Molecular mobility in epoxidized butadiene/styrene triblock copolymer

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Solid state nuclear magnetic resonance was carried out by the continuous wave and pulse methods for butadiene/styrene (B/S) triblock copolymers containing various amounts of epoxy groups. The effects of epoxidation on the second-order phase transition and molecular motion were examined. It was found that, with an increase in epoxy unit content from 0 to 0.31 groups/100 g copolymer, the glass transition temperature, T_g, in polybutadiene matrix increased from 201 to 264 K. The main minimum of the spin-lattice relaxation time was also shifted to higher temperatures. The activation energy determined from the slope of the low temperature curve $T_1 = f(1/T)$ was found to be 1.7 times higher in epoxidized copolymer containing 0.25 mol epoxy groups/100 g than in pure B/S copolymer.

(Keywords: epoxidized butadiene/styrene block copolymer; nuclear magnetic resonance; molecular motion; activation energy; glass transition temperature)

INTRODUCTION

Butadiene/styrene (B/S) triblock copolymers (or thermoplastic rubber) have a unique heterogeneous structure consisting of spherical polystyrene (PS) domains dispersed in a matrix of elastic polybutadiene (PB). The synthetic methods and properties of this material are described elsewhere[1–3]. Its chemical modification is of great importance, since it is the only available method of obtaining block diene copolymers with polar groups such as epoxy, ester and hydroxide[4,5]. Physical properties, especially molecular mobility, change during chemical modification of the matrix. The directions of such changes are not sufficiently understood.

Udipi[4] studied the epoxidation of B/S block copolymers and concluded that the epoxidation process does not affect the two phase domain structure of the block copolymer. Epoxidized B/S block copolymers have mechanical properties similar to those of thermoplastic elastomers[4].

In a B/S block copolymer with PB and PS blocks of relatively high molecular weight, two T_gs were observed corresponding to the glass transitions of the bulk homopolymers[2,6]. Mobility of the PB blocks was reduced by the presence of PS domains acting as some sorts of physical lattice nodes. This was confirmed by nuclear magnetic resonance (n.m.r.) and mechanical damping spectroscopy[8,9]. The glass transition temperatures of polybutadiene, polyisoprene and natural rubber modified by epoxidation increase more than that for unmodified polybutadiene[10,11]. The change in T_g depends upon the number of epoxy groups introduced and on chain microstructure. Due to the presence of epoxy rings, the flexibility of the free volume of the copolymers is reduced. The data in the literature does not provide a comprehensive view of the change in structure and chain mobility caused by epoxidation of B/S block copolymers. Among the methods for investigating this problem is n.m.r. analysis of solid polymers. We are not aware of any reports on the application of the method to studying the epoxidation process in copolymers of butadiene and styrene.

In this work continuous wave and pulse n.m.r. methods were used to investigate molecular mobility in epoxidized butadiene/styrene block copolymer. The temperature range used was 150–460 K. The choice of copolymer and methods should provide information on general molecular motions which are typical for glass transition phenomena in chemically modified PB matrix. It was also of interest to examine the spin-lattice relaxation time, T_1, in B/S block copolymer after epoxidation.

EXPERIMENTAL

Triblock butadiene–styrene (B/S) copolymer (manufactured by Philips Petroleum Co.) was used. Styrene content was 31 mol%. The ratio of 1,4 to 1,2 butadiene units was 0:0.15 as measured by ^{1}H n.m.r. in CCl_4. The number average molecular mass, $\bar{M}_n$, was 1.4×10^5 g mol^{-1} and the polydispersity index $\bar{M}_w/\bar{M}_n$ was 1.28 (gel permeation chromatography in THF).

The triblock copolymer was epoxidized by methods described elsewhere[4,12] by using formic or acetic acid and hydrogen peroxide. The epoxidation was carried out to obtain various conversions of double bonds in the polybutadiene chains. The content of epoxy groups in the

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Table 1 Resonance line width, ΔH (n.m.r.), and glass transition temperature, T_g, for B/S copolymers with different epoxy unit content

Polymer	Intrinsic viscosity $[\eta]$	Epoxy units (mol/100 g)	Degree of epoxidation (%)	Resonance line width ΔH (G)		Range of glass transition temperature ΔT (K)	T_g (K)
				153 K[a]	T_g zone[b]		
B/S	0.86	0	0	10.53	9.5	33	201.5
IEB/S	0.84	0.18	14.1	10.85	8.7	29	224.5
2EB/S	0.58	0.25	19.5	11.16	8.5	26	242
3EB/S	0.53	0.31	24.2	11.45	8.4	22	262

[a] Glassy state of copolymer
[b] Viscoelastic state of PBd matrix

copolymer was determined by titration of copolymer in HCl and dioxane solution against alcoholic NaOH[12]. The results are presented in *Table 1*. The limiting viscosity number in toluene was determined at 25°C with an Ubbelhode-type viscometer.

Using solid state n.m.r. analysis, the line width, ΔH, and the spin-lattice relaxation time, T_1, were determined as a function of temperature. A continuous wave spectrometer at 30 MHz and a pulse spectrometer were used. The equipment was assembled in the Institute of Mechanical Engineering at the Technical University of Poznań[13,14].

The widths of resonance lines were determined from recorded values of derivatives of n.m.r. absorption curves. The study was carried out over the temperature range 120–300 K on epoxidized block copolymers at three epoxidation levels and the original B/S copolymer. The results are shown in *Figures 1* and *2*. The spin-lattice relaxation time, T_1, was determined with pulse sequence $\pi/2 - \tau - \pi/2$ at temperatures between 160 and 500 K. The measurements were carried out for B/S and 2EB/S copolymer. The latter contained 0.25 epoxy groups per 100 g. Recovery of magnetization was non-exponential for both samples. Their decomposition into components is shown in *Figure 3*. The temperature dependences of relaxation time, T_1, for the copolymers are shown in *Figures 4* and *5*. The activation energy determined from the slope of the $T_1 = f(1/T)$ curve is an approximate value owing to the polydispersion of the polymer system.

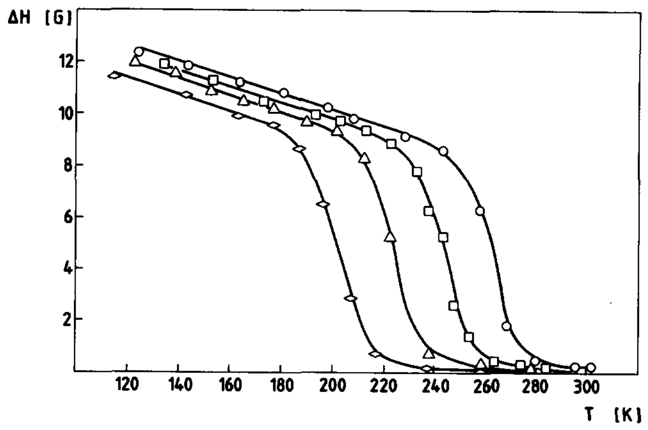


Figure 1 Dependence of resonance line width ΔH on temperature for B/S copolymer containing 0 (◇), 0.18 (△), 0.25 (□) and 0.31 (○) epoxy mol/100 g copolymer

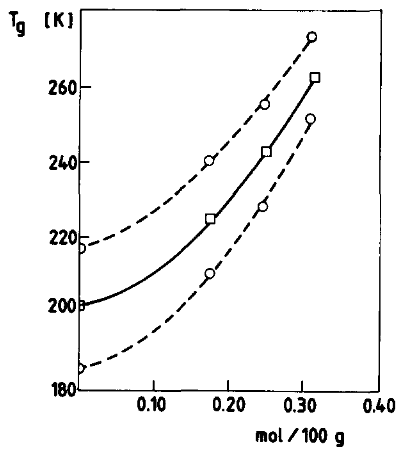
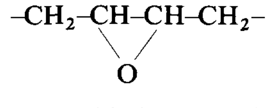


Figure 2 Influence of epoxy groups on glass transition temperature, T_g, in polybutadiene matrix as determined by solid state n.m.r. ○, Range of temperature for molecular relaxation of PBd matrix; □, average values

RESULTS AND DISCUSSION

The epoxidized B/S block copolymer contained varying amounts of epoxide groups (*Table 1*) and consisted of unchanged polystyrene suspended in polybutadiene matrix with randomly distributed internal epoxy units



$$-CH_2-\underset{\diagdown\,O\,\diagup}{CH-CH}-CH_2-$$

We assumed that the epoxidation took place mostly in the double bonds of the main polybutadiene chain. It is known that 1,4 butadiene units are much more reactive than 1,2 vinyl ones[12].

The n.m.r. resonance line width ΔH for all the copolymers examined fell abruptly from 10–11 to 0.5 G in the temperature range 180–270 K, as shown in *Figure 1*. The narrowing of the resonance line is due to an acceleration of molecular motion associated with passing the glass transition temperature. The T_g for B/S copolymer is 201.5 K (*Table 1* and *Figure 2*) and this value represents the T_g of the polybutadiene part. The T_g for polybutadiene lies in the range 170–210 K, depending on the microstructure of the chain[15] and the kind of method used for measurement. A 24% increase in the degree of epoxidation of PB matrix resulted in an increase in T_g by 61 K (*Figure 2* and *Table 1*). It appears that the activation energy of molecular motion accompanying this glass transition increases with increasing degree of epoxidation.

The increase in T_g is directly proportional to epoxy group content in the copolymer, if only a certain concentration limit is reached (*Figure 2*). A similar dependence was observed for low molecular weight epoxidized polybutadiene[10]. Burfield *et al.*[11] observed a

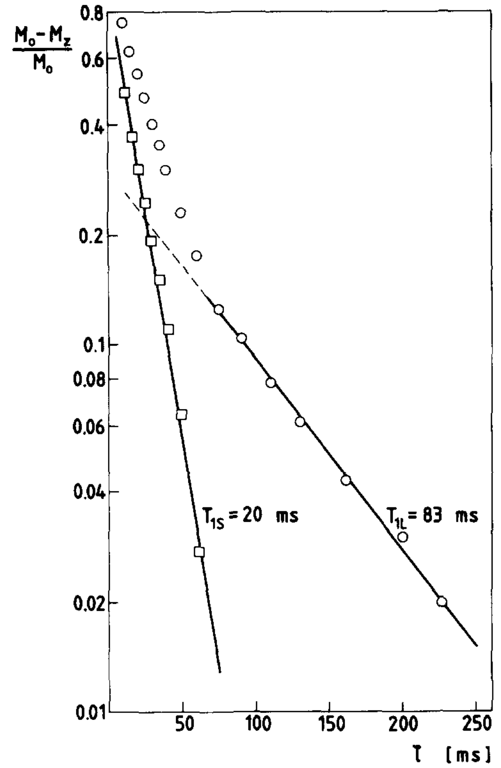
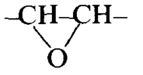
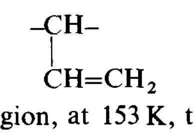


Figure 3 Recovery of magnetization in epoxidized 2EB/S copolymer at 295 K

linear dependence of T_g on epoxy group content in natural rubber. The temperature range ΔT over which the abrupt change in resonance line width is observed and which is identified with the glass transition zone decreases with increasing degree of epoxidation of PB; see *Table 1*. The narrowing glass transition zone could be attributed to approximately equal activation energies of thermal motion of particular chain segments after modification. The mobility of chain segments with the epoxy group



may be close to that of a segment with 1,2 vinyl units



$$\begin{array}{c}-CH- \\ | \\ CH{=}CH_2\end{array}$$

In the glassy state region, at 153 K, the line width ΔH increases with increasing degree of epoxidation (*Figure 1* and *Table 1*). The reduction in mobility seems to be due to steric hindrances, resulting from the presence of the three-membered epoxy rings. Measurements of relaxation time, T_1, reveal a non-exponential recovery of magnetization. This is related to the two phase structure of both the original (B/S) and the epoxidized copolymer (2EB/S). Likely results for non-epoxidized copolymer B/S have been obtained by Wardell *et al.*[7]. They explained the relaxation process in this copolymer by a simple two phase model. Between the phases is operative spin-diffusion. The long component of T_1 is related to PS blocks, the short one to PB blocks[7]. We suggest that for epoxidized copolymer 2EB/S the relaxation process can be described by the same mechanism of relaxation.

The main minimum of the relaxation time, T_1, for epoxidized copolymer (2EB/S) was found to occur at a higher temperature than that for B/S copolymer (*Figures 4* and *5*). The rate of nuclear relaxation of this minimum in PB was found to decrease after epoxidation. The activation energies determined from the slopes of low temperature curves were approximately 1.7 times higher in epoxidized 2EB/S copolymer than in B/S copolymer. All these facts confirm that epoxidation results in a higher rigidity of the copolymer structure. The activation energies determined from the high temperature slopes (above 450 K) are 1.4 times higher in epoxidized 2EB/S copolymer than in B/S copolymer (unmodified). This might also indicate a restriction on molecular mobility in epoxidized copolymer in the viscoelastic state. At high temperature, the disappearance of short components (*Figures 4* and *5*) is associated with the transition of a heterogeneous system into a homogeneous one. This interpretation of the experimental results is in agreement with the conclusions of Chang *et al.*[16]. In their viscometric studies they observed a homogeneous structure of triblock copolymer SBS above 448 K where Newtonian fluid behaviour occurred, in contrast to non-Newtonian behaviour at temperatures <448 K. The molecular relaxation of the homogeneous system at both the temperatures mentioned is of diffusion type.

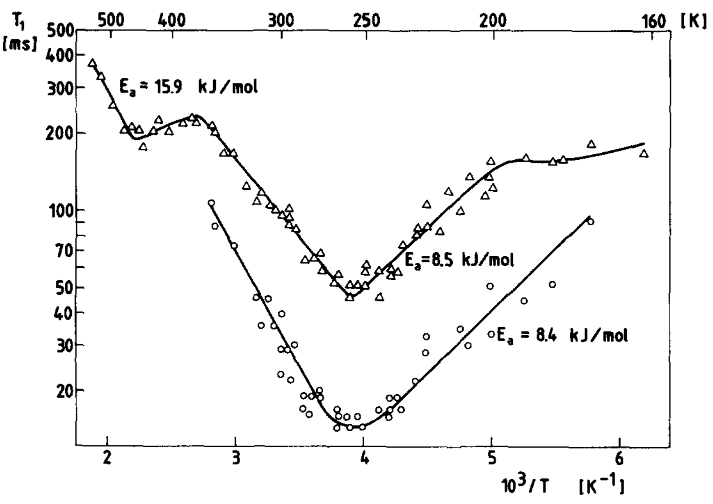


Figure 4 Spin-lattice relaxation time, T_1, *versus* reciprocal temperature in B/S copolymer: ○, polybutadiene phase; △, polystyrene phase

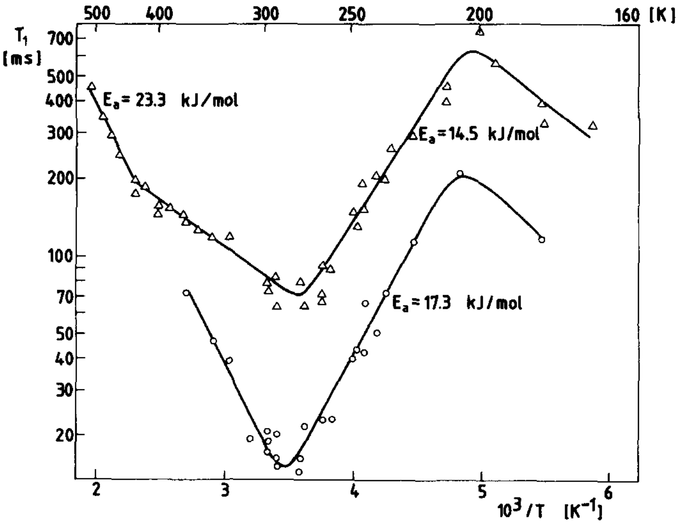


Figure 5 Spin-lattice relaxation time, T_1, *versus* reciprocal temperature in 2EB/S copolymer: ○, epoxidized polybutadiene; △, polystyrene

CONCLUSIONS

The results of solid state n.m.r. show that the morphology of partly epoxidized B/S triblock copolymer is similar to that of unmodified B/S copolymer. The structure is two phase, but in the molten state the initially heterogeneous structure becomes homogeneous as temperature increases. The temperature of this transition is lower for epoxidized copolymer than for the original copolymer.

The epoxidation of butadiene/styrene copolymer results in an increase in activation energies of molecular relaxation in polybutadiene matrix. The temperature for the minimum spin-lattice relaxation time and the glass transition temperature in PB matrix increase after epoxidation.

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