Structure of solution-grown *trans*-1,4-polyisoprene crystals: 2. D.s.c. studies of crystal form transformation

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Trans-1,4-polyisoprene (TPI) crystals were grown from hexane and amyl acetate solutions at various temperatures (−30 to 35°C) for periods of 0.5 to 263 h. The melting temperature (T_m) of the crystals was independent of the crystallization temperature (T_c) up to 5°C for hexane solution and 15°C for amyl acetate solution. Above these temperatures (T_r), T_m increased with T_c. On the other hand, below T_r a mixture of the α- and β-forms was obtained and above T_r only the α-form crystals were obtained. The transformation from the β- to the α-form was found to occur during crystallization. In the samples crystallized at 0°C, cyclic transformation between the two forms was observed. The inverse transformation from the α- to the β-form was observed during storage at room temperature for TPI crystals grown from amyl acetate solution at temperatures below T_r. This transformation was also observed for naturally occurring TPI (gutta percha and balata) crystals.

(Keywords: crystallization; *trans*-1,4-polyisoprene; conversion temperature)

INTRODUCTION

Trans-1,4-polyisoprene (TPI) crystals are grown from solution in a mixture of the α-form (monoclinic)[1,2] and the β-form (orthorhombic)[3]. It is also possible to prepare pure samples of either form. The α-form[4–6] was obtained by the precooling method which involves dissolution at an elevated temperature, precipitation, redissolution at a moderate temperature and crystallization at a constant temperature. Direct crystallization from solution, consisting of dissolution at an elevated temperature followed by isothermal crystallization, led to the formation of the β-form at lower crystallization temperatures and the α-form at higher crystallization temperatures[6,7]. The α-form grown from dilute solution without stirring was reported to melt at a temperature higher than the melting point of the β-form[8,9].

Irreversible transformation from the β- to the α-form was reported by Mandelkern *et al.*[10]. However, the conditions required for the transformation were not clarified. Cooper and Vaughan[11] reported that the transformation from the β- to the α-form occurs between 53 and 63°C. Leeper and Schlesinger[12] found it to occur between 64 and 72°C in the presence of liquid. Lovering and Wooden[13] suggested that β-form to α-form transformation occurred by fusion and crystallization. Woodward and coworkers[6] have investigated the transformation in various solutions and found that it occurs for synthetic, unfractionated TPI swollen with amyl acetate at 35°C for 17 h or with butyl acetate at 25°C for one day or at 35°C for 17 h.

In this work, the melting temperature of solution-grown TPI crystals obtained by direct crystallization in various conditions was examined. The crystal form which exhibited a high melting (HM) or low melting (LM) temperature was confirmed by X-ray diffraction. The relationship between the crystallization conditions, i.e. crystallization temperature, crystallization time and solvents used, and the resultant crystal form is reported herein. Finally, the transformation between the two crystal forms that occurs during crystallization and during storage of the crystals at room temperature is also reported.

EXPERIMENTAL

The materials used were synthetic *trans*-1,4-polyisoprene (TP301 from Kuraray Co.) with 99% *trans*-1,4 content ($\bar{M}_w = 1.4 \times 10^5$, $\bar{M}_n = 7.0 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.0$) and naturally occurring *trans*-1,4-polyisoprenes, gutta percha and balata, the microstructures of which were analysed by Tanaka *et al.*[14,15]. The polymers were purified by repeated precipitation from toluene solution into methanol.

Around 200 mg of TPI were dissolved in hexane at 60°C or in amyl acetate at 80°C to give a 0.2% (w/v) solution. The TPI solution was cooled directly in an ethanol bath to a certain crystallization temperature between −30 and 35°C and was held at this temperature for between 0.5 and 263 h. The solution-grown TPI crystals were filtered and washed with hexane or amyl

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acetate at the crystallization temperature and then dried *in vacuo* at room temperature.

D.s.c. measurements were carried out using a Rigaku PTC-10A or a Rigaku TAS-200 thermal analyser. The samples (about 2 mg) were heated from −20 to 100°C at a scanning rate of 10°C min^{-1}. The melting temperatures of the α-form and β-form were estimated from the maxima of the endothermic peaks without separating the overlapping peaks of the two forms. The d.s.c. measurements of samples that had been stored for one, two or three months in darkness at room temperature were also carried out in comparison with the freshly made samples.

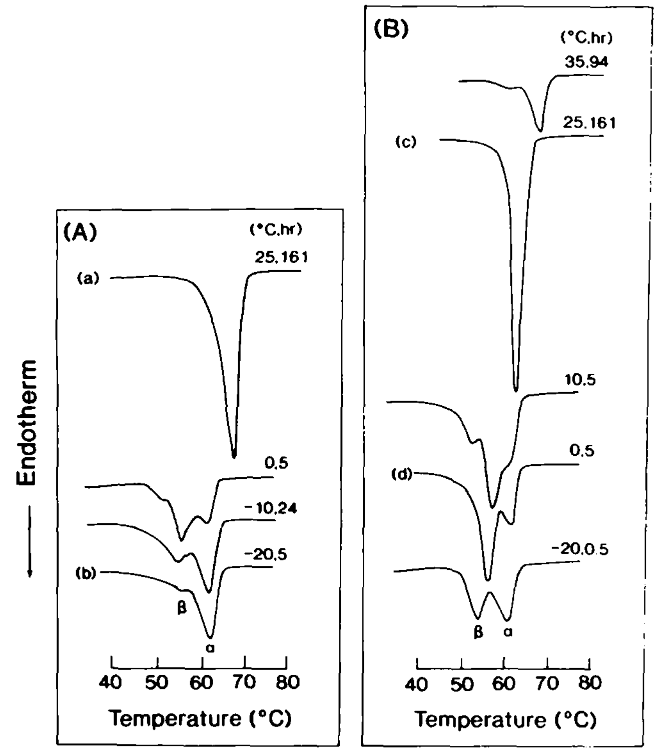


Figure 1 D.s.c. thermograms of TPI crystals grown from hexane (A) and amyl acetate (B) solutions. Scanning rate 10°C min^{-1}. The crystal forms of samples (a) to (d) were determined by X-ray diffraction

X-ray diffraction measurements were carried out with a Geigerflex (Rigaku Denki Co., Ltd) diffractometer. X-ray photographs were taken using nickel-filtered CuKα radiation. The *d*-spacings of the reflections were measured with a cylindrical camera of 50.0 mm radius. The diffraction patterns obtained were compared to those reported in the literature[2,3].

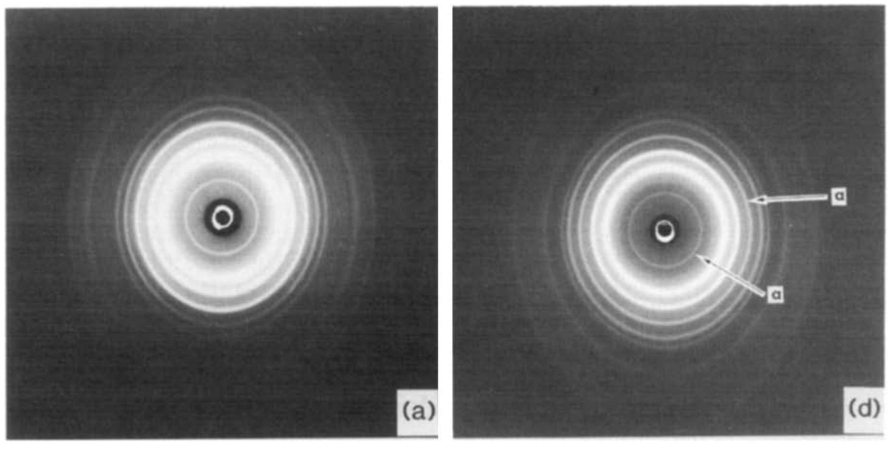
RESULTS AND DISCUSSION

Crystal form

Typical d.s.c. results are shown in *Figure 1*. At a T_c lower than 0°C for crystals grown from hexane and 10°C for crystals grown from amyl acetate, there appeared two endothermic peaks at low melting temperature (around 52–59°C) and high melting temperature (around 60–63°C). At a T_c higher than 0°C or 10°C, only the high melting temperature around 58–70°C was observed.

The crystal form in the samples (a) to (d) in *Figure 1*, which were crystallized at the temperature and period of time indicated in the figure, was determined by X-ray diffraction with reference to the reported X-ray diffraction patterns of the α-form and β-form[2,3]. Sample (d), which mainly exhibited the low melting temperature, gave the X-ray diffraction pattern of the β-form with some additional diffractions from the α-form. Samples (a) to (c), which exhibited the high melting temperature, gave the diffraction pattern of the α-form. The typical X-ray diffraction patterns of samples (a) and (d) are shown in *Figure 2*. The results of d.s.c. and X-ray diffraction are summarized along with the values of T_m in *Table 1*.

Figure 3 shows the effect of T_c on T_m for the solution-grown TPI crystals. Plot (A) demonstrates that at a T_c below 5°C for the hexane solutions, T_m for both LM and HM crystals is independent of T_c. For the amyl acetate solutions at a T_c below 15°C, the T_m of the HM crystal was independent of T_c. These findings suggest that the melting temperature of solution-grown TPI crystals does not always increase with T_c as reported[16]. The crystallization temperature at the discontinuity, or change of the slope, in *Figure 3* is defined as the 'conversion temperature'. The conversion temperatures are 5°C for the crystal grown in hexane solution and 15°C for the crystal grown in amyl acetate solution. It



α-TPI β-TPI

Figure 2 X-ray photographs of crystals grown from hexane at a T_c of 25°C for 161 h (sample a) and from amyl acetate at a T_c of 0°C for 5 h (sample d)

Table 1 Solution crystallization of synthetic *trans*-1,4-polyisoprene[a]

Solvent	T_d (°C)	T_c (°C)	t_c (h)	T_m (°C)		Crystal form
				LM	HM	
Hexane	60	−30	0.5	54.0	61.5	β, α
		−20	0.5	56.0	62.7	β, α
		−20	5	-	61.5	α
		−20	15	-	63.0	α
		−10	1	52.5	61.0	β, α
		−10	15	-	66.1	α
		−10	24	53.0	61.5	β, α
		−10	65	54.3	62.2	β, α
		0	0.5	56.0	61.0	β, α
		0	5	54.0	61.4	β, α
		0	24	55.0	61.4	β, α
		0	72	55.5	61.4	β, α
		5	1	-	58.2	α
		10	1	-	60.0	α
		10	48	-	62.0	α
		15	24	-	65.0	α
		20	24	-	66.0	α
		25	161	-	67.6	α
		30	263	-	69.9	α
Amyl acetate	80	−30	0.5	52.5	60.4	β, α
		−20	0.5	53.5	60.4	β, α
		−20	24	-	63.0	α
		−10	1	54.5	61.5	β, α
		−10	48	55.0	60.8	β, α
		−10	65	54.3	62.2	β, α
		0	0.5	54.4	61.2	β, α
		0	5	56.5	62.0	β, α
		0	72	55.5	61.4	β, α
		5	46	56.5	62.2	β, α
		10	2	57.2	62.2	β, α
		10	5	51.0, 57.0	61.0	β, α
		10	48	59.2	63.3	β, α
		15	24	-	60.8	α
		20	48	-	62.4	α
		25	161	-	64.0	α
		30	216	-	69.0	α
		35	94	-	69.3	α

[a] T_d, dissolution temperature; T_c, crystallization temperature; T_m, melting temperature; t_c, crystallization time; LM, low-melting crystalline form; HM, high-melting crystalline form

is interesting that the conversion temperature for the poor solvent (amyl acetate) is higher than that for the good solvent (hexane); the dissolution temperature is higher for the poor solvent than for the good solvent. The direct crystallization of TPI from both hexane and amyl acetate solutions at a T_c below the conversion temperature for each solvent gave a mixture of the two crystal forms; at a T_c above the conversion temperature only the α-form crystallized. The direct crystallization above the conversion temperature is isothermal, while the direct crystallization below the conversion temperature is non-isothermal; crystallization is complete before reaching the crystallization temperature. It was observed that the crystal form grown under isothermal crystallization conditions is more stable than that grown under non-isothermal crystallization conditions.

TRANSFORMATION OF CRYSTAL FORM

Transformation during crystallization

Figure 4 shows that the transformation between the two forms occurs at the indicated crystallization temperatures and periods of crystallization time. At a T_c of −20°C in both hexane and amyl acetate solutions, the endothermic peaks of the β-form gradually decrease and the endothermic peak of the α-form increases with crystallization time, and eventually only one endothermic peak of the α-form is observed. Therefore, it could be said that the β-form transforms to the α-form completely in crystallization times of up to 15 h for hexane and 24 h for amyl acetate. The β-form to α-form transformation also occurs when TPI is crystallized in amyl acetate solution at a T_c of 10°C. However, at 0°C cyclic

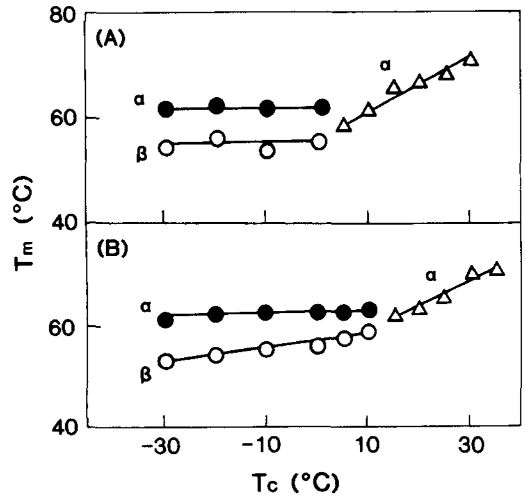


Figure 3 Plot of melting temperature (T_m) obtained from d.s.c. against crystallization temperature (T_c) of solution-grown TPI crystals grown from hexane (A) and amyl acetate (B)

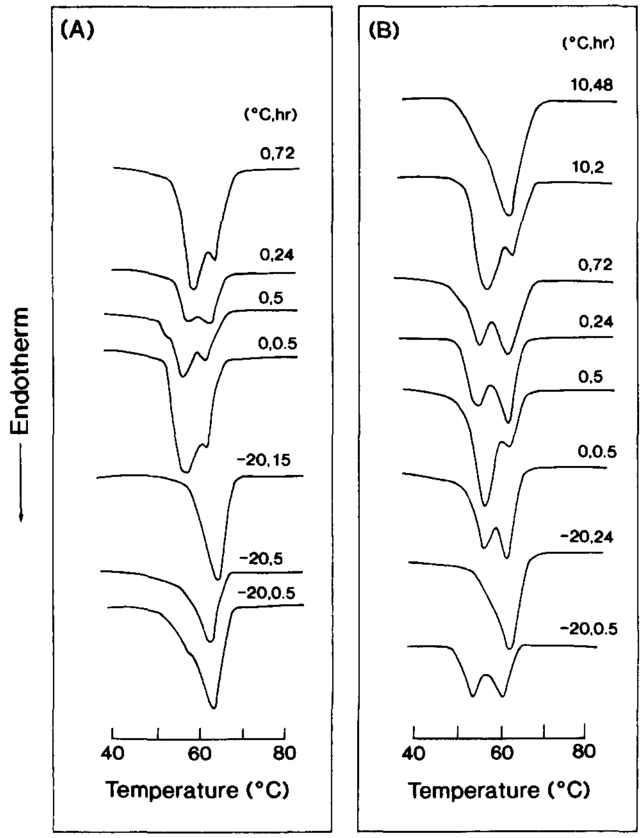


Figure 4 Comparison of d.s.c. thermograms for the transformation from β-form to α-form which occurs during crystallization in hexane (A) and in amyl acetate (B) at the indicated T_c and crystallization time

transformations between the two forms, i.e. α to β and β to α transformations, are observed for TPI crystals grown from both hexane and amyl acetate solutions. At the present time, no explanations for the cyclic transformations are available.

These results show that at a T_c below the conversion temperature the α-form is thermodynamically more stable than the β-form and that the β-form is kinetically favoured at all crystallization temperatures; TPI initially crystallizes in the β-form and the β to α transformation occurs in the course of crystallization.

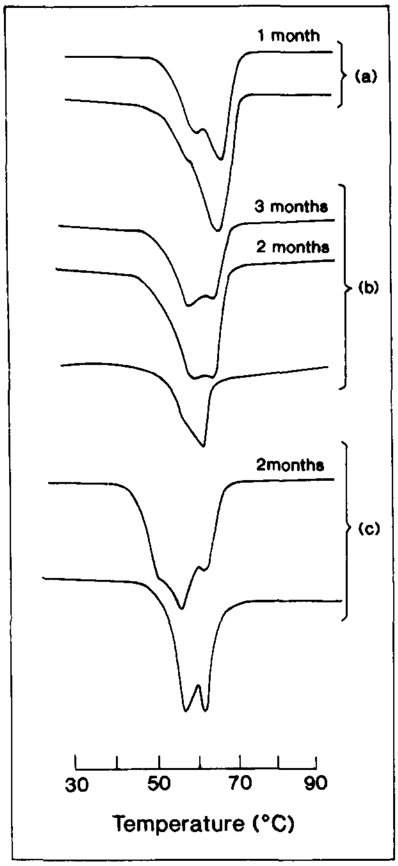


Figure 5 D.s.c. curves showing the α to β transformation that occurs during storage for TPI crystals grown in amyl acetate solution at -20°C for 24 h (sample a), 10°C for 48 h (sample b) and 5°C for 46 h (sample c)

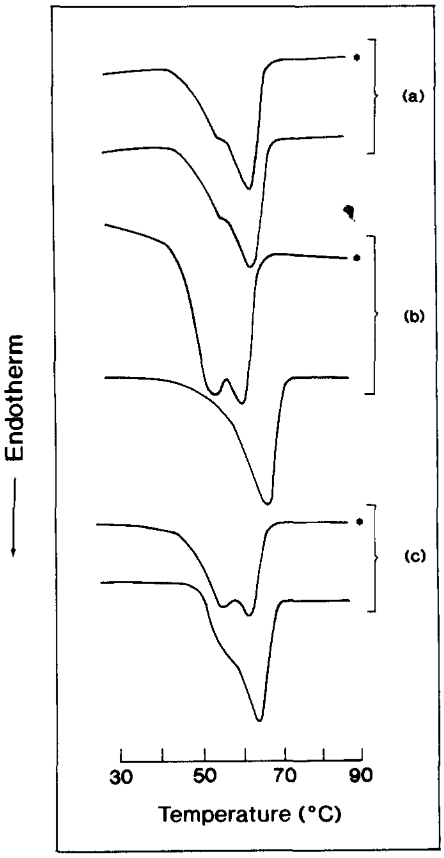


Figure 6 Comparison of d.s.c. thermograms of the α to β transformation that occurs during storage. The stored samples (*) were tested after one month of storage. The samples are synthetic TPI (sample a), gutta percha (sample b) and balata (sample c)

Transformation during storage

Figure 5 shows d.s.c. curves exhibiting the transformation from the α-form to the β-form during storage at room temperature for one to three months. The decrease in the endothermic peak of the α-form and the increase in the endothermic peak of the β-form for the stored TPI crystals can be clearly seen. This transformation was found to occur for synthetic TPI crystals when crystallized from amyl acetate solutions but not from hexane solutions. The α-TPI crystals grown from hexane solutions at a low T_c were more stable at room temperature than those grown from amyl acetate solutions.

Figure 6 shows the d.s.c. thermograms of the α to β transformation that occurred during storage for the naturally occurring *trans*-1,4-polyisoprenes gutta percha (b) and balata (c); the thermogram of synthetic *trans*-1,4-polyisoprene (a) grown from hexane solution is also shown for comparison. The α to β transformation was observed only for gutta percha and balata and not for the crystals of TP301. Hence, the α-form in naturally occurring TPI crystals is not as stable as that in synthetic TPI crystals grown from the same solvent. The stability of the α-form during storage might be assumed to depend on the solvent used, the T_c and the microstructure of TPI itself. Within the scope of this study, the detailed effect of storage on the stability of the α-form is not known.

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