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A kinetic study of the acceleration effect of substituted benzyl alcohols on the cationic photopolymerization rate of epoxidized natural oils

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Abstract

The rate of the cationic photopolymerization of epoxidized natural oils was enhanced by the addition of several mono, di and trisubstituted benzyl alcohols. The epoxidation of vegetable oils was achieved by using 30% hydrogen peroxide with methyl trioxo rhenium (MTO) as a phase transfer catalyst. Then, the effect of different methoxy-substituted benzyl alcohols on the curing rate was evaluated, using the real-time FT-IR technique. The overall result was an increase in the curing rate. The acceleration effect was explained on the basis of synergistic effects of two mechanisms, namely, the radical induced cationic photopolymerization and the activated monomer mechanism. Epoxidized oils with 2,5-dimethoxybenzyl alcohol as an accelerator exhibited the highest photopolymerization rate. Higher conversions were obtained using electron-transfer photosensitizers.

Keywords: Radical induced cationic photopolymerization; Benzyl alcohols; Real-time infrared spectroscopy

1. Introduction

The preparation of plastic materials based on natural plant oils, has become one of the more promising topics in material science. The triglicerides that constitute plant oils can be transformed into polymerizable monomers by several chemical modifications such as epoxidation, acrylation of epoxides, reaction with maleic anhydride, metathesis of double bonds, or transesterification, just to name a few. Thus, the versatility of the triglicerides has attracted the interest of many scientists in different research laboratories [1–3]. Besides, there are additional features that make plant oil triglicerides very attractive, like their inherent biodegradability and low cost. Another aspect of plant oil derivatives is that by using renewable resources, the world dependence on petroleum derivatives could be reduced in the future.

Epoxidized natural oils can be photopolymerized cationically. Crivello [4,5] studied the parameters that control this process in detail. Additionally, Wool [6] has reported the physical and mechanical properties obtained of composites derived from photocured epoxidized oils. Moreover, Soucek [7] and collaborators have focused their attention on the cationic photopolymerization of natural oils bearing epoxidized norbornylene groups.

It has been demonstrated by several investigators [8–10] that the curing rate of cycloaliphatic epoxides and vinyl ethers can be accelerated by means of the so-called radical induced cationic photopolymerization mechanism. In this mechanism, a source of radicals must be present in the cationic curable system. The radicals can be generated either from added radical-initiators like aromatic ketones and peroxide derivatives, or from monomers with labile hydrogen atoms.

For instance, in an earlier work [11] we reported the

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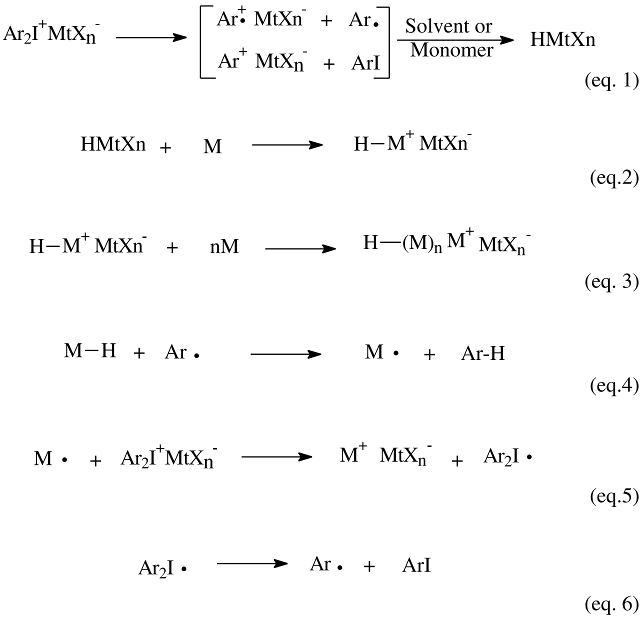
synthesis of cycloaliphatic epoxide monomers bearing substituted benzyl ether groups. These monomers exhibited elevated rates of photopolymerization. It was proposed that this rapid photopolymerization proceeded by two separate and distinct mechanisms. The first mechanism involved a conventional cationic polymerization catalyzed by the photogenerated Brønsted acid. A second, more complex redox mechanism also appeared to be taking place, in which aryl radicals derived from the photolysis of the photoinitiators abstract the labile benzylic hydrogen atoms of the monomer forming monomer-bound cations by a chain reaction mechanism. Details of these two proposed mechanisms are presented in Scheme 1.

The photolysis of a diaryliodonium salt leads to the formation of cations, radical and radical-cationic species. Thereafter, the cationic species interact with the monomer or impurities in the reaction mixture to generate a protonic acid corresponding to the anion of the diaryliodonium salt (Eq. (1)). The protonic acid is the primary species that initiates polymerization (Eq. (2)). In Scheme 1, polymerization (Eq. (3)) takes place via a dark, that is, a non-photochemical process. Usually, the radical products of the photolysis of a diaryliodonium salt do not participate in the cationic polymerization. However, when monomers bearing functional groups such as allyl, propargyl or benzyl ethers are present, these radicals can abstract the labile hydrogen atoms present in these groups to generate the corresponding carbon-centered resonance-stabilized free radicals (Eq. (4)). The subsequent redox interaction of these secondary radical species with the diaryliodonium salt results in the oxidation of the initially formed radical to the corresponding resonance stabilized cation with the reduction of the diaryliodonium salt to give a diaryliodine free radical (Eq. (5)). This radical is unstable and undergoes rapid decomposition to yield an aryliodide together with the regeneration of the aryl radical (Eq. (6)). The overall process can be viewed as a chain reaction in which during every cycle additional cationic species, $R^+ MtX_n^-$, are produced by the free radical induced decomposition of the photoinitiator. The cations generated by this chain reaction can initiate polymerization of the monomer. Thus, the mechanism can be characterized as a photoamplification process that results in the observed acceleration of the photopolymerization rate of the monomer through the generation of active cationic species through a ‘dark’ reaction.



$$Ar_2I^+MtX_n^- \longrightarrow \left[\begin{array}{l} Ar^{+\bullet}\,MtXn^- + Ar^{\bullet} \\ Ar^+\,MtX_n^- + ArI \end{array}\right] \xrightarrow[\text{Monomer}]{\text{Solvent or}} HMtXn \qquad \text{(eq. 1)}$$

$$HMtXn + M \longrightarrow H{-}M^+\,MtXn^- \qquad \text{(eq.2)}$$

$$H{-}M^+\,MtXn^- + nM \longrightarrow H{-}(M)_n\,M^+\,MtX_n^- \qquad \text{(eq. 3)}$$

$$M{-}H + Ar^{\bullet} \longrightarrow M^{\bullet} + Ar{-}H \qquad \text{(eq.4)}$$

$$M^{\bullet} + Ar_2I^+MtX_n^- \longrightarrow M^+\,MtX_n^- + Ar_2I^{\bullet} \qquad \text{(eq.5)}$$

$$Ar_2I^{\bullet} \longrightarrow Ar^{\bullet} + ArI \qquad \text{(eq. 6)}$$

Scheme 1.

In this study, four different vegetable oils were epoxidized and their performance as cationic photopolymerizable monomers was evaluated. The aim of this research was to improve the photopolymerization rate of epoxidized oils by means of the radical induced cationic photopolymerization mechanism. Here, the concept was to add the benzyl alcohols as additives. The alcohol group can react with the oxirane group of epoxidized oils by an acid-catalyzed addition reaction, fixing the benzyl moiety to the trigliceride. The produced benzyl ether can interact with the onium salt used as photoinitiator to generate benzyl cations in a similar fashion as in Eq. (5) of Scheme 1. The effect of different mono, di and trisusbstituted benzylic alcohols with methoxy groups, as accelerators of photopolymerization was evaluated by means of real time-FTIR.

2. Experimental section

2.1. Materials

Soybean, sunflower, corn and linseed oils were purchased in a local supermarket. These oils were epoxidized using the method reported by Marks and Larock [12]. All the rest of the organic starting materials and reagents were reagent-quality and were purchased from Aldrich Chemical Co and used as received. The onium salt cationic photoinitiators, (4-*n*-decyloxyphenyl) diphenyl sulfonium hexafluoroantimonate (DPDPS), and (4-*n*-decyloxyphenyl) phenyliodonium (DPPI) hexafluoroantimonate were prepared as described by Crivello [13,14]. ^{1}H and ^{13}C NMR spectra were obtained with a 200 MHz Varian Gemini 2000 spectrometer, at room temperature. Routine infrared spectra and photopolymerization kinetics were performed on a Magna Nicolet 550.

2.2. Studies of the rates of photoinitiated ring-opening cationic epoxide polymerization by Fourier transform real-time infrared spectroscopy (FT-RTIR)

The kinetics of the cationic photopolymerizations of the monomers synthesized during this investigation were monitored with FT-RTIR. A Nicolet Magna 550 Fourier transform infrared spectrometer equipped with a DTGS detector was fitted with a UVEXS model SCU 110 mercury lamp in which the light was carried through a flexible wand to the sample compartment. The end of the wand was placed at a predetermined distance and directed at an incident angle of 45° onto the sample window. The intensity of the UV irradiation was measured with a UV Process Supply Inc. Control cure radiometer. All kinetics experiments in this investigation were conducted at 25 °C with various light intensities.

Samples for kinetics analysis were prepared as follows. A homogeneous solution of the desired monomer with 1% mol of the designated photoinitiator and a determined amount of the accelerator was prepared (all concentrations are given as molar percentages with respect to the monomer, unless otherwise noted). The solutions were spread as thin films between two layers of 12 microns corona-treated oriented polypropylene films and then fixed to the metallic sample holder by means of magnetic strips. The course of the photopolymerization was followed by simultaneously monitoring both the decrease in the infrared absorption band at 830 cm^{-1} due to the epoxy group of the epoxidized oils and the increase of the band at 1160 cm^{-1} due to the polyether formed. Each kinetic run was carried out a minimum of five times. The resulting data were averaged and the conversion versus irradiation time curves is presented. The kinetic parameter, $R_p/[M_o]$, for selected kinetic runs was determined from the initial slopes of the irradiation time-conversion curves according to Eq. (8).

$$R_p/[M_o] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1})/(t_2 - t_1)$$

where R_p and $[M_o]$ are, respectively, the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times t_1 and t_2.

Data were collected at a rate of one spectrum per second. Data processing was performed with the OMNIC Series software.

3. Results and discussion

In a previous paper, [15] it was found that by using certain mono and disubstituted benzyl alcohols, the photopolymerization rate of monomers like 4-vinyl cyclohexene dioxide, limonene, and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexancarboxylate, can be accelerated. In this report we decided to further extend this research, using disubstituted and trisubstituted benzyl alcohols in monomers such as the epoxidized oils, where the effect of acceleration can be appreciated more clearly than in the aforementioned monomers that are very reactive inherently due to ring strain. In Table 1 are outlined the chemical structures of accelerators used in this study.

The epoxidation of the natural oils was carried out by the method reported by Marks and Larock (see reference in Section 2). This method is simple and effective. The oil is dissolved in chloroform and then 30% hydrogen peroxide is added dropwise. Methyl trioxo rhenium (MTO) was used as a phase transfer catalyst. The neutral to basic reaction conditions, eliminates the acid-catalyzed ring opening side reactions, which are normally a problem in epoxidation reactions. After the work up, neither the NMR nor the IR spectra showed signals for double bonds. We determined the oxirane content by the ASTM technique D 1652-97. The results are depicted in Table 2. Due to the larger level of initial unsaturation, the linseed oil has a higher value of oxirane content. The other oils have slightly lower values.

Fig. 1 shows a comparison of the kinetic curves of the photopolymerization of the four epoxidized oils when they are subjected to UV irradiation, using DPPI as the photoinitiator at 1% mol. It was found that the photopolymerization rate was rather low with conversions around 25%. This is an expected result if we consider that open chain epoxides are not as reactive as the cycloaliphatic epoxides. All of the four epoxidized oils showed the same trend with the linseed oil having the higher conversion (25%). This result agrees with that reported by Mathur [16], and Crivello [5], as they found as well, that the cationic cure rate of epoxidized oils is slow.

Fig. 2 shows a comparison of the rate of photopolymerization of epoxidized linseed oil with different monosubstituted benzyl alcohols. A curve in which no benzyl alcohol was used is included as baseline. It can be seen that the curves display three different stages. In the first one, the photopolymerization proceeds very slowly in the first 40 seconds, and its almost the same for all the cases; then there is a second stage where the polymerization rate increases, the increase depending on the accelerator used. In the third stage, the conversion levels off. It is very likely that in the first stage, some traces of basic impurities present retard the propagation process, and when there is enough acid generated, these impurities are neutralized and the epoxide ring-opening polymerization proceeds freely. In addition, during this period the attack of the benzyl alcohol onto the epoxide ring occurs. The nucleophilicity of the alcohol groups play an important role in this stage. Steric and

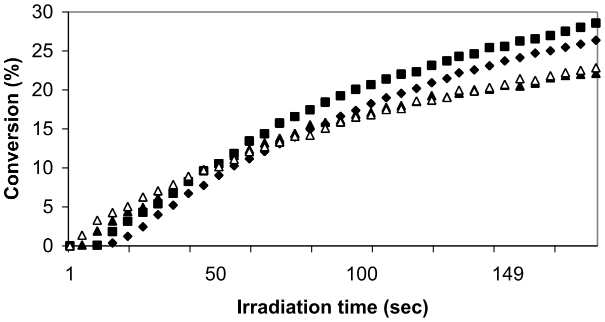
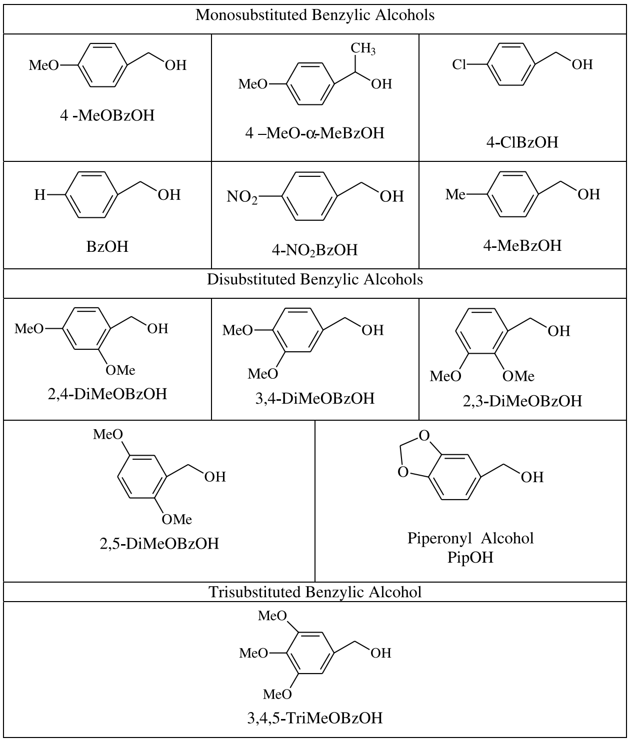


Fig. 1. Comparison of the cationic photopolymerization of vegetable epoxidized oils; corn (♦); soybean (▲); linseed (■); sunflower (△), (photoinitiator, 1.0% DPPI; light intensity 9.8 mW/cm^2).

Table 1
Chemical structures of compounds used as accelerators and photoinitiators of cationic photopolymerization of epoxidized oils



electronic effects induced by the substituents in the aromatic ring must control the rate of the addition of the benzyl alcohols to the epoxide group. Once attached, the benzyl alcohol can participate in another series of reactions where the transfer of protons between the chain-end generated oxonium and the epoxide group of monomer is involved. Penczek and Kubisa [17,18] have shown that in the presence of alcohols, the polymerization rate of epoxide monomers can undergo an acceleration effect. They have proposed an 'activated monomer mechanism'. According to this mechanism, there is a rapid exchange of proton when the oxonium propagating end reacts with an added alcohol (see Scheme 2). Then, there is a subsequent proton transfer from the growing chain to the monomer that thereafter can start new chains. As the terminal group is a hydroxyl group, the process continues until all monomer is consumed. Although this mechanism occurs to some extent during a normal ring opening polymerization due to the formation of terminal hydroxyl groups, the transfer of a proton is faster in Eq. (7) than in the propagation step described in Eq. (3) of Scheme 1. The resultant effect is an acceleration of the cationic curing rate.

Once the benzyl ether is incorporated into the chain, the labile benzyl hydrogen atoms can be abstracted by the photogenerated aryl radicals producing new benzyl radicals (see Scheme 3). These radicals can be oxidized by the onium salt to the corresponding benzyl cations (Eq. (10)). The regeneration of aryl radicals by the irreversible decomposition of diaryl iodine free radical constitutes a chain reaction that generates a large number of carbenium ions accelerating the consumption of the monomer. Thus,

Table 2
Oxirane oxygen content % of different epoxidized oils used in this study

Epoxidized oil	Oxirane oxygen content (%)
Soybean	7.0
Linseed	9.2
Sunflower	6.3
Corn	6.1

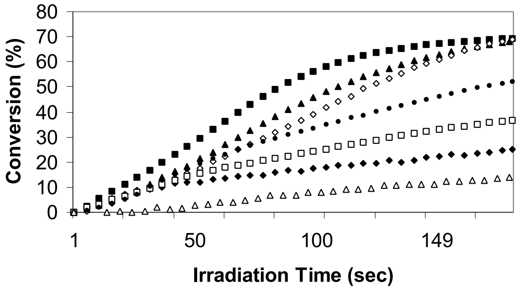
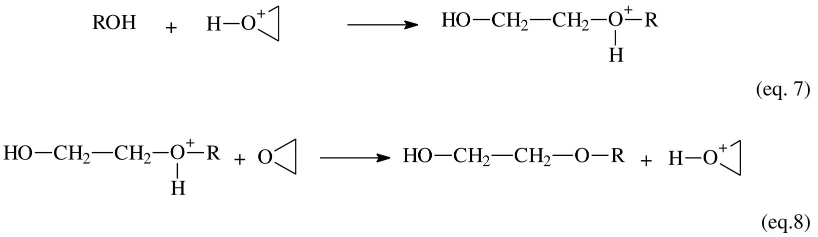


Fig. 2. Comparison of the effects of 20% various monosubstituted benzyl alcohols on the cationic ring-opening photopolymerization of epoxidized linseed oil, 4-MeOBzOH (■); 4-MeO-α-MeBzOH (▲); 4-MeBzOH (◇); 4-ClBzOH (□), 4-NO$_2$BzOH (△); BzOH (●); No BzOH (◆); (photoinitiator, 1.0% DPPI; light intensity 9.8 mW/cm^2).



Scheme 2.

combination of both mechanisms results in an evident acceleration effect of the photopolymerization rate of the epoxidized oil.

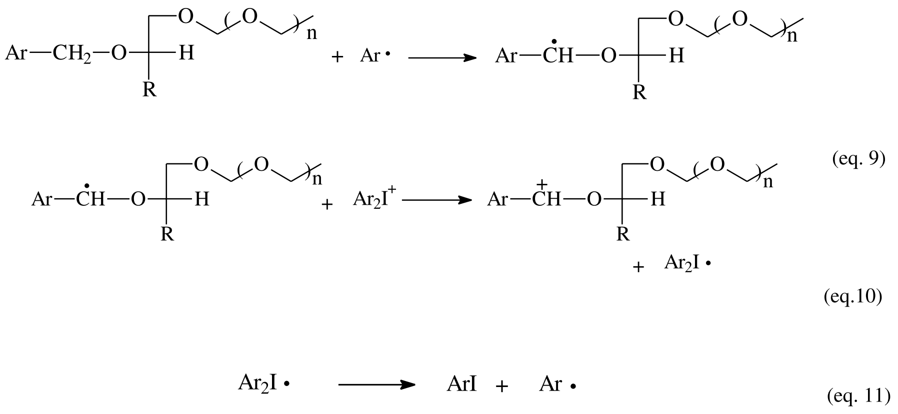
The second stage is affected by the nature of the substituent in the benzyl alcohol used as accelerator, increasing the polymerization rate with increasing activation of the aromatic ring with stronger electron donating substituents. The 4-MeOBzOH exhibited the highest polymerization rates, followed by 4-MeO-α-MeBzOH. Although in theory, the alcohol with α-methyl group would be more reactive because of the ease of abstraction of the tertiary hydrogen atoms, the hydroxyl group is sterically hindered and undergoes slower reaction with the initiating and propagating oxonium ions. 4-MeBzOH, BzOH, and 4-ClBzOH displayed the same polymerization rate in the first stage, but in the second stage the parameter $R_p/[M_0]$ were, respectively, 4.763×10^{-3}, 2.631×10^{-3} and $1.906\times10^{-3}\ \mathrm{s}^{-1}$. These values were determined from the slopes of the linear portions of the second stage in the irradiation time/conversion curves. The conversions obtained were augmented in the same order. It was also found that compared to benzyl alcohol, 4-nitrobenzyl alcohol induced a very sluggish photopolymerization rate even lower than the case where no benzyl alcohols were used.

In the third stage the rate of photopolymerization levels off as the monomer is consumed. The highly crosslinked matrix reduces the mobility as the gel point is reached. It can be deduced from the conversion level (around 60%) that the trapping of propagating cations is important.

The rate acceleration effects can be explained on the basis of the well-known relative abilities of substituents to stabilize both benzylic free radicals and benzyl carbocations. These reactive intermediates are generated by a series of reactions between the monomer and the photoinitiator as shown in Scheme 3. Hehre et al. [19] reported that the electron-donating *p*-methoxy group can stabilize the benzyl carbocation by 14 kcal/mol, while electron-withdrawing groups such as *p*-cyano and *p*-nitro groups are destabilizing, respectively, by 12 and 20 kcal/mol. In the case of the 4-ClBzOH, the $-I$ effect of chlorine is withdrawing sufficient electron density from the ring to deactivate it in comparison to BzOH.

Fig. 3 shows a comparison of the photopolymerization rates of epoxidized sunflower oil with 3,4,5-TriMeOBzOH and five different disubstituted benzyl alcohols including piperonyl alcohol (PipOH). It was observed that most of the dialkoxysubstituted benzyl alcohols included the PipOH displayed similar reactivities. There is a remarkable increase in the photopolymerization rate, when compared with the blank with no benzyl alcohol. Both 2,5-DiMeOBzOH and 3,4,5-TriMeOBzOH exhibited the highest acceleration effect on this epoxidized oil.

Again, we can explain these results on the basis of electronic effects induced by the position of the substituents in the aromatic ring of the benzyl alcohol. It has been recognized in the literature [20,21], that aromatic excited states are likely to exhibit reactivity different from that of corresponding ground states. Zimmerman et al. [22] studied the substituent effects in the photosolvolysis of benzyl



Scheme 3.

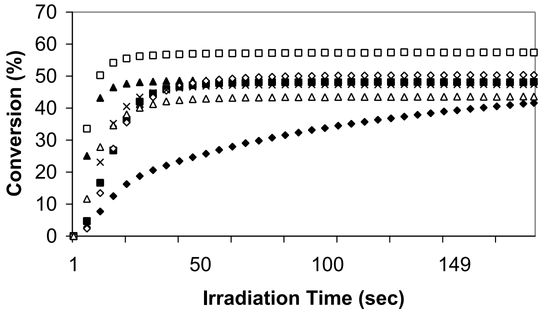


Fig. 3. Comparison of the effects of 20% various disubstituted benzyl alcohols on the cationic ring-opening photopolymerization of epoxidized sunflower oil, blank (◆) 2,3-DiMeOBzOH (◇); 2,4-DiMeOBzOH (■); 2,5-DiMeOBzOH (□); 3,4-DiMeOBzOH (×); PipOH (△); 3,4,5-TriMeOBzOH (▲); (photoinitiator, 1.0% DPPI; light intensity 11.1 mW/cm^2).

acetates. They found that in the photoreaction, the methoxy group in the *meta* position was strongly rate enhancing. This is in contrast with the ground state behavior. In the ground state the expected increased π-electron density was found at the *ortho* and *para* positions relative to an electron-donating substituent, while in the first excited state, selective electron transmission to the *ortho* and *meta* positions was noticed. The increased electron density at these sites helps to stabilize the positive charge of the benzyl cation intermediate. Thus, in the case of the 2,5-DiMeOBzOH the stronger activation in the *meta* and *ortho* positions of the aromatic ring results in a better stabilization of benzyl cation. The other alcohols like 2,3-DiMeOBzOH, 3,4-DiMeOBzOH and PipOH also have methoxy groups in the *meta* position. Nonetheless, the 2,4-DiMeOBzOH displayed a comparable behavior than the other alcohols meaning that the presence of both methoxy groups increases the electronic density almost to the same degree and hence, the reactivities are rather similar. The introduction of a third methoxy group results in slight increase of photopolymerization rate although comparable to the rate obtained with 2,5-DiMeOBzOH.

Fig. 4 shows a comparison of the different accelerators under the same conditions, using epoxidized sunflower oil as monomer. It was observed that going from BzOH to dimethoxybenzyl alcohols there is a progressive increase in the photopolymerization rate while the 3,4,5-TriMeOBzOH showed a similar reactivity than 3,4-DiMeOBzOH. The 2,5-DiMeOBzOH displayed the highest photopolymerization rate in these experiments.

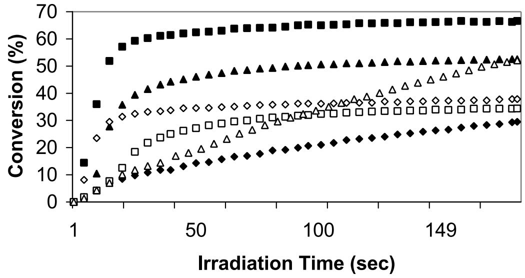


Fig. 4. RT-IR comparative study of the cationic photopolymerization of epoxidized sunflower oil with 20% of various accelerators, no BzOH (◆); BzOH (△); 4-MeOBzOH (□); 3,4-DiMeOBzOH (◇), 2,5-DiMeOBzOH (■), 3,4,5-TriMeOBzOH (▲); (photoinitiator, 1.0% DPPI; light intensity 9.8 mW/cm^2).

Accordingly, a study of the effect of the concentration of 2,5-DiMeOBzOH on the polymerization of epoxidized soybean oil was undertaken. The results are presented in Table 3. It can be seen that when 5% mol of 2,5-DiMeOBzOH is added to the epoxidized oil, there is an almost 3-fold increase in the photopolymerization rate. The effect is maximized at 20% of the alcohol. Increasing the concentration of the accelerator to 40% mol resulted in a decrease of the polymerization rate in comparison with the case of 20% mol. No attempts were made to optimize the concentration of the accelerator.

In order to improve the photo curing efficiency of epoxidized oils further it was decided to use photosensitizers. Its well known that by using photosensitizers [23–25], the absorption of UV light can be optimized resulting in a more efficient photolysis of the photoinitiators with the consequent increase in the number of initiating species. The overall effect is an apparent acceleration of the rate of polymerization of the monomer as compared to when no photosensitizer is used. These photosensitizers are believed to act through an electron transfer mechanism. A generalized mechanism proposed for the electron photosensitization of diaryliodonium salts is shown in Scheme 4. The photosensitizer absorbs light to give the corresponding excited species [PS]* (Eq. (9)) an excited state complex (exciplex) is formed as an intermediate between the onium salt and the excited photosensitizer (Eq. (10)). Then, the onium salt is reduced by a formal electron-transfer from the photosensitizer (Eq. (11)). The rapid decomposition of the resulting unstable diaryliodine free radical (12) prevents back electron-transfer and renders the overall process irreversible.

This photosensitization effect can be observed in Fig. 5 when the epoxidized corn oil was photopolymerized in the presence of 20% mol of 2,5-DiMeOBzOH with and without photosensitizers. The effect of perylene, anthracene and benzophenone was evaluated. There was no significant increase in the photopolymerization rate with these additives and the rate is already high when only the 2,5-

Table 3
Effect of the concentration of 2,5-DiMeOBzOH on the photopolymerization rate of epoxidized soybean oil

Concentration of 2,5-DiMeOBzOH	$R_p/[M_o]$ (10^{-2} s^{-1})	Acceleration factor
No alcohol	0.1821	–
5% alcohol	0.5013	2.75
10% alcohol	0.7189	3.94
20% alcohol	1.476	8.10
40% alcohol	0.929	5.10

$$[PS] \xrightarrow{h\nu} [PS]^{*} \qquad \text{(eq. 12)}$$

$$[PS]^{*} + Ar_2I^{+}MtX_n^{-} \longrightarrow [PS \cdots Ar_2I^{+}MtX_n^{-}]^{*} \qquad \text{(eq.13)}$$

$$[PS \cdots Ar_2I^{+}MtX_n^{-}]^{*} \longrightarrow [PS]^{\bullet+}\, MtX_n^{-} + Ar_2I^{\bullet} \qquad \text{(eq.14)}$$

$$Ar_2I^{\bullet} \longrightarrow ArI + Ar^{\bullet} \qquad \text{(eq.15)}$$

Scheme 4.

DiMeOBzOH is used. However, it was observed that the combined effect of the accelerator and the photosensitizers resulted in higher conversions, 96% for perylene and 94% for benzophenone. The less soluble anthracene had conversions of 85% while in the absence of the sensitizer the conversion was 55%.

4. Conclusions

The addition of substituted benzyl alcohols to epoxidized natural oils results in the acceleration of the rate of the onium salt-induced cationic photopolymerization. This effect can be ascribed to combined effect of two synergistic mechanisms. On one hand, we have a photoinitiated free-radical chain reaction that results in the generation of a large number of cationic species capable of initiating the ring opening polymerization of epoxides and on the other, we have the activated monomer mechanism, in which added alcohols promote the rapid transfer from protonated oxonium species to the monomer, speeding up the entire propagation process. We have found that 2,5-DiMeOBzOH displayed the higher polymerization rate when used at 20% mol concentration. Further enhancement of the cationic curing rate was achieved by using photosensitizers such as perylene and benzophenone. With this method, we have succeeded in increasing the rate and conversion of cationic photopolymerization of epoxidized oils. This strategy may be of interest for high speed coating and printing ink applications where epoxidized oils have found applications.

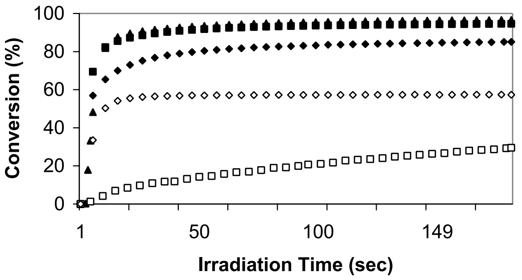


Fig. 5. Effect of photosensitizers on the photopolymerization of epoxidized corn oil in the presence of 20% 2,5-DiMeOBzOH, no photosensitizer (◇), perylene (■), anthracene (◆); benzophenone (▲); blank with no alcohol (□) (photoinitiator, 1.0% DPPI; light intensity 9.8 mW/cm^2).

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