

UV-Ignited Frontal Polymerization of an Epoxy Resin

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ABSTRACT: By combining frontal polymerization and radical-induced cationic polymerization, it was possible to cure thick samples of an epoxy monomer bleached by UV light. The effect of the relative amounts of cationic photoinitiator and radical initiator was thoroughly investigated and was related to the front's velocity and its maximum temperature. The materials obtained were characterized by quantitative conversion also in the deeper layers, not reached by UV light. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 2066–2072, 2004

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INTRODUCTION

UV-induced cationic photopolymerization of epoxy monomers is a well known process and one of great interest as a result of its significant number of industrial applications.^{1,2} The formulations are solvent-free; the production rates are high; and the energy required is much less than that required for thermal curing.

These advantages have led to the rapid growth of the technique in different fields, mainly in the production of films, inks, and coatings of a variety of substrates, including paper, metal, and wood. Moreover, a number of high-technology and electronic applications, such as the coating of optical fibers and fabrication of printed circuit boards, have been developed.³

Strong Lewis acid, often derived by the dissociation of a iodonium salt, is used as the initiator,

and this latter reaction is generally promoted by UV irradiation.^{4–6} However, the resulting photopolymerization is applicable only to thin materials. Indeed, because of the light-intensity gradient, this technique fails when thick parts have to be cured.

Nevertheless, photocuring has recently found applications in the production of thick polymers and composites.^{7,8} To effectively cure a thick section, the initiator system and wavelength must be carefully selected to ensure that light can effectively penetrate the sample. The initiator-rate profile resembles a wave front, and the depth of this front is determined by factors such as initiator concentration and molar absorptivity.^{9,10} It is desirable to have a low initiator concentration and to use photobleaching initiators, allowing more light to pass through the system to achieve thick-section curing.¹¹

In our work we aimed to overcome the important drawback of thick-section photopolymerization, by joining this to the so-called radical-induced cationic polymerization (RICP) and to frontal polymerization (FP).

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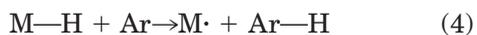
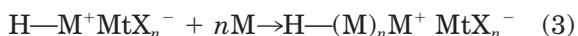
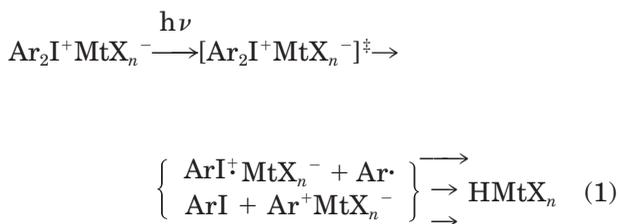
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In RICP experiments, a iodonium salt is dissociated by reaction with radicals instead of light irradiation. The mechanism involves the initial photoexcitation of the onium salt and then the decay of the resulting excited singlet state with both heterolytic and homolytic cleavages of the C–I or C–S bonds. Thus, free-radical, cation, and cation-radical fragments are simultaneously formed. The cationic species interact with a proton source, usually the monomer (M), to generate the strong Brønsted acid HMtX_n .

Initiation of polymerization takes place by protonation of the monomer (eq 2), and this is followed by the addition of other monomer molecules, thus resulting in chain growth (eq 3). The aryl radicals interact with monomers via the pathways shown in eq 4 by abstracting a hydrogen atom. In these reactions, secondary radical species are generated.

Redox interaction of these radical species with the diaryliodonium salts gives rise to carbocations and to an unstable diaryliodine radical (eq 5). In a subsequent reaction (eq 6), the diaryliodine radical decays irreversibly to generate an aryl iodide and an aryl-free radical.

The reactions shown in eqs 1–6 constitute a free-radical chain reaction in which the diaryliodonium salt photoinitiator is consumed by a nonphotochemical process. Also, carbocations are generated that ultimately initiate cationic polymerization:



From eqs 2–6, it may be concluded that the photochemically induced decomposition of the diaryliodonium salt photoinitiator can be greatly amplified by the redox cycle of eqs 1–6. This results in the very rapid and efficient generation of a large number of initiating cationic species by a nonphotochemical process,^{12,13} thus consuming the monomer in the deeper layers. This mechanism has been widely reported and discussed in the literature.^{14–19}

In principle, any photochemical source of free radicals can be used to start the aforementioned chain of reactions. It follows that radicals can be obtained also by heating a common radical initiator.

Alternatively, here we propose the use of FP as a way of generating the aforementioned radicals that produce cationic species that polymerize the epoxy monomer in the thicker parts of the sample where the light is not able to penetrate.

FP exploits heat production because of exothermicity of the polymerization reaction itself and its dispersion by thermal conduction. If the amount of dissipated heat is not too great, then a sufficient quantity of energy able to induce the polymerization of the monomer close to the hot zone is provided. The result is the formation of a hot polymerization front capable of self-sustaining and propagating throughout the reactor.^{20–36}

The first studies on FP were performed in the former Union of Soviet Socialist Republics on methyl methacrylate that was polymerized under drastic pressure conditions (>3000 atm).^{20,21} Several other vinyl monomers have been polymerized at ambient pressure by Pojman and coworkers.^{22–25} Also, epoxy monomers have been frontally polymerized by reaction with a stoichiometric amount of a curing agent by stepwise-growth kinetics.^{26–29}

In recent years, our group has started the investigation on this matter, paying particular attention to the possibility of finding new chemical systems that are able to bring about FP, such as polyurethanes,^{30,31} unsaturated polyester resins,^{32,33} polydicyclopentadiene,³⁴ and its interpenetrating polymer networks with polyacrylates.³⁵

As can be evinced by the references previously cited, a significant portion of FP literature has reported that the heat released during radical polymerizations induces the dissociation of initi-

ators that start new growing chains, thus allowing the traveling polymerization front to be self-sustaining.

In an analogous way, in this work we took advantage of the heat released during the polymerization of an epoxy monomer for promoting the dissociation of a radical initiator active in the subsequent RICP process that permits FP to occur. In such a way, the aforementioned limit of photopolymerization in the curing of thick materials has been overcome.

EXPERIMENTAL

Materials

3,4-Epoxy cyclohexylmethyl-3',4'-epoxy cyclohexanecarboxylate (CE) was purchased from Dow, dibenzoyl peroxide (BPO) from Fluka, and {4-[(2-hydroxytetradecyl)oxy]phenyl}phenyliodonium hexafluoroantimonate (HOPH) from Aldrich. All reagents were used as received.

UV-Ignited FP

All FP trials were carried out by dissolving various amounts of HOPH and BPO in CE (see Results and Discussion). The resulting mixtures were placed in glass tubes (16 mm i.d.), and the reactions were ignited by UV radiations (wavelength: 350 nm) produced by a UV generator EL 2000 instrument purchased from El-tra srl. The optical fiber cable was placed at about 1 cm from the surface of the solution and held in position until a hot propagating front started. The temperature profiles of each run were monitored with a K-type thermocouple, the junction of which was placed at about 1.5 cm from the bottom of the glass tube. The thermocouple was connected to a digital thermometer used for the reading and recording of temperature. The position of the front (± 0.5 mm) against time was also measured.

Polymer Characterization

Differential scanning calorimetry (DSC) was performed with a Mettler DSC 30 instrument in the range from 0 to 200 °C, with a heating rate of 20 °C/min. For each sample, two thermal scans were collected.

The gel content was determined by measuring the weight decrease after extraction with CHCl_3 for 24 h.

Table 1. Preliminary UV-Ignited FP Experiments

	BPO	HOPH	Results
First blank	No	No	No polymerization
Second blank	Yes	No	No polymerization
Third blank	No	Yes	Does not sustain front
Fourth blank	Yes	Yes	FP

The aforementioned analyses were performed on materials taken at about 4 cm from the bleached surface of the sample.

RESULTS AND DISCUSSION

In a first set of experiments, it was found that both the cationic photoinitiator and the thermal radical initiator were simultaneously necessary to obtain UV-ignited FP (see Table 1). First, even in the presence of relatively large amounts of BPO (up to 5 mol %), no polymerization was observed in the absence of HOPH. Second, only surface photopolymerization was noticed in the absence of BPO (for $0 \leq [\text{HOPH}] \leq 5$ mol %).

In a second set of experiments, the effect of the concentration of the two initiators was explored. First, the runs were performed with variation of the relative concentrations of the two compounds while their molar ratio was kept constant at $[\text{BPO}]/[\text{HOPH}] = 1.0$ mol/mol, that is, the minimum amount of BPO needed for FP to be self-sustaining.

Subsequently, the BPO concentration was varied in relation to a constant $[\text{HOPH}]/[\text{CE}]$ molar ratio ($= 1.0$ mol %). The BPO concentration was allowed to range from 0.67 to 3.0 mol %. Below 0.67 mol % FP did not self-sustain, whereas for amounts of initiator above 3.0 mol % no significant changes in front velocity (V_f) and its maximum temperature (T_{max}) were observed.

Figures 1 and 2 display the effect of the concentration of HOPH on V_f and T_{max} , respectively, at $[\text{HOPH}]/[\text{BPO}] = 1.0$ mol/mol.

In the considered range ($1.0 \leq [\text{HOPH}]/[\text{CE}] \leq 3.0$ mol %), V_f values were between 3.2 and 5.0 cm/min, corresponding to an increase of $[\text{HOPH}]/[\text{CE}]$ from 1 to 2 mol %, followed by a V_f decrease. T_{max} behaved in a similar way, increasing in the range of photoinitiator between 1 and 1.35 mol % (from 250 to 256 °C) and then decreasing to 232 °C at $[\text{HOPH}]/[\text{CE}] = 3.0$ mol %.

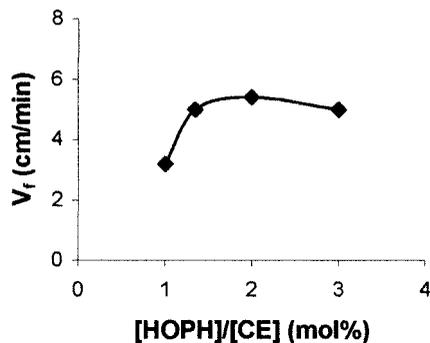


Figure 1. V_f as a function of the [HOPH]/[CE] molar ratio.

Figures 3 and 4 show the trends of V_f and T_{max} as functions of the BPO concentration when the [HOPH]/[CE] ratio was kept constant and equal to 1.0 mol %. In this case, V_f and T_{max} behaved differently. V_f exhibited a sharp increase from 1 to 6 cm/min when the [BPO]/[CE] ratio was raised from 0.5 to 3.0 mol %. In the same concentration range, T_{max} decreased from 297 °C to a plateau value placed at about 250 °C.

We investigated thermal properties to compare polymers obtained through FP, with the RICP method, with those prepared by usual cationic photopolymerization, that is, in the absence of radical initiators. DSC measurements were used to check whether the polymerization process was complete.

For the polymer samples obtained in the presence of both the cationic photoinitiator and the thermal radical initiator, only a weak exothermal signal relating to the occurrence of a residual thermal polymerization was evident (Fig. 5).

The hexothermal response completely disappeared when a second thermal scan was per-

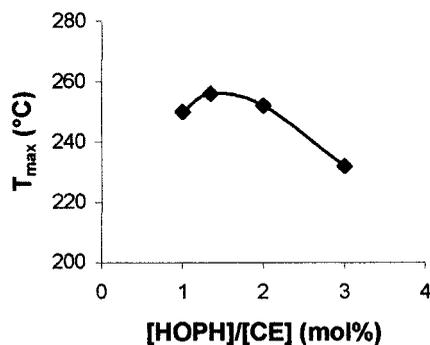


Figure 2. T_{max} as a function of the [HOPH]/[CE] molar ratio.

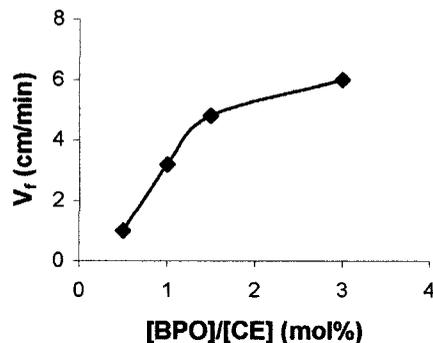


Figure 3. V_f as a function of the [BPO]/[CE] molar ratio.

formed on the same sample, and a glass-transition temperature became clearly evident around 100 °C (Fig. 6).

On the contrary, the DSC thermogram (Fig. 7) of the polymer sample obtained only in the presence of HOPH (by the traditional batch cationic photopolymerization method) exhibited a large exothermal peak having a maximum located at about 160 °C, attributable to the large amount of residual polymerization heat. By heating, an increase of network mobility was induced, and the residual acid was able to polymerize the unreacted epoxy groups trapped in the glassy polymer. This peak also disappeared when a second thermal scan was carried out on the same sample.

These data showed that in the presence of HOPH only, low conversion is obtained because while the surface is well cured, in the bulk only small amounts of epoxy groups are reached by UV light. The BPO presence allowed obtained polymers to have a higher conversion degree because of the occurrence of RICP, which enables the production of cationic species also in the deeper layers where light is not able to effectively penetrate.

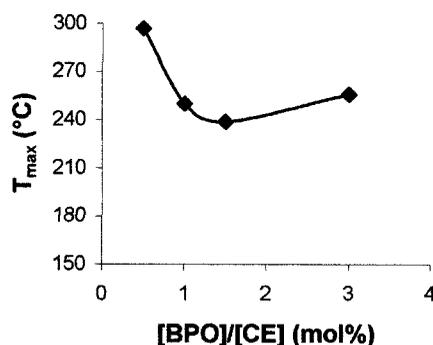


Figure 4. T_{max} as a function of the [BPO]/[CE] molar ratio.

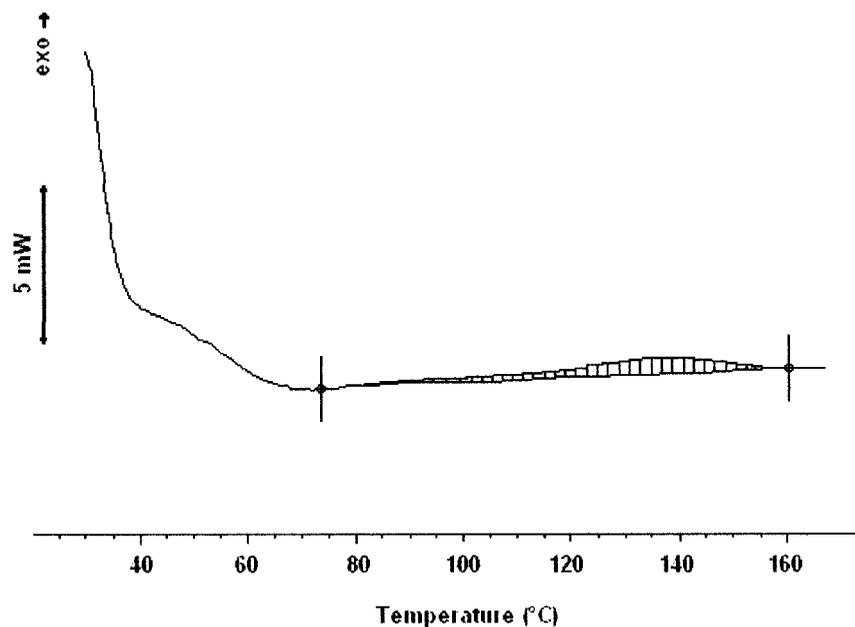


Figure 5. DSC thermogram of the photocured polymer in the presence of BPO and HOPH; first scan (sample F1: $[\text{HOPH}]/[\text{CE}] = 1.0$ mol %; $[\text{HOPH}] = [\text{BPO}]$).

To confirm the DSC data, gel-fraction extraction was performed. The gel content of the polymer obtained in the presence of HOPH only was 65%, whereas in the presence of HOPH and BPO, a result of 98% was reached.

CONCLUSIONS

By combining the FP technique with the UV-curing process, it was possible to overcome the limit of photopolymerization in the cur-

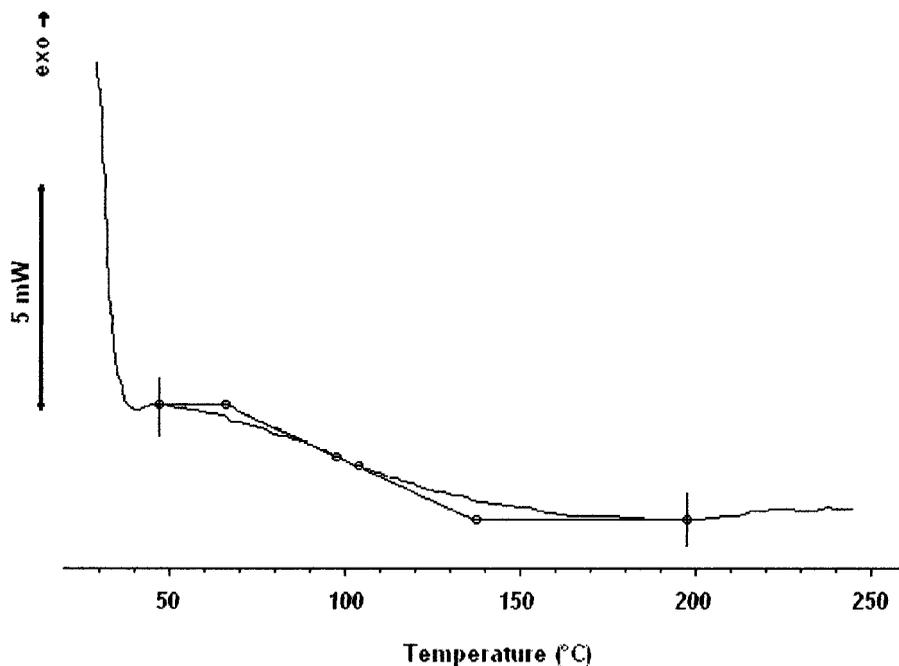


Figure 6. DSC thermogram of the photocured polymer in the presence of BPO and HOPH; second scan (sample F1).

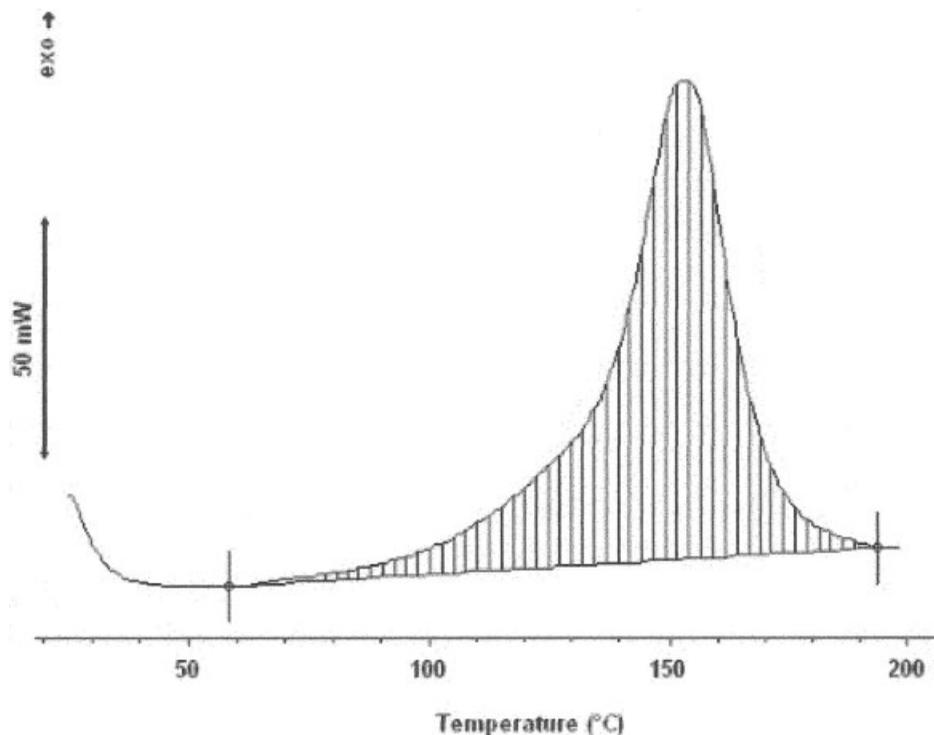


Figure 7. DSC thermogram of the photocured polymer obtained only in the presence of HOPH (sample B1: [HOPH]/[CE] = 1.0 mol %).

ing of thick materials, namely, epoxy monomers.

FP starts by the dissociation of a radical initiator promoted by the heat released during surface UV-induced polymerization. The carbon-centered radicals obtained are subsequently oxidized to carbocation by a iodonium salt photoinitiator. The carbocation formed is able to induce cationic polymerization of the thicker layers of the epoxy material.

A proper photoinitiator (HOPH)-radical initiator (BPO) ratio has been defined to obtain a self-sustaining polymerization front. The effect of the presence of a radical initiator was evidenced by DSC analysis, which showed that in the absence of BPO, low epoxy conversion is reached. On the contrary, in the presence of BPO a higher (almost quantitative) epoxy conversion is attained, as confirmed by DSC and the gel content.

This result opens the possibility of using the photopolymerization technique in a much larger number of applications.

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