Glass transition and crystallization phenomena in epoxidized *trans*-polyisoprene: a differential scanning calorimetry study

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The effect of epoxidation of *trans*-1,4-polyisoprene (TPI) on the glass transition temperature T_g and crystallization of the polymer has been investigated by differential scanning calorimetry. The value of T_g is shown to be linearly dependent on the extent of chain modification, and increases from 201 K for the unmodified polymer to 274 K for complete epoxidation. The modification inhibits the extent of crystallization, and above 25 mol% epoxidation little or no cold crystallization occurs at 263 K. The extent of crystallization is found to fit a previously proposed relationship: $\log(\Delta H_m) = \log k + n \log x_A$, where ΔH_m is the heat of fusion, k a constant, n the critical sequence length of repeating units for crystallization to occur and x_A the mole fraction of unmodified repeat units. For TPI, values of $n = 6$–7 are found for samples crystallized at 263 K.

(Keywords: *trans*-1,4-polyisoprene; epoxidation; differential scanning calorimetry glass transition; crystallization)

INTRODUCTION

Recently there has been renewed interest in the epoxidation of unsaturated polymers and the product derived from natural rubber (NR) is proving to be of considerable commercial interest. The physical properties of epoxidized natural rubber (ENR) have been shown[1–3] to be dependent on the epoxide content and this has meant that compositional analysis of the product is of some importance. Thermal analysis techniques, in particular the d.s.c. measurement of the glass transition temperature (T_g), have proved exceptionally useful since there is a linear correlation between T_g and epoxy content[3–5].

Trans-1,4-polyisoprene (TPI), the configurational isomer of NR, shows some distinct characteristics on d.s.c. examination[6]. Thus TPI has a marginally lower T_g ($\sim$4–5 K) in its amorphous state and more importantly is semicrystalline at ambient temperatures since the melting point is about 325 K. By contrast NR may only be crystallized by low-temperature storage since the melting point is close to 275 K[7]. Because of these significant differences it seemed of interest to examine the thermal properties of epoxidized TPI (ETPI) of varying composition to determine the dual effect of modification on both T_g and degree of crystallinity.

This paper therefore reports on the synthesis, characterization and thermal properties of a series of ETPI samples covering the compositional range from 0 to 75 mol%.

EXPERIMENTAL

Materials

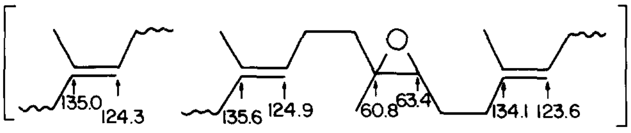
Synthetic *trans*-1,4-polyisoprene of about 99% isomeric purity was kindly supplied by Dunlop Ltd, UK. Peracetic acid was freshly prepared by the interaction between acetic anhydride and hydrogen peroxide, as described elsewhere[8].

Synthesis of epoxidized trans-*1,4-polyisoprene*

The modified polymer was prepared by the addition of appropriate amounts of freshly prepared peracetic acid to a 2% w/v stirred solution of TPI in chloroform at 273 K. After 5 h the product was isolated by methanol precipitation and purified by reprecipitation from chloroform. The product was vacuum dried at 323 K for 48 h.

Polymer characterization

The epoxy content of the samples was determined by either direct HBr titration[4,9] (epoxy content ≤ 15 mol%) or n.m.r. analysis[4,10,11], as detailed earlier. Whereas the proton n.m.r. spectrum of partially epoxidized TPI is effectively identical to the analogous *cis* polymer under moderate resolution, the ^{13}C n.m.r. spectrum is characterized by significant differences in chemical shift. For the latter, the observed shifts referenced to $CDCl_3$ at 77.04 ppm are summarized below for the olefinic and epoxide ring carbons at low levels of epoxidation:



As before, the epoxy content was determined from the ratio of the area of epoxy proton or carbon peaks to olefinic proton or carbon peaks, respectively. Relative areas of proton peaks were determined by weight ratio whereas carbon peaks were evaluated by electronic integration. The n.m.r. values presented in this paper are the mean of the carbon and proton determinations.

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Differential scanning calorimetry analysis

All d.s.c. measurements were made with a Perkin–Elmer DSC-2C calorimeter employing either a liquid-nitrogen sub-ambient cooling accessory (T_g measurements) or a two-stage cooling unit (fusion measurements). The instrument was calibrated as described in detail elsewhere[6,12]. For T_g measurements, the encapsulated sample ($\sim$10 mg) was heated at 400 K for 1 min and quench cooled to 150 K. The sample was then scanned at a rate of 20 K min^{-1} to a temperature at least 20 K above the observed transition. Quoted T_g values are the onset temperature as computed with the Thermal Analysis Data Station (TADS) program supplied by Perkin–Elmer.

Crystallization studies

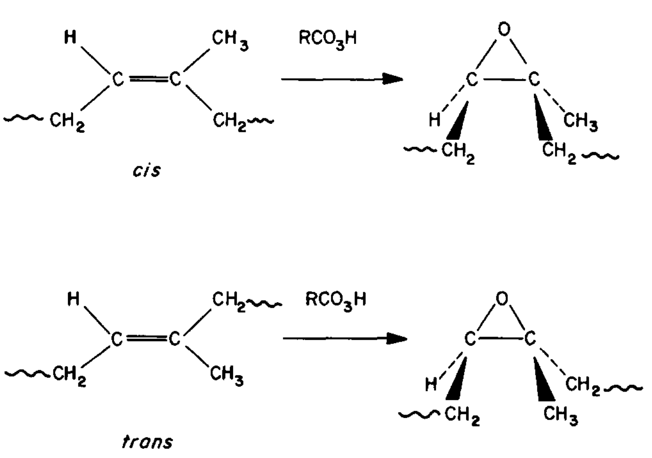
Preliminary studies showed that the as-prepared samples did not all exhibit observable fusion phenomena since the melting point (T_m) of some of the epoxidized polymers was below ambient temperatures. Accordingly, encapsulated samples were preconditioned by heating at 343 K, allowing to cool to ambient temperatures, followed by annealing at 263 K for 4 days. The samples were subsequently cooled to dry-ice temperatures and inserted into the D.S.C. at 210 K before scanning upwards at 20 K min^{-1}. Maximum and onset fusion temperatures were computed with the TADS program cited above.

RESULTS AND DISCUSSION

Synthesis and structure of epoxidized trans-1,4-polyisoprene

Epoxidized polymers are readily formed by the interaction of polydienes with peracids, and the reaction is essentially quantitative. For reactions at or below ambient temperatures and in the absence of strong acid catalysis, side-reactions are negligible. In the present studies, epoxidation was found to be essentially quantitative and no ring-opened products are detectable by ^{13}C n.m.r. (*Figure 1*).

An interesting feature of peracid epoxidation is that it is a concerted reaction occurring with retention of configuration. Thus the peracid epoxidation of *cis*- and *trans*-1,4-polyisoprene may be represented as:



and gives rise to distinct *cis* and *trans* epoxide units, respectively.

^{13}C n.m.r. studies confirm that this is the case since the secondary epoxide carbons have distinct chemical shifts of 64.5 and 63.4 ppm for the *cis* and *trans* epoxides, respectively. This difference is important because, as has been discussed elsewhere[13], it permits demonstration that the naturally occurring epoxide groups in NR, detected by ^{13}C n.m.r.[14], are of a *cis* configuration and hence must arise from a stereospecific route. This rules out a free-radical oxidation process, which is known to yield predominantly *trans* epoxide[15].

A consequence of the stereospecific nature of the epoxidation reaction is that the products derived from epoxidation of *cis*- and *trans*-1,4-polyisoprene are not

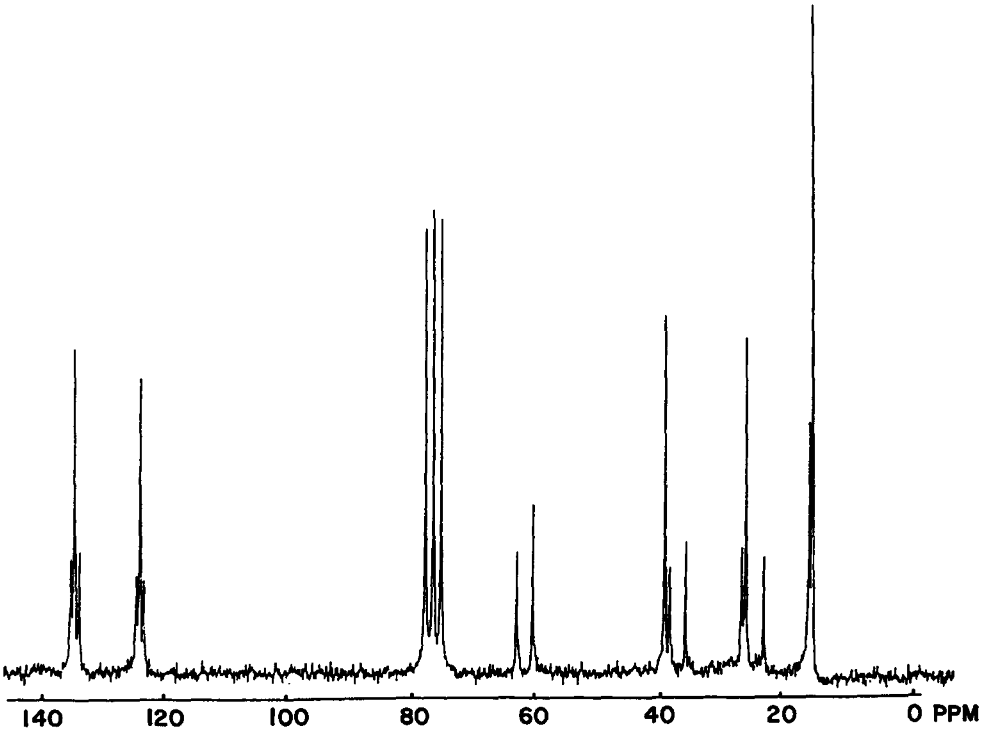


Figure 1 ^{13}C n.m.r. spectrum of partially epoxidized *trans*-1,4-polyisoprene

structurally identical and hence may exhibit different physical properties.

Glass transition temperature of epoxidized trans-*1,4-polyisoprene*

Progressive main-chain modification of polydienes invariably leads to an increase in the value of T_g because of lowered rotational freedom of the modified segments. Epoxide modification is no exception, as demonstrated in *Figure 2*, where the glass transition temperature increases in step with the level of modification. Exactly analogous behaviour has been observed elsewhere for epoxidized samples of polybutadiene[16] and NR[1–5].

In this case, the T_g of the quenched amorphous polymer is found to increase from a low of 201 K for unmodified TPI to an extrapolated value of 274 K for the completely epoxidized material. This is equivalent to a T_g increase of 0.73 K (mol%)$^{-1}$ and compares with a value of 0.85 K (mol%)$^{-1}$ observed[4] for ENR.

Crystallization behaviour

The thermal curve of the annealed unmodified TPI (*Figure 3*) shows a pronounced melting endotherm with $T_{m(max)} = 325$ K and enthalpy of fusion of 17.7 cal g^{-1}. This contrasts with values of $T_{m(onset)} = 277$ K and $\Delta H_m =$ 6.1 cal g^{-1} for NR samples crystallized under optimum conditions[7,12]. Clearly the *trans* isomer undergoes more extensive crystallization and forms more stable crystallites than the *cis* analogue. This is to be expected since the *trans* configuration is more readily packed into the crystal lattice.

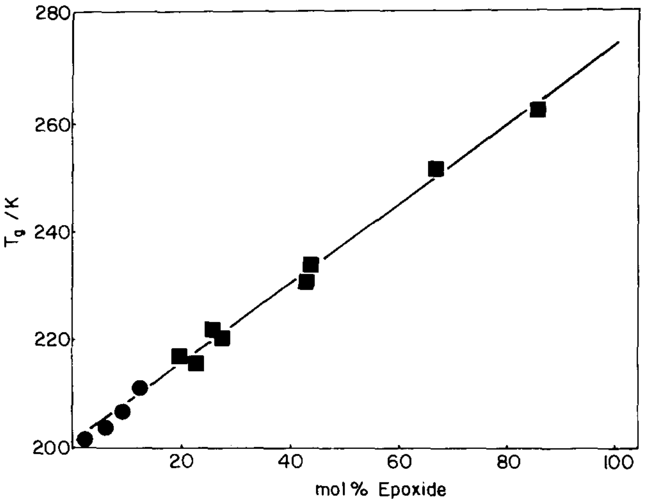


Figure 2 Relationship between the glass transition temperature and molar composition of epoxidized TPI: (●) data from HBr measurements; (■) mean of n.m.r. measurements

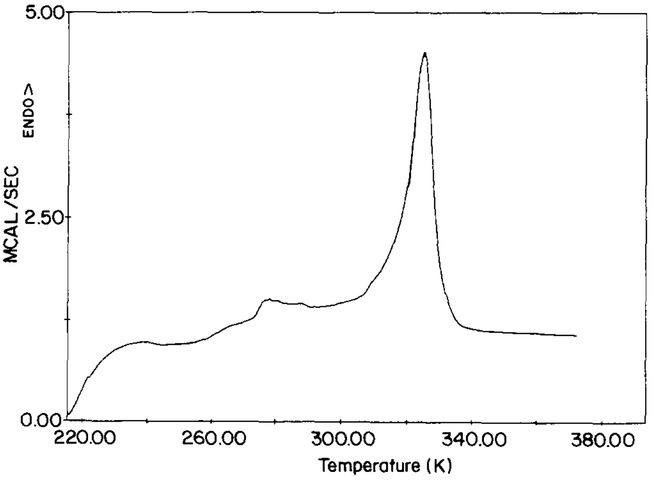


Figure 3 Thermal curve for unmodified TPI crystallized at 263 K for 4 days; scan rate = 20 K min^{-1}

Table 1 D.s.c. fusion data for crystallized epoxidized TPI[a]

Epoxy content (mol%)	$T_{m(onset)}$ (K)	$T_{m(max)}$ (K)	ΔH_m (cal g^{-1})
0	316	325	17.7
1.6	313	322	16.5
5.2	311	320	14.2
5.8	306	319	11.6
8.0	292	309	10.1
8.4	293	312	10.6
11.9	274	294	7.67
15.6	274	286	6.05
16.0	274	285	5.67
24.7	274	280	2.90

[a] Samples crystallized for 4 days at 263 K and scanned at 20 K min^{-1}

Incorporation of the oxirane ring into the polymer main chain is shown to have a significant effect on inhibition of crystallization (*Table 1*). Above 25 mol% little or no crystallization occurs and in the intermediate regions the melting temperature decreases progressively from 325 K for the unmodified material to as low as 280 K at 25 mol%. It is perhaps surprising that crystallization occurs at all at this level of modification and points to the fact that the oxirane ring exerts a rather small steric effect and that the overall chain configuration is retained on modification. The rather small steric effect of the oxirane ring is consistent with earlier observations relating to studies of strain-induced crystallization of ENR[2].

In previous crystallization studies of polypropylene[17], ethylene–propylene (EP) copolymers[18] and linear low-density polyethylene (LLDPE) copolymers[19,20] it has been shown that the extent of crystallization can be treated on a statistical basis. Thus for a polymer containing crystallizable units (A) randomly interspersed with non-crystallizable units (B), the observed extent of crystallization, as measured by the enthalpy of fusion (ΔH_m), is described by the relationship:

$$\Delta H_m = k x_A^n \qquad (1)$$

where k is a constant, x_A the mole fraction of crystallizable units and n the critical sequence length for crystallization. This equation may be expressed in a logarithmic form, which assists evaluation:

$$\log(\Delta H_m) = \log k + n \log x_A \qquad (2)$$

Since the peracid epoxidation of polyisoprenes is observed to be a random process[5,10], equation (2) should be applicable to ETPI samples. *Figure 4* confirms that such is the case. Evaluation of the slope of the logarithmic plot reveals a value of $n = 6.5$, and infers that at 263 K a minimum uninterrupted sequence length of between 6 and 7 repeat units or 24–28 main-chain carbon atoms is necessary for crystallization to occur. Values ranging between 10 and 20 main-chain carbon atoms have been deduced for ethylene copolymers studied at temperatures below 273 K[20].

Although it is difficult to make exact comparisons, it would appear the TPI forms less stable crystallites than

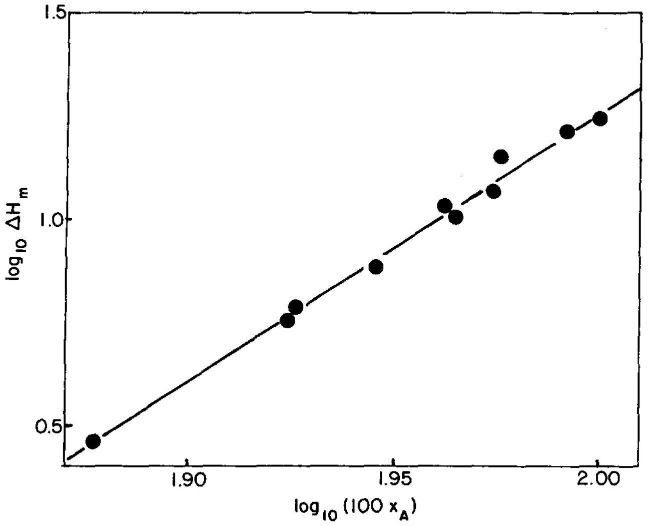


Figure 4 A logarithmic plot showing the relationship between ΔH_m and the molar composition of epoxidized TPI

polyethylene and this would be consistent with the added difficulty of accommodating the structurally rigid double bond into the crystal lattice.

A further comparison may also be made with very recent crystallization studies of TPI, where the polymer was crystallized from solution at 273 K[21]. By complete epoxidation of exposed isoprene units contained in folds, non-crystallizing chain ends and interlamellar traverses, the authors were able to demonstrate that the average number of repeat units in a chain traverse through the crystal core was approximately 15. This value is approximately twice the calculated minimum sequence length for crystallization to occur.

CONCLUSIONS

Epoxide modification of TPI leads to an increase in T_g that is very similar to the behaviour of its *cis* analogue, NR. The presence of the epoxide ring disrupts the process of crystallization and hence there is little tendency for cold crystallization above a 25 mol% composition. Analysis of the inhibition of crystallization indicates that the formation of stable crystallites requires a minimum uninterrupted sequence length of approximately 6–7 repeat units.

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