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Solution-grown crystal of *cis*-1,4 polyisoprene

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Synthetic *cis*-1,4 polyisoprene prepared by a Ziegler catalyst and naturally occurring *cis*-1,4 polyisoprenes from *Hevea brasiliensis* and *Lactarius volemus* were crystallized at −80 to −45°C from dilute hexane solution. The melting temperature, T_m, of these solution-grown crystals in hexane solution was determined by differential scanning calorimetry. The T_m value of natural rubber from *Hevea brasiliensis* was higher than that of low molecular weight rubber from *Lactarius volemus* and synthetic *cis*-1,4 polyisoprene, and was not varied by removing proteins, mixed fatty acids and linked fatty acids. For fractionated samples, the T_m value of rubber from *Lactarius volemus* decreased in proportion to the molecular weight, while that of natural rubber was independent of the molecular weight. © 1997 Elsevier Science Ltd.

(Keywords: natural rubber; *cis*-1,4,polyisoprene; melting temperature; crystallization temperature; impurity; d.s.c.)

INTRODUCTION

Structures and thermal properties of *cis*-1,4 polyisoprene crystal have been investigated mainly on the crystals grown from melt. Two different crystal forms were found for *cis*-1,4 polyisoprene by X-ray diffraction of the stretched film specimen[1-3]. These two forms were also observed by scanning electron microscopy[4,5], differential scanning calorimetry (d.s.c.)[6] and dilatometry[7]: α crystal with lower melting temperature and β crystal with higher melting temperature. The melting temperatures, T_m, of *cis*-1,4 polyisoprene increased linearly with the crystallization temperature, T_c. Thus, the equilibrium melting temperature, T_m^0, was estimated to be 39°C by dilatometry[7] or 35.5°C by optical turbidity measurement[8]. However, these determined T_m^0's would differ from T_m^0 of pure *cis*-1,4 polyisoprene, because natural rubber, thus far used, contained non-rubber components such as proteins and fatty acids as high as 2–3 wt%.

We have established a method of removing the proteins and fatty acids in natural rubber completely and have clarified the presence of the fatty acids linked to rubber molecule[9-11]. It has been found that the crystallization of natural rubber is accelerated by the synergistic effect of these mixed and linked fatty acid groups[12] and the green strength is enhanced by the presence of the linked fatty acids[10]. The linked fatty acids were presumed to be concerned with the chemical crosslinks of terminal groups and to govern the mechanical properties of the rubber.

The crystalline structure of diene rubber can be assessed by measuring a lamellar thickness of the solution-grown crystal using a small angle X-ray scattering[13] and ozonolysis-gel permeation chromatography[14,15], and some thermal properties can be measured by d.s.c.[16]. Thus, the influence of the branching and linked fatty acids will be clarified by comparison of the lamellar thickness and thermal properties of untreated rubber with highly purified rubbers. The lamellar thickness can be measured on the solution-grown crystal.

The crystallization of *cis*-1,4 polyisoprene grown from dilute solution has been only reported by Smith[17], who crystallized the ether-soluble low molecular weight fraction of natural rubber from ethyl ether solution. Smith used photography to detect the shape of crystal and obtained no information of thermal properties.

In this study, crystallization of *cis*-1,4 polyisoprene was carried out from dilute hexane solution of untreated-, deproteinized-, acetone-extracted- and transesterified-natural rubbers, low molecular weight naturally occurring *cis*-1,4 polyisoprene from sporophores of *Lactarius volemus*, and synthetic *cis*-1,4 polyisoprene. The crystallization temperature, T_c, dependence of T_m was investigated by d.s.c.

EXPERIMENTAL

Materials

Samples used were commercial synthetic *cis*-1,4 polyisoprene of JSR IR2200 (*cis*-1,4 98.5%, *trans*-1,4 1.2% and 3,4 0.3%) from Japan Synthetic Rubber Co. Ltd, commercial high-ammonia natural rubber latex (HA latex) and low molecular weight naturally occurring *cis*-1,4 polyisoprene from sporophores of *Lactarius volemus*. The synthetic *cis*-1,4 polyisoprene (CPI) was purified by reprecipitation from 1 w/v% toluene solution into methanol. The precipitate was dried under reduced pressure for more than 2 days. The HA latex was aggregated by the addition of methanol followed by centrifugation (untreated NR).

Enzymatic deproteinization of natural rubber was

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Table 1 Average molecular weight, molecular weight distribution, content of 3,4 units, nitrogen content (N_2%) and ester content of the samples

	$\overline{M}_n$ (10^4)	$\overline{M}_w$ (10^4)	$\overline{M}_w/\overline{M}_n$	3,4 (%)	N (%)	Ester (mmol kg^{-1})
CPI	20.3	104	5.10	0.3	0	0
Untreated NR	29.8	195	8.55	0	0.38	14.8
TE-NR	27.4	169	7.29	0	0.38	0
DPNR	24.6	140	7.80	0	0.01	14.8
AE-DPNR	31.8	122	5.25	0	0.01	4.5
TE-DPNR	20.8	119	7.76	0	0.01	0
LF-DPNR	4.4	15	7.35	0	–[a]	—
L-rubber	2.8	8.7	2.01	0	—	—

CPI, synthetic *cis*-1,4 polyisoprene; NR, natural rubber; TE-NR, transesterified NR; DPNR, deproteinized NR; AE-DPNR, acetone extracted DPNR; TE-DPNR, transesterified DPNR; LF-DPNR, lowest molecular weight fraction of DPNR; L-rubber, naturally occurring *cis*-1,4 polyisoprene from sporophores of *Lactarius volemus*

[a] Not examined

carried out by incubation of the HA latex diluted to about 30% dry rubber contents (DRC) with 0.04 w/v% proteolytic enzyme (Novo Industrials Alcalase 2.0T) and 1 w/v% sodium lauryl sulfate (SLS) for 12 h at 37°C followed by centrifugation[9]. The cream fraction was redispersed in 1 w/v% SLS to make 30% DRC and centrifuged again. The deproteinized natural rubber (DPNR) was extracted with acetone (AE-DPNR) in a Soxhlet apparatus for 24 h under nitrogen atmosphere in the dark and dried under reduced pressure for 3 days. Fractionation of DPNR was carried out by pouring methanol to 0.5 w/v% toluene solution. The lowest molecular weight fraction of DPNR (LF-DPNR) was obtained by adding methanol to a toluene solution of the rubber at 25°C in the usual way.

Transesterification of untreated NR (TE-NR) and DPNR (TE-DPNR) was carried out in toluene by reaction with fresh sodium methoxide at room temperature for 2 h followed by neutralization with dilute methanolic HCl[10].

Naturally occurring *cis*-1,4 polyisoprene (L-rubber)[18,19] from sporophores of *Lactarius volemus*, which did not contain protein, was obtained by the precipitation of hexane soluble fraction into methanol and purified in a similar way as synthetic CPI. The lowest molecular weight fraction of L-rubber was obtained by adding methanol to a toluene solution of the rubber at 25°C in the usual way. Some structural characteristics of the samples prepared are shown in *Table 1*.

Measurements

Nitrogen content of natural rubber samples was measured by a Yanako CHN CODER MT-5. Fatty acid ester content was determined by a Jasco FTIR 5300[10].

Gel permeation chromatography was carried out using a Jasco 880-PU as a high pressure pump and a Jasco 830-RI detector. Chloroform was used as an eluent.

Onset time of deposition of the solution-grown crystals at −80 to −45°C was determined by a visual observation as the time at which the hexane solution changed from transparent to opaque.

Measurements of melting temperature of the samples were made by a Seiko Instrument DSC 220 after isothermal crystallization of the rubbers in 1 wt% hexane solution was carried out at −70 to −45°C for 5 h in the d.s.c. sample chamber. The thermograms were obtained at the heating rate of 10°C min^{-1}.

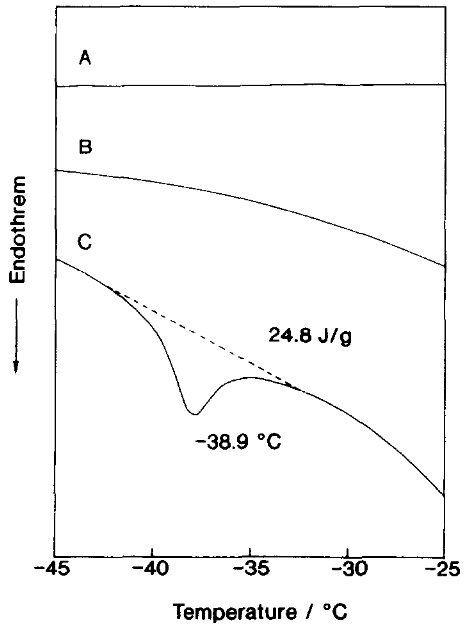

Figure 1 D.s.c. thermograms of (A) aluminium pan, (B) hexane, and (C) hexane solution of synthetic *cis*-1,4 polyisoprene crystallized at −70°C, respectively

RESULTS AND DISCUSSION

A white precipitate appeared when 1 w/v% hexane solutions of synthetic *cis*-1,4 polyisoprene (CPI), natural rubber (NR) and naturally occurring *cis*-1,4 polyisoprene from sporophores of *Lactarius volemus* (L-rubber) were cooled at the isothermal setting temperature of −70°C. The precipitate disappeared at room temperature. This disappearance of the precipitate suggests two possibilities, dissolution and melting. For the former, little heat transport for dissolution is expected to be measured. In contrast, for the latter, the heat of fusion of crystal can be shown in the d.s.c. thermogram as an endothermic peak.

In *Figure 1*, an endothermic peak of 24.8 J g^{-1} for the hexane solution of CPI cooled at −70°C is shown around −39°C. This was presumed to be due to the melting of the CPI crystal, since the endothermic peak was not observed in the thermograms of aluminium pan and hexane. Assuming that the equilibrium heat of fusion of CPI in hexane solution is the same as that of bulk specimen, i.e. 64.8 J g^{-1}, the degree of crystallinity of the

CPI crystal grown from the solution was estimated to be 38.3% from the ratio of the endothermic peak at 24.8 J g^{-1} to the equilibrium heat of fusion. It is noteworthy that the estimated degree of crystallinity of the CPI crystal grown from the solution is identical to the final degree of crystallinity of the crystal grown from melt[7].

The melting temperature of semi-crystalline polymers such as *cis*-1,4 polyisoprene[7] is dependent upon the crystallization temperature at which the polymer is crystallized. If the temperature necessary for the appearance of the endothermic peak in the d.s.c. thermogram is dependent on the cooling temperature, the white precipitate at low temperature can be proved as a crystal of the polymer. In the present work, a variation of the endothermic peak of the dilute hexane solution of CPI was investigated at an isothermal cooling temperature between −80 and −45°C. The temperature at which the endothermic peak top appeared, T_m, was significantly dependent on the isothermal cooling temperature, as shown in *Figure 2*. Plotting T_m vs T_c in *Figure 3*, the T_m was revealed to increase linearly as the isothermal cooling temperature increased. The increase in the T_m was, however, divided into two temperature regions bordering around −65°C. Below −65°C, the T_m could be regarded as a definite temperature, while it increased linearly with increasing the cooling temperature higher than −65°C. These two variations of T_m on the cooling temperature showed a similar trend to that of the melting temperature, T_m, of solution-grown crystal of polymer[7]. It was also reported that the lamellar thickness was observed to be independent of T_c at a certain low T_c[20–22]. Therefore, the white precipitates grown from the dilute hexane solution of CPI was concluded to be a solution-grown crystal.

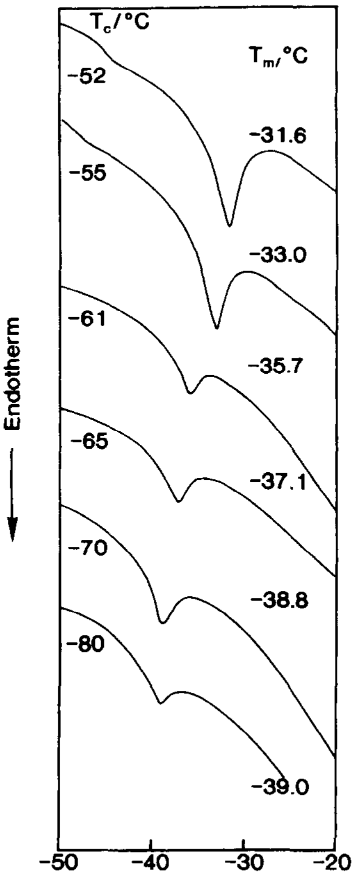

Figure 2 D.s.c. thermograms of hexane solution of synthetic *cis*-1,4 polyisoprene crystallized between −80 and −52°C

In *Figure 3*, CPI, NR and L-rubber showed a similar T_c-dependence of T_m and boundary temperature of about −65°C which was dependent on the size of vessel used for the crystallization[23]. However, the T_m value of CPI, NR and L-rubber was distinguished from each other at the same T_c. In order to clarify the origin of the difference in the T_m value, the effect of non-rubber components in NR, the difference in the molecular weight and content of *cis*-1,4 units on the T_m value were investigated.

With regard to NR, TE-NR, DPNR, AE-DPNR and TE-DPNR, a similar T_m vs T_c relationship was observed, despite the fact that they contained different non-rubber components as shown in *Table 1*. Along the T_m of these rubbers, equilibrium T_m was estimated to be −17.9°C by a Hoffman–Weeks plot[24], which was significantly lower than the T_m^0 of 39°C[7] or 35.5°C[8] determined for a NR crystal grown from melt. The lower equilibrium T_m value is due to the depression of melting temperature attributed to the presence of hexane as a solvent, as is evident from the depression of the mixtures of NR with dodecane, tetradecane or methyl oleate[25]. On the other hand, L-rubber and CPI showed distinctly separate lines (*Figure 3*). This demonstrates the negligible effect of non-rubber components, such as protein, mixed fatty acids and linked fatty acids, on the T_m of solution-grown crystal of *cis*-1,4 polyisoprene.

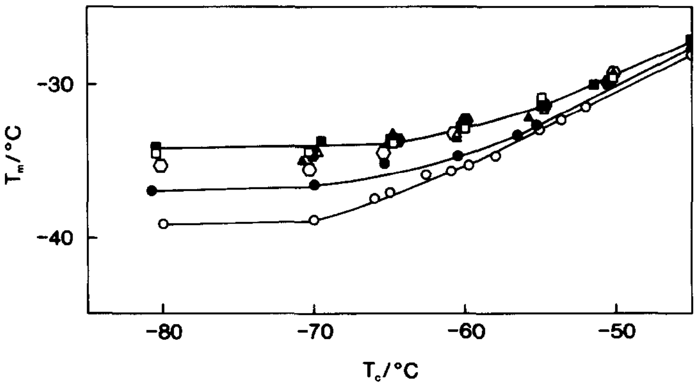

Figure 3 Dependence of melting temperature on crystallization temperature; (○) synthetic *cis*-1,4 polyisoprene, (□) untreated NR, (■) transesterified NR, (△) DPNR, (▲) acetone-extracted DPNR, (●) transesterified DPNR, (○) fractionated low molecular weight DPNR and (●) L-rubber, respectively

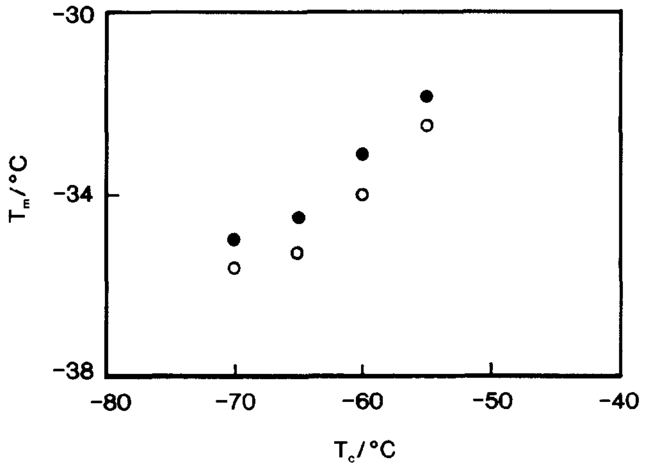

Figure 4 Dependence of melting temperature on crystallization temperature; (●) high molecular weight fraction and (○) low molecular weight fraction fractionated from L-rubber

The average molecular weight decreased in the order of natural rubber, lowest molecular weight fraction DPNR (LF-DPNR) and L-rubber, as shown in *Table 1*. In spite of the significant difference in the average molecular weight, the T_m value of LF-DPNR was the same as that of NR, while it was different from the T_m value of L-rubber which is a homologue of trans-esterified DPNR. It is well known that the T_m value increases with increasing molecular weight in the lower molecular weight region, but it does not change in the higher molecular weight region[26]. In order to ascertain the molecular weight dependence of T_m in the lower molecular weight region, the T_m value of fractionated L-rubbers was compared to each other. The T_m of two fractionated L-rubbers is shown in *Figure 4*. The high molecular weight fraction (1st fraction) of L-rubber, in which $\overline{M}_n = 3.50 \times 10^4$, $\overline{M}_w = 3.26 \times 10^5$ and $\overline{M}_w/\overline{M}_n = 9.33$, showed the T_m values to be higher than those of the low molecular weight fraction (5th fraction), in which $\overline{M}_n = 1.42 \times 10^4$, $\overline{M}_w = 5.29 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 3.73$. This suggests that the difference between the T_m value of LF-DPNR and L-rubber is due to the lower molecular weight nature of L-rubber. Thus, at the higher molecular weight fraction of natural rubber, the T_m value of *cis*-1,4 polyisoprene crystal grown from solution was clearly shown to be independent of the slight decrease in the average molecular weight by deproteinization and transesterification[10]. On the other hand, the content of 3,4 units in CPI can be related directly to the lowest T_m value. The heterogeneity in this microstructure resulted in the lower T_m value.

The determination of lamellar thickness of *cis*-1,4 polyisoprene crystal grown from solution will be presented in a subsequent paper.

CONCLUSION

cis-1,4 Polyisoprene was crystallized from hexane solution as a white precipitate. The melting temperature, T_m, of the solution grown crystal in hexane solution raised as the crystallization temperature, T_c, increased. The T_m value decreased in the order NR, L-rubber and CPI. The difference in T_m value was due to the molecular weight dependence of T_m at lower molecular weight and the presence of 3,4 units. At higher molecular weight, the non-rubber components such as protein, mixed and linked fatty acids in natural rubber were revealed to have little influence on the T_m value of the solution-grown crystal.

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