Thermodynamic Properties of Poly(ethylene glycol) and Poly(tetrahydrofuran). I. P—V—T Relations and Internal Pressure

Yoshiharu TSUJITA, Takuhei NOSE, and Toshio HATA

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

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ABSTRACT: P—V—T relations are measured for poly(ethylene glycol) (PEG) with different molecular weights over the temperature range from $-40°$ to 210°C and for poly(tetrahydrofuran) (PTHF) from $-40°$ to 170°C. The thermal expansion coefficient α, the compressibility β, and the internal pressure P_i are obtained and their temperature dependence is related to the molecular weight. The α and β of liquid PEG do not depend strongly on the molecular weight. On the other hand, the α of solid PEG becomes larger as the molecular weight increases, whereas the β is almost independent of molecular weight. These facts manifest themselves in the behavior of the internal pressure. In the liquid state the internal pressures of higher-molecular-weight PEG are approximately proportional to the second power of the reciprocal volume, but those of low-molecular-weight PEG and PTHF deviate from this rule. The results of internal pressure measurements are analyzed in terms of the theorem of corresponding states.
KEY WORDS P—V—T Relations / Thermodynamic Quantities / Internal Pressure / Polyethylene Glycol / Poly(tetrahydrofuran) /

For the purpose of thermodynamic studies of polymers, it is indispensable to determine the P—V—T (pressure—volume—temperature) relations, *i. e.*, the equation of state, because quantities characterising thermodynamic states can be derived from them. For example, internal pressure P_i, as one of such quantities, provides information about the intermolecular interactions.

Although many studies[1-11] have been reported on the P—V—T relations of polymers, the data and analyses for crystalline polymers do not yet seem complete enough to discuss thermodynamic states and the changes in thermodynamic quantities at the melting point. In this paper, thermodynamic quantities of typical polyethers, *i. e.*, poly(ethylene glycol) (PEG) and poly(tetrahydrofuran) (PTHF), are obtained and compared with those of polyethylene and eicosane reported previously.[12] Sims[13,14] measured thermal pressure coefficients of poly(ethylene glycol) and poly(tetrahydrofuran) in the vicinity of the melting temperature, but the samples used were low

molecular weight (1500 and 3000, respectively) and the measurements were limited to a narrow range of temperature. Becht and coworkers[15] have reported specific volume, thermal expansion coefficient, and compressibility for samples of PEG with different molecular weights in the liquid state, but not in the solid state.

For a quantitative study of the thermodynamic states of poly(ethylene glycol) and poly(tetrahydrofuran), the P—V—T relations were measured over a wide range, covering the crystalline and liquid states, by using a pressure apparatus recently developed in our laboratory.[12]

The thermodynamic quantities discussed here are: thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (1)$$

compressibility

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2)$$

internal pressure

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$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P \approx T\left(\frac{\partial P}{\partial T}\right)_V = T\frac{\alpha}{\beta} \qquad (3)$$

where V is volume, T temperature, P pressure, U internal energy, and S entropy. The solid samples used here may have had amorphous regions. To take into account the degree of crystallinity, we here adopted the two-phase model, as was done by Pastine,[16] and calculated the thermodynamic quantities of the crystalline region by use of the following equations. If it is assumed that temperature and pressure are the same in both amorphous and crystalline regions and that the degree of crystallinity is independent of T and P, we obtain for the two-phase model

$$v = (1-x)v_a + xv_c \qquad (4)$$

$$= (1-x)\alpha_a v_a/v + x\alpha_c v_c/v \qquad (5)$$

$$= (1-x)\beta_a v_a/v + x\beta_c v_c/v \qquad (6)$$

$$P_{ic} \approx T\alpha_c/\beta_c \qquad (7)$$

where the subscripts a and c designate amorphous and crystalline regions, respectively, V is specific volume, and x is the degree of crystallinity determined by the density method. For the numerical calculations the values of α and β extrapolated from the liquid state were taken to be α_a and β_a.

EXPERIMENTAL

Poly(ethylene glycol)s with narrow distributions of molecular weights, $M_n = 605$, 1020, and 7500, were obtained from Nippon Oil and Fats Co., Ltd., and designated PEG 600, PEG 1000, and PEG 6000, respectively. Molecular weights were determined by the end group analysis, and the distributions of molecular weights were checked by GPC, as shown in Figure 1. The solid samples of PEG were crystallized by slow cooling from the molten state. The degrees of crystallinity determined by the density method were 77.9% for PEG 600, 72.4% for PEG 1000, and 85.0% for PEG 6000. Poly(tetrahydrofuran) (PTHF) produced by cationic polymerization (molecular weight $M = 40000$, $M_n/M_w = 1.3$—1.5) was kindly provided by Dr. T. Fujimoto of
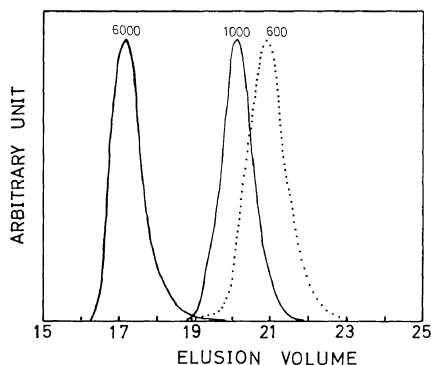

**Figure 1.** GPC measurement for PEG 600, PEG 1000, and PEG 6000.

Nagoya University. Measurements on solid PTHF were performed with the sample crystallized in a dilatometer at room temperature. Its degree of crystallinity determined by the density method was 61.4%. The pressure apparatus used here has been described in a previous paper.[12] Measurements at low temperatures, i.e., from room temperature to about −40°C, were improved by immersion of the apparatus into a freezing bath (Dry Ice—methanol mixture).

Although there are three possible methods of measurement, as mentioned elsewhere,[12] here the one was used in which volume—pressure relations are measured at constant temperature. The pressure was increased at a rate of nearly 10 kg/cm² min., and the measurements were made at intervals of 30—50 kg/cm².

RESULTS AND DISCUSSION

P—V—T Relations, Thermal Expansion Coefficient, and Compressibility.

Polyethyle Glycol. The V—T curves of solid PEG 6000 at pressures of 0, 200, and 400 kg/cm² and those of the same sample in the liquid state at 0, 100, 200, 300, 400, 500, 600, and 700 kg/cm² are shown in Figure 2. The values of α and β for $P = 0$ and those α_c and β_c calculated by eq 5 and 6 are shown as functions of temperature in Figures 3 and 4. Poly(ethylene glycol) exhibits sharper melting behaviors than polyethylene. That is, as shown in Figures 3 and 4, the thermal expansion coefficient α (or α_c) and the compressibility β (or β_c) at atmospheric pressure do not
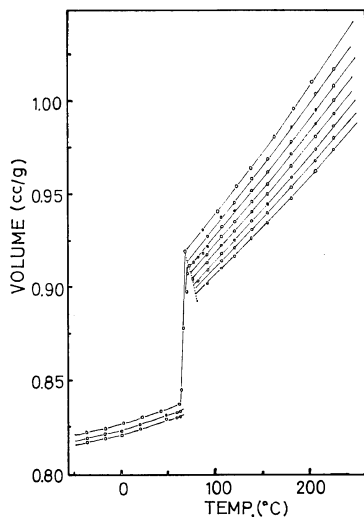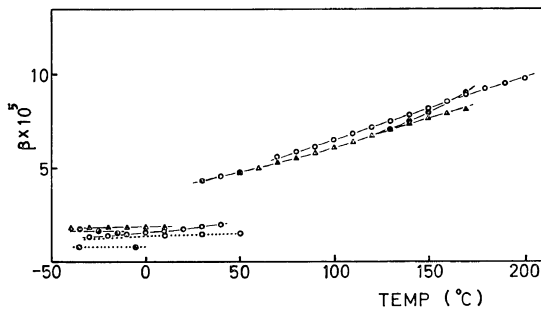
Figure 2. Volume *vs.* temperature relations at elevated pressures for PEG 6000. Pressure: 0, 200, 400 kg/cm² for the solid state; 0, 100, 200, 300, 400, 500, 600, 700 kg/cm² for the liquid state.
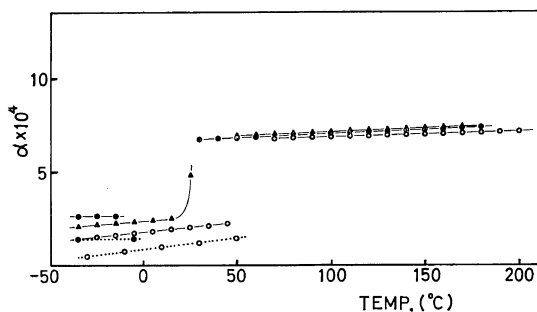
Figure 3. Temperature dependence of the thermal expansion coefficient α (deg^{-1}) for poly(ethylene glycol)s with various molecular weights: ●, PEG 600; ▲, PEG 1000; ○, PEG 6000; ——, observed values; ------, calculated values α_{c} (eq 5).

Figure 4. Temperature dependence of the compressibility β (kg/cm²)$^{-1}$ for poly(ethylene glycol)s with various molecular weights: ●, PEG 600; ▲, PEG 1000; ○, PEG 6000; ——, observed values; ------, calculated values β_{c} (eq 6).

exhibit before melting such an abrupt increase as observed in polyethylene. The temperature dependence of α, $d\alpha/dT$, in the liquid state is small but positive, in contrast with polyethylene and eicosane. In the solid region, the value of α (or α_{c}) for PEG 6000 is about one third that for polyethylene, whereas in the liquid region it is nearly the same for the two polymers. On the other hand, the value of β for PEG 6000 is about half that for polyethylene, both in the liquid and solid regions. The data

of α and β and the calculated values of α_{c} and β_{c} for PEG 600, PEG 1000, and PEG 6000 are shown as functions of temperature in Figures 3 and 4. The calculation of α_{c} for PEG 1000 involves large inaccuracy because a large part of the thermal expansion of the solid state is due to the amorphous region. For this reason the α_{c} of this sample is not shown in the figure. In the liquid state, the value of α and β do not depend greatly on molecular weight, a result which is in agreement with Becht's data.[15] On the other hand, in the solid state α (or α_{c}) is more sensitive to molecular weight than in the liquid state. The thermal expansion coefficient decreases with increasing molecular weight in the solid state. This fact seems to be associated with a more active molecular motion of lower-molecular-weight PEG in the vicinity of the melting temperature. On the contrary, the compressibility in the solid state does not depend on molecular weight. These facts lead to a large molecular-weight dependence of the internal pressure ($\approx T\alpha/\beta$) in the solid state, as described below.

Poly(tetrahydrofuran). The V—T curves of this polymer in the solid state at pressures of 0, 200, 400, 600, and 800 kg/cm² and those in the liquid state at pressures of 0, 100, 200, 300, 400, 500, 600, and 700 kg/cm² are shown in Figure 5. The thermal expansion coefficient α (and α_{c}) and the compressibility β (and β_{c}) at atmospheric pressure are shown in Figure 6. The thermal expansion coefficient in the solid state (or
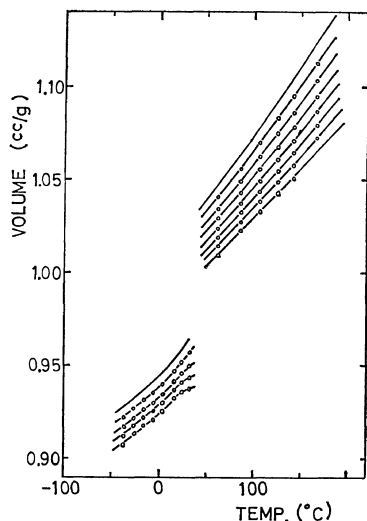
Figure 5. Volume *vs.* temperature relations at elevated pressures for poly(tetrahydrofuran). Pressure: 0, 200, 400, 600, 800 kg/cm² for the solid state; 0, 100, 200, 300, 400, 500, 600, 700 kg/cm² for the liquid state.
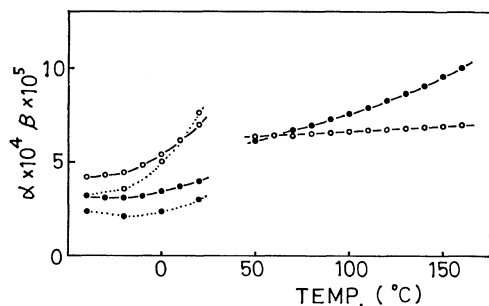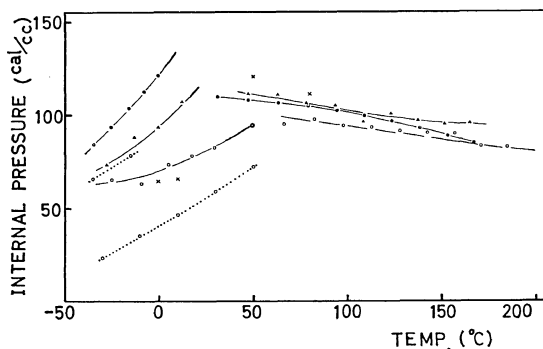

Figure 6. Temperature dependence of the thermal expansion coefficient α (deg⁻¹) (○) and the compressibility β (kg/cm²)⁻¹ (●) for poly(tetrahydrofuran): ——, observed values; ------, calculated values α_c and β_c (eq 5 and 6).

crystalline region) is larger than that of poly(ethylene glycol). As was observed for solid polyethylene, there is a broad region of premelting, which is reflected in the behavior of α (or α_c) and β (or β_c). The temperature dependence of α in the liquid state is positive and larger than that of PEG. The value and behavior of the compressibility in the liquid state are not much different from polyethylene and poly(ethylene glycol). Due to the tempera-
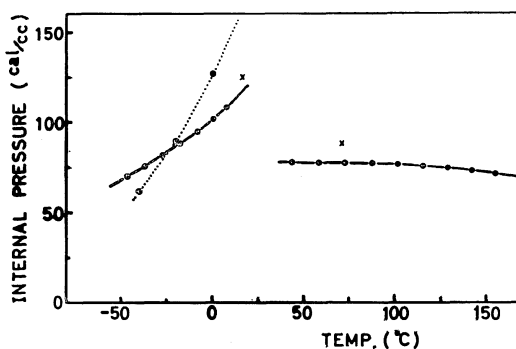
ture dependence of α and β, the internal pressure $P_i \approx T(\alpha/\beta)$ increases as temperature increases in the solid state, as will be described later.

The poly(tetrahydrofuran) employed here had a narrow distribution of molecular weight, but the $V-T$ relation did not show as sharp a melting region as that of poly(ethylene glycol). Therefore, premelting is not due to partial melting of low-molecular-weight fractions.

Internal Pressure. Internal pressure, P_i, is defined as the volume derivative of internal energy at constant temperature (see eq 3). It depends mainly on the intermolecular potential energy, and slightly on the intramolecular one, because the latter may have a small volume

Figure 7. Temperature dependence of the internal pressure of poly(ethylene glycol)s with various molecular weights: ●, PEG 600; ▲, PEG 1000; ○, PEG 6000; ——, observed values; ------, calculated values P_{ic} (eq 7); ×, Sims' data.

Figure 8. Temperature dependence of the internal pressure of poly(tetrahydrofuran): ——, observed values; ------, calculated values P_{ic} (eq 7); ×, Sims' data.

dependence. In order to describe a crystalline polymer with its molten state, two different curves of P_i vs. T will be needed, because of the difference in the volume dependence of the intermolecular potential between the crystalline and liquid states. Internal pressures of PEG and PTHF are as a function of temperature in Figures 7 and 8, respectively. The two branches of the P_i vs. T curves in Figures 7 and 8 correspond to the crystalline and liquid states. In these graphs, the data of Sims, et al.,[13,14] are also indicated by crosses; it does not agree with our data. The values of Sims, et al., in the solid region are smaller than ours for PEG but larger for PTHF, and in the liquid region they are larger than ours for both PEG and PTHF.

In the solid state the internal pressure of PEG increases as temperature increases; for PEG 6000, P_i is about 65 cal/cc at $-30°C$ and about 80 cal/cc at 25°C, and P_{ic} is about 20 cal/cc at $-30°C$ and about 55 cal/cc at 25°C. In the solid state, P_i becomes smaller with increasing molecular weight. This fact corresponds to a larger thermal expansion coefficient for lower molecular weight PEG. In the liquid state, P_i does not depend appreciably on molecular weight and decreases gradually with increasing temperature or volume.

The P_i for solid PTHF also increases as temperature increases; that is, P_i (or P_{ic}) ≈ 75 cal/cc at $-35°C$, 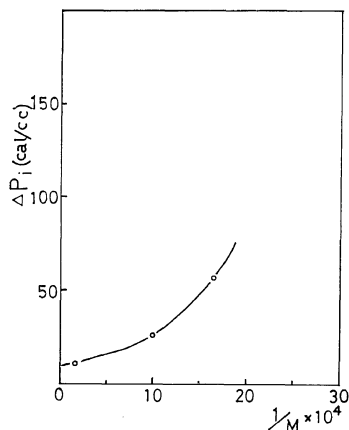and $P_{ic} \approx 100$ cal/cc and $P_i \approx 150$ cal/cc at 0°C. In the liquid state, P_i decreases gradually with increasing temperature or volume as in the case of polyethylene and poly(ethylene glycol).

The extrapolation of internal pressure data from the solid region to the melting temperature gives the hypothetical internal pressure of the solid state at the melting temperature. The changes of P_i at the melting point, $\Delta P_i = P_i$ (solid) $- P_i$ (liquid), were approximately equal to 10.8 cal/cc for PEG 6000, 26.3 cal/cc PEG 1000, and 56.4 cal/cc for PEG 600. They are plotted against reciprocal molecular weight in Figure 9. The dependence of ΔP_i on molecular weight is associated mainly with that of P_i in the solid state, since at the melting point the internal pressure of the liquid is almost the same for PEG of different molecular weights (Figure 7). Contrary to Sims' result ($\Delta P_i < 0$), the internal pressure of the solid is larger than that of the liquid. The value of ΔP_i for poly(tetrahydrofuran) is approximately equal to 67 cal/cc, when estimated from Figure 8. The ΔP_i of both polymers are positive, as in the case of polyethylene, but it was negative in eicosane. If ΔP_i is taken as $P_{ic} - P_i$ (liquid), the quantitative discussions made above should be altered, but the qualitative ones may remain the same.

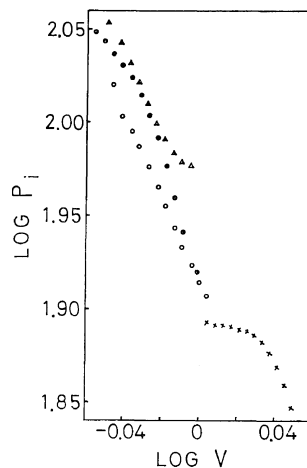Next, the dependence of internal pressure on volume in the liquid region is examined. Van

Figure 9. Relation between ΔP_i and reciprocal molecular weight M^{-1}.

Figure 10. Plots of $\log P_i$ vs. $\log V$: ●, PEG 600; ▲, PEG 1000; ○, PEG 6000; ×, polytetrahydrofuran.

der Waals' equation assumes P_i to be proportional to V^{-2}. Hildebrand, *et al.*,[17] and Allen, *et al.*,[18,19] showed experimentally that the internal pressure of the liquid is also proportional to V^{-2}. Bondi[20] concluded, however, from the data on low-molecular-weight liquids that P_i is not necessarily proportional to V^{-2}.

Figure 10 shows double logarithmically the relation between P_i and V for liquid polyethylene glycol and that for polytetrahydrofuran. It is seen that the data for PEG 1000 and PEG 6000 are fit by a straight line whose slope is about -2.3. This means that P_i for PEG 1000 and PEG 6000 are proportional to $V^{-2.3}$, in rough agreement with the assumption proposed by Hildebrand, *et al.*, and Allen, *et al.* For PEG 600, however, the linearity of the plot is not obtained, and the internal pressure can not be expressed as V^{-n} in the range of volume examined. For PEG 600 at lower temperatures P_i varies with $V^{-1.6}$ and at higher temperatures with V^{-4}. For PTHF, $\log P_i$ does not vary linearly with $\log V$; at lower temperatures $P_i \propto V^{-0.25}$, while at higher temperatures $P_i \propto V^{-2.4}$. As has been reported by the authors[12] and Bondi[20], internal pressures of polymer liquids are not always proportional to the second power of the reciprocal volume.

A meaningful comparison between polyethylene glycol and polytetrahydrofuran must be made at a corresponding state. According to the hole theory of polymer liquids proposed by Nose,[21] the reduced internal pressures in the liquid and crystalline state may be expressed as

$$\tilde{P}_{i\,\text{liquid}} = 0.699\, s(\tilde{V} - 1 + s)^{-2} \qquad (8)$$

$$\tilde{P}_{i\,\text{crystal}} = s\tilde{V}^{-3}(2.409 - 2.0218\,\tilde{V}^{-2}) \qquad (9)$$

where $\tilde{P}_i = P_i/P_i^* = P_i/(\varepsilon^* z'/\sigma^3)$ and $\tilde{V} = V/V^* = V/\sigma^3 N$ are reduced internal pressure and reduced volume, respectively, and s is a constant related to the coordination number. Here $\tilde{P}_{i\,\text{crystal}}$ was calculated by assuming that the crystalline state is a glassy state with no holes. Characteristic volume V^* is defined as the occupied volume, $\sigma^3 N$, where σ is the intermolecular distance at zero potential energy and N is the number of the segments, and is related to the volume at $0°K$, V_0, by $V_0 = 0.9161\,V^*$. By the use of a Spencer—Gilmore type equation V^* was

estimated to be 0.7987 cc/g for PEG 6000 and 0.8439 cc/g for PTHF (see Appendix). Next $P_i^*(=\varepsilon^* z'/\sigma^3)$, where ε^* is the minimum value of the potential energy and z' is coordination number per segment, was obtained by superimposing the experimental curve of P_i *vs.* V on the theoretical curve (eq 8) for the liquid state. The results obtained were 135 cal/cc for PEG 6000 and 133 cal/cc for PTHF. These values of P_i^* are similar to those of polyethylene and eicosane, which are 136 cal/cc and 141 cal/cc respectively.

Reduced internal pressures in the crystalline state were evaluated by use of these values by P_i^* and V^*. Figure 11 shows plots of $\tilde{P}_i$ (and
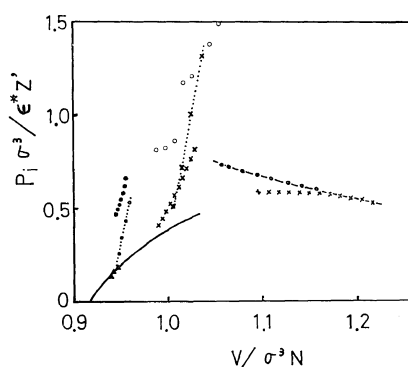
Figure 11. Reduced internal pressure *vs.* reduced volume for PEG 6000 (●) and poly(tetrahydrofuran) (×): ——, theoretical curve for the liquid state and the crystalline state; ------, calculated values (P_{ic}); ▲, eicosane; ○; polyethylene.

$\tilde{P}_{ic}$) *vs.* $\tilde{V}$ for PEG 6000 (●) and PTHF (×) with those for polyethylene (○) and eicosane (△). These plots are off the theoretical curve (the solid line) calculated from eq 9. The reduced values for P_{ic} (not P_i) should be compared with the theoretical curve for the crystalline state.

The crystalline state cannot be expressed by the present model (glass with no holes). Furthermore, the values of the reduced P_i of different polymers in the solid state do not merge on a single master curve. This fact implies that the theorem of corresponding states is not satisfied in the solid region, as long as one uses the same characteristic parameter P_i^* as that in the liquid state.
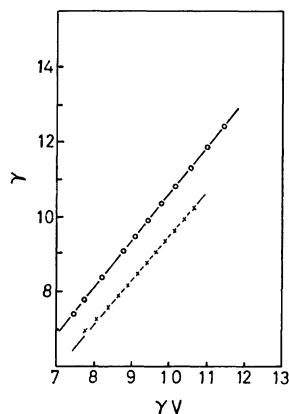
APPENDIX

In order to estimate V^* or V_0, we assume the Spencer—Gilmore[2,3] type equation for the liquid state, i.e.,

$$(P+P_i)(V-V_0)=nRT$$

By the use of the thermodynamic equation, $P+P_i=T\gamma(\gamma=(\partial P/\partial T)_V)$, the following equation can then be derived:

$$\gamma=\frac{1}{V_0}\gamma V-\frac{nR}{V_0}$$

From the slope of the plot of γ vs. γV in Figure 12, we estimate V_0 as 0.7987 cc/g for PEG 6000 and 0.8439 cc/g for poly(tetrahydrofuran).

Figure 12. Plots of thermal pressure coefficient γ vs. γV for PEG 6000 (◯) and poly(tetrahydrofuran) (×).

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