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EPOXY GRAFT FUNCTIONALIZATION OF POLY(BUTADIENE)

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Key Words: Poly(butadiene); Hydrosilation; 1,1,3,3-Tetramethyldisiloxane; 4-Vinyl-1,2-epoxycyclohexane; Crosslinking; Ultraviolet radiation

ABSTRACT

A novel strategy for the polymer analogous functionalization of poly(butadienes) with epoxy groups was developed. Siloxane, **I**, bearing both Si—H and epoxycyclohexyl functional groups was appended onto the pendant vinyl groups of the poly(1,2-butadiene) repeating units using a polymer analogous hydrosilation reaction. The modified poly(butadienes) were polymerized by exposure to ultraviolet radiation in the presence of cationic photoinitiators to give crosslinked networks. Thermal analysis of the resulting crosslinked poly(butadienes) showed that by varying the microstructure of the poly(butadiene) and the degree of epoxide substitution, materials with a wide range of properties could be obtained.

INTRODUCTION

In recent years, research efforts in this laboratory have been focused in the area of the exploration of novel photo- and e-beam-induced cationic epoxide ring-opening polymerizations and their applications. Of particular current interest is the application of these techniques for the fabrication of composite materials. One difficulty which has been encountered in the radiation-induced polymerization of low molecular weight, high functionality epoxy monomers is that brittle materials with poor impact properties result. Accordingly, current efforts in this laboratory have been directed toward finding means of reducing the inherent brittleness of the radiation-cured epoxy matricies. The incorporation of an elastomer in highly crosslinked polymers including traditional amine and anhydride-cured epoxy resins is a commonly employed technique used to improve their impact resistance [1-3]. The elastomer can be introduced either in particulate form or as a reactive liquid polymer miscible with the matrix which requires toughening. Under ideal conditions, the liquid elastomer should separate on curing to give a distinct elastomeric microphase within the crosslinked epoxy matrix. In all cases, it has been found that some tailoring or functionalization of the elastomeric modifier must be performed to make it at least partially compatible with the epoxy matrix resin.

One possible approach to the modification of UV- or e-beam-cured epoxy matrices is to employ elastomeric modifiers bearing epoxy groups which can copolymerize with the matrix resin during cure. There has been considerable recent activity in various groups aimed at the synthesis of epoxy-functionalized poly(butadienes) [4-7]. It has also been reported that the epoxidation of the internal double bonds resulting from 1,4-enchainment proceeds much more rapidly than the vinyl double bonds derived from 1,2-enchainment [4, 5, 7]. Therefore, this route for the functionalization of poly(butadiene) alters the polymer backbone and may disrupt the morphology and, consequently, the elastomeric nature of the poly(butadiene) modifier. Moreover, epoxidation reactions are usually not quantitative so it is difficult to control the degree of functionalization. Lastly, the work-up after epoxidation reactions on high polymers is also cumbersome. This communication reports on our attempts to develop new, epoxy functional impact modifiers which are compatible with the UV- and e-beam-induced cationic cure chemistry.

EXPERIMENTAL

Materials

All materials were used as received. Poly(butadiene), **PB420**, (36% 1,4-*cis*, 55% 1,4-*trans*, 9% 1,2-vinyl, M_w = 420,000 g/mol, T_g = −96°C) and poly(butadiene), **PB220**, (7% 1,4-*cis*, 93% 1,2-vinyl, M_w = 220,000 g/mol, T_m = 90°C) were purchased from Scientific Polymer Products, Inc. Poly(butadiene), **PB1**, (85% 1,2-vinyl, M_w = 1000 g/mol) was purchased from Polyscience, Inc. Karstedt's catalyst [platinum(0) complex of 1,3-divinyltetramethyldisiloxane] and 1,1,3,3-tetramethyldisiloxane were purchased from Hüls America Inc. Wilkinson's catalyst [tris(triphenylphosphine)rhodium(I) chloride] was obtained from Aldrich Chemical Company. 4-Vinyl-1,2-epoxycyclohexane oxide was obtained from the Union Carbide Corp. and used without further purification. The photoinitiator, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10), was prepared as described previously [8].

Measurements

Routine infrared spectra and real-time infrared spectra were run on a Midac M-1300 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled MCT detector. Gas chromatographic (GC) analyses were performed on a Hewlett-

Packard HP-5890 Gas Chromatograph equipped with a 5-m 5% methylsilicone column and a flame ionization detector. ^{1}H-NMR spectra were obtained using a Varian XL-200 MHz spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as an internal standard. Gel permeation chromatographic (GPC) analyses were carried out using a Hewlett-Packard HP-1090M HPLC equipped with a refractive index detector and μ-styragel columns (particle size 5 μm, mixed 34-24 Å pore sizes). $CHCl_3$ was used as eluent at a flow rate of 1.0 mL/min. The GPC was calibrated using polystyrene standards, and all molecular weight data are reported relative to those standards. Differential scanning calorimetry and thermal gravimetric analyses were performed on a Perkin-Elmer DSC-7 instrument in a nitrogen atmosphere at a heating rate of 20°C/minute.

Synthesis of 1-[2-(3{7-Oxabicyclo[4.1.0]heptyl})ethyl]-1,1,3,3-tetramethyldisiloxane (I)

A 250-mL round-bottomed flask was charged with 20.1 g (0.15 mol) of 1,1,3,3-tetramethyldisiloxane and 18.6 g (0.15 mol) of 3-vinyl-7-oxabicyclo[4.1.0]-heptane. The reaction flask was equipped with a magnetic stirrer and a reflux condenser. To this solution was added approximately 5 mg of tris(triphenylphosphine)rhodium(I) chloride as a catalyst, and the reaction mixture was heated to 80-85°C for 6 hours. The reaction was followed using gas chromatography by monitoring the disappearance of the starting materials and the appearance of the products. After the completion of the reaction, pure product **I** was obtained by fractional vacuum distillation with a boiling point of 86°C at 0.025 mmHg. The isolated yield was 35 g (90% based on the starting epoxide).

Procedure for the Synthesis of Epoxy Functional Poly(Butadienes)

Functionalization of PB420 to Give a 1% Graft Density (**PB420-1**) and a 7% Graft Density (**PB420-7**)

Poly(butadiene) **PB420** (1 g, 1.66 mmol of 1,2-vinyl units) was dissolved in 50 mL of toluene and placed in a two-necked 100 mL round-bottomed flask. **I** was added (0.045 g for the synthesis of **PB420-1** or 0.33 g for the synthesis of **PB420-7**) to the flask, and the reaction mixture was heated to 60°C. One drop of Karstedt's catalyst was added, and the hydrosilation reactions were monitored by following the disappearance of the Si—H band at 2117 cm^{-1} in the infrared spectrum. The reactions were over in approximately 2-3 hours. Under the same conditions, the identical reactions using Wilkinson's catalyst required approximately 24 hours at 90°C for completion. After cooling, the reaction mixtures were poured with stirring into 150 mL methanol to precipitate the grafted poly(butadiene) polymers. The precipitated poly(butadiene)s were washed with additional methanol and dried in vacuo at 60°C for 8 hours.

Functionalization of PB1 to Give a 60% Graft Density (**PB1-60**)

PB1 (1 g, 15.7 mmol of 1,2-vinyl units) was placed in a two-necked 100 mL round-bottomed flask. **I** (1.8 g) was added to the flask, and the mixture was heated to 50°C. One drop of Karstedt's catalyst was added. A vigorous exotherm resulted, and the reaction temperature was maintained between 50 to 55 °C with the aid of a water bath. It was later found that adding compound **I** in a dropwise fashion provided better temperature control of the reaction. The reaction was monitored by the disappearance of the Si—H band at 2117 cm^{-1} in the infrared spectrum. When all the Si—H groups had reacted, an additional 1.0 g of **I** was added. The reaction was completed in approximately 2 hours to give a viscous polymer. The total amount of **I** added was sufficient to react with approximately 70% of the available pendant 1,2-vinyl groups of **PB1**. When a stoichiometric amount of **I** (i.e., 4.0 g) was added at the beginning of the reaction, a crosslinked gel was obtained.

Functionalization of **PB220** to Give a 2% Graft Density (**PB220-2**), a 7% Graft Density (**PB220-7**), and a 31% Graft Density (**PB220-31**)

PB220 (1 g, 17.2 mmol of 1,2-vinyl units) was dissolved in 25 mL of toluene and placed in a two-necked 50 mL round-bottomed flask. **I** (1.5 g for synthesis of **PB220-31** or 0.35 g for the synthesis of **PB220-7** or 0.0085 g for the synthesis of **PB220-2**) was added to the flask and then heated to 60°C. One drop of Karstedt's catalyst was added. The reactions were monitored by IR spectroscopy as described previously. The reactions required approximately 2 hours for completion. Then the reaction mixtures were poured with stirring into 150 mL of methanol to precipitate the grafted poly(butadiene) polymers. The precipitated polymers were dried in vacuo at 60°C for 8 hours.

Thin-Film Photopolymerization and Thermal Analysis

A mixture of the epoxy functional elastomer, **PB1-60** containing 0.5 mol% of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) photoinitiator per mole epoxy groups in the polymer was drawn onto steel panels to a thickness of approximately 15 μm. The films were then irradiated using a 200-W medium-pressure mercury lamp. Epoxy functionalized poly(butadiene)s **PB420-1**, **PB220-2**, **PB220-7**, and **PB220-31** were dissolved in chloroform. IOC10 (0.5 mol% of per mol epoxy groups) was added to the chloroform solution, and the mixture was drawn onto steel panels. When most of the chloroform had evaporated, the films were irradiated using a 200-W medium-pressure mercury lamp. No attempt was made to dry the latter films completely before exposing them to UV. The crosslinked films were subsequently vacuum dried at 0.025 mmHg for 48 hours at room temperature to remove entrapped solvent before performing thermal analyses.

Real-Time Infrared Spectroscopy (RTIR)

Decker and Moussa [9] described the use of real-time infrared spectroscopy to monitor the kinetics of photopolymerizations. These authors employed a dispersive instrument for their measurements. Yang [10] was the first to use a Fourier transform instrument and has discussed its advantages. The apparatus used for these measurements consisted of a Midac M-1300 Fourier Transform Infrared Spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The spectrometer was fitted with a UVEXS Co., SCU 110 model, UV ultraviolet light source equipped with a fiber optic cable and a remote shutter. The probe of fiber optic cable was focused at a 45° angle onto the sample holder. The distance between the UV source and the sample was adjusted to give a radiation intensity of 16 mJ/cm^2s as measured by a radiometer sensitive to 363 cm^{-1}.

Photopolymerizations were carried out at room temperature. Samples for RTIR analyses were prepared as described in the preceding section, and then the polymer-photoinitiator mixtures were cast as thin films (~15 μm) onto a sodium chloride plate which was then placed in the FT-IR instrument. No deliberate effort was made to remove chloroform from the films except for the evaporation that took place during the experiment under ambient conditions. The effect of residual amounts of chloroform present in the films was neglected for RTIR purposes.

A typical run consisted of exposing the sample to UV irradiation while simultaneously recording the IR spectra. Spectra were recorded at a rate of up to 270 spectra per minute with a resolution of 4 cm^{-1}. As the polymerization proceeds, the concentration of the epoxide groups taking part in polymerization decreases, resulting in a corresponding decrease in the integrated areas of the bands at 835-845 cm^{-1} due to the epoxide groups. The conversion of the functional group at differernt times can be expressed as

$$\text{Conversion} = \frac{A_{t_0} - A_t}{A_{t_0}} \tag{1}$$

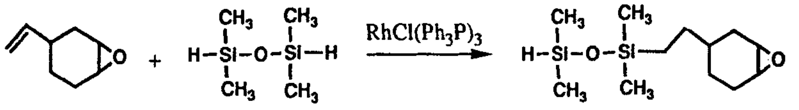
where A_{t_0} is the sum of the integrated areas of the bands corresponding to the epoxide groups at time zero, and A_t is the sum of the integrated areas of the same bands at time *t*. The data was collected using a Bitwise 486 PC, analyzed using Grams 386 software, and then plotted as conversion versus irradiation time curves.

The conversion versus irradiation time curves give a profile of the photopolymerization reactions of these materials. The steepest slopes of the curves are a measure of the rates of polymerization. Typically, the conversion increases with the passage of time until a maximum value of the conversion is reached.

RESULTS AND DISCUSSION

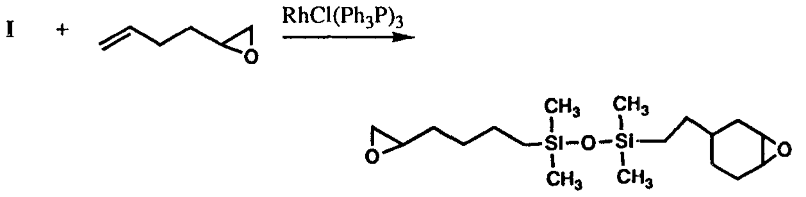
Synthetic Approach

The strategy that we have taken for the epoxy graft functionalization of poly(butadiene) is based on the use of a polymer analogous hydrosilation reaction with an epoxide substrate bearing a highly reactive Si—H group. Previously, we showed [11] that 1,1,3,3-tetramethyldisiloxane can be regioselectively hydrosilylated according to Eq. (2) to give compound **I** in greater than 96% yield in which only one Si—H group has reacted. Later, it was shown that **I** could be used in a second hydrosilation step to synthesize (Eq. 3) ambifunctional monomers containing two different types of epoxy functional groups [12], as for example, **II**.



I

(2)



II

(3)

It appeared that a polymer analogous hydrosilation reaction employing **I** might be an excellent method for the grafting of highly reactive epoxycyclohexyl groups onto the poly(butadiene) main chain. It has been found that cycloaliphatic epoxy compounds undergo UV-induced cationic polymerization at rates much higher than either terminal or internal open-chain epoxides [13]. Further, since the hydrosilation reaction is normally either quantitative or nearly quantitative, the graft density can be precisely tailored by controlling the stoichiometry.

Guo et al. [14] investigated the hydrosilations of various silanes onto various poly(butadiene)s using Wilkinson's catalyst [tris(triphenylphosphine)rhodium(I) chloride]. They found that the reaction takes place selectively at the vinyl double bond of the 1,2-repeat units and essentially not at all at the internal double bonds of the 1,4-repeat units. Hydrosilation is, therefore, a potentially convenient regioselective route to graft polymerizable epoxides as pendant functional groups onto the 1,2-repeat units of poly(butadiene) without substantially disrupting the elastomeric character of the backbone. Lastly, incorporation of the cycloaliphatic epoxy functionality into diene-based elastomers would result in crosslinkable elastomers that would be most probably compatible with epoxy resins employed as matrix resins for composite and other applications.

Synthesis and Characterization of Epoxy Functional Poly(Butadienes)

Three poly(butadienes) with different microstructures, (**PB420**, M_W 420000 g/mol, 36% *cis*-1,4, 55% *trans*-1,4, 9% 1,2-vinyl content; **PB220**, M_W 220000 g/mol, 7% *cis*-1,4, 93% 1,2-vinyl content; and **PB1**, M_W 1000 g/mol, 85% 1,2-vinyl content) were used in this study. In our initial experiments, precursor **I** was grafted by hydrosilation onto **PB420** at 90°C using Wilkinson's catalyst. The reaction was conveniently followed by monitoring the disappearance of the Si—H band at 2117 cm^{-1} in the infrared spectrum. This reaction required approximately 36 hours for complete hydrosilation. In contrast, repeating the reaction and using the platinum-containing Karstedt's catalyst required only 2 hours at 60°C for completion. After this time, the IR spectrum showed the complete disappearance of the 2117 cm^{-1} band. The ^{1}H-NMR spectrum of the grafted polymer shows prominent bands due to the epoxy protons which resonate at 3.1 ppm and a band at 0.0 ppm assigned to the protons of the methyl groups attached to the silicon atoms. The integrated peak intensities of the protons of the epoxide group in the ^{1}H-NMR spectrum matched well with the calculated values, indicating that the epoxide groups were preserved in the reaction. A GPC run of the two reaction products, however, showed that the molecular weight of poly(butadiene) had decreased in both cases after the grafting reaction. This suggests that the reaction conditions for hydrosilation also bring about main-chain scission in the polymer backbone. For this reason, the effects of the reaction conditions on the molecular weight of a typical poly(butadiene) polymer were briefly investigated to determine the optimum conditions which would minimize main-chain scission during hydrosilation. A series of experiments were conducted in which 1) a toluene solution of **PB420** was first heated at 90°C, 2) heated and stirred at 90°C, 3) heated and stirred at 90°C in the presence of Wilkinson's catalyst, 4) heated and stirred at 90°C in the presence of Wilkinson's catalyst and tri-*n*-hexylsilane (THS), and 5) heated and stirred at 90°C in the presence of Wilkinson's catalyst together with pentamethyldisiloxane (PMDS). The GPC molecular weights were measured at different times during each of these treatments and are shown graphically in Fig. 1. It can be seen from this figure that on simply heating a solution of poly(butadiene), the molecular weight drops from 450,000 to 260,000 g/mol in 22 hours and thereafter remains stable until the end of experiment at 92 hours. In a stirred solution the chain scission process does not stop after 22 hours but continues to occur until the end of the experiment at 92 hours where the molecular weight drops to 50,000 g/mol. The slight drop in molecular weight on heating probably results from oxidative cleavage of weak linkages in the chain. At the same time, the drop in molecular weight that resulted from stirring can be attributed to mechanical shearing of the polymer chains. It is further seen from Fig. 1 that the addition of Wilkinson's catalyst to a stirred and heated solution accelerates the chain scission process. Further, the addition of silanes markedly speeds up the chain scission process such that the molecular weight falls sharply to 80,000 g/mol in 2 hours and thereafter the process slows down. In contrast, the molecular weight after 2 hours of heat treatment and stirring in the presence of Wilkinson's

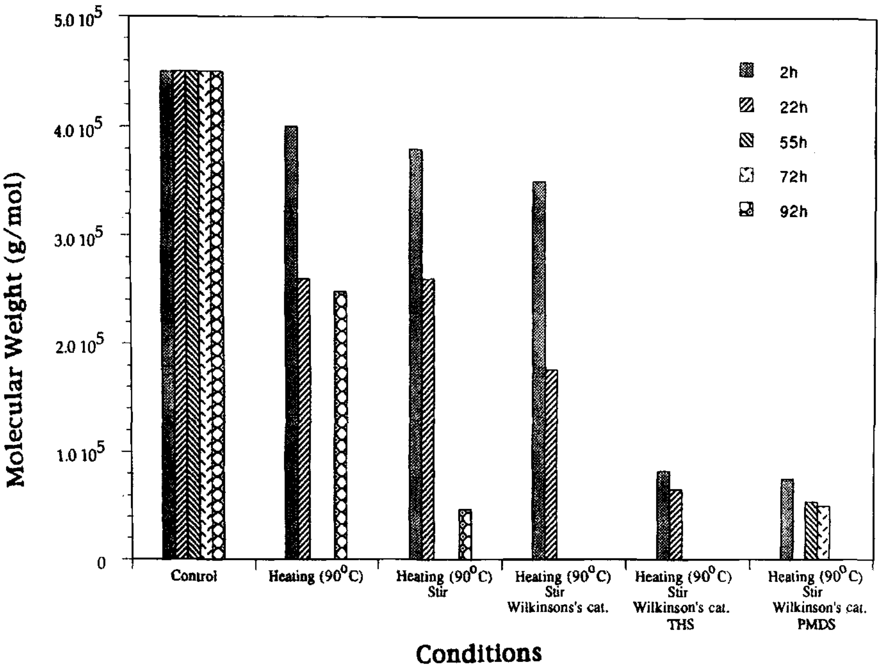


FIG. 1. Molecular weights of **PB420** as a function of reaction conditions.

catalyst was 350,000 g/mol. This phenomenon of molecular weight reduction appears to be dependant on the type of microstructure present in the poly(butadiene). While **PB420** with a very high 1,4-repeating unit content undergoes molecular weight reduction under the above conditions, no such drop in molecular weight was observed in the reactions involving **PB220** which has predominantly the poly(1,2-butadiene) structure.

The results of the chain scission study suggests that in order to prevent an excessive drop in the molecular weight of poly(butadiene) during hydrosilation, the reaction should be carried out at temperatures lower than 90°C and in the presence of the more active Karstedt's catalyst. Accordingly, reactions in the presence of Karstedt's catalyst were designed to maintain a stoichiometric excess of vinyl groups on the poly(butadiene) backbone. The excess vinyl groups act to keep the platinum metal in a complexed form and prevents the formation of colloidal platinum which is known to open the epoxide ring, causing crosslink formation [15]. Following this strategy, a series of different graft density poly(butadiene)s were synthesized which are shown in Table 1. An overall graft density as high as 60% was achieved for **PB1**. Approximately 7 of a total of 9% of the vinyl groups in **PB420** could be grafted without gelation. The maximum overall graft density achieved on **PB220** was 30%. Attempts to further increase the graft density resulted in gelation. For example, when 54% of the repeat units in **PB220** were grafted, the polymer did not redissolve in chloroform after precipitation and drying.

Figure 2 shows the GPC traces of **PB1** before and after (**PB1-60**) grafting 60% of the vinyl repeat units with **I**. The molecular weight of this polymer more than doubles after grafting. There was no perceivable viscosity change after grafting. **PB420-1** with 1% and **PB420-7** with 7% of the repeat units grafted were both rubbery materials. In Fig. 3 (Curve a) is shown the GPC trace of **PB420** before hydrosilation reaction. After completion of the grafting reaction using Karstedt's catalyst (Fig. 3, Curve b), there is a shift toward lower molecular weight. A very large drop in molecular weight is observed (Fig. 3, Curve c) when the reaction was carried out using Wilkinson's catalyst.

TABLE 1. Characteristics of Epoxy Grafted Poly(Butadienes)

Grafted polybutadiene	Appearance	M_n Before grafting	M_n After grafting	% Grafting Calcd	% Grafting Expt[a]
PB1-60	Viscous, liquid	2,100	5,800	59.0	60.0
PB220-2	Leathery	87,000	115,000	1.8	1.7
PB220-7	Rubbery	87,000	133,000	7.3	7.2
PB220-31	Tacky	87,000	161,000	31.0	31.8
PB220-52[b]	Tacky	87,000	215,000	50.0	–
PB420-1	Rubbery	231,000	182,000	0.94	0.85
PB420-7	Rubbery	231,000	186,000	6.9	6.7

[a] Determined by ^{1}HNMR.
[b] Partially soluble.

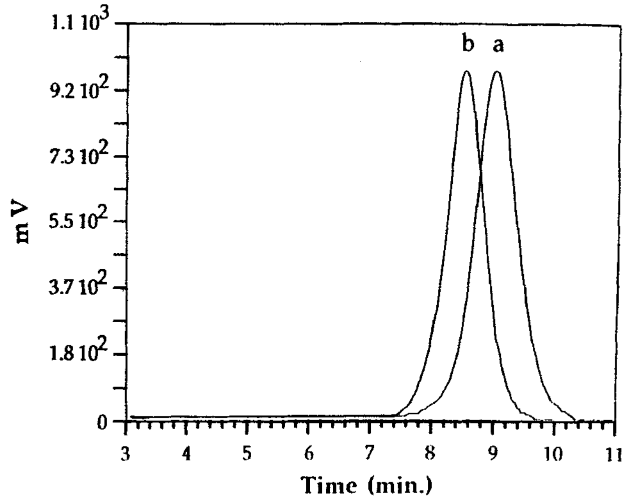


FIG. 2. GPC trace of poly(butadiene): (a) **PB1** before grafting and (b) after grafting by hydrosilation (**PB1-60**).

An effect of the graft density on the physical state of certain poly(butadiene)s has also been noted. For example **PB220-2** with 2% grafted **I** was leathery, while 7% grafted was clearly elastomeric. **PB220-31** with 31% grafted **I** was a viscous, tacky material. In Fig. 4 it can be seen that the molecular weights of the grafted products were higher than the starting poly(butadiene)s and increased with increasing graft density. The change in appearance from leathery in **PB220-2** to rubbery in

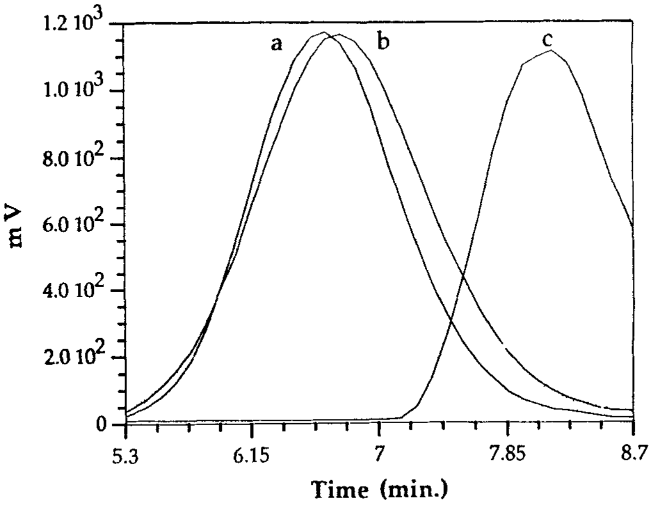


FIG. 3. GPC trace of poly(butadiene): (a) **PB420** before grafting, (b) after grafting by hydrosilation with Karstedt's catalyst (**PB420-1**), and (c) after grafting by hydrosilation with Wilkinson's catalyst (**PB420-1**).

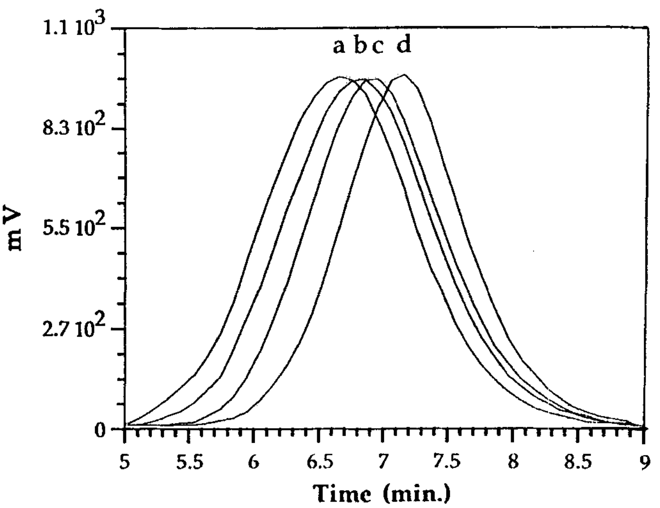


FIG. 4. GPC trace of poly(butadiene) with different extents of grafting: (a) **PB220-31** 31% grafting, (b) **PB220-7** 7% grafting, (c) **PB220-2** 2% grafting, and (d) **PB220** before grafting.

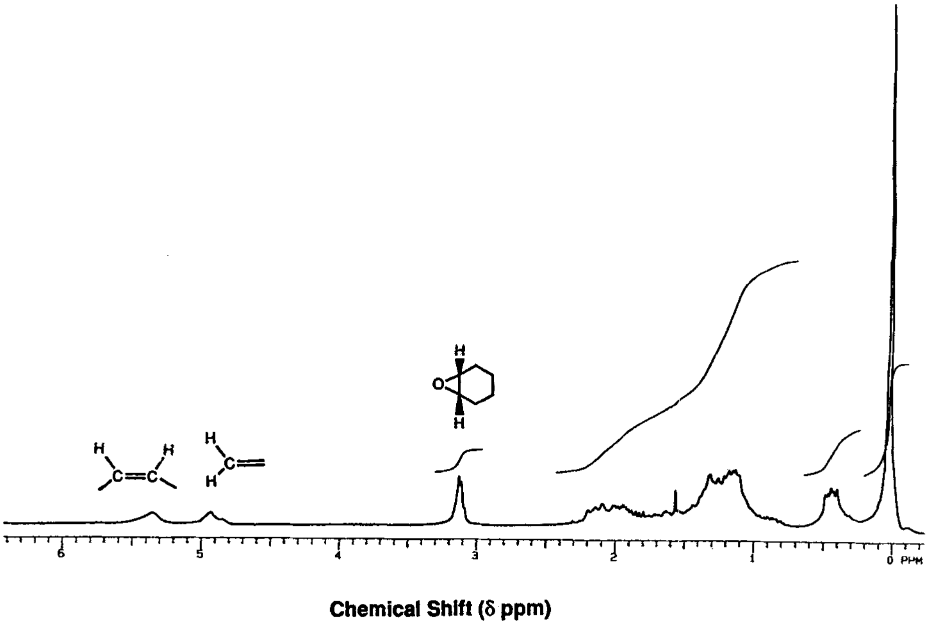


FIG. 5. 200 MHz ^{1}H-NMR spectrum of **PB1-60**.

PB220-7 is attributed to the fact that a 7% graft density in the latter was able to suppress the crystallinity and lower the T_g of the parent poly(butadiene) (**PB220**). A further increase in graft density to 31% has a plasticizing effect which makes this high molecular weight polymer tacky and viscous.

Figures 5, 6, and 7, respectively, show the ^{1}H-NMR spectra of **PB1-60, PB420-1,-7** and **PB220-2,-7,-31**. All the spectra of the grafted polymers contain peaks due to the epoxy group at 3.1 ppm and the 12 protons of the methyl groups attached to

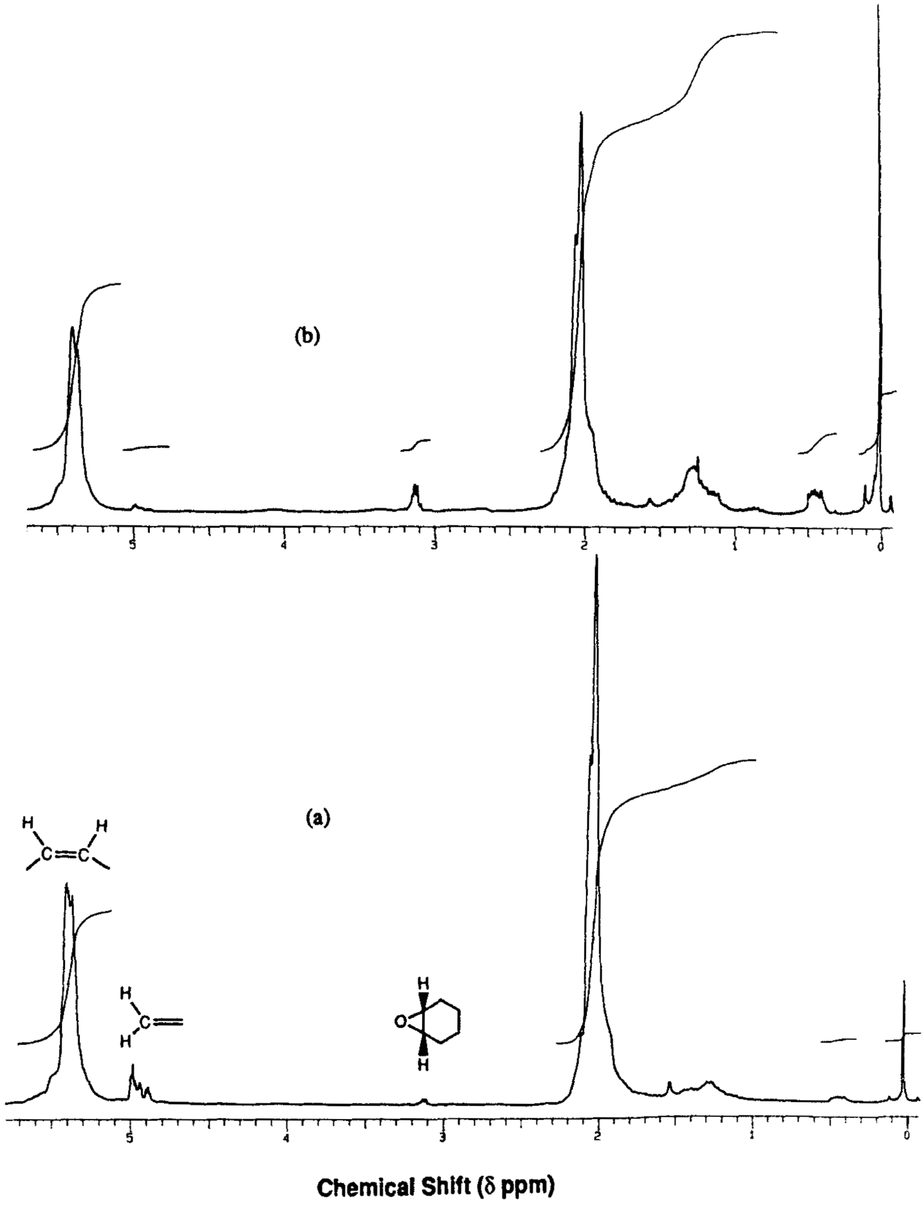


FIG. 6. 200 MHz ^{1}H-NMR spectrum of (a) **PB420-1** and (b) **PB420-7** .

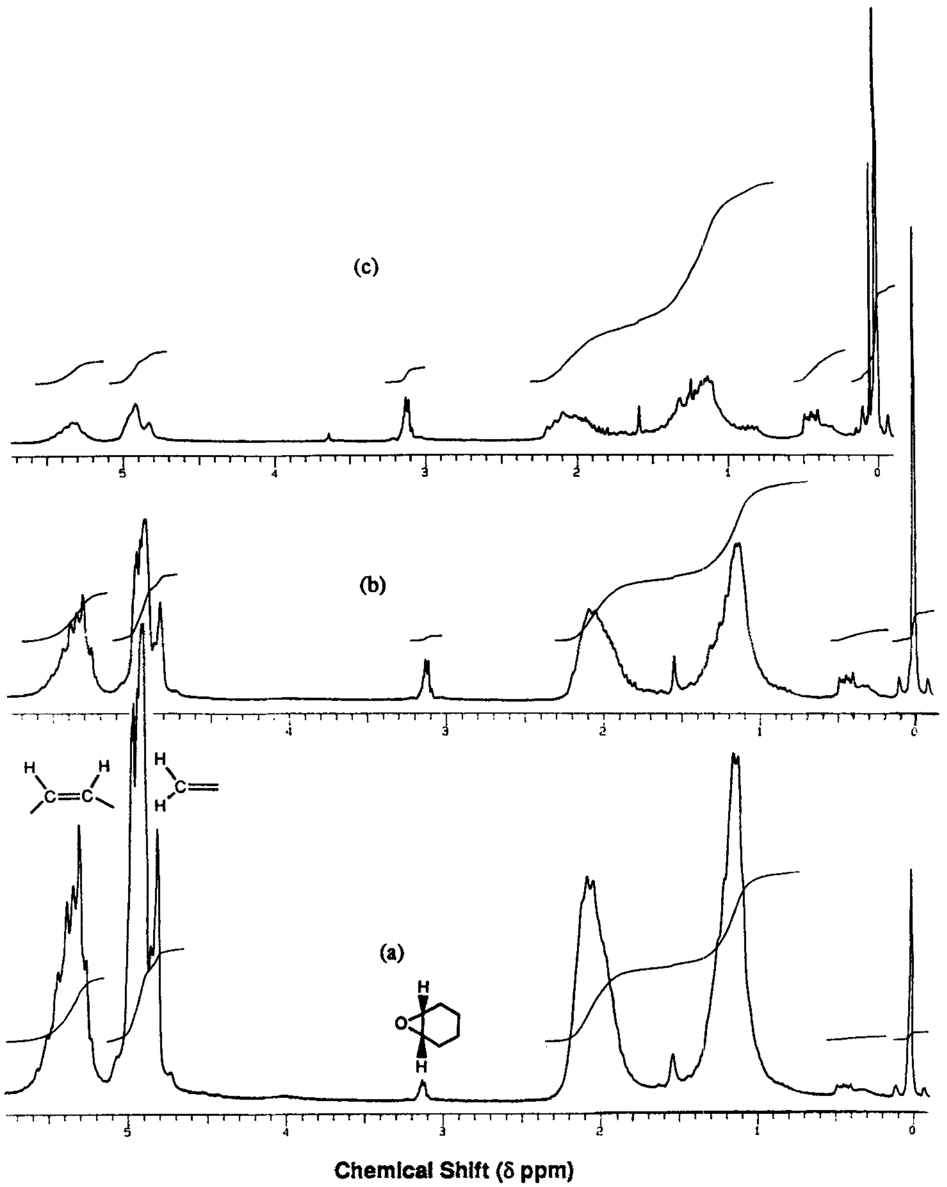


FIG. 7. 200 MHz ^{1}H-NMR spectrum of (a) **PB220-2**, (b) **PB220-7**, and (c) **PG220-31**.

silicon at 0 ppm. The resonance in the region of δ = 4.8–5.0 ppm corresponds to the two terminal vinylic protons of the 1,2-vinyl units of poly(butadiene). It can be seen in Figs. 6 and 7 that as the graft density increases, the intensity of the peaks at 3.1 ppm (epoxy) and 0 ppm (methyl—Si) increase as the vinyl protons at 4.9 ppm decrease. The graft density calculated from the integrated intensities of peaks at 3.1 and 4.9 ppm corresponded well with the theoretically calculated values and are reported in Table 1.

The methanol-precipitated and vacuum-dried grafted poly(butadienes) were stable with respect to crosslinking on storage and could be redissolved in toluene and chloroform. UV irradiation of the grafted poly(butadiene)s in the presence of the photoinitiator IOC10 gave crosslinked films which ranged from flexible and elastic to rigid and tough depending on the graft density of the starting functionalized poly(butadiene). The color of the UV-cured films varied from colorless to pale yellow. After UV curing, the crosslinked films were completely insoluble in chloroform and toluene.

Real-Time Infrared Spectroscopic Analysis (RTIR)

Figure 8 shows the IR spectrum of **PB1-60**. The shoulder at 886 cm^{-1} is assigned to the epoxide group. Since the graft density in other modified poly(butadiene)s is low, the epoxide absorptions in the IR spectra of the other samples were somewhat more obscured. Nevertheless, the sensitivity of the FT-RTIR technique and the mathematical routines of the Grams software made it possible to directly record the conversion versus irradiation time profiles during the course of photopolymerization even in samples with low epoxy graft content.

In Fig. 9 are plotted the RTIR conversion versus irradiation time curves for five grafted poly(butadiene)s. An inspection of this figure shows that the crosslinking reaction starts after an induction periods of about 10 seconds. The conversions after 600 seconds ranged from 67 to 80%. A conversion of 67% for **PB1-60** means that on, an average, 40% of the repeat units on the poly(butadiene) backbone

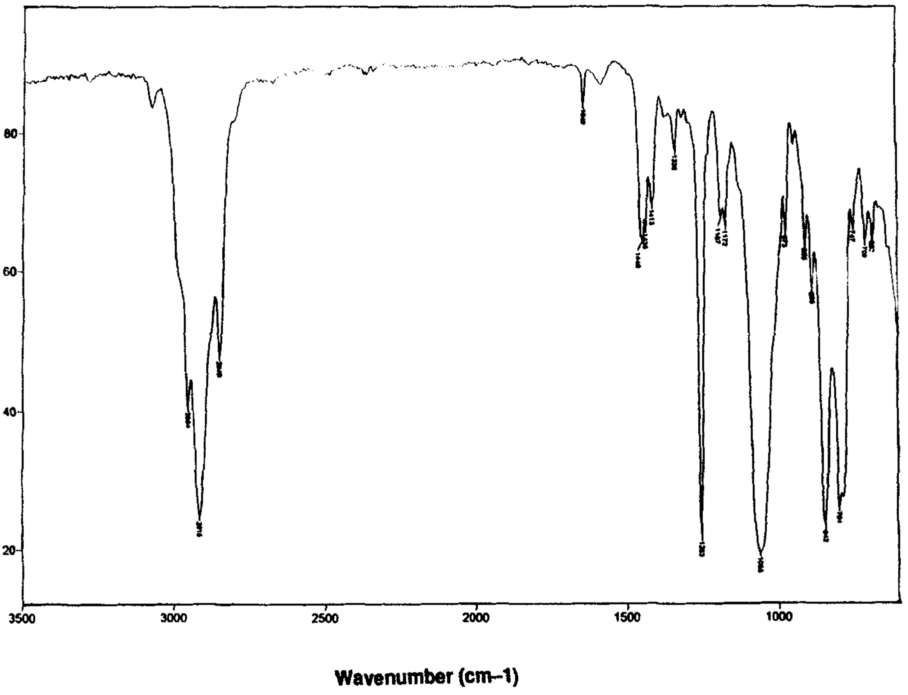


FIG. 8. FT-IR of grafted poly(butadiene) **PB1-60**.

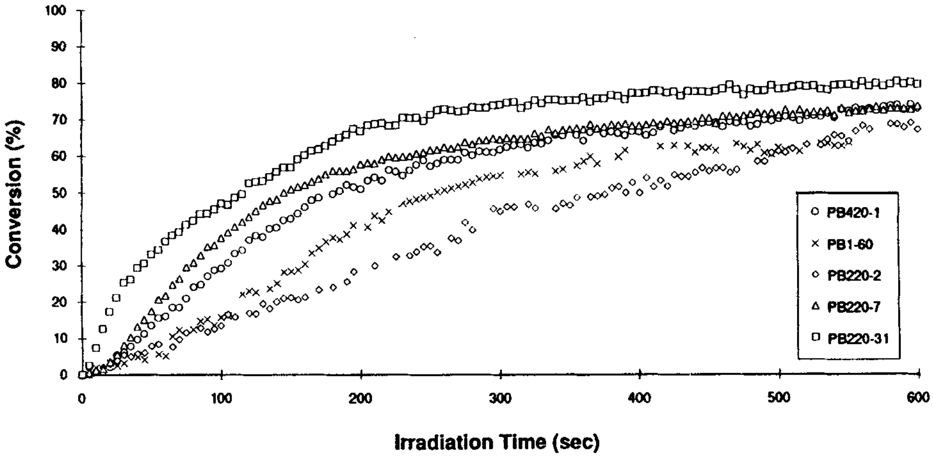


FIG. 9. Plot of the conversion of epoxy groups as a function of irradiation time for various grafted poly(butadienes).

participate in the crosslinking reaction which lends rigidity and a high T_g for this polymer. Figure 9 shows the RTIR curve for the cationic polymerization of **PB420-1**. After an induction period of about 15 seconds, a conversion of 55% is reached in 240 seconds which is followed by a retardation in the reaction rate as the mobility of the reacting functional groups is restricted by the crosslinked matrix which is formed. The resulting poly(butadiene) has a calculated crosslink density of approximately 0.5%, which accounts for the elastomeric nature of the polymer.

The rate of epoxide ring-opening polymerization, among other factors, depends on the concentration of the epoxy groups present and the mobility of the poly(butadiene) backbone (i.e., T_g). **PB220-31** exhibits the highest polymerization rate due to its high epoxy content. The rates decrease considerably as the epoxy contents decrease to 7% in **PB220-7** and to 2% in **PB220-2**, other factors remaining constant. The conversion in these latter samples continues to increase gradually until the end of the experiment at 600 seconds. The conversation rate of polymerization for **PB1-60** is among the lowest even though it has the highest epoxy content (60%). The reason is that the T_g of the polymer rises rapidly wiht increasing crosslink density, resulting in both a sluggish cure reaction and a poor conversoin.

Thermal Analysis of Photocrosslinked Films

The TGA curves of several photocrosslinked poly(butadiene)s are given in Fig. 10. An inspection of this figure shows that crosslinked **PB220-2** and **PB220-7** are thermally stable to temperatures in excess of 450°C in a nitrogen atmosphere. As the graft density goes up in **PB220-31** and **PB60-1**, the onset of decomposition is reduced to approximately 400°C. It was shown in an earlier publication [4] that a film of **PB420** shows a sharp loss in weight at around 350°C. Introduction and crosslinking of 1% of an epoxycyclohexyl graft onto this polymer increases the thermal decomposition temperature to about 400°C.

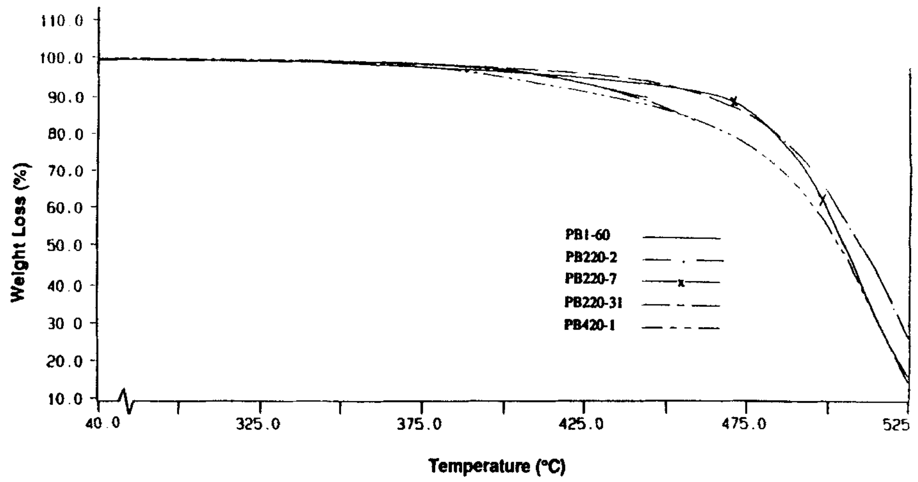


FIG. 10. Thermal decomposition profiles under nitrogen at a heating rate of 20°C/min for various photopolymerized epoxy functionalized poly(butadiene)s.

In all the photocrosslinked polymers derived from **PB220**, the crystalline and the amorphous phases give rise to distinct melting and glass transition peaks. According to the manufacturer's specifications, **PB220** has 29% crystallinity and shows a melting peak at 90°C. Grafting 2% of **I** onto this polymer to give **PB220-2** partially disrupts the crystallinity in the polymer chains and lowers the melting peak to 44°C (Fig. 11, Curve a). A similar drop in the melting peak to 41°C is observed for a 7% graft for **PB220-7** (Fig. 11, Curve b). T_gs are also observed for **PB220-2** and **PB220-7** of 7.6 and 15°C, respectively. The increase in T_g is reasonable because of the higher crosslink density in the latter polymer. **PB220-31** also exhibits a melting peak at 48°C and a much higher T_g of 85°C. The higher, 31% graft density in this polymer restricts the chain mobility which results in a sharp rise in the T_g. It should be noted that these samples have a heterogeneous microstructure, and thus the T_g is derived from the amorphous segments while the T_m is from the crystalline portion of the **PB220** structure. On subjecting **PB220-7** and **PB220-31** to a second heating cycle, one does not observe the melting peak, whereas for **PB220-2** the melting peak becomes broad and shifts to 56°C on reheating. One may speculate that the presence of a higher crosslink density in **PB220-7** and **PB220-31** does not allow the crystallites to reform after the heating cycle. A reviewer has also pointed out that the ^{1}H-NMR spectra (Fig. 7) show that these polymers possess considerable amounts of unreacted 1,4-*cis*-PB units (δ = 5.3-5.4 ppm). These units may serve as plasticers that partially prevent the reformation of crystallites on cooling.

The T_g value reported by the manufacturer for **PB420** is −96°C. On grafting **I** and photocrosslinking, the T_g of **PB420-1** increases to −38°C. Thus, the crosslinked polymer is still flexible and elastomeric at room temperature. In contrast, the highly crosslinked polymer obtained from **PB1-60** exhibits an exceptionally high T_g of 226°C and displays typical highly crosslinked rigid, brittle thermoset characteristics.

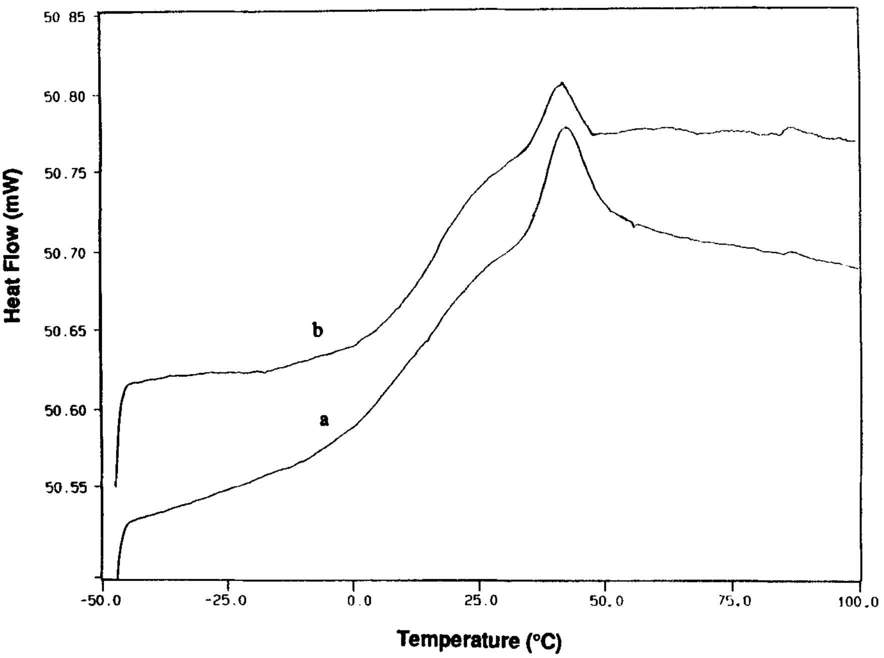


FIG. 11. DSC profile for photocrosslinked (a) **PB220-2** and (b) **PB220-7**.

CONCLUSIONS

Grafting of epoxy cyclohexyl groups on to the backbone of poly(butadiene)s using a polymer analogous hydrosilation reaction is an efficient method of producing photocrosslinkable polymers. By appropriate control of the stoichiometery, it is possible to control the graft density. Various modified poly(butadiene)s exhibiting a range of properties were synthesized. For example, crosslinked poly(butadiene)s with T_g spanning a range from -38 to 226°C were obtained possessing elastomeric and thermoset properties. These polymers have many potential applications in coating, adhesives, impact modification, and photoresists.

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