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Radical-Promoted Visible Light Photoinitiated Cationic Polymerization of Epoxides

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Herein is described the development of a three-component photoinitiator system that employs the free radical promoted decomposition of diaryliodonium salts for the visible light induced cationic polymerization of epoxides. A long wavelength, titanium-complex free radical photoinitiator is used to generate radicals that abstract hydrogen atoms from benzyl alcohol synergists. The resulting benzyl radical species efficiently reduce diaryliodonium salts thereby generating oxycarbenium ions that spontaneously fragment to form the corresponding aldehyde and a Brønsted superacid. The superacid subsequently initiates the cationic ring-opening polymerization of a wide variety of epoxide monomers.

Keywords: Cationic photopolymerization, epoxides, visible light, photosensitization

1 Introduction

Recently, we have been engaged in the development of cationic photopolymerization systems that employ low intensity visible light. Related systems based on the free radical photopolymerizations of multifunctional acrylate and methacrylate monomers have been known for some time and are currently employed in a variety of medical/dental applications including for example; the manufacture of catheters and quick setting dental composites and restoratives. They also find widespread use in many adhesive applications, for example, in the assembly of small appliances, syringes, eye glasses, speakers and audio equipment, and for the encapsulation of electronic and photonic devices. While the visible light sensitive free radical systems described above currently find considerable use, they do have certain inherent drawbacks such as high volume shrinkage, poor adhesion and low thermal resistance that limit their utility in certain applications. On the other hand, cationically photopolymerizable epoxide monomers display much lower volume shrinkages during polymerization and also feature excellent adhesion to many different types of substrates. The oxidative and thermal resistance of crosslinked polymers derived from the ring-opening polymerizations of epoxide monomers is also significantly better than those

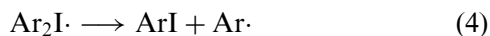
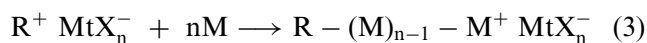
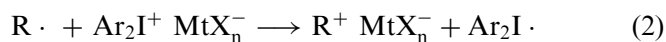
produced by the photoinduced free radical polymerization of acrylate and methacrylate monomers.

Accordingly, efforts in this laboratory over the past several years have been directed towards an investigation of visible light cationic photoinitiating systems. Simple cationic photoinitiators; diaryliodonium and triarylsulfonium salts, do not absorb in the visible region of the electromagnetic spectrum and can only be used where UV light is available. To use these photoinitiators for visible light induced cationic polymerizations, it is necessary to employ various methods to broaden their spectral sensitivity. The main approach that has been applied to broaden the spectral sensitivity of these photoinitiators is to use electron-transfer photosensitizers. We have reported that diaryliodonium salts are particularly amenable to photosensitization and that suitable electron-transfer photosensitizers for these compounds at wavelengths from 400–500 nm are polynuclear aromatic compounds (1,2,3) and their substituted analogues (4,5) carbazoles (6) and phenothiazines (7). Recently, we also reported that the naturally occurring dye, curcumin is a photosensitizer for diaryliodonium salts that spans the spectral region from 300–500 nm (8).

A major deficit of existing visible light sensitive cationic photopolymerization systems is their rather poor sensitivity at low intensity light levels that manifests itself in slow polymerization rates. It was the objective of this investigation to examine alternatives to electron-transfer photosensitization in an attempt to improve the response of these systems. One approach that we have been exploring is free radical promoted cationic photopolymerization. A general

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mechanism involving a four-step sequence of reactions is depicted in Scheme 1.



Sch. 1. Mechanism of free radical promoted cationic photopolymerization

The first step of the mechanism involves the unimolecular photoinduced homolytic fragmentation of a compound (PI) to yield two free radicals (Eq. 1). One or both of the free radicals can reduce a diaryliodonium salt (Eq. 2) yielding a carbocation and the diaryliodine free radical. The carbocation can initiate the cationic polymerization of suitable vinyl or heterocyclic monomers (Eq. 3). At the same time, the unstable diaryliodine free radical spontaneously decomposes (Eq. 4) to yield an aryl iodide and a highly reactive aryl radical. This latter species may, directly or through a subsequent series of reactions, reduce additional molecules of the diaryliodonium salt starting a chain reaction. Thus, a cycle is set up whereby the free radical promoted chain induced decomposition of diaryliodonium salts has the potential of chemically amplifying the effect of the photons absorbed by the system. Optimally, such a system can generate many propagating cationic centers by the absorption of a single photon of light.

The use of free radical promoted cationic polymerization to broaden and increase the spectral response of diaryliodonium salt photoinitiators has been described by a number of investigators. Ledwith (9,10), Baumann (11,12), Timpe (13) and Klemm (14) were the chief early workers in this field. Yagci and his coworkers (15–18) have explored many aspects of this area and have also extended free radical promoted cationic polymerizations to include N-alkoxyppyridinium salt cationic photoinitiators. In work from this laboratory (19), we have described the synergistic rate accelerating effects of free radical photoinitiators such as 2,2-diethoxy-2-phenylacetophenone on the diaryliodonium salt UV photoinitiated cationic photopolymerizations of a variety of epoxide monomers. In a recent publication (20), Yagci and his coworkers have described the development of a visible light sensitive system based on acylgermanes in combination with diaryliodonium salts for the free radical promoted cationic polymerization of epoxides and highly reactive vinyl monomers such as vinyl ethers and N-vinyl carbazole. Fouassier and his coworkers (21,22) have reported that the UV laser and visible light irradiation of aromatic ketones in the presence of disilanes, and silanes and germanes generates respectively, silyl and germynyl radicals that efficiently reduce diaryliodonium salts. In a cascade of reactions similar to those shown in Scheme

1, this system can be employed for the visible light photoinitiated cationic polymerization of epoxide monomers (23). In a recent paper from this laboratory (24), we have described a novel visible light sensitive system based on free radical promoted cationic polymerization. This system generated radicals capable of oxidation by diaryliodonium salts through the reaction of photoexcited camphorquinone with benzyl alcohols.

The present communication describes the development of a new and efficient visible light sensitive cationic photoinitiator system and its application to the polymerization of epoxide monomers and epoxide-functional oligomers.

2 Experimental

2.1 Materials

Irgacure 784 (bis(η^5 -cyclopentadienyl)bis[2,6-difluoro-3-(1-H-pyrrol-1-yl)phenyl]titanium) and Rhodorsil 2746 (4-isopropylphenyl-4'-methylphenyliodonium tetrakis(pentafluorophenyl)borate) were provided as a gift by the Ciba Specialty Chemicals, Inc. Basel, Switzerland. Limonene dioxide (1-methyl-4-(2-methyloxiranyl)oxabicyclo[4.1.0]heptane) was received as a gift from the Viking Chemical Co., Minneapolis, MN. 3,4-Epoxy cyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (ERL-4221) was purchased from the Union Carbide Corp. (now Dow Chemical, Midland, MI). All other monomers, reagents and chemicals were used as purchased from the Aldrich Chemical Co., Milwaukee, WI. The diaryliodonium salts, (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF₆) and (4-n-octyloxyphenyl)phenyliodonium hexafluorophosphate (OPPI PF₆) were prepared and purified by previously described methods (25).

2.2 Optical Pyrometry

General descriptions of the apparatus, sample preparation methods and analytical techniques used in the optical pyrometric analysis of photopolymerization reactions were given in previous publications from this laboratory (26–28). Figure 1 shows the modifications made to the OP apparatus for conducting visible light photopolymerization studies. A standard Panasonic SXGA-6000 (Model PT-D7700U) DLP™ Projector was mounted at a distance of 62 cm from the irradiation cabinet and a square beam from the projector was admitted into the apparatus through a 3 cm × 3 cm square aperture cut into the side of the cabinet. The beam was directed onto a mirror mounted at 45° to the horizontal and from there onto the underside of a thin film liquid sample sandwiched between two fluorinated polyethylene films mounted in a plastic 5 cm × 5 cm slide frame. The projector was fitted with a neutral density filter and all photopolymerizations were carried out at a light intensity of 8.5 mW/cm² unless otherwise noted. The

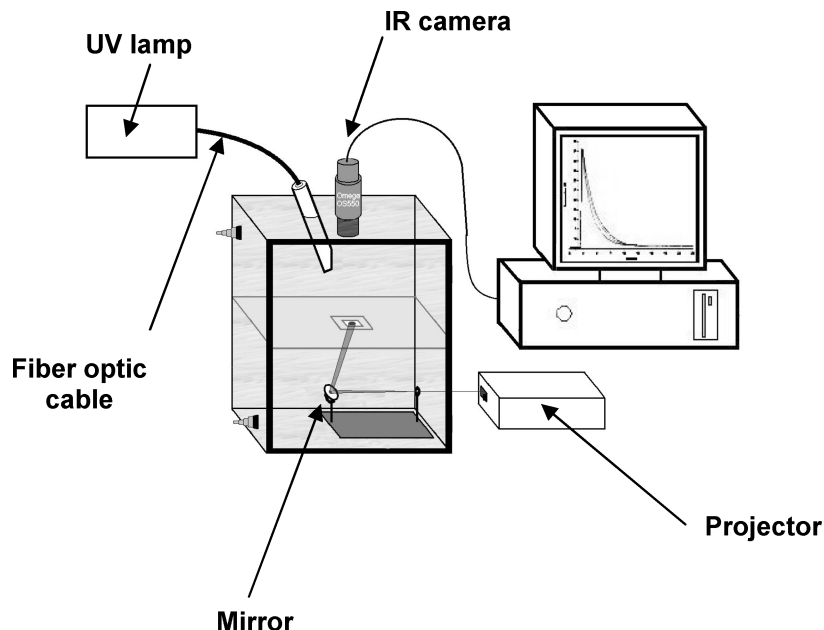


Fig. 1. Modified optical pyrometry apparatus for visible light polymerization studies.

course of the photopolymerization was monitored with an infrared camera mounted above the sample with the focal point of the camera at the focal plane. Light intensity measurements were made at the sample plane with the aid of a PRC Krochmann RadioLux 111 Radiometer (Berlin, Germany). The major emission bands provided by the projector are at 440, 552 and 609 nm.

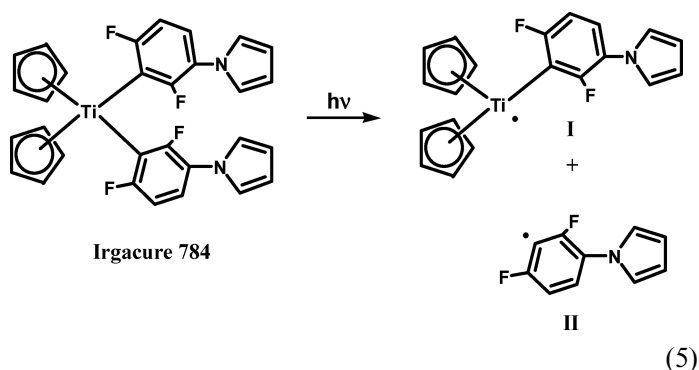
3 Results and Discussion

3.1 General Approach

The first task in achieving a visible light sensitive free radical promoted cationic polymerization is to select a free radical photoinitiator that absorbs strongly at wavelengths from 400 to 700 nm and efficiently generates free radicals on irradiation. In addition, neither the photoinitiator nor its photofragmentation products should inhibit or retard the cationic polymerization. On the basis of these two requirements it was possible to eliminate most common free radical photoinitiators. As a result, our attention centered on the commercially available photoinitiator, Irgacure 784 (bis(η^5 -cyclopentadienyl)bis[2,6-difluoro-3-(1-H-pyrrol-1-yl)phenyl]titanium) which possesses strong absorption bands at 405 and 480 nm with an appreciable tail absorption extending out to 560 nm. A search of the literature revealed that Irgacure 784 has previously been used together with diphenyliodonium hexafluorophosphate or N-ethoxy-2-methylpyridinium hexafluorophosphate by Yagci et al. (29,30) in the free promoted cationic photopolymerization the very reactive monomers; cyclohexene oxide, N-vinylcarbazole and n-butyl vinyl ether. Long irradiation times (30–180 min) under an atmosphere of nitro-

gen with 460 nm light (100 W Xenon lamp) were required to achieve appreciable conversions. Under the above experimental conditions, the photopolymerization of the bis-cycloaliphatic epoxy monomer 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (ERL-4221) did not take place. No explanation was given for this behavior.

The mechanism of the photolysis and subsequent initiation of radical polymerizations by Irgacure 784 and other titanocene complexes has been investigated by several groups of workers (31–33). On the basis of radical trapping studies that were conducted (34), it was suggested that during the irradiation two of the ligands of the complex are ultimately removed most probably by a step-wise process involving the initial formation of a titanium centered radical (I) and a aryl radical (II) (Eq. 5). Presumably, both species can initiate the free radical polymerization reactions. However, it appears that these same species do not efficiently reduce diaryliodonium or N-alkoxy-pyridinium salts by a direct interaction process. Considering the structure of the two radical species, this is not surprising since their oxidation would not be an easy process.



With the above mentioned (29,30) previous results in mind, it was decided to undertake a brief examination of the visible light free radical promoted cationic polymerization of epoxide monomers using Irgacure 784 as the free radical photoinitiator and diaryliodonium salts as the cationic initiator. To aid in these studies, we used optical pyrometry (infrared thermography) to evaluate the speed and efficiency of the visible light-driven polymerizations. Optical pyrometry (OP) is a convenient, highly reliable technique that was developed in this laboratory for remotely monitoring free radical and cationic photopolymerization reactions (22–24). This technique is based on the principle that free radical and cationic addition polymerizations are highly exothermic events. When neat monomers are irradiated in the presence of appropriate photoinitiators, the exothermicity of the polymerization reaction manifests itself in a measurable elevation in the temperature of the sample. Using an infrared camera (i.e. an optical pyrometer), the course of the evolution of the temperature of a sample is remotely monitored in real time as a function of the irradiation time at a constant irradiation intensity. The OP technique is especially well suited to the study of the photopolymerizations of multifunctional monomers that undergo crosslinking polymerizations. It has been further shown (26) that the initial portion of the temperature vs. time curve of an optical pyrometry trace is proportional to the corresponding conversion vs. time plots as determined by either real-time infrared spectroscopy (RTIR) or by differential scanning photocalorimetry (DSP). As detailed in the Experimental portion of this article, the OP apparatus that was originally designed to study UV induced photopolymerization reactions was further modified for the study photopolymerizations conducted under controlled visible light irradiation conditions. In the present instance, the photopolymerizations were conducted

at a rather low light intensity of 8.5–19 mW/cm² using a commercially available computer image projection system.

3.2 Studies of the Visible Light Photopolymerizations of Epoxy Monomers

Figure 2 shows a study of the visible light induced photopolymerization of ERL-4221 conducted in the presence of Irgacure 784 together with (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF₆) as the cationic initiator. Initial studies showed that polymerization of ERL-4221 does not take place when the monomer containing only either Irgacure 784 or OPPI SbF₆ is irradiated under the same conditions. The results depicted in Figure 2 verifies, as Yagci et al. had previously shown (29,30), that the polymerization of this monomer does not take place even after 5 min of continuous irradiation when both free radical and cationic photoinitiators are present. However, as may be noted in the same figure, when 20% by weight of 4-methoxybenzyl alcohol (MeOBzOH) were added, the polymerization proceeds vigorously after a brief induction period. In this latter case, the sample attains a maximum temperature of 164°C. A similar study is shown in Figure 3 in which 4-vinylcyclohexene dioxide was present as the monomer. As with ERL-4221, the photopolymerization of this very reactive difunctional monomer does not take place in the absence of the benzyl alcohol. Similarly, a number of other common epoxide monomers were evaluated and found respond to photopolymerization mediated by this three-component photoinitiator. Among these are: cyclohexene oxide, limonene dioxide, 1,2-epoxybutane and epoxidized linseed oil.

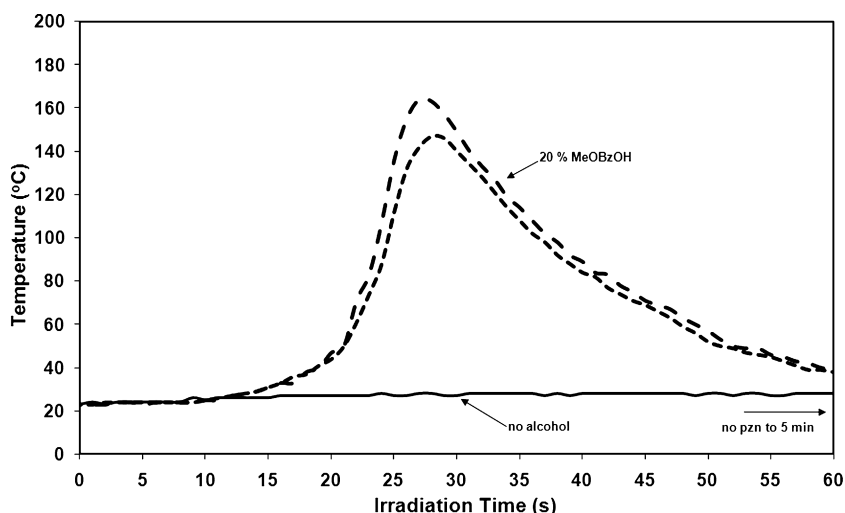


Fig. 2. OP study of the photopolymerization of ERL-4221 with 2.5% (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF₆), 1.5% Irgacure 784 in the presence and absence of 4-methoxybenzyl alcohol (MeOBzOH).

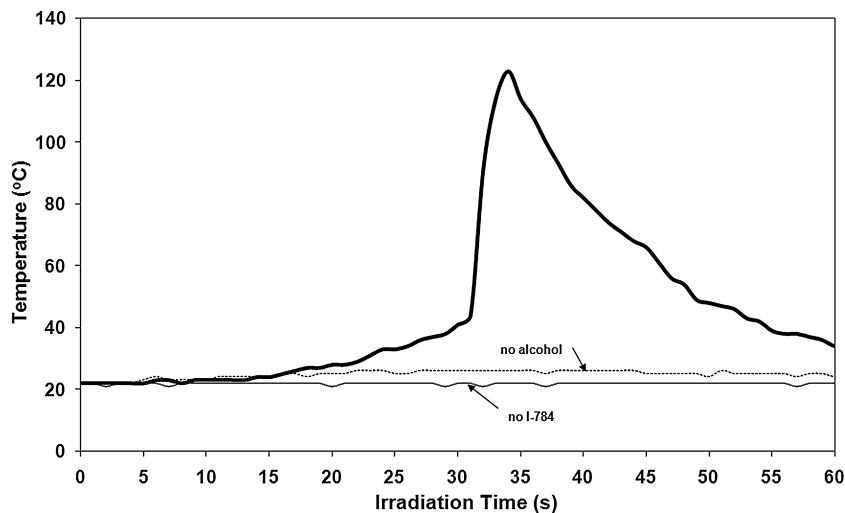
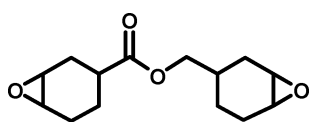
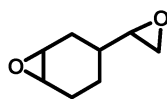


Fig. 3. OP study of the photopolymerization of 4-vinylcyclohexene dioxide with 2.5% OPPI SbF_6 , 1.5% Irgacure 784 in the presence and absence of MeOBzOH.



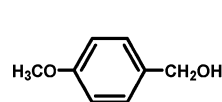
ERL-4221-4221



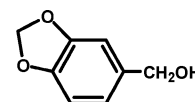
4-vinylcyclohexene dioxide

MeOBzOH may be replaced by other benzylic alcohols in the three-component photoinitiator system. Benzyl alcohol is considerably less reactive than MeOBzOH as also are 4-nitrobenzyl alcohol and 4-chlorobenzyl alcohol. However, as Figure 4 shows, piperonyl alcohol functions well in this new three-component photoinitiator system. 2-Phenethyl alcohol, a secondary benzylic alcohol, exhibits approximately the same reactivity as MeOBzOH. Since MeOBzOH is readily obtained and comparatively inexpensive, many

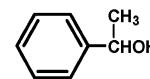
of the subsequent studies were conducted with this benzylic alcohol. Figure 5 shows the effect of varying the concentration of MeOBzOH while holding the other two components of the photoinitiator system constant. While there was a clear increase in the polymerization rate as the concentration of MeOBzOH is increased, the maximum effect was observed at approximately 20%. A further increase to 25% of MeOBzOH did not appreciably modify the response of the system as judged by comparing the OP curves.



MeOBzOH



piperonyl alcohol



2-phenethyl alcohol

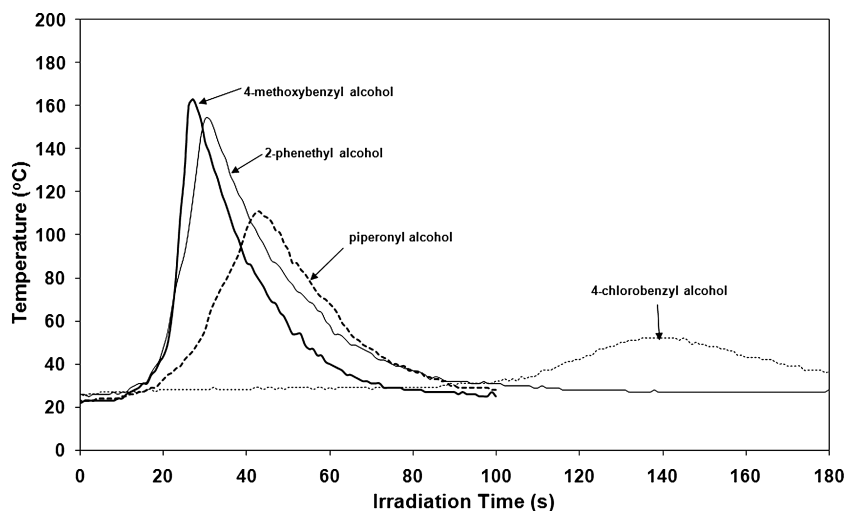


Fig. 4. Comparison of the effects of 20% various benzylic alcohols on the cationic ring-opening photopolymerization of ERL-4221 with 2.5% OPPI SbF_6 and 1.5% Irgacure 784.

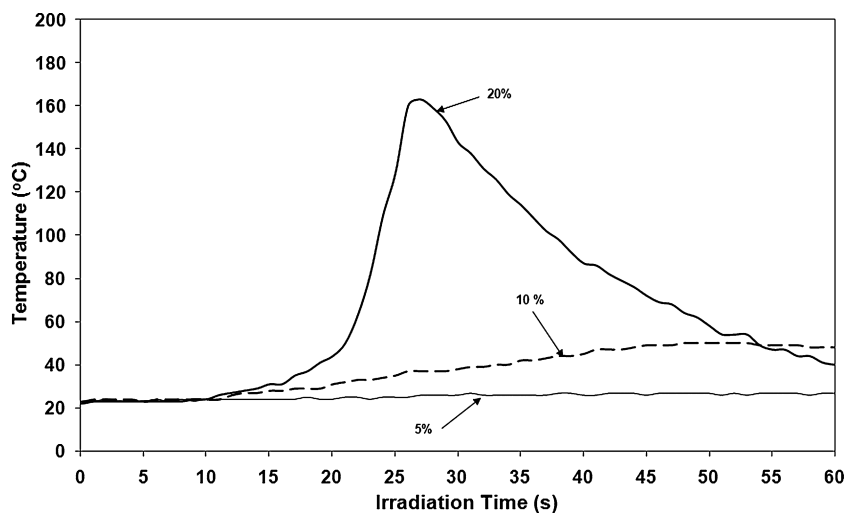
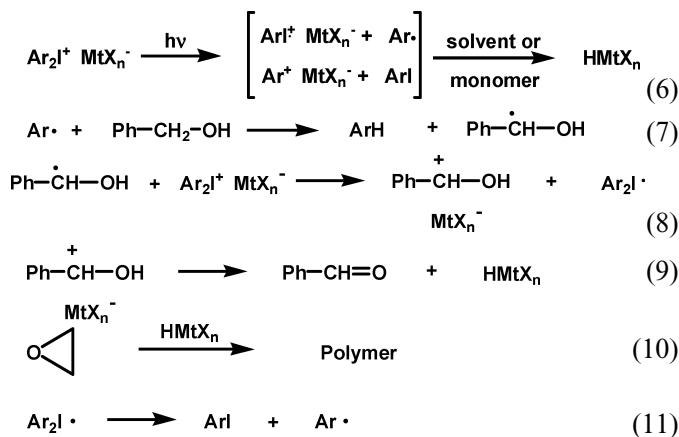


Fig. 5. Effect of the concentration of MeOBzOH on the cationic ring-opening photopolymerization of ERL-4221. (photoinitiator, 2.5% OPPI SbF₆ and 2.0% Irgacure 784)

3.3 Mechanistic Studies

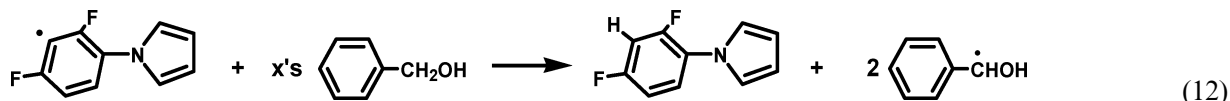
Previously (35), we have reported that benzyl alcohols markedly accelerate the UV-induced cationic ring-opening photopolymerizations of epoxides. This effect was observed only when diaryliodonium salts were employed as photoinitiators and does not occur when triarylsulfonium salts are used. A mechanism that rationalizes the observed results was proposed and is depicted in Scheme 2. In this Scheme, the mechanism is illustrated with benzyl alcohol and ethylene oxide for the sake of simplicity. The photolysis of a diaryliodonium salt yields an aryl radical and a diaryliodonium cation-radical (Eq. 6). Interaction of the aryl radical with solvents, monomers or trace impurities yields protonic acids capable of initiating cationic ring-opening polymerizations. At the same time, the aryl radical can abstract hydrogen atoms from benzyl alcohol to yield the corresponding benzyl radical (Eq. 7). These latter species reduce diaryliodonium salts thereby producing α -hydroxybenzyl carbocations and diaryliodonium radicals (Eq. 8). α -Hydroxybenzyl cations can undergo spontaneous deprotonation to give the corresponding benzaldehydes (Eq. 9). Cationic ring-opening polymerization, as shown in Equation 10, results from the attack by the protonic acid, HMTX_n, on the epoxide monomer. Lastly, the diaryliodonium radical is unstable and decays with the formation of an aryl iodine compound and the regeneration of the aryl radical (Eq. 11). In effect, a photoinitiated free radical chain induced decomposition process is set up which results in the consumption of the diaryliodonium salt by a non-photochemical process and, at the same time, produces reactive species that serve as initiators for cationic polymerization. The apparent UV photopolymerization rate acceleration observed when the benzyl alcohol is present derives from an increase in the concentration of initiating species that result from the combination of both the direct photo-

and non-photochemical (i.e., radical promoted) initiation processes.



Sch. 2. Mechanism of the acceleration of cationic photopolymerization by benzyl alcohols

Based on this prior work, we now propose that a similar mechanism may account for the visible light-induced photopolymerization of epoxides when MeOBzOH and other benzyl alcohols are added to the monomer containing both Irgacure 784 and OPPI SbF₆. As depicted in Equation 5, the irradiation of Irgacure 784 with visible light generates radical species such as **I** and **II**. It is now proposed that these species abstract hydrogen atoms from the benzyl alcohol to generate α -hydroxybenzyl radicals as shown in equation 12 and that these species are responsible for the reduction of the diaryliodonium salt together with consequent initiation of cationic polymerization as described in Scheme 2.



There is considerable evidence for the presence of free radicals as intermediates in the three-component photoinitiator induced cationic polymerization of epoxide monomers. It has been observed that the free radical promoted visible light induced cationic epoxide photopolymerizations characteristically display a prominent induction period that ends abruptly and is followed by the very rapid exothermic polymerization of the epoxide monomer. In contrast, the UV induced cationic polymerizations of epoxides such as ERL-4221 and 4-vinylcyclohexene dioxide by diaryliodonium salts take place either without or after very short induction periods. This is an indication of the presence of oxygen inhibition effects in these former radical promoted photopolymerizations. The samples for analysis by OP are prepared by sandwiching the liquid photopolymer between two fluoropolymer films. For this reason, the samples contain some dissolved oxygen that intercepts the photogenerated free radicals preventing the free radical promoted reduction of the diaryliodonium salt and the subsequent cationic epoxide polymerization. When all the oxygen in the samples is consumed by the photogenerated free radicals, it cannot be effectively replaced from the atmosphere within the time frame of the experiment and polymerization ensues at this point. Additional evidence for the presence of radicals is shown in Figure 6. When 3% nitrobenzene is added to the monomer-photoinitiator mixture as a free radical inhibitor, there is a total suppression of the visible light induced cationic photopolymerization reaction.

The results of the study of the effect of the structure of the benzyl alcohol that was depicted in Figure 4 can also be interpreted in view of the mechanism shown in Scheme 2 together with Equation 12. Benzyl alcohols bearing electron-donating substituents that stabilize the α -hydroxybenzyl radicals and the corresponding α -hydroxybenzyl cations by resonance interaction would be predicted to facilitate the overall photopolymerization reaction. This explains the superior reactivity of MeOBzOH and piperonyl alcohol as compared to benzyl alcohol in the reaction. The high reactivity of 2-phenethylalcohol provides further support for the mechanism since this compound would be expected to undergo facile hydrogen abstraction at the tertiary benzylic position. In addition, the generation of a carbocation at the same position through oxidation by the diaryliodonium salt would also be favored on the basis of stability considerations. As noted in equation 9 of Scheme 2, α -hydroxybenzyl cations deprotonate to yield a strong Brønsted acid and the corresponding benzaldehyde. The irradiation of a dichloromethane solution containing 6% OPPI SbF₆, 6% Irgacure 784 and 20% benzyl alcohol was irradiated for 10 min and then analyzed by gas chromatography for the presence of benzaldehyde. Traces of benzaldehyde were detected in the sample on the basis of its retention time by a comparison with the retention time of an authentic sample. Under the strongly acidic conditions of the reaction mixture, benzaldehyde undergoes a variety of further reactions.

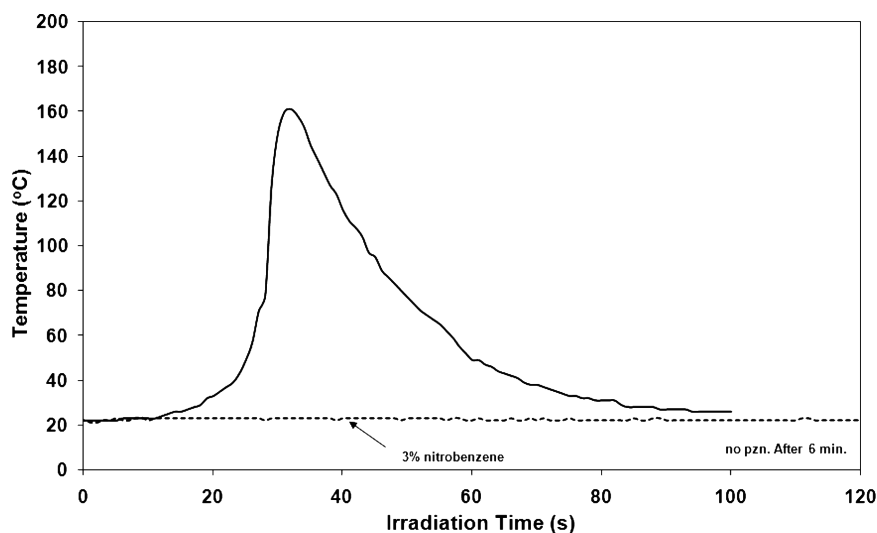


Fig. 6. Effect of nitrobenzene on the photopolymerization of ERL-4221 with 1.0% Irgacure 784, 2.5% OPPI SbF₆ and 20% MeOBzOH.

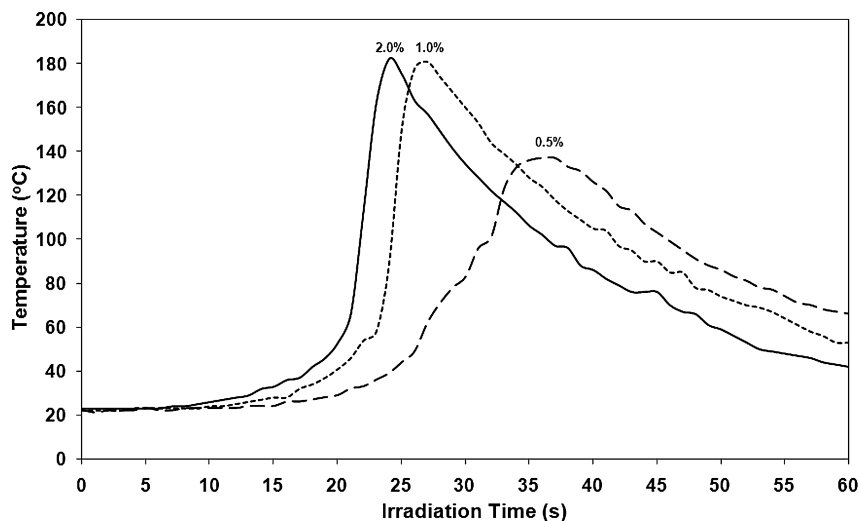


Fig. 7. OP study of the photopolymerization of ERL-4221 in the presence of various amounts of Irgacure 784 with 2.5% OPPI SbF_6 and 20% MeOBzOH.

The proposed mechanism by which the cationic photopolymerization proceeds involves, as the critical initial step, the irreversible photolysis of the titanium complex to form radicals. This is observed by a dramatic bleaching of the reaction mixture during the photopolymerizations from its initial orange color to a colorless polymer.

3.4 Effect of Variation of Experimental Parameters

A number of other experimental parameters were systematically varied to evaluate their effects on the cationic ring-opening polymerizations of epoxide monomers by this new three-component photoinitiator system. As in the previous studies, ERL-4221 was employed as the monomer. For example, as shown in Figure 7, the effects of modifying the concentration of Irgacure 784 were investigated. In gen-

eral, the higher the Irgacure 784 concentration, shorter the induction period and the sharper the temperature versus irradiation time curve. This suggests that at a constant light intensity the number of propagating centers generated by photolysis increases with an increase in the Irgacure 784 concentration. It may also be noted that the effect on the photopolymerization is greatest when the Irgacure 784 concentration is increased from 0.5% to 1.0% and that there is a lesser effect when it is further increased to 2%. A complementary study is depicted in Figure 8 in which the OPPI SbF_6 concentration was varied from 1.0–2.5%. Very little change in the polymerization response of the monomer, ERL-4221, was observed over this concentration range. In contrast, the replacement of OPPI SbF_6 with Rhodorsil 2746 as shown in Figure 9, led to a considerable lengthening of the induction period. This is unusual, since in previous

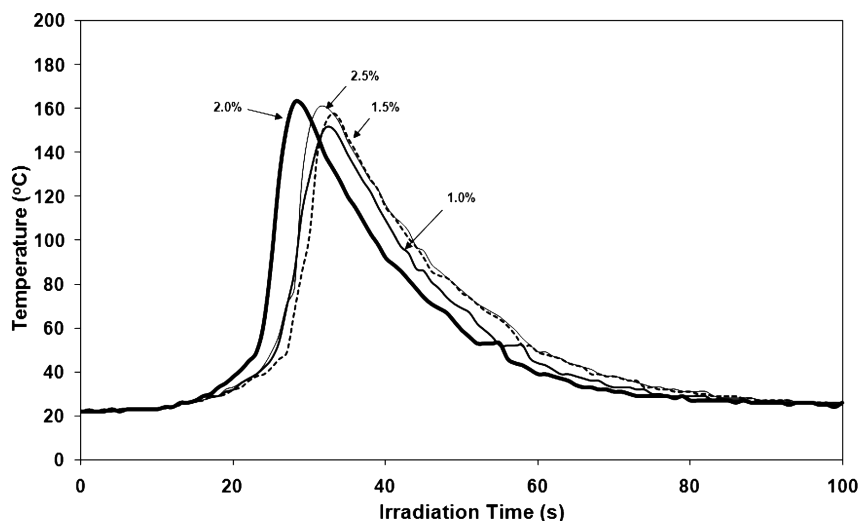


Fig. 8. OP study of the effect of the concentration of OPPI SbF_6 on the cationic photopolymerizations of ERL-4221 with 1.0% Irgacure 784 and 20% MeOBzOH.

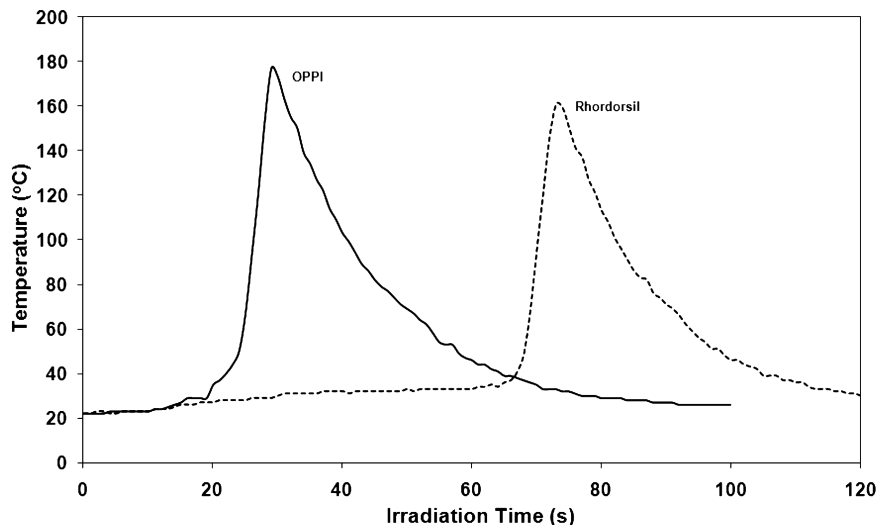
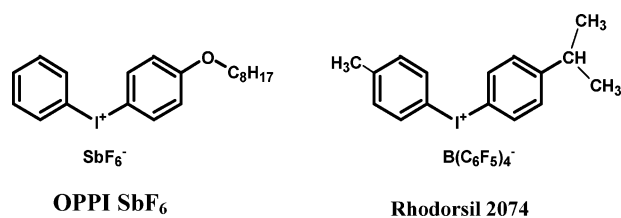


Fig. 9. Comparison of the effects of 2.0% of the photoinitiators OPPI SbF_6^- and Rhodorsil 2074 on the cationic ring-opening photopolymerization of ERL-4221 in the presence of 1.0% Irgacure 784 and 20% MeOBzOH.

work (36), we had observed that these two photoinitiators behaved similarly in UV induced photopolymerizations.



The effect of varying the light intensity in a typical free radical promoted cationic photopolymerization of ERL-4221 is shown in Figure 10. Increasing the light intensity produces a corresponding increase in the concentration of

photogenerated radicals that consume oxygen dissolved in the sample thereby shortening the induction period. Once the induction period is overcome, cationic polymerization of the monomer proceeds at nearly the same rate in both cases.

Epoxide monomers containing the three-component photoinitiator are stable at room temperature for months provided they are stored in the dark. Exposure of these same mixtures to laboratory-level visible light results in polymerization within 16–24 h. When a 2.0 g sample of ERL-4221 with 2.5% OPPI SbF_6^- and 1.5% Irgacure 784 was poured into an aluminum cup and placed in direct sunlight, highly exothermic polymerization took place within 30 sec and resulted in a solid crosslinked casting.

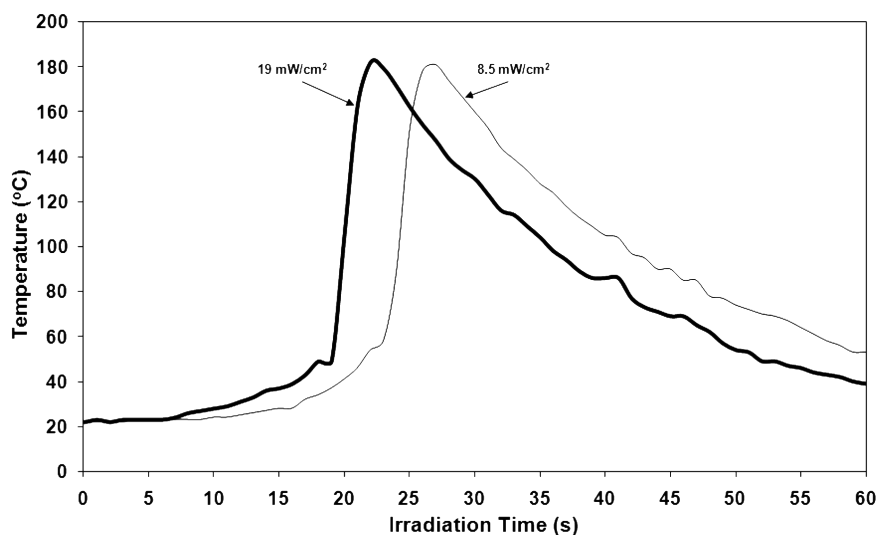


Fig. 10. The effect of the variation in the light intensity on the photopolymerization of ERL-4221 carried out with 20% of MeOBzOH, 2.5% OPPI SbF_6^- and 1.0% Irgacure 784.

4 Conclusions

The visible light induced cationic photopolymerization of epoxide monomers has been investigated using a free radical promoted three-component photoinitiator system. The photoinitiator consists of a titanocene complex that produces free radicals on irradiation with visible light. Subsequently, the primary radical species interact with benzyl alcohols to abstract hydrogen atoms to generate α -hydroxybenzyl radicals. These latter species are further oxidized by diaryliodonium salts bearing non-nucleophilic anions to form the corresponding benzaldehydes with the concomitant formation of strong Brønsted superacids. Catalysis of the ring-opening polymerization of epoxides takes place by attack of the superacids on the monomer. The proposed mechanism is supported by the observation that the polymerization is inhibited by free radical inhibitors and by molecular oxygen. In addition, the observation of the presence of benzaldehyde in the reaction mixture is a direct evidence of the proposed redox reaction between the diaryliodonium salt and benzyl alcohol-derived radical species. Further evidence for the proposed mechanism is provided by the results obtained from a study of substituent effects in the benzyl alcohols. Those substituents that tend to stabilize benzyl radicals and benzyl cations tend to accelerate the photopolymerization of the monomer while at the same time, substituents that destabilize these same intermediates retard the polymerization of the monomer.

The development of a practical visible light photoinitiator system for the rapid photopolymerization of epoxide monomers makes it possible to consider these systems for wide use in many applications. Of most current interest are medical and dental applications in which the use of epoxy resins offers a variety of chemical and mechanical performance advantages along with a very low order of skin, eye and oral toxicity.

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