Thermodynamic Properties of Polyethylene and Eicosane. II. Conformational Entropy of Melting

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ABSTRACT: The entropy of melting ΔS_m is divided into three parts according to Starkweather and Boyd: the entropy change due to disordering of molecular arrangements ΔS_{dis} at constant volume, the change of chain conformations ΔS_c and the entropy arising from the change of volume ΔS_v. ΔS_v was evaluated from the experimental results on the P—V—T relations for linear polyethylene and eicosane, where the volume dependence of the value of $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ is taken into consideration. ΔS_{dis} was estimated with the aid of the thermodynamic data for simple spherical molecules such as Ar and CCl_4. As results the conformational entropy of melting ΔS_c was obtained as 1.51 cal/CH_2 mol deg for polyethylene and 1.94 cal/CH_2 mol deg for eicosane, which are in good agreement with the theoretical predictions of several authors.

KEY WORDS Polyethylene / Eicosane / Entropy of Melting / P—V—T Relations / Conformational Entropy / Disordering Entropy / Clausius—Clapeyron Equation /

Melting phenomena of crystalline polymers differ from those of low-molecular-weight substances in various ways. The most characteristic aspect of polymer melting is considered to be in the fact that change of chain conformation occurs on melting and may play an important role in the entropy of melting, besides the change of volume and molecular orderliness as in low molecular weight crystals. Therefore it would be fruitful to distinguish these effects on the entropy of melting, and to discuss them separately.

Mandelkern[1] firstly proposed dividing the entropy of melting ΔS_m into two parts, the one at constant volume $(\Delta S_m)_V$ and the other due to the volume change ΔS_v. Succeedingly Starkweather and Boyd[2] tried to divide $(\Delta S_m)_V$ into a further two parts, the entropy change due to the change of molecular arrangements from order to disorder (the disordering entropy ΔS_{dis}) and the one due to the change of chain conformations on melting (the conformational entropy ΔS_c), that is,

$$\Delta S_m = (\Delta S_m)_V + \Delta S_v \qquad (1)$$
$$= (\Delta S_{dis} + \Delta S_c) + \Delta S_v \qquad (2)$$

In this paper an attempt is made to estimate these three terms of the entropy of melting on the basis of the experimental results for the pressure—volume—temperature (P—V—T) relations of linear polyethylene and eicosane, using a different method to that of Starkweather and Boyd.

EXPERIMENTAL

The sample used in this study were a linear polyethylene (unfractionated Hizex $\bar{M} = 34000$) presented by Mitsui Petroleum Co. and eicosane (99.9-% purity). The apparatus was the same as in the preceding paper.[3] Quantities needed for the discussion, *i.e.*, the volume change on melting ΔV_m, the pressure dependence of the melting temperature dT_m/dP and the dependence of thermal pressure coefficient on volume, were obtained from the P—V—T relations. In order to determine the value of dT_m/dP, the measurements of the P—V—T relationship were made in the vicinity of the melting temperatures, that is, V—T measurements at constant pressures. The heating rate was kept carefully 0.3°C/min for each pressure. The values of dT_m/dP were 0.0276°C/kg cm^2 for polyethylene and 0.0214°C/kg cm^2 for eicosane at atmospheric pressure.

ESTIMATIONS OF ENTROPY OF MELTING AND ITS COMPONENTS

One can obtain the entropy of melting from the thermodynamic quantities. As shown in the following, ΔS_v was derived first and $(\Delta S_m)_V$ necessarily obtained from eq 1. Next ΔS_{dis} was estimated, and ΔS_c then evaluated as $(\Delta S_m)_V - \Delta S_{dis}$.

Entropy of Melting

With the use of the values of dT_m/dP above obtained, the entropy of melting was calculated by the Clausius—Clapeyron equation

$$\frac{dT_m}{dP} = \frac{\Delta V_m}{\Delta S_m} \qquad (3)$$

where ΔV_m is the volume change on melting and ΔS_m is the entropy of melting. ΔV_m was obtained by the extrapolation of volume in the temperature region below that in which the pre-melting occurs, to that at the melting temperature. The value of ΔV_m for polyethylene of 100-% crystallinity was calculated by dividing the observed value with its crystallinity of 0.782. The observed value of eicosane was considered to be that for 100-% crystallinity. ΔS_m thus obtained by eq 3 were 2.53 cal/CH_2 mol deg for polyethylene and 3.50 cal/CH_2 mol deg for eicosane.

The Entropy Change due to the Volume Change ΔS_v

ΔS_v can be evaluated with the use of the Maxwell's relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, as

$$\Delta S_V = \int \left(\frac{\partial P}{\partial T}\right)_V dV \qquad (4)$$

Thermal pressure coefficient $(\partial P/\partial T)_V = \gamma$ varies with volume as shown in Figure 1 for instance in the liquid state. It is more reasonable to take into consideration this dependence of γ on volume in the calculation. As was discussed in the previous paper, internal pressure P_i, which is approximately equal to $T\gamma$, increases continuously as volume decreases in the liquid state. Therefore γ may also increases with volume decreasing, although the volume dependence of γ is not exactly estimated for the wide range of volume. Hence we assume here that γ increases as volume decreases with the same slope
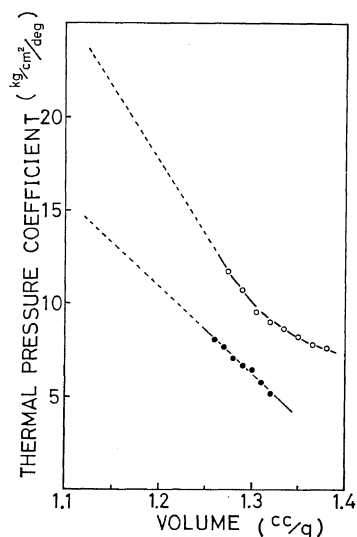

Figure 1. Relation between thermal pressure coefficient and specific volume: ●, PE; ○, eicosane.

of γ vs. V curve as that in the vicinity of the melting point in the liquid state, as shown by the dotted lines in Figure 1. Values of ΔS_v thus obtained are 0.91 cal/CH_2 mol deg for polyethylene and 1.44 cal/CH_2 mol deg for eicosane.

The Disordering Entropy ΔS_{dis}

If one considers a simple spherical molecule of low molecular weight, it has no intramolecular freedom, therefore ΔS_c is equal to zero. In this case one can write eq 1 and 2 as

$$\Delta S_{dis} = (\Delta S_m)_V = \Delta S_m - \Delta S_V \qquad (5)$$

Argon (Ar) and carbon tetrachloride (CCl_4) were chosen as such typical molecules. ΔS_m and $\Delta S_v = \int (\partial P/\partial T)_V dV$ were calculated in the same manner as above described, by the use of necessary data from Bridgman's paper[5] and the Critical Table.[6] ΔS_{dis} thus obtained were 0.94 cal/mol deg for Ar and 0.97 cal/mol deg for CCl_4 which are surprisingly close to each other. In Table I the thermodynamic quantities used are summarized.

If one can assume that this disordering entropy of melting per mole is independent of substances including polymers, one can calculate ΔS_c, using the mean value of ΔS_{dis}, 0.95 cal/mol deg. However, in the case of polymeric substances there

Table I. Thermodynamic quantities on melting of Ar and CCl₄

	Ar	CCl₄
dT_m/dP, deg/kg cm²	0.0238	0.0393
ΔV_m, cc/g	0.0795	0.0258
ΔS_m, cal/mol deg	3.13	2.37
ΔS_v	2.19	1.40
$(\Delta S_m)V$	0.94	0.97

is a further problem of how to choose the mole unit. This unit is considered to be the one which has three external degrees of freedom. If one accepts the corresponding state theorem recently developed for polymer liquids, one can determine the size of such a unit. According to Nose[7] this unit has about nine -CH₂- groups for polyethylene and about eight for eicosane. Thus ΔS_{dis} must be 0.11 cal/CH₂ mol deg for polyethylene and 0.12 cal/CH₂ mol deg for eicosane.

The Conformational Entropy ΔS_c

By subtracting ΔS_{dis} from $(\Delta S_m)_V$ one obtains the values of ΔS_c as 1.51 cal/CH₂ mol deg for polyethylene and 1.94 cal/CH₂ mol deg for eicosane.

Values of various entropies estimated above are tabulated in Table II including thermodynamic quantities on melting.

Table II. Thermodynamic quantities on melting of eicosane and polyethylene

	Eicosane	Polyethylene
T_m, °C	39.3	134.0
Crystallinity, %		78.2
dT_m/dP, deg/kg cm²	0.0214	0.0276
ΔV_m, cc/g	0.228	0.213
ΔS_m, cal/CH₂ mol deg	3.50	2.53
ΔH_m, cal/CH₂ mol	1094	1030
ΔS_v, cal/CH₂ mol deg	1.44	0.91
$(\Delta S_m)V$	2.06	1.62
ΔS_{dis}	0.12	0.11
ΔS_c	1.94	1.51

DISCUSSION

The estimation made by Starkweather, *et al.*, differs from this in the estimation method. Starkweather, *et al.*, first calculated ΔS_c theo-

retically and then obtained ΔS_{dis}. On the contrary in this study ΔS_{dis} was first estimated using various assumptions and then ΔS_c obtained.

In the evaluation of ΔS_v, Starkweather and other authors assumed a constant value for the thermal pressure coefficient $\gamma = (\partial P/\partial T)_V$. If the same assumption is made, ΔS_v is given as 0.54 cal/CH₂ mol deg with the use of the authors' data for polyethylene which agrees with the values of Starkweather, *et al.*,[2] and Quinn, *et al.*[3] However taking into consideration of the dependence of γ on volume, ΔS_v was evaluated as 0.91 cal/CH₂ mol deg for polyethylene and 1.44 cal/CH₂ mol deg for eicosane. In comparison of this result with the value of Starkweather, *et al.*, their value for polyethylene is as small as 62% of this. Starkweather and Boyd have calculated ΔS_c with the use of the partition function of Flory,[8] in which the energy difference between *trans* and *gauche* conformations is taken into consideration, to obtain $\Delta S_c = 1.59$— 1.70 cal/CH₂ mol deg for polyethylene. Kirschenbaum[9] has also evaluated the change in conformational entropy of fusion by considering the rotational isomers and pentane effect and obtained the value of 1.8 cal/CH₂ mol deg. Smith[10] calculated the configurational entropy of a single chain, considering the disallowance of *gauche—gauche prime* or its inverse conformation, and gave the value of 1.59—1.68 cal/ CH₂ mol deg. These values calculated by several authors are fairly in good agreements with the authors' experimental results and this seems to confirm the validity of their treatment for ΔS_{dis}.

Introducing Broadhurst's empirical equation, which relates the melting temperature of *n*-hydrocarbon to the number of carbon atoms, to Smith's equation, one obtains the dependency of the configurational entropy of a single chain on molecular weight, from which it is concluded that the conformational entropy of eicosane must be larger than that of polyethylene. It coincides with the results of this study.

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