Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Photoinitiated Cationic Polymerization of Epoxidized Elastomers

James V. Crivello[a]; Bo Yang[a]
[a] Department of Chemistry, Center for Polymer Synthesis Rensselaer Polytechnic Institute Troy, New York

To cite this Article Crivello, James V. and Yang, Bo(1994) 'Synthesis and Photoinitiated Cationic Polymerization of Epoxidized Elastomers', Journal of Macromolecular Science, Part A, 31: 5, 517 — 533
To link to this Article: DOI: 10.1080/10601329409349735
URL: http://dx.doi.org/10.1080/10601329409349735

J.M.S.—PURE APPL. CHEM., A31(5), pp. 517–533 (1994)

SYNTHESIS AND PHOTOINITIATED CATIONIC POLYMERIZATION OF EPOXIDIZED ELASTOMERS

JAMES V. CRIVELLO* and BO YANG

Department of Chemistry
Center for Polymer Synthesis
Rensselaer Polytechnic Institute
Troy, New York 12180

Key Words: Epoxidized elastomers; Phase transfer epoxidation; Cationic photopolymerization; Real-time infrared spectroscopy

ABSTRACT

Low and high molecular weight *cis*-1,4-poly(isoprene), 1,4-poly(butadiene), and 1,2-poly(butadiene) were epoxidized using a tungsten-based redox phase transfer catalyst and hydrogen peroxide. The epoxidation reaction was studied with respect to the influence of the structure on the rate and extent of epoxidation. A study of the photoinduced cationic crosslinking of these oligomers and polymers was carried out in the presence of UV light. Specialized photoinitiators consisting of diaryliodonium salts bearing long alkoxy chains attached to the aromatic rings were prepared and used in these studies. The effects of the structure of the epoxidized elastomer, its level of epoxidation, and the concentration and type of photoinitiator on the rate and extent of crosslinking polymerization were studied.

INTRODUCTION

One of the main focuses of interest in this laboratory has been the study of the photoinitiated cationic ring-opening polymerization of multifunctional epoxides

[1-3]. The very low energy requirements, solvent-free process, high polymerization rate, excellent properties, and insensitivity toward oxygen make these crosslinking polymerizations especially attractive for such commercial applications as coatings, inks, adhesives, and photoresists. Until recently, much attention has been devoted to the investigation of the polymerization of simple, low molecular weight epoxide-containing monomers. However, it was recognized that the range of chemical and mechanical properties obtainable with these conventional materials is limited. For example, by photopolymerizing such low molecular weight high functionality monomers it is difficult to obtain polymers having high degrees of flexibility and elongation. In an effort to circumvent these limitations, we have begun to investigate the possibility of incorporating the epoxy functionality into oligomeric and high molecular weight elastomers which can be photocrosslinked or "photovulcanized" to produce networks that combine the properties of rubbers and epoxy resins. Similar considerations have led Decker and his coworkers [4] to modify diene polymers by attaching acrylic ester groups and Kennedy et al. [5] to prepare epoxy telechelic poly(isobutylenes). Both of these groups studied the UV-induced crosslinking of the respective functionalized elastomers. Such materials have considerable potential applications in coatings, adhesives, and photolithography. This paper concerns the synthesis, characterization, and photoinitiated cationic crosslinking of both low and high molecular weight partially epoxidized *cis*-1,4-poly(isoprene), 1,4-poly(butadiene), and 1,2-poly(butadiene).

EXPERIMENTAL

Materials

All materials were used as received. Hydrogen peroxide (30%) was obtained from Fluka-Chemika. Tungstic acid (99%), methyltricaprylammonium chloride (Aliquat 336), squalene (97%), *cis*-1-4-poly(isoprene) (1,4-PIP, M_w = 800,000 g/mol) and poly(butadiene) (1,4-PBD, 36% 1,4-*cis*, 55% 1,4-*trans*, 9% 1,2-vinyl, M_w = 420,000 g/mol) were purchased from Aldrich Chemical Co. *cis*-1,4-Poly(isoprene) (1,4-PIP, LIR-30, MW = 29,000 g/mol) was obtained from Kuray Co. 1,2-Poly(butadiene) (1,2-PBD, Ricon 152, 85% 1,2-vinyl, 15% 1,4-*cis* and *trans*, M_w = 1600 g/mol) was received from Ricon Resins. 1,4-Poly(butadiene) (1,4-PBD, Polyoil 110, 78% 1,4-*cis*, 21% 1,4-*trans*, and 1% 1,2-vinyl, MW = 1700 g/mol) was purchased from Hüls America. The photoinitiators used were prepared as described previously [6]. Methyltricaprylammoniumtetrakis(diperoxotungsto)phosphate (MTTP) was prepared by the method of Venturello et al. [7].

General Procedures for Epoxidation

Epoxidation of Liquid Elastomers

The following procedure for the epoxidation of *cis*-1,4-poly(isoprene) is typical of that used for all of the liquid elastomers described in this investigation. Into a 250-mL three-necked round-bottom flask fitted with a thermometer, a reflux condenser, a pressure-equalizing addition funnel, and a magnetic stirrer were placed 6.3 g (0.097 mol) *cis*-1,4-poly(isoprene), 100 mL toluene, and 0.15 g (6.7×10^{-5}

mol) MTTP phase transfer catalyst. The polymer solution was heated to 55°C, then 5 mL of 30% hydrogen peroxide was added dropwise within 5 minutes. The reaction temperature was then raised and maintained at 60°C. The resulting biphasic reaction mixture was vigorously stirred and the course of the reaction monitored by ^1H NMR. After the desired degree of epoxidation was achieved, the water and organic layers were separated. The organic layer was washed with distilled water to remove catalyst residues and traces of hydrogen peroxide, dried over anhydrous Na_2SO_4, and the toluene removed on a rotary evaporator. The pale yellow viscous product was dried overnight under vacuum.

Epoxidation of High Molecular Weight Elastomers

Solid elastomer (5.0 g) was dissolved in 50 mL toluene in a 100-mL three-necked glass flask equipped with a thermometer, a reflux condenser, and a magnetic stirrer. The polymer solution was heated to 50°C and the phase transfer catalyst was introduced, followed by the addition of a measured volume of 30% hydrogen peroxide. The reaction temperature was raised and maintained at 60°C. Samples were withdrawn at various time intervals, precipitated into methanol, and then subjected to ^1H-NMR analysis. The coagulated polymer was dried overnight at 50°C under vacuum.

Epoxidation of Squalene

Into a 100-mL three-necked round-bottom flask fitted with a thermometer, a reflux condenser, a pressure-equalizing addition funnel, and a magnetic stirrer were placed 5 g squalene and 0.7 g MTTP phase transfer catalyst. The polymer solution was heated to 55°C, then 30 mL of 30% hydrogen peroxide was added dropwise within 10 minutes. The reaction temperature was raised and maintained at 60°C. The resulting biphasic reaction mixture was vigorously stirred and the course of the reaction monitored by ^1H-NMR. After the epoxidation was completed as judged by the disappearance of the olefinic protons at $\delta = 5.45$ ppm, the water and organic layers were separated. The organic layer was washed with distilled water to remove catalyst residues and traces of hydrogen peroxide, and then dried over anhydrous Na_2SO_4. The final product was dried overnight under vacuum. The yield of squalene hexaepoxide was 6.13 g (100% conversion).

Analysis. Calculated for $C_{30}H_{50}O_6$: C, 71.15%; H, 9.88%; Found: C, 71.11%; H, 9.82%.

Characterization of Epoxidized Elastomers

^1H-NMR spectra of the products were obtained on a Varian XL-200 spectrometer using $CDCl_3$ as the solvent and tetramethysilane as an internal reference. The conversion of double bonds during epoxidation was calculated from the ^1H-NMR spectra using Eq. (1):

$$\%\ \text{conversion} = [I_e/(I_e + I_d)](100) \tag{1}$$

where I_e is the integrated area of the peak at $\delta = 2.9$–3.1 ppm due to the protons on the epoxide carbons, and I_d is the integrated area of the peak at $\delta = 5.07$–5.50 ppm assigned to the protons on the carbons of the double bonds.

Molecular weights and molecular weight dispersities of the high molecular weight elastomers and their epoxidized analogues were determined in toluene using a Hewlett-Packard Model 1090 Gel Permeation Chromatograph. All GPC measurements were carried out on μ-styragel columns (particle size 5 μm, mixed 34–24 Å pore sizes), and the molecular weights are reported relative to monodisperse polystyrene standards.

Thin-Film Photopolymerizations

Photopolymerizations of the partially epoxidized liquid elastomers were carried out in the absence of solvents but in the presence of 0.5 mol % of either (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10SbF$_6$) or (4-decyloxyphenyl)phenyliodonium hexafluorophosphate (IOC-10PF$_6$) as photoinitiators. Solutions of the epoxidized liquid elastomers containing various amounts of the photoinitiators were drawn onto 8 in. × 4 in. cold rolled steel panels (Q-Panel Co.) using a BYK-Gardner AG-4301 film casting knife for chemical and mechanical property measurements. The thickness of the cured films was 3 mils (76 μm). The epoxidized elastomers were photopolymerized using a Fusion Systems Inc. Laboratory UV Cure Processor. The apparatus consisted of a microwave-activated 300-W UV lamp configured perpendicular to the travel of the conveyor belt and mounted at a distance of 10 cm from the belt. The radiation dose required to cure the epoxide was measured using a UV Process Supply Inc. Control Cure Radiometer.

Kinetic Studies by RTIR

The rate of the UV-induced crosslinking of the partially epoxidized liquid elastomers was studied by real-time infrared spectroscopy (RTIR). The apparatus used in this work consisted of a Buck Scientific Model 500 Infrared Spectrometer which was equipped with a UVEXS Co. SCU 110 UV lamp fitted with a fiber optic cable. The probe of the fiber optic cable was positioned so that the UV irradiation was directed onto the sample window of the spectrometer. The intensity of the irradiation could be varied by fixing the probe at various distances from the sample. All studies were conducted using broad band, unfiltered UV light. The polymerizations were carried out at room temperature in the presence of air. Solutions of the epoxidized liquid elastomers containing 0.5 mol % of the photoinitiators were cast onto thin polyethylene films using a wire-wound metal bar to a thickness of 1.2 mils (30.5 μm) and 2.4 mils (70 μm). The samples were irradiated at a UV intensity of 20 mW/cm^2 with a probe distance of 5 cm from the sample. The photopolymerizations were monitored by following the decrease of the characteristic epoxide absorption band (880–890 cm^{-1}) as a function of time upon UV exposure. Residual double bond absorption at 1667 cm^{-1} in the partially epoxidized elastomer was taken as an internal reference for the percent conversion calculation.

Characterization of the Photocured Elastomers

Thermogravimetric analyses were performed under nitrogen using a Perkin-Elmer Series 7 Thermogravimetric Analyser at a heating rate of 20°C/min.

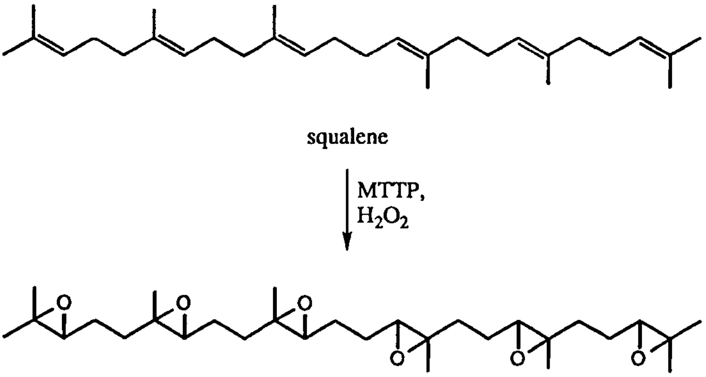
The gel content of the UV-cured epoxidized elastomers was measured by immersing preweighed 3 mil films of the photocured epoxidized polymer in acetone for 8 hours followed by drying over night at 50°C in a vacuum oven. The gel content was calculated from the weight ratio of the insoluble polymer to the initial sample. Impact testing was performed on a Gardner Impact Tester using a 4-lb weight according to ASTM D 2794-84. Solvent resistance of the photocured elastomers was determined by applying a MEK (methyl ethyl ketone) saturated cotton swab to the cured film in a back and forth motion. One back and forth motion constituted one double rub (MEK double rubs). The end point was reached when erosion of the substrate surface was noted.

RESULTS AND DISCUSSION

Redox Phase Transfer Catalyzed Epoxidation of Unsaturated Elastomers

Unsaturated polymers can be epoxidized using a number of well-established techniques involving peracids as the oxidants [8–12]. However, of particular interest to this work was a novel phase transfer method for the epoxidation of olefins by Venturello et al. [7]. More recently, Hay et al. [13] extended this reaction to the epoxidation of unsaturated polymers. A modification of the Hay procedure was used in this work. The phase transfer catalyzed method is advantageous in that it is efficient, simplifies work-up and avoids the use of peracids. It is also a very economical method of epoxidization.

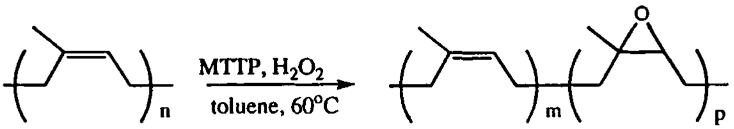
We began these investigations with a study of the phase transfer epoxidation of the model compound, squalene, which is structurally related to *cis*-1,4-poly(isoprene). Squalene undergoes exhaustive epoxidation in the presence of hydrogen peroxide and the redox phase transfer catalyst methyltricaprylammoniumtetrakis(diperoxotungsto)phosphate (MTTP) to give the hexaepoxide as shown in Eq. (2).



eq. 2

Squalene hexaepoxide was obtained as a crystalline solid upon workup of the reaction mixture and purification of the resulting oil. This compound was identical in all respects to that described in the literature [14]. Figure 1 shows the ^{1}H-NMR spectrum of this compound. The spectrum shows that no significant side reactions such as acid-catalyzed epoxide ring-opening occurred under the conditions of the phase transfer catalyzed epoxidation reaction.

After the successful completion of the model compound studies, the phase transfer catalyzed epoxidation was extended to several different unsaturated elastomers. Specifically, three different unsaturated oligomers and two high molecular weight elastomers were epoxidized: *cis*-1,4-poly(isoprene) (1,4-EPIP, low and high MW) 1,4-poly(butadiene) (1,4-EPBD, low and high MW), and 1,2-poly(butadiene) (1,2-EPBD). Equation (3) shows the general synthetic scheme employed for the epoxidation of unsaturated high and low molecular weight elastomers using hydrogen peroxide and MTTP as the catalyst in a biphasic aqueous/toluene system.



eq. 3

The course of the epoxidation reaction was conveniently followed using ^{1}H-NMR spectroscopy. A ^{1}H-NMR study of the epoxidation of 1,4-poly(butadiene) (1,4-PBD) is shown in Fig. 2. In the spectrum of the unsaturated precursor polymer, the peak at δ = 5.47 ppm is assigned to the protons on the carbons of the double bonds in the polymer. As the epoxidation proceeds, a new peak appears and in-

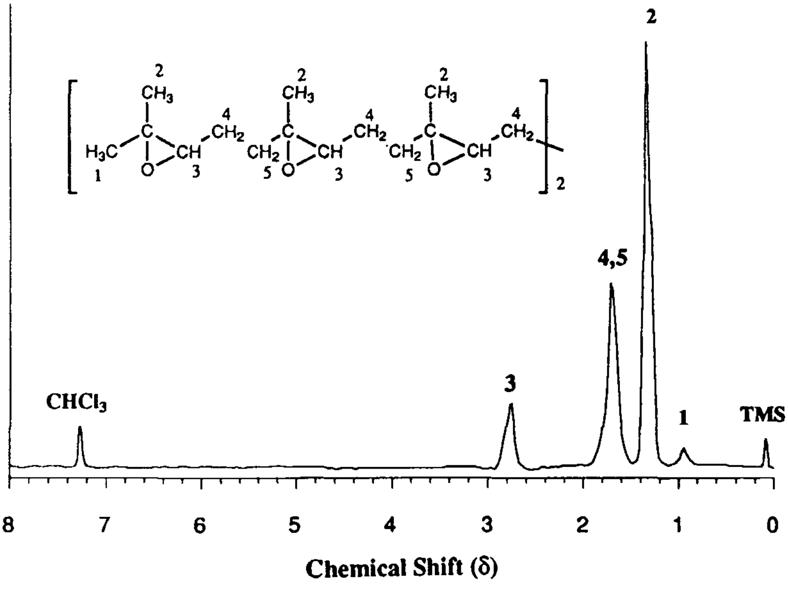


FIG. 1. ^{1}H-NMR spectrum of squalene hexaepoxide in $CDCl_3$.

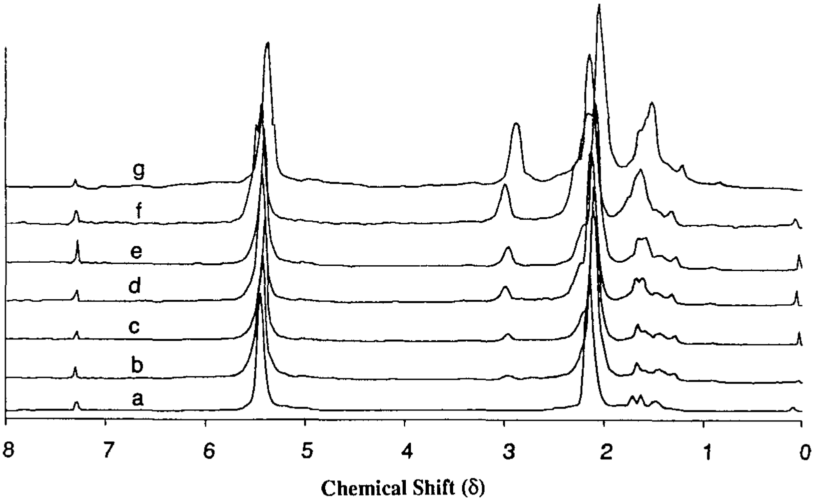


FIG. 2. ^{1}H-NMR spectra of the epoxidation of 14-PBD with time. Reaction after: (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, and (g) 120 minutes.

creases at $\delta = 3.0$ ppm due to the protons on the carbons of the epoxide groups while the intensity of the peak at $\delta = 5.47$ ppm concomitantly decreases.

It has been found that by appropriate manipulation of the reaction conditions, reaction time, and concentrations of reagents, it is possible to control the reaction to achieve any degree of epoxidation desired. Table 1 gives the experimental conditions used for the phase transfer epoxidation of three different unsaturated elastomers to 15 and 30% epoxidation of the double bonds. In this paper the percent epoxidation is denoted by values given in parentheses following the polymer. Thus, the designation; 1,4-EPIP (30%) indicates epoxidized *cis*-1,4-poly(isoprene) in which 30% of the double bonds have been converted to epoxide groups. In general,

TABLE 1. Experimental Conditions for the Phase Transfer Epoxidation of Unsaturated Elastomers[a]

Epoxidized elastomer	Elastomer, g	Catalyst, g	Reaction time, minutes
1,4-EPIP (15%)	6.3	0.15	36
1,4-EPIP (30%)	6.3	0.15	75
1,2-EPBD (15%)	5	0.45	64
1,2-EPBD (30%)	5	0.45	125
1,4-EPBD (15%)	5	0.15	44
1,4-EPBD (30%)	5	0.15	85

[a] Reactions carried out using 5 mL of 35% H_2O_2 in 100 mL toluene at 60°C.

the conversion of double bonds to epoxide groups increases with increasing reaction time for each polymer. However, considerable differences in the rate at which various polymers undergo epoxidation were observed, and these correlate with their structures. Figure 3 gives a comparison of rates of epoxidation of three different polymers together with the model compound squalene. Squalene is the most reactive substrate followed by 1,4-PIP and 1,4-PBD, while 1,2-PBD undergoes very sluggish epoxidation. These results are in accord with the usual reactivity observed for the epoxidation of small molecule olefins; i.e., trisubstituted > disubstituted > monosubstituted olefins.

The GPC analyses of the elastomers before and after epoxidation give insight into the epoxidation process and its influence on the molecular weight of the epoxidized polymers. As can be seen in Table 2, for high molecular weight poly(isoprene), the molecular weight distribution shows no significant change after epoxidation. But both the M_n and the M_w decrease after epoxidation. The extent of the decrease is proportional to the degree of epoxidation to which the reaction is carried. This strongly suggests that chain scission of the polymer backbone occurs during epoxidation. In contrast, the epoxidation of 1,4-PBD shows an increase in both M_n and M_w with increasing degree of epoxidation. However, there is no significant change in the molecular weight distribution. While the mechanism for this increase in molecular weight is still unknown, it may be speculated that it is due to a small amount of acid-induced crosslinking reaction during epoxidation. In this investigation the objective was to produce materials which upon crosslinking exhibit a high degree of flexibility and/or elongation. Hence, the maximum extent of the epoxidations carried out in these studies was 30%.

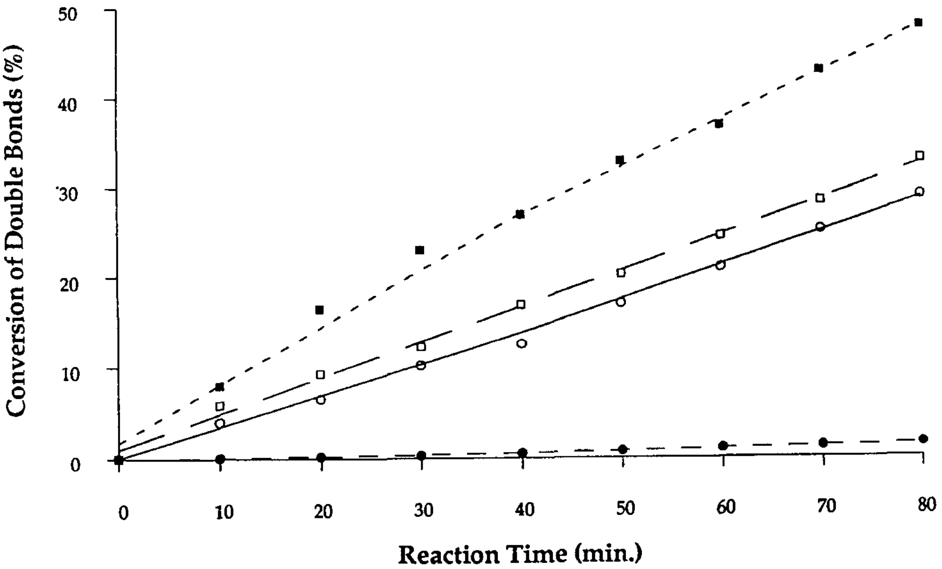


FIG. 3. Rate of phase transfer epoxidation for different oligomeric elastomers: (■) squalene; (□) 1,4-PIP; (○) 1,4-PBD; (●) 1,2-PBD.

TABLE 2. Molecular Weight Changes during the Epoxidation of Unsaturated Elastomers

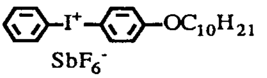
Polymer	M_n (g/mol)	M_w (g/mol)	MWD
1,4-PIP[a]	157,900	808,200	5.1
1,4-EPIP (15%)	107,900	655,900	6.1
1,4-EPIP (30%)	77,700	456,900	5.9
1,4-PBD[b]	56,000	360,700	6.4
1,4-EPBD (15%)	72,100	565,300	7.8
1,4-EPBD (30%)	111,500	648,300	5.8

[a] 97% 1,4-*cis*.

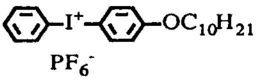
[b] 36% 1,4-*cis*; 55% 1,4-*trans*; 9% 1,2-vinyl.

Photoinitiated Cationic Polymerization

Initial attempts in this laboratory to carry out the photoinitiated cationic polymerization of the epoxidized elastomers prepared during the course of this work met with failure. In these studies a number of simple triarylsulfonium and diaryliodonium salts were used as photoinitiators. It was observed that such photoinitiators were nearly insoluble in the highly nonpolar hydrocarbon elastomers. Failure of these polymerizations is due mainly to the incompatibility of the photoinitiators and the epoxidized polymers. We recently described the synthesis of unsymmetrical diaryliodonium salts bearing long alkoxy chains in the para position of one of the aromatic rings [6]. It was observed that a number of these cationic photoinitiators were readily soluble in the epoxidized elastomers. Accordingly, the two diaryliodonium salts, (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10SbF$_6$) and (4-decyloxyphenyl)phenyliodonium hexafluorophosphate (IOC-10PF$_6$), depicted below, were employed as photoinitiators for the photopolymerization studies conducted during the course of these investigations.



IOC-10SbF$_6$



IOC-10PF$_6$

These two compounds are readily prepared by a straightforward synthesis. Both of the photoinitiators are colorless, crystalline compounds which can be readily purified by recrystallization. Further, the above photoinitiators have their major absorption band at 247 nm, which closely matches the 254 nm emission band of conventional mercury arc lamps. Thus, they are very efficient as cationic photoinitiators having quantum yields for photolysis of approximately 0.7. Solutions of the photoinitiators in the epoxidized elastomers can be prepared simply by stirring the crystalline compounds together with the polymers with slight heating.

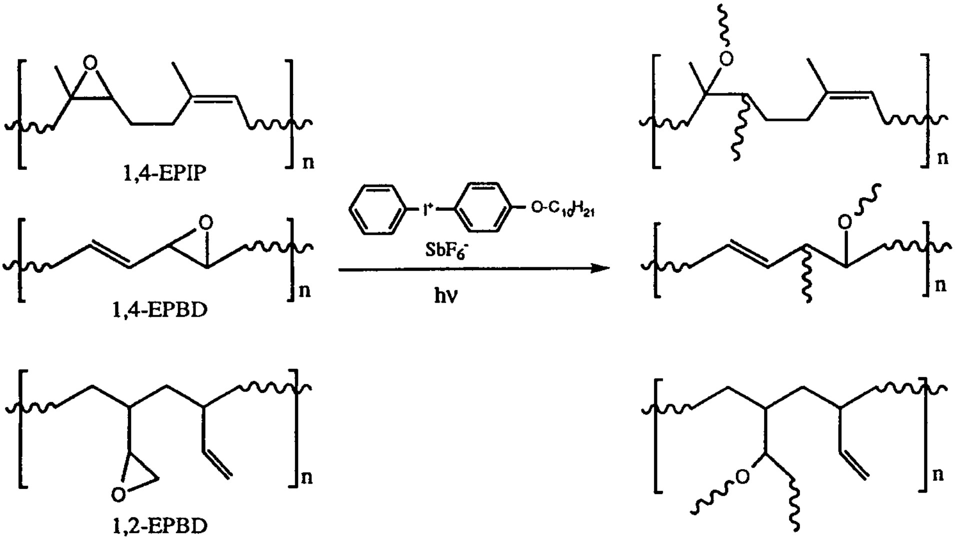
UV irradiation of films of the three epoxidized liquid elastomers containing 0.5 mol% of the photoinitiators give colorless, transparent, flexible, crosslinked polymers. This process is depicted in Scheme 1.

The photopolymerization of 1,2-EPBD gives fingernail creasible films which are tough plastics. These latter materials are not elastomeric. At the same time, the photoinduced crosslinking polymerization of 1,4-EPBD and *cis*-1,4-EPIP give materials which are clearly elastomeric with high elongations. The films obtained in all cases are insoluble in all common solvents due to crosslinking.

Real-time infrared spectroscopy (RTIR) was used to obtain kinetic data on the photoinduced cationic crosslinking polymerization of the epoxidized elastomers. This recently developed analytical technique makes it possible to directly record the conversion vs time profile during the course of a photopolymerization [15]. The ring-opening polymerization of the epoxy group and the concurrent appearance of ether linkages in the polymer networks can be easily monitored by infrared spectroscopy. For example, the IR spectra of a 1,4-EPBD film, before and after crosslinking, is shown in Fig. 4. The band at 880 cm^{-1} due to the epoxy groups has markedly decreased after irradiation while the linear ether band at 1100 cm^{-1} increased. Using RTIR, the rate of polymerization at any time in the reaction can be calculated according to

$$R_p = [M]_0([\text{conversion}]_{t2} - [\text{conversion}]_{t1})/(t_2 - t_1) \tag{4}$$

where R_p is the relative rate of polymerization, $[M]_0$ is the initial concentration of epoxy groups, and $[\text{conversion}]_{t2}$ and $[\text{conversion}]_{t1}$ are respectively, the conversions at times t_1 and t_2 calculated according to Eq. 1. In Table 3 are given the maximum rates of polymerization and the conversions after 300 seconds of UV irradiation for three different liquid epoxidized polymers taken from the RTIR curves. As shown



SCHEME 1.

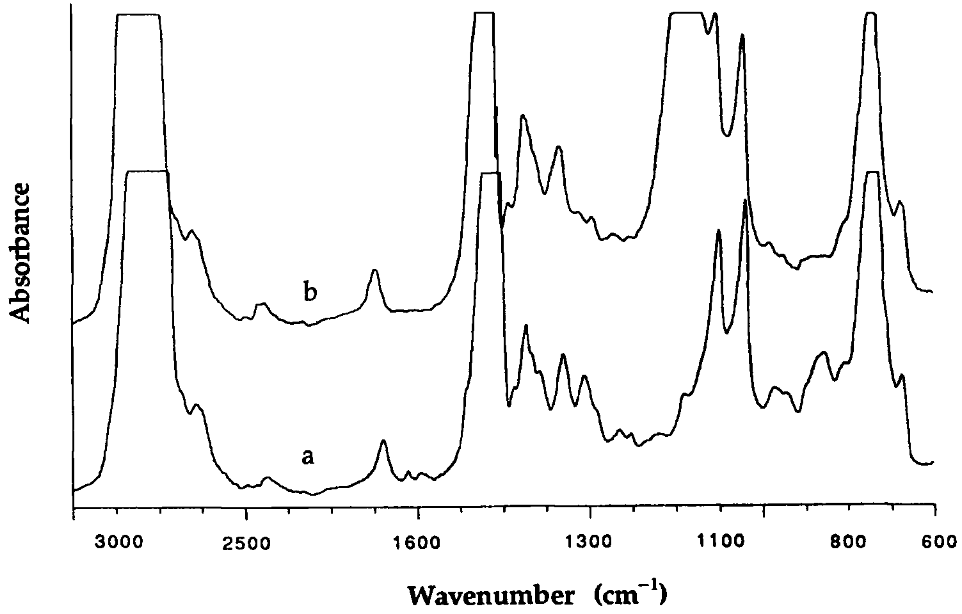


FIG. 4. IR spectra of 1,4-EPBD (30%): (a) before photopolymerization; (b) after photopolymerization.

TABLE 3. RTIR Kinetic Data for the Photopolymerization of Various Epoxidized Elastomers[a]

Epoxidized elastomer	$[M]_0$,[b] mol·L^{-1}	R_p,[c] mol·L^{-1}·s^{-1}	Extent of conversion, %[d]
1,2-EPBD (30%)	4.1	0.92	30.4
1,2-EPBD (15%)	2.1	0.52	31.2
1,4-EPBD (30%)	4.1	0.62	19.3
1,4-EPBD (15%)	2.1	0.34	18.5
cis-1,4-EPIP (30%)	3.3	0.32	11.6
cis-1,4-EPIP (15%)	1.7	0.16	11.0

[a] In air at a UV intensity of 20 mW/cm^2. Photoinitiator: 0.5 mol% IOC-10SbF6.

[b] Initial epoxide concentration.

[c] Maximum rate of polymerization.

[d] After 300 seconds of UV irradiation.

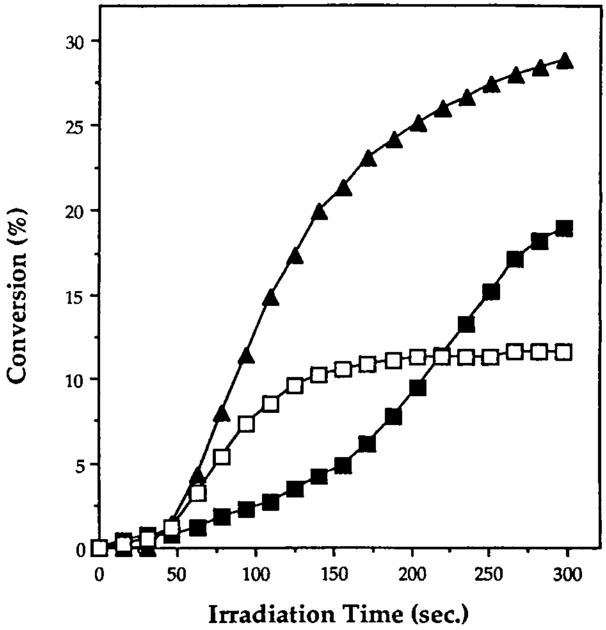


FIG. 5. RTIR comparison of the cationic photopolymerization of three epoxidized elastomers with same epoxide content: (▲) 1,2-EPBD (30%); (■) 1,4-EPBD (30%); (□) 1,4-EPIP (30%).

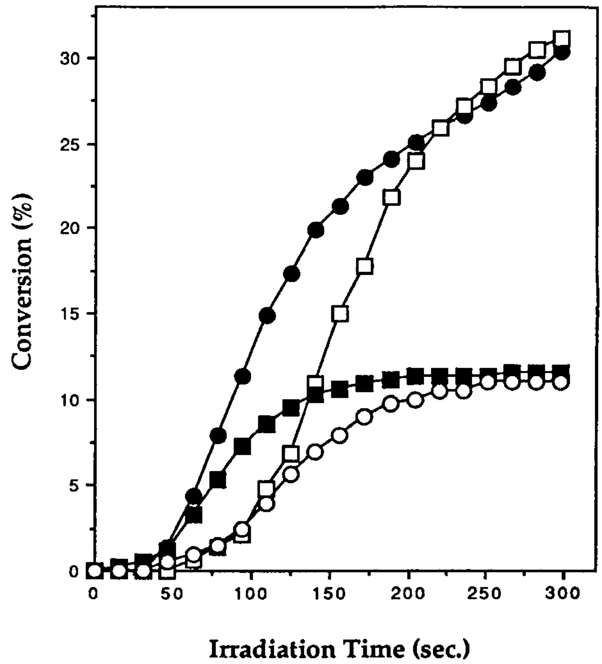


FIG. 6. RTIR study of the effect of the epoxide content on the cationic photopolymerization of (●) 1,2-EPBD (30%); (□) 1,2-EPBD (15%); (■) 1,4-EPIP (30%); (○) 1,4-EPIP (15%).

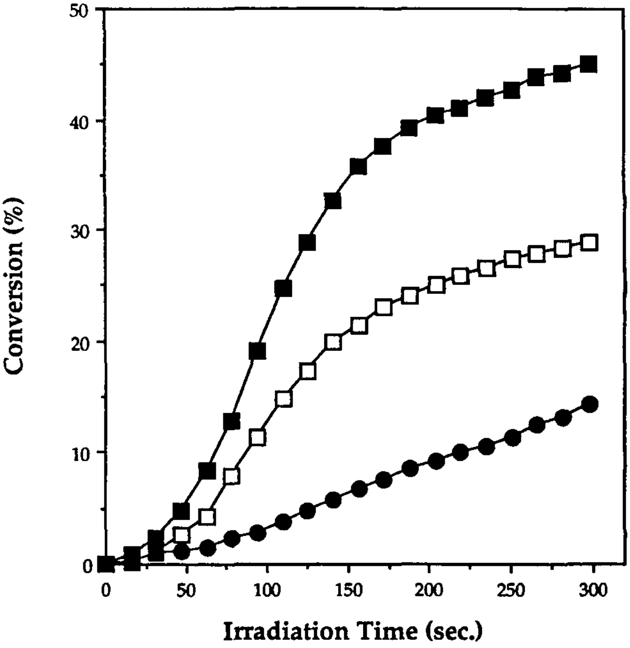


FIG. 7. RTIR study of the effect of the photoinitiator concentration on the cationic photopolymerization of 1,2-EPBD (30%); (■) 1% IOC-10SbF$_6$; (□) 0.5% IOC-10SbF$_6$; (●) 0.25% IOC-10SbF$_6$.

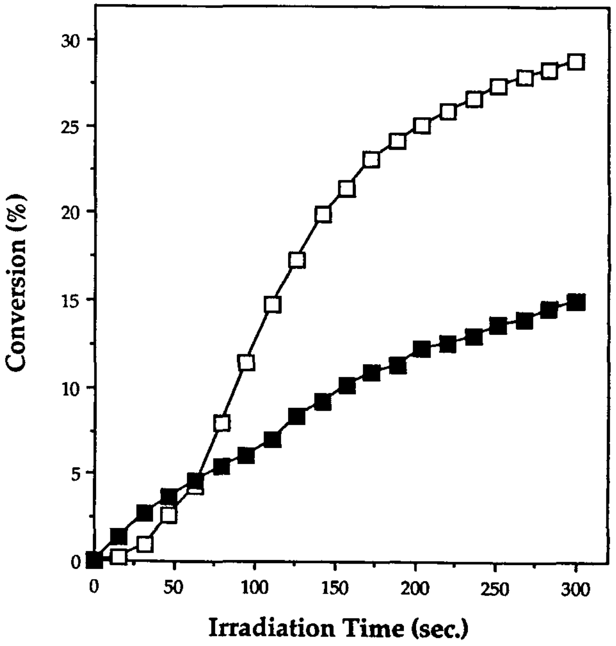


FIG. 8. RTIR study of the cationic photopolymerization of 1,2-EPBD (30%) with different photoinitiators: (□) 0.5% IOC-10 SbF$_6$; (■) 0.5% IOC-10PF$_6$.

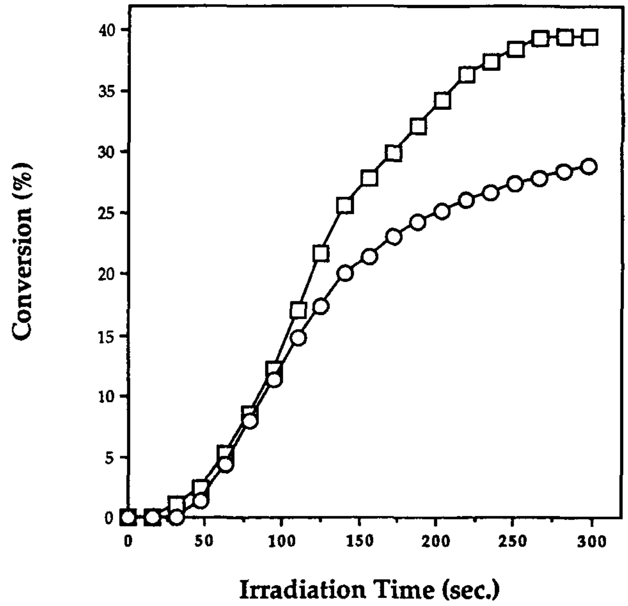


FIG. 9. RTIR study of the effect of film thickness on the cationic photopolymerization of 1,2-EPBD (30%) using 0.5% IOC-10SbF$_6$: (□) 1.2 mil (30.5 μm); (○) 2.4 mil (70.0 μm).

in Fig. 5, for the same degree of epoxidation (30 or 15%), 1,2-EPBD always gives a higher rate of epoxide ring-opening polymerization and a higher degree of conversion than either 1,4-EPBD or EPIP. This is because that 1,2-EPBD contains more highly reactive and less sterically hindered terminal and pendant rather than internal epoxy groups.

The rate of epoxide ring-opening polymerization and the conversion at any given moment of the reaction depends on the epoxide content of the elastomer. Figure 6 shows a comparison of the conversion vs time plots for the photopolymer-

TABLE 4. Properties of Photocrosslinked Epoxidized Elastomers[a]

Epoxidized elastomer	Gel content, %	Solvent resistance (MEK double rubs)	Gardner impact, ft-lb
1,4-EPIP (15%)	98.5	~500	~140
1,4-EPIP (30%)	97.5	~700	~160
1,2-EPBD (15%)	99.7	~700	~100
1,2-EPBD (30%)	97.1	~1200	~40
1,4-EPBD (15%)	96.4	~600	~120
1,4-EPBD (30%)	98.4	~800	~80

[a] *Curing conditions: 0.5 mol% IOC-10SbF$_6$; UV dose, 1100 mJ/cm^2; film thickness, 3* mil.

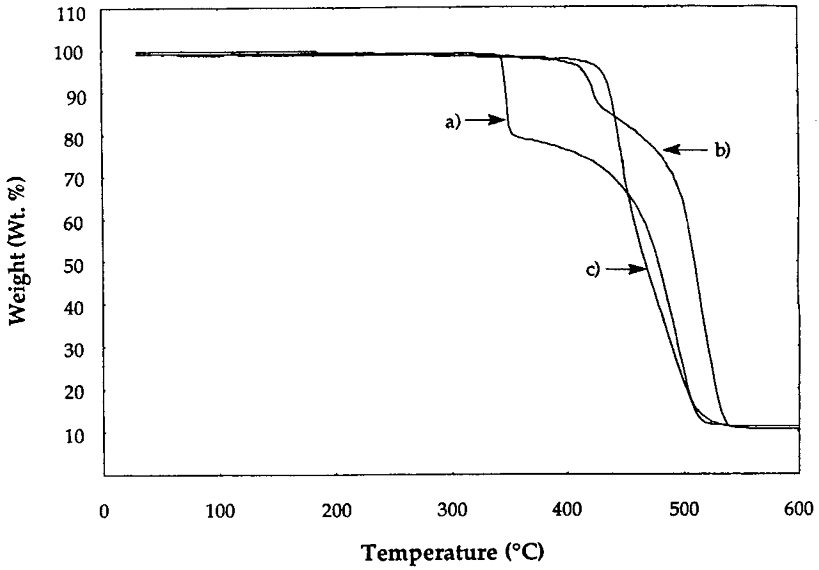


FIG. 10. TGA curves for (a) 1,4-PBD, (b) photocrosslinked 1,4-EPBD (15%), and (c) photocrosslinked 1,4-EPBD (30%) in nitrogen at a heating rate of 20°C/min.

izations of 1,2-EPBD and 1,4-EPIP with epoxide contents of 15 and 30%. Higher rates of epoxide ring-opening polymerization were observed with higher epoxide contents in all cases. However, the final conversions are independent of the epoxide content. In Fig. 7 are given the conversion vs time plots for the photopolymerization of 1,2-EPBD (30%) with different concentrations of the photoinitiator, IOC-10SbF$_6$. Both the rate of polymerization and the extent of conversion increase as the concentration of the photoinitiator increases from 0.25 to 1.0 mol%.

Varying the reactivity of the photoinitiator by changing the anion can bring significant changes both in the rate of polymerization and in the final conversion. As may be seen in Fig. 8, for photoinitiator IOC-10PF$_6$ bearing the PF$_6$-anion, compared to IOC-10SbF$_6$, the rate of the crosslinking polymerization of 1,2-EPBD (30%) substantially decreases and the extent of conversion is reduced by almost one-half. This result can be explained by considering both the nucleophilicity of the two anions and their stability toward abstraction of a fluorine atom by the propagating cation. Since SbF$_6^-$, is both less nucleophilic and more stable than PF$_6^-$, it exhibits an intrinsically higher reactivity as well as a decreased tendency toward termination [16].

The influence of film thickness on the rate of photopolymerization and extent of conversion of 1,4-EPBD (30%) using IOC-10SbF$_6$ was also studied, and the results are given in Fig. 9. As the film thickness was increased from 1.2 to 2.4 mils, the rate of polymerization and the extent of conversion of epoxide groups to give crosslinking sites decrease probably due to UV screening effects by the polymer, the photoinitiator, and the fragments derived from the photoinitiator.

Some preliminary properties of the photocured epoxidized unsaturated oligomers prepared during this investigation are given in Table 4. The properties of the oligomers are clearly a function of the number of epoxy groups present in the starting polymer and the degree of crosslinking. As can be seen from the data in Table 4, all the crosslinked elastomers gave very high gel contents. In the MEK double rub tests, 1,2-EPBD (30%) was the most resistant material. This reflects the high crosslinking density which is the result of a combination of the high epoxide content (30%) and high reactivity of 1,2-EPBD toward photoinitiated cationic polymerization. At the same time, the high crosslink density of this crosslinked oligomer reduces the impact resistance of this elastomer. In contrast, 1,4-EPBD and *cis*-1,4-EPIP were swelled by MEK but had good extensibility as indicated by their impact resistance.

The crosslinked networks formed from the epoxidized elastomers have improved thermal stability over their linear unsaturated precursors. Figure 10 shows the results of a TGA analysis under nitrogen of high molecular weight 1,4-PBD films and the same films after epoxidation and photocrosslinking. The films are stable up to 350°C, at which point the unsaturated elastomer films start losing weight while the cured films retain their original weight until up to approximately 400°C. Thereafter, a sharp decrease in weight of the films was observed with complete degradation by about 520°C.

CONCLUSIONS

The epoxidation of unsaturated elastomers using a tungsten-based redox phase transfer catalyst and hydrogen peroxide is an efficient method to produce photocrosslinkable polymers. By appropriate manipulation of the reaction conditions and concentration of reagents it is possible to control the reaction to achieve any degree of epoxidation desired. RTIR kinetic studies show that the rate and extent of epoxidation is dependent on the structure of starting unsaturated polymers. In the presence of UV radiation and a soluble photoinitiator consisting of diaryliodonium salts bearing long alkoxy chains attached to the aromatic rings, the functionalized elastomers can be photocrosslinked to produce networks. A kinetic investigation by RTIR spectroscopy has shown that the rate and extent of photoinduced crosslinking polymerizations were greatly dependent on the structure of the epoxidized elastomers, its level of epoxidation, and the concentration and type of initiator. These polymers have many potential applications as coatings, adhesives, and photoresists.

ACKNOWLEDGMENT

We gratefully acknowledge support of this research by the U.S. Department of Energy.

REFERENCES

[1] J. V. Crivello and J. H. W. Lam, *Coatings Plast. Prep.*, *39*, 31 (1978).
[2] J. V. Crivello, *Polym. Mater. Sci. Eng. Prep.*, *60*, 217 (1989).
[3] J. V. Crivello, *Soc. Plast. Eng.*, *Conf. Prepr.* Regional Technical Conference, Mid-Hudson Section, 11 (1991).

[4] H. Le. Xuan and C. Decker, *J. Polym. Sci., Polym. Chem. Ed.*, *31*, 769 (1993).
[5] J. A. Puskas, G. Kaszas, and J. P. Kennedy, *J. Macromol. Sci., Pure Appl. Chem.*, *A28*(1), 6 (1991).
[6] J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.*, *27*, 3951 (1989).
[7] C. Venturello and R. D'Aloisio, *J. Org. Chem.*, *53*, 1553 (1988).
[8] G.-H. Hsiue and J.-M. Yang, *J. Polym. Sci., Polym. Chem. Ed.*, *28*, 3761 (1990).
[9] H.-D. W. Zagefka, *Adv. in Org. Coatings Sci. Technol.*, *12*, 58 (1990).
[10] D. Zuchowska, *Polymer*, *21*, 514 (1980).
[11] N. V. Bac, L. Terlemezyan, and M. Mihailov, *J. Appl. Polym. Sci.*, *42*, 2965 (1991).
[12] S. Varughese, D. K. Tripathy, and S. K. De, *J. Adhes. Sci. Technol.*, *4*(10), 847 (1990).
[13] X. Jian and A. S. Hay, *J. Polym. Sci., Polym. Chem. Ed.*, *29*, 547 (1991).
[14] B. L. V. Duuren and F. L. Schmitt, *J. Org. Chem.*, *25*, 1761 (1960).
[15] C. Decker and K. Moussa, *J. Polym. Sci., Polym. Chem. Ed.*, *28*, 3429 (1990).
[16] J. V. Crivello, *Adv. Polym. Sci.*, *62*, 1 (1984).

Received July 6, 1993
Revision received August 16, 1993