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INVESTIGATION OF THE USE OF POLY(3,4-EPOXY-1-BUTENE) IN FREE RADICAL PHOTOPOLYMERIZATIONS

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ABSTRACT

The use of poly(3,4-epoxy-1-butene) (polyEPB) in photoinduced free radical polymerizations has been investigated. It was observed that the inclusion of polyEPB into these photopolymerizations has several beneficial effects. In combination with aromatic ketones, polyEPB functions as a hydrogen donor to form a highly effective photoinitiator for the polymerization of acrylate monomers. At the same time, polyEPB undergoes facile autoxidation that serves to mitigate inhibition effects due to oxygen during free radical photopolymerizations. PolyEPB is an effective chain transfer agent that tends to increase both the rate and conversion in photoinduced crosslinking polymerizations in which multifunctional monomers are employed. Lastly, polyEPB is a interesting matrix-modifying agent that becomes incorporated into the resin matrix during photopolymerization due to photoinduced grafting reactions.

Key Words: Free radical photopolymerization; Poly(3,4-epoxy-1-butene); Acrylate photopolymerizations

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INTRODUCTION

Photoinduced free radical polymerization reactions are finding uses today in a wide variety of industrial processes.[1] For example, they are a mainstay of the wood coatings industry and are widely employed as protective and decorative coatings for metals, plastics and paper, as well as for photocurable printing inks and adhesives. This area of polymer chemistry is growing rapidly due to the inherent low energy requirements of this technology as well as to the elimination of the use of organic solvents and the consequent air and water pollution that accompanies their use. In addition, the polymers that are formed possess excellent chemical resistance and mechanical properties. Free radical polymerizations have reached reasonably large commercial usage in the past decade and their usage is currently growing at an overall rate of approximately 15% per year. This growth is expected to continue as industry becomes more aware of the manifold benefits of UV curing and as more restrictive environmental legislation mandating lower volatile organic compound emissions is enacted.

For these reasons, research and development continues apace in the study of free radical polymerizations. Current research efforts are mainly directed in three major areas,[2]: 1) the design and synthesis of new photoinitiator systems, 2) the development of novel monomers and 3) the discovery of additives that modify either the cure characteristics or enhance the mechanical performance of existing photopolymerizable acrylate and methacrylate systems. This paper describes the results of investigations using poly(3,4-epoxy-1-butene) (polyEPB) as a component of novel photoinitiator systems and as a matrix modifier in photoinitiated free radical photopolymerizations.

EXPERIMENTAL

Materials

Poly(3,4-epoxy-1-butene) (polyEPB) was used as received from Eastman Chemical Company, Kingsport, TN. This oligomer was prepared by the BF_3 etherate catalyzed ring-opening polymerization of 3,4-epoxy-1-butene carried out in the presence of 1,4-butanediol. The hydroxyl-terminated oligomer used in this work had a 1,2/1,4 content of 95/5 and a GPC determined M_n of 1413 g/mol (polystyrene standards). The acrylic monomers used in this investigation were purified by distillation prior to use. Triethanolamine and the aromatic ketones described in this work were used as purchased from Aldrich Chemical Company (Milwaukee, WI) unless otherwise noted. Esacure KB-1 (2,2-dimethoxy-2-phenylacetophenone) was kindly supplied as a gift by Sartomer Company (Exton, PA). Other reagents and solvents were obtained from various commercial sources and used as received.

Routine infrared spectra were obtained using a Midac-M1300 Fourier transform Infrared spectrometer. Gas chromatographic (GC) analyses were performed using a Hewlett-Packard 5890 Gas Chromatograph equipped with a 10 m 5% OV-17 phenylsilicone capillary column and a flame ionization detector. ^{1}H NMR experiments were carried out using either a Varian XL-200 (200 MHz) or an Inova-300 spectrometer at room temperature with chloroform as the solvent and employing tetramethylsilane (TMS) as an internal standard. Thermal gravimetric analyses were carried out in air at a heating rate of 40°C/min using a Perkin-Elmer (Stamford, CT) Thermal Analyzer equipped with a TGA-7 module. Gel Permeation Chromatography (GPC) was carried out with the aid of a Hewlett-Packard, Gel Permeation Chromatograph equipped with a refractive index detector and μ-styragel columns (particle size 5 μm; mixed 24–34 Å pores). Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Elemental analyses (EA) were performed by Atlantic Microlabs, Norcross, GA.

Photopolymerization Studies Using Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR)

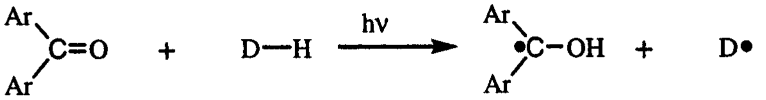
Photopolymerizations of the acrylic monomers were monitored using real-time infrared spectroscopy (FT-RTIR). A Midac M-1300 FTIR spectrometer (Midac Corp., Irvine, CA) equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector was used. The instrument was fitted with a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a flexible liquid optic wand. The end of this wand was directed at an incident angle of 45° onto the sample window and the distance from the window varied from 6–18 cm to control the light intensity. UV light intensities were measured with the aid of a UV Process Supply, Inc. radiometer (Chicago, IL) at the sample window. A light intensity of 10 mW/cm^2 was employed for all the studies conducted in this work.

Photopolymerizations were carried out at room temperature in neat solutions of the acrylate monomers containing various concentrations of polyEPB and an aromatic ketone as the photoinitiator system. Irradiations were carried out using broadband (i.e., unfiltered) UV irradiation. All concentrations reported in this paper are given in units of mol% with respect to the acrylate monomer unless otherwise noted. Several drops of the monomer/photoinitiator solutions were placed on a 12 μm oriented and corona treated polypropylene film (General Electric Capacitor Dept., Hudson Falls, NY), covered with an identical polypropylene film, and then mounted in 5 cm × 5 cm slide frames. Samples (uncovered) were prepared by knife coating the monomer/photoinitiator mixtures onto a single polypropylene film. The thickness of the liquid monomer films was estimated at 10–25 μm. Infrared spectra were collected at a rate of 1 spectrum per second using LabCalc, data acquisition software obtained from the Galactic Industries Corp. (Salem, NH) and were processed using GRAMS-386 software from the same company. During irradiation, the decrease in the absorbance band due to the double bonds at $1640\,\mathrm{cm}^{-1}$ of the respective acrylic monomers was monitored. Three to five runs were performed for each kinetic study and the results averaged to give the final conversion versus time curves. Under these conditions, the run-to-run reproducibility was approximately ±5%.

RESULTS AND DISCUSSION

Free Radical Photoinitiator Systems Based on PolyEPB

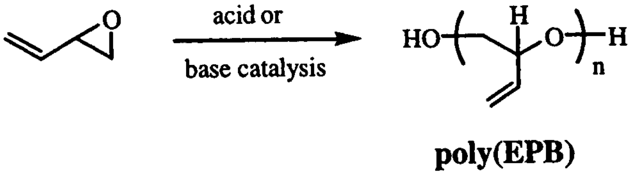
There are two major classes of high quantum yield photoinitiator systems currently used in free radical polymerizations.[4] The first of these are photofragmentation photoinitiators that undergo Norrish type I carbon-carbon bond cleavages upon excitation with UV light. These systems have the advantage of simplicity and high quantum yield but suffer from a relatively high cost and an inherent thermal instability that limits pot life in the presence of highly reactive multifunctional acrylate and methacrylate monomers. A second, frequently used class of photoinitiator systems is hydrogen abstraction photoinitiators that consist of an aromatic ketone in combination with a hydrogen donor. Upon excitation, the aromatic ketone undergoes efficient crossover from the initially formed excited singlet to the excited triplet state. The excited triplet ketone exhibits diradical character that manifests itself in the abstractraction of hydrogen atoms from the donor. This reaction is depicted schematically below in Eq. (1) where D-H represents a hydrogen donor.



(1)

The diarylhydroxymethyl free radical typically dimerizes while the radical, D•, formed by hydrogen abstraction can initiate the polymerization of a vinyl monomer. Typical aromatic ketones used for this purpose are benzophenone, Michler's ketone and 2-isopropylthioxanthone. A wide variety of hydrogen donor synergists have been employed, however, the most commonly used are diethanolamine, methyldiethanolamine and triethanolamine. Hydrogen abstraction photoinitiators have the advantage that they are inexpensive and display excellent thermal stability in formulations with multifuntional monomers. This latter feature is due to the fact that radical species are formed only on irradiation with light, consequently, thermal activation of these systems cannot occur.

Hydroxyl terminated oligomeric poly(3,4-epoxy-1-butene)s (polyEPB) are readily available from the acid or base catalyzed ring-opening polymerization of 3,4-epoxy-1-butene in the presence of alkane diols or triols (Eq. (2)).[3] While the pathway for polymerization of EPB takes place by epoxide ring-opening generating repeating units bearing pendant vinyl groups (1,2-polymerization), some 1,4-polymerization (5–30%) also takes place under acid catalysis with the cooperative involvement of both the epoxide and vinyl groups (Eq. (2)).[3] For the sake of simplicity in Eq. (2) and elsewhere in this article, the structure of polyEPB will be represented by its majority repeat unit.



(2)

We proposed that polyEPB might be a potentially interesting and inexpensive hydrogen donor synergist for free radical polymerizations. PolyEPB can be viewed as a polymeric tertiary allylic ether that possesses an easily abstractable hydrogen atom at each repeating unit along the polymer backbone. Thus, polyEPB can potentially function as a hydrogen donor that together with an aromatic ketone may initiate polymerization under UV irradiation. Accordingly, we have investigated the effect of adding polyEPB to aryl ketones in the presence of typical acrylate monomers. These reactions were followed using Fourier transform real-time infrared spectroscopy (FT-RTIR). This technique involves monitoring the change in the intensity of characteristic IR bands of the acrylate groups at 1640 cm^{-1} undergoing photopolymerization as a function of time. Decker and Moussa,[5,6] as well as ourselves[7,8] have described the use of this technique to follow the kinetics of rapid photopolymerization reactions. Figure 1 shows the results of the photopolymerization of 1,6-hexanediol diacrylate carried out in the presence of 8.0 mol% polyEPB and 2.0 mol% benzophenone. Included for comparison in this study are the results obtained for the polymerization of this same monomer in the presence of 8.0 mol% of triethanolamine. When either polyEPB or triethanolamine were omitted, no polymerization of the acrylate monomer was noted. Although triethanolamine appears to be more effective, polyEPB clearly functions as an efficient hydrogen donor in this system. A similar study is shown in Fig. 2 in which polyEPB and triethanolamine are again compared in the polymerization of 1,6-hexanediol diacrylate. The aromatic ketone employed in this case was 2-isopropylthioxanthone (ITX). As the data shows, polyEPB is superior to triethanolamine as a hydrogen donor in this case. A study of the effect of the polyEPB concentration on the rate of photopolymerization of 1,6-hexanediol diacrylate is shown in Fig. 3. PolyEPB is more

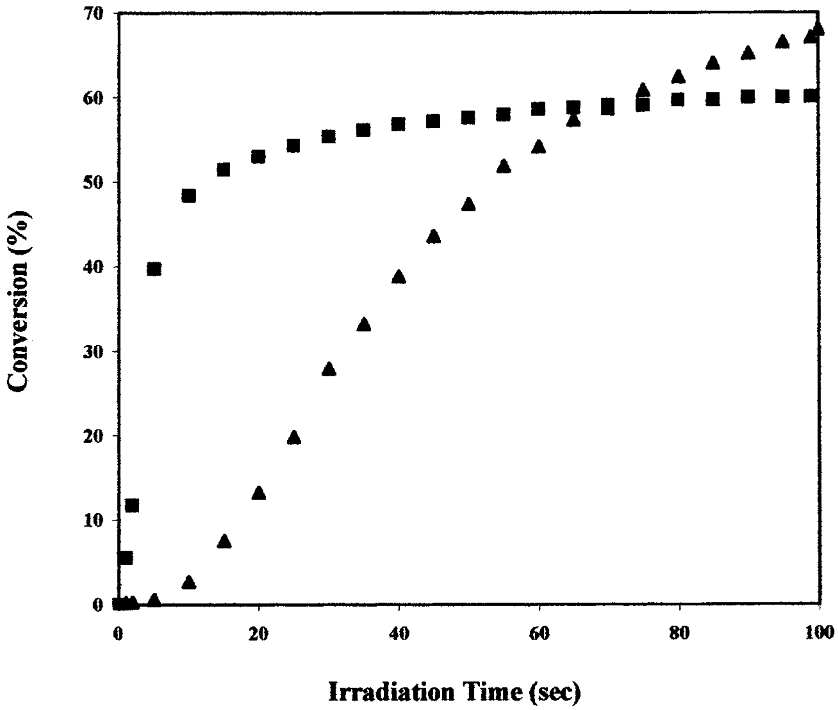


Figure 1. RTIR study of the photopolymerization of 1,6-hexanediol diacrylate with 2.0 mol% benzophenone in the presence of 8.0 mol% polyEPB (▲) and 8.0 mol% triethanolamine (■). Light intensity 10 mW/cm^2.

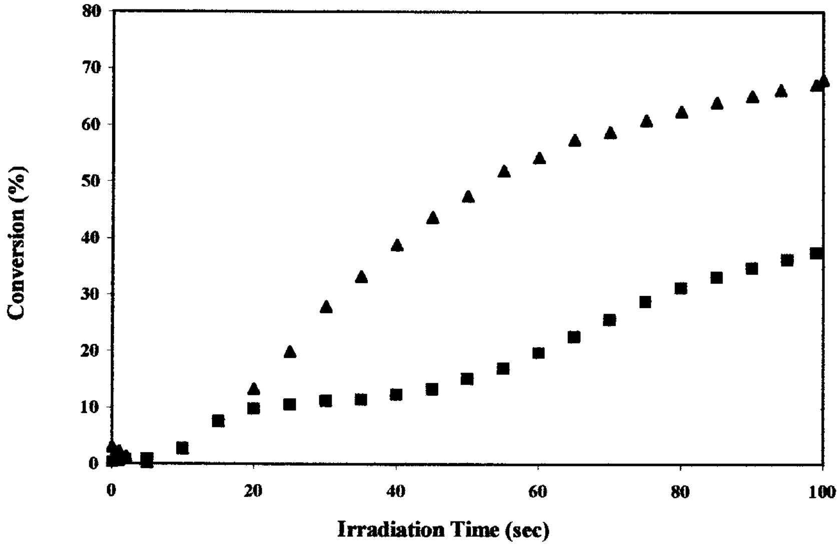


Figure 2. Comparison of the polymerization of 1,6-hexanediol diacrylate with 2.0 mol% 2-isopropylthioxanthone in the presence of 8.0 mol% polyEPB (▲) and 8.0 mol% triethanolamine (■). Light intensity 10 mW/cm^2.

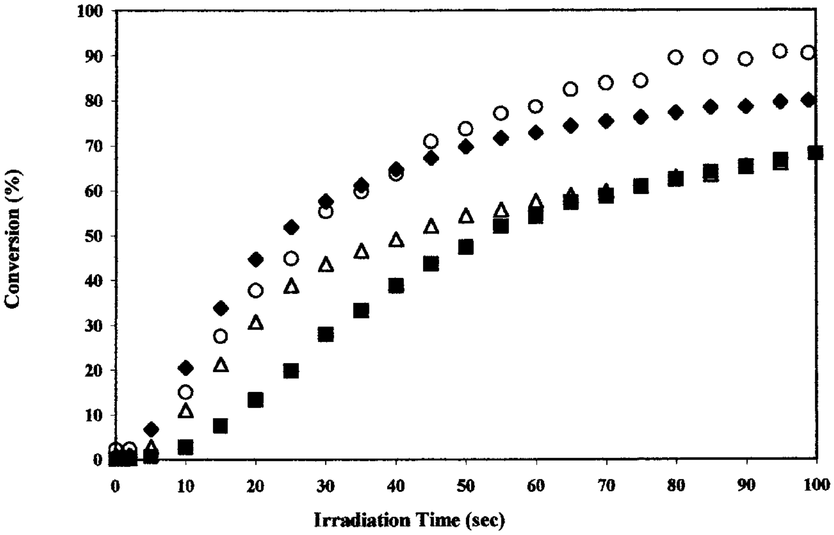
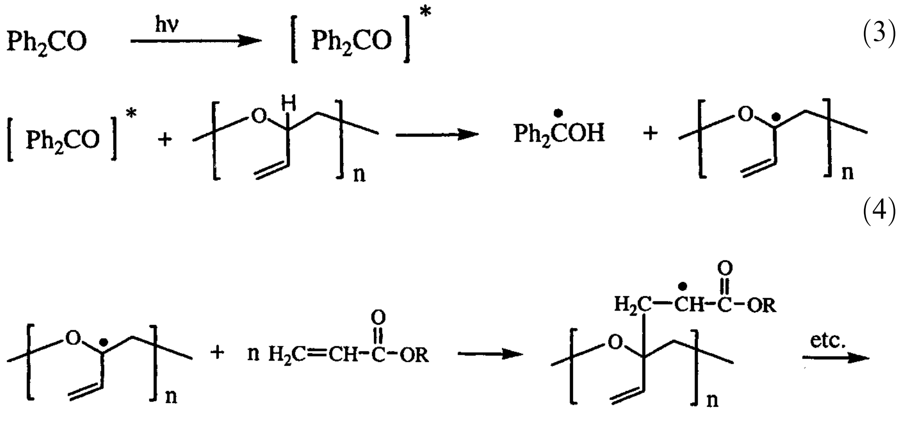


Figure 3. Study of the effect of polyEPB concentration on the photopolymerization of 1,6-hexanediol diacrylate in the presence of 2.0 mol% benzophenone. (■), 5.0 mol%; (△), 8 mol%; (◆), 15 mol%; and (○), 20 mol% polyEPB. Light intensity 10 mW/cm^2.

effective at higher concentrations and the difference between 15 and 20 mol% (based on repeat units of polyEPB with respect to 1,6-hexanediol diacrylate) is minimal. In the following, Sch. 1 is shown the proposed mechanism for free radical photoinitiation involving polyEPB as a hydrogen donor.

Benzophenone is depicted in the above scheme as the prototypical aromatic ketone. On photoexcitation (Eq. (3)), the excited benzophone abstracts hydrogen from at some of the repeat units along the poly(EPB)



(3)

(4)

(5)

Scheme 1.

backbone (Eq. (4)). For simplicity, only the specific sites where hydrogen abstraction has occurred are shown in Eq. (4) and elsewhere in this article. Thereafter, acrylate polymerization can take place at the radical sites generated along the polymer backbone to give an acrylate grafted polyEPB polymer (Eq. (5)). To provide further evidence for this reaction, an 80:20 w/w mixture of isobornyl acrylate and polyEPB containing 2.0 wt% of benzophenone was prepared and irradiated with UV light for 2 min. The polymer that was obtained was dissolved in chloroform and precipitated into methanol. This procedure was repeated twice more to free the polymer from residual monomer. The ^{1}H NMR spectrum of the dried polymer is shown in Fig. 4. Comparison with the spectra of authentic samples of polyEPB and isobornyl acrylate show that the polymer obtained bears a series of new methyl bands that can be attributed to the isobornyl group of the acrylate-grafted polymer. The polymer also contains resonances that can be attributed to the pendant double bond of polyEPB. In summary, it appears that as the mechanism shown in Eq. (4) suggests, acrylate groups are efficiently grafted onto the backbone of polyEPB during photoinitiated free radical polymerization.

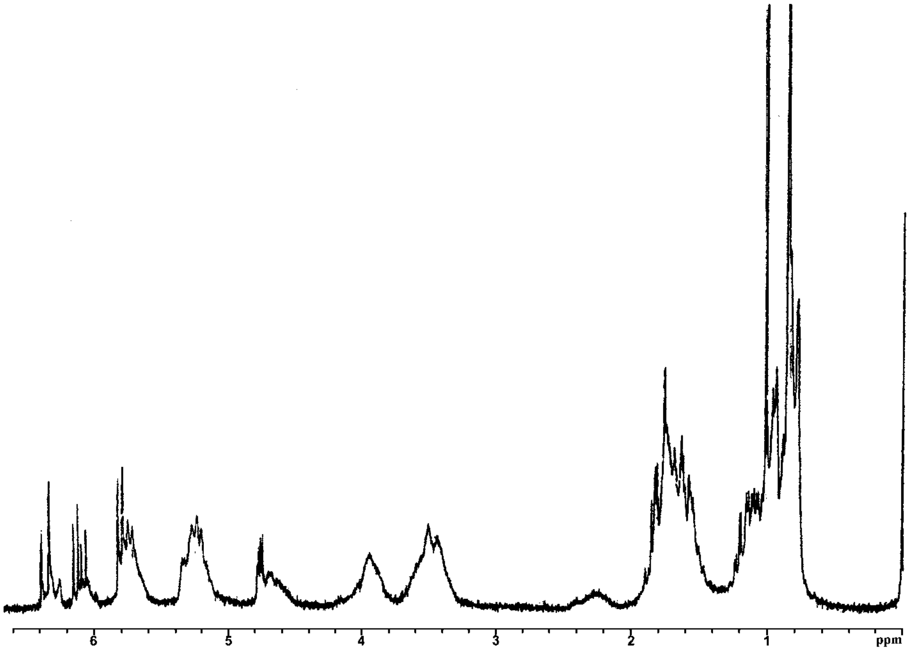
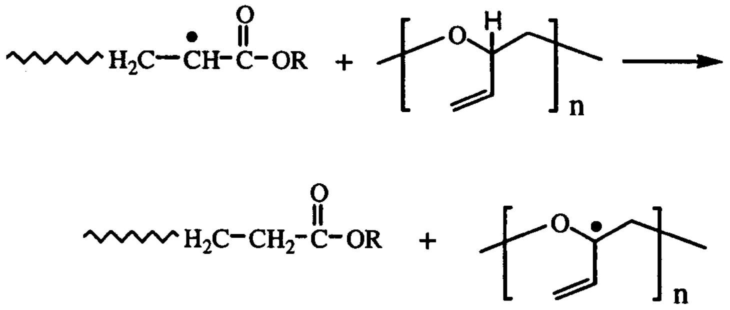


Figure 4. ^{1}H NMR spectrum of polyEPB-graft-poly(isobornyl acrylate).

PolyEPB as a Chain Transfer Agent

In addition to providing grafting sites along the chain for polymer attachment and growth, polyEPB would be expected to function as a chain transfer agent during polymerization. The mechanism proposed for chain transfer involving polyEPB is depicted in Eq. (6).



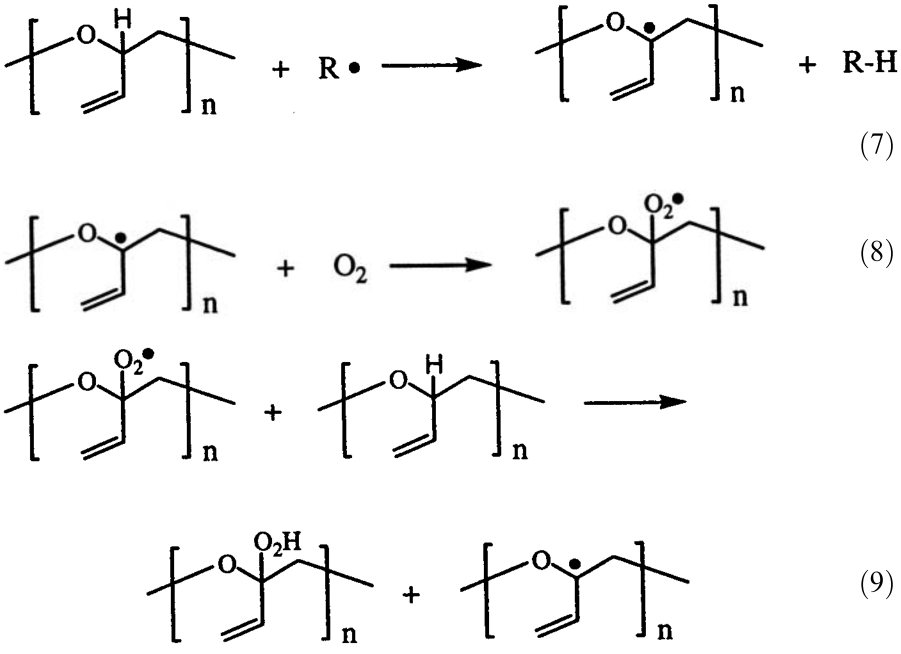
(6)

Hydrogen abstraction by the growing acrylate chain results in termination of that chain to form "dead" chains and at the same time generates potential new graft sites along the backbone of polyEPB. Typically, when multifuctional monomers are employed in photopolymerizations, the ultimate conversions are low due to occlusion of the growing free radical sites within the crosslinked matrix. However, the presence of a chain transfer agent should increase the overall conversion in these systems by mobilizing the reactive free radicals to more accessible sites. Evidence of this can be seen in Figs.1 and 2 in which the polymerizations containing polyEPB proceed to higher conversions than those in which triethanolamine was used as a hydrogen donor.

There is one interesting advantage of the use of polyEPB as compared to conventional chain transfer agents in free radical polymerizations. While the usual chain transfer agents have a strong molecular weight lowering effect on the resulting acrylate polymer, due to the presence of multiple hydrogen abstraction (i.e., chain transfer and graft) sites along the backbone, polyEPB should produce polymers with higher molecular weights (or higher crosslink densities).

PolyEPB as an Additive to Reduce Oxygen Inhibition Effects

One of the most difficult problems to overcome in free radical photopolymerizations is the sensitivity of these reactions to the presence of oxygen. The well known[9] "oxygen inhibition effect" is responsible for delayed and incomplete photopolymerizations and contributes to poor mechanical properties and chemical resistance particularly in thin film applications. To overcome this problem, two major strategies are commonly practiced. Simply carrying out such polymerizations in an inert atmosphere such as nitrogen suffices to alleviate the problem altogether. However, this is not always an acceptable or practical solution that can be used in all cases and especially for many low cost, high-speed applications. Additives that rapidly consume dissolved molecular oxygen in the film undergoing photopolymerization can also be used to minimize oxygen inhibition. Typically, the additives that are most useful are those that undergo facile autoxidation such as amines. PolyEPB undergoes autoxidation by virtue of the presence of the easily abstracted tertiary allylic ether hydrogen atoms situated along the backbone. Accordingly, we proposed that the addition of polyEPB to photocurable acrylate and methacrylate monomers should result in the mitigation of the oxygen inhibition effect by virtue of the reaction mechanism depicted in Sch. 2.



Scheme 2.

Free radical species ($R^{\bullet}$) generated by photolysis of a photofragmentation initiator can abstract the labile tertiary allylic protons on the backbone of polyEPB as shown in Eq. (7). This is followed by rapid reaction of the resulting polymer-bound radicals with dissolved oxygen present in the monomer (Eq. (8)). The hydroperoxy radicals formed in this latter reaction can further abstract hydrogen atoms from the backbone of polyEPB (Eq. (9)) regenerating the starting polymeric radicals. This free radical chain reaction consumes and quickly depletes the monomer film of oxygen. Usually, the depletion of oxygen occurs more rapidly than its rate of replacement by

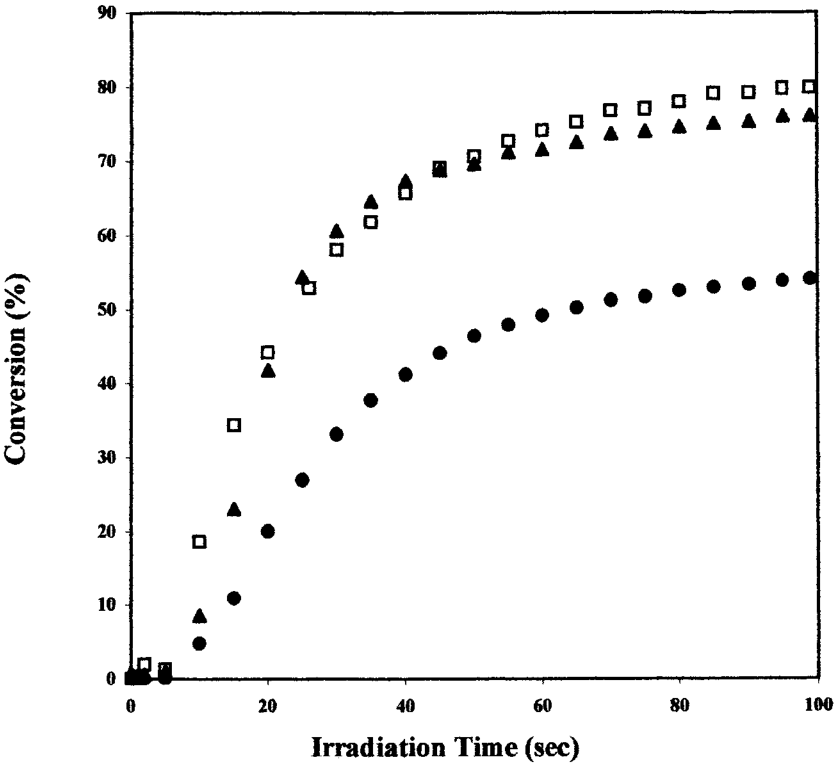


Figure 5. Study of the photopolymerization of 1,6-hexanediol diacrylate containing 4.0 mol% polyEPB and 2.0 mol% 2,2-dimethoxy-2-phenylacetophenone. Covered (▲), uncovered (□), and uncovered with no polyEPB (●). Light intensity 10 mW/cm^2.

diffusion into the monomer film allowing free radical polymerization of the acrylate monomer to proceed.

We have sought experimental evidence for the above mechanism in photocurable acrylate mixtures containing polyEPB. Shown in Fig. 5 are the results of a FT-RTIR study of the polymerization of 1,6-hexanediol diacrylate containing 4 mol% polyEPB carried out open to the air and also covered with a film of oriented polypropylene. These latter samples contain a small amount of dissolved oxygen but once it is consumed, the oxygen cannot be replaced by diffusion as with the former samples. Included in this study for comparison is a kinetic curve for the photopolymerization of pure 1,6-hexanediol diacrylate in air. In all three cases, 2,2-dimethoxy-2-phenylacetophenone (Esacure KB-1, Sartomer Corp.) was used as the photoinitiator. The results depicted in Fig. 5 clearly show the advantage of the inclusion of polyEPB into photocurable free radical formulations. The rates of polymerization of samples containing polyEPB was the same in either a covered or uncovered state. In contrast, under the same irradiation conditions, the polymerization of pure 1,6-hexanediol diacrylate carried out in the presence

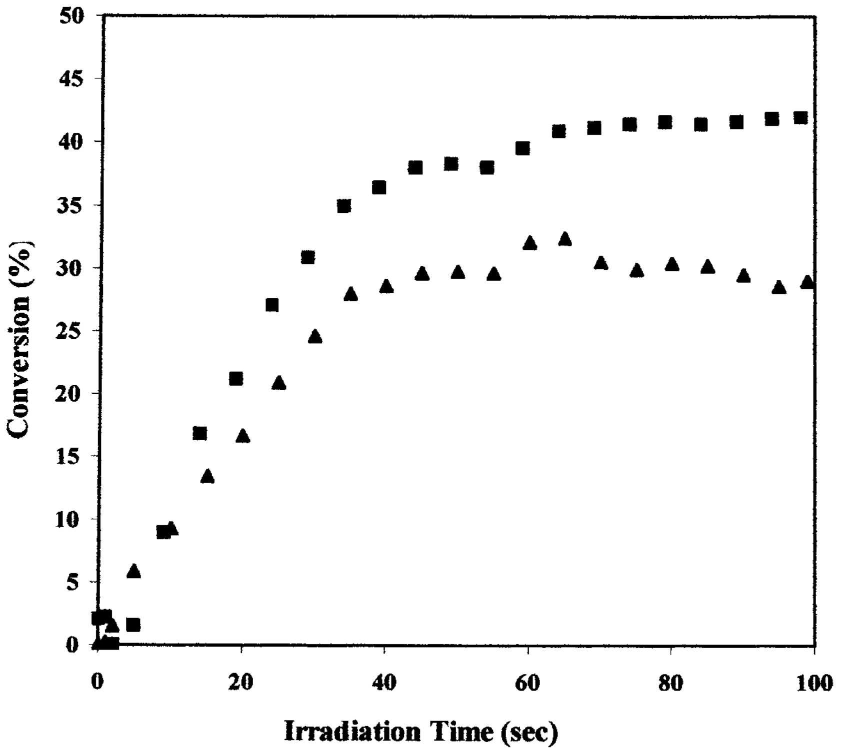


Figure 6. Study of the photopolymerization of n-butylacrylate containing 8.0 mol% polyEPB and 2.0 mol% 2-isopropylthioxanthone. Covered (■), uncovered (▲). Light intensity 10 mW/cm^2.

of oxygen was much slower and displayed an induction period consistent with an oxygen inhibition effect.

A similar study is shown in Fig. 6 in which the polymerization of n-butyl acrylate was carried out with 8.0 mol% polyEPB in covered and uncovered samples. In this case, 2.0 mol% 2-isopropylthioxanthone was used as the photoinitiator. Analogous results were observed when benzophenone or Michler's ketone was substituted for 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator. Very little difference was observed between the polymerization rates in samples containing polyEPB carried out in covered and uncovered mode. As noted before, these acrylate monomers do not polymerize when aromatic ketones are used in the absence of polyEPB. In this experiment, polyEPB plays a dual role. First, it functions as a hydrogen donor as part of the photoinitiator system and second, as an oxygen scavanger to reduce the inhibiting effects of oxygen.

The magnitude of the oxygen inhibition effect and its reduction depends somewhat on the type of monomer employed. Figure 7 gives the results of a study of the photopolymerization of trimethylolpropane triacrylate

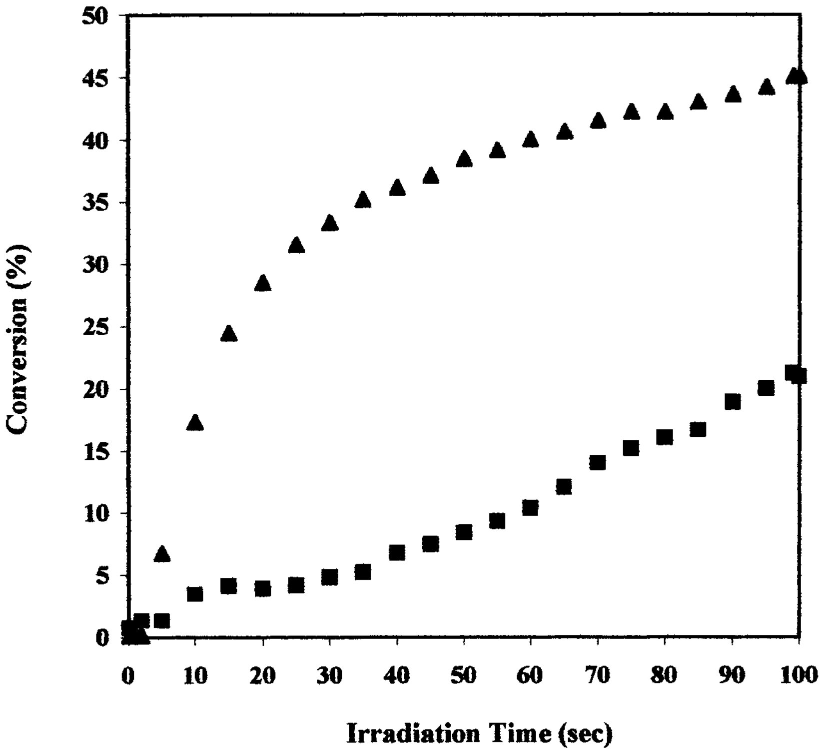


Figure 7. Comparison of the polymerization of trimethylopropane triacrylate with 2.0 mol% 2-isopropylthioxanthone in the presence of 8.0 mol% polyEPB. covered (▲), uncovered (■). Light intensity 10 mW/cm^2.

using 2-isopropylthioxanthone as the aromatic ketone and polyEPB. Covering the sample to exclude oxygen has a strong accelerating effect on the photopolymerization. Taken together, the results shown in Figs. 5–7 are indicative of the ability of polyEPB to strongly reduce oxygen inhibition in photoinitiated free radical systems. For this reason, we suggest that polyEPB may find use as an additive in this field of application.

CONCLUSION

PolyEPB is a highly useful additive and matrix modifier for photoinitiated free radical crosslinking polymerizations. Work in this laboratory has uncovered several beneficial functions that this material can serve in these polymerizations. In particular, we have demonstrated that polyEPB can function as a hydrogen donor together with aromatic ketones to form an efficient photoinitiating system for these polymerizations reactions. PolyEPB can increase conversions in photocurable multifunctional acrylate systems due to both chain transfer and grafting effects. During photopolymerization, grafting of the acrylate monomer onto the backbone of polyEPB takes place. Thus, polyEPB becomes an integral part of the final resin matrix. We have also demonstrated that polyEPB can substantially reduce oxygen inhibition effects in photoinduced free radical polymerization systems leading to lower cost curing processes through the elimination of the use of nitrogen as an inerting gas.

In addition, polyEPB has other properties that make it valuable for free radical photocuring processes. PolyEPB is an oligomeric material with some film-forming characteristics. This makes it attractive for use in coating and ink formulations that require viscoelastic properties for optimal deposition, flow and adhesion characteristics. It is likely that the oligomeric nature of polyEPB will also confer a low level of oral toxicity, eye and skin irritation.

ACKNOWLEDGMENT

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