Synthesis of an Oxetane-Functionalized Hemispiroorthocarbonate Used as a Low-Shrinkage Additive in the Cationic Ultraviolet Curing of Oxetane Monomers

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ABSTRACT: The synthesis of an hemispiroorthocarbonate functionalized with an oxetane group is reported. The obtained monomer was used as a slow shrinkable additive in the cationic ultraviolet curing of a commercially available dioxetane resin. We evidenced polymer network flexibilization by increasing the oxetane-functionalized hemispiroorthocarbonate content in the photocurable formulation. It was demonstrated that spiroorthocarbonate acted as a shrinkage reduction additive and reached expansion on volume after polymerization in the presence of 50 wt % of the functionalized spiroorthocarbonate. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1780–1787, 2009

Key words: cationic polymerization; coatings; photopolymerization

INTRODUCTION

Volume shrinkage, which usually occurs during polymerization, can often cause a large buildup of internal stress in the polymer network and volumetric and dimensional changes, which are responsible for inaccuracy in shapes and a decrease in the mechanical strength or adhesiveness properties.

For these reasons, the suppression or reduction of volume shrinkage is of great importance in the design of materials requiring precise dimensions and for the preparation of composites. One way to make low-shrinkage/low-stress polymeric materials is the incorporation of spiroorthocarbonates, spiroorthoesters, and other strained bicyclic monomers into curable formulations, as proposed by Bailey[1] in 1983.

Polymerizations and copolymerizations that proceed without shrinkage or with expansion in volume through the use of spirocompounds as additives have been intensively studied during the last 20 years[2,3] and were reviewed extensively by Rokicki.[4] In a poly-

cyclic monomer during ring-opening polymerization, for every bond that goes from a Van der Waals distance to a covalent distance, at least two bonds go from a covalent distance to a near Van der Waals distance. This results in essentially zero shrinkage or expansion upon polymerization for polycyclic ring-opening monomers.[5]

One of the most efficient monomers for such a polymerization is spiroorthocarbonates whose polymerization occurs with volume expansion.[6] The high volume expansion may be based on the release of the very compact structure of the starting monomer by the successive double ring-opening polymerization mode. The flexibility introduced into the epoxy network by spiroorthocarbonate copolymerization also reduces the internal stress in the resin.[7]

Copolymerization between a dioxirane and a 1,5,7,11-tetraoxospiro[5.5]undecane, with boron trifluoride as catalyst and elevated temperature, was shown to have zero shrinkage.[8] Also, the cationic photopolymerization of a spiroorthocarbonate with an aromatic dioxirane gave rise to a copolymerization reaction.[9]

Our joint groups, in the frame of a cooperation project, recently proposed the use of an epoxy-functionalized spiroorthocarbonate as a low shrinkage additive in an epoxy-based cationic ultraviolet (UV)-curable formulation.[10]

The UV-induced polymerization technique is gaining increasing importance in the field of coatings because of its peculiar characteristics:[11] it can be

considered an environmental friendly technique because it is a solvent-free process, and it is usually carried out at room temperature, which, therefore, guarantees the saving of energy. Furthermore, it induces polymer formation with a fast transformation of the liquid monomer into a solid film with tailored physical–chemical and mechanical properties.

The cationic photoinduced process presents some advantages over the radical one,[12] in particular, a lack of inhibition by oxygen, low shrinkage, good mechanical properties of UV-cured materials, and good adhesion properties to various substrates. In addition, the monomers employed are generally characterized by low irritation and toxicity properties; between them, oxetanes monomers have received increasing attention.[13–19] The high oxetane ring strain, very similar to that of epoxides, and the higher basicity of the oxetane heterocyclic oxygen than that for the oxirane oxygen in epoxides make this class of resin an interesting alternative in cationic UV-curing applications.

Therefore, by pursuing an investigation into the low shrinkable polymerization process, we proposed the synthesis of an oxetane-functionalized spiroorthocarbonate (OXT SOC) to be used as low-shrinkage additive in cationic UV curing of a commercially available dioxetane monomer. The cationic UV-induced polymerization process was investigated and elucidated by means of a real-time Fourier transform infrared (FTIR) investigation, and the properties of UV cured films were evaluated.

EXPERIMENTAL

Materials

Pentaerythritol, diethyl carbonate, potassium hydroxide, molecular sieves, tetraethyl orthocarbonate (TEOC), triethyl amine, and p-toluensulfonic acid were all reagent grade and were purchased from Aldrich Co. (USA). The following monomers were used in this study: bis[1-ethyl(3-oxetanyl)]methyl ether (OXT-221 or DOX) from Toagosei (Japan) and the synthesized oxetane-functionalized hemispiroorthocarbonate (HOXT SOC), which was prepared on purpose, as described later. The structures of the monomers were as follows:

DOX

HOXT SOC
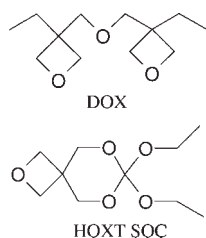
A commercially available mixture of antimonate sulfonium salts (UVI 6976) was supplied from Dow; it was given as a solution with propylene carbonate (50% w/w), and it was added to the curable mixtures at a concentration equal to 2% (w/w).

Synthetic procedure for HOXT SOC

Preparation of oxetane diol (DIOL)

Into a 100-mL, round-bottom flask fitted with a magnetic stirrer, thermometer, microdistilling head, and dry ice trap was placed a mixture of 7 g (0.051 mol) of pentaerythritol, 6.07 g (0.051 mol) of diethyl carbonate, and 0.05 g (0.00089 mol) of potassium hydroxide dissolved in 2 mL of absolute alcohol. The mixture was refluxed until the pot temperature fell below 105°C, and then ethanol was removed by distillation while the head temperature was kept at 76°C. Distillation was continued until the pot temperature rose to 140–150°C. When heated above 180°C, the system was subjected to a vacuum (2 mmHg). As a result of this treatment, carbon dioxide was released. The evolution was rapid, and a white solid appeared in the trap. A semisolid was formed in the reaction flask. It was washed with acetone, and the extracts were collected and put together. After evaporation of the solvent, the obtained residue was purified by column chromatography with acetone as an eluent. A viscous liquid (4.7 g) was obtained in a 77.55% yield.

^{1}H-NMR (CDCl$_3$, 300 MHz, δ, ppm): 3.75 (d, 2H, CH_2—OH), 4.0 (t, 1 H, CH$_2$—OH), 4.35 (s, 4 H, —CH$_2$—O—CH$_2$—)

Preparation of HOXT SOC

In a three-necked, 250-mL, round-bottom flask provided with magnetic stirrer, condenser, nitrogen inlet, and thermometer were placed 5 g (0.042 mol) of DIOL and 4.03 g (0.021 mol) of TEOC. Then, 100 mL of dried toluene was added, followed by 0.120 g (6.3×10^{-4} mol) of p-toluenesulfone and 2 g of molecular sieves, and then, the system was flushed with nitrogen to set anhydrous conditions. After 10 min, 0.86 g (8.4×10^{-3} mol) of triethyl amine was added to the flask. The mixture was refluxed to reach 95°C. The reaction was discontinued after 8 h. The reaction mixture was filtered, and the solvent was evaporated. The residue was purified by column chromatography with silica gel as the stationary phase and hexane : ethyl acetate 90 : 10 as the eluent. A viscous liquid was obtained in a 57% yield.

^{1}H-NMR (CDCl$_3$, 300 MHz, δ, ppm): 1.2 (t, 3 H, CH$_3$—CH$_2$—), 3.6 (q, 2 H, CH$_3$—CH_2—), −4.1 (s, 4H, C—CH$_2$—O—), 4.45 (s, 4H, —CH$_2$—O—CH$_2$—)

Sample preparation and characterization

Photocurable formulations were prepared by the addition of the HOXT SOC monomer to the oxetane

resin (DOX) in the range between 10 and 50 mol %. To all the mixtures, 2 wt % of cationic photoinitiator was added. The formulations were coated and irradiated with a UV lamp (Hg low-pressure lamp, Italquart, Milano) for 2 min in air with a light intensity on the surface of the samples of about 35 mW/cm^2.

The kinetics of the photopolymerization were determined by real-time FTIR spectroscopy with a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induced the polymerization, and the IR beam, which analyzed *in situ* the extent of the reaction. The oxetane ring-opening conversion was followed by the monitoring of the decrease in the absorbance due to the oxetane ring centered at 980 cm^{-1}. A medium-pressure mercury lamp (Omnicure Hamamatsu) equipped with an optical guide was used to induce the photopolymerization (the light intensity on the surface of the sample was about 50 mW/cm^2).

Dynamic mechanical thermal analyses (DMTAs) were performed with a Rheometric Scientific MKIII instrument (United Kingdom) at a frequency of 1 Hz in the tensile configuration.

The gel content was determined on the cured films by measurement of the weight loss after 24 h of extraction with chloroform at room temperature according to the standard test method ASTM D 2765-84.

Shrinkage measurements were obtained by measurement of the density of the system before and after curing. We measured the solution density by weighing a precise amount of liquid formulation. The density of the cured film was measured by means of a Sartorius balance YDK01 with a density determination kit. Archimedes' principle was applied to determine the specific gravity of a solid with this measuring device: a solid immersed in a liquid is exposed to the force of buoyancy. The value of this force is the same as that of the weight of the liquid displaced by the volume of the solid. The density measurements were performed with the Sartorius hydrostatic balance, which enabled us to weigh the solid in air and in a liquid. The specific gravity of a solid (ρ) is determined when the density of the liquid [$\rho(l)$] causing buoyancy is known through the following formula:

$$\rho = W(a)\rho(l)/W(a) - W(l)$$

where $W(a)$ is the weight of the solid in air and $W(l)$ is the weight of the solid in liquid.

The chosen liquid was ethanol with a density value at 25°C of 0.78506. The specific volume of the system before and after curing was defined as the inverse of the density, and the shrinkage was calculated with the following formula:

$$\Delta = [V_p - V_l/V_l] \times 100$$

where Δ is the volume change, V_p is the specific volume of the cured polymer, and V_l is the specific volume of the starting liquid formulation.

RESULTS AND DISCUSSION

Synthesis of HOXT SOC

The synthesis of HOXT SOC was carried out in two stages (see Scheme 1). In the first stage, DIOL was prepared by means of the transesterification of the pentaerythritol with diethyl carbonate with potassium hydroxide as a catalyst. Once the transesterified intermediate was formed, the reaction mixture was heated at 180°C *in vacuo*; this resulted in the release of carbon dioxide to form DIOL. The diol was transetherified with TEOC in the presence of *p*-toluensulfonic acid. A mixture of both HOXT SOC and OXT SOC was obtained, with the latter formed in minor proportion (25% w/w). The reaction mixture was resolved by column chromatography. In Figure 1 is shown the proton spectrum of the obtained HOXT SOC. The peaks at 4.1 and 4.45 ppm correspond to the protons of the oxetane moiety, whereas the peaks at 1.2 and 3.6 ppm correspond to the ethyl groups.

Figure 2 shows the IR spectra of DIOL, which was used as the starting material, and HOXT SOC. The broad peak at 3350 cm^{-1}, which corresponded to the OH groups of the diol, completely disappeared, which means that the transetherification reaction proceeded quantitatively. The peak corresponding to the oxetane group was located at 940 cm^{-1}.

During the synthesis of the oxetane spiroorthocarbonate, either HOXT SOC or OXT SOC was formed. Although an equivalent DIOL : TEOC ratio of 2 : 1 was used, HOXT SOC was formed preferentially. This might have been due to the high strain in the bicycle spiroorthocarbonate, induced by the relatively small molecules of DIOL when it was etherified with the
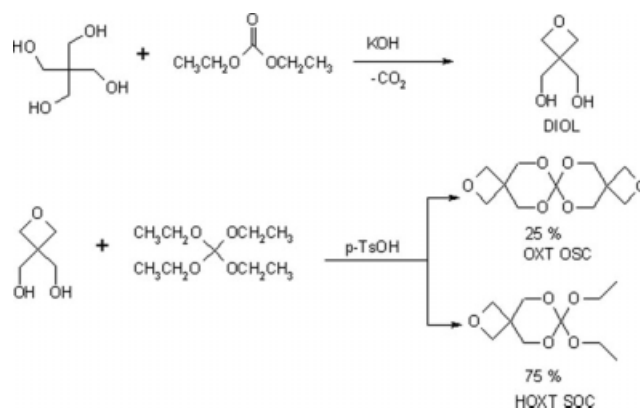
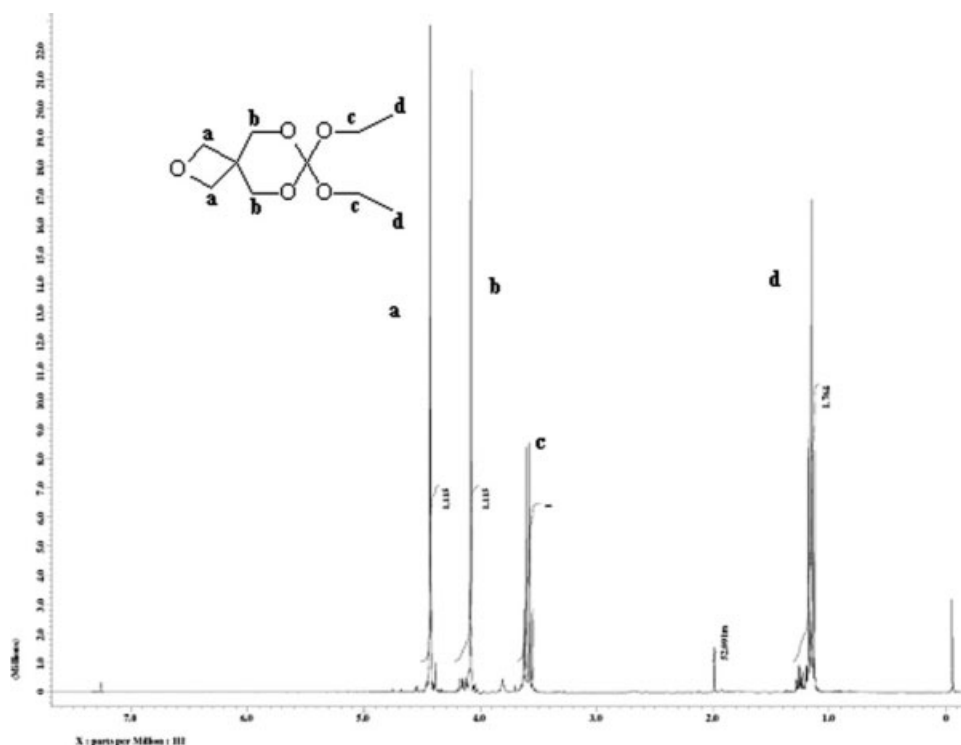**Scheme 1** Synthetic methodology for the preparation of OXT SOC.

Figure 1 ¹H-NMR spectrum of HOXT SOC.

TEOC. Thus, because we were obtaining HOXT SOC in major proportion, it was of interest to evaluate the activity of this compound as an antishrinkng additive after separation of the HOXT SOC.

Investigation of the cationic photocuring process

First, the reactivity of the pure monomers was investigated toward a cationic UV-induced polymerization process by means of real-time FTIR analysis. In Figure 3, the conversion curves as a function of irradiation time are reported for both the DOX and HOXT SOC pristine monomers and for their 1 : 1 molar ratio mixture. Although the plateau value gave the final oxetane group conversion, the slope of the curve gave an indication of the polymerization rate.

The pure oxetane-functionalized spiroorthocarbonate resin HOXT SOC showed a high reactivity in acid
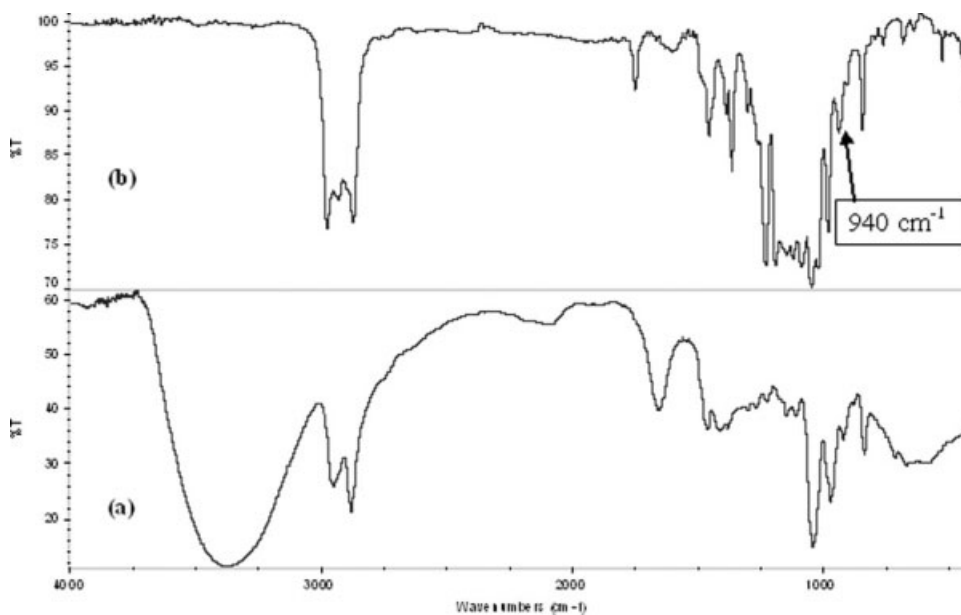

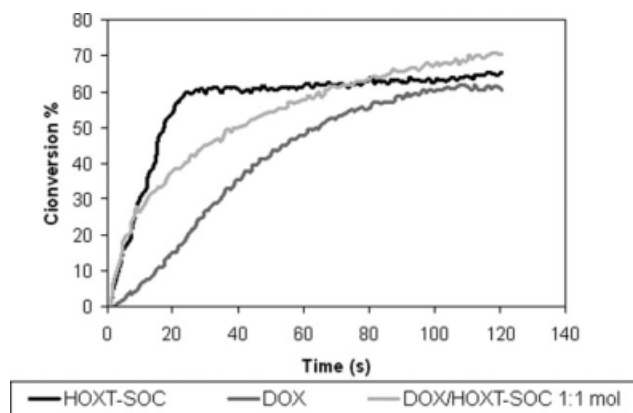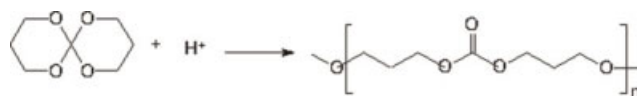**Figure 2** IR spectra of (a) the starting DIOL and (b) the hemispiroorthocarbonate HOXT SOC.

Figure 3 Real-time FTIR conversion curves for the pure HOXT SOC monomer, the DOX monomer, and the DOX/HOXT SOC mixture (1 : 1 molar ratio).

Scheme 2 Mechanism for spiroorthocarbonate ring-opening polymerization.

tion activated by the generated photoacid. Also evident was the appearance of a strong peak centered 1750 cm^{-1}, which was attributable to the carbonate carbonyl group; this was due to the spiroorthocarbonate ring-opening polymerization reaction, as depicted in Scheme 2. Furthermore, the C—O band absorption, centered at 1270 cm^{-1}, clearly increased after UV curing, which indicated polyethercarbonate formation. All of this evidence was in agreement with a double ring-opening polymerization of the spiroorthocarbonate monomer, which involved both the oxetane ring and spiroorthocarbonate ring.

The pure DOX resin showed a lower oxetane reactivity with a lower polymerization rate (see Fig. 3). This was attributed to the high glass-transition temperature (T_g) values of the network that was formed during the cationic ring-opening polymerization of the DOX monomer; because of the high reactivity in network formation, the system reached gelation and vitrification quite rapidly. As a result, the reactive species diffusion was hindered, and a lower monomer reactivity and oxetane group conversion were achieved. This early vitrification effect did not allow the complete oxetane group conversion, and a high content of reactive groups were trapped in the glassy
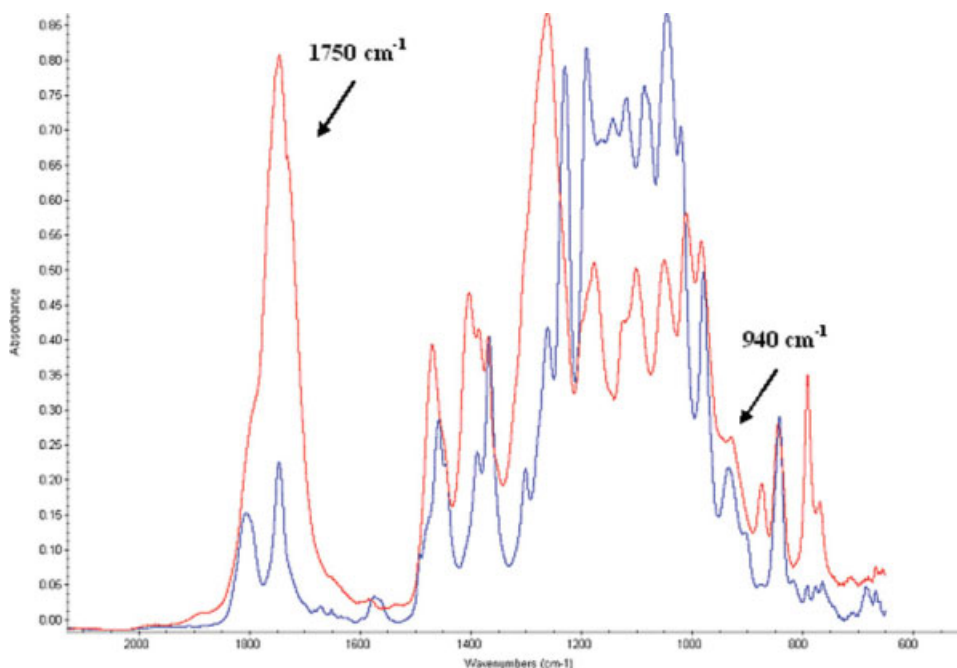
conditions, which read 65% oxetane conversion after 2 min of irradiation (see Fig. 3). On the other hand, it a leveling of the oxetane final conversion was evident, which could be probably explained by proton consumption by the spiroorthocarbonate ring-opening polymerization, which occurred simultaneously with the oxetane ring-opening polymerization. A proposed mechanism for spiroorthocarbonate ring-opening polymerization, simplified for the nonfunctionalized spiroorthocarbonate monomer, is shown in Scheme 2.

In Figure 4, the FTIR spectra of HOXT SOC, before and after UV curing, are shown. We observed a strong decrease of the oxetane peak centered at 980 cm^{-1}, due to the oxetane ring-opening polymerization reac-

Figure 4 FTIR spectra of the HOXT SOC pristine system before and after UV curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
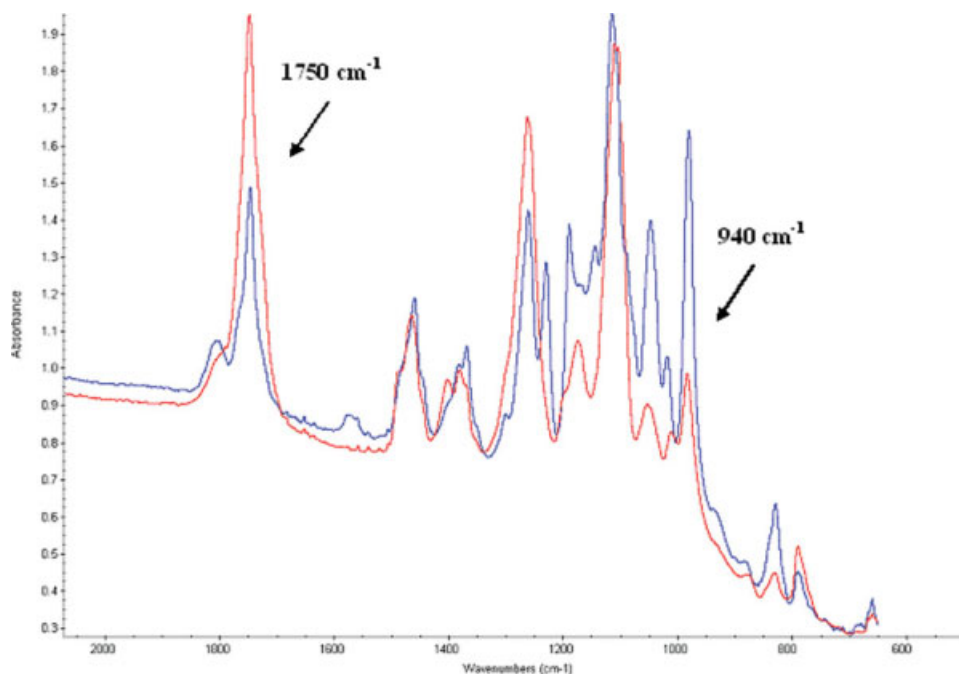
Figure 5 FTIR spectra of the DOX/HOXT SOC mixture (1 : 1 molar ratio) before (blue spectra) and after (red spectra) UV curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

polymer network. When the HOXT SOC monomer was added to the DOX resin in a 1 : 1 molar ratio, increases in the oxetane ring-opening polymerization rate and oxetane final conversion were achieved with respect the pristine DOX monomer (see Fig. 3). It is possible to explain this result on the basis of a flexibilization effect induced by the insertion into the oxetane-based polymeric network of the spiroorthocarbonate flexible structure.

A copolymerization process between the DOX and HOXT SOC monomers is proposed on the basis of the FTIR investigation of the DOX/HOXT SOC 1 : 1 mol formulation.

In Figure 5, the FTIR spectra of the DOX/HOXT SOC 1 : 1 molar ratio before and after UV curing are reported. A strong decrease in the oxetane peak centered at 940 cm^{-1} was observed, as expected from the oxetane ring-opening polymerization reaction. Furthermore, as observed for the pure spiroorthocarbonate monomer, the appearance of a carbonate carbonyl group centered at 1750 cm^{-1} and attributed to the spiroorthocarbonate ring-opening polymerization reaction was clearly evident after UV curing. This evidence was in accordance with a copolymerization mechanism.

Therefore, OXT SOC could react both via a spiro ring-opening copolymerization with the DOX oxetane groups (as depicted in Scheme 3 in a simplified way with a nonfunctional spiroorthocarbonate monomer) or via an oxetane ring-opening copolymerization. In both cases, it was possible to foresee a copolymerization mechanism between the two monomers. These results are in agreement with a previous literature investigation reporting a copolymerization reaction between spiroorthocarbonate and an oxirane monomer.[9]

Characterization of the cured films

Dynamic mechanical characterization of the UV cured films was performed by means of DMTA, which allowed the evaluation of the elastic component
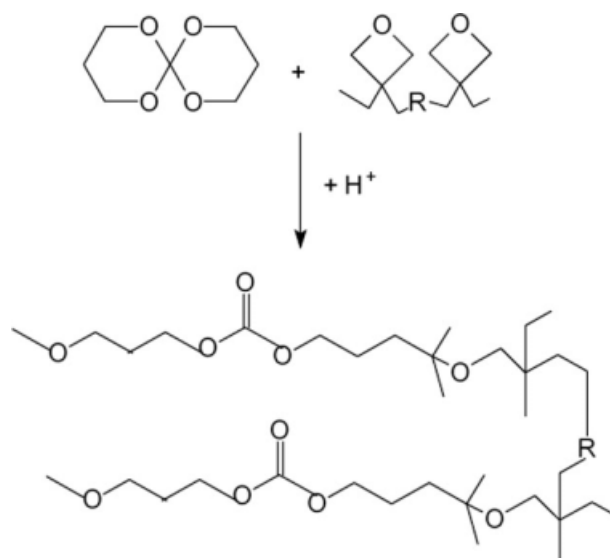
Scheme 3 Proposed copolymerization mechanism between spiro ring-opening polymerization and oxetane ring-opening polymerization.

[storage modulus (E')] and viscous component [loss modulus (E'')] of the materials in a large temperature interval.

In the T_g region, a clear decrease of E' was evident, whereas the tan δ curve (tan δ = E''/E') showed a maximum, which was assumed to be the T_g of the cured films[20] (see Fig. 6).

It was possible to observe a shift in the maximum of the tan δ curves toward lower values with increasing amount of HOXT SOC in the DOX photocurable formulation; at the same time, a decrease in E' was evident. The T_g data are collected in Table I, together with the gel content values.

The flexibilization of the DOX photocured films by the addition of HOXT SOC monomer was due both to the introduction of very flexible structures in the photocured polymer network and to the reduction of the crosslinking density because of the presence of the monofunctional oxetane additive.

These results are in accordance with the kinetic data previously discussed. Because the HOXT SOC
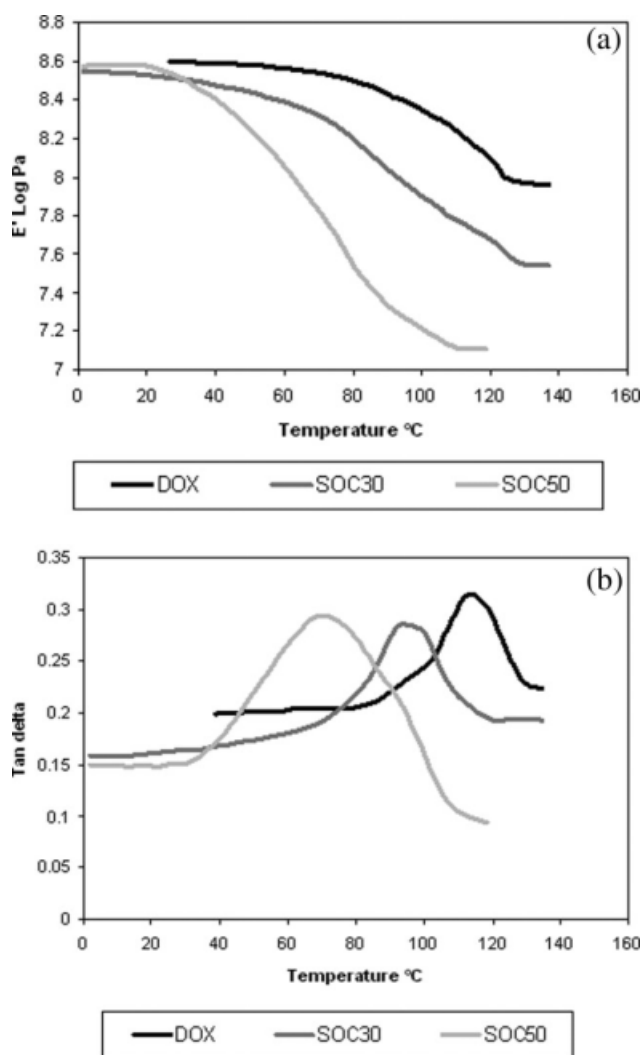
TABLE I
T_g Data

Sample	Gel content (%)	T_g from DMTA (°C)	Shrinkage change
DOX	94	115	−4.21
90 : 10 DOX/HOXT SOC	97	100	−3.60
70 : 30 DOX/HOXT SOC	98	96	−3.64
50 : 50 DOX/HOXT SOC	97	70	0.95

monomer acted as a flexibilizing reactive diluent, a higher mobility of reactive species could be obtained; as a result, an increase in the photopolymerization rate and oxetane group conversion was achieved, as demonstrated by real-time FTIR investigations.

The presence of a single tan δ peak in all of the cured films was further evidence of a copolymerization mechanism between the DOX and HOXT SOC monomers.

The copolymerization reaction between DOX and HOXT SOC was also strongly supported by high gel content values for all of the investigated systems (always >97%; see Table I), which indicated that the monofunctional additive was linked into the polymeric network via a copolymerization reaction instead of the formation of a linear extractable polymer via an homopolymerization reaction.

Shrinkage measurements

The efficiency of HOXT SOC as a low-shrinkable additive was determined by measurement of the density of the starting formulations and of the corresponding cured films. The calculated shrinkages are reported in Table I.

A decrease in the shrinkage extent upon photopolymerization was evidenced in the cured films obtained in the presence of HOXT SOC. A slight expansion of volume during polymerization was even reached by the photocuring of the DOX/HOXT SOC 1 : 1 molar ratio formulation.

Even if it is difficult to explain the unexpected nonlinear behavior, we can conclude that HOXT SOC acted as shrinkage reduction or expandable monomer additive for oxetane UV-curable formulations if added in the proper amount. These results are in agreement with those of previous investigations reported in the literature.[4,10]

CONCLUSIONS

HOXT SOC was synthesized with the aim to reduce shrinkage during the cationic photopolymerization of oxetane monomers. The HOXT SOC and the dioxetane resin DOX were compatible in the range between 5 and 50 mol % spiroorthocarbonate. The

Figure 6   DMTA curves for the cured films.

formulations, under UV irradiation, gave rise to transparent cured copolymeric networks. A flexibilization increase was evidenced by an increase in the spiroorthocarbonate content in the photocurable formulation. A copolymerization reaction was proposed on the basis of FTIR investigation and confirmed by the presence of a single tan δ peak in the DMTA thermogram and very high gel content values. Shrinkage during photopolymerization was calculated by measurement of the density of the starting formulations and of the corresponding cured films; it was demonstrated that spiroorthocarbonate acted as shrinkage reduction additive, and it even induced a slight expansion in volume during polymerization when added at a 1 : 1 molar ratio with the DOX monomer.

The results of this study are in agreement with previous investigations performed by our groups and show the strong efficiency of the use of strained bicyclic monomers as low shrinkable additives in the cationic UV curing process.

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