# Comparative d.s.c. studies of the crystallization of natural rubber and its synthetic analogues

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A comparative d.s.c. crystallization study has shown that deproteinized natural rubber (DPNR) undergoes crystallization much more readily than synthetic analogues of 99% *cis*-1,4 purity. Acetone extracted DPNR is closer in behaviour to the synthetic materials whereas, the latter, when doped with 1% w/w stearic acid or rubber extract approach the crystallization character of DPNR. The differences in crystallization behaviour are thus largely, but not entirely, due to the presence of nucleating impurities in the natural product. Secondary rate effects may also be caused by slight differences in polymer microstructure or variation in molecular weight distribution. The maximum extent of crystallinity observed under the most favourable conditions approaches 40% for the DPNR samples as determined from the observed heat of fusion of the crystalline regions.

**(Keywords: differential scanning calorimetry (d.s.c.); natural rubber; synthetic polyisoprenes; nucleating impurities)**

## INTRODUCTION

Although the high *cis*-1,4-microstructure of natural rubber can be largely duplicated by synthetic polyisoprene analogues, nevertheless there remain important differences in the properties of the elastomers—some of which have been discussed in earlier publications[1,2]. Distinctive characteristics of the raw rubbers encompass both differences in chemical and physical properties. The former differences are apparent in studies relating to oxidation, *storage hardening* or vulcanization, whereas, the latter show themselves in comparisons of the rheological and strength properties of the materials.

The fundamental causes of these differences are, however, generally not well understood and it is believed that various factors may influence the comparative properties of the elastomers. Thus small differences in microstructure, variation in molecular weight and molecular weight distributions, the presence of *abnormal groups*[3] or non-rubber impurities in natural rubber, have all been cited to explain one or more of the distinctive characteristics delineated above.

An important determinant of elastomeric properties is the morphology of the material. Thus the variable tendency of elastomers to crystallize is one major reason for differences in physical characteristics. The ideal rubber should not be susceptible to crystallization at low temperatures, either on storage or in service as concimitant hardening may prove deleterious to processing efficiency or end product use. Conversely, the ability to crystallize under strain is a prized asset as the resulting rubber crystallites provide a reinforcing effect leading to a higher strength material. These conflicting constraints have stimulated the investigation of factors influencing rubber crystallization and, *inter alia*, have led to the development of modified natural rubbers which are far more resistant to low temperature crystallization[4].

The earliest detailed crystallization studies largely employed dilatometric techniques[5–12], but subsequently, electron microscopic[13–15], X-ray diffraction[16], calorimetric[15–17] and most recently optical turbidmetric[18,19] methods have been utilized. In this work we wish to describe preliminary comparative studies of the crystallization of both natural rubber and synthetic polyisoprenes as revealed by d.s.c. examination. Particular attention has been paid to the influence of non-rubber impurities on the crystallization phenomenon.

## EXPERIMENTAL

### *Materials*

Natural rubber (DPNR grade) and Kuraprene IR10 (a high *cis*-1,4-polyisoprene) were made available by the Rubber Research Institute of Malaysia. A further synthetic high *cis* polyisoprene (Natysyn 2200) was kindly provided by Goodyear, USA. The synthetic materials were used as received.

A 5 g sample of DPNR (%N = 0.14) 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 an atmosphere of oxygen-free 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 sheeted on a two roll mill and again dried for a further 48 h. The rubber as purified is designated DPNR-AE (%N = 0.11).

A small sample of this rubber (0.5 g) was subsequently dissolved in 50 ml of chloroform under nitrogen and in the dark, the solution filtered, and the rubber precipitated by

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pouring into excess methanol. The precipitated rubber was subsequently dried for 48 h under high vacuum, and designated DPNR-AER (%N = 0.10).

### *D.s.c. 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 the purge gas. In order to ensure good reproducibility the cooling unit was switched on for at least 2 h before calibration and allowed to run continuously for periods of up to 6 days. The instrument was calibrated[20] with respect to the melting transitions of water ($T_{onset} = 273.15$ K) and indium ($T_{onset} = 429.78$ K) using a scan rate of 10 K min$^{-1}$.

Rubber samples (10–15 mg) were encapsulated in the standard aluminium pans, heated at 400 K for 10 min and cooled rapidly to the crystallization temperature (248 K) where the sample was maintained for the periods as indicated. At the end of the crystallization period the sample was rapidly cooled to 210 K and the temperature scanned through to 400 K at a heating rate of 20 K min$^{-1}$.

The melting points and heats of fusion were determined with the Thermal Analysis Data Station (TADS) standard program supplied by Perkin-Elmer.

## RESULTS AND DISCUSSION

### *Crystallization of DPNR and synthetic* cis-*1,4-polyisoprenes*

D.s.c. examination of NR samples crystallized at 248 K show well defined melting endotherms for crystallization periods in excess of one hour with crystal growth approximately 75% complete after 3 h (*Figure 1*, *Table 1*). This is quite consistent with the dilatometrically observed[8] crystallization rates of unextracted NR, at this temperature, which are characterized by rapid crystal growth after an initial induction period of around 40 min. The initial period is associated with the slow nucleation of spherulite growth centres. The form of the melting curves showing distinct multiple melting transitions at high levels of crystallinity are quite similar to earlier d.s.c. observations[15] at similar scan rates.

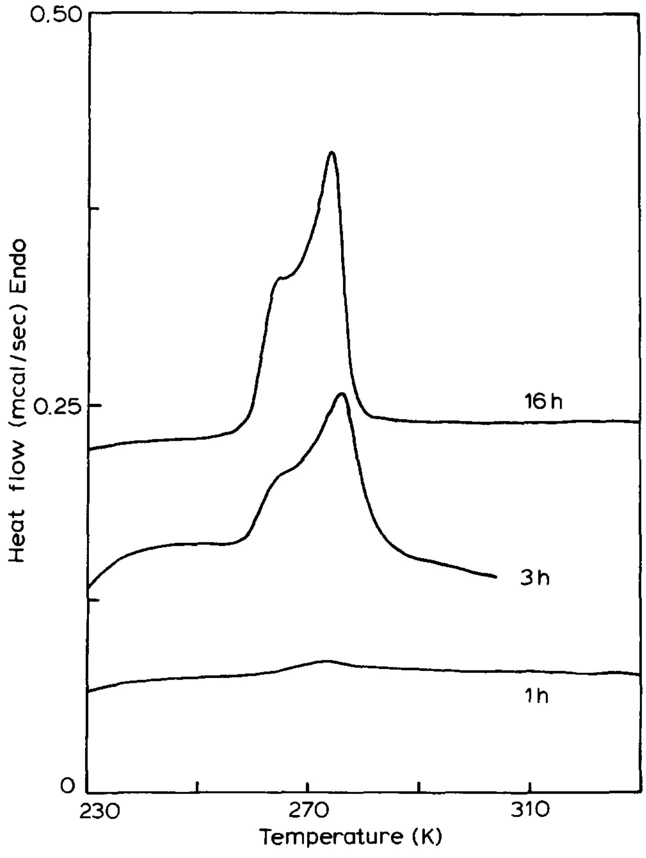

**Figure 1** Melting endotherms of DPNR samples crystallized for various periods at 248 K. (Scans normalized to 1 mg sample size)

**Table 1** Crystallization data for DPNR samples

| Sample | Crystallization[a] time (h) | $T_{max}$[b] (K) | $\Delta H_m$[c] (cal g$^{-1}$) |
|---|---|---|---|
| DPNR | 1 | – | – |
| | 3 | 276 | 4.3 |
| | 16 | 277 | 5.8 ± 0.1[d] |
| DPNR-AE | 3 | – | trace only |
| | 16 | 276 | 1.8 |
| DPNR-AER | 16 | 276 | 1.2 |
| DPNR-AE + 1% Stearic acid | 3 | 274 | 3.8 |
| | 16 | 275 | 6.1 |

[a] All samples crystallized at 228 K

[b] The melting temperature corresponding to the temperature maximum in the melting endotherm

[c] The heat of fusion of the combined melting endotherms

[d] Mean of three determinations

By contrast, the two synthetic samples of *cis*-1,4-polyisoprene show negligible crystallinity after 3 h and only reach about 10% of the DPNR value after 16 h (*Figure 2*, *Table 2*). Quite clearly the crystal growth rates of the synthetic analogues are very much retarded compared to the NR sample. In earlier studies two main explanations have been advanced to rationalize this behaviour: (i) nucleation is assisted in NR by the presence of non-rubber impurities[8,10]; and (ii) the spherulitic growth rates in synthetic polyisoprenes are reduced because of structural irregularities in the rubber mainchain[12,17]. In this particular case $^{13}$C-n.m.r. analysis[22] of the two synthetic rubbers reveal a high degree of regularity in the polymer microstructure (Natsyn-2200: *cis*-1,4 98.4%, *trans*-1,4 1.0% and 3,4 0.6%; Kuraprene IR-10: *cis*-1,4 98.9%, *trans*-1,4 0.7% and 3,4 0.4%) and taking into account the rather small retardation effect of *trans*-1,4 units[4], it seems unlikely that these small differences could explain the distinct crystallization behaviour of the rubbers.

### *Crystallization of purified DPNR*

Acetone extraction of the DPNR sample led to a reduction of about 4% in the weight of the material and this is believed to be principally due to removal of low molecular weight non-rubbers such as fatty acids. This purification had a dramatic effect on the rate of crystallization with minimal observable crystallinity after 3 h and a reduced extent after 16 h (*Table 1*, *Figure 2*). Reprecipitation of the extracted rubber led to a further reduction in the crystallization rate. The crystallinity of the purified NR after 16 h although much reduced is still somewhat greater than the synthetic analogues. This may reflect incomplete removal of nucleating impurities or the intrusion of a secondary factor influencing the crystallization process.

**Table 2** Crystallization data for synthetic polyisoprene samples

| Sample | Crystallization time (h) | $T_{max}$ (K) | $\Delta H_m$ (cal g$^{-1}$) |
|---|---|---|---|
| Natsyn 2200 | 3 | – | n.d. |
| | 16 | 274 | 0.59 ± 0.03 |
| Natsyn 2200 + 1% Stearic Acid | 3 | 273 | 0.09 |
| | 16 | 275 | 4.6 |
| Natsyn 2200 + 3.5% w/w Rubber Extract | 16 | 274 | 4.5 |
| Kuraprene IR-10 | 16 | 274 | 0.59 |
| Kuraprene IR-10 + 1% Stearic Acid | 16 | 276 | 4.3 |

Conditions as for *Table 1*. n.d. – no detectable melting transition

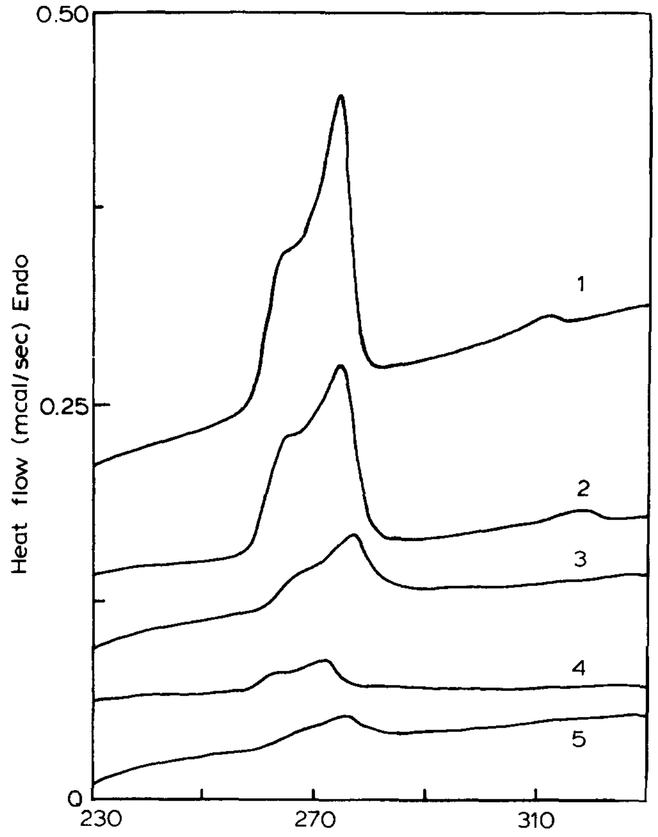

**Figure 2** Comparison of the melting endotherms of various rubber samples crystallized for 16 h at 248 K: 1-DPNR-AE+1% stearic acid; 2-Natsyn-2200+1% stearic acid; 3-DPNR-AE; 5-Kuraprene IR-10. (Scans normalized to 1 mg sample size)

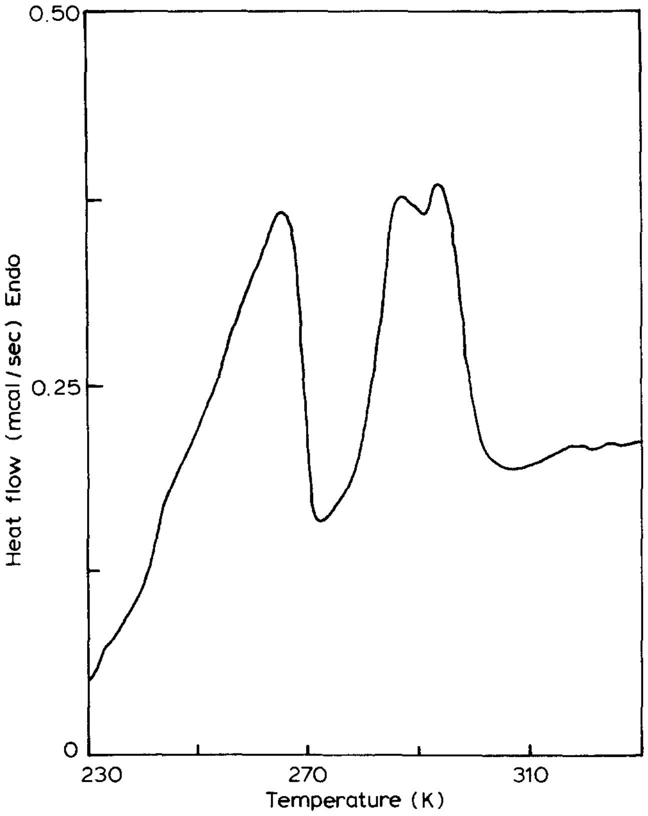

**Figure 3** Melting transitions of rubber extract cooled rapidly to 210 K. (Sample weight 6.3 mg)

D.s.c. analysis of the acetone extract (*Figure 3*) showed the presence of at least two distinct crystallizable species with maximum melting temperatures of approximately 265 K and 287 K respectively. Such species when present in the rubber matrix would provide nuclei for crystal growth at the temperature employed in this study (248 K).

An expanded d.s.c. scan of the unextracted DPNR (*Figure 4*) shows the presence of an additional crystallizable species with maximum melting temperatures of 326 K. (The peaks due to the acetone extractable material are largely submerged under the rubber crystallization peak). There is evidence that the above impurities are not completely removed by extraction/reprecipitation and hence may influence the crystallization patterns.

### *Crystallization of doped samples*

If the acetone extract is responsible for the enhanced crystallizability of the material then addition of the extract to the synthetic polymer should have an activating effect. This is indeed the case (*Table 2*, *Figure 2*). However, the extent and rate of crystallization is still lower than the analogous DPNR sample as judged by the heat of fusion ($\Delta H_m$) after both 3 and 16 h periods (compare *Tables 1* and *2*).

Stearic acid has been long known to serve as a nucleating agent and addition of this species at a 1% w/w level to both DPNR-AE and synthetic rubber samples leads to enhanced crystallizability as in the case of the addition of the rubber extract. However, again the natural sample demonstrates a greater facility in crystallization. Rather interestingly in the case of the DPNR sample, $\Delta H_m$ is somewhat higher after crystallization in the presence of stearic acid than for the original unextracted sample (*Table 1*). This suggests that stearic acid added at a 1% level is in fact slightly superior in action to the original acetone soluble non-rubbers at a 4% w/w level.

### *Crystallization of polymer blends*

Blends of DPNR with Natsyn (2200) were prepared at

**Table 3** Crystallization behaviour of DPNR)NATSYN blends

| Composition of blend | Crystallization time (h) | $T_{max}$ (K) | $\Delta H_m$ (cal g$^{-1}$) |
|---|---|---|---|
| 10% DPNR | 16 | 273 | 0.77 |
| 25% DPNR | 16 | 273 | 3.5 |
| 50% DPNR | 3 | 273 | 0.35 |
| | 16 | 274 | 5.6 |

Conditions as for *Table i*

various levels of NR content and subjected to overnight crystallization. There is a clear interaction between the two materials (*Table 3*). At low levels of NR (10% w/w) the crystallization appears inhibited possibly due to a dilution of the nucleating impurities and the extent of crystallization ($\Delta H_m = 0.77$ cal g$^{-1}$) is only slightly more than for the unblended Natsyn ($0.59 \pm 0.03$ cal g$^{-1}$). In contrast at levels exceeding 25% w/w a synergistic effect[12] is observable and the 50/50 blend develops a crystallinity approaching that of the original DPNR. This would appear to suggest that the concentration of structural defects in the sy‘nthetic material is not sufficient to interfere with the extent of crystallization *vis à vis* NR.

### *Extent of crystallization*

Using the average of the two literature values[16,21] for the heat of fusion for natural rubber crystals (15.5 cal g$^{-1}$) it is possible to estimate the degree of crystallinity of the various samples studied. This reveals a maximum observed value of almost 40% for extracted DPNR doped with 1% stearic acid. Unpurified DPNR samples show crystallinity of 28% after 3 h and 37% after 16 h at 248 K. Unblended but doped synthetic rubbers (stearic acid or rubber extract) shows a maximum crystallinity of just below 30% after overnight crystallization.

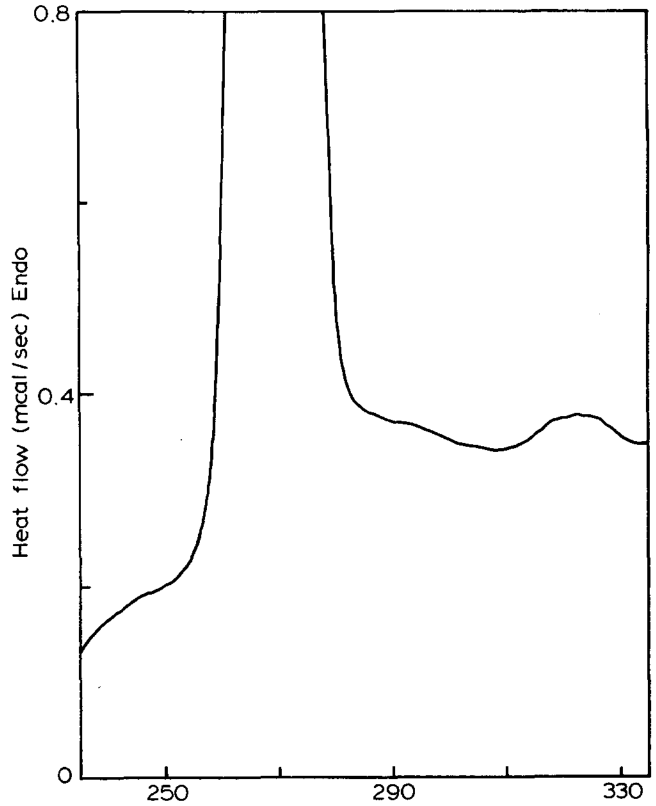

**Figure 4** Expanded d.s.c. scan of crystallized DPNR showing the presence of crystallizable non-rubber impurities. (Sample weight 15 mg)

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