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Thermodynamics of Polymeric Fluids – Effect of Volume on the Configurational Entropy of Chain Molecules

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SUMMARY: Various conformation-dependent properties of chain molecules have been successfully treated within the rotational isomeric state approximation. The conformation entropy is one of such properties which can be readily defined by the partition function, the sum of all possible configurations of the chain. Flexible polymers often exhibit crystallization and in some cases liquid-crystallization as well. In these first-order transitions, changes in the spatial arrangement of polymer chains are considered to be a major factor involved. In order to explicitly determine the conformational contribution to the melting entropy, the latent entropy observed under the isobaric condition must be corrected for the volume change. The entropy separation 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 molecules. Finally thermodynamic significance of the conformation entropy in these transitions is emphasized on the basis of the critical studies of the entropy–volume relation of chain molecules in the liquid state.

Formulation of Conformation Entropy

Conformation entropy S^{conf} may be defined as

$$S^{\mathrm{conf}} = \mathrm{k} \ln Z + \mathrm{k}T(\mathrm{d}\ln Z / \mathrm{d}T) \qquad (1)$$

where Z represents configuration partition function:

$$Z = \mathrm{J}^* \, \mathrm{U}_1^{(\mathrm{n})} \, \mathrm{J} \qquad (2)$$

where J* and J are the row and column vectors, respectively, taking care of the initial and terminal bonds of the chain comprising n bonds. Enumeration of all possible configurations can be performed by the matrix multiplication of the conformational

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statistical weight matrix U_i defined within the rotational isomeric state (RIS) approximation.[1] Having U_i properly defined for bond i, calculation of the average of any conformation-dependent properties is straightforward. Usefulness of the conformation partition function thus defined has been demonstrated by a vast majority of successful examples: various properties of polymer chains have been studied in dilute solution as well as in the bulk molten state by both experimental and theoretical techniques.[1]

The conformation entropy defined by eq. 1 is directly related to the flexibility or rigidity of given polymer chains. Thermodynamic properties of the bulk are known to be largely affected by the flexibility of the polymer chain. Attempts to elucidate the contribution arising from the conformational flexibility are rather limited however. In order to predict the bulk properties from a given first-order structure, as required in the molecular design of polymeric materials, such information is fundamentally important. In this work, an effort has been made to elucidate the role of conformation entropy in determining the phase transitions of chain molecules.

Role of Conformation Entropy in Determining the Phase Transition

As depicted in Fig. 1, the mechanism involved in the melting of crystals is largely differentbetween polymeric and monomeric globular compounds. While the destruction of long-range order, i.e., the randomization of centers of gravity, is the major contribution to the entropy of melting in low molecular weight compounds, changes in the spatial arrangement of polymer chains are considered to be the major factor in the other. The role of rotational isomerism in the melting behavior has thus been an important issue in the history of polymer science.[2] In the molten amorphous state, chain molecules are assumed to take random-coil arrangements unperturbed by the long-range interactions along the chain, while the chains are confined in a well-ordered single conformation in the crystalline state, thus Z=1. The conformational entropy change ΔS^{conf} can be calculated by taking the difference between these two states. Strictly speaking, however, the validity of the treatment is guaranteed only for an isolated single chain. In order to extract the conformational contribution to the melting entropy, the value observed under the isobaric condition must be corrected for the volume change.

According to Mandelkern's formulation[2], the increase in entropy due to the volume-expansion at the melting point can be conventionally estimated by

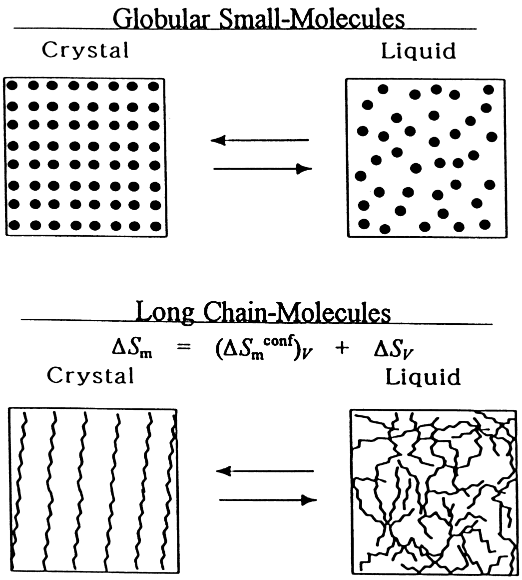

Fig. 1: Schematic representation of the phase transition for globular and chain molecules.

$$\Delta S_V = (\alpha/\beta)\Delta V = \gamma\Delta V \qquad (3)$$

where α, β, and γ respectively denote thermal expansion coefficient, isothermal compressibility, and thermal pressure coefficient

$$\gamma = (P/T)_V = (S/V)_T \qquad (4)$$

The constant-volume entropy change $(\Delta S_m)_V$ at the melting point can then be derived from the relation

$$(\Delta S_m)_V = (\Delta S_m)_P - \Delta S_V \qquad (5)$$

where $(\Delta S_m)_P$ is the melting entropy observed under the atmospheric pressure.

The values of $(\Delta S_m)_V$ have been estimated for a variety of polymers and often shown to be in reasonable agreement with those of the conformation entropy calculated according to the RIS approximation.[3] For chain molecules, a major contribution to the melting entropy arises from the internal rotation around the constituent bonds.

In the real system, volume expansion or contraction takes place at the transition due to the density difference between the two phases in equilibrium. The entropy separation according to eqs. 3-5 is a hypothetical process assuming 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.[4-6] Wunderlich et al.[6] pointed out that the volume dependence of γ during the compression from the liquid to the solid volume may not be negligible, and thereby leads to a significant underestimate of the ΔS_V term. They proposed to adopt an integration form such as

$$\Delta S_V=\gamma\,(V)\,\mathrm{d}\,V \qquad (6)$$

to replace eq. 3. To what extent the entropy of the system including 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. The phase rule however dictates that the direct determination of the γ (V) function at the melting point is impossible.

The Entropy -Volume Relation of Polymer Fluids

The γ vs. specific volume (v_{sp}) relations derived for linear polyethylene (PE) in the range 160~260 are reproduced in Fig. 2.[7] The slope of the curves indicates the susceptibility of γ

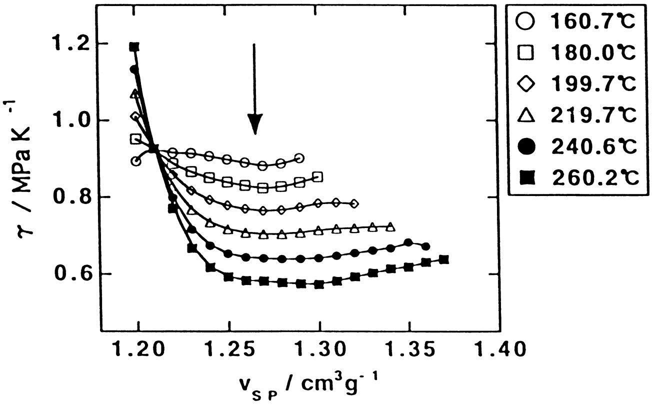

Fig. 2: The γ-v_{sp} relation at given temperatures, obtained from the analysis of *PVT* data reported for PE in the molten state.[8] The specific volume at the melting point is indicated by the arrow.

to the volume change at given temperatures. The γ value remains relatively insensitive to the change in v_{sp} over a fairly wide range around a shallow minimum. The γ value tends to be enhanced in the vicinity of the lower end of the curve. The slope of the γ-v_{sp} curve becomes steeperhighly negative) especially when high-temperature samples are compressed under high pressure (cf. the curve for 260.2). Such a tendency is less marked for curves obtained at lower temperatures. The v_{sp} value at the melting point (133) is indicated by the arrow. The results shown in Fig. 2 suggest that γ may not be appreciably affected by the compression or expansion of the volume over a certain range as long as the system remains highly fluid. The γ-v_{sp} relation determined as above does not however guarantee that the conformation of chain molecules are also unaltered by the volume change.

MD Simulation of n-Undecane in the Liquid State

In order to obtain further insight into the problem, MD simulations were carried out using the software package InsightII/Discover.[9] Several initial chain conformations were constructed using the Amorphous Cell program with the COMPASS force field.[10] Calculations were extended to temperatures lower than the melting point (-25.6) of n-undecane.[11]

The γ-v_{sp} relations obtained from the experimental *PVT* data and MD simulations are shown separately in Figs. 3a and 3b. At lower temperatures, conformational transition takes place less frequently around a given bond, leading to a larger fluctuation in the calculated *PVT* relation.It should be noted that the general trend exhibited by the γ-v_{sp} curves (Figs. 3a and 3b) resembles those previously obtained from the analysis of the *PVT* data of PE (Fig. 1). The γ values remain quite insensitive to the specific volume v_{sp} over a wide range. The curves derived under high-temperature and high-pressure conditions tend to go up abruptly as the specific volume v_{sp} decreases beyond certain limiting values. As temperature increases, the γ-v_{sp} curve tends to shift upward. In the region where γ values are going up rapidly ($v_{sp} < \sim 1.3$ cm^{3}g^{-1}), all γ-v_{sp} curves tend to merge.

Variation of the bond conformation was studied within the RIS approximation. Average values of the trans fraction f_t were elucidated for the terminal C_2-C_3 and the central C_5-C_6 bonds as a function

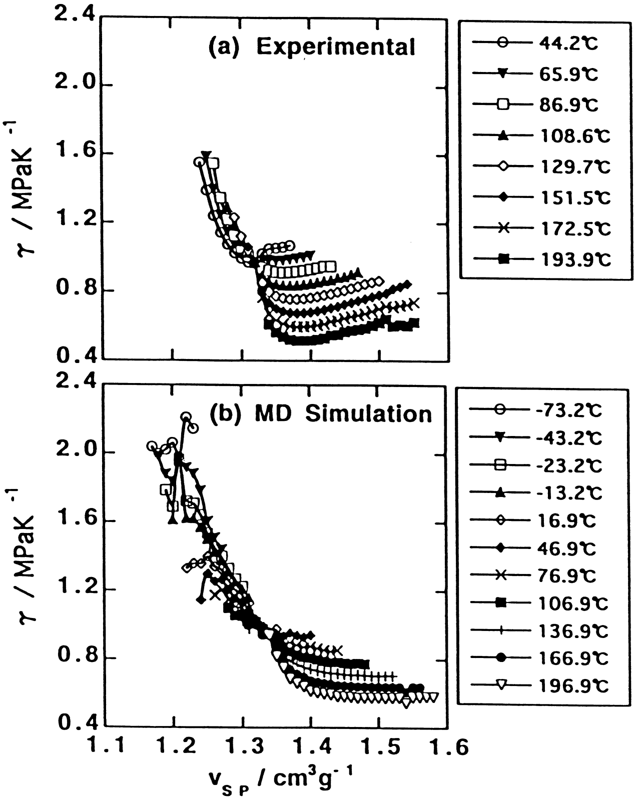

Fig. 3: The γ-v_{sp} curves for given temperatures: (a) Obtained by the analysis of experimental *PVT* data and (b) MD simulation. A wider range of specific volume is covered in the latter diagram.

of temperature and pressure. Both f_t values tend to decrease with temperature, while they remain nearly invariant with pressure. The spatial configuration of n-undecane is apparently not much affected by the compression of the bulk volume within the range examined. It is interesting to note that the bond conformation remains unaltered even in the range $v_{sp} < \sim 1.3$ cm^{3}g^{-1}, where the magnitude of γ is increasing rapidly. The trans-gauche transition around the C-Cbond occurs quite frequently as long as temperatures are kept sufficiently high. At lower temperatures, however, conformational transition tends to deviate from the ergodic behavior.

Integration of eq. 6 along the γ-v_{sp} path as illustrated in Fig. 2 or 3 leads to a pressurized liquid having the crystal volume, in which internal rotations are highly restricted, and perhaps bond lengths and bond angles are displaced as well, from the mean position encountered in the free chain. Our goal is to find a hypothetical process (cf. eqs. 3-5) in which the volume of the liquid can be compressed to that of the crystal without creating too much intermolecular conflicts on the intramolecular bond rotation and rearrangement of the spatial configuration of the chain. Fluidity must be guaranteed during compression.

In the vicinity of the phase transition point, some possible pretransition effect makes an accurate experimental determination of the γ-v_{sp} relation difficult. In the practical application, the relation $\gamma=\alpha/\beta$ (eq. 3) is often used to estimate γ at the transition by extrapolation from higher temperatures. The value of γ thus obtained can be adopted in the prescription set forth by eqs. 3-5. For the purpose at hand, this process should not be excluded because of its simplicity unless a more prevailing form of γ (V) is known.

Concluding Remarks

The lattice theories of polymeric fluids constructed on the basis of random conformation of chains have been successfully applied to various *PVT* properties of polymers in the melt. [12-14] In these theories, an arbitrarily chosen portion of a given chain molecule called segment serves as a unit interspersing the configuration space available to the system. The intermolecular degrees of freedom of segments constituting the chain are often expressed as 3c after Prigogine[15], although the definition of parameter c is rather intuitive. Treatment of free volumes is somewhat divergent among the theoretical models employed. This c is however the only parameter representing the neighbor-dependent character of the segment in the individual chain molecules. The values of c estimated from experimental data exhibit little correlation with the conformational characteristics, such as flexibility or stiffness, of the chain.

The γ-v_{sp} curves shown above do not quite agree with the prediction from the equation of state theories.[12-14] Such deviation suggests that changes in the local structure of liquid are not appropriately reflected in the theoretical expressions. As shown in many examples obtained by the analysis of experimental data, [7] a plateau region or even some moderate increase in γ is often observed as v_{sp} increases beyond a shallow minimum: i.e., in the high-temperature and low-pressure region. At this moment, however, we cannot offer any reasonable explanation for the complicated behavior revealed in the experimental γ-v_{sp} relation.

The phase transition entropies of chain molecules, after corrected for the volume change as specified in eqs. 3-5, have been compared with the conformation entropies derived by using the RIS analysis of a single chain.[3,16] The treatment has been extended to the analysis of the isotropic–liquid crystalline phase transition of mainchain-type compounds in which flexible spacers joining mesogenic units play a major role.[9,17] The transition entropies estimated in these two different methods exhibit good correspondence for both crystallization and liquid-crystallization. The importance of the conformation entropy in determining the physical properties of the aggregated bulk state has thus been demonstrated. The conformation entropy is not the only conceivable entropy for the polymer systems however. In liquid crystals, the role of the orientational entropy along the polymer chain should not be underestimated. These are the forthcoming subjects inviting us to pursue.

Finally, I would like to point out the need of a refined equation of state theory in which the spatial configuration of polymer chains is precisely taken into account. The PRISM theory, an off-lattice continuum treatment of polymeric liquids, recently developed by Curro and Schweizer[18] is apparently a promising effort along this line.

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References

1) (a) P. J. Flory, „*Statistical Mechanics of Chain Molecules*", Interscience, New York, 1969. (b) A. Abe, „*Comprehensive Polymer Science*", Vol. 2, Ed by C. Booth and C. Price, Pergamon Press, Oxford, 1989; Chap. 2, p.49-69. (c) W. L. Mattice and U. W. Suter, „*Conformational Theory of Large Molecules*", Interscience, New York, 1994.

2) L. Mandelkern, „*Crystallization of Polymers*", McGraw-Hill, New York, 1964; Chap. 5.

3) (a) I. Kirshenbaum, *J. Polym. Sci., Part A*, **3**, 1869 (1965). (b) R. P. Smith, *J. Polym. Sci., Part A-2*, **4**, 869 (1966). (c) A. E. Tonelli, *J. Phys. Chem.*, **52**, 4749 (1970); *J. Phys. Chem.*, **56**, 5533 (1972). (d) J. E. Mark, *J. Chem. Phys.*, **67**, 3300 (1977). (e) P. R. Sundararajan, *J.*

Appl. Polym. Sci., **22**, 1391 (1978). (f) A. Abe, *Macromolecules*, **13**, 546 (1980).

4) (a) Y. Tsujita, T. Nose, and T. Hata, *Polym. J.*, **3**, 587 (1972). (b) Y. Tsujita, T. Nose, and T. Hata, *Polym. J.*, **5**, 201 (1973). (c) Y. Tsujita, T. Nose, and T. Hata, *Polym. J.*, **6**, 51 (1974).

5) A. Turturro and U. Bianchi, *J. Chem. Phys.*, **62**, 1668 (1975); U. Bianchi and A. Turturro, *J. Chem. Phys.*, **65**, 697 (1976).

6) (a) F. E. Karasz, P. R. Couchman, and D. Klempner, *Macromolecules*, **10**, 88 (1977). (b) B. Wunderlich and G. Czornyj, *Macromolecules*, **10**, 906 (1977). (c) M. Naoki and T. Tomomatsu, *Macromolecules*, **13**, 322 (1980). (d) T. Bleha, *Polymer*, **26**, 1638 (1985).

7) A. Abe, T. Takeda, and T. Hiejima, *Macromol. Symp.*, **152**, 255 (2000); A. Abe, T. Takeda, T. Hiejima, and H. Furuya, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **41** (1), 337 (2000).

8) P. Zoller and D. Walsh, „*Standard Pressure-Volume-Temperature Data for Polymers*“, Tech. Pub. Co., Lancaster, 1995.

9) A. Abe, T. Takeda, T. Hiejima, and H. Furuya, *Macromolecules*, submitted.

10) H. Sun, *J. Phys. Chem., B.*, **102**, 7338 (1998).

11) (a) M.G. Broadhurst, J. Res. Nat. Bur. Stand., **66A**, 241 (1962). (b) J. G. Hust and R. E. Schramm, *J. Chem. Eng. Data*, **21**, 7 (1976).

12) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507, 3515 (1964); P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965); A. Abe and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1838 (1965).

13) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969); R. Simha,. *Macromolecules*, **10**, 1025 (1977).

14) T. Nose, *Polym. J.*, **2**, 124, 427, 437 (1971).

15) I. Prigogine, A. Bellemans, and V. Mathot, „*The Molecular Theory of Solutions*,“ North-Holland Pub., Amsterdam, 1957.

16) A. Abe, T. Takeda, T. Hiejima, and H. Furuya, *Polym. J.*, **31**, 728 (1999).

17) A. Abe, *Rep. Prog. Polym. Phys. Jpn.*, in press.

18) K. S. Schweizer and J. G. Curro, *Phys. Rev. Lett.* **58**, 246 (1987); K. G. Honnell, J. G. Curro, and K. S. Schweizer, *Macromolecules*, **23**, 3496 (1990).