Structure of solution-grown *trans*-1,4-polyisoprene crystals: 3. Thermodynamic properties of α-TPI crystals

Ploenpit Boochathum*, Yasuyuki Tanaka and Kenji Okuyama
Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

(*Received 30 April 1992; revised 30 November 1992*)

The thermodynamic properties of α-type *trans*-1,4-polyisoprene crystals grown from solution were investigated by differential scanning calorimetry and X-ray diffraction. The equilibrium melting temperature estimated from the plot of melting temperature against crystallization temperature was found to be 101.5°C. The surface free energy calculated from the slope of the plot of melting temperature against reciprocal lamellar thickness was found to be 9.6 kJ mol^{-1}, in good agreement with Keller and Martuscelli's work. The lamellar thickness of α-TPI crystals grown at high crystallization temperatures (10–35°C) increased with the increase of crystallization temperature. At low crystallization temperatures, e.g. −10 and −20°C, the lamellar thickness was greater than the expected value. This may be caused by the occurrence of isothermal thickening. At such low temperatures, the lamellar thickness was independent of crystallization temperature. The chain-folded lamellae of α-TPI crystals grown from hexane were estimated to have looser and longer surface folds than those grown from amyl acetate at the same crystallization temperature. Based on the crystallinity data, the stem lengths of lamellae grown from hexane were found to be slightly shorter than those of lamellae grown from amyl acetate. These findings are in agreement with the results determined by ozonolysis–g.p.c. measurements.

(Keywords: α-TPI; lamellar thickness; equilibrium melting temperature)

INTRODUCTION

The thermodynamic properties of *trans*-1,4-polyisoprene (TPI) crystals, in particular the equilibrium melting temperature and surface free energy, have been reported by many researchers[1–7]. However, their results varied and did not agree with the theoretical values.

Attempts to determine the chain-folded structure of polymer crystals have been made by applying various methods of analysis[8–11], even though those experiments did not always give direct information on the chain-folded structure. Recently, we have successfully applied etching, using ozonolytic degradation in combination with high-resolution g.p.c. measurements, to the determination of the structures of chain-folded lamellae of solution-grown polyisoprene and polybutadiene crystals in both quantitative and qualitative analyses[12,13].

In the work described herein, the equilibrium melting temperature (T_m°) and surface free energy (σ_e) for α-TPI crystals were determined using several physicochemical methods and compared to the theoretical values. The chain-folded structure of α-TPI crystals grown from hexane solution was also determined and compared with that of crystals from amyl acetate solution.

EXPERIMENTAL

Materials

Synthetic *trans*-1,4-polyisoprene (TP301 from Kuraray Co.) with 99% *trans*-1,4 content by ^{1}H n.m.r. was used. G.p.c. showed this sample to have an $\bar{M}_w$ of 1.4×10^5, an $\bar{M}_n$ of 7.0×10^4 and an $\bar{M}_w/\bar{M}_n$ ratio of 2.0. The unfractionated sample was purified before use by precipitation from toluene solution into methanol.

Crystallization from solution

TPI was dissolved at 60°C in hexane and 80°C in amyl acetate. The concentration used was 0.2% w/v. Once the TPI had completely dissolved, the solutions were rapidly cooled in a temperature-controlled bath for a period of time. The solution-grown TPI crystals thus obtained were filtered and washed with hexane or amyl acetate at the crystallization temperature. The washed crystals were dried at room temperature *in vacuo* in order to remove residual solvent.

Differential scanning calorimetry

The melting temperatures of the TPI crystals were determined by differential scanning calorimetry (TAS-200 1.2, Rigaku). About 2 mg of the dried crystalline sample were placed in a d.s.c. pan and heated from −20 to 100°C with a scanning rate of 10°C min^{-1}.

X-ray diffraction

The lamellar thicknesses of α-TPI crystals were determined from the spacings of small-angle X-ray scatterings from the powder specimens. These diffraction patterns were recorded with an imaging plate (DIP-100, MAC Science Co.) using monochromatized CuKα radiation from an X-ray generator (ROTAFLEX RU-200, Rigaku). The camera length used was 320 mm.

---

*To whom correspondence should be addressed. Present address: Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology, Thonburi, Bangkok 10140, Thailand

0032-3861/93/173699–05

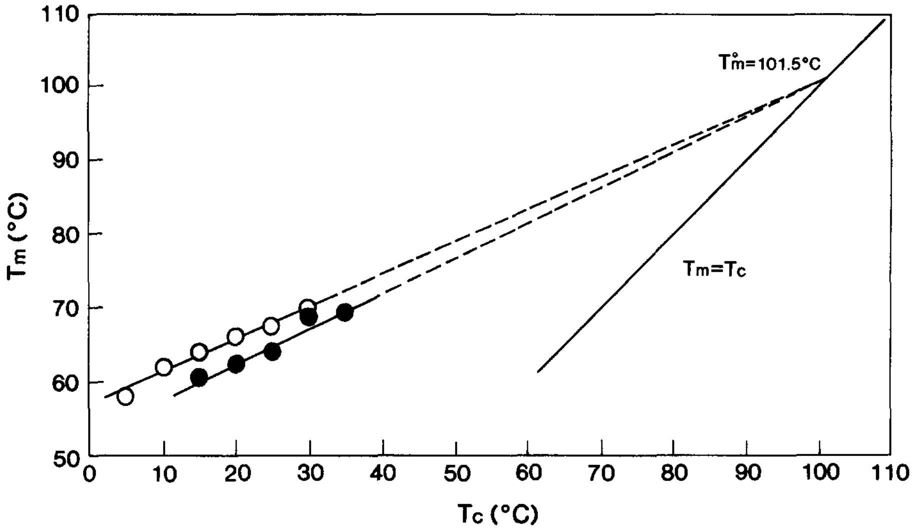

Figure 1 The relationship between melting temperature and crystallization temperature for α-TPI crystals grown from hexane (○) and amyl acetate (●) (data from ref. 15)

Density measurements

The densities of some crystal samples were determined by the flotation method using a mixture of ethanol and acetic acid. The densities were measured by using five pycnometers having a nominal volume of 25 cm^3. The weight-fraction crystallinity was calculated by the same method as in an earlier paper[13].

RESULTS AND DISCUSSION

Thermodynamic properties

The plot of melting temperature against crystallization temperature by a least-squares method gave a straight line for both hexane and amyl acetate, as shown in *Figure 1*. The equilibrium melting temperature was estimated by extrapolating these lines to a straight line where T_m and T_c are equal.

For α-TPI grown from hexane

$$T_m = 57.020 + 0.439T_c \quad (1)$$

and for α-TPI grown from amyl acetate

$$T_m = 53.300 + 0.472T_c \quad (2)$$

The equilibrium melting temperatures of α-TPI crystals grown from hexane and amyl acetate were found to be equal, being 101.5°C. The slopes of the lines in *Figure 1* are in very good agreement with that predicted by the theoretical equation (0.5) derived by Gopalan and Mandelkern[14]

$$T_m = (a/2n)T_c + T_m^\circ[1 - (a/2n)] \quad (3)$$

where a is the ratio of the interfacial free energy of a chain emerging from the basal plane of a mature crystal (σ_{ee}) to that of a chain emerging from a nucleus of critical size (σ_{en}), and n is the ratio of the thickness in chain units of a mature crystal (ζ) to that of a crystal nucleus of critical size (ζ^*). If a/n is a constant or if $\zeta = \zeta^*$ and $\sigma_{ee} = \sigma_{en}$, a further reduction of equation (3) to

$$T_m = 1/2(T_m^\circ + T_c) \quad (4)$$

is achieved. Equation (4) is the expression used as the basis of the extrapolation method.

Table 1 Summary of equilibrium melting temperatures obtained by various researchers for α-TPI crystals

Source	T_m° (°C)
Mandelkern *et al.*[1]	74.0
Lovering and Wooden[3]	87.0
Flanagan and Rijke[4]	82.4
Davies and Long[6]	89.0
Boochathum *et al.*	101.5

The equilibrium melting temperature obtained from this study is, however, higher than those obtained from previous studies[1,3,4,6]. *Table 1* compares the equilibrium melting temperatures obtained by various researchers with the result obtained in this study. The reasons for the variation in T_m° might be as follows.

First, it might be due to purification of the crystal form. It was found in our previous study that α-TPI in a mixture of the two forms (α and β) has a lower melting temperature than the pure form grown at the same crystallization temperature. For example, pure α-TPI crystals grown from hexane and amyl acetate at −20°C melt at the same temperature of 63.0°C, while the mixture melts at 61.5°C from hexane and 60.4°C from amyl acetate. The same result was also reported[15] for crystals grown at −10°C. Therefore, the impurity is believed to lower the equilibrium melting temperature. For the TPI crystals prepared in this study, the purity of the crystal form was checked by d.s.c. measurements. The single endotherm peak demonstrated the existence of the α-form alone.

Secondly, the melting temperature of TPI crystals grown at a low crystallization temperature or under high supercooling was not linearly related to that of crystals grown under isothermal conditions when plotted against crystallization temperature. This could cause a lower equilibrium melting temperature as well. In this work, crystallizations at isothermal and high supercooling conditions were clearly separated by a characteristic temperature, defined as the conversion temperature[15]. Furthermore, it might be concluded that the equilibrium melting temperature obtained in this study is quite reasonable since the slopes of the linear equations obtained from the plot of the experimental data are close to the theoretically derived value.

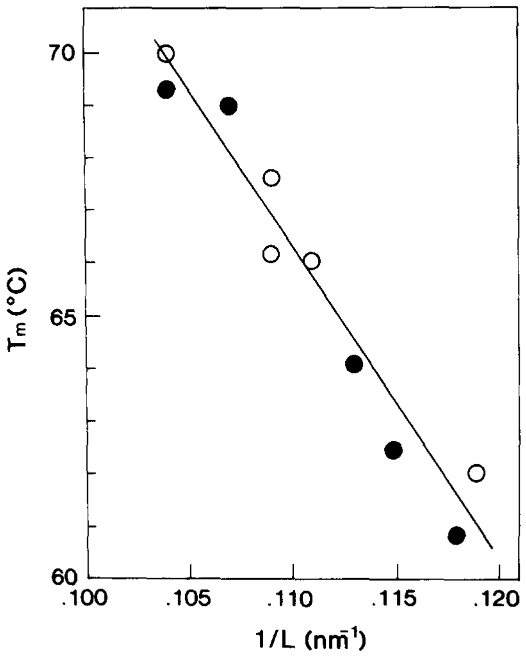

Figure 2 The relationship between melting temperature and reciprocal lamellar thickness for α-TPI crystals grown from hexane (○) and amyl acetate (●)

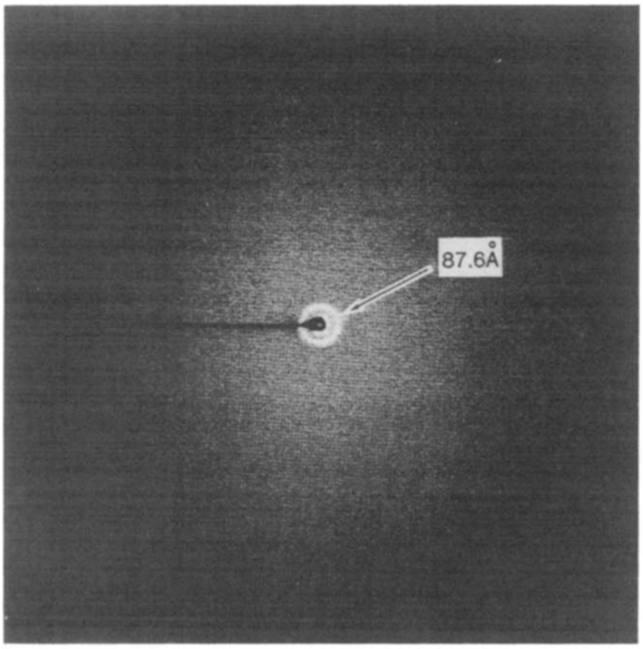

Figure 3 The small-angle scattering for an α-TPI crystal grown from amyl acetate at −20°C over 24 h

Another important thermodynamic parameter is the surface free energy σ_e which is obtained from the slope of the plot of melting temperature (T_m) against reciprocal lamellar thickness ($1/L$)

$$T_m = T_m^\circ[1-(2\sigma_e)/L\Delta H_f] \qquad (5)$$

where ΔH_f has been found[1] to be 12.9 kJ mol^{-1}. The plot of T_m against $1/L$ is shown in *Figure 2*. The lamellar thicknesses of the samples were measured by using a small-angle X-ray scattering method. An example of X-ray scattering for an α-TPI crystal grown from amyl acetate at −20°C over 24 h is shown in *Figure 3*. Again, by using the least-squares method, the surface free energy was found to be 9.6 kJ mol^{-1}, in good agreement with the result obtained by Keller and Martuscelli[5] (9.9 kJ mol^{-1}). However, the equilibrium melting temperature obtained from this calculation, 132.2°C, is greater than that obtained through the use of equation (4) (101.5°C).

Surface-folded structure

Figure 4 shows the relationship between the lamellar thickness of an α-TPI crystal and crystallization temperature in the range −20 to 35°C. It is obvious that lamellar thickness increases when the crystallization temperature increases in the range 10–35°C. Here, the lamellar thicknesses of α-TPI crystals grown in hexane solution were found to be slightly greater than those of crystals grown in amyl acetate solution at any crystallization temperature. According to previous findings[16], when ΔT ($\Delta T = T_m^\circ - T_c$) is large enough, the lamellar thickness is constant. In the case of this study, for crystallization at supercooling temperatures[15] of −10 and −20°C, the lamellar thicknesses of α-TPI crystals grown from hexane solution as well as from amyl acetate solution were not found to be constant. They were somewhat longer than the expected value (84 Å, the shortest one obtained by high-temperature crystallization). The resulting unusual thickness might be due to the occurrence of the phenomenon called 'isothermal thickening'[16–18]. At certain low crystallization temperatures, the lamellar thickness was observed to be independent of crystallization temperature.

According to Fischer and Schmidt[19], the density of the polymer lamellae is related to that of the subcell, ρ_c, by the following equation

$$\rho = \rho_c - (\text{constant}/L) \qquad (6)$$

where L is the lamellar thickness and ρ_c is equal to 1.05 g cm^{-3} for α-TPI crystals[20]. *Figure 5* shows the plot of the density against the reciprocal lamellar thickness for some α-TPI crystals grown in hexane solution and

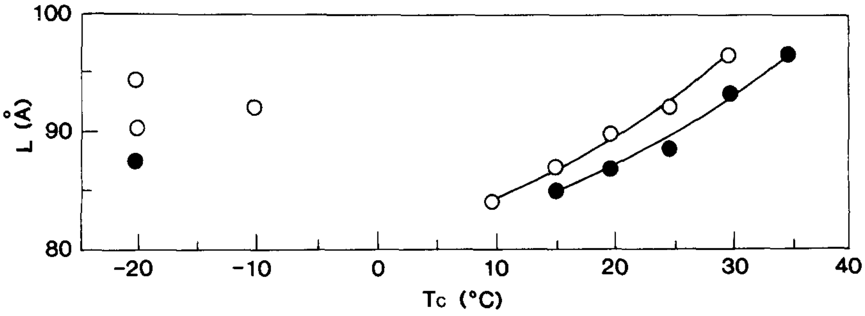

Figure 4 The relationship between lamellar thickness and crystallization temperature for α-TPI crystals grown from hexane (○) and amyl acetate (●)

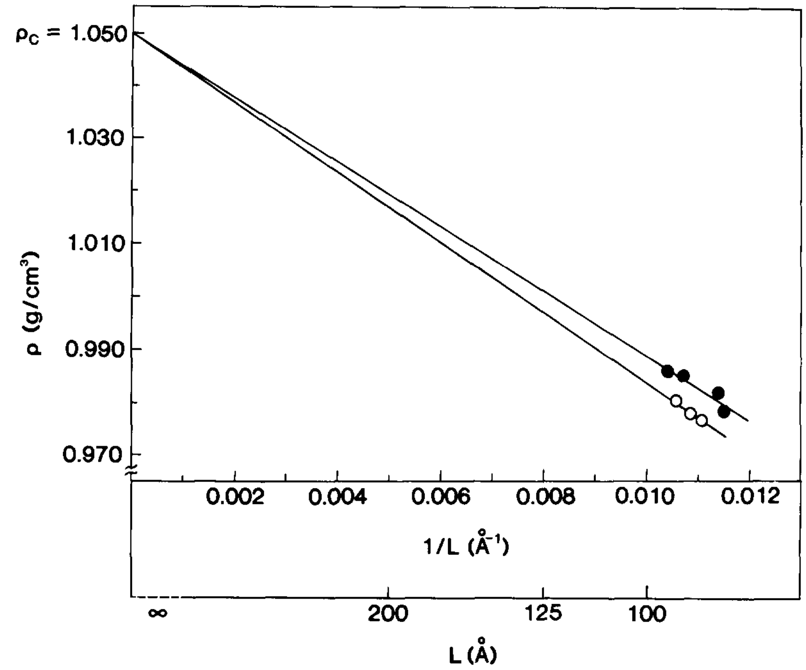

Figure 5 The relationship between density and reciprocal lamellar thickness for α-TPI crystals grown from hexane (○) and amyl acetate (●)

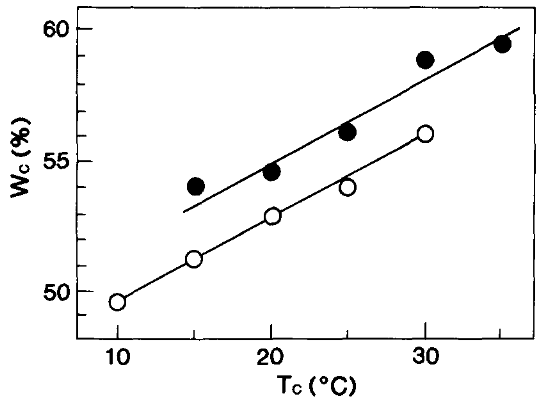

Figure 6 The relationship between weight-fraction crystallinity and crystallization temperature for α-TPI crystals grown from hexane (○) and amyl acetate (●)

Table 2 Summary of densities in connection with lamellar thicknesses for α-TPI crystals grown from hexane and amyl acetate

Solvent	T_c (°C)	ρ (g cm^{-3})	L (Å)	$1/L$ (Å^{-1})
Hexane	−20	0.9804	94.3	0.0106
	10	0.9712^a	84.1	0.0119
	15	0.9740^a	86.9	0.0115
	20	0.9765	89.9	0.0111
	25	0.9778	92.0	0.0109
	30	0.9811^a	96.5	0.0104
Amyl acetate	−20	0.9822	87.6	0.0114
	15	0.9780^a	85.0	0.0118
	20	0.9785	86.9	0.0115
	25	0.9811^a	88.3	0.0113
	30	0.9850	93.6	0.0107
	35	0.9860	96.5	0.0104

^{a}Extrapolated values

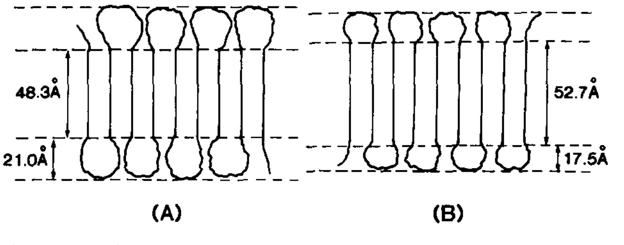

Figure 7 Schematic representation of the proposed structures of chain-folded lamellae grown from hexane (A) and amyl acetate (B)

amyl acetate solution. The plots both give a linear relationship that satisfies equation (6). Accordingly, this relationship could be used as the standard curve for density determination. Owing to the difficulty in density measurement of the samples which have powder form, their densities were obtained by extrapolation to this standard curve. Some extrapolated and experimental values of density for α-TPI crystals grown from hexane and amyl acetate are listed in *Table 2*.

Figure 6 shows the plot of the weight-fraction crystallinities, obtained from the experimental and/or estimated densities by extrapolation, against crystallization temperature. The relationship was found to be linear in which the weight-fraction crystallinity increased with the increase of the crystallization temperature. The crystallinities of α-TPI crystals grown in amyl acetate solution were appreciably greater than those of crystals grown in hexane solution at any crystallization temperature. This implies that α-TPI lamellae grown from amyl acetate have longer crystalline stem lengths. Based on the results obtained from *Figures 4* and *6*, the chain-folded lamellae grown in hexane solution might have longer and looser surface folds as compared to those lamellae grown in amyl acetate solution, as shown schematically in *Figure 7*. These findings are in agreement with previous results obtained by the ozonolysis–g.p.c. method[13] in which the stem lengths of lamellae grown from hexane and from amyl acetate were found to be 11 and 12 isoprene units, respectively. By using 4.39 Å for the crystallographic repeat distance in the chain direction of the α-TPI crystal[21], the stem length and surface fold length were calculated to be 48.3 Å and 21.0 Å, respectively, for lamellae from hexane and 52.7 Å and 17.5 Å, respectively, for lamellae from amyl acetate.

CONCLUSIONS

The equilibrium melting temperature of the solution-grown α-TPI crystals grown from both hexane and amyl acetate was found to be 101.5°C. The surface free energy was estimated to be 9.6 kJ mol^{-1}. The α-TPI lamellae grown from hexane were found to have slightly shorter crystalline stem lengths but looser and longer surface folds as compared to the lamellae grown from amyl acetate.

ACKNOWLEDGEMENT

We are grateful to Emeritus Professor Yozo Chatani for his critical reading of this manuscript and his helpful advice.

REFERENCES

1 Mandelkern, L., Quinn, F. A. and Roberts, D. E. *J. Am. Chem. Soc.* 1956, **78**, 926
2 Lovering, E. G. and Wooden, D. C. *J. Polym. Sci. (A-2)* 1969, **7**, 1639
3 Lovering, E. G. and Wooden, D. C. *J. Polym. Sci. (A-2)* 1971, **9**, 175
4 Flanagan, R. D. and Rijke, A. M. *J. Polym. Sci. (A-2)* 1972, **10**, 1207
5 Keller, A. and Martuscelli, E. *Makromol. Chem.* 1972, **151**, 189
6 Davies, C. K. L. and Long, O. E. *J. Mater. Sci.* 1979, **14**, 2529
7 Mukherji, S. and Woodward, A. E. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 793
8 Patel, G. N. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 2259
9 Priest, D. J. *J. Polym. Sci. (A-2)* 1971, **9**, 1777
10 Keller, A., Martuscelli, E., Priest, D. J. and Udagawa, Y. *J. Polym. Sci. (A-2)* 1971, **9**, 1807
11 Schilling, F. C., Bovey, F. A., Anandakumaran, K. and Woodward, A. E. *Macromolecules* 1985, **18**, 2688
12 Tanaka, Y., Boochathum, P., Shimizu, M. and Mita, K. *Polymer* 1993, **34**, 1097
13 Boochathum, P., Shimizu, M., Mita, K. and Tanaka, Y. *Polymer* 1993, **34**, 2564
14 Gopalan, M. and Mandelkern, L. *J. Phys. Chem.* 1967, **71**, 3833
15 Boochathum, P., Tanaka, Y. and Okuyama, K. *Polymer* 1993, **34**, 3694
16 Norman, M. and Mario, T. 'Polymers, Liquid Crystals, and Low-dimensional Solids', Plenum Press, New York, 1984, p. 71
17 Kawai, T. *Koll. Z. Z. Polym.* 1969, **229**, 116
18 Hoffman, J. D. and Weeks, J. J. *J. Chem. Phys.* 1965, **42**, 4301
19 Fischer, E. W. and Schmidt, G. F. *Angew. Chem.* 1962, **74**, 551
20 Fisher, D. *Proc. Phys. Soc. London* 1953, **66**, 7
21 Takahashi, Y., Sato, T., Tadokoro, H. and Tanaka, Y. *J. Polym. Sci., Polym. Phys. Edn* 1973, **11**, 233