Polybutadiene modified by epoxidation: 2. The effect of epoxy groups on the crosslinking process with dicumyl peroxide

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The process of crosslinking sodium and n-butyllithium polybutadienes as well as the products of their modification obtained by epoxidation has been studied. It has been found that the crosslinking efficiency of epoxy-1,2-polybutadiene is half that of the starting polybutadiene. However, the crosslinking efficiency of epoxy-1,4-polybutadiene was found to be similar to that of the starting 1,4-polybutadiene. The shift in glass transition temperature for epoxy-polybutadienes brought about by the change in the chemical composition $(\Delta T_g)_M$ was found to be 67 K for 1,4-polybutadiene, and 51 K for 1,2-polybutadiene. The effect of the epoxy groups and crosslinks on the glass transition temperatures of modified crosslinked polymers is also discussed.

INTRODUCTION

In our previous work Part 1[1] the reactivities of polybutadienes of differing structure during their epoxidation with peracetic acid were investigated, as well as the effect of epoxy groups on the polymer solution viscosity. In the present work the effect of the chemical structures of epoxypolybutadienes on their crosslinking efficiency with dicumyl peroxide as well as their glass transition temperature is discussed. It is known that the epoxy groups formed in the polymer and the crosslinks bring about a decrease in the elasticity of the system. In this work we tried to separate the effect of chemical modification from that of crosslinking on the glass transition temperature of low-molecular weight polybutadienes.

EXPERIMENTAL

Crosslinking of polybutadiene

Epoxypolybutadiene and polybutadiene was mixed with dicumyl peroxide (17.7 mmol/100g of polymer) dissolved in small amount of benzene. After homogenization the solvent was distilled off under reduced pressure. The heat of the crosslinking reaction was measured by the d.s.c. method with a Perkin-Elmer DSC-1B instrument using heating rates of 4, 8, and 16 deg. min^{-1}. Benzoic acid was used as a standard in the reaction heat calculations. The analysis of the thermograms was carried out according to a method given in references 2–4.

The curing of polybutadienes was carried out by pressing a mixture in a metal mould at 423K for 2 h under a pressure of 0.98 MPa.

The glass transition temperature (T_g) of crosslinked polybutadienes and epoxypolybutadienes was determined by d.s.c. at a heating rate of 32 deg. min^{-1}.

RESULTS AND DISCUSSION

The modification of polybutadiene by epoxidation affects its properties in the solid phase. The glass transition temperature, T_g, markedly increases with increasing epoxy ring content in the chain (*Figure 1*) which indicates a decrease in the chain flexibility. The T_g shift caused a change in the chemical composition of the polymer $(\Delta T_g)_M$ is larger for 1,4-polybutadiene (1,4-PB) than for 1,2-polybutadiene (1,2-PB). Thus it may be suggested that the presence of epoxy groups in the main chain has a stronger influence on the decrease of the molecular flexibility of the chain than have those present in the side groups.

Crosslinking initiated by dicumyl peroxide

The effect of epoxy groups on crosslinking via double bonds was determined from the thermal effect of the reaction. The crosslinking efficiency was determined as the amount of heat of reaction in relation to one unit of butadiene containing the double bond $\Delta H_{>C=C<}$

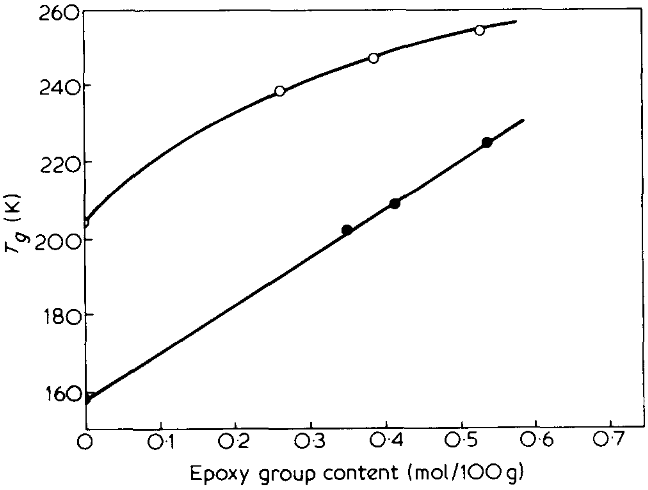

Figure 1 Dependence of glass transition temperature on the epoxy group content in (○), 1,2-polybutadiene and (●), 1,4-polybutadiene

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Table 1 Crosslinking of polybutadienes and epoxypolybutadiene initiated with dicumyl peroxide at a concentration of 17.7 mmol/100 g

Property	Polybutadiene		Epoxypolybutadiene	
	1,2–	1,4–	1,2–	1,4–
I. Polymer characteristics				
double bond content [from iodine number] (mol/100 g)	1.44	1.59	0.76	0.96
Weight fraction of polymer units [from n.m.r] (wt.%)				
1,2-configuration	72.0	15.6	46.9	14.7
1,4-configuration	28.0	84.4	–	41.8
epoxy group content (mol/100 g)	–	–	0.580	0.577
glass transition temperature (K)	214	168	255	225
II. Crosslinking process				
total heat of reaction, ΔH_t, kJ/g				
ΔH_t, kJ/g	0.749	0.171	0.402	0.149
$\Delta H_{>C=C<}$ kJ mol^{-1}	52.56	10.76	52.75	15.53
ΔH_{DCP} kJ mol^{-1}	4506	971	2272	916
activation energy, (kJ mol^{-1})	141.4	100.0	123.0	117.6
III. Crosslinked polymer characteristics				
epoxy group number decrease (%)	–	–	1.0	11.5
gel content (%)	96.9	97.1	95.4	102.0

Table 2 Degree of reaction of double bonds in polybutadiene and epoxypolybutadiene in the radical reaction

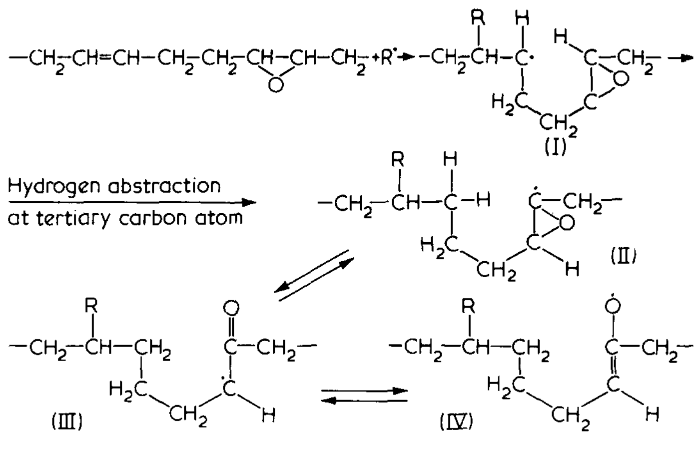
Polymer	Relative loss of double bonds*	
	1,2-configuration (1640 cm^{-1})	1,4-configuration (965 cm^{-1})
1,2–PB	0.20	0.21
1,2–EPB	0.13	–
1,4–PB	–	0.17
1,4–EPB	–	0.47

* Relative loss of double bonds was calculated from changes in the i.r. spectrum: $T = 423$K, $t = 2$ h

and per mol of dicumyl peroxide used ΔH_{DCP}; the results are given in *Table 1*. The crosslinking efficiency of 1,4-PB is ~4 times lower than that of 1,2-PB. This agrees well with a decreased double bond content of the 1,2-configuration in this polymer. It also agrees with other literature data concerning the crosslinking of high-molecular weight polydienes. The crosslinking efficiency of epoxy-1,2-polybutadiene (1,2-EPB) with dicumyl peroxide is lower than that of the starting polybutadiene. This may be caused by the lower double bond content, especially of those of 1,2-configuration, in the polymer. However, the crosslinking efficiency of epoxy-1,2-polybutadiene (1,2-EPB) is slightly higher than that for the starting (1,4-PB). This may be explained by the i.r. spectra of crosslinked polubutadiene and crosslinked epoxypolybutadiene.

The i.r. spectra of 1,2-PB and 1,2-EPB after crosslinking exhibit strong absorption bands at 1710–1730 cm^{-1} (C=O stretching mode) and 3400–3500 cm^{-1} (O–H stretching mode). The presence of these groups indicates that the radical reaction is associated with oxidative side-reactions which result in carboxyl group formation whose content in 1,2-PB and 1,2-EPB is similar. A decrease of the absorption band corresponding to double bonds indicates their active role in the radical reaction (*Table 2*). This is in agreement with literature data on high molecular weight polydienes[5–7].

In the spectrum of 1,4-PB after crosslinking no new absorption bands were observed, though the intensity of the double bond band, especially that of the 1,4-trans configuration, was markedly lower (*Table 2*). However, several additional absorption bands at 1050, 1170, 1710–1750 and 3300–3450 cm^{-1} were observed in the spectrum of 1,4-EPB after radical reaction. A significant increase in the intensity of the absorption band at 967 cm^{-1}, corresponding to the 1,4-trans configuration of double bonds, was also found (*Table 2*). The general features of the 1,4-EPB i.r. spectra as compared with those of 1,4-PB and 1,2-EPB, i.e. the presence of other bands (1050 and 1170) and the higher content of carbonyl and hydroxyl groups as compared with that of 1,2-EPB, indicate that transformation of epoxy groups has taken place. This process was further confirmed by chemical analysis from which a loss of 11% of the epoxy groups was found (*Table 1*). There is a probability that during the crosslinking reaction of the 1,4-EPB which is initiated by free radicals, carbonyl groups and ether bridges are formed according to the following scheme:

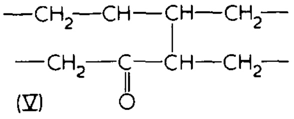


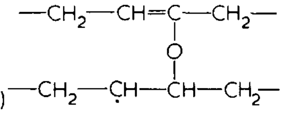
Further the intermolecular reaction between macroradicals (structures II, III and IV) and double bonds in the

Table 3 Glass transition temperature of crosslinked modified polybutadienes

Sample	Content in starting polymer mol/100 g		Glass transition temperature, (K) T_g*	(ΔT_g)	$(\Delta T_g)_M$	$(\Delta T_g)_\nu$
	Epoxy	Double bonds				
1,2–PB	–	1.44	280	66	–	66
1,2–EPB	0.271	1.05	286	72	25	47
1,2–EPB	0.386	0.93	295	81	33	48
1,2–EPB	0.555	0.78	294	80	41	39
1,4–PB	–	1.59	200	32	–	32
1,4–EPB	0.470	1.11	278	110	40	69
1,4–EPB	0.525	0.96	273	105	57	48

chains of 1,4-EPB with crosslinking bridge formation may be as follows:


(V)

(VI)


The formation of structures I–IV can proceed only if the epoxy groups and double bonds are contained in adjacent polymer units. This is possible only in 1,4-EPB, for n-butyllithium polybutadiene contains blocks of *cis*-1,4-PB and *trans*-1,4-PB[8] and the existence of blocks of such a kind in 1,2-PB is of low probability. Furthermore, 1,2-EPB contains only double bonds of 1,2-configurations.

That the number of crosslinks formed in 1,4-EPB is higher than in 1,2-EPB, was confirmed by T_g determinations of crosslinked as well as modified polybutadienes. The T_g for crosslinked polymers was shifted towards higher temperatures with increasing epoxy groups content in the chain (*Table 3*). This shift is thought to be partially due to an epoxy group effect (effect of modification, $(\Delta T_g)_M$), and an intermolecular crosslinking effect (effect of crosslinking, $(\Delta T_a)_v$). The later was calculated using the Fox–Loshaek assumption[9]:

$$T_g - T_{g0} = (\Delta T_g) = (\Delta T_g)_M + (\Delta T_g)_v$$

where T_g— glass transition temperature of crosslinked epoxypolybutadiene,

T_{g0}—glass transition temperature of starting polybutadiene,

$(\Delta T_g)_M - T_g$ of epoxypolybutadiene minus T_g of polybutadiene.

It can be seen from *Table 3* that the effect of modification at epoxy group content equal to 0.55 mol/100 g is more pronounced than the effect of the crosslinks formed. The modification of 1,4-PB through epoxidation causes $(\Delta T_g)_v$ values to increase. This indicates that the epoxy groups enhance the crosslinking density in agreement with the i.r. data.

CONCLUSIONS

A decrease in the 1,2-double bond content in polybutadienes through their oxidation to epoxy groups brings about a considerable decrease in the efficiency of crosslinking with organic peroxides, while a decrease in the double bond content in the main chain 1,4-configuration was found to have no effect on crosslinking efficiency. It was further established that macroradicals promote inter- and intramolecular rearrangements of the epoxy rings in the chain of 1,4-PB, but those contained in both the main chain and the side-groups of 1,2-PB were not affected during this free-radical process.

The modification of polybutadiene via epoxidation tends to increase the glass transition temperature, T_g, of both linear and crosslinked polymers. The epoxy groups in the main chain have a stronger effect than have those in the side-groups. An increase in the epoxy group content in the main chain of 1,2-PB causes the effect of crosslinking on T_g to decrease, but the opposite effect was observed for 1,4-PB.

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