Possibility of ordered regions in isotactic polypropylene glasses from heat capacity

Nobuyuki Tanaka*

Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu 376, Japan

For isotactic polypropylene, the enthalpy and entropy differences between a glass and a crystal, ΔH^{gc} and ΔS^{gc}, and between a glass and a liquid, ΔH^{ag} and ΔS^{ag}, were discussed via conformational analysis. ΔH^{gc} and ΔS^{gc} are mostly attributed to the difference in bending and torsional vibration modes between a glass and a crystal. ΔH^{ag} and ΔS^{ag} are nearly equal to the sum of h^{conf} and h^{int}, and that of $(s^{conf} - s_0^{conf})$ and s^{int}, respectively. Here h^{conf} and s^{conf} are the conformational enthalpy and entropy per molar structural unit, s_0^{conf} ($= 0.38$ J mol^{-1} K^{-1}) is s^{conf} at 0 K, and h^{int} and s^{int} are the intermolecular interaction enthalpy and entropy per molar structural unit. The value of ΔH^{ag} at 0 K, 5.6 kJ mol^{-1}, is almost equal to the cohesive energy of a CH_3 residue, 5.7 kJ mol^{-1}. In a glass, the existence of localized ordered regions with enthalpy 6.78 to 9.29 kJ mol^{-1} was predicted. The conformational analysis further showed that many rod-like sequences with right- and left-handed helices may be contained in a glass.

(Keywords: polypropylene; ordered regions; glass transition)

INTRODUCTION

Studies[1-5] on the heat capacity of polymers have concentrated on the computational prediction of the temperature dependence of the heat capacity in the melting and glass transitions. Already it has been clarified[1-3] that the isochoric heat capacity, C_v, for a glass and a crystal should be the sum of the contributions from torsional and bending vibration modes and side-group vibration modes, which can be measured by use of infra-red, Raman and neutron spectroscopies[6,7]. According to the ATHAS database[8] on heat capacity, the values of $H^a - H^c$ and $S^a - S^c$ for nylon-6 and nylon-6,6 are constant below the glass transition temperature, T_g, where H^a and H^c are the enthalpies and S^a and S^c are the entropies per molar structural unit for amorphous and crystalline states. From this result, it is predicted that the amorphous states[8] for nylon-6 and nylon-6,6 are glassy liquids[9]. For isotactic polypropylene (iPP), $H^a - H^c$ and $S^a - S^c$ increase with increasing temperature, although in the cryogenic range below 70 K, h^{conf} is zero and s^{conf} is constant. Here h^{conf} and s^{conf} are the conformational enthalpy and entropy per molar structural unit. This result suggests that the heat capacity for a glass is not similar to that for a crystal.

In this paper, first, the origin of the heat-capacity difference between a glass and a crystal is discussed thermodynamically. Secondly, the enthalpy for a liquid (hypothesized) is investigated. The remarkable difference between its enthalpy and the glass transition enthalpy at T_g gives the possibility of ordered regions in a glass[9].

*At the time of this work, the author was at the University of Tennessee, Knoxville, TN 37996-1600, USA

THEORETICAL TREATMENT

Heat capacity

The enthalpy and entropy per molar structural unit, H^q and S^q, for a crystal ($q = c$) and a glass ($q = g$) are given by[1-3]:

$$H^q = H_0^q + \int_0^T C_p^q \, dT$$

$$= H_0^q + \int_0^T C_{vib\alpha}^q \, dT + \int_0^T C_{vib\beta}^q \, dT + \int_0^T C_{ext}^q \, dT \quad (1)$$

and

$$S^q = S_0^q + \int_0^T (C_p^q/T) \, dT$$

$$= S_0^q + \int_0^T (C_{vib\alpha}^q/T) \, dT + \int_0^T (C_{vib\beta}^q/T) \, dT + \int_0^T (C_{ext}^q/T) \, dT$$

$$(2)$$

Here H_0^q and S_0^q are H^q and S^q at 0 K, C_p^q is the isobaric heat capacity, $C_{vib\alpha}^q$ is the heat capacity relating to the bending and torsional vibration modes, $C_{vib\beta}^q$ is the heat capacity due to the vibration modes of side groups, and C_{ext}^q ($= C_p^q - C_v^q$) is the external part of the heat capacity. On the right-hand sides of equations (1) and (2), the third terms are almost not influenced by the states of a polymer[10], i.e. $C_{vib\beta}^c \approx C_{vib\beta}^g$, and the fourth terms are small in the temperature range below T_g. Therefore, if $C_{ext}^c \approx C_{ext}^g$, the enthalpy and entropy differences between a glass and a crystal, ΔH^{gc} ($= H^g - H^c$) and ΔS^{gc}
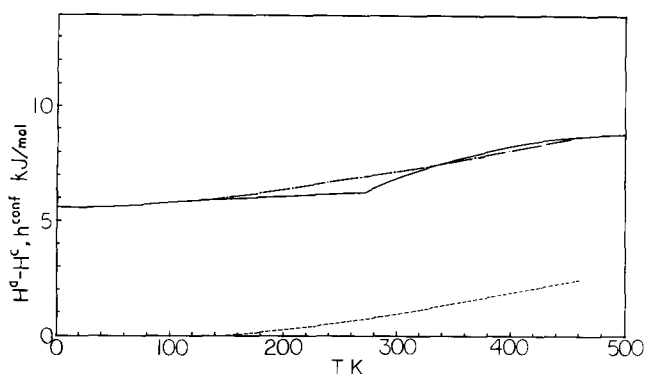
Figure 1 The relationships between h^{conf} and T for an RIS model of iPP (broken curve), and between $H^a - H^c$ and T for iPP (full curve, ATHAS data; chain curve, predicted curve for a liquid)
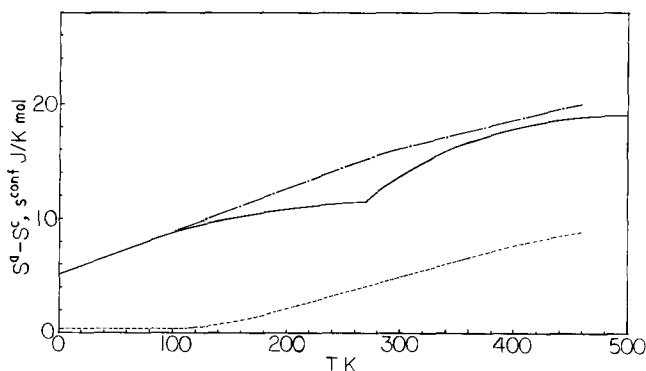
Figure 2 The relationships between s^{conf} and T for an RIS model of iPP (broken curve), and between $S^a - S^c$ and T for iPP (full curve, ATHAS data; chain curve, predicted curve for a liquid)

$(=S^g - S^c)$, are given by:

$$\Delta H^{gc} \approx \int_0^T (C^g_{vib\alpha} - C^c_{vib\alpha}) \, dT + \Delta H^{gc}_0 \qquad (3)$$

$$\Delta S^{gc} \approx \int_0^T (C^g_{vib\alpha}/T - C^c_{vib\alpha}/T) \, dT + \Delta S^{gc}_0 \qquad (4)$$

where ΔH^{gc}_0 and ΔS^{gc}_0 are ΔH^{gc} and ΔS^{gc} at 0 K. ΔH^{gc} and ΔS^{gc} are mostly attributed to the difference in bending and torsional vibration modes between a glass and a crystal. *Figure 1* shows the plots of h^{conf} and ΔH $(=H^a - H^c)$ against T for iPP. *Figure 2* shows the plots of s^{conf} and ΔS $(=S^a - S^c)$ against T for iPP. Here:

$$h^{conf} = RT^2(\partial \ln Z/\partial T)/x$$

and

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

Z is the conformational partition function per chain, R is the gas constant and x is the degree of polymerization. The values of h^{conf} and s^{conf} were calculated for a rotational isomeric state (RIS) model[11,12] with *trans*, *gauche* and *gauche'* isomers. In the cryogenic range below 70 K, h^{conf} is zero and s^{conf} is constant (0.38 J mol^{-1} K^{-1}). With increasing temperature from 70 K, h^{conf} and s^{conf} increased gradually. In the temperature range below T_g, ΔH and ΔS quoted from the ATHAS databank[8] increased gradually with increasing temperature. Above T_g, ΔH and ΔS increased with larger slopes, reflecting that the amorphous state below T_g was a glassy liquid[9].

Considering that, in the cryogenic range below 70 K, h^{conf} is zero and s^{conf} is constant, it is predicted that the increases of ΔH and ΔS in this temperature range are almost totally due to the increases of ΔH^{gc} and ΔS^{gc}. For a liquid (hypothesized) below T_g, H^a and S^a should contain[4,9,10] h^{conf} and s^{conf}, respectively. Therefore, ΔH and ΔS between a liquid (hypothesized) and a crystal are given as follows:

$$\Delta H \approx (h^{conf} - h^{conf}_0) + h^{int} + (\Delta H^{gc} - \Delta H^{gc}_0) \qquad (5)$$

$$\Delta S \approx (s^{conf} - s^{conf}_0) + s^{int} + (\Delta S^{gc} - \Delta S^{gc}_0) \qquad (6)$$

where h^{int} and s^{int} are the intermolecular interaction enthalpy and entropy per molar structural unit for a glass, and h^{conf}_0 and s^{conf}_0 are h^{conf} and s^{conf} at 0 K, respectively. At 0 K, $h^{int} = \Delta H_0$ and $s^{int} = \Delta S_0$. ΔH_0 and ΔS_0 are ΔH and ΔS at 0 K. From equations (5) and (6), ΔH^{ag} $(=H^a - H^g)$ and ΔS^{ag} $(=S^a - S^g)$ are derived:

$$\Delta H^{ag} \approx h^{conf} + h^{int} \qquad (h^{conf}_0 = 0 \text{ for iPP}) \qquad (7)$$

$$\Delta S^{ag} \approx (s^{conf} - s^{conf}_0) + s^{int} \qquad (8)$$

Equation (7) has already been predicted in ref. 9. The ATHAS data[8] value of ΔH_0 $(\approx \Delta H^{ag}_0)$, 5.6 kJ mol^{-1}, is almost equal to the cohesive energy[13] of a CH$_3$ residue, 5.7 kJ mol^{-1}, where ΔH^{ag}_0 is ΔH^{ag} at 0 K. The chain curves in *Figures 1* and *2* show the curves of ΔH and ΔS predicted by equations (5) and (6), where ΔH and ΔS are approximated to $h^{conf} + \Delta H^*$ and $(s^{conf} - s^{conf}_0) + \Delta S^*$, respectively, and ΔH^* and ΔS^* are ATHAS data. Above T_g, ΔH^* and ΔS^* are approximated to those at T_g. In the temperature range above 350 K, the predicted curves of ΔH and ΔS are very close to those from ATHAS data (experimental). This approximation means that h^{int} and s^{int} are almost constant above T_g. Next, the conformations for an isolated chain of iPP in the cryogenic range ($\leqslant 70$ K) are investigated. *Figure 3* shows the chemical structure of iPP with $x = 100$. *Table 1* shows the 100 kinds of conformations that an RIS model of iPP with $x = 100$ can take independently of temperature in the cryogenic range below 70 K. The conformations are composed of sequences with right- and/or left-handed helices. Accordingly, a chain is rod-like. From the number of conformations, $s^{conf} = 0.38$ J mol^{-1} K^{-1} is obtained regardless of temperature. Thus it is predicted that many rod-like sequences with right- or left-handed helices are contained at random in a glass. A structure like this for a glass may take torsional and bending vibration modes different from a crystal.

Glass transition

Figure 4 shows the schematic curves of C_p and H^a for a polymer in the vicinity of T_g (here the onset temperature of the C_p jump, T^b_g)[4]. Here, in order to analyse the glass transition behaviour of a polymer, the following scheme was hypothesized first. In the cooling process from the
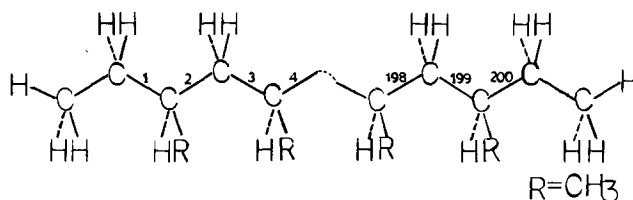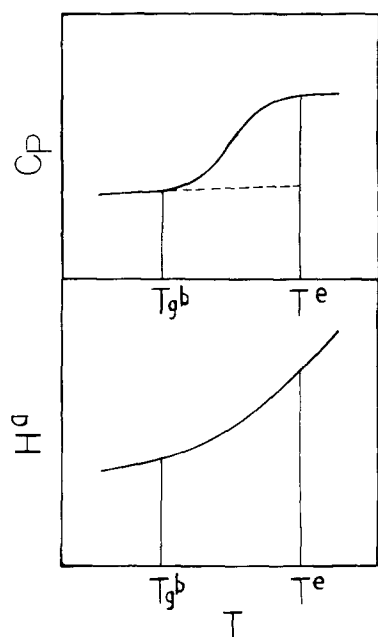

Figure 3 The chemical structure of iPP $(x = 100)$

Table 1 The 100 kinds of conformations for iPP $(x = 100)$ below 70 K[a]

No. of conf.	Bonds														
	1	2	3	4	5	6	7	...	194	195	196	197	198	199	200
1	T	T	G'	T	G'	T	G'		T	G'	T	G'	T	G'	T
2	T	G	T	T	G'	T	G'		T	G'	T	G'	T	G'	T
3	T	G	T	G	T	T	G'		T	G'	T	G'	T	G'	T
4	T	G	T	G	T	G	T		T	G'	T	G'	T	G'	T
⋮															
97	T	G	T	G	T	G	T		T	G'	T	G'	T	G'	T
98	T	G	T	G	T	G	T		G	T	T	G'	T	G'	T
99	T	G	T	G	T	G	T		G	T	G	T	T	G'	T
100	T	G	T	G	T	G	T		G	T	G	T	G	T	T

[a] T, *trans* isomer; G, *gauche* isomer; G', *gauche'* isomer

Figure 4 Schematic curves of C_p and H^a in the vicinity of T_g^b for a polymer. The broken line is C_p^g for a polymer glass (hypothesized)

melt, the localized solid parts with ordered regions are generated from a temperature T^e $(> T_g^b)$. The glass formation at T_g^b locks these into a glass and leads to a heterogenous glass. In the heating process from a temperature below T_g^b, the melting of solid parts is initiated at T_g^b and has disappeared at T^e, though in the temperature range between T_g^b and T^e the solid parts remain in thermodynamic equilibrium with the molten parts. A scheme like this was predicted on the basis of the experimental result that the C_p jump at T_g for many polymers does not occur vertically. The enthalpy per molar structural unit, h_s, for solid parts generated near T_g^b is given by[4]:

$$h_s \approx h_g + \Delta h \tag{9}$$

and

$$\Delta h \approx \int_{T_g^b}^{T^c} C_p \, dT - \int_{T_g^b}^{T^c} C_p^g \, dT$$

where h_g is the glass transition enthalpy per molar structural unit and Δh is the heat change per molar structural unit relating to the disappearance of solid parts in the heating process. C_p is the observed isobaric heat capacity, C_g^p is the isobaric heat capacity for a superheated

polymer glass (hypothesized), and T^e is the temperature at which, in the heating process from a temperature below T_g, C_p coincides with that of a pure liquid. Recently it has been clarified that Δh in equation (9) is linked to the conformational free energy per molar structural unit, f^{conf}:

$$f^{conf} = h^{conf} - Ts^{conf} = -(RT\ln Z)/x \tag{10}$$

f^{conf} is divided into two conformational free energies: (1) f_1^{conf} with a partition function Z_t as a function of temperature, and (2) f_2^{conf} with a partition function Z_0 regardless of temperature:

$$f^{conf} = f_1^{conf} + f_2^{conf} \tag{11}$$

with

$$f_1^{conf} = -(RT \ln Z_t)/x \qquad f_2^{conf} = -(RT \ln Z_0)/x$$

For iPP, the value of $Z_0^{1/x}$ is x (see *Table 1*). The conformational enthalpy and entropy in f_1^{conf} $(= h_1^{conf} - Ts_1^{conf})$, h_1^{conf} and s_1^{conf}, are given by:

$$h_1^{conf} = [RT^2(\partial \ln Z_t/\partial T)]/x$$
$$= [RT^2(\partial \ln Z/\partial T)]/x \quad (= h^{conf}) \tag{12}$$
$$s_1^{conf} = R[\ln Z_t + T(\partial \ln Z_t/\partial T)]/x$$
$$= R[\ln Z_t + T(\partial \ln Z/\partial T)]/x \tag{13}$$

Therefore the transition from an amorphous state with Z_0 to a liquid state is accompanied by the absorption of the heat equivalent to $-f_1^{conf}$, because h_2^{conf} is zero, and s_2^{conf} $(= R(\ln Z_0)/x = \text{constant})$ is the common entropy for both an amorphous state with Z_0 and a liquid state. Here let us hypothesize the localized solid parts with ordered regions in a glass, which are residual even after the disappearance of glassy state at T_g^b, and take $-f_1^{conf}$ for Δh in equation (9). In this case, h_s is given by:

$$h_s = h_s^{conf} + h_s^{int} = h_g - f_1^{conf} \tag{14}$$

where h_s^{conf} $(= h^{conf} = h_1^{conf})$ and h_s^{int} $(= h^{int} + h^{int'})$ are the conformational enthalpy and the intermolecular interaction enthalpy per molar structural unit for solid parts, respectively. The value of h^{int} $(= h_g^{int})$ is approximated to the molar cohesive energy for a CH_3 residue[13], 5.69 kJ mol^{-1}; h_g^{int} is h^{int} for a glass. In this case, $h^{int'}$ is derived as:

$$h^{int'} = (RT \ln Z_t)/x \tag{15}$$

The total cohesive enthalpy per molar structural unit, h_0, for a glass containing solid parts is given by[4]:

$$h_0 = h_g + h_s \qquad (h_s > h_g) \tag{16}$$

Table 2 The numerical values (kJ mol^{-1}) of h_g, h_s, h_0, h_0^+, $H^a - H_0^c$ and $H^a - H^c$ at T_g for iPP[a]

Polymer	T_g (K)	$H^a - H_0^c$	$H^a - H^c$	h_g	h_s	h_0	h_0^+
iPP	270	15.94*	6.22*	6.44	6.78 (9.29)	13.22 (15.73)	14.10–15.82

[a] The values marked with an asterisk contain h^{conf} at T_g, 0.75 kJ mol^{-1}. The values of h_s and h_0 in parentheses are those in the case that $h^{int'}$ is 2.85 kJ mol^{-1}, the value of the cohesive energy of a CH_2 residue[13]

Table 2 shows the values of h_g, h_s, h_0 and h_0^+ (reference value[12]), together with $(H^a - H_0^c)$ and $(H^a - H^c)$. As shown in *Table 2*, though the value of h_0 is a little smaller than the minimum value of h_0^+, the value of $H^a - H_0^c$ is almost equal to the maximum value of h_0^+. Taking the molar cohesive energy of CH_2, 2.85 kJ mol^{-1}, for $h^{int'}$, $h_0 = 15.73$ kJ mol^{-1} is obtained. This value is almost equal to the maximum value of h_0^+ and the value of $H^a - H_0^c$. Therefore in iPP glasses, the existence of localized ordered parts with $h_s = 6.78$ to 9.29 kJ mol^{-1} is predicted.

ACKNOWLEDGEMENT

REFERENCES

1 Lau, S.-F. and Wunderlich, B. *J. Thermal Anal.* 1983, **28**, 59
2 Grebowicz, J., Lau, S.-F. and Wunderlich, B. *J. Polym. Sci.* 1984, **71**, 19
3 Cheban, Y. V., Lau, S.-F. and Wunderlich, B. *Colloid Polym. Sci.* 1982, **269**, 9
4 Tanaka, N. *Polymer* 1992, **33**, 623
5 Sumpter, B. G., Noid, D. W. and Wunderlich, B. *J. Chem. Phys.* 1990, **93**, 6875
6 Miyazawa, T. *J. Polym. Sci. (C)* 1964, **7**, 5916
7 Takeuchi, H., Higgins, J. S., Hill, A., Maconnachie, A., Allen, G. and Stirling, G. C. *Polymer* 1982, **23**, 499
8 ATHAS databank (1992 Recommended Data)
9 Tanaka, N. and Wunderlich, B. *Bull. Am. Phys. Soc.* 1992, **37**, 420
10 Loufakis, K. and Wunderlich, B. *J. Am. Chem. Soc.* 1988, **92**, 4205
11 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969
12 Tanaka, N. *Sen-i Gakkaishi* 1990, **46**, 487
13 Bunn, C. W. *J. Polym. Sci.* 1955, **16**, 323