

Structure of solution-grown *trans*-1,4-polyisoprene crystals: 4. Effect of concentration on crystal form and melting temperature

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The crystallization of synthetic *trans*-1,4-polyisoprene (TPI) was carried out in 0.05 to 20.0% (wt/vol) hexane, octane and amyl acetate solutions and the melting temperature, T_m , of the resulting crystals was measured by differential scanning calorimetry (d.s.c.). The crystal form and T_m of the crystals were independent of the concentration of the solutions. On crystallization at low temperatures, TPI crystals appeared before the TPI solutions reached the desired crystallization temperature, T_c , and the T_m was independent of the T_c . This phenomenon was quantitatively analysed with respect to the *conversion temperature* and the crystallization conditions. In contrast, at high temperatures, TPI crystals were observed after the TPI solutions reached a given T_c , and the T_m was dependent on the T_c . Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The crystallization of synthetic *trans*-1,4-polyisoprene (TPI) from solution has been investigated for many years^{1–6}. Recently, we have shown that the crystal form of solution-grown TPI crystals is dependent on the crystallization temperature (T_c), crystallization time (t_c), and the solvent from which the crystals were grown^{7–9}. For example, when TPI was crystallized at lower T_c s, two crystal forms, known as the α - and β -forms, were observed, and the transformation between the α - and β -crystals was found to occur in the course of crystallization for longer t_c s, as well as during storage of the crystals. On the other hand, only the α -crystal was grown from hexane and amyl acetate solutions at a T_c higher than 5 and 10°C, respectively, and their melting temperatures (T_m s) increased with increasing T_c . A similar tendency was also observed by other workers^{10–12}. However, details of the low-temperature crystallization were not given.

In our recent investigations, the ozonolysis-gel permeation chromatography (g.p.c.) method was shown to be a powerful technique to determine the number of isoprene units per stem in a solution-grown TPI crystal, with this number being proportional to the lamellar thickness at lower temperatures. This indicates the possibility of a direct observation of the number of

isoprene units per stem in a single crystal, if the single crystal is grown at lower temperatures. However, high-supercooling crystallization at lower T_c s gave a mixture of the α - and β -forms and their T_m s were independent of T_c ⁸. In order to obtain single crystals at lower values of the T_c , it is necessary to investigate the crystallization conditions in detail at lower temperatures.

In the present work, the influence of the concentrations of the TPI solutions on the crystal form and melting temperature was investigated. A clear explanation was also sought for the phenomenon that the T_m is independent of T_c when crystallization was carried out at temperatures lower than a certain temperature, referred to as the *conversion temperature*, which was defined as the crystallization temperature at the discontinuity in the T_m versus T_c plot⁸. The conversion temperature was found to be concerned with the heat flux and rate of crystallization.

EXPERIMENTAL

The material used in this work was commercially obtained synthetic *trans*-1,4-polyisoprene (TP301, Kuraray Co.) with 98.7% *trans*-1,4 content, $\bar{M}_w = 1.4 \times 10^5$, $\bar{M}_n = 7.0 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.0$. Purification of the polymer was carried out by repeated precipitation from toluene solution into methanol.

The 0.05–20.0% (wt/vol) solutions of TPI in hexane,

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octane and amyl acetate were prepared by dissolving the TPI at temperatures of 60°C for hexane and octane solutions, and at 80°C for amyl acetate solution. The TPI crystals were grown directly from solutions placed in a cooling bath at a fixed crystallization temperature of -20°C. The solution-grown TPI crystals were filtered and then dried *in vacuo* at room temperature. D.s.c. measurements were carried out by using a Seiko Instrument DSC 220. Details of the crystallization procedure and the d.s.c. measurements have been described in a previous paper⁸.

RESULTS AND DISCUSSION

The concentration dependence of crystal form and melting temperature

Figure 1 shows typical d.s.c. thermograms for TPI crystals grown from 0.05–20.0% (wt/vol) hexane solutions at -20°C for 5 h. According to previous work^{1,8}, the two endothermic peaks at ca. 60 and 50°C in the d.s.c. thermograms were attributed to melting of the α - and β -form crystals, respectively. For each concentration of solution in this study, however, only a single endothermic peak for the α -form crystal was identified, with no peak being observed for the β -form crystal. This demonstrates that only crystals of the α -form can be obtained at a T_c lower than 0°C.

Table 1 summarizes the crystal forms of the TPI crystals obtained from hexane, octane and amyl acetate solutions ranging in concentration from 0.05 to 20.0% (wt/vol) at the same T_c of -20°C for 5 h. It was clear that the crystal forms were not influenced by the concentration of solution, but only by the nature of the solvents used. For hexane and octane solutions, only the α -form occurred at all of the concentrations that were used. On the other hand, TPI crystals grown from amyl acetate gave the α -form at concentrations in the range from 0.20 to 1.00% (wt/vol), with a mixture of the α - and β -forms being observed at concentrations of 0.05, 0.10 and 0.50%

Table 1 Crystal forms of TPI grown in various concentrations of solution at a T_c of -20°C for 5 h

Solvent	Concentration (% (wt/vol))	Crystal form
Hexane	0.05	α
	0.10	α
	0.20	α
	0.50	α
	1.00	α
	3.00	α
	10.0	α
	20.0	α
Octane	0.05	α
	0.10	α
	0.20	α
	0.50	α
	1.00	α
	2.00	α
Amyl acetate	0.05	α, β
	0.10	α, β
	0.20	α
	0.35	α
	0.50	α
		α, β'
	1.00	α

^a Repeated crystallization

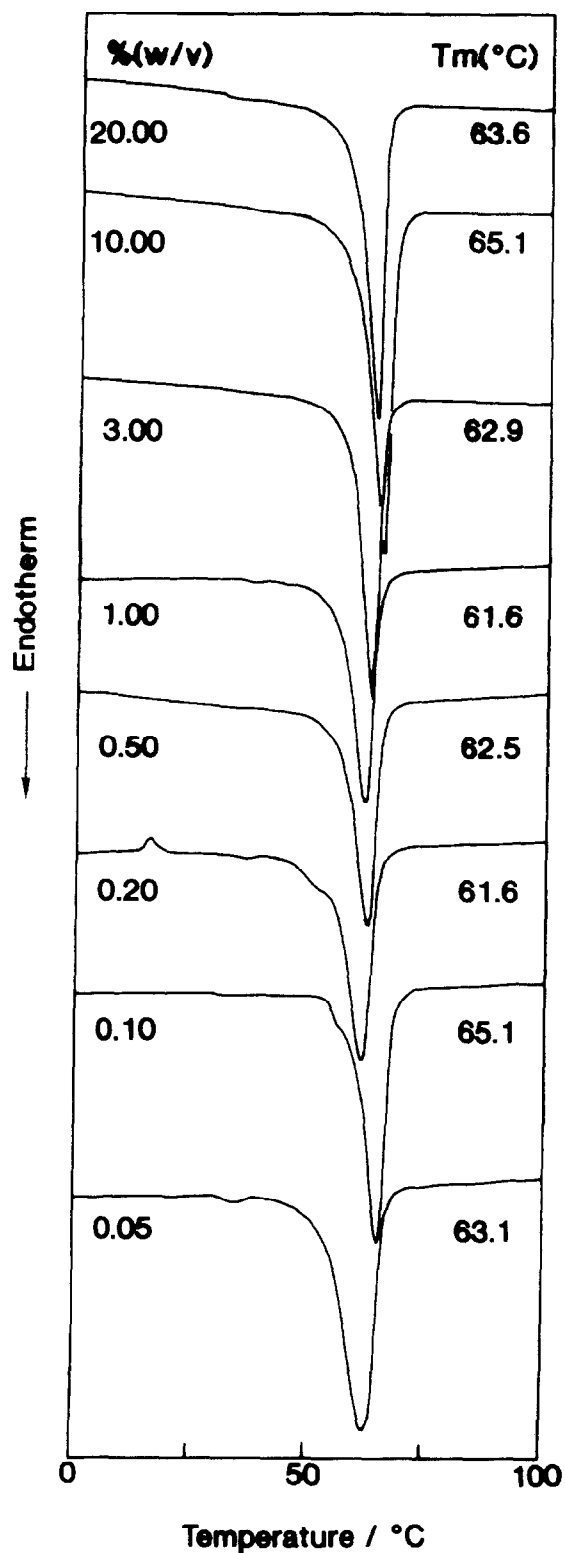


Figure 1 D.s.c. thermograms of TPI crystals grown from hexane solutions at -20°C for 5 h at various concentrations

(wt/vol). Therefore, the kind of crystal form obtained was found to be due to the influence of the solvent being used and the T_c .

In Table 1, the crystal form grown in the first crystallization experiment from a 0.50% (wt/vol) amyl acetate solution is compared with those grown by repeated crystallization. These crystallizations from amyl acetate solutions gave either the α -form or a

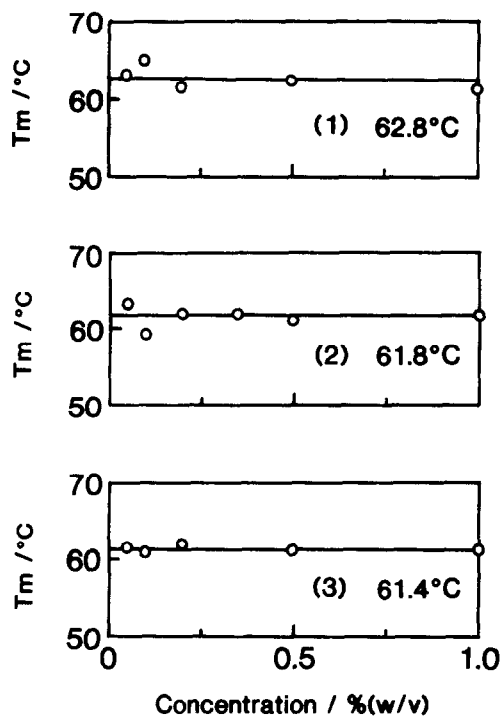


Figure 2 Concentration dependence of T_m for TPI crystals grown from various solvents: (1) hexane; (2) amyl acetate; (3) octane

mixture of the α - and β -forms. This might be because transformation between the α - and β -forms took place when amyl acetate was used as the solvent.

Figure 2 shows the concentration dependence of T_m for α -form crystals grown at -20°C for 5 h. At all of the concentrations in the range from 0.05 to 1.00% (wt/vol), the observed T_m values were found to be independent of the concentration. TPI crystals grown from octane and amyl acetate solutions melted, on the average, at 61.4 and 61.8°C, respectively, while those grown from hexane solution melted at 62.8°C (average value).

Concentration dependence of conversion temperature

The plot of T_m against T_c for TPI crystals grown from 0.10% (wt/vol) hexane, octane, or amyl acetate solutions is shown in Figure 3. Thus in this study, the conversion temperature obtained for α -TPI crystals grown from hexane solution was found to be 10°C , while the corresponding temperature from amyl acetate and octane was 15°C . These values for the conversion temperature are in agreement with those obtained for crystals grown from 0.20% (wt/vol) solutions⁸. Figure 4 shows a plot of T_m against T_c for TPI crystals grown from hexane solutions ranging in concentration from 1.00 to 20.0% (wt/vol). All solutions showed the same conversion temperature of 10°C . This suggests that the concentration of the crystallization solution has no effect on the conversion temperature. On the other hand, this parameter was dependent on the size and shape of the vessel used for crystallization, and on the solvent employed.

Crystallization at any temperature below the conversion temperature was expected to be that of the high-supercooling crystallization type, providing that T_m was independent of T_c . On the contrary, the T_m of a TPI crystal grown at isothermal crystallization temperatures higher than the conversion temperature was

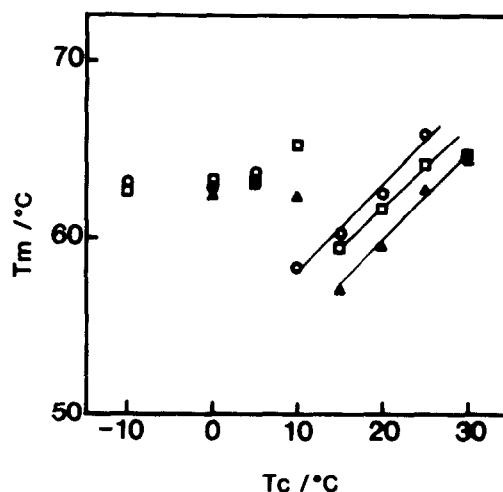


Figure 3 Plot of T_m against T_c for solution-grown α -TPI crystals: (○) hexane; (△) amyl acetate; (□) octane

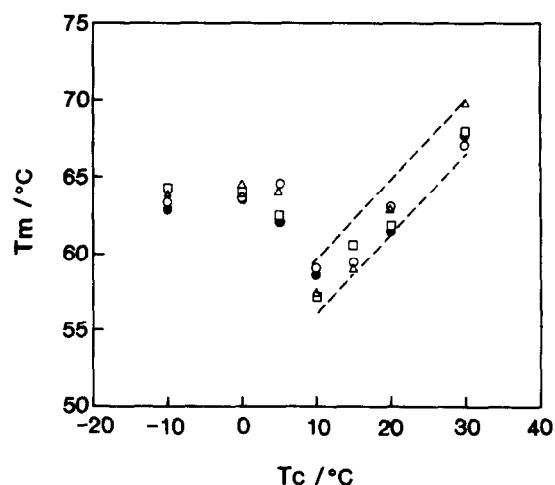


Figure 4 Plot of T_m against T_c for solution-grown α -TPI crystals at various concentrations in hexane: (○) 1; (△) 5; (□) 10; (●) 20% (wt/vol)

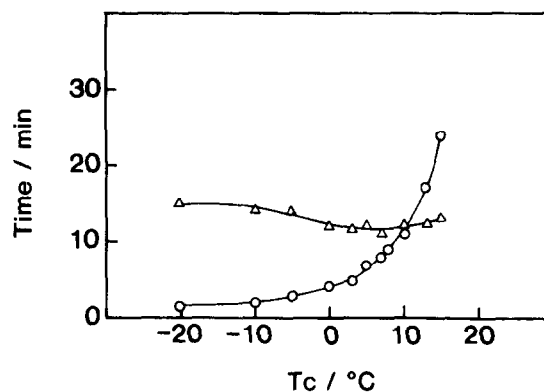


Figure 5 Plots, as a function of T_c , of the time required for TPI solutions to achieve the T_c (△), and the onset time for the emergence of crystals (○)

found to increase as T_c increased for all of the solvents used here. Crystallization under high-supercooling and low-supercooling conditions can be clearly explained by the following observations.

It took 10–15 min under the conditions employed in these experiments for the hexane solutions to achieve the steady-state condition after the temperature was reduced to T_c from the dissolution temperature. As expected, the higher the value of T_c , then the shorter was the time required to achieve a desired T_c . On the other hand, crystals could be clearly observed in the period from 2 to 25 min, depending on the crystallization temperature. The time required to achieve a given T_c and the time required for the emergence of crystals to be visually recognized is shown in Figure 5. The time required for the emergence of crystals, which is inversely proportional to the rate of crystallization, increased as the difference between T_m and T_c decreased. At a T_c lower than 10°C, the crystals emerged before the TPI solution had reached a given T_c . In contrast, at a T_c higher than 10°C, the crystals were observed after the solution reached T_c . As can be remarkably seen from Figure 5, the temperature at which both curves intersect is exactly equal to the observed conversion temperature of 10°C. However, this value might be shifted due to the difference in the size and shape of the vessel used for crystallization, and as a result of the specific solvent used in the experiment. Thus, it was shown that both the time required for the solutions to achieve the crystallization temperature and the onset time for the emergence of crystals are influenced by the value of the conversion temperature. As a result, this observation supports the fact that the conversion temperature is characteristic of the experimental conditions, and is also useful in distinguishing between high-supercooling crystallization and low-supercooling crystallization of TPI from

solution. Single crystals were presumed to grow at lower temperatures by a suitable choice of crystallization conditions.

In conclusion, α -form crystals of TPI can be grown from hexane and octane solutions at lower T_c s. The concentration of the crystallization solution has no influence on the crystal form and melting temperature of the α -TPI crystals that are obtained.

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