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Role of conformation entropy in determining the phase transitions of polymeric systems

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SUMMARY: A conventional method of estimating conformational entropy change at the melting point of polymers has been set forth in Mandelkern's book. The entropy separation according to this method involves a hypothetical assumption that the volume of the isotropic fluid may be compressed to that of the solid state without affecting the configurational part of the entropy of chain molecules. In this work, we have extensively examined the volume dependence of thermal pressure coefficient γ for various polymeric systems, for which the *PVT* data are available in Zoller's handbook. The γ values were found to be quite insensitive to the variation of volume in the range where the system remains highly fluid. The concept of the transitions previously proposed seems to be supported by the present analysis.

Introduction

A conventional method to estimate conformational entropy change at the melting point of polymers has been described in its simplest form by Mandelkern:1)

$$(\Delta S_{\mathrm{tr}})_V = (\Delta S_{\mathrm{tr}})_P - \Delta S_V \qquad (1)$$

where $(\Delta S_{\mathrm{tr}})_V$ and $(\Delta S_{\mathrm{tr}})_P$ indicate the entropy changes at the phase transition, respectively, for the constant-volume and constant-pressure conditions. The contribution ΔS_V from the volume change ΔS_{tr} at the transition can be estimated by

$$\Delta S_V = (\alpha/\beta)\Delta V_{\mathrm{tr}} = \gamma\Delta V_{\mathrm{tr}} \qquad (2)$$

where α, β and γ respectively denote the thermal expansion coefficient, isothermal compressibility, and thermal pressure coefficient. The values of $(\Delta S_{\mathrm{tr}})_V$ have been estimated for a variety of polymers and usually shown to be in a reasonable agreement with those of the conformational entropy calculated according to the rotational isomeric state (RIS)

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approximation[1,2]. This method has been adopted in the estimation of the constant-volume transition entropy at the isotropic - liquid crystal interphase of mainchain dimer and trimer liquid crystals in our previous work[3,4].

The entropy separation according to eqs. 1 and 2 involves a hypothetical assumption that the volume of the isotropic fluid may be compressed to that of the solid state without affecting the configurational part of the entropy of chain molecules. The validity of such an assumption has been questioned by several authors[5-7]. The thermal pressure coefficient is defined as the change of entropy with volume, i.e.,

$$\gamma = (\partial P/\partial T)_V = (\partial S/\partial V)_T \tag{3}$$

It has been pointed out that the volume dependence of γ during the compression from the liquid to solid volumes may not be negligible, and thereby leads to a significant underestimate of the ΔS_V term. It should then be more reasonable to adopt an integration form such as

$$\Delta S_V = \int \gamma(V)dV \tag{4}$$

to replace eq. 2. To what extent the configuration of chain molecules could be affected by the compression of the bulk volume is apparently an important point which must be carefully investigated. In view of these arguments, we have extensively examined the volume dependence of thermal pressure coefficient γ for various chain molecules in the fluid state, the *PVT* data required for the analysis being taken from handbooks[8,9].

Procedure and results

The analysis was performed for various liquids including polymers as well as low molecular weight chain molecules. An example is shown for polyethylene (PE) in Fig. 1. The *P-T* isochores (Fig. 1 a) were first deduced from the *PVT* data assembled by Zoller et al.[8]. The curve fitting becomes less satisfactory for the experimental data obtained at higher temperatures (>260°C). The values of $\gamma=(\partial P/\partial T)_V$ can be calculated for given

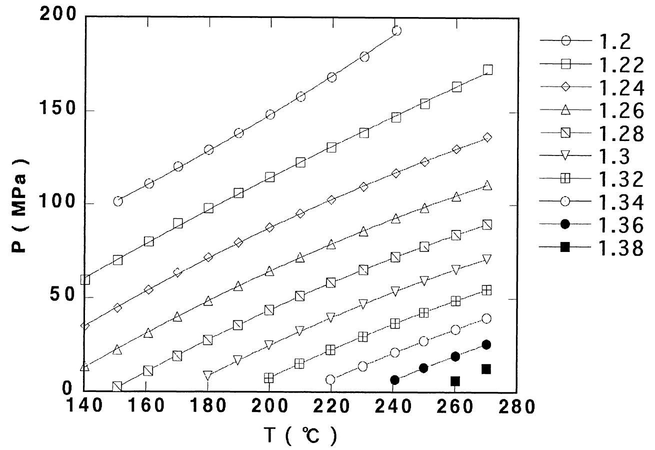

Fig. 1 a: The *P-T* isochore for a molten PE sample: *PVT* data taken from literature[8]. The specific volumes are indicated to the individual curves

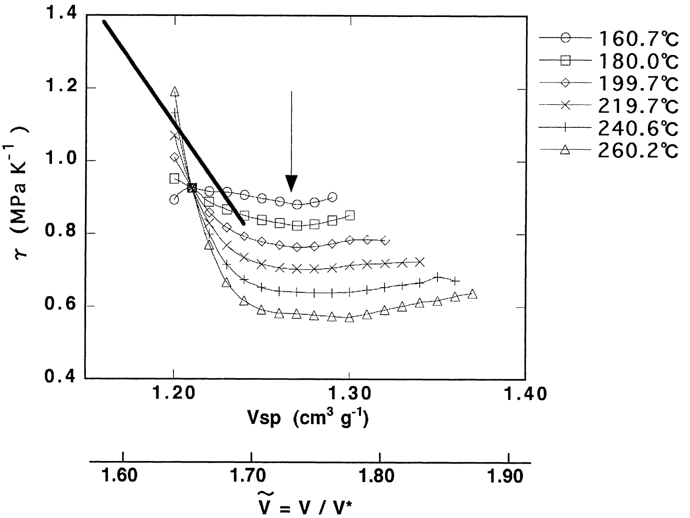

Fig.1 b: Variation of γ with v_{sp} calculated from the isochore (Fig.1 a). Temperatures are shown for the individual curves by using symbols. The v_{sp} value at the melting point (133°C) is indicated by the arrow. The γ–v_{sp} relation derived by Robertson[10] is illustrated for the melting temperature of the present PE sample by the heavy line in the upper-left corner. The $\tilde{v}$ values are indicated on the line shown below the abscissa temperatures by using this diagram. The γ vs. specific volume (ν_{sp}) relations thus derived in the range 160 - 260°C are illustrated in Fig. 1 b.

The slope of the curve indicates the susceptibility of γ to the volume change. The γ value remains relatively insensitive to the change in ν_{sp} around a shallow minimum. The value tends to be enhanced in the vicinity of the lower end of the curve where the system is approaching to the transition range. The slope of the γ-ν_{sp} curve becomes steeper (highly negative) when high-temperature samples are compressed under high-pressure (e.g. curve for 260°C). Such a tendency is less marked for curves obtained at lower temperatures. The specific volume of the liquid phase estimated at the transition temperature (133.0°C) at P=0 is shown by the arrow in Fig. 1 b. In practice, of course, the liquid could not be compressed to the crystal volume at the melting point. The experimental γ-ν_{sp} curves indicated are inevitably those obtained at sufficiently high temperatures. As the temperature approaches the melting point, the slope of the γ-ν_{sp} curve in the lower ν_{sp} region tends to be moderate. An extrapolation of the γ-T relation (cf. Fig. 1 b) along the line ν_{sp} = 1.267 cm^3g^{-1} (indicated by the arrow) gives γ = 0.97 $MPaK^{-1}$ at 133.0°C. The γ-ν_{sp} relation of PE has been previously estimated from the paraffin data by Robertson:[10)] the linear function $\gamma = 9.4–6.9\ \nu_{sp}$ derived for the melting temperature is also illustrated (heavy line) for comparison in Fig l b. Use of Robertson's expression in calculating the constant-volume melting entropy[5)] could not be fully supported.

The *PVT* data of other conventional polymers such as polyoxyethylene (POE), *cis*-1,4-polybutadiene (PB), and atactic polystyrene (PS) also assembled in Zoller's handbook are treated similarly[8)]. The results are shown in Figs. 2-4, where temperatures adopted for the analysis are distinguished by symbols. The polymers examined above possess quite divergent *PVT* characteristics. That is, (1) the POE crystal melts at around 64°C under an ordinary pressure, (2) the melting point of PB crystal is much lower (~2°C) *(PVT* data below 30°C are not included in Zoller's handbook), and (3) an atactic PS does not crystallize under any condition. Although the range of the data points are somewhat limited in some examples, the γ-ν_{sp} relation exhibits similar trends with those of PE in all cases. The specific volume of the liquid POE at the melting point is estimated to be 0.91 cm^3g^{-1}

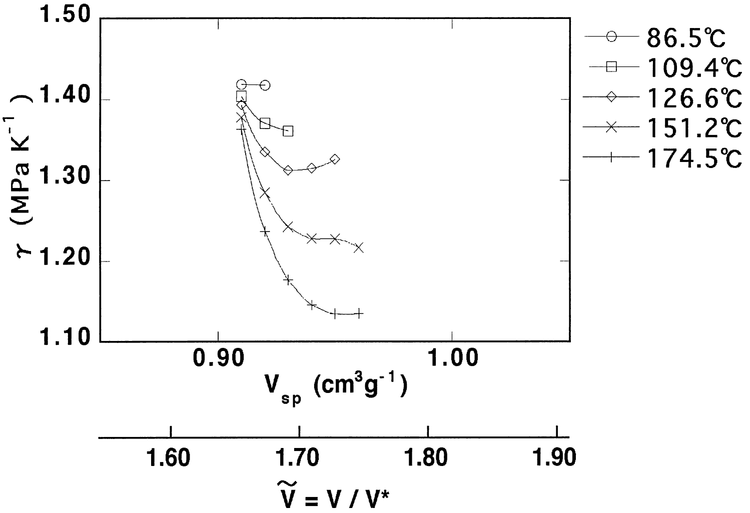

Fig. 2: The γ–v_{sp} relation for a molten POE sample: *PVT* data taken from literature[8]. Temperatures are shown for the individual curves

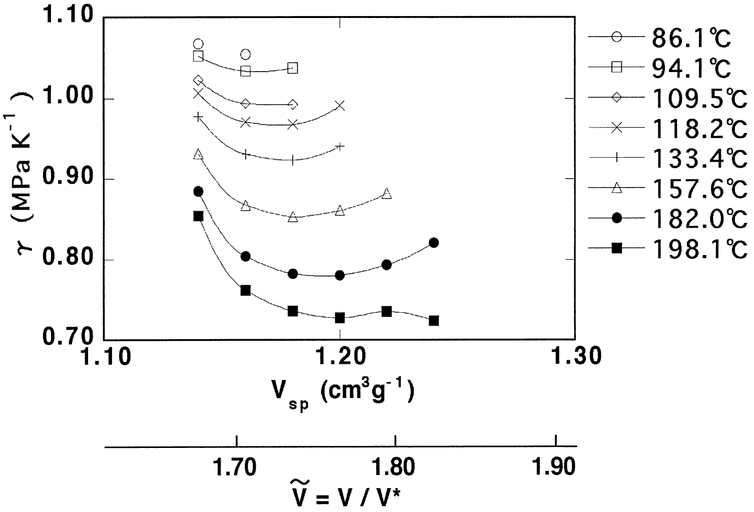

Fig. 3: The γ–v_{sp} relation for a molten PB sample: *PVT* data taken from literature[8]. Temperatures are shown for the individual curves

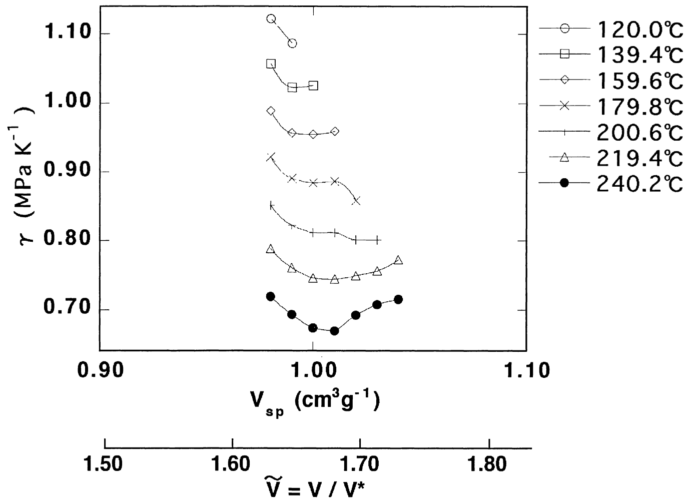

Fig. 4: The γ–v_{sp} relation for a molten PS sample: *PVT* data taken from literature[8]. Temperatures are shown for the individual curves

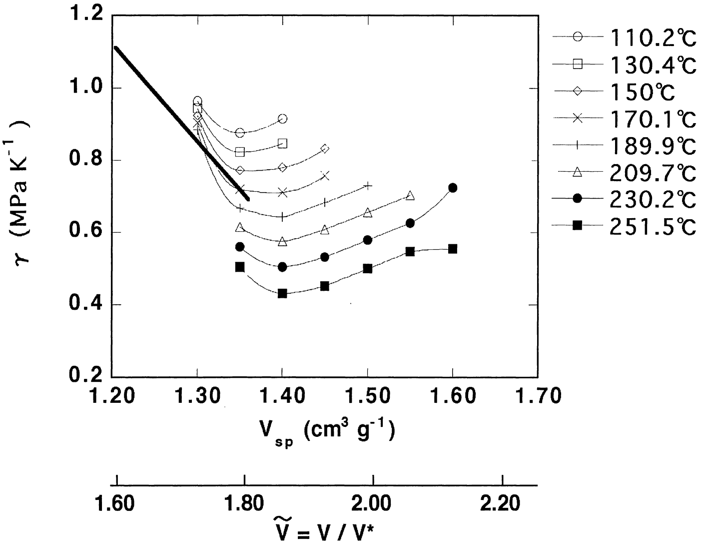

Fig. 5: The γ–v_{sp} relation for n-hexadecane: *PVT* data taken from literature[8]. Temperatures are shown for the individual curves. The heavy line indicates the relation reported for n-heptadecane by Turturro and Bianchi[11]

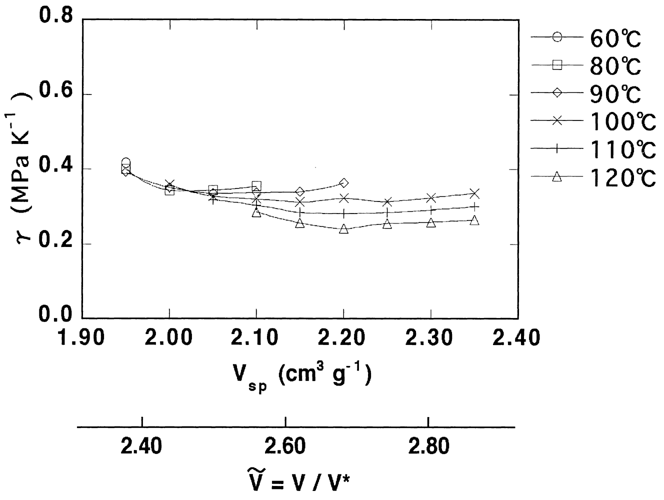

Fig. 6: The γ–v_{sp} relation for 2-methylpropane: *PVT* data taken from literature[9]. Temperatures are shown for the individual curves

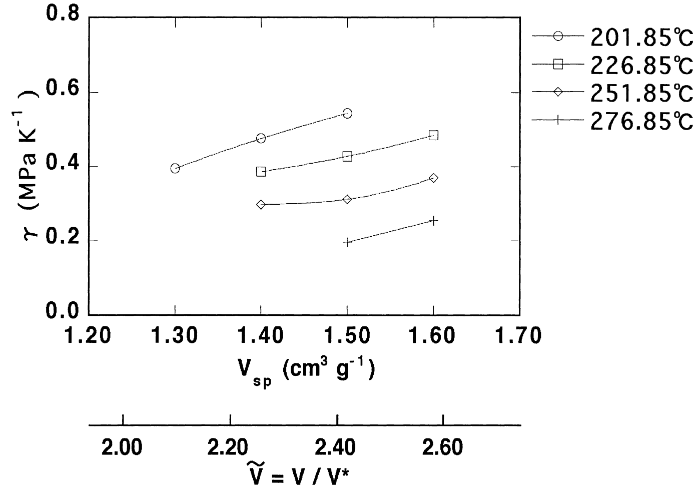

Fig. 7: The γ–v_{sp} relation for benzene: *PVT* data taken from literature[9]. Temperatures are shown for the individual curves

from the *V-T* relation[8)]. In conventional semicrystalline polymer systems, the difference between the crystalline and molten specific volumes at the melting point should be of the order of 0.1 cm^3g^{-1}.

The results shown in Figs. 1-4 suggest that γ may not be appreciably affected by the compression or expansion of the volume by this amount as long as the system remains highly fluid. Following the aforementioned arguments, the volume of the isotropic fluid may be compressed to that of the solid state or vice versa while the configurational entropy of chain molecules remains invariant. The temperature dependence of the configurational entropy estimated for an isolated single chain by the conventional RIS model is known to be very small within the temperature range considered in this work.

The analysis was extended to include smaller molecules such as various linear and branched paraffins, and for comparison, a globular molecule[9)]. The results are illustrated for n-hexadecane, 2-methylpropane, and benzene, respectively, in Figs. 5-7. Although absolute values are divergent in both γ and ν_{sp}, the general characteristics of various plots are more or less similar to those found for polymer samples shown above. Comparison indicates that the enhancement of γ in the small ν_{sp} region is a general phenomenon, not a unique feature of polymeric chain molecules. In Fig 5, the γ-ν_{sp} relation reported for n-heptadecane by Turturro and Bianchi[11)] is illustrated by a heavy line in the upper-left corner. In their estimation, the slope of a given *P- T* isochore is assumed to be invariant over a wide range of temperature. As manifestly shown in Fig.1a, however, the slopes of the *P-T* curve are mostly non-linear, thus suggesting that the value of γ varies as a function of volume ν_{sp} as well as temperature *T*.

Discussion

At this stage, it would be natural to consider the use of reduced volumes $\tilde{\nu}$ instead of specific volumes ν_{sp}, by taking a ratio to the core volume ν^*. The values of the core volume $\nu^*(cm^3g^{-1})$ were calculated from the van der Waals volumes listed in Bondi's table[12)]. The reduced volumes calculated in this manner are indicated on the scale shown below the abscissa in each figure. The core volume is often used to define the free volume $f = (\nu_{sp}-\nu^*)/\nu^*$. It is interesting to note that the γ values become relatively insensitive to the volume, and the slopes tend to be flat at around $\tilde{v}$ = 1.6-1.8 in most of the figures. For the two small molecules, i.e., 2-methylpropane and benzene, experimental data are available only for larger values of $\tilde{v}$. The magnitude of $\tilde{v}$ $(= v_{sp}/v^*)$ vary with the value of core volume (v^*) used. If the core volumes are adopted from the other sources (e.g., Flory's equation of state[13)]), numerical values of $\tilde{v}$ should become smaller. At any rate, these observations suggest that the γ values remain quite insensitive to the volume change, whether or not the molecule is chain-like or globular, as long as the intermolecular distance is larger than a certain limit.

As depicted in Fig. 1 b, the previous arguments on the validity of eq. 2 were focused on the functional form of the γ-v_{sp} relation in the immediate vicinity of the transition region. The entropy separation due to eqs. 1-3 requires a hypothetical process in which the volume of the liquid is compressed to that of the crystal without affecting the configurational part of the entropy of chain molecules. The aforementioned analysis suggests that this condition may be fulfilled for a highly fluid system. On the other hand, the γ-v_{sp} relation in the vicinity of the melting point may include some pretransition effect widely known for various systems. It makes an accurate experimental determination of the γ-v_{sp} relation difficult. Accordingly, in the present state of the art, the adoption of a simple expression as set forth by eqs. 1-3 may be more preferable, or at least should not be excluded because of its simplicity unless the functional form of $\gamma(V)$ is accurately known. As suggested by Würflinger[14)], use of an equation of state could be helpful in elucidating thermodynamic characteristics of a liquid in the transition range, provided that the required parameters of the expression are well established.

In this paper, we have just concentrated in investigating the volume dependence of γ. In treating the transition entropy of real systems, contribution from the so-called communal entropy ΔS_d is often considered by introducing an extra term in eq. 1:[11,15,16)]

$$(\Delta S_{\mathrm{tr}})_V = (\Delta S_{\mathrm{tr}})_P - \Delta S_V - \Delta S_{\mathrm{d}} \qquad (5)$$

The physical definition of the ΔS_d term is still obscure for polymeric systems, in which the external degrees of freedom are largely restricted by the chain connectivity. In general, contribution from this source to the total entropy change is assumed to be small for polymeric chains. In our previous treatment of liquid crystals, the constant-volume transition entropy estimated without consideration for the ΔS_d term were compared directly with those calculated on the basis of the ^{2}H NMR data.

Concluding remarks

In most cases, some moderate increase in γ is systematically observed as v_{sp} increases beyond a shallow minimum: i,e., in the high-temperature and low-pressure region. The equation of state theories available in the literature[13,17,18)] normally predict certain distinct volume-dependence of γ. At this moment, however, we cannot offer any reasonable explanation for the complicated behavior revealed in the experimental γ-v_{sp} relation. Studies are in progress in both theory and experiment toward a deeper understanding of such characteristics.

Acknowledgment

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