Cold crystallization of natural rubber and its synthetic analogues: The influence of chain microstructure*

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The crystalizabilities of eight synthetic high *cis*-1,4-polyisoprene rubbers have been compared with that of purified natural rubber by differential scanning calorimetry measurements. The detailed microstructure of the rubbers as determined by ^{13}C and ^{1}H nuclear magnetic resonance have also been studied. Whereas natural rubber is characterized by an essentially sterically pure main chain of 100% *cis*-1,4 content, the structure of the synthetic rubbers spans the range 90.9 to 99.1 mol% *cis*-1,4 content with varying amounts of *trans*-1,4 and 3,4 units. The study shows that the purified natural rubber samples undergo cold crystallization more readily than the synthetic analogues and this is attributable to the more perfect microstructure of the natural product. Generally the crystallizability of the rubbers correlates with the average *cis* sequence lengths of the polymer main chain.

(Keywords: cold crystallization; natural rubber; polyisoprene; microstructure; nuclear magnetic resonance; differential scanning calorimetry)

INTRODUCTION

The crystallization of rubbers is an important phenomenon which has been investigated intensively over the years. Thus the property of stress-induced crystallization is crucial in enhancing the performance properties of rubbers, whereas the ability to cold-crystallize is generally a disadvantageous characteristic. Although the microstructure of natural rubber can be closely imitated by synthetic polyisoprene analogues, it is of some moment that the crystallization behaviours of the materials vary widely. Thus in a recent investigation[1], employing a calorimetric technique, it was shown that deproteinized natural rubber (DPNR) undergoes crystallization much more readily than synthetic analogues of 99% *cis*-1,4 purity. The difference in crystallizability was shown to be due, at least in part, to the presence of nucleating impurities in the natural product, as had indeed been suggested earlier[2]. However, comparative measurements with acetone-extracted DPNR and stearic acid-doped *cis*-1,4-polyisoprene revealed that a secondary factor was probably operative. It was speculated that small differences in polymer microstructure or molecular weight distribution might have an important influence on the rate of crystallization.

In order to probe the importance of microstructure in crystallization, it was decided to examine the behaviour of synthetic polyisoprenes of different but known microstructure in comparison with purified natural rubber samples. The results of such a study are now reported in this paper.

EXPERIMENTAL

Materials

Natural rubber (DPNR grade) was made available by the Rubber Research Institute of Malaysia. Synthetic rubbers, as stated in the text, are all commercially available high *cis*-1,4-polyisoprene samples, and were used as received for crystallization studies.

DPNR (0.14% N) was further purified by the following procedure. A 5 g sample was sheeted by a single pass on a cold two-roll mill. The sheeted rubber was wrapped in aluminium foil and acetone-extracted in the dark, in a Soxhlet extractor, under nitrogen. After extraction for 24 h the rubber was dried under high vacuum at room temperature, in the dark, for a further 24 h. The rubber was then again sheeted on a two-roll mill and vacuum dried for a further 48 h. The rubber as purified is designated DPNR-AE (0.11% N).

Doped samples of rubber containing 1% w/w of stearic acid were prepared by blending appropriate quantities of the technical grade additive with the rubber on a cold mill.

Nuclear magnetic resonance measurements

Measurements were made on deuterochloroform solutions of the rubbers at 50°C employing a JEOL FX-

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200 spectrometer operated under the following conditions:

	^1H n.m.r.	^{13}C n.m.r.
Data points	8000, double	16 000, double
Sweep width	2000 Hz	8000 Hz
Obs. freq.	199.5 MHz	50.1 MHz
Pulse width	10 μs (45°)	10 μs (45°)
Pulse delay	5.0 s	12.0 s
Acquisition time	2.0480 s	1.0240 s
Sample conc.	12 mg/0.6 ml	300 mg/6 ml

Differential scanning calorimetry measurements

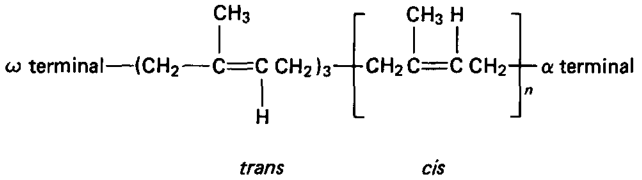
All measurements were made with a Perkin–Elmer DSC-2C calorimeter equipped with an Intracooler II two-stage cooling unit and a dry-box assembly. Dry nitrogen was employed as a purge gas. In order to ensure good reproducibility, the cooling unit was switched on at least 2 h before calibration and allowed to run continuously for periods of up to 6 days. The instrument was calibrated with respect to the melting transitions of water ($T_{\mathrm{onset}} = 273.15$ K) and indium ($T_{\mathrm{onset}} = 429.78$ K) at a scan rate of 10 K min^{-1}.

Rubber samples, about 15 mg, were encapsulated in standard aluminium pans. Two distinct procedures were used for carrying out crystallization. In the first procedure, the rubber sample was held at 400 K for 1 min in the d.s.c. instrument and then rapidly cooled to and held at the temperature of crystallization. In the second procedure, the encapsulated samples were heated at 400 K in an air oven (1 min) and then placed in a chest freezer set at the crystallization temperature. At the end of the annealing period the samples were removed from the freezer and cooled by packing in dry ice. The samples were then transferred to the dry-box of the d.s.c. instrument at dry ice temperature and inserted in the d.s.c. cell at a temperature some 30 K below the crystallization temperature.

In both procedures, the samples were subsequently cooled to 210 K and heated through the melting range at scan rates of 20 K min^{-1}.

RESULTS AND DISCUSSION

Recent high-resolution n.m.r. studies[3–5] of naturally occurring *cis*-polyisoprenes show that the basic polymer structure is essentially a pure *cis*-1,4 main chain capped with terminal groups arising from the biosynthetic precursors:



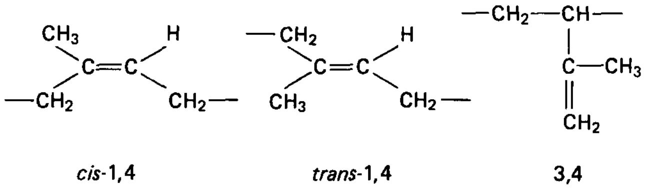
$$\omega\ \text{terminal}-(CH_2-\underset{H}{\overset{CH_3}{C}}=C\,CH_2)_3-\left[CH_2\overset{CH_3}{C}=\overset{H}{C}\,CH_2\right]_n-\alpha\ \text{terminal}$$

(I)

Whereas polyisoprenes extracted from the leaves of golden rod (*Solidago altissima*) and sunflower (*Helianthus annuus*) show the complete structure outlined schematically above, the low-molecular-weight natural rubbers (*Hevea brasiliensis*) so far studied show only the long *cis* sequences and terminal *trans–trans–trans* group. In addition the presence of low concentrations of epoxide and ester groups have been detected in certain *Hevea* rubbers and their determination supports earlier reports[6] of oxygenated groups in natural rubber.

The importance of the above observations in the current context is that whole natural rubber samples, assuming that they are structurally analogous to the low-molecular-weight ($\bar{M}_n = 10\,000$) fractions examined, should be characterized by very long *cis* sequence lengths.

By contrast, the polymerization of isoprene by lithium or Ziegler-type catalysts gives rise to a macromolecule of predominantly *cis*-1,4 (II) microstructure interspersed with *trans*-1,4 (III) and 3,4 (IV) units.



(II) (III) (IV)

The relative content of *cis*-1,4, *trans*-1,4 and 3,4 units may be determined by both ^1H and ^{13}C n.m.r. using assignments and methods described earlier[7,8]. In this study the reported values are based on ^{13}C n.m.r. analysis employing the relative intensity of the methyl carbon which resonates at 23.25 ppm (*cis*), 18.74 ppm (3,4 unit) and 15.76 ppm (*trans*). Additional values for the 3,4 unit content have been determined by ^1H n.m.r. based on the ratio of the olefinic proton resonances which occur at 4.85 and 4.89 ppm (3,4 unit) and 5.25 ppm (*cis* and *trans*).

The content of the isomeric units for the eight synthetic rubber samples are summarized in *Table 1*. With the exception of the Cariflex rubber with a *cis* content of only about 91 mol %, the other samples have somewhat similar microstructure with values in the range 98.3 to 99.1 mol % *cis* units. The determination of the isomeric distribution in the Cariflex sample was triplicated with one set of measurements obtained using gated decoupling. (The gated decoupling technique is very difficult to apply for signals lower in intensity than about 0.5 % due to the low signal/noise ratio.) Comparison of duplicated measurements under similar experimental conditions shows acceptable reproducibility. However, values of the 3,4 unit content measured by ^{13}C and ^1H techniques are not in good agreement despite the excellent reproducibility of the proton measurements. It seems likely that the values deduced from ^1H observations are inflated because of the inclusion of resonances due to terminal 3,4 units which

Table 1 Microstructure of synthetic polyisoprenes

	^{13}C n.m.r.			^1H n.m.r.	
Sample	*cis*-1,4	*trans*-1,4	3,4	3,4	
Ameripol SN 600	99.1	0.6	0.3	0.5	[a]
Nipol IR 2200	98.9	0.8	0.3	0.8	0.8
Kuraprene IR 10	98.8	1.0	0.2	0.7	0.7
CPS-IR	98.9	0.8	0.4	0.6	[a]
JSR IR 2200	98.5	1.2	0.3	1.0	0.9
SKI-3	98.4	1.2	0.4	0.7	0.7
Natsyn 2200	98.3	1.4	0.3	0.8	0.7
Cariflex	90.9	5.2	3.9		
	90.3	5.6	4.1	4.4	4.5
Cariflex	(89.6)[b]	(5.8)[b]	(4.6)[b]		

[a] Gelation of sample precluded measurement

[b] Values obtained by gated decoupling measurement (nuclear Overhauser effect suppressed)

are not counted by the ^{13}C measurement. Work is in hand with model compounds to attempt to resolve this discrepancy.

Comparative crystallization

The synthetic rubber samples together with natural rubber (*Hevea*) samples were crystallized under two distinct sets of conditions. One set of rubbers was doped with 1% w/w of stearic acid whereas the second set was used as received. The reasons for adding stearic acid were twofold: first to mask the effect of any nucleating impurities in the samples and secondly to accelerate the rate of crystallization so as to facilitate the measurements.

The heats of fusion of the various samples under three different crystallization conditions are summarized in *Table 2*. Since the heat of fusion is directly proportional to the crystallinity of the sample, the numerical value thereof may be taken as an index of the sample crystallizability. Inspection of the tabulated results shows that measurements with doped samples after short crystallization times (7 h) are more discerning, in terms of differentiating tendency of crystallize, than longer-term storage of as-received rubbers.

It is immediately apparent that for the series of stearic acid-doped rubbers (column A) the natural rubber sample shows greater facility in crystallization than any of the synthetic analogues. The importance of adding stearic acid to mask the effect of nucleating impurities is seen in column B where the purified natural rubber apparently crystallizes less readily than the Nipol IR2200. This reversal of trend is almost certainly due to the presence of impurities such as antioxidants, which may promote crystallization in the unpurified synthetic rubbers. Further purification of deproteinised natural rubber samples by treatment with $LiAlH_4$ in addition to acetone extraction was not found to inhibit crystallization further compared to the acetone-extracted sample.

Crystallization of the as-received rubbers for 163 h at 239 K (column D) provides samples of somewhat similar crystallinity and with the usual form of melting curve as previously described[1]. The maximum melting temperature (T_{max}) was observed to fall within the range 272–274 K, which is, as expected, slightly lower than that observed for rubbers crystallized at 248 K[1]. The sole exception to the above pattern is the Cariflex sample which showed a T_{max} of 253 K. This must correspond to the formation of much less stable crystallites and must be a direct consequence of the short uninterrupted *cis* sequence lengths.

Table 2 Heats of fusion of both natural and synthetic rubbers after crystallization under varying conditions

Sample	*cis*-1,4 content (mol%)	⟨*cis*⟩[a]	ΔH_m (cal g^{-1})			
			A[b]	B[c]	C[d]	D[e]
DPNR	(100)	–	–	5.8	6.1	6.0
DPNR-AE	(100)	–	3.8	1.8	5.9	6.0
Ameripol SN 600	99.1	110	0.60	0.6	3.5	5.5
Nipol IR 2200	98.9	90	1.8	3.8	5.2	5.3
Kuraprene IR 10	98.8	82	0.99	1.1	4.5	5.7
CPS-IR	98.8	82	0.42	–	3.3	5.5
JSR IR 2200	98.5	66	0.42	–	3.5	5.3
SKI-3	98.4	62	0.63	1.7	4.4	5.5
Natsyn 2200	98.3	58	0.63	–	3.0	5.4
Cariflex	90.9	10	n.d.	–	0	0.43

[a] Average *cis* sequence length assuming random distribution
[b] As-received or purified rubbers, crystallized 16 h at 248 K
[c] Stearic acid-doped, crystallized 7 h at 248 K
[d] As-received rubbers, crystallized 41 h at 243 K
[e] As-received rubbers, crystallized 163 h at 239 K

Table 3 Relationship between heat of fusion and microstructure for grouped rubbers

Group	*cis* content (mol%)	ΔH_m (cal g)[a]
1	100	3.8
2	98.8–99.1	0.95
3	98.3–98.5	0.56
4	90.9	0

[a] Stearic acid-doped rubbers, crystallized for 7 h at 248 K. Values averaged over rubbers in group

An examination of the relationship between crystallizability and microstructure, using the data based on column A, does not provide a completely clear-cut trend. Thus whereas it is evident that the natural rubber samples with the most uniform microstructure show the highest proclivity to crystallize and that the Cariflex rubber with only 90.9 mol% *cis* structure is most resistant, the order of the remaining synthetic rubbers is not strictly regimented according to their microstructure. Probably the most notable exception is the Ameripol sample, which, although having the highest average *cis* sequence length, is only mid-range as far as facility in crystallization is concerned. Whereas individual rubbers may appear out of order, there does appear to be a distinct trend if the rubbers are grouped according to their approximate *cis* content (*Table 3*), and this confirms the importance of microstructure in determining the crystallizability of polyisoprene rubbers.

The reason for the apparent individual exceptions to the general trend relating crystallization rate and microstructure is not clear. The exceptions may partially reflect the difficulty in precise quantitative determination of microstructure by n.m.r. or may be related to differences in *MW* and/or *MWD* among the samples since crystallization rates have been shown to be dependent on *MW* in LLDPE samples[9].

CONCLUSION

Natural rubber (*Hevea braziliensis*) undergoes cold crystallization more rapidly than any of the high *cis*-1,4 synthetic rubber analogues examined. The difference in behaviour has been shown to be mainly due to two factors:

(i) the presence of low-molecular-weight nucleating impurities in natural rubber; and

(ii) the more perfect microstructure in the natural product.

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