

A Hole Theory of Polymer Liquids and Glasses. III. Glass Transition and Glassy State; Heat Capacity Change at Glass Transition Temperature and Excess Enthalpy

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ABSTRACT: In order to interpret the change in heat capacity ΔC_p at glass transition temperature and the excess enthalpy H_e of polymer liquids and glasses relative to the crystals, a hole theory is presented in which both the hole fraction and the state of chain conformation are assumed to be frozen-in in the glassy state. In this treatment, ΔC_p and H_e are both divided into two parts: one associated with intersegmental and the other with intrasegmental interactions. The relations $TV(\Delta\alpha)^2/\Delta C_p^{\text{inter}}\Delta\beta=1$ and $TV(\Delta\alpha)^2/\Delta C_p\Delta\beta\leq 1$ are derived, where T is temperature, V is volume, $\Delta\alpha$ and $\Delta\beta$ are the differences in the thermal expansion coefficient and compressibility between the liquid and glassy states respectively, and $\Delta C_p^{\text{inter}}$ is the part of ΔC_p attributable to intersegmental interactions. Using the results of this theory, the experimental observations for ΔC_p and H_e are compared and analyzed, bringing in at times the principle of corresponding states.

KEY WORDS Hole Theory / Polymer / Glass Transition / Heat Capacity / Excess Enthalpy /

In the preceding paper¹ we explained the glassy state by the hole theory, in which the glassy state was distinguished from the liquid and crystalline states by the freezing of holes which respect to intersegmental interactions. In this paper we deal with the thermodynamic properties which reflect both inter- and intra-segmental interactions, *i.e.*, changes in heat capacity ΔC_p at glass transition temperature and "excess enthalpy" H_e of the liquid and glass relative to the crystal, whereas in the previous paper¹ we considered the problems concerned with intersegmental interactions only, *e.g.*, internal pressure. Since the glassy state may be regarded as a frozen liquid such that the polymer chains cannot change their conformations and that the segments cannot exchange their mean positions with each other, both holes and chain conformation are frozen-in in the glassy state. Therefore each of the above quantities ΔC_p and H_e may consist of two elements: one associated with holes, intersegmental interactions, and the other associated with conformation of chain backbones, intrasegmental interactions.

Here we present a general hole theory incorporating the previous one, and derive a few relations between thermodynamic quantities such as ΔC_p , H_e , $\Delta\beta$, and $\Delta\alpha$, where $\Delta\beta$ and $\Delta\alpha$ are respectively the differences in compressibility and the thermal expansion coefficient between the liquid and glassy states. From the theoretical results we try to analyze the experimental observations, using at times the principle of corresponding states.

THEORY

Model

We consider a system in which N segments are on M lattice sites ($M \geq N$). Thus there are $(M-N)$ empty sites or holes. If we denote the cell volume by v^* , then $M/N = V/Nv^* \equiv V/V^* \equiv \tilde{V}$, where V is volume, and hence the quantity $(1-\tilde{V}^{-1})$ represents the hole fraction. In developing the theory further, we make the following two assumptions.

Assumption 1. The change in the cell volume with pressure and temperature is essentially independent of the hole fraction or \tilde{V} . This

implies that the thermal expansion coefficient and compressibility of the cell volume are almost continuous at the glass transition, and that the glasses of different hole fractions have almost the same cell volume, the same thermal expansion coefficient and the same compressibility (see APPENDIX in the preceding paper¹).

Assumption 2. The free energy of the system is expressed by the sum of two kinds of free energy: one associated with the internal degrees of freedom or intrasegmental interactions, including the so-called short range interaction related to the chain conformation, and the other associated with the external degrees of freedom or intersegmental interactions. The former is considered to be independent of volume, and depends on temperature alone in the zero-th approximation. On the other hand, the latter should be dependent upon the hole fraction, the mean distance between nearest neighbor segments and temperature T . Hence it can be regarded as a function of \tilde{V} , V^* , and T . Thus the assumption is represented by

$$F = U - TS = U_1(T) - TS_1(T) + U_2(\tilde{V}, V^*, T) - TS_2(\tilde{V}, V^*, T) \quad (1)$$

where U is the internal energy and S the entropy, and the subscripts 1 and 2 refer to intrasegmental interactions, respectively. In general U_1 and U_2 , or S_1 and S_2 cannot be expressed separately since, for example, the admissible number of arrangements of the polymer chain on the lattice and the conformational state of chain backbones may be mutually affected. However Gibbs and DiMarzio² have shown, with a lattice theory, the possibility that the partition functions for intra- and inter-molecular interactions are formally expressed separately. Thus we may reasonably use the expression of eq 1 in zero-th approximation. The free energy in our previous paper^{1,3} was also expressed in the form of eq 1; the partition function corresponding to $U_1 - TS_1$ was represented by the implicit form $J(T)$, whereas that corresponding to $(U_2 - TS_2)$ was given in the explicit form. The preceding model showed that Assumption 1 is valid at pressure much less than internal pressure and that the dependence of the $T-P-V^*$ relation on \tilde{V} is only slight even at higher pressure.

In the glassy state, which is considered here to be a quasi-equilibrium state, it is assumed that the holes and the conformation of the chain backbones are completely frozen in. Thus, in the glassy state, the hole fraction or \tilde{V} is assumed to be constant and the part of $U_1 - TS_1$ associated with the hindered rotation about chain backbones is also assumed not to vary. On the other hand, in the liquid state, \tilde{V} and V^* are both allowed to change so as to minimize the free energy.

In the present theory in which inter- and intra-segmental interactions are separately expressed, both ΔC_p and H_e are also represented by the sum of two parts:

$$\Delta C_p = \Delta C_p^{\text{inter}} + \Delta C_p^{\text{intra}} \quad (2)$$

$$H_e = H_e^{\text{inter}} + H_e^{\text{intra}} \quad (3)$$

where superscripts inter and intra refer to inter- and intra-segmental interactions, respectively. From the definitions for these quantities, we have

$$\Delta C_p = \Delta(\partial H_e / \partial T)_p,$$

$$\Delta C_p^{\text{inter}} = \Delta(\partial H_e^{\text{inter}} / \partial T)_p,$$

$$\Delta C_p^{\text{intra}} = \Delta(\partial H_e^{\text{intra}} / \partial T)_p,$$

where the symbol Δ denotes the difference between the liquid and glassy states. Since the the equation of state and $\Delta C_p^{\text{inter}}$ are both determined by a volume-dependent part of free energy, some relation among $\Delta C_p^{\text{inter}}$, $\Delta\beta$ and $\Delta\alpha$ is expected, which will be derived in the next section. The expressions for $\Delta C_p^{\text{inter}}$ and H_e^{inter} will be also derived by using the explicit form for U_2 given in the previous paper.^{1,3} Finally, we will present a simple rotational-isomeric model for the conformational energy of a chain backbone and express $\Delta C_p^{\text{intra}}$ and H_e^{intra} with two parameters involved in the model.

$\Delta C_p^{\text{inter}}$ and H_e^{inter}

First we will express the the heat capacity C_p^{inter} at constant pressure arising from inter-molecular interactions. From the definition of the heat capacity, we have

$$\begin{aligned} C_{p1}^{\text{inter}} &= T(\partial S_2 / \partial \tilde{V})_{V^*, T} (\partial \tilde{V} / \partial T)_p^{-1} \\ &\quad + T(\partial S_2 / \partial V^*)_{\tilde{V}, T} (\partial V^* / \partial T)_p^{-1} + T(\partial S_2 / \partial T)_{\tilde{V}, V^*} \\ &= T(\partial S_2 / \partial \tilde{V})_{V^*, T} \tilde{V} \{ \partial \ln V / \partial T \}_p^{-1} \\ &\quad - (\partial \ln V^* / \partial T)_p^{-1} + T(\partial S_2 / \partial V^*)_{\tilde{V}, T} \\ &\quad \times (\partial \ln V^* / \partial T)_p^{-1} + T(\partial S_2 / \partial T)_{\tilde{V}, V^*} \end{aligned} \quad (4)$$

for the liquid state, and

$$C_{pg}^{\text{inter}} = T(\partial S_2/\partial V^*)_{\tilde{V},T}(\partial V^*/\partial T)_{\tilde{V},P} + T(\partial S_2/\partial T)_{\tilde{V},V^*} \quad (5)$$

for the glassy state, where the symbols *l* and *g* as subscripts and superscripts refer to the liquid and glassy states respectively. From eq 4 and 5, we can derive $\Delta C_p^{\text{inter}}$ as

$$\Delta C_p^{\text{inter}} \equiv C_{pl}^{\text{inter}} - C_{pg}^{\text{inter}} = T(\partial S_2/\partial \tilde{V})_{V^*,T} \tilde{V}(\alpha_l - \alpha_g) \quad (6)$$

using the relation $(\partial \ln V^*/\partial T)_P^l = (\partial \ln V^*/\partial T)_{\tilde{V},P} = \alpha_g$ (Assumption 1), where α_l and α_g are the thermal expansion coefficients $(\partial \ln V/\partial T)_P$ in the liquid and glassy states. The relation $P = -(\partial F/\partial V)_T = -(\partial F/\partial V)_{V^*,T} = \{T(\partial S_2/\partial \tilde{V})_{V^*,T} - (\partial U_2/\partial \tilde{V})_{V^*,T}\}/V^*$ can be derived from the condition that the volume of the cell is determined so as to minimize the free energy of the system (see APPENDIX of the preceding paper¹). With this relation, $\Delta C_p^{\text{inter}}$ may be expressed in an alternative form

$$\Delta C_p^{\text{inter}} = \{(\partial U_2/\partial \tilde{V})_{V^*,T} + PV^*\}(\alpha_l - \alpha_g) \quad (7)$$

Next we will express the quantity $(\partial S_2/\partial \tilde{V})_{V^*,T}$ in terms of α and compressibility $\beta \equiv -(\partial \ln V/\partial P)_T$ in order to relate $\Delta C_p^{\text{inter}}$ to the changes of α and β at glass transition temperature. Thermal pressure coefficient $(\partial P/\partial T)_V \equiv \alpha/\beta$ is given by

$$\begin{aligned} (\partial P/\partial T)_V^l &= \alpha_l/\beta_l \equiv (\partial S/\partial V)_T^l \\ &= (\partial S_2/\partial \tilde{V})_{V^*,T}/V^* + \{(\partial S_2/\partial V^*)_{\tilde{V},T} \\ &\quad - (\tilde{V}/V^*)\}(\partial S_2/\partial \tilde{V})_{V^*,T}(\partial V^*/\partial V)_T^l \quad (8) \end{aligned}$$

for the liquid state and

$$\begin{aligned} (\partial P/\partial T)_V^g &= \alpha_g/\beta_g \equiv (\partial S/\partial V)_T^g \\ &= (\partial S_2/\partial V^*)_{\tilde{V},T}(\partial V^*/\partial V)_T^g \\ &= (\partial S_2/\partial V^*)_{\tilde{V},T}/\tilde{V} \quad (9) \end{aligned}$$

for the glassy state.

Accordingly, combining eq 8 and 9, and using the relation $\tilde{V}(\partial V^*/\partial V)_T = \beta_g/\beta_l$ (Assumption 1), we obtain

$$(\partial S_2/\partial \tilde{V})_{V^*,T}/V^* = \Delta\alpha/\Delta\beta \quad (10)$$

where $\Delta\alpha = \alpha_l - \alpha_g$ and $\Delta\beta = \beta_l - \beta_g$.

Finally, substituting eq 10 into eq 6, we have the expression

$$\Delta C_p^{\text{inter}} = TV(\Delta\alpha)^2/\Delta\beta \quad (11)$$

If $\Delta C_p^{\text{inter}}$ is replaced by ΔC_p , this equation becomes identical with the well known equation $\Delta C_p \Delta\beta / TV(\Delta\alpha)^2 = 1$ which holds for a thermodynamical second order transition. In the present theory, since $\Delta C_p^{\text{intra}} = \Delta C_p - \Delta C_p^{\text{inter}} \geq 0$, it follows that

$$TV(\Delta\alpha)^2/\Delta C_p \Delta\beta = \Delta C_p^{\text{inter}}/\Delta C_p \leq 1 \quad (12)$$

Heat capacity at constant pressure C_p and that at constant volume C_v are related to each other by the equation $C_p = C_v + TV\alpha^2/\beta$. Therefore we have

$$\Delta C_p^{\text{inter}} = \Delta C_v^{\text{inter}} + \Delta(TV\alpha^2/\beta) \quad (13)$$

noting $\Delta C_p^{\text{intra}} = \Delta C_v^{\text{intra}}$ from Assumption 2. From eq 11 and 13, we have

$$\frac{\Delta C_v^{\text{inter}}}{\Delta C_p^{\text{inter}}} = \frac{(1 - \alpha_l \beta_g / \alpha_g \beta_l)^2}{(\beta_g / \beta_l)(\alpha_l / \alpha_g - 1)^2} \quad (14)$$

$$= \frac{(1 - P_{1l}/P_{1g})^2 P_{1l} \alpha_g}{(\alpha_l / \alpha_g - 1)^2 P_{1g} \alpha_l} \quad (14')$$

where P_1 is internal pressure defined by $(\partial U/\partial V)_T$ and the relation $P_1 = T\alpha/\beta - P = T\alpha/\beta$ is used. As can be seen from this equation, $\Delta C_v^{\text{inter}}$ is not zero but positive, and thus it follows that $\Delta C_v > \Delta C_v^{\text{intra}}$.

According to the previous hole theory,^{1,3} the expression for U_2 is given by

$$U_2 = -N\varepsilon^* z' Ks(\tilde{V} - 1 + s)^{-1} \quad (15)$$

where z' is the mean coordination number of a lattice site, *i.e.*, $s = z'/z$, and $-\varepsilon^* zK$ is the lattice energy, intersegmental interaction energy per segment, represented by

$$-\varepsilon^* z' K = \varepsilon^* z' \{1.0109(\sigma^3 N/V^*)^4 - 2.409(\sigma^3 N/V^*)^2\}/2 \quad (16)$$

Here the symbols ε^* and σ are the parameters involved in the Lennard-Jones 12-6 potential expressed as $u(r_{ij}) = 4\varepsilon^* \{(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6\}$ where $u(r_{ij})$ is the potential energy of interaction between segments *i* and *j* as a function of separation r_{ij} . If we use the expression in eq 15 for U_2 , the quantity $\Delta C_p^{\text{inter}}$ is derived from eq 7 as

$$\Delta C_p^{\text{inter}} = N\varepsilon^* z' Ks(\tilde{V}_g - 1 + s)^{-2} \tilde{V}_g \Delta\alpha \quad (17)$$

at atmospheric pressure ($P=0$).

We note here that, if the corresponding states principle for polymer liquids⁴ is assumed, $\Delta C_p^{\text{inter}}$ of a molar unit having three external degrees of freedom, which is denoted here by $\Delta C_p^{\text{inter}}$ may be a universal function of the reduced variables, as shown in the following. We let $3c$ designate the external degrees of freedom per segment. Then, $\Delta C_p^{\text{inter}}$ is expressed as $\Delta C_p^{\text{inter}} N_A / cN$, where N_A is Avogadro's number. The principle of corresponding states for the equation of state is assumed here, and U_2 is also assumed to be expressed as $U_2 = N\varepsilon^* z' \times f(\tilde{V}, \tilde{T}, V^* / \sigma^3 N)$, where the function f is a universal one and the reduced temperature \tilde{T} is defined as $ckT / \varepsilon^* z'$. It then follows that

$$\begin{aligned} \Delta C_p^{\text{inter}} &= \Delta C_p^{\text{inter}} N_A / cN = \Delta(\partial U_2 / \partial T)_p N_A / cN \\ &= \frac{\varepsilon^* z' N_A}{c} \Delta(\partial f / \partial T)_p \\ &= R \{ (\partial f / \partial \tilde{T})_{\tilde{V}} - (\partial f / \partial \tilde{T})_{\tilde{V}, \tilde{P}} \} \end{aligned} \quad (18)$$

where R is kN_A , the gas constant, and \tilde{P} is the reduced pressure. The right side of eq 18 is a function of the reduced variables. Accordingly, provided that the reduced variables at glass transition temperature T_g are independent of the substance, which holds roughly as shown in the preceding report,¹ the change in heat capacity $\Delta C_p^{\text{inter}}$ at T_g for a molar unit having three external degrees of freedom should have the same value for any substance. This result is identical with the statement presented by Wunderlich⁵ based on the hole theory of Hirai and Eyring.⁵ In Wunderlich's treatment, however, the choice of a unit seems uncertain, whereas in the present case such a structural unit may be determined, for example, by the method described in the previous paper.³ Transforming eq 11, we obtain the expression for $\Delta C_p^{\text{inter}}$ as

$$\begin{aligned} \Delta C_p^{\text{inter}} &= R \tilde{T}_g \tilde{V}_g' (\Delta \tilde{\alpha}')^2 / \Delta \tilde{\beta}' \\ &= R \tilde{V}_g' \Delta \tilde{\alpha}' (1 - \tilde{\alpha}_g' / \tilde{\alpha}_1') \tilde{P}'_{11} \\ &\quad \times \{ 1 - (\tilde{\alpha}_g' / \tilde{\alpha}_1') (\tilde{P}'_{11} / \tilde{P}'_{1g}) \}^{-1} \end{aligned} \quad (19)$$

where \tilde{V}' , $\tilde{\alpha}'$, $\tilde{\beta}'$, and \tilde{P}'_i are defined as $V / \sigma^3 N$, $(\partial \ln \tilde{V}' / \partial \tilde{T})_{\tilde{P}}$, $\beta \varepsilon^* z' / \sigma^3$, and $P_i \sigma^3 / \varepsilon^* z'$, respectively (therefore $\tilde{P}'_i = \tilde{T} \tilde{\alpha}' / \tilde{\beta}'$ at $P=0$). On the other hand, it follows from eq 17 that an alternative form for $\Delta C_p^{\text{inter}}$ is given by

$$\Delta C_p^{\text{inter}} = RKs(\tilde{V}_g - 1 + s)^{-2} \tilde{V}_g \Delta \tilde{\alpha}' \quad (20)$$

This section will end with a convenient estimate of the excess enthalpy H_e^{inter} based on the expression for U_2 given by eq 15 with eq 16. It is assumed here that a perfect crystalline state, the reference state, may be described as the case of $\tilde{V}=1$ in the hole model, *i.e.*, as the case in which the hole fraction is zero. The excess enthalpy H_e^{inter} relative to the crystal may then be given as

$$\begin{aligned} H_e^{\text{inter}} &\cong U_1^{\text{inter}} - U_c^{\text{inter}} \\ &= -\varepsilon^* Nz' K [s(\tilde{V} - 1 + s)^{-1} - 1] \\ &= \varepsilon^* Nz' K (\tilde{V} - 1) / (\tilde{V} - 1 + s) \end{aligned} \quad (21)$$

for the liquid state, where U_1^{inter} is U_2 in the liquid state and U_c is that in the crystalline state, and

$$H_e^{\text{inter}} \cong \varepsilon^* Nz' K (\tilde{V}_g - 1) / (\tilde{V}_g - 1 + s) \quad (22)$$

for the glassy state.

C_p^{intra} and H_e^{intra} —A Simple Model for the Conformational Energy of Chain Backbones

In this section, we will make a simple analysis of the change in heat capacity at T_g and the excess enthalpy attributable to intrasegmental interactions. Both these quantities may be related to the hindered rotation about polymer chain backbones, since other degrees of freedom of intrasegmental interactions may show almost the same features in different states, *i.e.*, in the liquid, glassy, and crystalline states, at the same temperature.

We now represent the partition function $J(T)^R$ for the hindered rotations about chain backbones with the simplest rotational-isomeric approximation as follows

$$J(T)^R = \left\{ \sum_{i=1}^m w_i \exp(-\varepsilon_i / kT) \right\}^m \quad (23)$$

where each unit of the main chain has w_i rotational isomers which have the energy ε_i , hence $\sum_{i=1}^m w_i$ is the total number of rotational isomers for each unit, and m is the total number of rotational units in the system. Thus the enthalpy, $H(T)^R$ associated with chain conformation may be derived from the partition function, eq 23, as

$$H(T)^R = -kT^2 (\partial \ln J^R / \partial T)$$

$$=m\sum_{i=1}^n\{w_i\varepsilon_i\exp(-\varepsilon_i/kT)\}/\sum_{i=1}^nw_i\exp(-\varepsilon_i/kT) \quad (24)$$

The heat capacity C_p^R associated with the rotation of chain backbones may then be expressed as

$$C_p^R=(\partial H^R/\partial T) \quad (25)$$

and the excess enthalpy H_e^{intra} as

$$H_e^{\text{intra}}=\begin{cases} H(T)^R-H_c^R & \text{in the liquid state} \\ H(T_g)^R-H_c^R & \text{in the glassy state} \end{cases} \quad (26)$$

Here, H_c^R denotes H^R in the crystalline state, and it is assumed that in the glassy state the rotation about chain backbones is frozen-in in the conformational state at which the glass has been formed. Accordingly, C_p^R of the glassy state is zero. Hence the quantity $\Delta C_p^{\text{intra}}$ may be equal to C_p^R of the liquid state at T_g .

Considering the case of two isomers of different energies ($n=2$), and assuming that in the crystalline state every rotational unit is in the conformational state 1 ($i=1$), we have from eq 24, 25, and 26

$$H_e^{\text{intra}}=m\Delta\varepsilon w\exp(-\Delta\varepsilon/kT)/(1+w\exp(\Delta\varepsilon/kT)) \quad (27)$$

for the liquid state, and

$$\Delta C_p^{\text{intra}}=mk(\Delta\varepsilon/kT)^2w\exp(-\Delta\varepsilon/kT)/\times\{1+w\exp(-\Delta\varepsilon/kT)\}^2 \quad (28)$$

where $\Delta\varepsilon=\varepsilon_2-\varepsilon_1$ ($\varepsilon_1\leq\varepsilon_2$), and $w=w_2/w_1$. From these equations we readily derive the relations at T_g represented by

$$\Delta\varepsilon/kT=T\Delta C_p^{\text{intra}}/H_e^{\text{intra}}+H_e^{\text{intra}}/mkT \quad (29)$$

$$w=(\Delta H^{\text{intra}})^2\exp(\Delta\varepsilon/kT)/(mkT^2\Delta C_p^{\text{intra}}) \quad (30)$$

ANALYSIS OF EXPERIMENTAL OBSERVATIONS AND DISCUSSION

$\Delta C_p^{\text{inter}}$ and H_e^{inter}

In Table I, we show the values of $TV(\Delta\alpha)^2/\Delta C_p\Delta\beta$ for polymers calculated from published data. The value of $TV(\Delta\alpha)^2/\Delta C_p\Delta\beta$, which is $\Delta C_p^{\text{inter}}/\Delta C_p$ according to the present theory (eq 12), is less than unity and about 0.6 in most cases. This fact agrees with the theoretical prediction represented by eq 12. The fact that

this ratio is less than unity implies, in general, that two or more "ordering parameters" are necessary to specify a glassy state.⁷ The present theory has essentially two ordering parameters: one is the hole fraction representing intersegmental interactions and the other represents the state of chain conformation.

We now evaluate $\Delta C_p^{\text{inter}}$ and $\Delta C_v^{\text{inter}}$ with the average values of the reduced variables for some polymers which were obtained in the preceding paper.¹ Required values for the calculation are as follows: $\bar{V}_g'=1.083$, $V_g^*/\sigma^3N=0.997$, $\bar{\alpha}_g'=2.27$, $\bar{\alpha}_1'=5.10$, $\bar{P}'_{11}=0.616$, and $\bar{P}'_{ig}=0.386$. (\bar{P}'_{11} and \bar{P}'_{ig} are the averages for poly(vinyl acetate)⁸ and poly(methyl methacrylate).⁹) Considering $\Delta C_v^{\text{inter}}/\Delta C_p^{\text{inter}}=\Delta C_v^{\text{inter}}/\Delta C_p^{\text{inter}}$, $\alpha_1/\alpha_g=\bar{\alpha}_1'/\bar{\alpha}_g'$, and $P_{11}/P_{ig}=\bar{P}'_{11}/\bar{P}'_{ig}$, and using eq 14 and 19 with the above values, we have

$$\Delta C_p^{\text{inter}}=3.61R=7.18\text{ cal/mol}$$

$$\Delta C_v^{\text{inter}}/\Delta C_p^{\text{inter}}=0.163_5$$

$$\Delta C_v^{\text{inter}}=1.17_3\text{ cal/mol}$$

$$\Delta C_p^{\text{inter}}-\Delta C_v^{\text{inter}}=\Delta(TV\alpha^2/\beta)=6.01\text{ cal/mol}$$

On the other hand, using eq 14' and 20 with eq 16, we have

$$\Delta C_p^{\text{inter}}=2.12R=4.22\text{ cal/mol}$$

$$\Delta C_v^{\text{inter}}/\Delta C_p^{\text{inter}}=0.069_4,$$

where we used $s=10/12$ and the theoretical value 0.707 for P_{ig}/P_{11} calculated from the expression for U_2 of eq 15 in the preceding paper.¹ The value of $\Delta C_p^{\text{inter}}$ obtained from eq 20 is much lower than that from eq 19, probably because the model for U_2 (eq 15) gives the lower value of $(\partial U_2/\partial \bar{V})_{V^*,T}$. This may be also responsible for the fact that the constant cell volume model in the previous paper³ gives a lower value of P_{11} . The latter value for $\Delta C_v^{\text{inter}}/\Delta C_p^{\text{inter}}$ is much lower than the former because it is sensitive to the ratio P_{11}/P_{ig} , to which the theory gives a value lower than the experimental one.¹

According to the present analysis, a considerable amount of $\Delta C_v^{\text{inter}}$ is expected and we cannot regard ΔC_v as the change in heat capacity $\Delta C_v^{\text{intra}}$ associated with intrasegmental interactions only. In other words, the quantity ΔC_v may include the change in heat capacity arising from the changeability of the mean posi-

Table I. Various thermodynamic

Polymer	$T_g, ^\circ\text{K}$	$V_g, \text{cc/g}$	$\alpha_1 \times 10^4, ^\circ\text{K}^{-1}$	$\alpha_g \times 10^4, ^\circ\text{K}^{-1}$	$\beta_1 \times 10^5, \text{cm}^2/\text{kg}$	$\beta_g \times 10^5, \text{cal}/\text{deg g}$	
Polystyrene ^a	362	0.97	5.45 ^b	2.46 ^b	4.72 ^b	3.16 ^b	
Poly(methyl methacrylate) ^b	384	0.855	5.52	2.58	5.07	3.84	
Poly(vinyl chloride) {	^d	353	0.75	3.76	1.61	3.89	3.30
	^e	348	0.725	5.70	1.99	4.23	2.42
Poly(vinyl acetate) {	^g	294	0.836	5.93	2.28	3.84	2.32
	^h	298	0.855	$\Delta\alpha$ 4.0		$\Delta\beta$ 1.56 ⁱ	

^a ref 10, ^b ref 9, ^c ref 11, ^d ref 9 and 12, ^e ref 13, ^f ref 5, ^g ref 8, ^h ref 14, ⁱ ref 15.

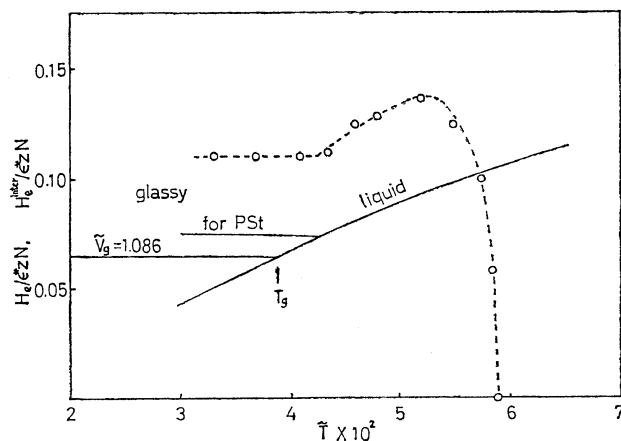


Figure 1. Calculated reduced excess enthalpy $H_e^{\text{inter}}/\epsilon^*z'N$ associated with intersegmental interactions and experimental excess enthalpy H_e of polystyrene divided by $\epsilon^*z'N$: —, curve for $H_e^{\text{inter}}/\epsilon^*z'N$ calculated from eq 21 and 22; \circ , experimental value of $H_e/\epsilon^*z'N$ for polystyrene¹⁰ ($\epsilon^*z'N=118 \text{ cal/g}$)³.

tion of the center of the segment in the liquid state, in addition to the change in heat capacity for intrasegmental degrees of freedom associated with the hindered rotation about main chains.

In Table I, the values of the change in various kinds of heat capacity at T_g for several polymers are shown, being calculated from published data with eq 11 and 14. Such values as $\Delta C_p^{\text{inter}}$, $\Delta C_v^{\text{inter}}$, and $\Delta C_p^{\text{intra}}$ are greatly dependent on the values of α_g/α_l and P_{ig}/P_{il} , and therefore it is very difficult to obtain these values accurately. For the same reason the constancy of the obtained values of $\Delta C_p^{\text{inter}}$ in Table I is poor because the principle of corresponding states for the equation of state is not sufficiently well satisfied.

The theoretical results for H_e^{inter} expressed by eq 21 and 22 are illustrated in Figure 1, being compared with the experimental total ex-

cess-enthalpy for polystyrene¹⁰ derived by $\epsilon^*z'N$. The value of $\epsilon^*z'N$ used is that obtained in the previous paper,³ and the total excess enthalpy was estimated by converting the observed excess enthalpy relative to the 39-% crystalline to 100-%. The calculated curve of $H_e^{\text{inter}}/\epsilon^*z'N$ for polystyrene glass is evaluated from eq 22 with $V_g/V_g^* = 1.097$ given in the preceding report.¹ The excess enthalpy H_e^{inter} arising from intersegmental interactions associated with the hole is about two thirds of the total excess enthalpy H_e . The remaining portion of the excess enthalpy $H_e - H_e^{\text{inter}}$ may be attributed to intrasegmental interactions, namely, the conformational energy of hindered rotation about chain backbones.

$\Delta C_p^{\text{intra}}$ and H^{intra}

Subtracting the calculated H_e^{inter} from the observed H_e , we have the values of H_e^{intra} for polystyrene and show them in Figure 2. The

quantities at glass transition

ΔC_p , cal/deg g	$\Delta C_p^{\text{inter}}$, cal/deg g	$\Delta C_p^{\text{inter}'}$, cal/mol	$\Delta C_v^{\text{inter}}$, cal/deg g	$\Delta C_p^{\text{intra}} = \Delta C_p - \Delta C_p^{\text{inter}}$ cal/deg g	$TV(\Delta\alpha)^2 / \Delta C_p \Delta\beta$
0.075	0.048 ₆	7.0 ₉	0.0050	0.026 ₃	0.65
0.086 ^c	0.056 ₁	8.1 ₄	0.011 ₅	0.029 ₉	0.65
0.068 ^f	0.033 ₃	—	0.0093	0.034 ₇	0.49
	0.048 ₁	—	0.0039	0.019 ₉	0.71
0.10 ^h	0.052 ₁	4.8 ₄	0.0040	0.047 ₀	0.52
	0.063 ₂	5.8 ₇	—	0.036 ₈	0.63

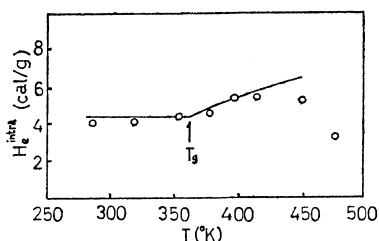


Figure 2. Excess enthalpy H_e^{intra} associated with intrasegmental interactions for polystyrene: —, curve of H_e^{intra} calculated from eq 27 with $\Delta\epsilon = 1.76$ kcal/mol and $w = 1.76$; O, values of H_e^{inter} calculated by subtracting the calculated H_e^{inter} (eq 21 and 22) from the experimental H_e .¹⁰

value of H_e^{intra} at T_g , 362°K, thus obtained is 4.49 cal/g. The value of $\Delta C_p^{\text{intra}}$ for polystyrene is estimated to be 0.026₃ cal/deg g as shown in Table I. Using eq 29 and 30 with these values of H_e^{intra} at T_g and $\Delta C_p^{\text{intra}}$, and taking a half of a repeating unit as a rotational unit, we have 1.76 kcal/mol for $\Delta\epsilon$ and 1.76 for w . With these values, H_e^{intra} in the liquid state is calculated from eq 27 and illustrated by a solid line in Figure 2. The calculated curve shows the reasonable increase in H_e^{intra} above T_g . The value of $\Delta\epsilon$ obtained here is fairly close to the 1.67 kcal/mol evaluated by Gibbs and DiMarzio² with their theory of glass transition in which $w = 2$. Although the physical meanings of $\Delta\epsilon$ and w obtained experimentally are not sufficiently clear due to the simplicity of the model, the values for $\Delta\epsilon$ and w obtained above appear to show reasonable magnitudes. Therefore the value of H_e^{intra} estimated as $H_e - H_e^{\text{inter}}$ may reasonably be expected, and hence H_e^{inter} evaluated by eq 21 and 22 may also be said to give reasonable magnitude and temperature dependence.

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LIST OF SYMBOLS

- C_p , heat capacity at constant pressure
- C_v , heat capacity at constant volume
- C_p' , heat capacity at constant pressure of a molar unit having three external degrees of freedom
- C_v' , heat capacity at constant volume of a molar unit having three external degrees of freedom
- c , one third of external degrees of freedom
- c , as subscript designate the crystalline state
- F , Helmholtz free energy
- g , subscript and superscript for glassy state (except in T_g , \tilde{T}_g , V_g , \tilde{V}_g^* , and \tilde{V}_g' , where g refers to glass transition point.)
- g , as subscript in T_g , \tilde{T}_g , V_g , \tilde{V}_g^* , V_g^* , and \tilde{V}_g' designate the glass transition point.
- H_e , excess enthalpy relative to the crystal
- $H(T)^R$, enthalpy associated with the hindered rotation about chain backbones
- inter, superscript for intersegmental interactions
- intra, superscript for intrasegmental interactions
- $J(T)^R$, partition function associated with the hindered rotation about chain backbones
- K , function defined by eq 16
- k , Boltzmann's constant
- l , subscript and superscript for liquid state
- M , total number of lattice sites in system
- m , total number of rotational units in system
- N , total number of segments in system
- N_A , Avogadro's number
- n , number of rotational isomers having different energies per rotational unit

P , pressure
 \bar{P} , reduced pressure, $P\sigma^3/\varepsilon^*z'$
 P_i , internal pressure, $(\partial U/\partial V)_T$
 \bar{P}_i' , reduced internal pressure defined as $\bar{P}_i' \equiv P_i\sigma^3/\varepsilon^*z'$
 R , gas constant per mole
 S , entropy
 s , ratio of coordination number of a segment to a lattice site, z'/z
 T , temperature
 \bar{T} , reduced temperature defined as $\bar{T} \equiv ckT/\varepsilon^*z'$
 U , internal energy
 V , volume
 \bar{V} , reduced volume defined as $\bar{V} = V/V^* = M/N$
 V^* , volume of cells occupied by segments, v^*N
 \bar{V}' , reduced volume defined as $\bar{V}' = V/\sigma^3N$
 v^* , volume of a cell
 w , ratio of w_2 to w_1 , w_2/w_1
 w_i , number of rotational isomers per rotational unit which have energy ε_i
 z , coordination number of a lattice site
 z' , coordination number of a segment
 α , thermal expansion coefficient
 $\bar{\alpha}'$, reduced quantity of thermal expansion coefficient defined as $\bar{\alpha}' = (\partial \ln \bar{V}'/\partial \bar{T})_{\bar{p}} = \alpha\varepsilon^*z'/ck$
 β , isothermal compressibility
 $\bar{\beta}'$, reduced isothermal compressibility defined as $\bar{\beta}' = \beta\varepsilon^*z'/\sigma^3$
 Δ , difference between the liquid and glassy states (except in $\Delta\varepsilon$)
 ε^* , potential energy at minimum of potential energy curve of Lennard-Jones 12-6 potential
 ε_i , potential energy of rotational isomer i
 $\Delta\varepsilon$, difference in potential energy between

two rotational isomers 2 and 1, $\varepsilon_2 - \varepsilon_1$ ($\varepsilon_2 \geq \varepsilon_1$)
 σ , distance between segment centers at which potential energy is zero in Lennard-Jones 12-6 potential
 1, as subscript designates the intrasegmental interactions (except in ε_1 and w_1)
 2, as subscript designates the intersegmental interactions (except in ε_2 and w_2)

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