

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

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(Received 3 January 1989; accepted 24 February 1989)

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 shown¹⁻³ 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 content³⁻⁵.

Trans-1,4-polyisoprene (TPI), the configurational isomer of NR, shows some distinct characteristics on d.s.c. examination⁶. Thus TPI has a marginally lower T_g (~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 K⁷. 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

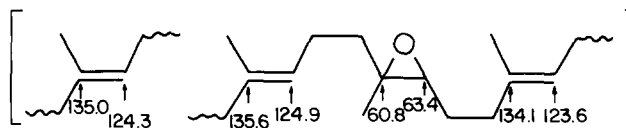
acid was freshly prepared by the interaction between acetic anhydride and hydrogen peroxide, as described elsewhere⁸.

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 ¹³C n.m.r. spectrum is characterized by significant differences in chemical shift. For the latter, the observed shifts referenced to CDCl₃ 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 (~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.

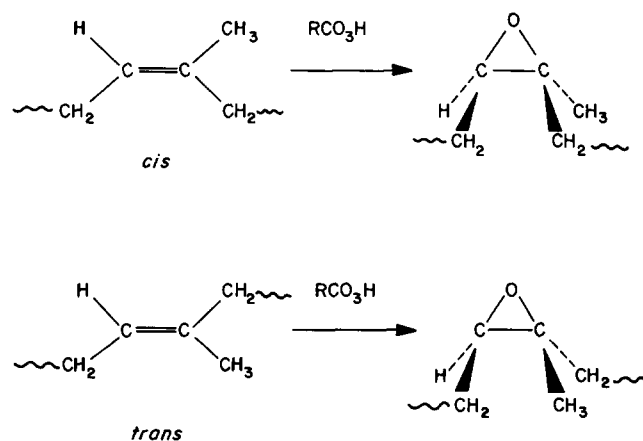
RESULTS AND DISCUSSION

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 ¹³C 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.

¹³C 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 elsewhere¹³, it permits demonstration that the naturally occurring epoxide groups in NR, detected by ¹³C 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* epoxide¹⁵.

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

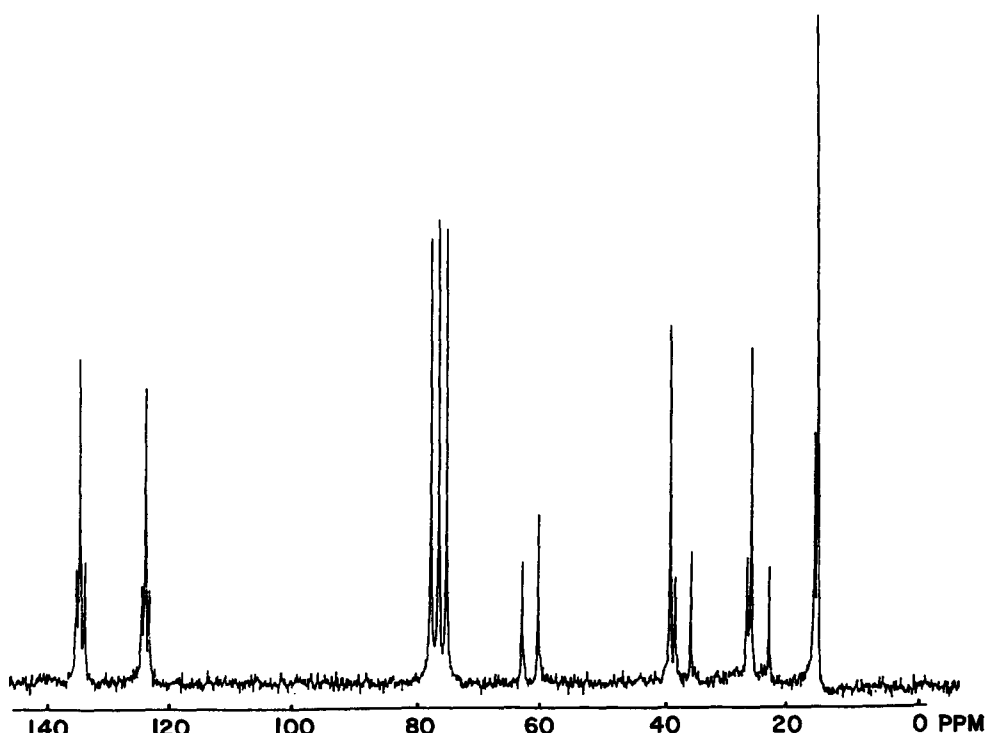


Figure 1 ¹³C n.m.r. spectrum of partially epoxidized *trans*-1,4-polyisoprene

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