Polybutadiene modified by epoxidation. 1. Effect of polybutadiene microstructure on the reactivity of double bonds

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The reactivity of low-molecular weight sodium polybutadiene (1,2-PB) and n-butyllithium polybutadiene (1,4-PB) has been studied during epoxidation with peracetic acid. The effect of the epoxy groups formed on the polymer solution viscosity has also been investigated. It was found that the rate constant of 1,4-PB epoxidation is ~1.9 times greater than that for 1,2-PB of a similar molecular weight. The reactivity of various structural polymer unit forms was studied by spectroscopic methods (i.r. and ^{1}H n.m.r.); it was found that reactivity depends on chain microstructure in the following way:

for 1,2-PB: trans-1,4 > *cis*-1,4 ⩾ 1,2

for 1,4-PB: cis-1,4 > *trans*-1,4 ⩾ 1,2

An increase in the limiting viscosity number was observed with increasing epoxy content in the 1,2-PB chain, but the opposite effect was observed for 1,4-PB. The solubility parameter, δ, for both kinds of epoxy polybutadiene was found to be similar (19.8×10^3 J$^{1/2}$ · m$^{-3/2}$).

INTRODUCTION

Epoxidation of polydienes with various organic peracids has been studied by many authors[1–9], who have investigated the kinetics of the reaction, the reactivity of the double bonds and the effect of some reaction parameters on the number of epoxy groups introduced into the polymer chain. In the oxidation of polybutadiene with peracids the double bonds of the pendant vinyl groups were found to be less reactive than the double bonds in the main chain[2–5]. The reactivity of the latter depends on the *cis–trans* isomerism, but there is no unanimity as to which of these isomers is more reactive[3,4].

The epoxidation of polybutadiene with peracetic acid proceeds only partly, and after the reaction there are two kinds of epoxy rings, depending on the chain microstructure – i.e. epoxy groups in the main chain (internal groups) and in pendant groups (external groups).

These active centres can participate in crosslinking through both epoxy groups and double bonds, and a knowledge of the influence of epoxy groups on the properties and crosslinking of epoxypolybutadienes is of considerable importance.

In our earlier papers[10,11] the optimization of the epoxidation of low molecular weight poly(butadiene-co-styrene) was reported as well as the influence of styrene content on the rate of epoxidation of double bonds in poly- and copolybutadiene obtained in the presence of sodium metal as catalyst.

The present paper deals with the reactivity of polybutadienes of varying structure during epoxidation with peracetic acid as well as the effect of the epoxy groups obtained on the conformation of the macromolecule in solution and its glass transition temperature. These epoxypolybutadienes were crosslinked with dicumyl peroxide, and the effect of the polymer chemical structure on crosslinking efficiency is discussed in Part 2[12].

EXPERIMENTAL

Chemical modification of polybutadiene

Polybutadiene was obtained by anionic polymerization in a hydrocarbon solvent in the presence of a metallic sodium dispersion[13,14] or n-butyllithium[15] as catalysts. The sodium polybutadiene is referred to as 1,2-polybutadiene (1,2-PB), and n-butyllithium polybutadiene as 1,4-polybutadiene (1,4-PB). Characterization of these polymers is given in *Table 1.*

The epoxidation of polybutadiene was carried out in toluene solutions using acetic acid and hydrogen peroxide, a 60 wt % aqueous solution in a 1:2 molar ratio, in the presence of a strong-acid cation exchanger, Xenonit SD. The concentration of hydrogen peroxide was 1 mole per mole of double bonds. In all experiments a constant stirring rate was used, and the temperature of the reaction was kept at 303 to 318K to within ±0.5K.

Samples of the reaction mixture were taken periodically, neutralized with anhydrous sodium carbonate, dried over anhydrous magnesium sulphate and finally separated by distillation under reduced pressure at 308K.

Epoxidized polybutadiene containing 0.58 mole epoxy groups was obtained under optimized conditions as reported earlier[10].

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Table 1 Effect of polymer type on the reaction rate of epoxidation, k_2, and $\tau_{0.25}$ value at various temperatures

	Polybutadiene		
Property	1,2-	1,2-	1,4-
Limiting viscosity number $[\eta]$ (toluene, 298K)	0.216	0.470	0.170
Number-average molecular weight, $\bar{M}_n$	4000	6100	6000
Double bond content, mol (100 g)$^{-1}$			
1,2-configuration	1.10	0.99	0.22
1,4-configuration	0.41	0.42	1.37
$k_2' \times 10^{-5}$ dm^3 mol^{-1} s^{-1} at			
303K	2.95	3.55	6.67
308K	4.33	5.00	7.83
313K	7.30	8.51	6.83
318K	10.17	13.33	–
Quarter-time of the reaction $\tau_{0.25}$ ks at			
303K	11.0	7.2	3.3
308K	8.7	5.4	2.4
313K	5.2	3.6	2.6
318K	3.2	2.0	–

Analyses

Polymer molecular weights were determined by vapour pressure osmometry with a Mechrolab instrument using benzene as solvent. The polymer microstructure was determined by i.r. spectroscopy with a Perkin–Elmer instrument (CCl_4 solutions), and ^1H n.m.r. spectra were recorded with a Tesla BS-487 instrument (8 wt % CCl_4 solutions) using TMS as an internal standard.

The epoxy group content was determined by addition of HCl in dioxane solution; the degree of conversion of double bonds to epoxy groups was calculated from the following relationship:

$$x' = C_e/C_0$$

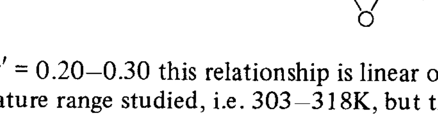
where C_e is the epoxy group content, in mole (100 g of polymer)$^{-1}$ and C_0 is the content of butadiene units containing double bonds, in mole (100 g)$^{-1}$.

Viscosities were determined in an Ubbelhode-type viscometer at 298K, and the limiting viscosity number was determined by a graphical method.

RESULTS AND DISCUSSION

The epoxidation of low-molecular-weight polybutadienes of various structures was carried out with peracetic acid formed *in situ* from acetic acid and hydrogen peroxide.

The degree of conversion of double bonds into epoxy groups, x', during the reaction according to the scheme below for 1,2-PB is shown in *Figure 1.*



Up to $x' = 0.20$–0.30 this relationship is linear over the temperature range studied, i.e. 303–318K, but the slope of the curve changes after a certain degree of epoxidation had been reached.

A decrease in the epoxy group formation rate at 313 and 318K after 4 and 6 ks, respectively, may be brought about by secondary reactions of the epoxy ring causing ring-opening under the influence of reaction substrates (CH_3COOH). The effect of these secondary reactions becomes more pronounced with increasing time of epoxidation, i.e., with an increase in the epoxy group content in the macromolecule; this was confirmed by i.r. data. *Figure 2* shows spectra of 1,2-BP epoxidized at 318K after various reaction times. The presence of hydroxyacetyl groups was identified by the absorption band at 1740 cm^{-1} which appeared in the reaction product spectra after 9 ks at 318K, and after 12 ks at 303K.

The linear character of the relationship shown in *Figure 1* may indicate that initially the reaction mechanism may be second order with respect to the reaction product.

Epoxidation of high molecular weight polydienes proceeds according to a second order reaction mechanism[6,8,9]. The reaction rate constant, k_2', was evaluated from a relationship describing a second order reaction at equimolar concentrations of reagents and after the previous introduction of a degree of transformation of functional groups at the time t:

$$k_2't = 1/C_0(1 - x')$$

where C_0 is the initial concentration of double bonds in the polymer (mol cm^{-3}); x' is the degree of transformation of double bonds into epoxy groups; and k_2' is the combined reaction rate constant of the reaction giving epoxy group formation along the chain.

A plot of $1/C_0(1 - x')$ vs. reaction time at 303K is shown in *Figure 3. Table 1* gives values of the calculated rate constant, k_2', up to a degree of conversion of the double bonds of $x' = 0.25$, as calculated by the least-squares method. The effect of the viscosity of the polymer solution on the peracetic acid diffusion rate into the organic phase was neglected in the kinetic analysis. It was found that the rate constant, k_2', increases with increasing temperature indicating that the process proceeds in a kinetically-controlled region. The rate constant for 1,4-PB is 2.3 times as high as that for 1,2-PB at similar viscosities of their toluene solutions $[\eta]$, and is 1.9 times as high as that for 1,2-PB of a similar molecular weight. The higher reactivity of 1,4-PB as compared with that of 1,2-PB is related to differences in the reactivity of double bonds of different configuration. The relative reactivities of particular structural forms of polybutadiene were determined by i.r. and ^1H n.m.r. The

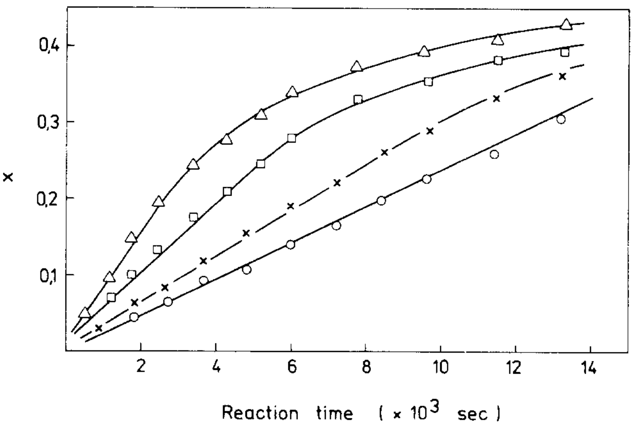


Figure 1 Dependence of degree of conversion of double bonds, x', on the time of epoxidation for 1,2-polybutadiene. ○, 303K; x, 308K; □, 313K; △, 318K

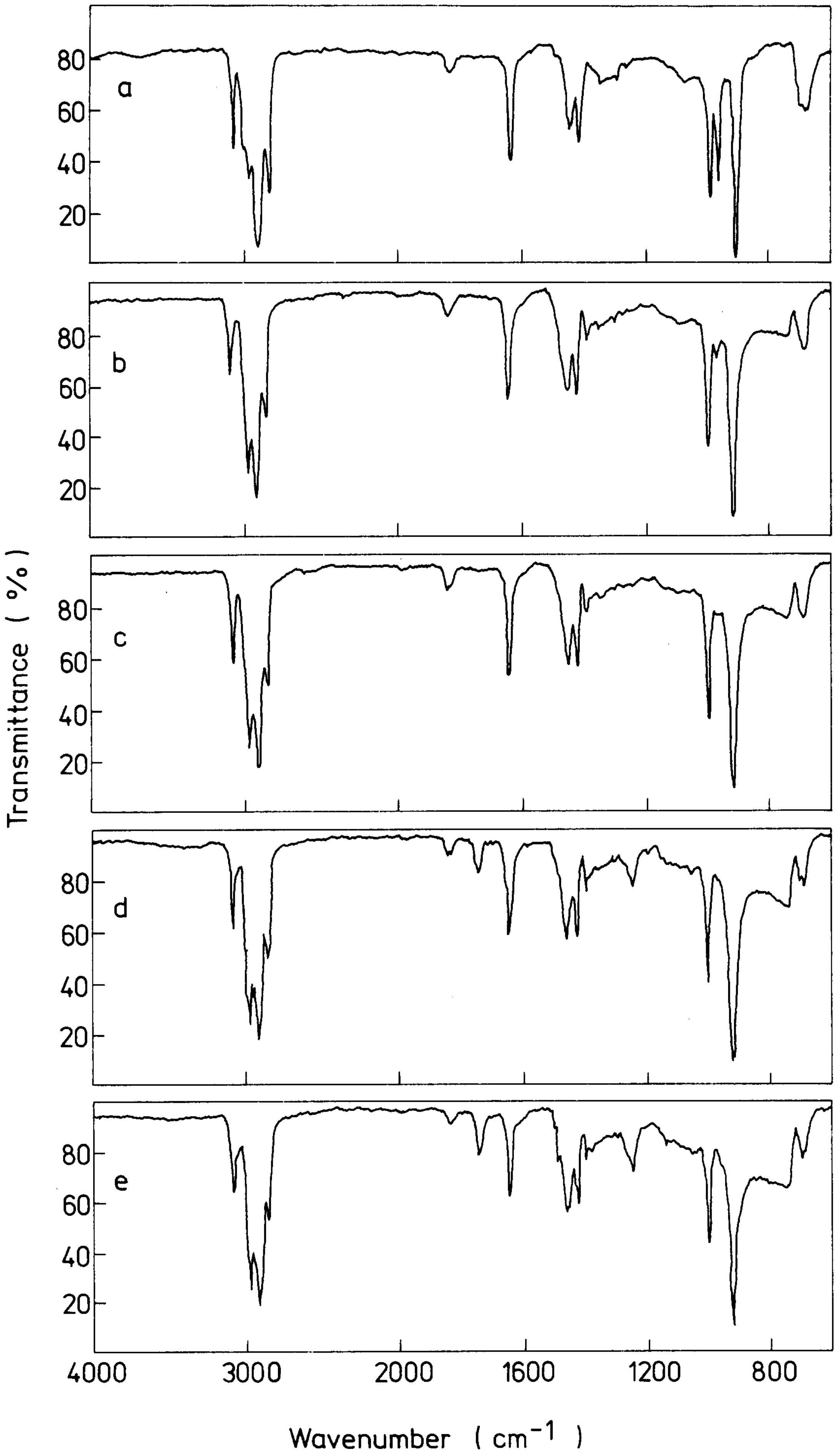


Figure 2 Infrared spectra of 1,2-polybutadiene after various reaction times (ks) at 318K: (a) 0; (b) 3.0; (c) 5.0; (d) 9.0; (e) 15.6

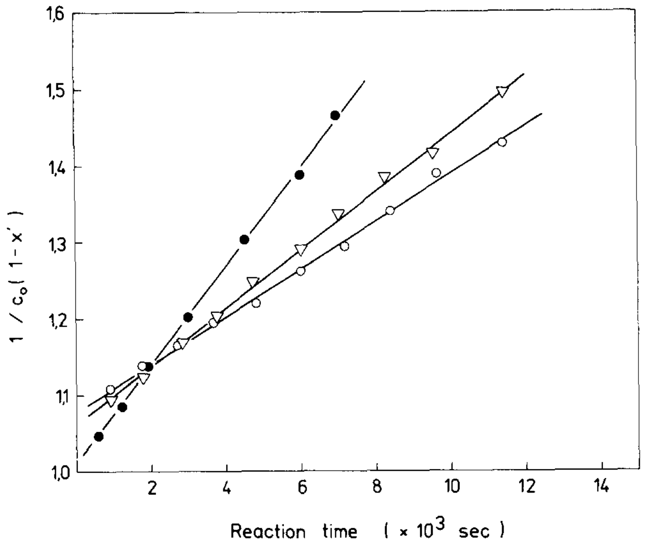


Figure 3 Relationship between $1/c_0$ $(1-x')$ and epoxidation time at time at 303K: ○, 1,2-polybutadiene, $[\eta] = 0.216$; ▽, 1,2-polybutadiene, $[\eta] = 0.470$; ●, 1,4-polybutadiene, $[\eta] = 0.170$

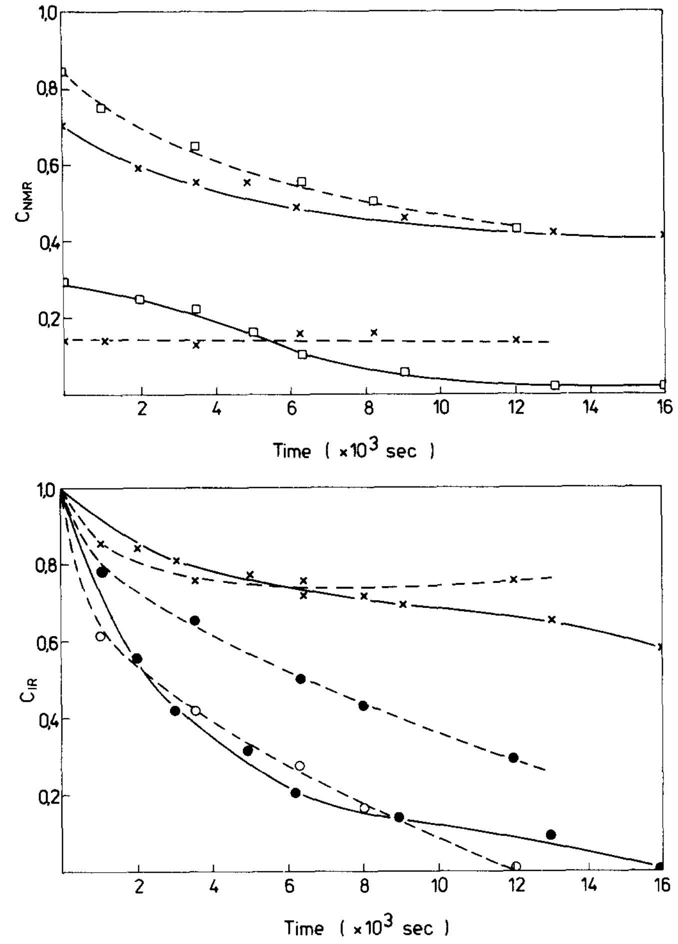


Figure 4 Degree of conversion of double bonds in butadiene units during epoxidation at 303K: 1,2-polybutadiene, solid line; 1,4-polybutadiene, broken line: x, 1.2; □, 1.4; ●, *trans*-1,4; ○, *cis*-1,4

results are shown in *Figure 4*. For the interpretation of i.r. and ^{1}H n.m.r. spectra the data reported by Tanaka *et al.*[16], Durbetakie and Miles[17], and Silverstein and Bassler[18] were assumed. A relative decrease in the content of *cis*-1,4 units in 1,2-PB is not shown in *Figure 4*, since the absorption characteristics for the *cis*-1,4- structure at 700–750 cm^{-1} are broad and thus difficult to interpret quantitatively (*Figure 5*). Some absorption bands derived 1,2-double bonds are also present in this region. In the case of 1,4-PB this band practically vanishes with increasing reaction times, but in the case of 1,2-PB its character considerably changes, becoming better shaped, narrower and separated into two bands. One band, at 700 cm^{-1}, may be assigned to blocks of isotactic 1,2-PB; the second, at 730 cm^{-1}, indicates the presence of *cis*-1,4 butadiene units. The existence of *cis*-1,4 double bonds in 1,2-PB after oxidation was also confirmed by combined i.r. and n.m.r. spectroscopy. The presence of the 1,4-structure was found in the ^{1}H n.m.r. spectra; however the absence of the 974 cm^{-1} band indicated that the *trans*-1,4 structure was not present.

Under specific reaction conditions (T = 303K) the *cis*-1,4 double bonds in 1,4-PB were found to react totally, whereas those in 1,2-PB reacted only partly. They were found to react totally only at higher degrees of oxidation and at higher temperatures.

^{1}H n.m.r. studies confirmed the structural form of PB units involved in the reaction, and the structure of the epoxy rings was identified. For epoxidized 1,2-PB and 1,4-PB, two absorption peaks were observed with chemical shifts, δ, from 2 to 3 ppm. The intensity of the peaks increased with the progress of the oxidation reaction (*Figure 6*), and they can be assigned to *cis*-1,4 (2.9 ppm) and *trans*-1,4 (3.1 ppm) epoxy groups. However, in view of the unchanged intensity of peaks corresponding to double bonds of 1,2-configuration, the presence of epoxy end-groups in the chain can be excluded.

The absorption spectrum of epoxy end-groups during the oxidation of 1,2-PB overlaps with the signals of protons of the *cis*-1,4 form. This is indicated by an increase in the intensity and width of the absorption peak at δ = 2.8 ppm during the course of the reaction, and a concomitant decrease in the intensity of signals related to vinyl protons $-C\underline{H}{=}C\underline{H}_2$ (δ = 5.3 ppm, *Figure 6*).

The structure of epoxy ring-containing groups in poly-

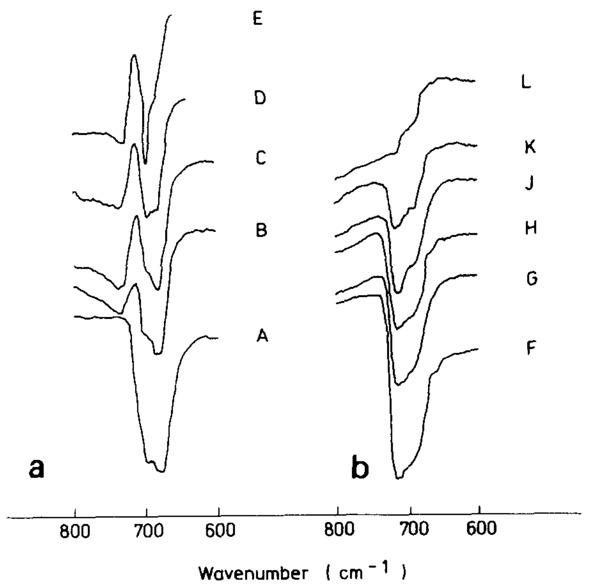


Figure 5 Infra-red spectra of (a) 1,2-polybutadiene, and (b) 1,4-polybutadiene in the 600–800 cm^{-1} region after various times of epoxidation at 303K (in ks): A, 0; B, 3.0; C, 4.9; D, 9.0; E, 12.0; F, 0; G, 0.9; H, 2.1; J, 3.3; K, 6.3; L, 12.0

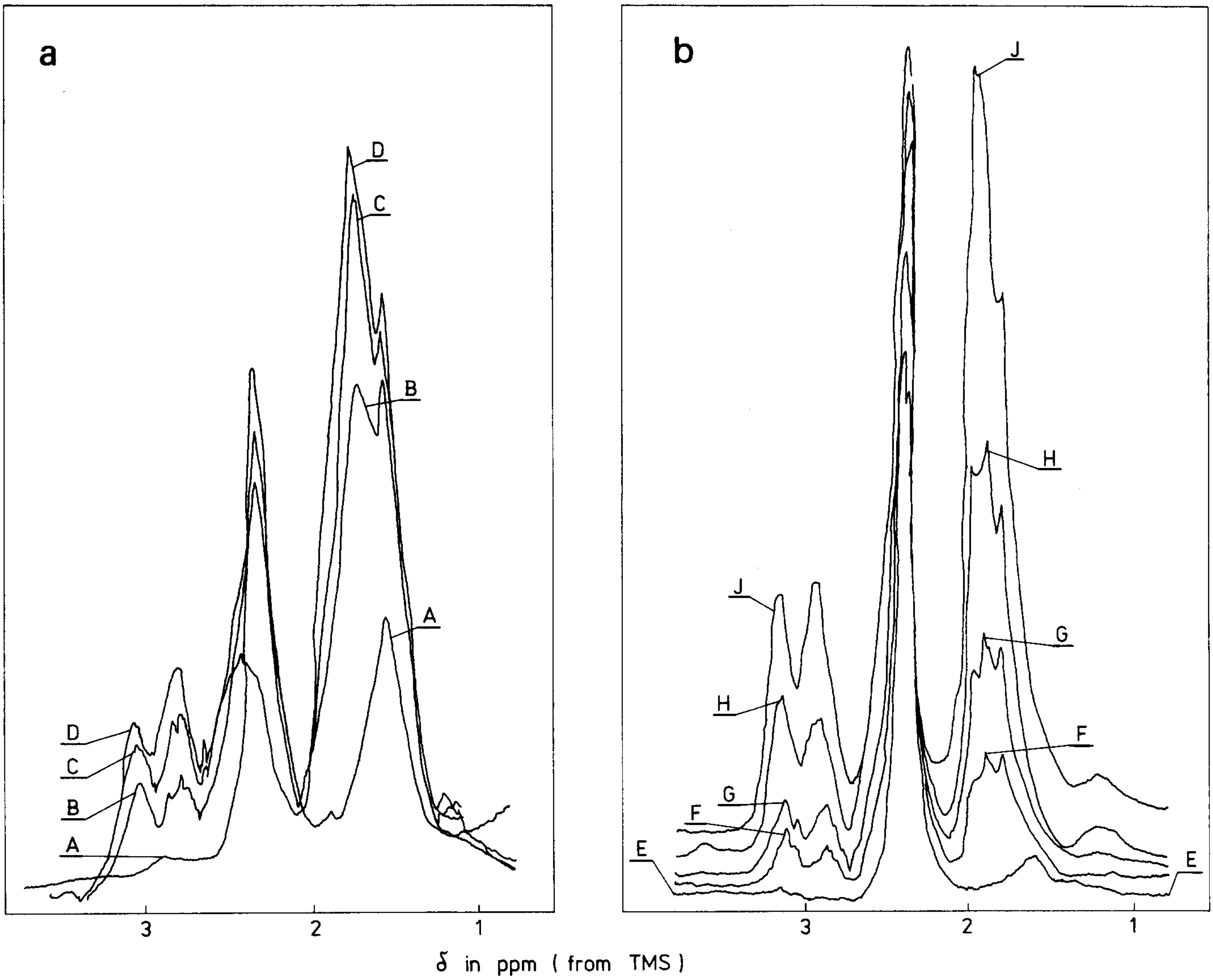
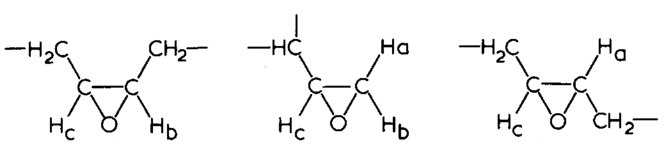


Figure 6 ^{1}H n.m.r. spectra of (a) 1,2-polybutadiene and (b) 1,4-polybutadiene with various epoxy group contents: A, 0; B, 0.270; C, 0.356; D, 0.459; E, 0; F, 0.271; G, 0.403; H, 0.493; J, 0.571 in mol (100 g)$^{-1}$ (80 MHz, CCl$_4$, TMS)

butadiene chains is shown below:



In the ^{1}H n.m.r. spectrum of the epoxidized 1,4-PB there are two well-shaped signals derived from H$_b$ protons of the *cis*-epoxy groups, and H$_c$ protons of the *trans*-groups; this is in agreement with the data of Silverstein and Bassler[18] for low molecular weight compounds. However, in the epoxidized 1,2-PB, H$_b$ protons of the epoxy end-groups overlap with the signals of the H$_b$ protons of the *cis* form.

The broad signal at 2.83 ppm for epoxy-1,2-polybutadiene (1,2-EPB) should be assigned to *cis*-1,4 and 1,2 protons, and that at 3.0 ppm should be assigned to *trans*-1,4 groups. Unfortunately, even using a 100 MHz instrument and a thermodynamically better solvent (deuterated chloroform), we were unable to separate all three structural forms in 1,2-EPB.

Within the limits of the spectroscopic methods we may say that during the epoxidation of 1,2-PB only a portion of the *cis*-1,4 and 1,2 double bonds are active, but virtually all *trans*-1,4 bonds react. On the other hand, in the case of 1,4-PB, the *cis*-1,4 double bonds react totally, the *trans*-1,4 only partly, and the 1,2-double bonds are practically inactive. This data indicates that the fraction of double bonds in polybutadiene and the reaction rate depends on the chemical structure of the macromolecule, i.e., its primary-order structure. In 1,2-PB, as shown by statistical calculations, the probability of the existence of 1,2-PB blocks of the triad, tetrad and pentad-type is 1.00, 0.95 and 0.97, respectively. However, Mochel[19] showed that in n-butyllithium 1,4-PB the *cis*-1,4 and *trans*-1,4 units form blocks which are separated by isolated 1,2-butadiene units. The distribution and the content of 1,2-butadiene units markedly affect the polymer conformation.

In *Figure 7* the dependence of the limiting viscosity number on the epoxy group content is shown for both polybutadienes. The relationship between viscosity and epoxy group content for 1,2-PB is characterized by the presence of a maximum at 0.3–0.4 mole (100 g of epoxy group)$^{-1}$. This viscosity change indicates the influence of the epoxy rings on the conformational shape of the macromolecule and may be interpreted as follows.

The viscosity increase observed along with an increase in the epoxy ring content in polybutadiene may arise from electrostatic repulsion between polar groups and from en-

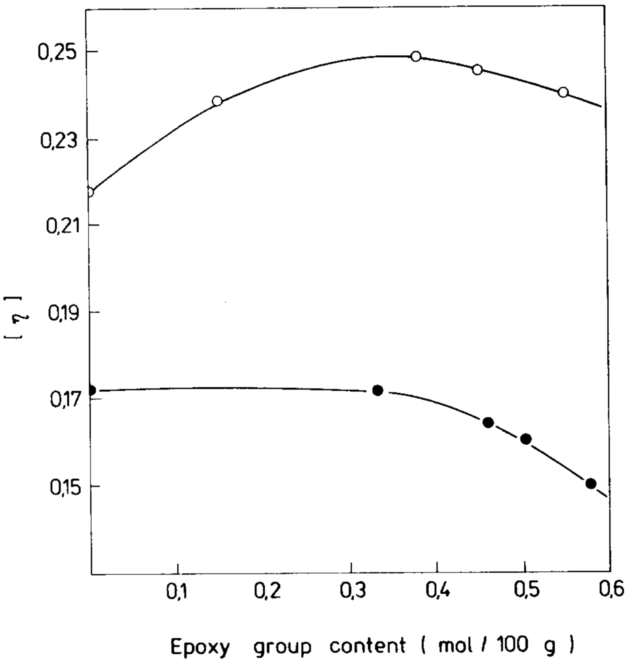


Figure 7 Relationship between epoxide group content and limiting viscosity number in toluene at 298K in: ○, 1,2-polybutadiene and ●, 1,4-polybutadiene

hanced polymer–solvent interactions, both of which tend to expand individual macromolecular coils. After a certain limiting epoxy group concentration has been reached, the subsequent decrease in the solution viscosity may be caused by deterioration of the thermodynamic properties of the solvent. The solubility parameters for polybutadiene, toluene and epoxypolybutadiene are 16.8 x 10^3, 18.2 x 10^3 and 19.8 x 10^3 $J^{1/2}$ $m^{-3/2}$, respectively. The limiting viscosity number of all epoxidized 1,2-polybutadienes is higher than that for the starting polybutadiene, but for 1,4-PB the reverse relation has been found, and as the epoxy group content increases, the limiting viscosity number decreases.

The relation between solution viscosity and epoxy group content in 1,2-PB is similar to that reported by Tutorski *et al.*[20] for high-molecular weight 1,4-polyisoprene. This similarity is probably related to the presence of side groups – vinyl and methyl – which influence the molecular conformation in solution.

The cohesion energy density values, δ, for epoxypolybutadienes, obtained by graphical estimation on the basis of the relation between the limiting viscosity number, [η], and the solvent solubility parameter, were found to be 19.8 x 10^3 $J^{1/2}$ $m^{-3/2}$ for both epoxypolybutadienes, independent of their microstructure (*Table 2*). This is considerably higher than the value for polybutadiene – 16.8 x 10^3 $J^{1/2}$ $m^{-3/2}$, ref 21 – and can be brought about by the presence of epoxy groups. The microstructure of low molecular weight epoxypolybutadienes and the fraction of symmetrically and unsymmetrically substituted epoxy groups in the chain at the same total concentration do not have any marked effect on the cohesion energy value, but may cause decoiling of the individual polymer coils. The proof of this is the considerably higher density of low molecular weight 1,2-PB and 1,2-EPB as compared with 1,4-PB and 1,4-EPB (*Figure 7, Table 2*).

The marked increase in the degree of reaction of the vinyl groups in 1,2-PB as compared with that for 1,4-PB may arise from conformational effects in the chain, i.e. in the secondary structure. During the reaction of double bonds with organic peracid an unstable transient 5-membered complex is formed[23,24]. The process of its formation is permitted by the availability of vinyl groups in the decoiled (1,2-PB) than in the coiled (1,4-PB) chain.

Table 2 Limiting viscosity number of epoxypolybutadienes

	Epoxypolybutadiene	
Property	1,2-	1,4-
Number-average molecular weight, $\bar{M}_n$	5300	6400
Epoxy group content, mol (100 g)$^{-1}$	0.587	0.577
[η] at 298K, dl/g in:		
toluene	0.342	0.150
sym-tetrachloroethane	0.585	0.228
acetone	0.165	0.100

Solubility parameters, δ, for toluene, sym-tetrachloroethane and acetone are 18.2, 19.8, and 20.3 x 10^3 $J^{1/2}$. $m^{-3/2}$ (see ref 22)

CONCLUSIONS

The reactivity of different structural polybutadiene units in epoxidation depends on the chain microstructure, and it decreases in the following order:

in sodium 1,2-polybutadiene: 1,4-*trans* > 1,4-*cis* ⩾ 1,2

in n-butyllithium polybutadiene: 1,4-*cis* > 1,4-*trans* ⩾ 1,2

Differences in reactivity of 1,2-double bonds are probably due to the different chain conformations of these polymers.

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