g and X_A for an RIS model of P/E copolymer. $h^c(X_A)$ and $s^c(X_A)$ were calculated using the conformational parameters of i-PP[3] and PE[3]. T_g = 263 K and 148 K were adopted for i-PP[12] and PE[16], respectively. The T_g against X_A curves were obtained for the two values (0.05 and 0.5) of the first-order parameter η, expressing the statistical weight of the $\overline{\text{gauche}}$ relative to the gauche state in i-PP. The two curves for η = 0.05 and η = 0.5 were almost identical. Taking P as component A, T_g decreases with decreasing X_A. The value of T_g at X_A = 0 is not equal to T_g (= 148 K) of PE, whereas if E is selected as component A, T_g increases slightly with decreasing X_A. In this case, the value of T_g at X_A = 0 is also not equal to T_g of i-PP. However, it is of interest that the values at each composition of two damping peaks β and γ for the glide modulus obtained by Flocke[17] and Kline *et al.*[18] except for the β value of PE and the γ value of PP lie near these T_g against X_A curves. The calculated results appear to support the presence of two glass transition points for E/P copolymers, as pointed out for i-PP by Muus *et al.*[19].

Figure 5 shows the relationship between T_g and X_A for an RIS model (3 states) of a-PP, with the statistical weight η = 0.2 at 25°C. a-PP was treated as a binary random copolymer composed of meso and racemi diads. Calculations of $h^c(X_A)$ and $s^c(X_A)$ were performed using the conforma-

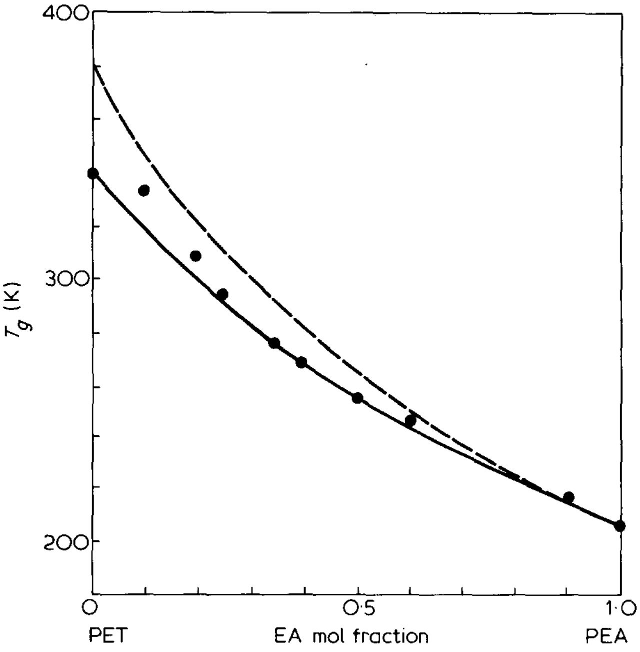

Figure 3 Relation between T_g and EA mole fraction for ET/EA copolymer with unit A = ET (solid curve) or EA (dashed curve). h^ν = 2 900 cal mol^{-1}. ●, experimental values by Edgar[15]

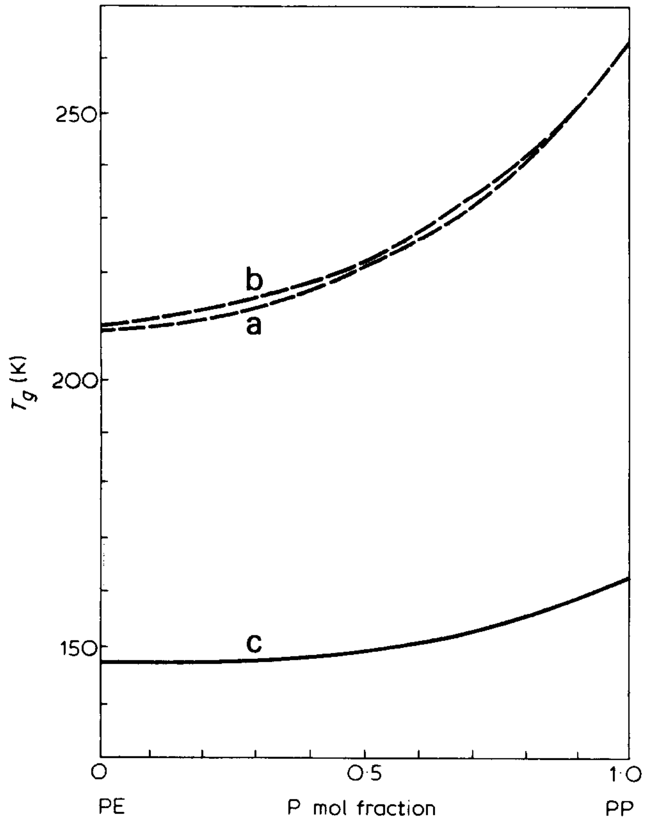

Figure 4 Relation between T_g and P mole fraction for E/P copolymer with unit A = P (dashed curves) or E (solid curves), (a) $\eta = 0.05$, (b) $\eta = 0.5$, (c) $\eta = 0.05$ and 0.5

tional parameters of i-PP and s-PP[3]. For i-PP and s-PP, T_s = 267 K was used for both[20,21]. In the case of $\eta = 0.2$, the concave curves obtained, depending on whether unit A is meso or racemi diad, are much the same. The experimental values of T_g for a-PP[22–27] are 10 ~ 15° less than T_g of i-PP and s-PP. Accordingly, the results at $\eta = 0.2$ may be supported experimentally. $\eta = 0.2$ appears to be the adequate first-order statistical weight of the gauche relative to the gauche state. In the case of $\eta \neq 0.2$, the two curves were not in agreement at all.

On the basis of the results in *Figures 1–5*, it is concluded that the composite dependence of T_g for the above copolymers and for a-PP may be governed by the first and second-order relative interaction energies about a skeletal bond, relating to their conformational characteristics.

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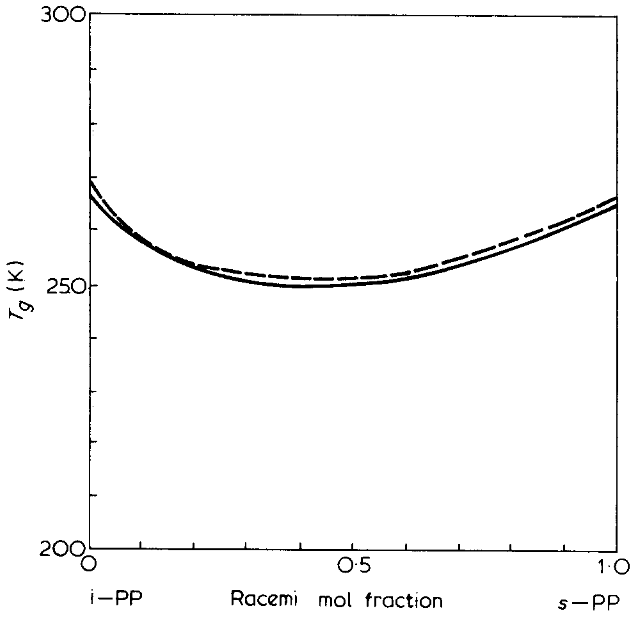

Figure 5 Relation between T_g and racemi diad mole fraction for a-PP with unit A of meso diad (solid curve) or racemi diad (dashed curve). $\eta = 0.2$

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