Conformational effects on isobaric and constant volume specific heats in polymers

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An equation was derived for the isobaric specific heat change ΔC_p at T_g for polymers by use of the configurational partition function normalized per unit volume for the polymer liquid. Eliminating the contributions of the conformational and free volume specific heat changes, the remaining contribution to ΔC_p, relating to the thermal wave-length and the excess specific heat change, was considered thermodynamically. In order to investigate the causes of the abrupt change in C_p at T_g as observed in many polymers, for PE, PET, nylon-6 and PP, the conformational specific heat C^c was calculated in the temperature range from 50 K to melting temperature. The characteristic temperature dependence of C^c with a peak temperature of 100 K for PE, PET and nylon-6, 250 K near T_g (263 K) for i-PP and about 320 K for s-PP was obtained. At T_g of PE, PET and nylon-6, no peculiar change in C^c was found. The abrupt change in C_p at T_g may be attributed almost entirely to the change in the free volume specific heat C^f.

INTRODUCTION

The isobaric specific heat change ΔC_p at T_g for polymers, that is, the difference between the isobaric specific heats of the frozen solid and the fluid at a given temperature in the vicinity of T_g, have been considered to consist of the three components, (1) the conformational specific heat change ΔC^c, (2) the free volume specific heat change ΔC^f, and (3) the miscellaneous specific heat change ΔC^m, related to the various additional modes of energy input which are required to raise the temperature of the liquid[1]. Roe and Tonelli have also reported[1] that the conformation contribution ΔC^c to ΔC_p is very small, the free volume contribution ΔC^f is roughly a third to a half of the total magnitude of ΔC_p, and the miscellaneous contribution ΔC^m is as large as ΔC^f.

In this paper, an equation for the isobaric specific heat change ΔC_p at T_g will be derived by use of the configurational partition function[2] normalized per unit volume, taking into account both the conformational character and the free volume of the polymer liquid. Eliminating the contributions of the conformational and free volume specific heat changes, the remainder contribution, relating to the thermal wave-length and the excess specific heat change will be considered thermodynamically. The correctness of the equation for the remainder contribution will be discussed on the basis of the Roe and Tonelli's data[1] of the constant volume specific heat change ΔC_v for several polymers. In the next place, in order to investigate the causes of the abrupt change in C_p at T_g as observed in many polymers, for polyethylene (PE), poly(ethylene terephthalate) (PET), nylon-6, isotactic and syndiotactic polypropylene (i-PP and s-PP), the conformational specific heat C^c will be calculated in the temperature range from 50 K to melting temperature.

THEORETICAL AND DISCUSSION

Isobaric and constant volume specific heats

The isobaric specific heat change ΔC_p at T_g for the polymers can be derived by use of the configurational partition function Ω normalized per unit volume proposed in the preceding paper[2].

$$\Delta C_p = \left[\frac{d}{dT}\left\{RT^2\left(\frac{d\ln\Omega}{dT}\right)\right\}\right]_p$$

$$= \left[\frac{d}{dT}\left\{\left(RT^2\frac{d\ln Z(T)}{dT}\right)/x\right\}\right]_p -$$

$$\left[\frac{d}{dT}\left(RT^2\frac{d\ln v_f}{dT}\right)\right]_p + \frac{dU_0}{dT} + \frac{3}{2}R \qquad (1)$$

where $Z(T)$ is the conformational partition function of an isolated chain at T, v_f the free volume per structural unit, U_0 the intermolecular cohesive enthalpy per molar structural unit, x the degree of polymerization, and R the gas constant. The first and second terms in the right hand side of equation (1) are respectively equal to the conformational specific heat change ΔC^c and the free volume specific heat change ΔC^f, and the third term dU_0/dT the excess specific heat change.

The constant volume specific heat change ΔC_v at T_g can be derived by the thermodynamic equation:

$$\Delta C_v = \Delta C_p - TV\Delta(\alpha^2/\beta) \qquad (2)$$

where α and β refer to the thermal expansion coefficient and

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Table 1 The numerical values of ΔC_v and ΔC^c for several polymers

Polymer	ΔC_v cal/g K from Eq.(2)[1]	from Eq.(3)	ΔC^c cal/g K[1]
PS	0.042	0.041–0.047	0.011–0.017
a-PMMA	0.044	0.039	0.009
i-PMMA	0.067	0.043	0.013
PVAc	0.087	0.048–0.053	0.013–0.018
PVC	0.051	0.061	0.013

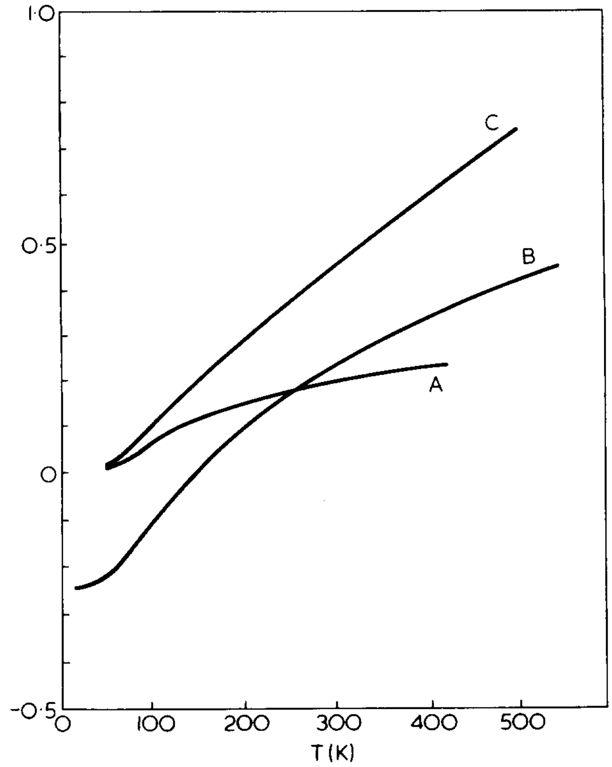

Figure 1 Conformational enthalpy E^c vs. temperature: (A), PE; (B), PET; (C), nylon-6

isothermal compressibility, respectively. $TV\Delta(\alpha^2/\beta)$ is equal to the free volume contribution ΔC^f approximately[1]. Therefore, from equation (1)

$$\Delta C_v \approx \Delta C^c + \frac{dU_0}{dT} + \frac{3}{2}R \qquad (3)$$

The term $(dU_0/dT + 3R/2)$ in equation (3) may be related to the miscellaneous contribution to ΔC_p described in Roe and Tonelli's article[1]. The numerical values of ΔC_v for polystyrene (PS), polymethylmethacrylate (PMMA), poly(vinyl acetate) (PVA$_C$) and poly(vinyl chloride) (PVC), calculated from equation (2) and from equation (3) under the approximation of $dU_0/dT \approx 0$, are listed in *Table 1*, together with the numerical values of ΔC^c [1].

As seen in *Table 1*, the values of ΔC_v from equation (2) are in good agreement with those from equation (3). This result indicates that the constant volume specific heat change ΔC_v at T_g can be evaluated theoretically by use of equation (3) and the calculated values of ΔC^c.

Conformation contribution C^c *to* C_p

Figures 1 and *2* show respectively the conformational

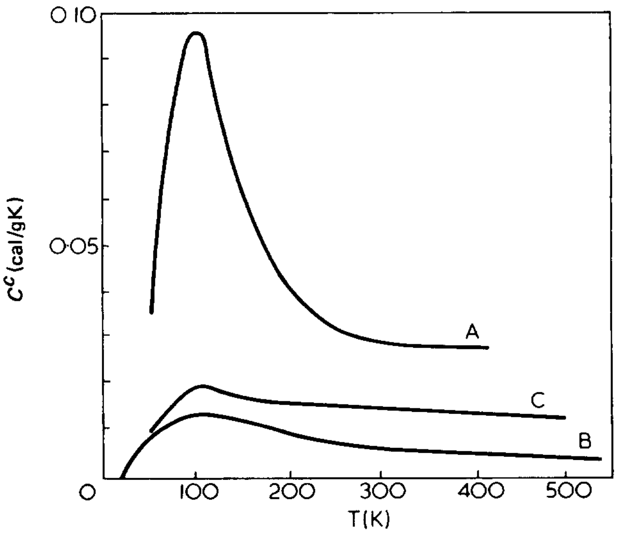

Figure 2 Conformational specific heat C^c *vs.* temperature: (A) PE (B), PET; (C), nylon-6

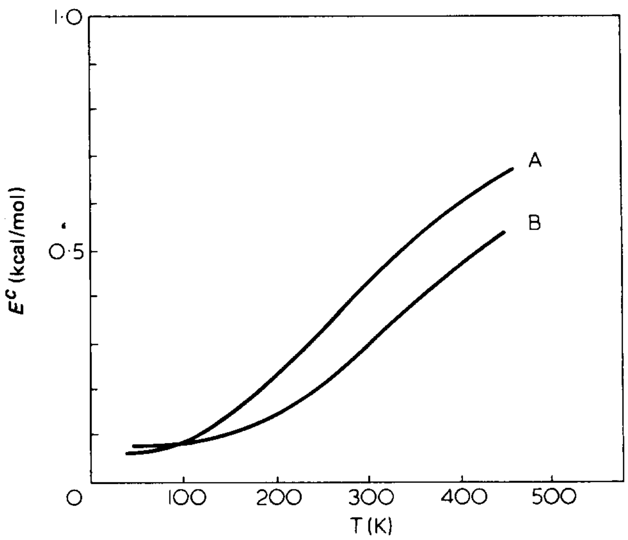

Figure 3 Conformational enthalpy E^c *vs.* temperature: (A), i-PP; (B), s-PP

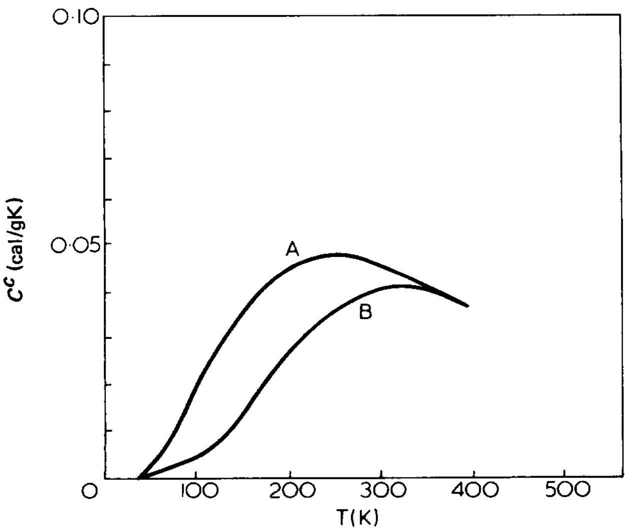

Figure 4 Conformational specific heat C^c *vs.* temperature: (A), i-PP; (B), s-PP

enthalpy[*] E^c vs. T and the C^c (= dE^c/dT) vs. T curves for PE, PET and nylon-6. The values of C^c were obtained by the graphical differentiation method of the E^c *vs.* T curves in *Figure 1.* As seen in *Figure 2,* for these polymers the common peak temperature of 100 K was obtained. These peaks may be related to the motions of ethylene units contained in these polymer chains. At T_g of PE, PET and nylon-6, respectively, 153 K, 323 K and 342 K[3], no characteristic change in C^c was found. Therefore, the abrupt change in C_p at T_g observed for nylon-6[4] and PET[5] may be attributed mainly to the change in C^f. *Figures 3* and *4* show respectively the E^c *vs.* T and the C^c *vs.* T curves for i-PP and s-PP. For i-PP, the C^c *vs.* T curve has a peak temperature of 250 K near T_g (263 K)[3]. For s-PP, C^c has a similar peak at about 320 K. These changes in C^c near T_g for PP seem to have almost no influence on the discontinuous increment of dC_p/dT at T_g[6–8]. The abrupt change in C_p at T_g may be mainly attributed to the change in C^f as well as PET and nylon-6.

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[*] The calculation of E^c has been performed by use of a rotational isomeric model with three states[9] for PE, PET and nylon-6, and five states[10] for PP. For PE and PP, in which the dependences of x on E^c have been found, the values at $x = \infty$ for PE and $x = 200$ for PP are used.