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Analysis of Melting Entropy and Effect of Volume on the Conformational Entropy of *trans*-Polyisoprene

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ABSTRACT: Some discussions on the problems and the criticisms in the experimental analysis of the melting entropy as the sum of two or three independent contributions are given by considering volume effects on each contribution. It is shown that the criticism proposed by Karasz, Couchman, and Klempner on the concept of the entropy separation is drawn on the basis of erroneous neglects of a temperature-dependent contribution to the entropy and of volume dependences of some thermodynamic variables. A reliable value of the entropy due to volume change can be obtained from the thermal-pressure coefficient of the liquid state, and, in this estimation, the contribution of the communal entropy is expected to be negligible. The melting properties of *trans*-polyisoprene were obtained by measuring the melting temperature under elevated pressures at a heating rate of 0.3 K/h and the pressure–volume–temperature relations for both liquid and semicrystalline regions. The comparison of the experimental conformational entropy with the one calculated for an isolated unperturbed chain revealed the conformational entropy of *trans*-polyisoprene to be affected by volume change in the high-density region but only slightly in the low-density region. Thus the average conformations in the bulk polymer may be regarded to be the same as that of an isolated chain in the ordinary-liquid region. A differential scanning calorimeter was also used to determine the latent heat and the Clausius–Clapeyron equation was ascertained to apply to the melting of the semicrystalline phase within experimental uncertainties.

The increment of entropy in the liquid state from that in the crystalline state at the same temperature and pressure has been frequently analyzed by dividing it into inter- and intramolecular contributions. This seems to follow from the fact that most statistical models used to treat thermodynamic properties of polymer liquids and solutions lead to a partition function constituted by independent factors such as intramolecular conformations of the chain, intermolecular configurations, and a communal term. The entropy-separation concept above leads to the following expressions on the melting point at which the increment of entropy can directly be obtained as the melting entropy ΔS_m: for simple molecules which have no intramolecular degrees of freedom,[1]

$$\Delta S_m = \Delta S_v + \Delta S_d \tag{1}$$

and for polyatomic molecules,[2-17]

$$\Delta S_m = \Delta S_v + S_c \tag{2a}$$

or

$$\Delta S_m = \Delta S_v + \Delta S_d + S_c \tag{2b}$$

where ΔS_v is the entropy due to volume change, ΔS_d the communal entropy, and S_c the intramolecular conformational entropy which can be assumed to vanish in the crystalline state. These simple equations include some vagueness and several criticisms have been proposed.

The communal entropy term in eq 2b, introduced by Starkweather and Boyd[4] and employed by Tsujita, Nose, and Hata[11] and Turturro and Bianchi[13] has been assumed to be constant, though miscellaneous methods were adopted in its evaluation. However, Kirkwood,[17] in his critical study on the cell models, showed S_d to be a function of volume V and temperature T, but its functional dependence remained obscure. Furthermore, a doubt was cast upon its existence in polymer liquids by Smith.[6]

The isothermal entropy change made by the change in volume is determined by

$$\Delta S_v = \int_{V^c_m}^{V^l} \gamma \, dV \tag{3a}$$

$$\Delta S_v \simeq \gamma(V^l_m - V^c_m) = \gamma \Delta V_m \tag{3b}$$

where V^l_m and V^c_m are the volume of the liquid and crystalline phase, respectively, at the melting temperature T_m, and γ is the thermal-pressure coefficient. Since the approximation in eq 3b with liquid γ underevaluates ΔS_v,[7,13] the inclusion of terms which account for the volume dependence of γ, i.e., eq 3a, has recently been applied by some investigators.[11,13] Wunderlich and Czornyj,[15] however, demonstrated on polyethylene that the refined determination from eq 3a with eq 2a resulted in a larger deviation in the S_c value from that for an isolated unperturbed chain and suggested that S_c might depend on volume.

A criticism on the entropy-separation concept was proposed by Karasz, Couchman, and Klempner[14] from considerations on thermodynamic paths of calculation of ΔS_v. They applied, in addition to eq 3b, the isobaric paths to calculate ΔS_v and used the approximation

$$\Delta S_v \simeq (C_P/TV\alpha)\Delta V_m \tag{4}$$

where C_P and α are the isobaric heat capacity and the thermal expansivity, respectively. They showed a discordance in the ΔS_v values from four paths of calculation by using liquid and crystalline quantities in each of eq 3b and 4 for several polymers and concluded that the entropy-separation concept is incorrect. However, it will be shown that their criticism was drawn on the basis of an erroneous neglect of temperature and volume dependences of some thermodynamic variables.

The above problems included in the experimental analysis on the basis of the entropy-separation concept may be summarized as follows: (1) the evaluation of ΔS_v; (2) the existence of ΔS_d; (3) the constancy of ΔS_d if ΔS_d is required; and (4) the volume dependence of S_c. The purpose of this paper is first to examine problems (1) to (3) and second to attempt to elucidate the effect of volume on the conformational entropy by analyzing the melting properties at elevated pressures for *trans*-polyisoprene (*trans*-PIP).

In order to apply the thermodynamic analysis to melting, the melting temperature should be the equilibrium melting temperature $T_m{}^0$ of the fully-extended-chain crystal. The thermodynamic quantities at $T_m{}^0$ for polymers cannot at present be determined directly and must be calculated by an extrapolation method.[18,19] From a practical point of view, since it seems quite difficult to know the pressure effect on the thermodynamic quantities at $T_m{}^0$, we apply

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the analysis on the melting points determined at a relatively slow heating rate of 0.3 K/h, after examining the validity of one of the necessary conditions of the equilibrium transition, i.e., the Clausius–Clapeyron equation.

Experimental Section

Material. Natural gutta-percha in lump form was first crushed and dissolved in benzene. After being centrifuged, the solution was passed through a glass filter and the gutta-percha was reprecipitated with methanol. The crude sample was purified by repeated swelling with toluene and benzene and deswelling with acetone and methanol. Then the benzene solution was lyophilized. All the processes were conducted rapidly in the absence of light as much as feasible. The number average molecular weight $\bar{M}_n$, the weight average $\bar{M}_w$, and the ratio $\bar{M}_w/\bar{M}_n$ determined by the gel-permiation chromatography were 105 000, 313 000, and 2.96, respectively. From the osmometric measurement, $\bar{M}_n$ was 75 000.

The crystal modification α form of *trans*-PIP can be obtained by slowly cooling the molten sample.[20] Therefore, in order to avoid a crystallization of the β form, the gutta-percha purified in the manner above was always allowed to crystallize in vacuo at a cooling rate of 0.3 K/h after being heated to 100 °C. The thus prepared sample is referred to as sample A.

Melting Temperature and PVT Relations. The measurements of the melting temperatures and the PVT relations of gutta-percha were carried out by dilatometers set in a pressure vessel which was immerzed in a water bath controlled to an accuracy of ±0.01 °C. Changes in the mercury level of the dilatometer were read by measuring the emf of a variable differential transformer (Shinko Electric Co.) induced by a piece of permalloy set on the top of the mercury column. The PVT data for mercury taken from ref 21 and 22 were used to calibrate the emf of the transformer by using a mercury-filled dilatometer and to calculate the specific volume of the sample. The temperature was measured by a thermocouple inserted in the pressure cell and the pressure by a Heise bourdon tube gauge with the automatic thermal compensator (Dresser Ind.). Details of the pressure cell used and the treatment of data are given elsewhere.[23]

After elevating the pressure to each desired value at room temperature, four V–T isobars, 1, 150, 300, and 500 kg cm^{-2}, were measured for sample A at a heating rate of 0.3 K/h to give the melting temperature at each pressure. Isothermal experiments were also carried out to give the PVT relations at a 7 K interval through the semicrystalline region 270–305 K and at a 5 K interval through the liquid region 330–370 K. The pressure was changed by a 20 kg cm^{-2} interval in the 1–100 kg cm^{-2} region and by 50 kg cm^{-2} in the 150–550 kg cm^{-2} region. The sample used in the isothermal experiments on the semicrystalline phase is referred to as sample B which was prepared by allowing sample A to stand under 500 kg cm^{-2} at room temperature for 2 days.

Latent Heat. The direct measurement of the latent heat was made by a differential scanning calorimeter (Model DSC-1B, Perkin-Elmer). The sample temperature in the DSC-1B was calibrated with the melting temperatures of standard materials, i.e., mercury, water, gallium, and indium, which were fitted to the second-order polynomials in the programmed temperature by the least-squares method. The measurement of the heat capacity with DSC-1B was made by O'Neill's method,[24] i.e., by a superposition of recorder traces with an empty pan, the samples, and α-alumina as a standard of which heat capacity data were taken from those of Onodera et al.[25] The DSC measurements were carried out on seven different masses of sample A scanned at 8 K/min through a temperature range of 240–360 K. From the data of the heat capacity, the latent heat was determined in two ways: (1) measuring the area under the heat-capacity curve of a melting peak; and (2) taking the height of the discontinuity in the enthalpy curve calculated by numerical integration of the heat capacity. The latent heat of mercury was also measured in the same procedure to clarify the uncertainty included in the determination above.

Results

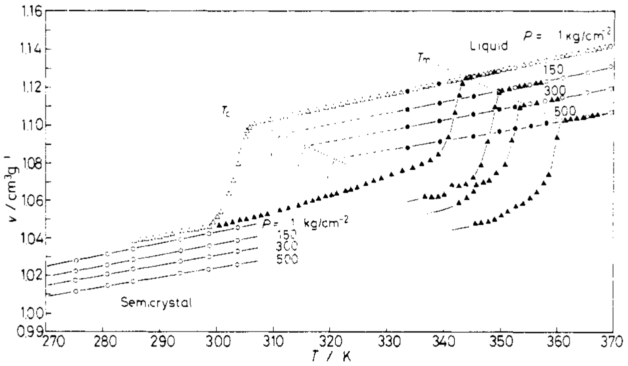

Figure 1. *PVT* relations of *trans*-polyisoprene: circles, isothermal measurements, (○) liquid and sample B, (●) liquid below T_m, not used in the melting entropy analysis; triangles, isobaric measurements, (△) cooling processes, (▲) heating processes; solid lines, isobars; dotted lines, melting and crystallization traces. Some data on cooling processes are omitted and replaced with broken lines.

The results of the PVT experiments are summarized in Figure 1. The crystal structure of the α form of *trans*-PIP was determined from X-ray diffraction by Takahashi et al.[20] From their unit-cell parameters, the specific volume of the pure crystal was obtained at 0.952 cm^3 g^{-1} at 25 °C. The crystallinities were determined from the PVT data in the semicrystalline phase by separating its volume, expansion coefficient $(\partial V/\partial T)_P$, and compression coefficient $(\partial V/\partial P)_T$ into pure-liquid and pure-crystal contributions. When appropriate crystallinities are given, both samples A and B should give the same values of $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ for the pure crystal. Thus determined crystallinities by the least-squares analysis are 35.6 ± 0.4% for sample A and 39.3 ± 0.4% for sample B. The resulting α and the compressibility β at 1 atm for the pure crystal are $(2.69 \pm 0.7) \times 10^{-4}$ K^{-1} and $(1.55 \pm 0.9) \times 10^{-5}$ kg^{-1} cm^2, respectively. The rather large uncertainties of these values are mainly due to the following situation.

As is generally observed in polymers, the apparent melting temperature differs appreciably from the crystallization temperature, T_c, as shown in Figure 1. When the molten sample was cooled to the region between T_m and T_c, apparent behaviors of the sample seemed to be the same as those of the liquid above T_m, but we observed a slight retardation effect on volume at higher pressures in our experimental time scale of about 1 h, which might be due to local crystallizations. Thus we cannot expect reliable data for the volume derivatives in that region. This made it necessary for us to extrapolate the liquid properties above T_m to the semicrystalline region (270–305 K) in order to obtain the pure-liquid properties in that region.

The thermal–pressure coefficients were determined from the slopes of P–T isochores, which were accurately linear in both the liquid and semicrystalline phases. The results are shown in Figure 2. The liquid γ above T_m is represented by the linear expression in V as

$$\gamma = -31.5V + 44.0 \quad (\text{kg cm}^{-2}\ \text{K}^{-1}) \qquad (5)$$

which is indicated by the solid line in Figure 2, where the deviation bands are delineated by shading.

The melting temperatures taken at the points where the isobaric volume curves measured at the heating rate of 0.3 K/h suddenly break to form slowly changing plateau regions in the liquid are listed in Table I. The consequent pressure dependence of the melting temperature, $\mathrm{d}T_m/\mathrm{d}P$, is regarded to be constant in our experimental pressure range within experimental errors and obtained as 0.326 ± 0.004 K MPa^{-1}, which is greater than the value 0.284 ± 0.003 K MPa^{-1} for $\mathrm{d}T_c/\mathrm{d}P$ determined by cooling measurements at a rate of 0.3 K/h. The liquid volumes at the melting points were directly measured and those of the

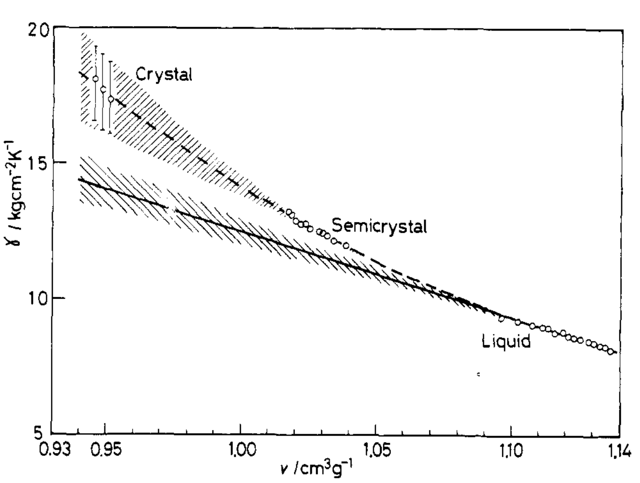

Figure 2. Thermal–pressure coefficient as a function of volume for *trans*-polyisoprene. Deviation bands are delineated by shading.

Table I
Effects of Pressure on the Melting of *trans*-Polyisoprene

P, kg cm^{-2}	T_m, K	$V^l{}_m$, cm^3 g^{-1}	$V^c{}_m$, cm^3 g^{-1}	ΔV_m, cm^3 g^{-1}	ΔS_m,^{a} J K^{-1} g^{-1}
1	344.2 ± 0.3	1.1252	0.963	0.162	0.496 ± 0.010
150	350.0 ± 0.7	1.1181	0.962	0.156	0.477 ± 0.010
300	353.4 ± 0.7	1.1103	0.961	0.149	0.458 ± 0.010
500	360.5 ± 0.7	1.1020	0.959	0.143	0.437 ± 0.010

^{a} From the Clausius-Clapeyron equation.

pure crystal were estimated from extrapolations of the V–T relations of the pure crystal. They are listed in Table I, which also tabulates the values of the melting entropy ΔS_m determined from the Clausius–Clapeyron equation,

$$dT_m/dP = \Delta V_m/\Delta S_m \quad (6)$$

The calorimetric latent heat ΔH_m determined by measuring the area bounded by the heat-capacity curve of the melting peak and that extrapolated from the liquid and the semicrystalline region to the melting temperature has a mean value of 160.6 ± 1.7 J g^{-1} for seven samples. On the other hand, the value of ΔH_m determined from the discontinuity of the numerically integrated heat-capacity curve is 164.9 ± 1.2 J g^{-1}. Thus the scatter in the DSC measurement is ±2.2%. The latent heat of mercury, determined by the same procedure, was compared with the value 2.33 kJ mol^{-1} from calorimetry,[26] and the deviation of this procedure was given as −2.1%. Considering the uncertainties in the crystallinity and the melting temperature, the melting entropy for *trans*-PIP from the DSC measurement is determined here to be 0.472 ± 0.026 J K^{-1} g^{-1}, which represents an over-all uncertainty of ±5.5%.

The ΔS_m value from the DSC measurement agrees with that from the melting volume in Table I within experimental uncertainties. It may be stated that the Clausius–Clapeyron equation applies approximately to the melting of the semicrystalline phase of *trans*-PIP. However, a discrepancy of about 5% between them would indicate the limit of the thermodynamic analysis described hereinafter. The ΔS_m value in the present study agrees within experimental error with the value 0.545 ± 0.065 J K^{-1} g^{-1} determined from the melting point depression of the solution by Mandelkern et al.[27]

Discussion

The Entropy-Separation Concept and the Entropy Due to Volume Change. We shall attempt to clarify the assumptions involved in the experimental analysis with eq 1 and 2 based on the entropy-separation concept. Following the traditional polymer-liquid theories based on the lattice-like models,[28–31] the entropy is assumed to be constituted by three or four contributions, other than the constant one: S_k referred here to as the kinetic entropy which is a function of temperature only; S_v, the volume entropy which is considered to be corresponding to the equation of state term in the liquid theories above; S_c, the intramolecular conformational entropy; and/or S_d, the communal entropy which is assumed to be zero in the crystalline phase. As a further approximation, we take an expectation that the constant term and the kinetic and volume entropies are the same in the liquid as in the crystal, when the volume and the temperature of the liquid are identical with those of the crystal. In conflict with the liquid theories above, we first consider that S_c and S_d depend on volume as well as temperature. The liquid and crystalline entropy at the same T and P are then

$$S^l(T,P) = S^l(T,V^l) = \text{constant} + S_k(T) + S_v(T,V^l) + S_c(T,V^l) + S_d(T,V^l) \quad (7)$$

$$S^c(T,P) = S^c(T,V^c) = \text{constant} + S_k(T) + S_v(T,V^c) \quad (8)$$

where superscripts l and c index the liquid and the crystal, respectively. Following the consideration of Karasz et al.,[14] we will estimate ΔS_v in eq 2 along four thermodynamic paths, which are schematically shown in Figure 3.

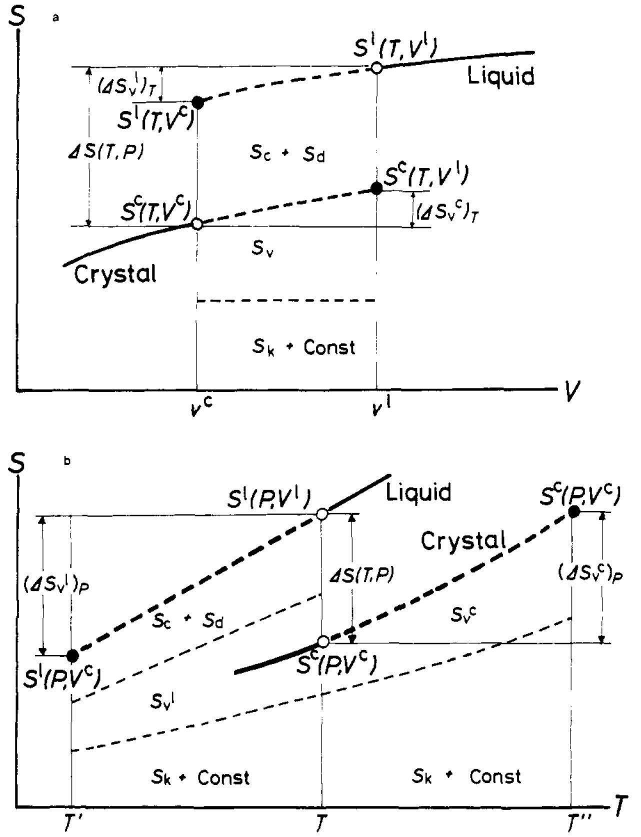

Figure 3. (a) Isothermal variation of entropy with volume: open circles, equilibrium entropies; solid circles, hypothetical entropies for the compressed liquid [$V^l(P',T) = V^c(P,T)$] and for the expanded crystal [$V^c(P'',T) = V^l(P,T)$]; solid lines, equilibrium isotherms; broken lines, isothermal extrapolations; thin broken lines, dissection into contributions to the entropy. (b) Isobaric variation of entropy with temperature: open circles, equilibrium entropies; solid circles, hypothetical entropies for the contracted liquid [$V^l(P,T') = V^c(P,T)$] and for the expanded crystal [$V^c(P,T'') = V^l(P,T)$]; solid lines, equilibrium isobars; broken lines, isobaric extrapolations; thin broken lines, dissection into contributions to the entropy.

From a consideration of a change in entropy of the liquid associated with an isothermal compression from V^{l} to V^{c} (see Figure 3a), the increment of entropy of the liquid from that of the crystal at the same T and P is given by

$$\Delta S(T,P) = [\Delta S_{\mathrm{v}}^{\mathrm{l}}]_T + S_{\mathrm{c}}(T,V^{\mathrm{c}}) + S_{\mathrm{d}}(T,V^{\mathrm{c}}) \quad (9\mathrm{a})$$

$$[\Delta S_{\mathrm{v}}^{\mathrm{l}}]_T \equiv S^{\mathrm{l}}(T,V^{\mathrm{l}}) - S^{\mathrm{l}}(T,V^{\mathrm{c}}) = \int_{V^{\mathrm{c}}}^{V^{\mathrm{l}}} \gamma^{\mathrm{l}}\, \mathrm{d}V \quad (10\mathrm{a})$$

These are equivalent to eq 2b and 3a. However, it should be noted that, if S_{c} or S_{d} depend on volume, the analysis from eq 9a may give S_{c} and S_{d} of the compressed system. From an isothermal expansion of the crystal from V^{c} to V^{l} (see Figure 3a), the entropy increment is given by

$$\Delta S(T,P) = [\Delta S_{\mathrm{v}}^{\mathrm{c}}]_T + S_{\mathrm{c}}(T,V^{\mathrm{l}}) + S_{\mathrm{v}}(T,V^{\mathrm{l}}) \quad (9\mathrm{b})$$

$$[\Delta S_{\mathrm{v}}^{\mathrm{c}}]_T \equiv \int_{V^{\mathrm{c}}}^{V^{\mathrm{l}}} \gamma^{\mathrm{c}}\, \mathrm{d}V \quad (10\mathrm{b})$$

If S_{c} and S_{d} are independent of volume, γ^{l} should be identical with γ^{c} from the entropy-separation concept adopted in this study.

Similar expressions of the entropy increment may also be given by considering isobaric paths.[1,14] As is shown in Figure 3b, if it is expected that $S_{\mathrm{v}}^{\mathrm{l}}(P,V) = S_{\mathrm{v}}^{\mathrm{c}}(P,V)$, corresponding expressions are easily obtained as

$$\Delta S(T,P) = S_{\mathrm{k}}(T') - S_{\mathrm{k}}(T) + [\Delta S_{\mathrm{v}}^{\mathrm{l}}]_P + S_{\mathrm{c}}(P,T') + S_{\mathrm{d}}(P,T') \quad (9\mathrm{c})$$

$$\Delta S(T,P) = S_{\mathrm{k}}(T) - S_{\mathrm{k}}(T'') + [\Delta S_{\mathrm{v}}^{\mathrm{c}}]_P + S_{\mathrm{c}}(P,T'') + S_{\mathrm{d}}(P,T'') \quad (9\mathrm{d})$$

with the definitions of

$$[\Delta S_{\mathrm{v}}^{\mathrm{l}}]_P \equiv \int_{V^{\mathrm{c}}}^{V^{\mathrm{l}}} (C_P^{\mathrm{l}}/TV^{\mathrm{l}}\alpha^{\mathrm{l}})\, \mathrm{d}V = \int_{T'}^{T} (C_P^{\mathrm{l}}/T)\, \mathrm{d}T \quad (10\mathrm{c})$$

$$[\Delta S_{\mathrm{v}}^{\mathrm{c}}]_P \equiv \int_{V^{\mathrm{c}}}^{V^{\mathrm{l}}} (C_P^{\mathrm{c}}/TV^{\mathrm{c}}\alpha^{\mathrm{c}})\, \mathrm{d}V = \int_{T}^{T''} (C_P^{\mathrm{c}}/T)\, \mathrm{d}T \quad (10\mathrm{d})$$

where T' is the temperature when the liquid volume reduces isobarically to the crystal volume at T and T'' is the temperature when the crystal volume expands isobarically to the liquid volume at T. It is found that the ΔS_{v} term in eq 2 corresponds to the kinetic and volume terms in eq 9c and 9d.

In the isothermal paths of eq 9a and 9b, the objective is to measure γ in a volume range which covers the change in volume at the melting point. In many cases, the liquid γ is regarded as a function of volume only, i.e., P–T isochores are linear. Although this is not precisely true, it proves to be a good approximation for most liquids.[32] Therefore, when γ is measured at T somewhat higher than T_{m}, in a volume range which covers a major portion of ΔV_{m}, by elevating the pressure and extrapolating to T_{m}, eq 10a may give an appropriate ΔS_{v} value. On the contrary, it may hardly be possible to allow the crystal volume to approach the liquid volume, unless the melting takes place under high pressure.

In the estimation of ΔS_{v} from the isobaric paths of eq 9c and 9d, the superheating and the supercooling over a wide temperature range are required to cover ΔV_{m}, since T' and T'' are anticipated to be very far from T_{m}, e.g., in polyethylene, $T_{\mathrm{m}}^0 - T' \simeq 248$ K and $T'' - T_{\mathrm{m}}^0 \simeq 265$ K from the V–T relations.[33,34] In addition, one may encounter another difficulty in obtaining the kinetic contribution, which comprises a major portion of the liquid and crystal entropy. The temperature dependences of the kinetic and conformational entropy cannot be ignored as shown in Figure 3b. That is, the approximation eq 4 is quite unreasonable and the inequality among the ΔS_{v} values from eq 3b and 4 with the liquid and crystalline quantities may have nothing to do with the denial of the entropy-separation concept.

Table II
Contributions to the Melting Entropy[b]

P, kg cm^{-2}	$[\Delta S_{\mathrm{v}}^{l}]_T$ ($\pm$0.3)	S_{c}(exptl) ($\pm$1.0)	S_{c}(calcd)
1	12.0	21.8	22.18 (22.9)[a]
150	11.7	20.8	22.23
300	11.3	19.8	22.28
500	11.0	18.8	22.35

[a] Calculated by Tonelli[10] with the statistical weight matrices by Mark.[52] [b] J K^{-1}/mol of repeating unit.

Consequently, we are left with only the analysis based on eq 9a and 10a. The values of $[\Delta S_{\mathrm{v}}^{\mathrm{l}}]_T$ are listed in Table II. Employing the $\gamma^{\mathrm{l}} = \gamma^{\mathrm{c}}$ curve which is indicated by the broken line in Figure 2, the value of ΔS_{v} is obtained as 13.0 ± 0.2 J K^{-1} mol^{-1}, which is close to the value of $[\Delta S_{\mathrm{v}}^{\mathrm{l}}]_T$.

The Communal Entropy. As the communal entropy problem inherent in the solid-like liquid theories is still unsolved, various methods of estimation have been applied. Starkweather and Boyd[4] expected S_{d} of the repeating unit of the polymer chain to be similar to the corresponding quantity in metals[1] and required its value to be ca. 0.9R. By assuming the melting point to be a corresponding state and comparing the S_{d} for Ar and CCl_4 to that for polymers, Tsujita, Nose, and Hata estimated the S_{d} value per mole of segment as 0.48R.[11] Turturro and Bianchi[13] employed Temperley's equation[35] which accounts for a whole molecular communality in polymer liquids and requires S_{d} to vanish at the long-chain extreme. In all of these cases, S_{d} is regarded as a substantial constant.

Kirkwood[17] defined S_{d} as the entropy difference between an unconstrained system and a restricted system having the center of each particle stay within its own cell and showed it to be a function of V and T. However, its functional dependence on V and T remained unknown, excepting its limiting values: R at $V \to \infty$ and zero at the high-density extreme.[17] In accordance with Kirkwood's definition of S_{d}, Monte-Carlo calculations of S_{d} for hard spheres have been made.[36,37] Hoover and Ree[36] revealed that S_{d} for hard spheres is nearly a linear function of density V_0/V, where V_0 is the close-packed volume, in the low-density region and approaches zero near the solid density ($V_0/V \simeq 0.736$). This suggests that the volume effect on S_{d} may not be ignored.

In order to elucidate the volume effect on S_{d} in the real systems, we attempt to analyze ΔS_{m} at elevated pressures for the simple spherical molecules Ar and CCl_4. A corresponding comparison between the simple liquids and the polymer liquids may be achieved by an appropriate selection of a volume-reduction parameter. On this line, we employ the characteristic parameter in the equation of state proposed by Flory et al.,[29,38] hereafter referred to as Flory's equation of state, for two reasons: (1) the reduced equation of state

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/\tilde{V}\tilde{T} \quad (11)$$

$$\tilde{V} = V/V^*,\ \tilde{T} = T/T^*,\ \tilde{P} = P/P^*,\ P^*V^*/T^* = cR \quad (12)$$

where $3c$ is the number of external degrees of freedom per segment,[28] applies to simple liquids[39] as well as polymer liquids; and (2) the equation satisfies the law of corresponding state.[40] The numerical evaluation of the reduction parameters for Ar and CCl_4 and *trans*-PIP was

Table III
The Reduction Parameters of Flory's Equation of State at the Atmospheric Melting Temperature

	Ar^a	CCl$_4$^{a}	*trans*-PIP
V^*, cm^3 mol^{-1}	21.795	74.084	64.840
P^*, bar	3035	5830	4038
T^*, K	1319	4507	7502

^{a} Calculated from the data tabulated by Rowlinson.[32]

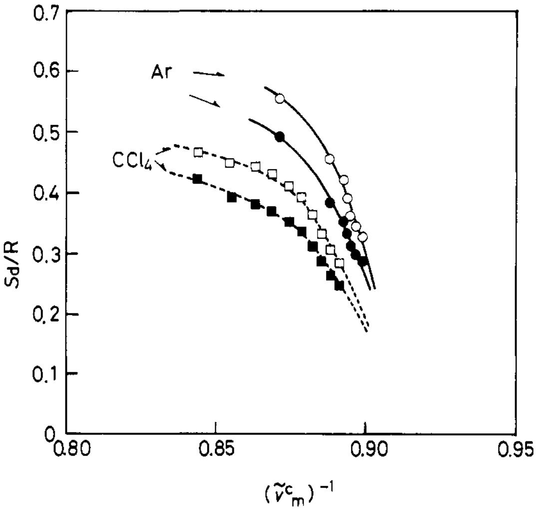

Figure 4. Communal entropy as a function of reduced density: circles, Ar, (○) γ from ref 32, (●) γ from ref 48; squares, CCl$_4$, (□) γ from ref 32, (■) γ from ref 49.

carried out according to the procedure presented by Flory et al.[29] The temperature was chosen as the atmospheric melting temperature. The results are listed in Table III.

Flory's partition function includes the same communal entropy factor e^{3cR}[38] as Rice's.[41] Considering the result of Hoover and Ree,[36] the value $3cR$ for $S_{\rm d}$, even if true,[42] should be regarded as the low-density extreme. Notwithstanding this contradiction, the qualitative success of the equation in the prediction of the excess volume for various solutions[43] leads us to expect Flory's equation of state parameter to give an appropriate correspondence in terms of volume in the rather qualitative comparisons of the present study. It is well known that the reduction parameters depend on temperature and pressure.[44] These slight dependences, however, scarcely alter the present comparison.

The values of $S_{\rm d}$ for Ar and CCl$_4$ were calculated in the following manner by using eq 9a and 10a with $S_{\rm c} = 0$. The $\Delta S_{\rm m}$ values at various pressures were determined from the Clausius–Clapeyron equation (eq 6), combining the $\mathrm{d}T_{\rm m}/\mathrm{d}P$ data from Simon's equation collected by Babb[45] and the $\Delta V_{\rm m}$ data for Ar by Bridgman[46] and for CCl$_4$ by Brickwedde.[47] The data of γ for Ar[32,48] and CCl$_4$[32,49] were fitted to the second-order polynomials in V by the least-squares method and the latter were integrated in eq 10a to give $\Delta S_{\rm v}$ with $V_{\rm m}{}^{\rm l}$ calculated from eq 11 and $V_{\rm m}{}^{\rm c}$ from $V_{\rm m}{}^{\rm l} - V_{\rm m}$. It should be noted that the corresponding volume for the analysis by eq 9a is the hypothetical one when it equals the crystalline volume at $T_{\rm m}$, i.e., $\tilde{V}^{-1} = (\tilde{V}_{\rm m}{}^{\rm c})^{-1}$.

As shown in Figure 4, the $S_{\rm d}$'s for both Ar and CCl$_4$ decrease with increasing density and seem to approach zero at $\tilde{V}^{-1} \sim 0.92$. This agrees qualitatively with the result for hard spheres.[36] Thus the volume effect on $S_{\rm d}$ may not be negligible below $\tilde{V}^{-1} \sim 0.92$ in the real systems as well.

In the polymer liquids, however, $(\tilde{V}_{\rm m}{}^{\rm c})^{-1}$ has a larger value, e.g., 0.990 at 1 atm in polyethylene[29,15] and 0.988 at 1 atm in *trans*-PIP. This may suggest, if the correspondence of $S_{\rm d}$ to the density in the simple liquids is similar to that in the polymer liquids, that the contribution of $S_{\rm d}$ to $\Delta S_{\rm m}$ can be ignored in the analysis by eq 9a, notwithstanding the ambiguity of the independent existence of $S_{\rm d}$ in the polymer liquids. On the contrary, the $S_{\rm d}$ contribution may not be ignored in the analysis by eq 9b, since $\tilde{V}^{-1} = (\tilde{V}_{\rm m}{}^{\rm l})^{-1}$ which has a smaller value, e.g., 0.851 at 1 atm in *trans*-PIP.

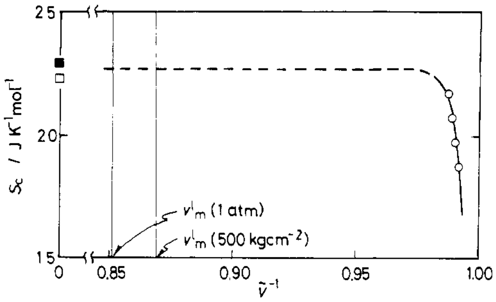

Figure 5. Conformational entropy as a function of reduced density for *trans*-polyisoprene: circles, experimental; squares, calculation from the rotational isomeric state model, (■) by Tonelli (ref 10) and (□) by the authors.

The Conformational Entropy. The conformational entropy of a single isolated unperturbed chain may be obtained from the partition function evaluated by the matrix method,[10,50,51] if the rotational isomeric state model of the polymer chain is adopted. Calculations in the above fashion were presented by Tonelli[10] for many polymers and his result for *trans*-PIP from the statistical weight matrices determined by Mark[52] is shown in Table II. We also carried out a similar calculation for *trans*-PIP at each melting point by using the refined statistical weight matrices by Abe and Flory.[53] The results are not effectively different from that by Tonelli, as shown in Table II.

On the basis of the preceding discussion, the experimental evaluation of the conformational entropy was made on the melting points at several pressures by using eq 9a with the communal entropy contribution ignored. The results are compared with those of the isolated chain in Table II. At the atmospheric melting temperature, the experimental value agrees with that of the isolated chain in the limit of the experimental uncertainty. As the pressure increases, a deviation appears and reaches the value of 19% at 500 kg cm^{-2}, exceeding the experimental uncertainties. This arises from the difference in pressure dependence of each conformational entropy. Since the conformational partition function for the isolated chain is a function of temperature only, the conformational entropy for the isolated chain increases slightly with pressure because of increasing melting temperature whereas the experimental one decreases. It should be emphasized again that the experimental conformational entropy, as shown in eq 9a, was determined on a hypothetical compressed system for which the volume was identical with the crystalline volume at the melting point. Hence the experimental volume region lies toward the high density.

In order to elucidate graphically the volume dependence, plots of the conformational entropy against the reduced density are shown in Figure 5, where the ranges of experimental uncertainties are omitted to avoid complexity. Although a large volume dependence of the conformational entropy is observed near $\tilde{V}^{-1} \sim 1$, a precipitous fall of the dependence may presumably occur as the volume increases. If this is true, it is expected that the conformational entropy may be little affected in the low-density region as indicated by the broken line in Figure 5. The plateau region appears to be ranging from $\tilde{V}^{-1} \sim 0.97$–0, which corresponds approximately to the pressure region below 3000 kg cm^{-2}. This may offer further experimentally corroborating evidence for the postulate that the average conformation of a chain in the bulk polymer should be the same as that of an isolated unperturbed chain.

It should here be remarked that the present experimental analysis of conformational entropy is made on the metastable melting temperature T_m determined by the slow-heating measurements. This is based only on the idea that the Clausius–Clapeyron equation applies approximately to the melting at T_m. T_m is lower by 8.4 ± 0.8 K than T_m^0 estimated by Flanagan and Rijke.[19b] If dT_m^0/dP is assumed to be the same as dT_m/dP, similar analysis at T_m^0 gives the value of S_c(exptl) as 22.4 J K^{-1} mol^{-1}, which is greater than that at T_m by about 2%. This deviation scarcely alters the rather qualitative conclusion of the present study. However, a quantitative estimation of greater precision may require further considerations on the stability and structure of the semicrystal, as well as on the models.

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