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Synthesis and Photoinitiated Cationic Polymerization of Epoxidized Castor Oil and Its Derivatives

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SYNTHESIS AND PHOTOINITIATED CATIONIC POLYMERIZATION OF EPOXIDIZED CASTOR OIL AND ITS DERIVATIVES*

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Key Words: Castor Oil, Epoxidized Castor Oil, Photopolymerization

ABSTRACT

In this communication we describe the synthesis of epoxidized castor oil (ECO) as an interesting and inexpensive biorenewable monomer by an efficient and low cost epoxidation process. Also described are studies of the photoinitiated cationic polymerization of ECO using diaryliodonium salt photoinitiators. The influence of the structure and the concentration of the photoinitiator on the polymerization are reported. The ability of photosensitizers to accelerate the photopolymerization was also studied. Studies comparing the photopolymerization behavior of ECO with other commercially available epoxidized linseed and soybean oils and with other types of synthetic epoxy monomers were conducted. The excellent reactivity of ECO can be ascribed to the presence of both epoxy and hydroxyl groups in the molecule which permits this material to polymerize mainly by an activated monomer mechanism.

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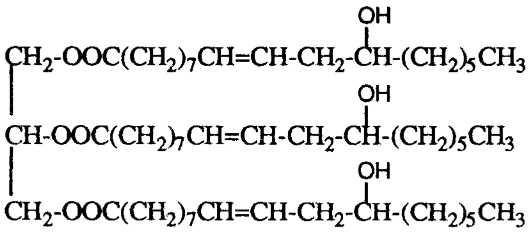
* Please note that this paper originally appeared in A35(1), pp. 1–20. However, due to an error in the printing process, some of the text ran out of order. For the sake of clarity, we are reprinting the paper in its entirety.

INTRODUCTION

Today, one of the challenges in polymer chemistry is to develop polymeric materials from inexpensive, environmentally compatible and renewable sources of starting materials while using the least energy input possible. In this laboratory we have undertaken a program of research to modify unsaturated plant oils to provide inexpensive monomers which will polymerize rapidly under photoinitiated cationic polymerization conditions. Previously, this group has described the use of a number of epoxidized triglyceride oils as starting materials to make crosslinked polymer networks [1]. Photopolymerization or "UV curing" offers a rapid, environmentally compatible and economically attractive method for preparing three dimensional polymer networks [2]. Consequently, UV curing has been widely used for thin film applications such as coatings, inks and adhesives. Due to the development of diaryliodonium and diarylsulfonium salts as two classes of practical cationic photoinitiators [3], this area of polymer photochemistry has enjoyed rapid development over the past two decades and has been applied to the polymerization of a wide range of monomer types [4, 5, 6, 7].

Castor oil (**I**) is an inexpensive, biorenewable, large-scale commodity material. Its worldwide production in 1995 was 492,254 thousand metric tons [8], of which more than 80% is produced in Asia.



$$\begin{array}{l} CH_2\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH_2\text{-}\overset{OH}{C}H\text{-}(CH_2)_5CH_3 \\ | \\ CH\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH_2\text{-}\overset{OH}{C}H\text{-}(CH_2)_5CH_3 \\ | \\ CH_2\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH_2\text{-}\overset{OH}{C}H\text{-}(CH_2)_5CH_3 \end{array}$$

I

Native and modified castor oils are currently used in many commercial polymer related applications including: plasticizers, nylon intermediates and polyurethanes. Further, castor oil is an attractive starting material for the synthesis of monomers and polymers because it contains on the average three hydroxyl and three olefinic groups per molecule that can be utilized for introduction of other types of reactive and polymerizable functional groups.

In this communication, we report the preparation and photopolymerization of epoxidized castor oil and other epoxidized castor oil derivatives as novel monomers. A comparison of these materials with related epoxidized vegetable oils is also provided to understand their potential reactivity and utility in relation to the broad family of epoxidized vegetable oil monomers.

EXPERIMENTAL

Materials

Castor oil (**I**) and dehydrated castor oil (Castung® oil, **II**) were supplied by CasChem, Inc., Bayonne, New Jersey. Epoxidized linseed (Vikoflex 7190) and soybean oils (Vikoflex 7170) were obtained from Elf Atochem North America, Inc., Bloomington, MN. Diglycidyl ether oligomer (DER 331) was provided by Dow Chemical Company, Midland, MI. 3,4-Epoxycyclohexylmethyl 3',4'-epoxy-cyclohexanecarboxylate (CY 179) was supplied by Ciba-Geigy Corporation. Oxone®, 18-crown-6-ether, methyltri-n-octylamine and 30 wt % hydrogen peroxide were procured from Aldrich Chemical Co., Milwaukee, WI. Hydrogen peroxide (70 wt %) was obtained from FMC Corporation, Philadelphia, PA. MTTP was synthesized according to the procedure reported in literature [9]. The diaryliodonium salts used in this work (**V**) were prepared as described previously [10].

Methods

^1H NMR spectra were recorded on a Varian XL-200 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal reference. Routine infrared spectra were obtained using a MIDAC Model M1300 FTIR. The percent oxirane oxygen of the epoxidized oils was determined according to ASTM D-1652-88.

Epoxidation of Castor Oil

Procedure A: Using 30% Hydrogen Peroxide

To a 5 L three-necked flask equipped with a thermometer, addition funnel, condenser and mechanical stirrer were added castor oil (500 g, 0.54 mol) and methyltri-n-octylammonium diperoxotungstophosphate (MTTP, 3 g, 1.33 mmol). The temperature of the reaction flask was gradually brought to 60°C and 1070 mL (8.7 mol, 30% aqueous solution) hydrogen peroxide was added with stirring over the course of 4 hours using the addition funnel. The reaction mixture was vigorously stirred for an additional 4 hours before allowing it to cool to room temperature. Toluene (1 L) was added to extract the product and the organic layer separated and dried over anhydrous sodium sulfate. After the removal of the solvent on a rotary evaporator, epoxidized castor oil (ECO) was recovered in 94% yield. ^1H NMR spectrum of the product revealed that 75% conversion of the double bonds to epoxide groups had taken place. The oxirane oxygen content was determined by ASTM method D-1652-90 and found to be 3.6 %.

Table 1 gives the ^1H NMR chemical shifts for both castor oil and ECO.

TABLE 1. ^{1}H NMR Spectral Assignments ($CDCl_3$, TMS, δ ppm)

Assignments	Chemical Shift (δ, ppm)	
	Castor oil	Epoxidized castor oil
$CH_2\,\mathbf{CH_3}$	0.9	0.9
$\mathbf{CH_2}CH_3$	1.3	1.0-1.8
$\mathbf{CH_2}CH{=}CH\mathbf{CH_2}$	2.0, 2.2	-
$CO\mathbf{CH_2}$	2.3	2.3
	-	2.9, 3.1
$\mathbf{CH_2}OCO$	4.0-4.4	4.0-4.4
$(O)CH_2\mathbf{CH}(O)CH_2(O)$	5.2-5.3	5.2-5.3
$CH_2\mathbf{CH{=}CH}CH_2$	5.3-5.7	-

Procedure B: Using 70% Hydrogen Peroxide

To a 3 L three-necked flask equipped with a thermometer, condenser and mechanical stirrer were added castor oil (500 g, 0.54 mol) and MTTP (3 g, 1.33 mmol). After thoroughly mixing the MTTP and castor oil at 60°C, powdered calcium carbonate (6.65 g, 50 molar excess over MTTP) was introduced and stirred. Hydrogen peroxide (102 mL of 70% aqueous solution) was added dropwise with stirring over the course of 2 hours with the aid of a syringe pump. The reaction mixture was kept at 60°C under vigorous stirring conditions for 9 hours before allowing it to cool to room temperature. Chloroform (1 L) was added to extract the product and the resulting solution dried over anhydrous sodium sulfate. After the removal of the solvent on a rotary evaporator, there were obtained 495 g (90% yield) of ECO. The oxirane oxygen content by titration was found to be 3.7 %.

Epoxidation of Castung® Oil

To a 3 L three-necked flask equipped with a thermometer, condenser, two addition funnels and a mechanical stirrer was added (11.2 g, 0.013 mol) of Castung® oil and 0.25 g (0.95 mmol) of 18-crown-6-ether along with 50 mL each of acetone and dichloromethane. After the introduction of 200 mL of 7.4 pH phosphate buffer, the contents of the flask were cooled to -5 °C and Oxone® (120 g in 500 mL deionized water) was added dropwise. During the reaction, a 2N aqueous NaOH solution was added dropwise along with Oxone® to maintain the pH at approximately 7.4. Complete addition of Oxone® required 4 hours and thereafter the reaction mixture was stirred overnight at 2°C. The reaction mixture was filtered, diluted with dichloromethane, dried over anhydrous sodium sulfate and the solvents stripped off using a rotary evaporator. There were recovered 11.9 g (96% yield) of epoxidized Castung® oil (ECT). Titrimetric determination gave an oxirane oxygen content of 6.7%.

IR spectral analysis: Castung®, 3020 ($\nu_{C\text{-}H}$ unsaturated), 1750 cm^{-1} ($\nu_{C=O}$ ester); ECT, 1750 ($\nu_{C=O}$ ester), 820 and 840 cm^{-1} ($\nu_{C\text{-}O}$ epoxy).

Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR)

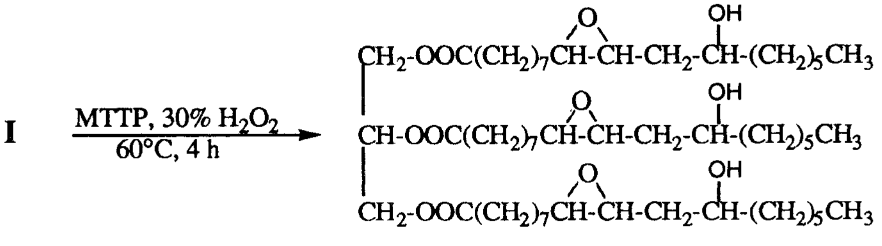
Kinetic and conversion data for the cationic photopolymeriztion of the castor oil based monomers were obtained using Fourier transform real-time infrared analysis (FT-RTIR). This method involves the monitoring of an appropriate IR band due to the polymerizing group while simultaneously irradiating the thin film sample with UV light. Measurements were performed on a Midac Model M1300 Fourier Transform Infrared Spectrometer equipped with a liquid nitrogen cooled MCD detector (Midac Corp, Irvine, CA). The instrument was fitted with a UVEXS Co (Sunnyvale, CA) SCU 110 UV lamp equipped with a flexible liquid optic cable directed at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light with an intensity of 1150-1400 mJ/cm^2 min. Samples were prepared by mixing 1.0 g of the epoxidized oil in a vial with a predetermined amount of the appropriate photoinitiator and the contents of the vial were vigorously agitated in a VWR-2 vortexer to obtain a good dispersion of the photoinitiator. The vial was then gently heated and mixed in an ultrasonic bath for 1 hour to dissolve the photoinitiator. Two drops of the sample were placed between thin (13 μm) films of polypropylene and then this sandwich was mounted between 5 cm x 5 cm photographic slide frames. The progress of the polymerizations of the were determined quantitatively by monitoring the formation of a new band assigned to the polyether chromophor at 1160 cm^{-1}. The decrease of the epoxy peaks at 830 cm^{-1} was used to compute the overall conversion. The data was collected on a Bit-Wise Co. (Albany, NY) 486 PC computer, reduced and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. (Salem, NH) Grams 386, Version 3.0 software package. Light intensity measurements were made with the aid of an International Light Co. (Chicago, IL) Control-Cure Radiometer.

RESULTS AND DISCUSSION

Synthesis of Epoxidized Castor Oil (ECO) and Epoxidized Castung Oil (ECT)

Previously [7], we have noted that due to the lack of reactive functionalities, plant oils (glycerol triesters of unsaturated fatty acids) are not directly amenable to cationic polymerization. However, the olefinic double bonds of these oils can be readily transformed into cationically polymerizable epoxy groups through simple epoxidation reactions using peracetic acid. An exception to this rule is castor oil. The preparation of epoxidized castor oil (ECO) using peracetic acid in glacial acetic acid at 20-25°C has been described in the literature [11]. A more recent review of the literature contains few references to the preparation of this material suggesting that it has found few applications as compared to other epoxidized vegetable oils.

We have recently described a new method for the epoxidation of unsaturated vegetable oils [7] which is based on the work of Venturello and D'Aloisio [8]. This method involves the use of the tungsten-based phase-transfer catalyst, methyltri-n-octylammonium diperoxotungstophosphate (MTTP), and aqueous hydrogen peroxide. Typically, the epoxidation is rapid, efficient and gives quantitative yields of the desired epoxidized vegetable oils. Further, no solvents are required for the epoxidation reaction. The epoxidation of castor oil using MTTP was successfully carried out and is depicted in Equation 1.

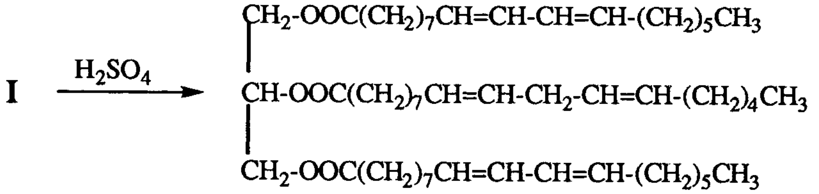


$$\mathrm{I}\ \xrightarrow[60^{\circ}C,\ 4\ h]{MTTP,\ 30\%\ H_2O_2}\ \begin{array}{l} CH_2\text{-}OOC(CH_2)_7\overset{O}{CH\text{-}CH}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}(CH_2)_5CH_3 \\ CH\text{-}OOC(CH_2)_7\overset{O}{CH\text{-}CH}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}(CH_2)_5CH_3 \\ CH_2\text{-}OOC(CH_2)_7\overset{O}{CH\text{-}CH}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}(CH_2)_5CH_3 \end{array} \qquad (1)$$

ECO

In this laboratory, both 30% and 70% aqueous hydrogen peroxide have been used for this epoxidation. When 70% hydrogen peroxide is used, the level of epoxidation obtained in the final product was low due to competing ring-opening side reactions of the epoxide groups under the reaction conditions. This difficulty was overcome through the incorporation of solid, powdered calcium carbonate in the reaction mixture to control the pH. Both methods of MTTP epoxidation were equally effective giving ECO with a maximum oxirane oxygen content of 3.6-3.7% Based on this determination, it can be calculated that each ECO molecule contains an average of 2.3 epoxy groups.

When castor oil is treated with sulfuric or other strong acids it undergoes facile dehydration to give the highly unsaturated oil known as Castung® oil [12]. A generalized structure for Castung® oil, **II**, is shown below in Equation 2.



$$\mathrm{I}\ \xrightarrow{H_2SO_4}\ \begin{array}{l} CH_2\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_5CH_3 \\ | \\ CH\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4CH_3 \\ | \\ CH_2\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_5CH_3 \end{array} \qquad (2)$$

II

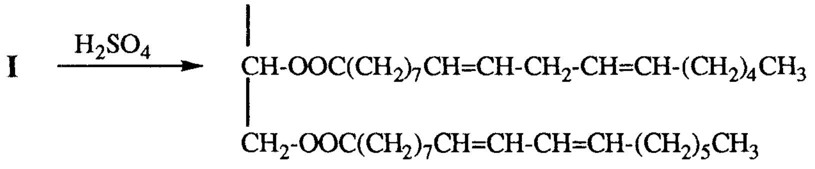
The actual structure of Castung® oil is far more complicated than the structure shown. Both conjugated and non-conjugated double bonds are present in the oil. The position and number of conjugated double bonds can vary from molecule to molecule and from sample to sample depending on the method of preparation. **II** used in this study had a ratio of 28:72 of conjugated to non-conjugated double bonds.

Epoxidation of **II** with hydrogen peroxide and the MTTP catalyst resulted in inefficient epoxidation (approximately 60% by ^1H NMR after 24 hours reaction). During the reaction, the pH of the reaction mixture fell to 4.0. Under these conditions, ring-opening of the initially formed epoxy groups was observed to take place as a major and facile side reaction. Incorporation of solid calcium carbonate into the reaction mixture to control the pH was not effective in increasing the level of epoxidation. In contrast, it was found that epoxidation of **II** using potassium monoperoxysulfate (Oxone®) in the presence of acetone proceeds smoothly and without detrimental ring-opening side reactions, provided that the pH of the reaction mixture is maintained at 7.4 with the aid of a phosphate buffer [13, 14]. Using Oxone® epoxidized Castung® (ECT) with an oxirane oxygen content of 6.7% was obtained. Fully epoxidized ECT has a molecular weight of 975.4 g/mol with a calculated oxirane oxygen content of 9.8%. Thus, the ECT prepared in this study has approximately four epoxy groups per molecule.

Cationic Photopolymerization of ECO and ECT

Photoinitiator Effects

Like many epoxidized vegetable oils, ECO and ECT are hydrophobic monomers of low polarity. For this reason, the solubility of simple, unsubstituted diaryliodonium and triarylsulfonium salt photoinitiators in these monomers is very limited. In this investigation, we have employed diaryliodonium photoinitiators based on the (4-n-decyloxyphenyl)-phenyliodonium cation (IOC10) with the three anions shown [15].



$$\mathbf{I} \xrightarrow{H_2SO_4} \begin{array}{l} | \\ CH\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4CH_3 \\ | \\ CH_2\text{-}OOC(CH_2)_7CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_5CH_3 \end{array} \qquad (2)$$

II

Due to the unsymmetrical structure of these compounds and the presence of the decyloxy group in the molecule, these photoinitiators are more soluble in both ECO and ECT than their unsubstituted analogues. Since the photosensitivity of these photoinitiators resides in the cation, their photolysis rates are identical and independent of the anion present. The mechanism of the photolysis of diaryliodonium salts has been investigated [16, 17, 18] and it has been shown that the primary species responsible for the initiation of cationic polymerization is the Brønsted acid corresponding to the anion originally present in the photoinitiator. Thus, for the above photoinitiators, photolysis would be expected to produce respectively, HPF_6, $HAsF_6$, and $HSbF_6$. These acids may all be classified as "super acids"[19] which efficiently and quantitatively protonate and initiate the cationic ring-opening polymerization of epoxides [20].

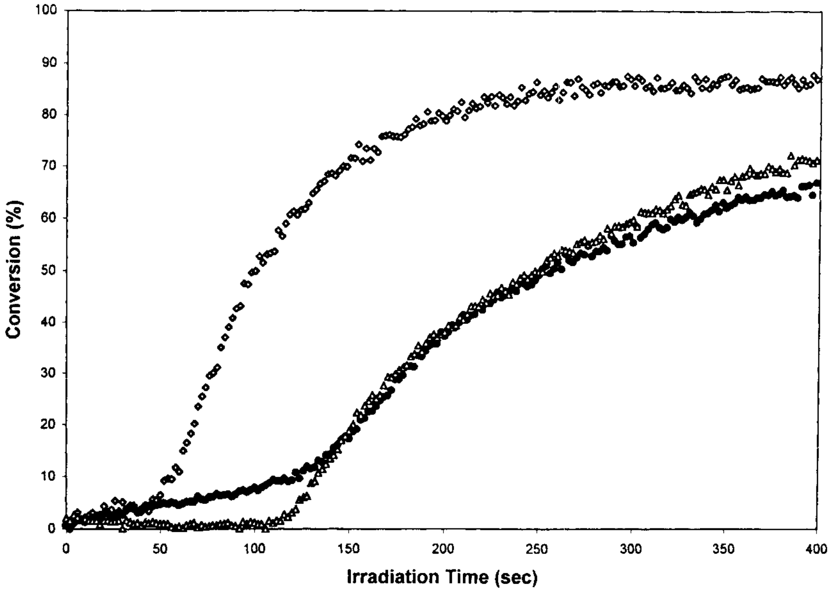


Figure 1. Effect of the IOC10 counterion on the rate of polymerization of ECO (1.5 mol% photoinitiator). ● ,AsF_6^-; ◊, SbF_6^-; Δ PF_6^-.

Figure 1 shows a comparison of the polymerization of ECO (3.7% oxirane oxygen) containing 1.5 mol% of the three photoinitiators shown above. This comparison was made using an analytical technique known as Fourier transform real-time infrared spectroscopy (FT-RTIR) [21]. Employing this method, the course of the photopolymerizations was followed by simultaneously monitoring both the decrease in the infrared absorption of the epoxy group (830 cm^{-1}) and the increase of the band (1160 cm^{-1}) due to the linear ether formed as a function of irradiation time. The curves display three different regions corresponding to three different kinetic processes. The first region consists of an induction period in which little polymerization of ECO is taking place. As may be noted, the length of this period decreases in the order $SbF_6^- > AsF_6^- \sim PF_6^-$. Two major factors are responsible for the induction period. As previously described, the epoxidation of **I** involved the use of a quaternary ammonium phase transfer catalyst. During reaction this catalyst tends to decompose generating amines. Due to the high molecular weight of the amines and their solubility in ECO, they could not be readily removed from the product. Consequently, there is always a level of basic impurities present in ECO prepared by this technique which must be neutralized by photogenerated acid before the epoxide ring-opening polymerization can proceed. The difference observed in the length of the inhibition period relates primarily to the respective solubilities of these photoinitators in ECO. IOC10 SbF_6^- is the most soluble of the three photoinitiators in ECO and for that reason, is most effective in reducing the induction period.

During the second stage of the polymerization, rapid consumption of epoxy groups takes place. The slope of the curves in this region are directly proportional to their corresponding rates of polymerization. Again, the order with respect to the anions: $SbF_6^- > AsF_6^- \sim PF_6^-$ is observed. The effects of anion on the rate of photopolymerization of epoxy monomers has been observed previously [22] and has been attributed to two factors namely: the nucleophilicity of the anion and its relative stability towards ion splitting reactions involving abstraction of a fluoride anion by the growing cationic chain end. The nucleophilicity of the anions increases and the stability of the three anions decrease in an inverse order as noted for their rates of polymerization. This is consistent with previous observations and confirms that IOC10 SbF_6^- is the most efficient photoinitiator for epoxide polymerization.

During the last stage of the polymerization, the rate of polymerization falls off as the monomer is exhausted and as the gel point is reached and mobility is reduced. Also during this period the glass transition temperature (T_g) rises and the polymerization rate falls as the phase change takes place. It should be noted that of the three photoinitiators, IOC10 SbF_6^- also gives the highest conversion in Figure 1. This effect is related to the high rate of exothermic polymerization initiated by this photoinitiator which raises the temperature of the sample and increases the mobility of the remaining functional groups.

Figure 2 shows the effect of different concentrations of IOC10 SbF_6^- on the polymerization of ECO. As the concentration is increased from 0.5 mol% to 1.0 mol%, there is a dramatic drop in the induction time. As the concentration is further increased, the induction time remains unaffected. This would tend to suggest that the rate of photolysis of the photoinitiator is limited by the light flux rather than by the photoinitiator concentration in these experiments. With the exception of the curve for 0.5 mol% IOC10 SbF_6^-, the slopes (i.e. rates) for all the other photo-initiator concentrations are substantially the same; again suggesting that the polymerizations are light limited. However, the conversions after 400 seconds are different and tend to be higher for higher photoinitiator concentrations. This may be rationalized as being due to the production of more acid upon prolonged irradiation for those samples with higher photoinitiator concentrations. It should be pointed out

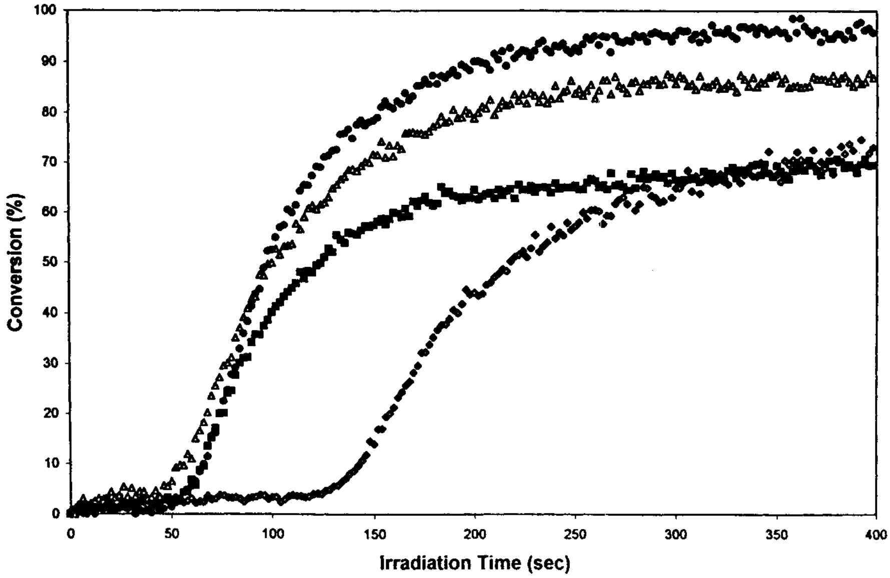
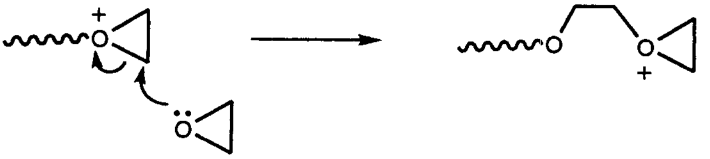


Figure 2. Effect of the IOC10 SbF_6^- concentration on the rate of polymerization of ECO. ●, 2 mol%; Δ 1.5 mol%; ■ 1 mol%; ◊, 0.5 mol%.

that conversion is also affected by sample thickness variations and that these experimental variations are difficult to avoid completely. Similar effects were observed for concentration studies with IOC10 PF_6^- and IOC10 AsF_6^-.

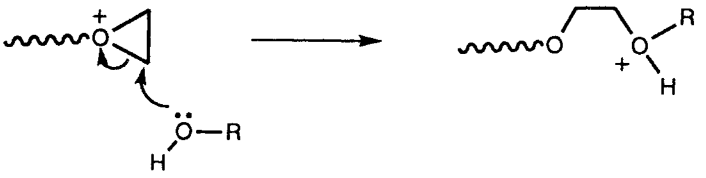
Mechanistic Considerations

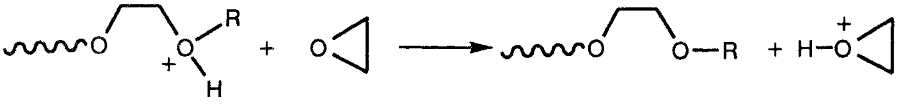
The molecular structure of ECO is different from other common epoxidized vegetable oils and synthetic epoxides in that in addition to the epoxide groups, there are three hydroxyl moieties. These structural differences translate into different behaviors in the polymerization of ECO as compared to other epoxide resins. The propagation step of the cationic ring-opening polymerization of epoxides involves the repeated S_N2 attack of an epoxide oxygen on the oxiranium cation end of the growing polymer chain as shown in Equation 3.



(3)

However, when an alcohol is present, it competes with the epoxide in the above reaction resulting in the formation of an ether linkage and the expulsion of a proton as depicted in Equations 4 and 5.


(4)


(5)

The above polymerization reaction has been termed to proceed by an "activated monomer mechanism" [23] since the propagation involves chain transfer from the growing polymer chain to the monomer. There are three major conclusions which can be drawn from a comparison of the above two polymerization mechanisms. First, the kinetics of the two mechanisms would be expected to be different. Further, since proton transfer is typically regarded as a very fast process, the latter polymerization would be expected to be faster than the former one. Second, in a crosslinking reaction, the latter mechanism permits greater mobility of the active site and would be expected to result in a higher conversion of epoxide functional groups. Third, the latter mechanism (Equations 4 and 5) generates short polyether chains with the number of hydroxyl groups equivalent to the moles of alcohol added, while the first mechanism gives a linear polyether structure with few hydroxyl groups. On the basis of these considerations, it would be expected that the polymerization of ECO would proceed faster and to a higher epoxide conversion than equivalent epoxidized vegetable oils without hydroxyl groups. Further, the chemical and mechanical properties of the crosslinked matrix which would be formed from ECO would be also be different. To test these conclusions, a number of studies were undertaken.

To further examine the effects of structure, ECO with different oxirane oxygen contents were prepared and then photopolymerized with 1.5 mol% IOC10 SbF_6^- photoinitiator. The results are presented in Figure 3. As the oxirane oxygen value increased from 2.4-6.7%, the induction period decreased from approximately 175 seconds to about 55 seconds. ECT with the highest oxirane oxygen (6.7%) but

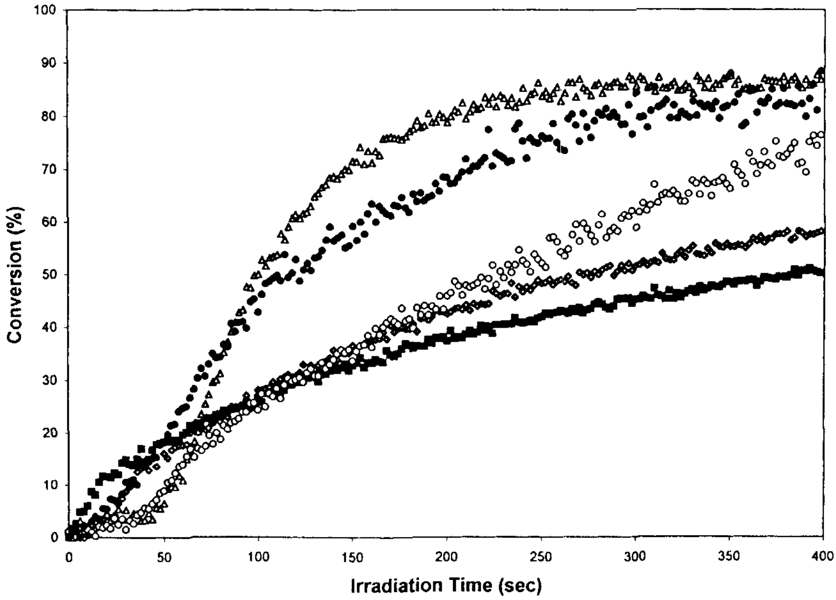


Figure 3. Effect of oxirane oxygen content on the photopolymerization of ECO and ECT. ○ , 6.7% ECT;■ , 3.7% ECO; ▲, 3.0% ECO; ◊ 2.4% ECO.

no hydroxyl groups undergoes photopolymerization at approximately the same rate as ECO with less than one half the oxirane oxygen (3.0%) content. All four monomers show an appreciable induction period.

Comparison and Copolymerization of ECO and ECT with Other Epoxy Monomers

Figure 4 compares the photopolymerization behavior of ECO with non-hydroxyl containing epoxidized linseed (e-linseed), soybean (e-soybean) and ECT oils. Several interesting features of these curves are noteworthy. It is worth pointing out that only ECO and ECT prepared under basic epoxidation conditions display pronounced inhibition periods. ECO has the highest rate of polymerization of any of the oils shown in this figure despite the fact that its oxirane oxygen content is the lowest of any of the oils present (e-linseed oil, 9.3%; e-soybean oil, 7.1% ECT, 6.7%). As predicted, the photopolymerization of ECO also proceeds to a higher conversion than the other oils. For the epoxidized linseed and soybean oils, the conversion versus time curves plateau at approximately 30% and even after 400 seconds of UV exposure the value does not increase beyond 60%. Both of these observations can be ascribed to the presence of hyroxyl groups in ECO and their

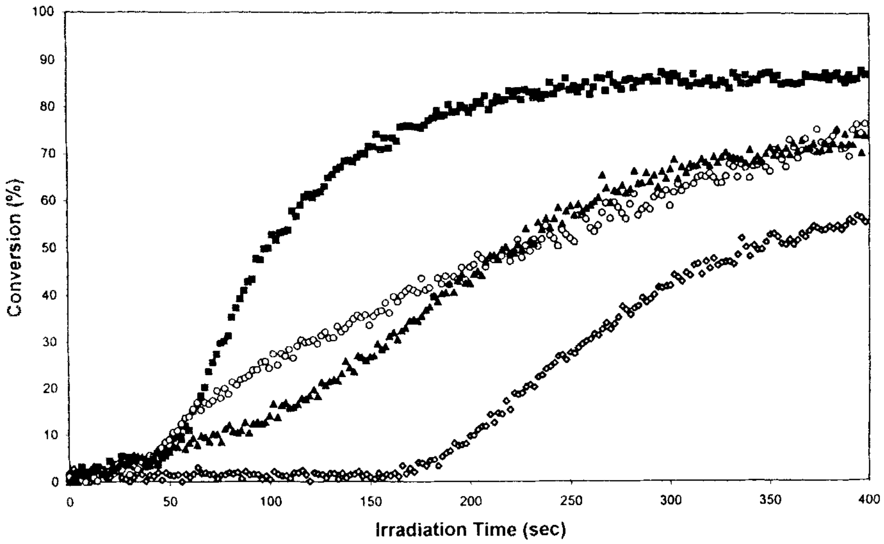


Figure 4. Behavior of epoxidized oils in photoinitiated cationic polymerization using 1.5 mol% IOC10 SbF_6^-. Δ, ECO; ○, ECT: ■, e-linseed oil; ◇, e-soybean oil; ●, ECO and e-linseed oil.

influence of the polymerization mechanism (Equations 4 and 5). To show the influence of the hydroxyl groups more clearly, a 50:50 molar mixture of ECO and e-linseed oil were photopolymerized. As shown in Figure 3, the resulting mixture undergoes photopolymerization at a greatly enhanced rate as compared to e-linseed oil alone due to a changeover from a simple ring-opening to an activated monomer mechanism of polymerization. Similar rate enhancing effects have been observed previously in the addition of alcohols to cationically photopolymerizable epoxy resins [24].

Figure 5 shows a comparative study of the photopolymerizations of ECO with bisphenol A digylcidyl ether modified resin DER 331 and a biscycloaliphatic epoxy monomer, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (CY179). The structures of these materials are shown below. Under identical conditions, both of the synthetic epoxy monomers undergo more rapid polymerization than ECO. Further, the two synthetic epoxy resins do not display an induction period. The polymerizations of all the monomers proceed to approx-

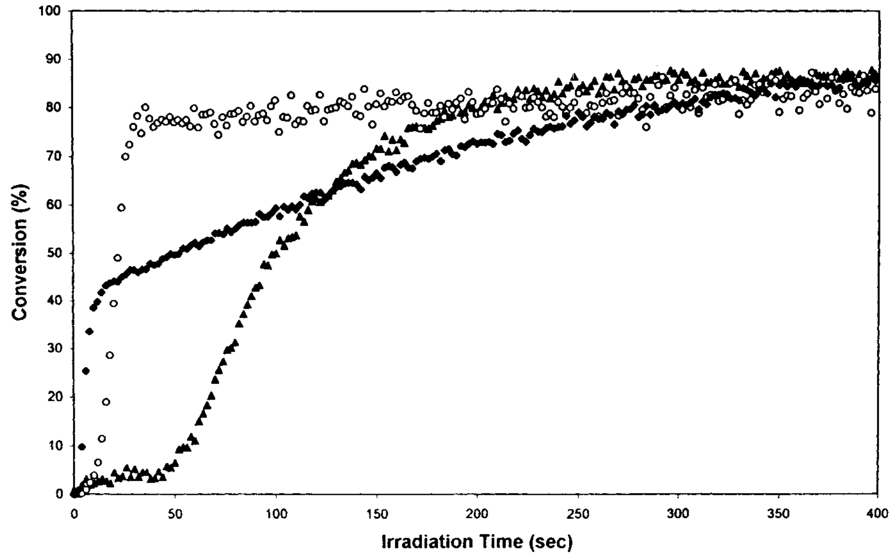
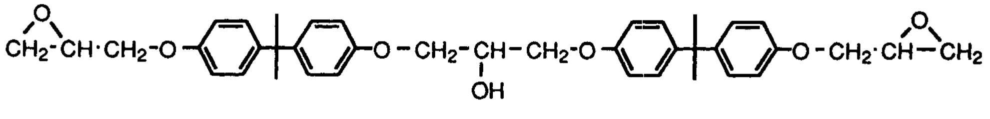
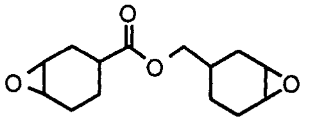


Figure 5. Comparison of the cure behavior of ○ DER 331; ♦, CY179 and ▲, ECO in photoinitiated cationic polymerization using 1.5 mol% IOC10 SbF_6^-.

imately the same ultimate (400 sec. irradiation) degree (~80%) of conversion. This is likely the result of the presence of hydroxyl groups in all three monomers.



DER 331



CY179

The profiles of the FT-RTIR curves are different for each of the monomers. and appears related to the quantity of hydroxyl groups present and their corresponding level of epoxidation. CY179 has the highest oxirane oxygen content

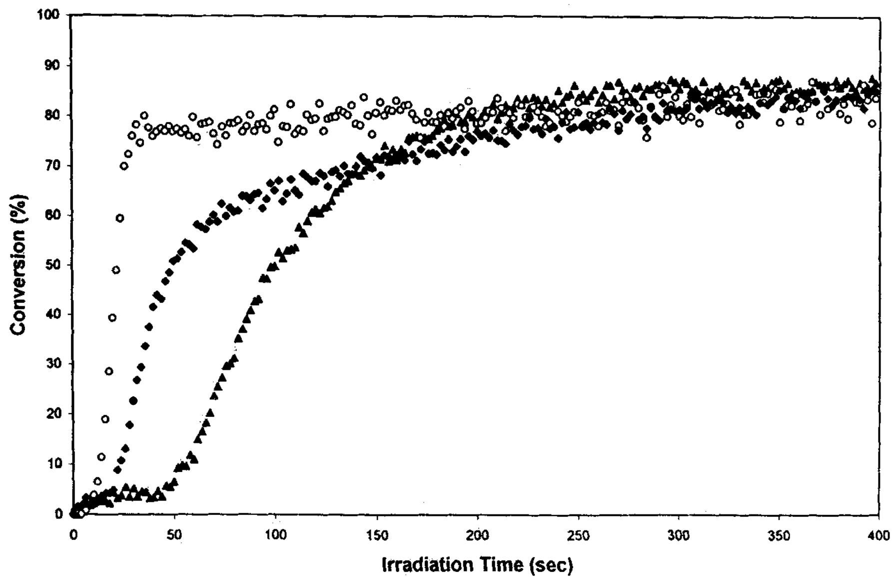


Figure 6. FT-RTIR study of the copolymerization of ECO and DER 331. ○, DER 331; ♦, 50:50 Copolymer; ▲, ECO.

(11.2-12.2%) and the lowest hydroxyl content (due to impurities and alcohols from ring-opening side reactions during synthesis). At the same time, DER 331 has an oxirane oxygen content of 8.4-8.8% and almost one hydroxyl per two epoxy groups while ECO has an oxirane oxygen content of 3.7% and three epoxy groups per molecule. CY179 undergoes rapid initial polymerization but the gel point is reached at low conversions (~45%) due to the high oxirane oxygen content and also the high T_g of the crosslinked matrix formed. Thereafter, polymerization proceeds slowly limited by diffusional effects in the gelled resin. In contrast, the photopolymerizations of both DER 331 and ECO plateau at much higher conversions.

Copolymerization of Epoxidized Castor Oil with DER 331 (III) and CY 179 (IV) Resins

The copolymerization of ECO with DER 331 and with CY179 (50/50 mole %) was carried out using 1.5 mole% IOC10 SbF_6- and the results are shown in Figures 6 and 7. Also shown for comparison in these two figures are the FT-RTIR curves for the corresponding homopolymerizations. In both cases, the rates of the copolymerizations are enhanced over the corresponding ELO homopolymerization. There is also a reduction of the induction period which may be attributed to a

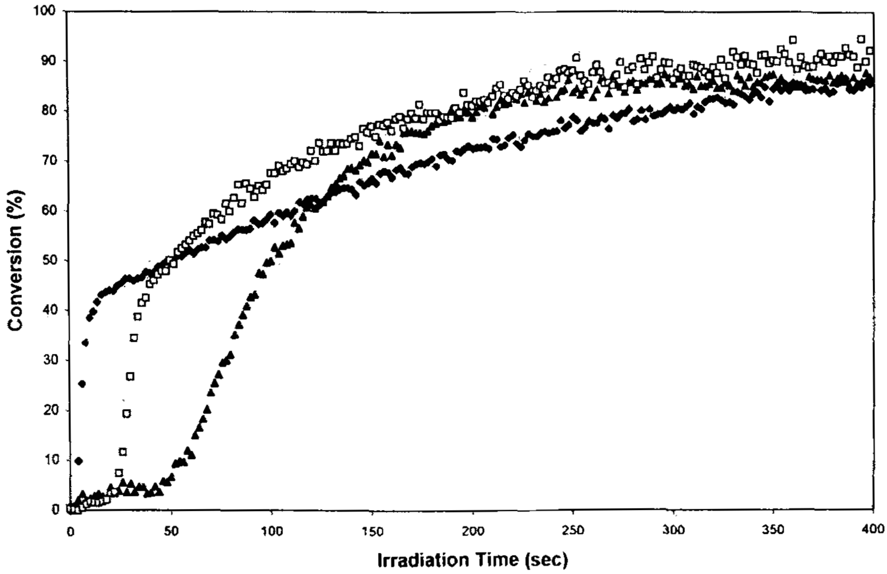


Figure 7. FT-RTIR study of the copolymerization of ECO and CY 179. ♦, CY 179; □, 50:50 Copolymer; ▲, ECO.

dillution effect which lowers the concentration of basic impurities present in ECO. The greatest effects are observed in the copolymerization of ECO with CY179 (Figure 7). In this case, the photopolymerization proceeds to a higher conversion than the homopolymerization of CY179 before the gel point is reached. Ultimate conversions (400 sec. irradiation) were not affected by copolymerization and reached 80-90%. Interestingly, copolymer films of DER 331 and epoxidized castor oil were more flexible and less colored than the homopolymer films of DER 331.

Photosensitized Polymerization of ECO

The diaryliodonium salt photoinitiators used in this study have poor absorbtivity in the 300-450 nm region. This greatly limits their efficiency of light utilization. Moreover, the screening effects of the photolysis products of the photoinitiator further limit their efficiency of photoabsorption. The use of photosensitizers can alleviate these problems [25]. Anthracene and 2-isopropylthioxanthone (ITX) are excellent photosensitizers for diaryliodonium salts and were used in this investigation. The results are presented in Figure 8. Included in this figure is a FT-RTIR curve for the unsensitized ECO polymerization as a control. Using both photosenstizers enhances the rate of polymerization of ECO. The

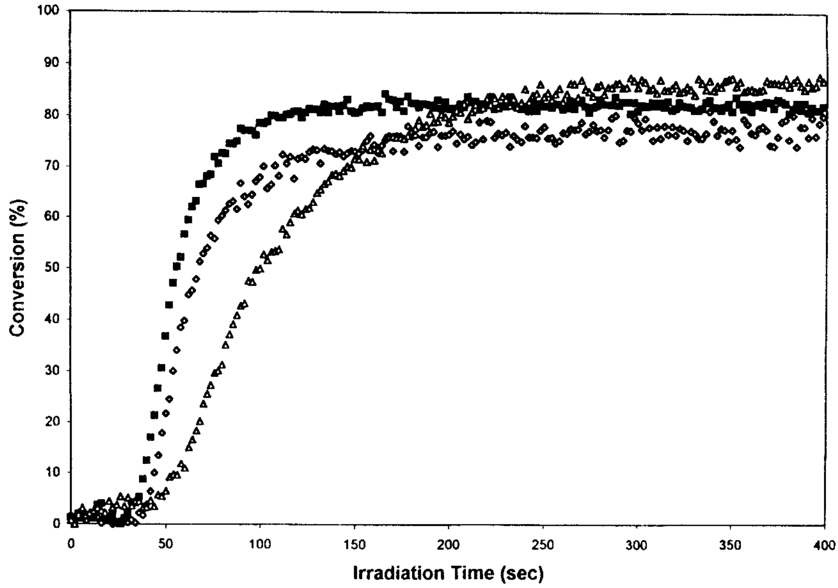


Figure 8. Effect of photosensitizer (0.15 mol%) on the photopolymerization of ECO in the presence of 1.5 mol% IOC10 SbF_6^-.
Δ, control; ◊, ITX; ■, anthracene.

conversions for all three curves are the same. By capturing more of the available light, photosensitized decomposition of the diaryliodonium salts produce more initiating species than the non-photosensitized decomposition. This, in turn, produces a higher effective rate of consumption of epoxide functional groups. It may also be noted that the length of the induction period is only slightly decreased by photosensitization.

CONCLUSIONS

Castor oil can be rapidly and efficiently epoxidized using the tungstophosphate phase transfer catalyst, MTTP and hydrogen peroxide. Epoxidized castor oil (ECO) displays excellent reactivity in photoinitiated cationic polymerization compared to other epoxidized vegetable oils which can be ascribed to the presence of the hydroxyl groups in the molecule. On the other hand, although the related derivative, epoxidized Castung® oil (ECT), has a higher epoxy content than ECO but no hydroxyl groups, its polymerization rate is much slower. It is proposed that ECO polymerizes mainly by an activated monomer mechanism whereas ECT undergoes polymerization by a typical cationic ring-opening mechanism. The photopolymerization rate of ECO is highest for diaryliodonium salts containing the SbF_6^- counterion and may be further accelerated through the use of photosensitizers such as anthracene and 2-isopropylthioxanthone. ECO copolymerizes well with both aromatic glycidyl ether and cycloaliphatic epoxy monomers to flexibilize these resin matrices. These results indicate a high potential for ECO as a low-cost, high reactivity photopolymerizable monomer and modifier in a wide variety of practical applications.

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