

# Prediction of ordered regions in nylon-6 and nylon-6,6 glasses from heat capacity

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The conformational and intermolecular contributions to the residual enthalpy  $\Delta H_0$  and entropy  $S_0^a$  at 0 K for amorphous nylon-6 and nylon-6,6 were investigated on the basis of the derivation of a new relationship between  $C_p$  and  $C_v$ . It was found that  $\Delta H_0$  contains only the intermolecular enthalpy for CONH residues in amorphous nylon-6 and nylon-6,6. The conformational contribution to  $S_0^a$  consists, on the basis of the conformations, of 49 kinds of rotational isomeric states for nylon-6 and 2401 ( $49 \times 49$ ) kinds for nylon-6,6, independently of temperature. The intermolecular contributions to  $S_0^a$  are only due to CONH residues in these polymers. Next, through the investigation of the conformational contributions to the glass transition, the possibility of ordered regions in nylon-6 and nylon-6,6 glasses was explored. The existence of localized and ordered parts with enthalpies of  $40.1 \text{ kJ mol}^{-1}$  for nylon-6 and  $80.7 \text{ kJ mol}^{-1}$  for nylon-6,6 is predicted. The enthalpies of the localized ordered parts are somewhat larger than the glass transition enthalpies of  $37.6 \text{ kJ mol}^{-1}$  for nylon-6 and  $75.2 \text{ kJ mol}^{-1}$  for nylon-6,6, respectively.

(Keywords: polyamide; ordered regions; heat capacity)

## INTRODUCTION

Heat-capacity measurements for many polymers<sup>1,2</sup> could prove that the entropy for the amorphous state is not zero at 0 K. Therefore, the measured entropy for the amorphous state at 0 K is called the residual entropy  $S_0^a$ . Similarly the enthalpy  $H_0^a$  remains higher than the crystalline enthalpy  $H_0^c$  at 0 K. For crystals,  $S_0^c$  is zero. As the temperature is increased, the initial contribution to the crystalline entropy  $S^c$  comes from intermolecular vibrations, followed by intramolecular bending and torsional vibration modes, as known from detailed analysis of the heat capacity<sup>2-4</sup>.

In this paper, first, the conformational and intermolecular contributions to  $H_0^a$  and  $S_0^a$  for amorphous nylon-6 (N6) and nylon-6,6 (N66) are investigated on the basis of the derivation of a new relationship between the isobaric heat capacity and the isochoric heat capacity,  $C_p$  and  $C_v$ . In the second stage, through the investigation of the conformational contribution to the glass transition, the possibilities of ordered regions in N6 and N66 glasses are discussed.

## CONFORMATIONAL CONTRIBUTIONS TO HEAT CAPACITY

The configurational partition function  $\Omega$  normalized per unit volume for a polymer liquid is expressed by<sup>5,6</sup>:

$$\Omega = \frac{Z^N}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3Nx/2} \left( \frac{q}{v_f} \right)^{Nx} \exp\left(-\frac{Nxh^{int}}{RT}\right) \quad (1)$$

with

$$v_f = qv \exp(-h^{int}/RT)$$

where  $N$  is the number of polymers,  $T$  is the absolute temperature,  $Z$  is the conformational partition function for a chain at  $T$ ,  $m$  is the mass of the structural unit,  $R$  is the gas constant,  $k$  is the Boltzmann constant,  $h$  is the Planck constant,  $h^{int}$  is the intermolecular interaction enthalpy per molar structural unit,  $x$  is the degree of polymerization,  $q$  ( $\leq 1$ ) is the packing factor of the core,  $v_f$  is the free volume per structural unit and  $v$  is the apparent volume per structural unit. [In ref. 5, the  $U_0$  in equation (1) should be revised to  $-U_0$ , though other equations do not need any revision.] Here  $U_0$  is  $h^{int}$ . From equation (1), the heat capacities,  $C_p$  and  $C_v$ , for a polymer liquid can be derived:

$$C_j = \left( \frac{\partial[(RT^2 \partial \ln \Omega / \partial T) / Nx]}{\partial T} \right)_j = \left( \frac{\partial h^{conf}}{\partial T} \right)_j + \frac{3R}{2} - \left( \frac{\partial(RT^2 \partial \ln v / \partial T)}{\partial T} \right)_j \quad (2)$$

with  $j = p$  or  $v$  and  $h^{conf} = (RT^2 \partial \ln Z / \partial T) / x$ .

According to thermodynamics,  $C_p$  and  $C_v$  are given as:  $C_p = [\partial H(P, T) / \partial T]_p$  with  $H(P, T) = G(P, T) - T[\partial G(P, T) / \partial T]_p$  and  $G(P, T) = -RT \ln \Omega(P, T)$ ; and  $C_v = [\partial U(V, T) / \partial T]_v$  with  $U(V, T) = F(V, T) - T[\partial F(V, T) / \partial T]_v$  and  $F(V, T) = -RT \ln \Omega(V, T)$ . Here  $H(P, T)$  and  $G(P, T)$  are the enthalpy and the Gibbs free energy as functions of  $P$  and  $T$ ,  $\Omega(P, T)$  is the partition function as a function

of  $P$  and  $T$ ,  $U(V, T)$  and  $F(V, T)$  are the internal energy and the Helmholtz free energy as functions of  $V$  and  $T$ ,  $\Omega(V, T)$  is the partition function as a function of  $V$  and  $T$ ,  $P$  is the pressure and  $V$  is the volume.  $\Omega(P, T)$  and  $\Omega(V, T)$  are given by equation (1). Thus  $C_p - C_v$  is represented by:

$$C_p - C_v = \left( \frac{\partial h^{\text{conf}}}{\partial T} \right)_p - \left( \frac{\partial h^{\text{conf}}}{\partial T} \right)_v - \left( \frac{\partial(RT^2 \partial \ln v / \partial T)}{\partial T} \right)_p \quad (3)$$

At  $T_g$ , assuming that the cohesive state of all polymer chains is a frozen quasi-equilibrium,  $f_{\text{flow}} (= h_{\text{flow}} - Ts_{\text{flow}}) = 0$  and  $s_{\text{flow}} = 0$  ( $h_{\text{flow}} = 0$ ), the former meaning the equilibrium and the latter the freezing of flow parts, should be accepted as the criteria<sup>5,6</sup> of  $T_g$  for polymers. When  $h_{\text{flow}}$  and  $s_{\text{flow}}$  are the enthalpy and entropy per molar structural unit for flow parts near  $T_g$ ,  $f_{\text{flow}}$  is given by<sup>5,6</sup>:

$$f_{\text{flow}} = h^{\text{conf}} - Ts^{\text{conf}} + h^{\text{int}} + RT \ln v_f - TS_d \quad (4)$$

with

$$s^{\text{conf}} = (R \ln Z + RT \partial \ln Z / \partial T) / x$$

and

$$S_d = R \ln(2\pi mkT/h^2)^{3/2} - (R/Nx) \ln N! + R \ln q$$

From equation (4) with  $f_{\text{flow}} = 0$ ,  $h^{\text{conf}}$  at  $T_g$  is derived:

$$h^{\text{conf}} = Ts^{\text{conf}} - (h^{\text{int}} + RT \ln v_f - TS_d) \quad (5)$$

Whereas at  $T_g$ , the conformational terms in equation (1),  $Z^N/N!$  and  $Z$ , are unity, the denominator  $N!$  should be changed to 1. From equation (1), for a glass at  $T_g$ , the next relation is obtained:

$$R \ln(2\pi mkT/h^2)^{3/2} = R \ln v \quad (6)$$

In this case, equation (5) is rewritten as:

$$h^{\text{conf}} = Ts^{\text{conf}} - (RT/Nx) \ln N! \quad (7)$$

From equations (3) and (7),  $C_p - C_v$  at a temperature  $T$  ( $= T_g$ ) on the hypothetical boundary line between glass and liquid phases is derived:

$$C_p - C_v = T \left( \frac{\partial s^{\text{conf}}}{\partial T} \right)_p - \left( \frac{\partial(RT^2 \partial \ln v / \partial T)}{\partial T} \right)_p \quad (8)$$

for

$$\begin{aligned} (\partial h^{\text{conf}} / \partial T)_p &= s^{\text{conf}} + T(\partial s^{\text{conf}} / \partial T)_p - (R/Nx) \ln N! \\ (\partial h^{\text{conf}} / \partial T)_v &\approx s^{\text{conf}} - (R/Nx) \ln N! \end{aligned} \quad (9)$$

From one of the criteria of  $T_g$ ,  $h_{\text{flow}} = 0$ , the second term on the right-hand side of equation (8) is derived<sup>6</sup>:

$$\left( \frac{\partial(RT^2 \partial \ln v / \partial T)}{\partial T} \right)_p = \left( \frac{\partial h^{\text{conf}}}{\partial T} \right)_p \quad (10)$$

Equation (10) is derived regardless of  $q$  in equation (1). In ref. 6,  $q$  is treated as a constant. Thus the goal of equation (8) is obtained:

$$C_p - C_v = -(\partial h^{\text{conf}} / \partial T)_v = T(\partial s^{\text{conf}} / \partial T)_p - (\partial h^{\text{conf}} / \partial T)_p \quad (11)$$

Figures 1 and 2 show the plots of  $h^{\text{conf}}$  and  $s^{\text{conf}}$  against  $T$  for the rotational isomeric states (RIS) models<sup>7</sup> of N6 and N66. In Figure 2, the relationship between ( $S^a - S^c$ )

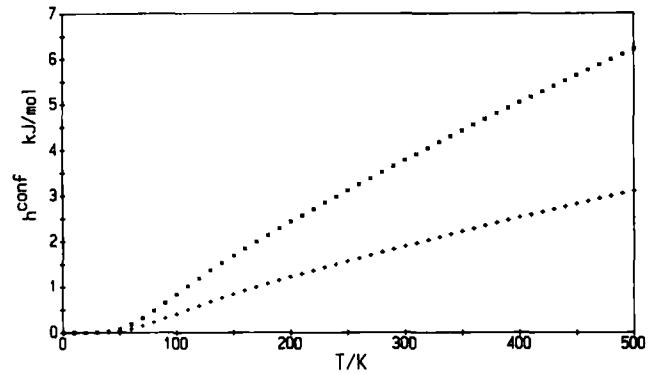


Figure 1 The relationships between  $h^{\text{conf}}$  and  $T$  for RIS models of N6 (+) and N66 (x)

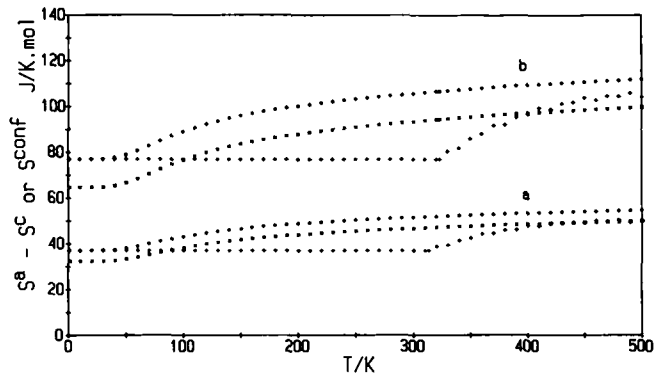


Figure 2 The relationships between  $s^{\text{conf}}$  and  $T$  for RIS models of (a) N6 and (b) N66 (x:  $s^{\text{conf}}$  data), and between  $S^a - S^c$  and  $T$  for (a) amorphous N6 and (b) amorphous N66 (+: ATHAS data;  $\blacklozenge$ : predicted data for liquids)

and  $T$  is also shown, together with the  $s^{\text{conf}}$  vs.  $T$  curve. The experimental values of entropies per molar structural unit,  $S^a$  and  $S^c$ , for amorphous and crystalline states of N6 and N66 were quoted from the ATHAS databank<sup>1</sup>. Here it should be noted that ATHAS data of  $S^a$  for N6 and N66 at  $T > 20$  K are those for a liquid glass (discussed below), whereas for many polymers in the cryogenic range ( $< 10$  K), the relation  $C_p \approx C_v$  has been obtained<sup>1</sup>. Substituting  $h^{\text{conf}'}$  for  $h^{\text{conf}}$  in this case, from equation (11) the next relation is obtained:

$$T(\partial s^{\text{conf}} / \partial T)_p = [\partial h^{\text{conf}'}/\partial T]_p \quad (12)$$

From equation (12),  $h^{\text{conf}'}$  is derived:

$$h^{\text{conf}'} = s^{\text{conf}} T + h_0^{\text{conf}} \quad (h_0^{\text{conf}} = \text{constant}) \quad (13)$$

where  $h_0^{\text{conf}}$  is the conformational enthalpy per molar structural unit at 0 K, which is zero for N6 and N66 (see Figure 1). Therefore it is understood that the residual enthalpy,  $\Delta H_0 (= H_0^a - H_0^c)$ , for N6 and N66 contains only the intermolecular enthalpy, where  $H_0^a$  and  $H_0^c$  are the enthalpies per molar structural unit at 0 K for amorphous and crystalline states, respectively. From ATHAS data<sup>1</sup> for N6, N66 and other nylons (N11, N12, N69, N610 and N612), the following relations on ( $H_0^a - H_0^c$ ) are found:

for  $[\text{CONH}(\text{CH}_2)_{n>5}]_x$  type nylon

$$H_0^a - H_0^c = 2.8n + \Delta H_6 \quad (14)$$

for  $[\text{NHCO}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_{n>6}]_x$  type nylon

$$H_0^a - H_0^c = 2.8n + \Delta H_{66} \quad (15)$$

where  $n$  is the number of  $\text{CH}_2$  residues, and  $\Delta H_6$  and  $\Delta H_{66}$  are  $\Delta H_0$  for N6 and N66. The coefficient in equations (14) and (15),  $2.8 \text{ kJ mol}^{-1}$ , is almost equal to the residual enthalpy at 0 K,  $2.7 \text{ kJ mol}^{-1}$  (ATHAS data<sup>1</sup>), and the cohesive energy,  $2.8 \text{ kJ mol}^{-1}$  (Bunn's data<sup>8</sup>), for polyethylene. Therefore it is predicted that  $\Delta H_6$  and  $\Delta H_{66}$  ( $\approx 2\Delta H_6$ ) contain only the intermolecular enthalpy of  $m \times \text{CONH}$  residue(s) ( $m=1$  for N6 and  $m=2$  for N66). This prediction is supported from the discussion on  $S_0^a$  for N6 and N66 (described below), and implies that N6 and N66 crystals (listed in ATHAS databank<sup>1</sup>) are the condensation<sup>2</sup> with loose packing of  $\text{CH}_2$  residues. As the values of  $\Delta H_0$  for N6 and N66, the cohesive energies of  $m \times \text{CONH}$  ( $m=1$  for N6 and  $m=2$  for N66),  $35.6 \text{ kJ mol}^{-1}$  and  $71.1 \text{ kJ mol}^{-1}$  (ref. 8), were adopted here. For N6 and N66 crystals with close packing of  $\text{CH}_2$  residues,  $(H_0^a - H_0^c)$  may be given by equation (14) or (15) with  $n=5$  for N6 and  $n=6$  for N66, respectively. Here  $(H_0^a - H_0^c)$  for N6 and N66 in this case is rewritten as  $(H_0^a - H_0^{c'})$ , where  $H_0^{c'}$  is the enthalpy per molar structural unit at 0 K for crystals with close packing of  $\text{CH}_2$  residues. The enthalpy difference between a liquid (hypothesized) and a crystal,  $\Delta H (=H^a - H^c)$ , is represented by:

$$\Delta H \approx h^{\text{conf}} + h^{\text{int}} \quad (16)$$

Figure 3 shows the  $\Delta H$  vs.  $T$  curves for N6 and N66, together with ATHAS data; here  $h^{\text{int}}$  is approximated to  $H_0^a - H_0^c$ . In the range of  $T < T_g$ , ATHAS data are equal to  $H_0^a - H_0^c$ .  $\Delta H$  is near the ATHAS data. The entropy  $S^a$  for the amorphous state can be calculated from the next equation, using the experimental values of  $(H^a - H_0^c)$  and  $(G^a - H_0^c)$ <sup>1</sup>:

$$S^a = [(H^a - H_0^c) - (G^a - H_0^c)]/T \quad (17)$$

with  $G^a = H^a - TS^a$ . From  $S^a = s^{\text{conf}} + s^{\text{int}}$ ,  $s^{\text{int}}$  is derived:

$$s^{\text{int}} = [(H^a - H_0^c) - (G^a - H_0^c)]/T - s^{\text{conf}} \quad (18)$$

where  $s^{\text{int}}$  is the intermolecular entropy per molar structural unit for the amorphous state. Table 1 shows the values of  $s^{\text{int}}$  at 1 K for N6 and N66, together with  $s^{\text{conf}}$  and  $S^a$  at 1 K. As shown in Table 1, it is noticeable that 87% of  $S^a$  for N6 and 84% of  $S^a$  for N66 are the conformational entropies, respectively.

Next, the conformation for N6 in the temperature range below 20 K is investigated. In this temperature

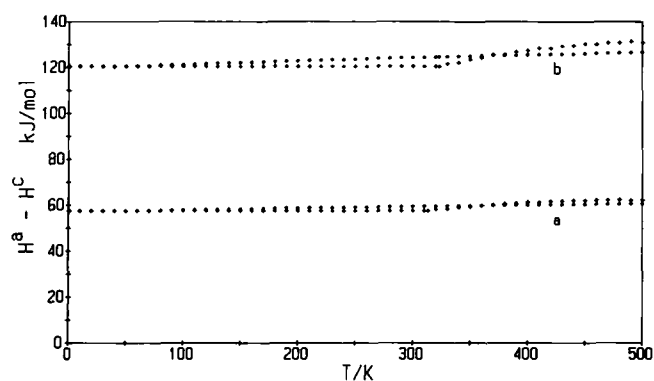


Figure 3 The relationships between  $H^a - H^c$  and  $T$  for (a) amorphous N6 and (b) amorphous N66 (+: ATHAS data revised on  $\Delta H_0$ ; ◆: predicted data for liquids)

Table 1 The numerical values of  $s^{\text{int}}$ ,  $s^{\text{conf}}$ ,  $S^a$  ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) and  $s^{\text{conf}}/S^a$  at 1 K for N6 and N66

Polymer	$T$ (K)	$s^{\text{conf}}$	$s^{\text{int}}$	$S^a$	$s^{\text{conf}}/S^a$
N6	1	32.4	4.7	37.1	0.87
N66	1	64.7	12.4	77.1	0.84

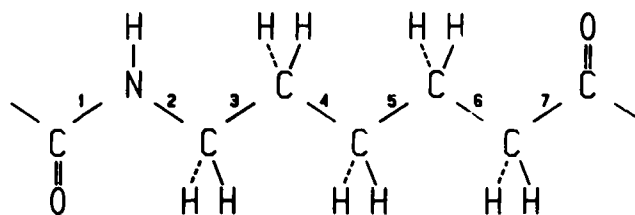


Figure 4 The chemical structure of the N6 structural unit

range,  $s^{\text{conf}}$  for N6 and N66 is constant. Table 2 shows the 49 kinds of conformations that the N6 structural unit can take in the temperature range below 20 K.

Figure 4 shows the chemical structure of the N6 structural unit. The structural unit takes on only *trans* isomer about the C-N bond, and C-C bonds 4 and 5, and *trans*, *gauche* and *gauche'* isomers about other bonds at each ratio shown in Table 2, because below 20 K the sequential probability  $p$  of an isomer about bond  $i$  ( $i=3-7$ ) to one about bond  $i+1$ —about bonds 3, 6 and 7, *gauche* → *gauche'*, *gauche'* → *gauche*, and about bonds 4 and 5, *trans* → *gauche* (*gauche'*), *gauche* → *gauche'*, *gauche'* → *gauche* (*gauche'*)—is approximated to zero. According to the conformational analysis for other aliphatic nylons, the 49 kinds of conformations for  $[\text{CONH}(\text{CH}_2)_{m \geq 4}]_x$  type nylon and 2401 ( $49 \times 49$ ) kinds for  $[\text{NHCO}(\text{CH}_2)_{m \geq 4} \text{CONH}(\text{CH}_2)_{n \geq 4}]_x$  type nylon are revealed in the cryogenic range ( $\leq 20 \text{ K}$ ). The former gives  $s^{\text{conf}} = 32.4 \text{ J K}^{-1} \text{ mol}^{-1}$  and the latter  $s^{\text{conf}} = 64.7 \text{ J K}^{-1} \text{ mol}^{-1}$ . These conformations for N6 and N66 should be in amorphous regions even above  $T_g$ . From ATHAS data<sup>1</sup> for other amorphous nylons (N11, N12, N69, N610 and N612), the following relations on  $s^{\text{int}}$  at 1 K are found:

for  $[\text{CONH}(\text{CH}_2)_{n > 5}]_x$  type nylon

$$s^{\text{int}} = 4.1n + s_6^{\text{int}} \quad (19)$$

for  $[\text{NHCO}(\text{CH}_2)_4 \text{CONH}(\text{CH}_2)_{n > 6}]_x$  type nylon

$$s^{\text{int}} = 4.1n + s_{66}^{\text{int}} \quad (20)$$

where  $s_6^{\text{int}}$  and  $s_{66}^{\text{int}}$  are  $s^{\text{int}}$  at 1 K for N6 and N66 (see Table 1). The coefficient,  $4.1 \text{ K}^{-1} \text{ mol}^{-1}$ , is almost equal to the residual entropy at 0 K,  $3.9 \text{ J K}^{-1} \text{ mol}^{-1}$  (ref. 1), for polyethylene. Therefore it is predicted that  $s_6^{\text{int}}$  and  $s_{66}^{\text{int}}$  ( $\approx 2s_6^{\text{int}}$ ) contain only the intermolecular entropy for CONH residues. Figure 2 also shows the comparison of  $s^{\text{conf}}$  with  $(S^a - S^c)$  for N6 and N66. ATHAS data of  $(S^a - S^c)$  are constant in the temperature range below  $T_g$  and increase with increasing temperature at  $T > T_g$ , whereas  $s^{\text{conf}}$  is constant in the temperature range below 20 K and increases gradually with increasing temperature at  $T > 20 \text{ K}$ . Therefore it is understood that the values of  $S^a$  at  $T$  ( $20 \text{ K} < T \leq T_g$ ) quoted from ATHAS databank<sup>1</sup> are those for a liquid glass. Because it is

Table 2 The 49 kinds of conformations for N6 structural unit below 20 K

No. conf. <sup>a</sup>	Bonds						
	1 C-N	2 N-C	3 C-C	4 C-C	5 C-C	6 C-C	7 C-C(=O)
1	T	T	T	T	T	T	T
2	T	T	T	T	T	T	G
3	T	T	T	T	T	T	G'
4	T	T	T	T	T	G	T
5	T	T	T	T	T	G	G
6	T	T	T	T	T	G'	T
7	T	T	T	T	T	G'	G'
8	T	T	G	T	T	T	T
9	T	T	G	T	T	T	G
10	T	T	G	T	T	T	G'
11	T	T	G	T	T	G	T
12	T	T	G	T	T	G	G
13	T	T	G	T	T	G'	T
14	T	T	G	T	T	G'	G'
15	T	T	G'	T	T	T	T
16	T	T	G'	T	T	T	G
17	T	T	G'	T	T	T	G'
18	T	T	G'	T	T	G	T
19	T	T	G'	T	T	G	G
20	T	T	G'	T	T	G'	T
21	T	T	G'	T	T	G'	G'
22	T	G	T	T	T	T	T
23	T	G	T	T	T	T	G
24	T	G	T	T	T	T	G'
25	T	G	T	T	T	G	T
26	T	G	T	T	T	G	G
27	T	G	T	T	T	G'	T
28	T	G	T	T	T	G'	G'
29	T	G	G	T	T	T	T
30	T	G	G	T	T	T	G
31	T	G	G	T	T	T	G'
32	T	G	G	T	T	G	T
33	T	G	G	T	T	G	G
34	T	G	G	T	T	G'	T
35	T	G	G	T	T	G'	G'
36	T	G'	T	T	T	T	T
37	T	G'	T	T	T	T	G
38	T	G'	T	T	T	T	G'
39	T	G'	T	T	T	G	T
40	T	G'	T	T	T	G	G
41	T	G'	T	T	T	G'	T
42	T	G'	T	T	T	G'	G'
43	T	G'	G'	T	T	T	T
44	T	G'	G'	T	T	T	G
45	T	G'	G'	T	T	T	G'
46	T	G'	G'	T	T	G	T
47	T	G'	G'	T	T	G	G
48	T	G'	G'	T	T	G'	T
49	T	G'	G'	T	T	G'	G'
T	49	21	21	49	49	21	21
G	0	14	14	0	0	14	14
G'	0	14	14	0	0	14	14

<sup>a</sup>The values in the last three lines show the numbers of *trans* (T), *gauche* (G) and *gauche'* (G') isomers about each bond in the 49 kinds of conformations

**Table 3** The numerical values of  $h_g$ ,  $h_s$ ,  $h_0$ ,  $h_0^*$ ,  $H^a - H_0^c$  and  $H^a - H^c$  ( $\text{kJ mol}^{-1}$ ) at  $T_g$  for N6 and N66

Polymer	$T_g$ (K)	$H^a - H_0^c$	$H^a - H^c$	$h_g$	$h_s$	$h_0$	$h_0^*$
N6	313	81.2	51.6	37.6	40.1	77.7	80.3
N66	323	162.7	103.1	75.2	80.7	155.9	159.0

assumed that below  $T_g$  the amorphous N6 listed in ATHAS databank<sup>1</sup> contains only 49 kinds of conformations independently of temperature, although above 20 K the existence of more than 49 kinds of conformations is expected from the  $s^{\text{conf}}$  vs.  $T$  curve (see Figure 2). In the temperature range below 20 K, there are only 49 kinds of conformations without the possibility of taking other conformations. Therefore the amorphous state at  $T < 20$  K should be distinguished with the state at  $T$  between 20 K and  $T_g$ , which is called a liquid glass state here. In the high-temperature range ( $> 400$  K),  $s^{\text{conf}}$  is almost equal to ATHAS data of  $(S^a - S^c)$  for N6 and somewhat smaller than that for N66. From these results, for liquids of N6 and N66, the relationships between  $(S^a - S^c)$  and  $T$  (Figure 2) are predicted, where  $S^a - S^c \approx s^{\text{int}} + s^{\text{conf}}$ . The predicted values of  $(S^a - S^c)$  at  $T > 400$  K are only  $s^{\text{int}}$  larger than ATHAS data. At a temperature near  $T_g$  in the cooling process from the melt, the conformation of a chain is restricted strongly by surrounding chains. Specifically, the chance of rotation about bonds 3–7 (see Figure 4) is decreased significantly because of the apparent increment of the rotational barrier, which leads to  $p = 0$ . As a result, it is assumed that the number of conformations per structural unit is concentrated gradually to 49 kinds (see Table 2). The chains that fail to take conformations of 49 kinds may be frozen in a glass as chains with strains. Annealing at a temperature below  $T_g$  for a glass may allow the release of conformational strains like this in the way to take conformations of 49 kinds.

### ORDERED REGIONS IN GLASSES

For a glass containing ordered parts, the total cohesive enthalpy per molar structural unit,  $h_0$ , is given as follows<sup>6,9</sup>:

$$h_0 \approx h_g + h_s \quad (h_s \approx h_g - f_1^{\text{conf}}) \quad (21)$$

with  $f_1^{\text{conf}} = -(RT \ln Z_t)/x$ , where  $h_g$  is the glass transition enthalpy per molar structural unit,  $h_s$  is the enthalpy per molar structural unit for ordered parts in a glass,  $Z_t (= Z/Z_0)$  is the term as a function of temperature in  $Z$ , and  $Z_0$  is the term regardless of temperature in  $Z$ . Table 3 shows the values of  $h_g$ ,  $h_s$ ,  $h_0$  and  $h_0^*$  (the value<sup>6</sup> from solubility parameter  $\delta = 13.6 (\text{cal cm}^{-3})^{1/2}$ ), together with  $(H^a - H_0^c)$  and  $(H^a - H^c)$ . As shown in Table 3, the values of  $h_0$  for N6 and N66 are almost equal to  $h_0^*$  and

$(H^a - H_0^c)$ . Accordingly in N6 and N66 glasses, the existence of localized ordered parts with  $h_s = 40.1 \text{ kJ mol}^{-1}$  for N6 and  $80.7 \text{ kJ mol}^{-1}$  for N66 is predicted. The enthalpies of the localized ordered parts are only somewhat larger than the glass transition enthalpies  $37.6 \text{ kJ mol}^{-1}$  for N6 and  $75.2 \text{ kJ mol}^{-1}$  for N66. Whereas regardless of the presence of ordered parts, each chain in a glass is frozen to  $Z = 1$ . Therefore the heat-capacity difference between a liquid and an ideal glass at the glass transition,  $\Delta C_j$  ( $j = p$  or  $v$ ), could be approximated to the difference between a liquid and a glass containing ordered parts. From equation (2),  $\Delta C_v (= C_v)$  is derived<sup>10</sup>:

$$\Delta C_v = (\partial h^{\text{conf}} / \partial T)_v + \frac{3}{2}R \quad (22)$$

For polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc) and poly(vinyl chloride) (PVC), the values<sup>10</sup> of  $\Delta C_v$  from equation (22) are in good agreement with those<sup>11,12</sup> calculated from the thermodynamic relation:

$$\Delta C_v = \Delta C_p - TV\Delta(\alpha^2/\beta) \quad (23)$$

where  $\alpha$  and  $\beta$  are the thermal expansion coefficient and isothermal compressibility, respectively.

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### REFERENCES

- 1 Wunderlich, B. ATHAS databank (1992 Recommended Data)
- 2 Wunderlich, B. 'Thermal Analysis', Academic Press, Boston, 1990
- 3 Grebowicz, J., Law, S.-F. and Wunderlich, B. *J. Polym. Sci. Symp.* 1984, **71**, 19
- 4 Cheban, Y. V., Law, S.-F. and Wunderlich, B. *Colloid Polym. Sci.* 1982, **269**, 9
- 5 Tanaka, N. *Polymer* 1978, **19**, 770
- 6 Tanaka, N. *Polymer* 1992, **33**, 623
- 7 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969
- 8 Bunn, C. W. *J. Polym. Sci.* 1955, **16**, 323
- 9 Tanaka, N. *Polymer* 1993, **34**, 4941
- 10 Tanaka, N. *Polymer* 1979, **20**, 593
- 11 Roe, R. J. and Tonelli, A. E. *Macromolecules* 1978, **11**, 114
- 12 Roe, R. J. and Tonelli, A. E. *Macromolecules* 1979, **12**, 878