Strain crystallization in random copolymers produced by epoxidation of *cis* 1,4-polyisoprene

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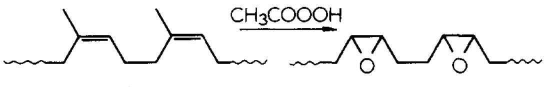
Cis 1,4-polyisoprene has been chemically modified by reaction with peracetic acid. By this method a series of random copolymers were produced containing epoxy co-units on the main chain. These materials have previously been shown to have a number of interesting properties. They exhibit a resistance to swelling by hydrocarbon oils and retain the high strength typical of *cis* 1,4-polyisoprene. The strain induced crystallization behaviour has been studied by X-ray techniques and it has been found, somewhat surprisingly, that the ability to crystallize is retained even by materials containing 95 mole % epoxy co-units. The volume of the polymer crystal unit cell increases considerably, by more than 8%, as the fraction of epoxy co-units on the main chain increased. These effects are attributed to the inclusion of the co-units in the polymer crystals. The high tensile strength of these copolymers is attributed to the retention of the ability to strain crystallize and to an increase in the glass transition temperature.

Keywords Crystallization; strain; polyisoprene; epoxidation; copolymer; strength

INTRODUCTION

The high fracture strain and tensile strength of crosslinked *cis* 1,4-polyisoprene (natural rubber) has long been attributed, in part, to the phenomenon of strain crystallization[1]. Crystallinities of up to 30% have been measured, depending on the elongation, temperature and crosslink density[2-4]. The introduction of *trans* 1,4 units on to the main chain of *cis* 1,4 polyisoprene and *cis* 1,4-polybutadiene, producing *cis/trans* random copolymers, has been shown to reduce considerably the tensile strength (*Figure 1*)[5,6]. It is well documented that copolymerization can affect crystallization and crystal structure in thermally crystallized copolymers. In particular, the crystallinity of such systems is often reduced considerably even at low comonomer concentrations[7-9]. This is partly due to the tendency of comonomer units to be rejected from the crystalline phase.

Elastomers best suited to applications requiring a good hydrocarbon oil resistance are those with polar groups on the polymer chain. It is possible to chemically modify *cis* 1,4-polyisoprene to produce a molecule with epoxy groups on the main chain. The natural rubber latex is reacted with peracetic acid resulting in the addition of oxygen at the C=C double bonds as shown below:



If this reaction is carried out under the correct conditions, a random copolymer results and the fraction of epoxy co-units can be accurately controlled[10]. While a number of authors[11-13] have studied the nature of this reaction, little has been reported on the mechanical properties of the modified polymers. Some published work[13], (*Figure 1*) suggested that the tensile strength of the polymers fell rapidly with increasing comonomer concentration. However, this observed reduction in

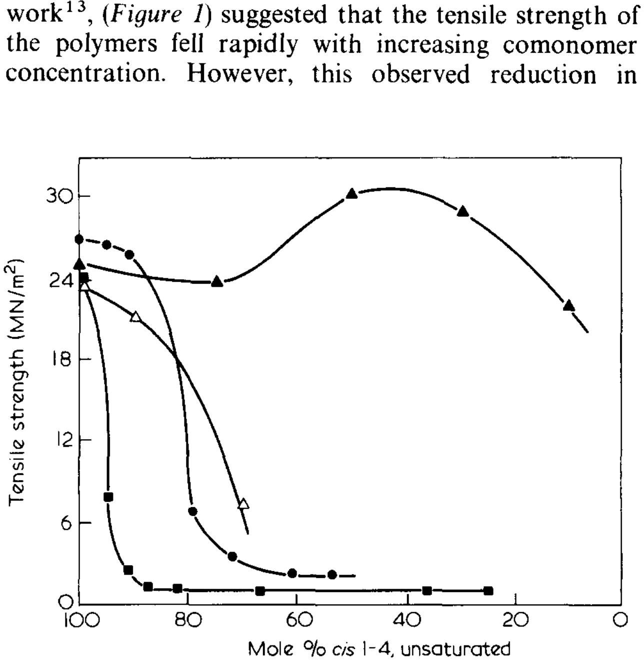


Figure 1 Tensile strength of random copolymers based on *cis* 1,4-polyisoprene. Epoxidized *cis* polyisoprene: (▲) present work; (△) ref 13; (●) isomerized *cis* polyisoprene, ref 5; (■) isomerized *cis* polybutadiene, ref 6

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tensile strength was associated with a large increase (56%) in hardness suggesting that during preparation some epoxide groups had ring-opened[10]. The material was thus no longer a pure random copolymer but contained other structures with high glass transition temperatures. More recent work[10] has shown that copolymers can be produced for which very little reduction in tensile strength is observed (*Figure 1*). This suggests that strain crystallization may occur in the copolymer to a not dissimilar extent from that of the homopolymer. Little data exist on strain crystallization of random copolymers but it is usually found that chemical modification of polymers, including *cis* 1,4-polyisoprene, greatly reduces their ability to crystallize. Thus the implication that crystallization of molecules containing up to 95 mole % co-units can occur is somewhat unexpected. It is known that the large driving force for crystallization provided by the strain energy causes homopolymers to strain crystallize at a temperature well above the melting point of crystals formed in unstrained polymers. It may be that a similar driving force will be of sufficient magnitude to cause a strained random copolymer to crystallize and that the resulting crystals may contain a significant proportion of co-units if these are not too different geometrically from the unmodified units.

The present work was undertaken to investigate the effect of partial expoxidation upon the strain crystallization behaviour and the nature of the crystalline phase in *cis* 1,4-polyisoprene.

EXPERIMENTAL

All materials were produced from an aqueous natural rubber (Hevea) latex concentrate with a 60% dry rubber content. The epoxidation reaction was carried out using the latex diluted to 20% dry rubber content with distilled water and stabilized with Ethomeen 18/60, a non-ionic surfactant. The resulting latex was cooled in an ice–water mixture and a 35 mass per unit volume % solution of peracetic acid (free from mineral acids) was added slowly over a period of two hours. The amount of peracetic acid was carefully controlled in order to ensure a stoichiometric balance of reactants, e.g. for an epoxidation level of 10 mole %, 0.1 moles of peracetic acid was required per mole of rubber. The temperature was maintained below 20°C for 16 hours, after which time the latex was coagulated by the addition of methanol. The coagulated rubber was thoroughly washed with water whilst lightly milling and then dried in air at 50°–60°C.

Table 1 Crosslinking formulation for epoxidized rubber

Constituent	Proportion by mass
Cis 1,4-polyisoprene (natural rubber)	100
Zinc oxide	5
Stearic acid	2
Flectol H	2
Sulphur	2.5
MOR	0.6

For epoxidation levels above 50%, the dry rubber content of the latex was further reduced to avoid high acid concentrations and the formation of epoxy ring-opening reaction products[10].

The epoxidized rubber was crosslinked using sulphur as the vulcanizing agent. Zinc oxide and stearic acid were used as the activator system together with 'Flectol H' as an anti-oxidant and a sulphenamide type accelerator, 2 (morpholinothio) benzothiazole (MOR). The exact formulation used is given in *Table 1*. In all cases, samples were crosslinked by hot pressing to comparable moduli as measured by a Monsanto rheometer at 150°C. The modulus at this temperature, remote from the glass transition temperature, is largely dependent on the crosslink density. This procedure ensures a similar crosslink density in all the samples. These data together with the cure times and tensile strength results are shown in *Table 2*.

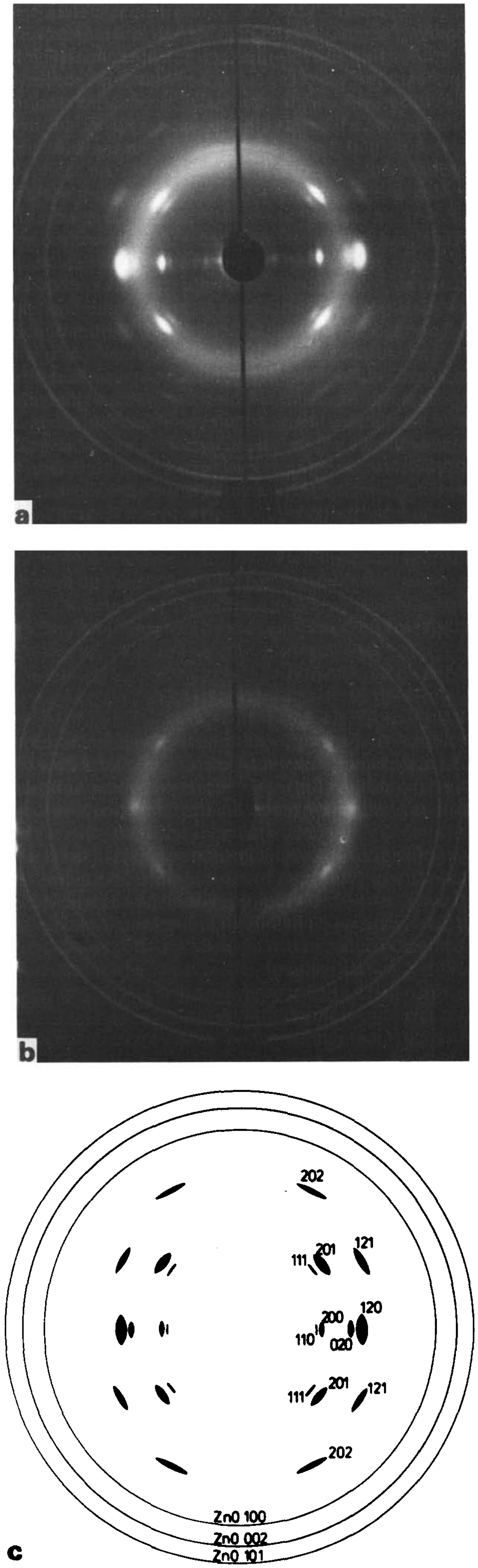
The degree of epoxidation was determined using '^{1}H n.m.r.' spectra and elemental oxygen analysis. The ^{1}H n.m.r. spectra were determined from solutions of the polymers in deuterochloroform (HMDS 0.05 ppm). The relative areas of the resonance peaks at $\delta = 5.05$ ppm, (for the olefinic *cis* 1,4-polyisoprene proton) and at $\delta = 2.75$ ppm (for the corresponding proton in the epoxidized molecule) were used. Good agreement was found between the two methods although there was a tendency for the ^{1}H n.m.r. technique to yield slightly higher values of epoxy content.

Glass transition temperatures were determined using a Perkin Elmer D.S.C. A 10 mg sample was heated at 10°C per minute over the temperature range -120°C to $+60$°C and the glass transition temperature (T_g) determined from the resulting d.s.c. traces. At a later stage of the work epoxide levels were determined routinely from T_g measurements based on an elemental oxygen ^{1}H n.m.r. calibration curve.

Wide angle X-ray diffraction techniques were used to measure the degree of crystallinity and the unit cell dimensions $(\underline{a},\underline{b},\underline{c})$ of the strained polymer samples. Nickel filtered Cu Kα radiation was used with an accelerating voltage of 40 kV and a 30 mA filament current. 1 cm wide strips of the polymer were stretched to the required extension at 20°C in approximately 25 s and

Table 2 Properties of polymers

Epoxidation level mole %	Cure time at 150°C/min	Monsanto Rheometer torque rise (Nm)	Physical properties		
			Stress at 100% extension (MN/m^2)	Tensile strength (MN/m^2)	Extension at break %
Cis 1,4-polyisoprene (natural rubber)	31	2.9	0.74	25.8	760
ENR – 25	33	2.8	0.69	24.1	789
ENR – 50	25	3.0	0.78	30.9	762
ENR – 70	21	3.0	0.96	28.4	622
ENR – 95	22	3.1	1.49	21.9	587



clamped in position. X-ray exposures of $1\frac{1}{2}$–2 hours at 20°C were made, depending on the particular polymer. A Statton box camera with pin-hole collimators was used and the diffraction patterns were recorded on flat plate film. The spacings and intensities of the diffraction maxima were measured using a Joyce and Leoble double-beam recording microdensitometer.

The polymers all contained a small proportion of unreacted zinc oxide which was used as an internal standard for the determination of the polymer crystal lattice spacings. The ZnO (100) and (002) reflections were used for calibration where $2\theta_{100} = 31.783°$ and $2\theta_{002} = 34.475°$. An orthorhombic unit cell was assumed for the polymer crystals[14,15] and the (200), (120) and (201) reflections were used for the calculation of the *a*, *b* and *c* lattice parameters.

The crystallinity of the samples was determined using a similar technique to that described by Field[16], Goppel and Arlman[17,18] and others[3,19], namely the comparison of amorphous halo intensities. This technique is the most suitable to the measurement of strain crystallization in elastomers as the principal amorphous halo is not seriously affected by the diffraction arcs from the crystalline phase and the totally amorphous polymer is available for separate study. The percentage crystallinity (χ_c) of a stretched specimen is assumed to be given by:

$$\chi_c = \frac{100(I_u - I_s)}{I_u}$$

where I_u is the intensity of the amorphous halo of the unstrained specimen at a given azimuthal angle and I_s is the intensity of the amorphous halo of the strained specimen at the same azimuthal angle. The intensities I_u and I_s are only comparable if the amorphous and semicrystalline specimens have the same scattering mass and absorption characteristics. If this is not the case, corrections must be applied to the measured intensity. The intensities of the polymer amorphous haloes were determined directly from the microdensitometer traces by measuring the peak height at a constant azimuthal angle. In order that the intensities I_u and I_s be comparable all measured values were standardized against the intensities of the zinc oxide internal standard reflections at the same azimuthal angle. As all the samples contained the same concentration of zinc oxide per unit volume, it was assumed the the intensity of the zinc oxide reflections was proportional to the thickness of the specimens.

RESULTS AND DISCUSSION

X-ray diffraction patterns from a *cis* 1,4-polyisoprene sample and from a sample containing 70 mole % epoxy co-units both stretched 400% are shown in *Figure 2a* and *b*, respectively. Both patterns show clear evidence of the presence of oriented polymer crystals in the samples. The diffraction arcs in the copolymer are less intense and have

Figure 2 X-ray diffractions patterns from *cis* 1,4-polyisoprene (a) and from a copolymer containing 70 mole % epoxy units (b). The pattern indexing is as in (c)

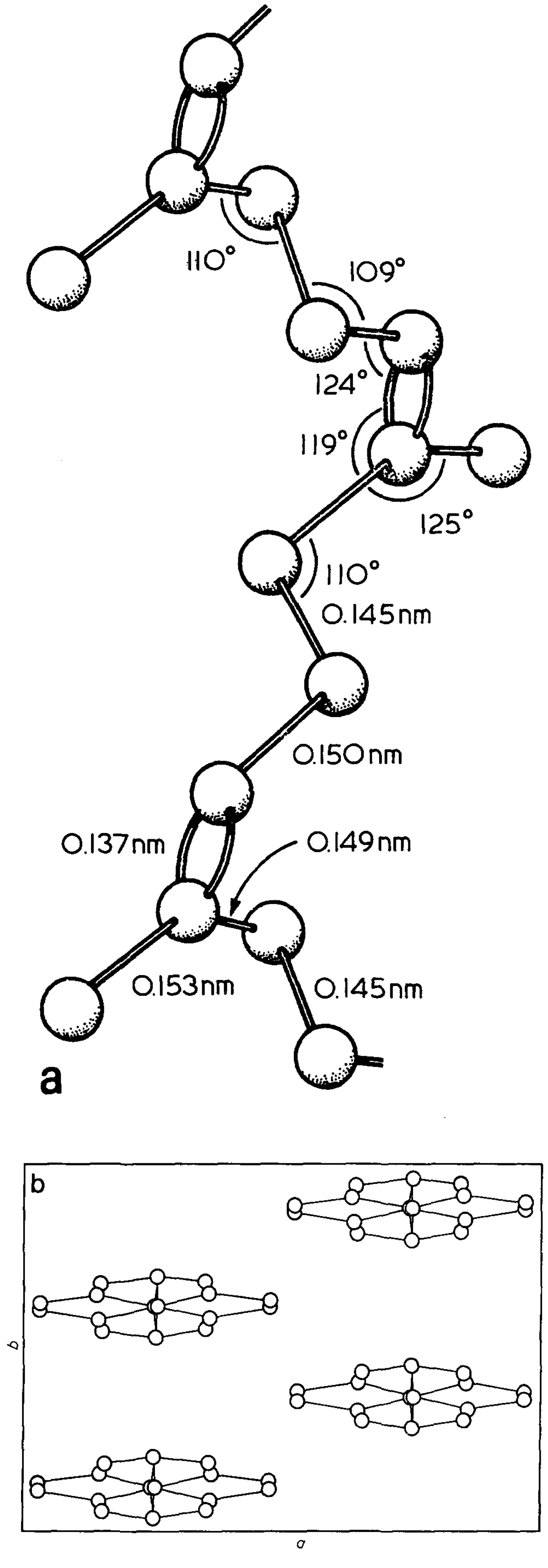


Figure 3 Molecular arrangement within the *cis* 1,4-polyisoprene unit cell (a) shows the two isoprene units in the *c* direction. (b) Shows the four molecules per unit cell projected onto the *a–b* base plane

moved to positions corresponding to larger interplanar spacings. The magnitude of the displacement is much greater than the width of a diffraction peak. The degree of polymer crystal orientation in the two samples is not dissimilar. The prominent diffraction rings from the zinc oxide standard are also seen, together with the diffuse maxima from the amorphous part of the semi-crystalline polymers.

The diffraction maxima from the samples were indexed (see *Figure 2c*) assuming an orthorhombic unit cell for the polymer crystals. The unit cell of *cis* 1,4-polyisoprene has been described as orthorhombic or monoclinic by various investigators[14,15,19,20]. However the monoclinic cells differ only in that one angle is 92° rather than 90°, a difference which does not significantly affect the calculation of the lattice parameters in the present study. Four long chain molecules pass through the unit cell parallel to the *c* axis. The *c* repeat length of each molecule contains two isoprene units as shown in *Figure 3a.* The arrangement of the four molecules within the unit cell is illustrated in *Figure 3b* which is a plane projection in the *c* direction on to the *a–b* base plane of the cell.

Some initial experiments were carried out to determine the effect of the magnitude of the strain on the 'apparent' lattice parameters of the crystals in *cis* 1,4-polyisoprene. These were designed to determine the degree of precision with which it was necessary to strain the samples. It can be seen (*Figure 4*) that the measured values of the lattice parameters *a*, *b* change as a function of strain. However the change is small in the region of 400% strain. It was therefore decided to strain all samples to 400% ± 10%. The explanation for the 'apparent' change in lattice parameter is not simple. The crystals form continuously during the straining process, no matter how rapid. There is some evidence to suggest that the final degree of crystallinity is dependent on the strain rate[22]. The crystals therefore form from a melt which is orientated to various degrees and they may themselves be subsequently strained, both effects being dependent on the applied stress. The measured 'apparent' lattice parameters hence depend both on the resulting lattice defect concentration in the crystals and the stress to which the crystals are subject. These effects are probably minimized at high strains, as the degree of crystallinity increases rapidly with strain and the majority of crystals are formed from the same melt at the same strain at a constant stress.

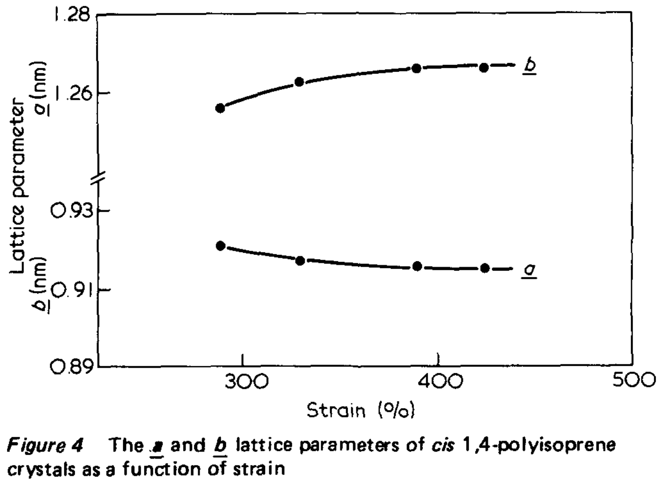
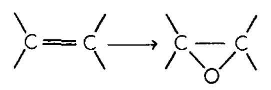


Figure 4 The *a* and *b* lattice parameters of *cis* 1,4-polyisoprene crystals as a function of strain

The variations in lattice parameters, calculated from the (200), (120) and (201) reflections, as a function of percentage epoxy co-units are shown in *Figures 5–7*. It can be seen that the value of $\underline{a}$ decreases considerably, $\underline{b}$ increases considerably and $\underline{c}$ increases slightly. The lattice parameters measured for *cis* 1,4-polyisoprene compare favourably with those determined by Kawai *et al.*[15] but are rather larger than those determined by Bunn[20]. The overall effect is a considerable increase in unit cell volume (*Table 3*) as the fraction of co-units on the polymer chain increases.

The percentage crystallinity in the samples was determined from the variation of the peak intensity of the amorphous halo. This was measured at a single azimuth (75°) which was accepted as being representative of the overall amorphous intensity. This has been shown to be true of orientated amorphous *cis* 1,4-polyisoprene[19]. The variation of percentage crystallinity with percentage co-units, for samples strained 400%, is shown in *Figure 8* and the numerical values are given in *Table 3*. The crystallinity of the *cis* 1,4-polyisoprene is comparable with that determined by Nyburg[3] and Goppel and Arlmann[18]. The percentage crystallinity remains practically constant in samples containing up to 50% co-units and then decreases considerably as the co-unit content increases further (*Figure 8*).

The samples being studied are random copolymers, confirmed by ^{13}C n.m.r. with a certain fraction of the C=C double bonds being replaced by epoxy units (as shown below) with retention of the *cis* configuration of the polymer backbone[23].



The unit cell dimensions and the fraction crystallinity in the samples are determined, in part, by the fraction of co-

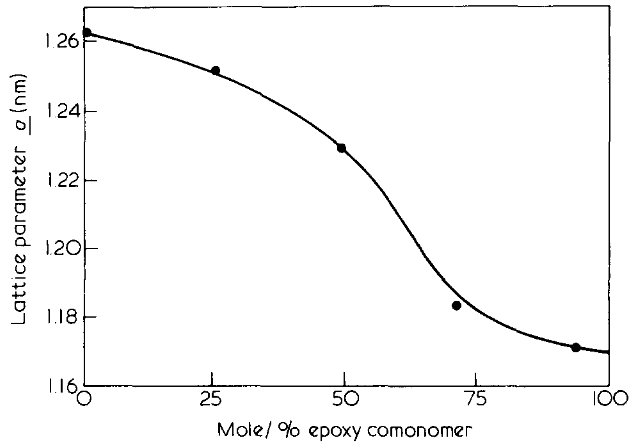


Figure 5 $\underline{a}$ Lattice parameter for the copolymers as a function of mole % epoxy comonomer

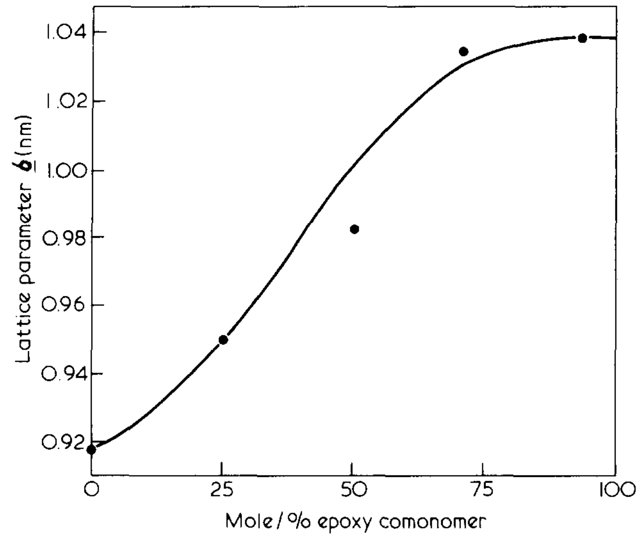


Figure 6 $\underline{b}$ Lattice parameter for the copolymers as a function of mole % epoxy comonomer

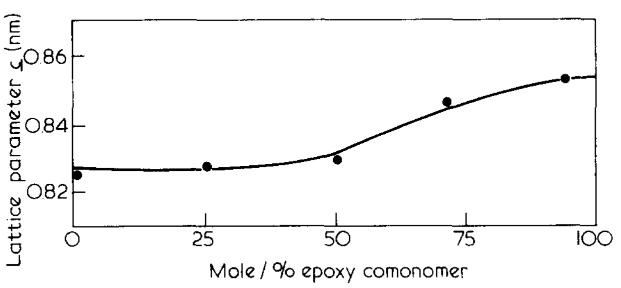


Figure 7 $\underline{c}$ Lattice parameter for the copolymers as a function of mole % epoxy comonomer

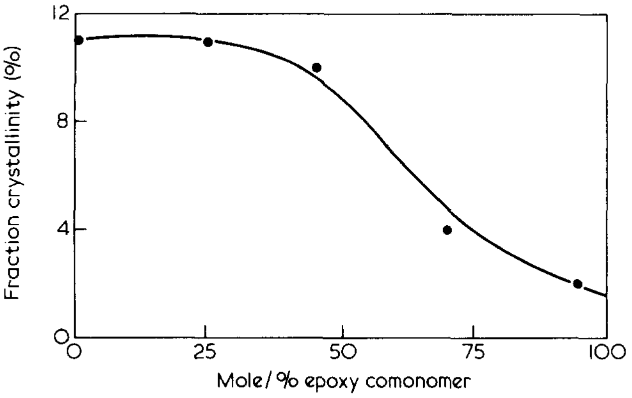


Figure 8 Strain crystallinity of the copolymers as a function of mole % epoxy comonomer for samples strained 400%

Table 3 Lattice parameters, unit cell volumes, degrees of crystallinity and glass transition temperatures for random copolymer samples

Sample	*a* lattice parameter (nm)	*b* lattice parameter (nm)	*c* lattice parameter (nm)	Unit cell volume (nm^3)	Degree of crystallinity (%)	Glass transition temperature (°C)
NR	1.263	0.917	0.824	0.955	11	−69
25 mole % ENR	1.254	0.950	0.827	0.985	11	−48
50 mole % ENR	1.230	0.982	0.827	0.999	10	−27
75 mole % ENR	1.183	1.035	0.846	1.036	4	−9
95 mole % ENR	1.172	1.038	0.852	1.036	2	+10

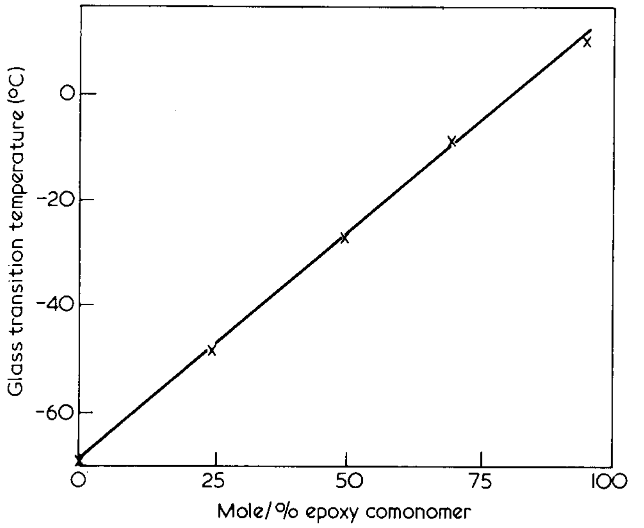
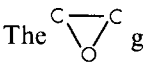


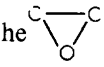
Figure 9 Glass transition temperatures of the copolymers as a function of mole % epoxy comonomer

units which are included in the crystals. Thermally induced crystallization of random copolymers generally takes place relatively slowly and considerable segregation of comonomer units into the amorphous phase normally occurs[9,24]. However, in the present case large numbers of comonomer units are likely to be incorporated into the crystals as a result of both the rapid crystallization rate and the large driving force for crystallization provided by the strain energy. When comonomer units are included in the crystalline phase of a copolymer, they are considered to behave as defects in a homopolymer matrix[25,26]. The inclusion of defects in a crystal lattice is known to dilate the crystal unit cell of short chain molecules[27] and has also been shown to have similar effects in some copolymer systems[27–29]. However the magnitude of the effect observed here appears to be much greater than that reported for any similar system.

In the present case the fact that the unit cell volume increases by 8.4% (*Table 3*) strongly suggests that a considerable fraction of the comonomer units are included in the crystals. Further support is given to this suggestion by the fact that the usually observed decrease in crystallinity in copolymer systems[7,8] is not observed until the polymer molecules contain more than 50% comonomer units (*Figure 8*). It should be noted that at these high concentrations the crystallinity decreases but the unit cell volume shows little change (*Table 3*) which suggests that a limit to the fraction of co-units which can be incorporated into the crystals is reached.

Although the overall unit cell volume increases with the fraction of co-units, *Figures 5–7* show that the lattice parameters change in different senses; $\underset{\sim}{a}$ decreases while $\underset{\sim}{b}$ and $\underset{\sim}{c}$ increase. The change in the c lattice parameter is considerably smaller than the changes in the other two dimensions. The c direction is the chain direction and any increase in $\underset{\sim}{c}$ is determined largely by the length of the co-unit. The  group is approximately 0.01 nm larger than the C=C double bond and would cause a corresponding increase in the length of the co-unit. The *cis* 1,4-polyisoprene unit cell contains two isoprene units in the c direction[20], *Figure 3a*. The maximum effect, due to this increase in bond length, would be a change of approximately 0.02 nm in $\underset{\sim}{c}$, which is comparable to the measured change (*Figure 7*). The $\underset{\sim}{a}$ and $\underset{\sim}{b}$ unit cell dimensions vary to a far greater extent. These variations must be due to configurational changes of the copolymer chains relative to each other within the unit cell, in order to incorporate the oxygen atoms (*Figure 3b*). The detailed X-ray work, necessary to specify the exact configurations of the copolymer molecules has not, as yet, been carried out.

At first sight it might be surprising that the epoxide group can be incorporated into the crystal lattice, in the strained polymer, so relatively easily when a *trans*-isoprene co-unit is incorporated only with great difficulty, if at all. This appears to be due to both geometrical and chemical factors. The *cis* configuration is rigorously maintained during the epoxidation and the oxygen atom occupies a relatively inconspicuous volume. Both these factors suggest that only minor geometrical rearrangements of the molecular packing are necessary on inclusion of epoxy groups. The inclusion of the polar epoxy groups is likely to lead to some hydrogen bonding between molecules. While this may aid inclusion it is probably responsible for the major changes in the $\underset{\sim}{a}$ and $\underset{\sim}{b}$ lattice parameters, $\underset{\sim}{a}$ decreasing and $\underset{\sim}{b}$ increasing with increasing mole % epoxy co-units.

This work was initially undertaken in an attempt to ascertain why the tensile strength of these epoxidized random copolymers remained high while that of other copolymers based on *cis* 1,4-polyisoprene decreased dramatically as the fraction of comonomer units on the molecules increased, (see *Figure 1*). It can now be seen that the explanation, in part, is that these copolymers retain the ability to strain crystallize and hence crack propagation is delayed until large strains are achieved and high energies are available. This is not however the complete explanation as the copolymers retain a high tensile strength even when the fractional crystallinity decreases (*Figure 1*). Furthermore the 50/50 copolymer has the maximum tensile strength (*Figure 1*. It was in an attempt to explain this phenomenon that the glass transition temperatures, T_g, of the copolymers were determined. It can be seen in *Figure 9* that T_g increases almost linearly with comonomer content, increasing by nearly 79°C to almost 10°C for the 95% epoxy sample. These results in themselves are evidence of the absence of chemical side reactions occurring during epoxidation which would cause epoxide ring-opening, resulting in hard thermoplastics with glass transition temperatures greater than 100°C[30,31]. The higher glass transition temperatures found in the present materials are probably the result of the hydrogen bonding between molecules, as the replacement of the C=C bond by the  epoxy group would certainly not make the molecule less flexible. The increase in the glass transition temperature with increasing comonomer fraction would clearly tend to increase the tensile strength if the fraction crystallinity remained constant and compensate for any drop as the crystallinity decreased. Furthermore the increase in the glass transition temperature would tend to cause a reduction in the strain to fracture. All these effects are in fact observed. The tensile strength increases when the crystallinity is constant and decreases as the crystallinity decreases (*Figure 1*, *Table 3*) and the strain to fracture continuously decreases as the comonomer content increases (*Table 2*).

CONCLUSIONS

Epoxy copolymers based on *cis* 1,4-polyisoprene strain crystallize even when containing 95 mol % epoxy co-units, although the degree of crystallinity is considerably diminished when more than 50 mole % epoxy co-units are present. The significant crystallization in samples containing up to 50 mole % epoxy co-units is the result of the co-units being included in the crystals giving rise to a considerable dilation of the unit cell. The magnitude of this dilation ($\simeq 8\%$ by volume and 10% in individual lattice constants) is much larger than any previously reported, to the authors' knowledge. The tensile strength of the random copolymers remains high as a result of the retention of the ability to strain crystallize and the increase in the glass transition temperature.

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