Thermodynamic Properties of Poly(ethylene glycol) and Poly(tetrahydrofuran)

II. Conformational Entropy of Melting

Yoshiharu TSUJITA, Takuhei NOSE, and Toshio HATA

*Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama 2-12-1, Meguro-ku, Tokyo, Japan.*

(Received June 20, 1973)

ABSTRACT: The entropy of melting ΔS_m was studied for poly(ethylene glycol) (PEG) and poly(tetrahydrofuran) (PTHF). The ΔS_m was divided into three parts: ΔS_{dis} , the entropy change due to disordering of the molecular arrangement at constant volume; ΔS_c , the one due to the change in chain conformation; and ΔS_v , the entropy arising from the change in volume. ΔS_v was evaluated from the experimental P - V - T relations for these polymers, with the volume dependence of $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ taken into consideration; ΔS_{dis} was estimated with the aid of thermodynamic data for simple spherical molecules. The resulting conformational entropies of melting per mole of bonds were 1.50 cal/deg for PEG with molecular weight $M_n=605$, 1.41 cal/deg for PEG with $M_n=1020$, 1.40 cal/deg for PEG with $M_n=7500$, and 1.53 cal/deg for PTHF with $M=40000$.

KEY WORDS Entropy of Melting / Conformational Entropy / Clausius-Clapeyron Equation / Thermal Pressure Coefficient / Pressure / Melting Point / Poly(ethylene glycol) / Poly(tetrahydrofuran) /

One of the most characteristic aspects of polymer melting is the change in chain conformation which occurs on melting. In this paper, in order to further our understanding of this effect on the thermodynamics of melting of crystalline polymers, the entropies of melting for poly(ethylene glycol)s (PEG) and poly(tetrahydrofuran) (PTHF) were estimated by the same method as in a preceding paper on polyethylene and eicosane.¹

The entropy of melting ΔS_m may be separated into three parts as has been proposed in a previous paper.¹ They are the disordering entropy ΔS_{dis} , the conformational entropy ΔS_c , and the entropy of melting due to volume change ΔS_v . From the data for pressure-volume-temperature (P - V - T) relations these three parts can be estimated. The entropy change ΔS_v is evaluated by application of the Maxwell relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$. In this case, it is important to take the volume dependence of $(\partial P/\partial T)_V$ into account, although Starkweather and Boyd² treated $(\partial P/\partial T)_V$ as constant. The disordering entropy ΔS_{dis} is ob-

tained from the entropy changes of disordering for Ar and CCl_4 . Finally, the conformational entropy ΔS_c is determined by subtracting these two parts from ΔS_m . The values of ΔS_c thus obtained for PEG of different molecular weights and that for PTHF are compared with those of polyethylene and eicosane.

EXPERIMENTAL

Materials and Experimental Methods

Three samples of poly(ethylene glycol) with different molecular weight were provided by Nippon Oil and Fats Company, Ltd. These were the same as those used in a previous paper.³ They are designated PEG 600, PEG 1000, and PEG 6000. Their molecular weights M are indicated in Table I. It was shown that these had narrow distributions of molecular weights. The sample of poly(tetrahydrofuran) used also had a narrow distribution of molecular weights ($M=40000$).³ It was a gift from Dr. T. Fujimoto of Nagoya University. The samples of PEG were crystallized by slow cool-

Table I. Thermodynamic quantities of melting

		PEG 600	PEG 1000	PEG 6000	PTHF
M		605	1020	7500	40000
T_m	°C	24.6	41.1	66.0	42.7
dT_m/dP	deg/kg cm	0.0123	0.0145	0.0154	0.0181
ΔV_m	cc/g	0.080 ₁	0.089 ₉	0.095 ₂	0.199
ΔS_m	cal/mol deg	6.71	6.40	6.38	11.14
ΔH_m	kcal/mol	2.00	2.01	2.16	3.52
ΔS_v	cal/mol deg	1.71	1.66	1.68	3.00
$(\Delta S_m)_v$	cal/mol deg	5.00	4.74	4.70	8.14
ΔS_{dis}	cal/mol deg	0.49	0.50	0.50	0.75
ΔS_c	cal/mol deg	4.51	4.24	4.20	7.39
$\Delta S_c/bond$	cal/mol deg	1.50	1.41	1.40	1.48

ing from the molten state; the sample of PTHF was crystallized at room temperature. The crystallinities determined by the density method were 77.9, 72.4, 85.0, and 61.4% for PEG 600, PEG 1000, PEG 6000, and PTHF, respectively. The volume change on melting, ΔV_m , the pressure dependence of the melting temperature, dT_m/dP , and the thermal pressure coefficient were derived from the P — V — T relations. The apparatus and procedures used for the measurements of the P — V — T relations have been described elsewhere.⁴

Experimental Results

Volumes of the solid state at the melting temperature T_m were estimated by extrapolation of the data at temperatures lower than the pre-

melting region. The values of ΔV_m for PEG and PTHF of 100% crystallinity were computed by dividing these values by the degrees of crystallinity, and are given in Table I. Melting temperatures at elevated pressures were obtained from measurements of the V — T relation at constant pressure, and they are shown for PEG 600 and PEG 1000 in Figure 1, for PEG 6000 in Figure 2, and for PTHF in Figure 3. The normal increase in T_m with pressure was not observed for PEG 1000 even at somewhat lower pressures. The cause for this is not clear at present. Since the abnormal phenomena, however, do not occur near atmospheric pressure, as seen in Figure 1, the value of dT_m/dP at atmospheric pressure, which is required for the

Figure 1. Pressure dependence of melting temperature for PEG 600 and 1000.

Figure 2. Pressure dependence of melting temperature for PEG 6000.

Figure 3. Pressure dependence of melting temperature for poly(tetrahydrofuran).

Figure 4. Correlation between thermal pressure coefficient and specific volume for PEG 600.

calculation of ΔS_m , can be determined. The values of such dT_m/dP for all samples are shown in Table I. From the P - V - T relations,³ thermal pressure coefficients $\gamma = (\partial P/\partial T)_V$ were obtained. The results are shown as functions of specific volume for PEG 600 in Figure 4 and for PTHF in Figure 5.

ESTIMATION OF ENTROPY OF MELTING AND ITS COMPONENTS

The entropy of melting ΔS_m is divided into

Figure 5. Correlation between thermal pressure coefficient and specific volume for poly(tetrahydrofuran).

three parts, *i.e.*,

$$\Delta S_m = (\Delta S_m)_V + \Delta S_V \quad (1)$$

$$= (\Delta S_{dis} + \Delta S_c) + \Delta S_V \quad (2)$$

where $(\Delta S_m)_V$ is the entropy of melting at constant volume. Since ΔS_m and ΔS_V can be experimentally obtained, $(\Delta S_m)_V$ is evaluated from eq 1. If ΔS_{dis} is estimated, ΔS_c is then evaluated as $(\Delta S_m)_V - \Delta S_{dis}$.

Entropy of Melting

The entropy of melting was calculated by the Clausius—Clapeyron equation

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

With substitution of the data for ΔV_m and dT_m/dP into eq 3, the molar entropies of melting per repeat unit were evaluated, and they are shown in Table I.

Entropy Change Due to Volume Change

The entropy change due to a change in volume can be evaluated by use of the Maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (4)$$

or

$$\Delta S_V = \int \left(\frac{\partial P}{\partial T} \right)_V dV = \int \gamma dV \quad (5)$$

The thermal pressure coefficient, γ , varies with volume as shown in Figures 4 and 5. Hence it is necessary to take this dependence of γ into account in the calculation of ΔS_V . As discussed in previous papers,^{3,4} the internal pressure P_i ,

which is approximately equal to $T\gamma$ near atmospheric pressure, increases continuously as the volume decreases in the liquid state. Therefore γ may also increase with the decrease in volume, although the volume dependence of γ cannot be exactly estimated for a wide range of volume. Hence it is assumed here that γ increases with volume at the same slope as in the vicinity of the melting point in the liquid state. This assumption is indicated by the dotted lines in Figures 4 and 5. The values of ΔS_V thus obtained by eq 5 are shown in Table I.

Disordering Entropy ΔS_{dis}

The disordering entropy was estimated by the same method as in a preceding paper.¹ Namely, it was assumed that the molar disordering entropy of melting is independent of the particular substance, even for polymers, and is 0.95 cal/mol deg. This value was derived from the experimental data for Ar and CCl₄ with the equation $\Delta S_{dis} = \Delta S_m - \Delta S_V$, and the assumption that $\Delta S_c = 0$ for such simple spherical molecules.¹ In the case of polymeric substances, we must confront another problem concerning the choice of mole unit. This unit is considered to be the one which has the same external degrees of freedom as simple spherical molecules, *i.e.*, three external degrees of freedom. The size of such a unit is estimated on the basis of a corresponding state theorem to be 1.90 times and 1.27 times the repeating unit for PEG 6000 and PTHF, respectively (see Appendix). The resulting disordering entropies are shown in Table I.

Conformational Entropy ΔS_c

By subtracting ΔS_{dis} from the configurational entropy (ΔS_m)_V, the conformational entropy ΔS_c is obtained and is given in Table I.

Other thermodynamic quantities related to melting are also shown in Table I.

DISCUSSION

The entropy of melting for PEG decreases with increasing molecular weight. The entropy of melting in PTHF lies between those of poly(ethylene glycol) and polyethylene when compared in the range of high molecular weight. The heat of fusion ΔH_m , evaluated from the thermodynamic equation $\Delta H_m = T_m \Delta S_m$, agrees

well with the ΔH_m (2.17 kcal/mol) obtained from differential scanning calorimetry. Mandelkern⁵ has obtained the heat of fusion from an analysis of the melting point depression caused by the addition of diluents. His value ΔH_m (1.98 kcal/mol) is a little smaller than ours. The heat of fusion increases with increasing molecular weight (see Table I).

Malcolm and Ritchie⁶ reported that the entropy of melting at constant volume for poly(ethylene glycol) with $M=5000$ is 4.22 cal/mol deg if the thermal pressure coefficient is assumed to be independent of volume.

Malcolm and Ritchie⁶, theoretically calculated the conformational entropy for PEG to be 3.35 cal/mol deg, assuming that the difference in potential energy between the *trans* and *gauche* forms of the C—C bonds in PEG is the same as in polyethylene and that the difference for the C—O bonds in PEG is the same as in poly(ethyleneoxide). On the other hand, Tonelli⁷ evaluated the intramolecular configurational entropy on melting for a single isolated polymer chain on the basis of the rotational isomeric state model, and obtained 5.10 cal/mol deg for poly(ethylene glycol). Our data for PEG fall between the values of these two authors. The ratios of ΔS_c to ΔS_m are 0.66–0.69 for both PEG and PTHF, whereas those for eicosane and polyethylene are 0.60–0.62. Thus the contribution of the conformational entropies of polyethers to the total entropy of melting is larger than that of polyethylene.

The conformational entropy ΔS_c tends to decrease as the molecular weight increases. These results for molecular weight dependence agree qualitatively with those derived from both Smith's equation⁸ and Broadhurst's empirical equation⁹ for *n*-hydrocarbons. The relation between conformational entropy and molecular weight for poly(ethylene glycol) coincides with those for eicosane and polyethylene.

APPENDIX

The corresponding state theorem is represented by the equation of state

$$f(\bar{P}, \bar{V}, \bar{T}) = 0 \quad (\text{A-1})$$

where f is a universal function, and $\bar{P} = P/P^*$,

$\tilde{V}=V/V^*$, and $\tilde{T}=T/T^*$ are the reduced pressure, volume, and temperature, respectively. Characteristic pressure, volume, and temperature can be written¹⁰

$$P^*=e^*/v^*, \quad V^*=v^*N, \quad \text{and} \quad T^*=e^*/ck \quad (\text{A-2})$$

where e^* is the intersegmental interaction parameter, v^* is the occupied volume of a segment, $3c$ is the number of external degrees of freedom per segment, and N is the total number of segments in the system. If eq A-1 and eq A-2 are combined, one can obtain the relation

$$P_i\alpha V_s/R=(c/M)\tilde{P}_i\tilde{\alpha}\tilde{V} \quad (\text{A-3})$$

where P_i is the internal pressure, α is the thermal expansion coefficient, V_s is the specific volume, R is the gas constant, $\tilde{P}_i$ is the reduced value of P_i , i.e., $\tilde{P}_i=P_i/P^*$, and $\tilde{\alpha}$ is the reduced value of α , i.e., $\tilde{\alpha}=\alpha T^*$. The quantity M/c represents the molecular weight of a unit having three external degrees of freedom. Since the value of $\tilde{P}_i\tilde{\alpha}\tilde{V}$ is the same for all substances at a corresponding state, M/c can be determined from eq A-3 by comparing the value of $P_i\alpha V_s/R$ at the corresponding state with that of a reference substance for which the value of M/c is known. It is assumed here that the melting point is a corresponding state. Since c is considered to be unity for Ar, $\tilde{P}_i\tilde{\alpha}\tilde{V}$ at the melting point is evaluated from the value of $P_i\alpha V_s/R$ of Ar at

the melting point. Then, the values of M/c for other substances can be calculated from the values of $P_i\alpha V_s/R$ at their melting points. For example, the values of $P_i\alpha V_s$ for PEG 6000 and PTHF are estimated to be 0.060 and 0.055 cal/g deg from P — V — T measurements.³ Thus the units of PEG 6000 and PTHF having three external degrees of freedom are 1.90 times and 1.27 times as large as the respective repeating units.

REFERENCES

1. Y. Tsujita, T. Nose, and T. Hata, *Polymer J.*, **3**, 587 (1972).
2. H. W. Starkweather and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).
3. Y. Tsujita, T. Nose, and T. Hata, *Polymer J.*, **5**, 201 (1973).
4. Y. Tsujita, T. Nose, and T. Hata, *ibid.*, **3**, 581 (1972).
5. L. Mandelkern, *J. Appl. Phys.*, **26**, 443 (1955).
6. G. N. Malcolm and G. L. D. Ritchie, *J. Phys. Chem.*, **66**, 852 (1962).
7. A. E. Tonelli, *J. Chem. Phys.*, **52**, 4749 (1970).
8. R. P. Smith, *J. Polym. Sci., Part A-2*, **4**, 869 (1962).
9. M. G. Broadhurst, *J. Chem. Phys.*, **36**, 2578 (1962).
10. I. Prigogine, "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam, 1957.