A Critical Study of the Entropy−Volume Relation of Chain Molecules in the Fluid State: Computer Simulation of *n*-Undecane and Comparison with Experimental *PVT* Data

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ABSTRACT: 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 molecules. In this work, we have extensively examined the volume dependence of thermal pressure coefficient $\gamma = (\delta P/\delta T)_V = (\delta S/\delta V)_T$ of *n*-undecane. Molecular dynamic simulations were performed using the software package Insight II/Discover. In the standard calculation, a cubic box containing 30 *n*-undecane molecules was used under the conventional periodic boundary conditions. The experimental observations were well reproduced by the MD simulation performed as above, and accordingly the γ vs specific volume (v_{sp}) relations derived from the simulation are favorably compared with those obtained from the experimental *PVT* data. The γ values remain quite insensitive to v_{sp} over a wide range at given temperatures. Values of the trans fraction were found to decrease with an increase in temperature, while they tend to remain quite insensitive to pressure (0−200 MPa). It was concluded on this basis that the aforementioned treatment of the volume change at the phase transition seems to be supported by the present analysis.

Introduction

The present work was motivated by the arguments regarding the estimation of volume correction for the fusion entropy of chain molecules. The increase in entropy due to the volume expansion at the melting point can be conventionally estimated as prescribed in Mandelkern's book[1]

$$\Delta S_V = (\alpha/\beta)\Delta V = \gamma \Delta V \tag{1}$$

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

$$\gamma = (\delta P/\delta T)_V = (\delta S/\delta V)_T \tag{2}$$

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

$$(\Delta S_m)_V = (\Delta S_m)_P - \Delta S_V \tag{3}$$

where $(\Delta S_m)_P$ is the melting entropy observed under 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 conformational entropy calculated according to the rotational isomeric state (RIS) approximation.[2,3] For chain molecules, major contribution to the melting entropy arises from the internal rotation around the constituent bonds. This method has also been adopted in the estimation of the constant-volume transition entropy at the isotropic ∼ liquid-crystal and liquid-crystal ∼ crystal phase boundaries of main-chain dimer and trimer compounds in our previous work.[4] The results thus obtained were compared with the conformational entropies deduced on the basis of the deuterium NMR spectroscopy.

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 1 and 2 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.[5] The validity of such an assumption has been questioned by several authors.[6−11] Wunderlich et al.[9] 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

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

to replace eq 1. 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 a direct determination of $\gamma(V)$ function at the melting point is impossible. At the phase boundary, a slight increase in pressure could immediately cause crystallization at this point.

In consideration of these controversial arguments, we have extensively examined the volume dependence of thermal pressure coefficient γ for various chain mol-

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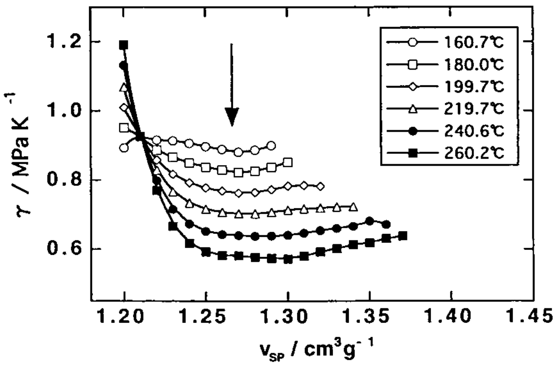

Figure 1. Variation of thermal pressure coefficient γ as a function of specific volume v_{sp} at given temperatures, obtained from the analysis of *PVT* data reported for polyethylene (PE) in the molten state.[12] The specific volume at the melting point is indicated by the arrow.

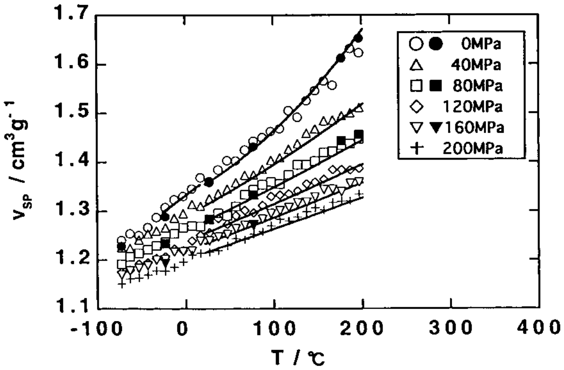

Figure 2. $v_{sp}-T$ isobars of liquid *n*-undecane. The specific volumes obtained by the NPT simulation (shown by symbols) are compared with those (curves) determined by the *PVT* experiment over the temperature range from 21.8 to 201.3 °C.[12] The result of the dilatometric measurement under atmospheric pressure (reported for the temperature range from −26.2 to 16.9 °C) is also indicated by a short curve.[17] Open symbols represent the results collected from the standard procedure (30 molecules, r_c = 9.5 Å, 50 ps runs). For comparison, the MD simulations performed on an expanded scale (64 molecules, r_c = 12.0 Å, 500 ps runs) are also included (filled symbols). The experimental observations are well reproduced by these MD simulations. The figure includes the results of calculations carried out down to −73.2 °C. The cooling of the system did not show any indication of crystallization far below the melting point (−25.6 °C) (see text).

ecules in the fluid state, the *PVT* data required for the analysis being taken from the handbooks.[12,13] The γ vs specific volume (v_{sp}) relations previously derived for linear polyethylene (PE) in the range 160−260 °C are reproduced in Figure 1.[14] The slope of the curves indicates the susceptibility of γ 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 $\gamma-v_{sp}$ curve becomes steeper (highly negative) especially when high-temperature samples are compressed under high pressure (cf. the curve for 260 °C). Such a tendency is less marked for curves obtained at lower temperatures. The v_{sp} value at the melting point (133 °C) is indicated by the arrow. The results shown in Figure 1 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 $\gamma-v_{sp}$ relation determined as above does not however guarantee that the conformation of chain molecules are also unaltered by the volume change.

To obtain further insight into the problem, we have attempted molecular dynamic (MD) simulation by employing *n*-undecane as a model system. The molecule comprises 10 skeletal C−C bonds (i.e., eight rotatable bonds), and thus the minimum requirements may be fulfilled. Experimental *PVT* data of *n*-undecane observed in the range of temperature 25−200 °C and pressure 0−200 MPa were assembled in the handbook of Zoller and Walsh.[12] The isochores and the isothermal $\gamma-v_{sp}$ curves calculated on the basis of the MD simulation will be compared with those derived from the experimental *PVT* data.

MD Simulation Using an Atomistic Model

Molecular mechanics and dynamic simulations were carried out using the software package InsightII/Discover provided by Molecular Simulations, Inc. (MSI). Several initial chain conformations were constructed using the amorphous cell program, the COMPASS force field[15] recently released from MSI being used in this work. In the standard calculation, a cubic box containing 30 *n*-undecane molecules was used under the conventional periodic boundary conditions. NVT and NPT simulations were performed with finite group-based cutoffs (r_c) and with tail corrections for van der Waals interactions. In this method, charged atoms are collected in small groups with those in a close proximity to form an atom group of a net charge of zero or almost zero. An atom near the center of each group is selected to act as a switching atom. When the distance between the switching atoms of two groups is less the cutoff distance, all the atom pairs in the two groups are included. If the distance is greater than the cutoff, they are all excluded. This procedure has been installed to prevent artifacts due to splitting of dipoles in the MSI Discover program. The effect of cutoff distances was examined at r_c = 8.0, 9.5, and 12.0 Å. NPT simulations were carried out using Berendsen pressure control method and Anderson stochastic temperature control. The time step used was 1 fs. All systems were equilibrated under the simulation conditions for at least 50 ps before collecting the trajectories for subsequent analysis. For NVT simulations, pressures and cohesive energies were evaluated over the last 5 ps of the simulations; for NPT simulations, densities were averaged over the 50 ps runs. The NPT data thus collected were used for the subsequent analysis. Calculations were extended to temperatures below the melting point (−25.6 °C) of *n*-undecane.[16,17]

Some of the calculations were carried out for a larger cell box containing 64 *n*-undecane molecules with r_c = 12.0 Å, the sampling time being extended up to 500 ps runs. Comparison with the results derived from the standard procedure will be demonstrated in appropriate figures.

Results and Discussion

Shown in Figure 2 are the isobars of *n*-undecane, where calculated values (open symbols) are compared with those experimentally obtained by the *PVT*[12] and dilatometric measurements.[17] The standard deviation for these calculated points is estimated to be of the order of ±0.01 cm^3/g: the magnitude tends to be slightly higher for the high-temperature−low-pressure region and lower for the opposite end. The result was found to be most satisfactory when the cutoff distance was set equal to $r_c = 9.5$ Å. The other r_c values led to slightly larger deviations, although differences are marginal, from the experimental observation. The results derived from larger scale simulations are shown by filled symbols. The specific volumes (filled symbols) estimated under a variety of conditions are consistent with those shown by open symbols as well as the corresponding (experimental) curves. Figure 2 includes the results calculated down to −73.2 °C at various pressures ranging from 0 to 200 MPa. The specific volumes at the melting equilibrium are reported to be 1.18 $cm^3\ g^{-1}$ (crystal) and 1.30 $cm^3\ g^{-1}$ (liquid)[17] under atmospheric pressure. During the MD simulation, unlike simple liquids, cooling of the system did not show any indication of crystallization below the melting point of *n*-undecane, and the density−temperature curves shown in the figure could be fitted by appropriate second-order polynomials over the entire temperature range at all pressures. The density−temperature plots calculated by stepwise cooling exhibit a plateau at around −100 °C, indicating a gradual transition to the glassy state. As pointed out by the reviewers, some further effort should be needed to ensure crystallization of the system at lower temperatures: e.g., adoption of a larger simulation box or an extended simulation time. Since our main concern is in the liquid state, we did not pursue this subject any further.

As shown in Figure 3a,b, the $P-T$ isochores obtained from experimental *PVT* observations are reasonably well reproduced by the computer simulation. These $P-T$ curves were approximated by the second-order polynomials, and the slopes of the curves thus estimated were plotted against specific volumes to yield the $\gamma-v_{sp}$ relation at given temperatures. The $\gamma-v_{sp}$ relations obtained from the experimental *PVT* data and MD simulations are shown separately in Figure 4a,b. 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 $\gamma-v_{sp}$ curves (Figure 4a,b) resembles those previously obtained from the analysis of *PVT* data of PE. This point is important since we have chosen liquid *n*-undecane as a model compound of PE. 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 $\gamma-v_{sp}$ 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 $\gamma-v_{sp}$ curves tend to merge. Each of the $\gamma-v_{sp}$ relations illustrated in Figure 4 indicates variation under an isothermal condition. In the previous discussion on PE,[14] these observations were used to conclude that the value of the isotropic fluid may be compressed to that of solid state or vice versa while the configurational entropy of chain molecules remains invariant.

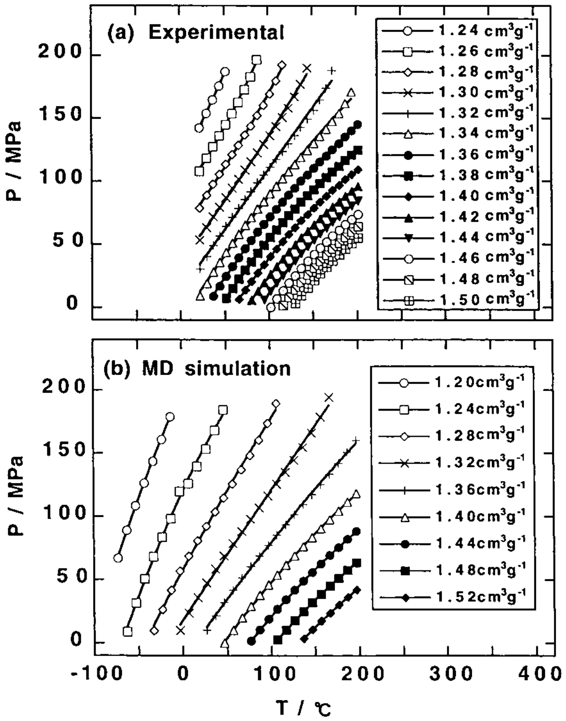

Figure 3. $P-T$ isochore of *n*-undecane, the specific volumes being indicated to the individual curves: (a) obtained by the analysis of experimental data and (b) MD simulation.

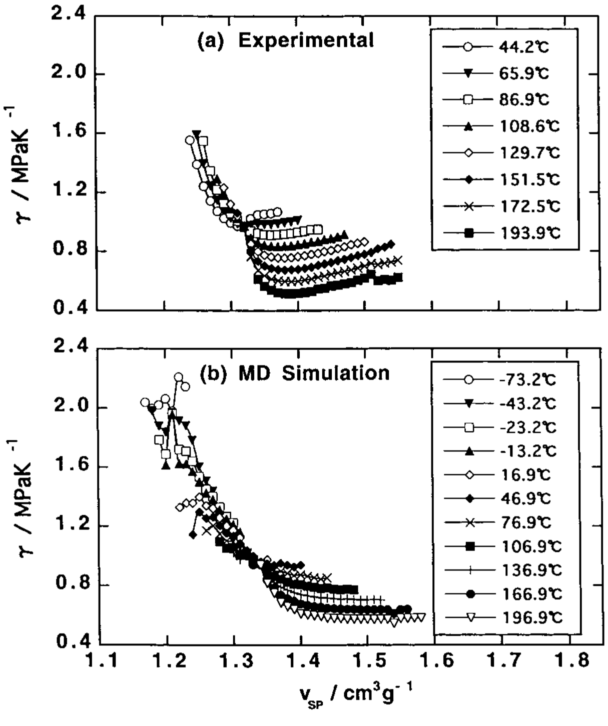

Figure 4. $\gamma-v_{sp}$ curves for given temperatures: (a) obtained by the analysis of experimental data and (b) MD simulation. A wider range of specific volume is covered in the latter diagram.

The conformation of *n*-undecane molecules has been investigated for representative ensembles. Examples of the pair correlation function g(*r*) are illustrated as a function of intermolecular distance *r* (carbon to carbon) in Figure 5, where the curves derived under a fixed pressure (Figure 5a) and a fixed temperature (Figure 5b) are shown separately. As temperature increases, the height of correlation peaks tends to lower. The correlation peaks become broadened at higher temperatures, indicating that the structure of the liquid tends to be more disordered. The position of the peaks (r_{max}) shifts slightly toward higher values as the molecular packing becomes less dense by lowering pressure or increasing temperature. As shown in Figure 5b, the structure of the liquid remains nearly unaffected by the applied pressure within the range investigated. The results of calculation carried out by employing a larger simulation

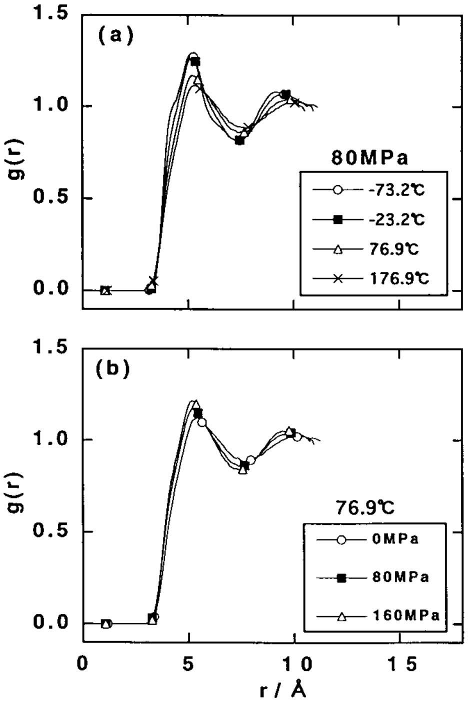

Figure 5. Examples of pair correlation function $g(r)$ obtained by the MD simulation, r designating the intermolecular carbon−carbon distance: (a) variation with temperature at a given pressure (80 MPa) and (b) variation with pressure at a given temperature (76.9 °C).

box for the temperature of 76.9 °C were found to be nearly identical at given pressures (0, 80, 160 MPa) as those shown in Figure 5b and thus are not included here.

Variation of the conformation was studied in terms of the trans fraction f_t for given bonds, where averages were taken over the entire ensemble. The averages taken over all constituent bonds are plotted in Figure 6. Figure 6a,b indicates the f_t values vs temperature plots calculated under two different conditions. Despite the difference in the size of the cell and the sampling time used in the two simulations, the results are very similar, and thus the figures are shown separately. The bond conformation was also investigated around the terminal C_2-C_3 as well as the C_5-C_6 bond. The values of f_t tends to be slightly lower for the terminal, although the data points scatter appreciably around the lines derived using the least-squares method. The values estimated at 0 MPa and 25 °C are $f_t(C_2-C_3) = 0.71 \pm 0.05$ and $f_t(C_5-C_6) = 0.75 \pm 0.05$, while those taken from the curves shown in parts a and b of Figure 6 are respectively $f_t(\text{all C}-\text{C}) = 0.73 \pm 0.02$ and 0.75 ± 0.02. The slope of the curves corresponds to a trans−gauche energy difference $\Delta E = 2.9 \pm 0.3$ kJ/mol as estimated by assuming a simple Boltzmann relation. The value of ΔE thus derived is in the range of those conventionally adopted for n-alkanes.[18] To examine the effect of the size of the simulation box, calculations were further extended to include a system containing 128 molecules with $r_c = 15.0$ Å at 0 MPa for the temperature of 76.9 °C: the f_t values sampled over 50−200 ps runs were found to remain nearly constant. The value (0.69) obtained after 200 ps runs exactly coincides with that from the smaller cell (64 molecules, $r_c = 12.0$ Å, 500 ps runs) and thus is not included in Figure 6b.

The effect of pressure is shown explicitly in Figure 7, where f_t values are plotted against pressure at given temperatures (−23.2, 76.9, 176.9 °C). In these averages, a small difference between the inner and terminal bond conformation is ignored. The corresponding results obtained from larger scale simulations are distinguished by using filled symbols: f_t values thus derived tend to be slightly higher than those of the open symbols in the lower temperature region. Although the data points are scattered around the least-squares lines drawn for given temperatures (±a few percent), the bond conformation tends to remain invariant with pressure as an average. As the applied pressure increases, the specific volume

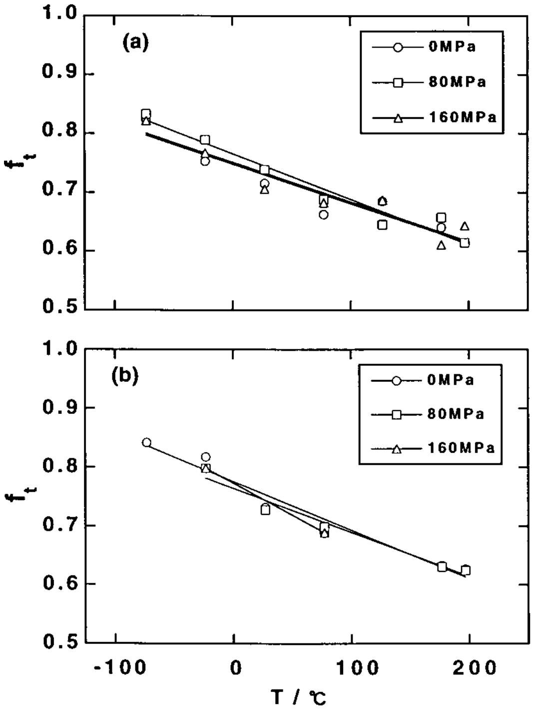

Figure 6. Bond conformation of n-undecane as a function of temperature. Averages of f_t for all C−C bonds estimated at given pressures: (a) those calculated by using the standard simulation box (30 molecules, $r_c = 9.5$ Å, 50 ps runs) and (b) those obtained by using a larger simulation box (64 molecules, $r_c = 12.0$ Å, 500 ps runs). To facilitate comparison, lines are drawn through the individual set of symbols (0, 80, 160 MPa) by the least-squares method, indicating that the effect of pressure is insignificant.

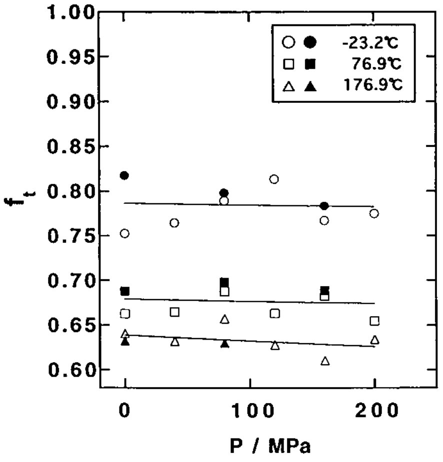

Figure 7. Bond conformation (f_t) as a function of pressure estimated by the standard procedure (open symbols), temperatures being indicated in the figure. Filled symbols are those derived from larger size simulations (64 molecules, $r_c = 12.0$ Å, 500 ps runs). For the sake of comparison, lines are drawn for given temperatures by the least-squares method.

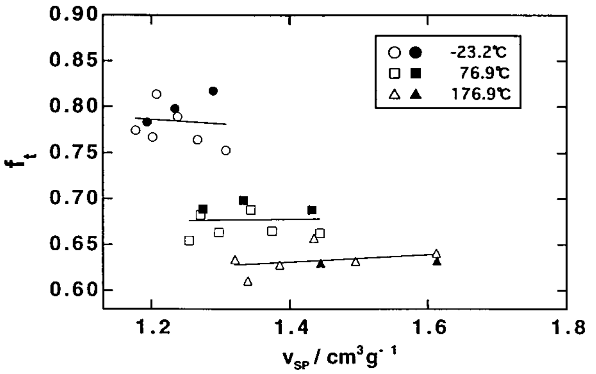

Figure 8. Bond conformation as a function of specific volume. The f_t values appeared in the preceding figure are plotted against specific volumes. See legends to Figure 7.

v_{sp} decreases. In Figure 8, the same f_t values are plotted as a function of v_{sp}. In brief, the spatial configuration of *n*-undecane is not significantly affected by the compression of the bulk volume within the range (<200 MPa) examined.[19] It is interesting to note here 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–C bond occurs quite frequently as long as temperatures are kept sufficiently high. At lower temperatures, however, conformational transition tends to deviate from the ergodic behavior.[22]

Concluding Remarks

The equation-of-state theories available in the literature[23–25] normally predict a certain distinct volume dependence of γ.[7b] According to the Flory model,[23] for example, γ is given as

$$\gamma = P/T + (P^*/T)(v_{sp}^{*2}/v_{sp}^{2}) \tag{5}$$

where P^* designates the characteristic pressure and v_{sp}^* the core volume. The right-hand side of eq 5 consists of two terms, i.e., the ideal gas term and the van der Waals interaction term. The steep rise of the $\gamma - v_{sp}$ curve observed with decreasing v_{sp} (at higher compression) probably arises from the intermolecular correlation. Integration of eq 4 along the $\gamma - v_{sp}$ path as illustrated in Figure 4b leads to a pressurized liquid having crystal volume, in which internal rotations are restricted, and perhaps bond lengths and bond angles are also displaced from the mean values encountered in the free chain. Our goal is to find a hypothetical process (cf. eq 3) in which the volume of the liquid can be compressed to that of the crystal without creating too much intermolecular conflicts: the intramolecular bond rotation and thus the rearrangement of the spatial configuration of the chain should be permitted even when the entire volume is reduced. Fluidity must be guaranteed during compression. As shown above, in a highly fluid state, the values of γ are apparently not much depend on the volume.

The entropy of fusion of *n*-undecane is reported to be $(\Delta S_m)_P = 89.6$ J mol^{-1} K^{-1}.[16] Adoption of $\gamma = 1.2$ MPa K^{-1} in eq 1 yields $\Delta S_V = 18.0$ J mol^{-1} K^{-1}, leading to $(\Delta S_m)_V = 71.6$ J mol^{-1} K^{-1}, in an approximate agreement with the configurational entropy ($\Delta S^{conf} = 61.9$ J mol^{-1} K^{-1}) estimated by the RIS model.[26] *n*-Alkanes comprising an odd number of carbons ($n = 11-43$) are however known to exhibit the rotator solid phase in the vicinity of the melting point.[16] In *n*-undecane, the low-temperature orthogonal form turns into the hexagonal (rotator) packing at −36.6 °C. The value of $(\Delta S_m)_P$ cited above corresponds to the melting (−25.6 °C) of the latter phase. Such a pretransition phenomenon makes a quantitative comparison difficult.

The $\gamma - v_{sp}$ curves shown in this work and the previous papers[14] as well do not quite agree with the prediction from the equation-of-state theories (cf. eq 5). 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,[14] 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 $\gamma - v_{sp}$ relation.

In this work, we have just concentrated in investigating the volume dependence of γ in the liquid state. In treating the transition entropy of real systems, contributions from the so-called communal entropy as well as other residual entropies are often considered by introducing an extra term ΔS_d in eq 1:[8,10,27]

$$(\Delta S_{tr})_V = (\Delta S_{tr})_P - \Delta S_V - \Delta S_d \tag{6}$$

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.[27]

In the vicinity of the phase transition point, some possible pretransition effect makes an accurate experimental determination of the $\gamma - v_{sp}$ relation difficult. In the practical application, the relation $\gamma = \alpha/\beta$ (eq 1) 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 1–3. For the purpose at hand, this process should not be excluded because of its simplicity unless a more prevailing form of $\gamma(V)$ is known.

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(2) Conformational entropy S^{conf} may be defined as $S^{conf} = k \ln Z + kT(\mathrm{d} \ln Z/\mathrm{d}T)$, where Z represents configuration partition function and k is the Boltzmann factor. Enumeration of all possible configurations can be performed by the matrix-multiplication method within the RIS approximation.[3] 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.

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(5) The concept prescribed in eqs 1−3 should be in principle applicable to both expansion from the crystalline state and compression of the molten amorphous state. In practice, the treatment requires a reasonable estimation of γ along the path to the hypothetical fluid state.[6] In this regard, the latter approach may be more tractable in the actual application.

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