

PHOSPHORYLATED COPOLYMERS CONTAINING PENDANT, CROSSLINKABLE SPIROORTHOESTER MOIETIES

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Abstract

The synthesis of a novel spiroorthoester containing monomer, 1,4,6-trioxaspiro[4,4]-2-nonylmethyl acrylate, is presented. This monomer was polymerized via a free-radical system to yield the homopolymer and a series of copolymers with phosphorus-containing comonomers. Diethyl vinyl phosphonate, allyldiphenyl phosphine oxide, and diethyl(methacryloyloxymethyl)phosphonate were used in various feed ratios to produce copolymers with different phosphorus concentrations containing crosslinkable spiroorthoester side-chain units. The crosslinking of the polymers was performed cationically with ytterbium triflate, and in all cases, the expansion of the polymer was observed. Moreover, the incorporation of phosphorus into the copolymers increases the limiting oxygen indices, regardless of the percentage of phosphorus used.

Keywords: cationic polymerization; copolymerization; crosslinking; flame retardance; heteroatom-containing polymers; radical copolymerization; spiroorthoesters; ytterbium triflate

INTRODUCTION

A major concern for the production of polymeric materials is shrinkage upon crosslinking or curing. This is a particular problem in the coating, casting, molding and microelectronics industries. It can cause poor adhesion to a substrate, delamination, microvoids, and microcracks, which in turn can reduce the durability of a product. A number of different techniques have been employed to reduce shrinkage, such as the addition of fillers and curing at lower temperatures. However, these methods are not totally efficient as the shrinkage is due to the crosslinking reaction rather than as a consequence of production methods.

The most effective method of solving this problem is to use monomers with groups that undergo polymerization with nearly zero shrinkage or expansion. A number of cyclic monomers have been reported that appear to maintain their volume or actually expand during the double ring-opening polymerization.¹⁻⁵ Among these are the spiroorthoesters (SOEs); these materials are easily prepared from epoxides and lactones and exhibit a wide variety of structures.⁶⁻⁸ The addition of a vinyl or acrylate for radical polymerization allows the SOE moiety to be carried into the polymeric system for later crosslinking.⁹ Copolymers containing SOE moieties can be crosslinked, without significant shrinkage, by cationic double ring-opening polymerization by Lewis acid catalysts.

The flammability of organic polymers has become a major research interest in recent years because of the increasing use of polymeric materials in both domestic and public environments. Although halogen-containing flame retardants are exceptionally efficient, they have clear disadvantages, as they generate toxic and corrosive gases during thermal degradation. In recent times, developments in the chemistry of halogen-free flame-retardant polymers have involved the incorporation of a number of heteroelements such as P, Si, B, and N, and other miscellaneous elements.¹⁰ For years, phosphorylation has been considered one of the most efficient means of conferring flame retardancy on synthetic polymer materials.¹¹⁻¹³

In this article, the radical copolymerization of SOE and a phosphorus-containing comonomer is presented. The shrinkage effects of the copolymer during cationic cross-linking reactions are assessed by gas pycnometry. The flame-retardant properties of the polymers are determined by limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

Epibromohydrin (Fluka), γ -butirolactone (γ -BL; Aldrich), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$; Aldrich),

triethylamine (Fluka), acrylic acid (Aldrich), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; Aldrich), 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (Aldrich), diethyl vinyl phosphonate (DEVP; Aldrich), allyldiphenylphosphine oxide (ADPPO; Aldrich), methacryloyl chloride (Aldrich), diethylhydroxymethylphosphonate (Aldrich), ytterbium (III) trifluoromethanesulfonate [Yb(OTf)₃; Aldrich] were used as received. 2,2'-Azobisisobutyronitrile (AIBN; Aldrich) which was recrystallized from methanol before use. All solvents were purified with standard procedures.

Instrumentation

¹H NMR (400 MHz), ¹³C NMR (100.6 MHz), and ³¹P NMR (161.9 MHz) spectra were obtained with a Varian Gemini 400-MHz Fourier transform spectrometer with CDCl₃ as the solvent and tetramethylsilane or phosphoric acid as the internal standard.

Crosslinking studies were performed on a Mettler DSC-821e thermal analyzer in covered Al pans under N₂ at a scanning rate of 10 °C/min. The determination of the glass transition temperatures (T_g's) was carried out on a Mettler DSC-822e thermal analyzer in covered Al pans under N₂ at scanning rate of 20 °C/min.

The isothermal polymerization process at 80 °C was monitored with

an FTIR-680 Plus spectrophotometer with a resolution of 4 cm⁻¹ in the absorbance mode. An attenuated-total-reflection accessory with thermal control and a diamond crystal was used to obtain Fourier transform infrared/attenuated total reflection (FTIR-ATR) spectra.

Thermogravimetric analyses (TGAs) were performed with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 8 mg were degraded between 30 and 800 °C at a heating rate of 10 °C/min under nitrogen and air atmospheres.

The molecular weight distribution of the polymers was determined with a Waters gel permeation chromatograph equipped with a Waters 510 differential refractive-index detector (RID-6A from Shimadzu). The gel permeation chromatograph was operated using three Waters Shodex columns (K80M, 5-μ mixed-D gel, and 3-μ mixed-E gel) at a nominal flow rate of 1 mL/min and with a sample concentration of 0.1% in tetrahydrofuran as the solvent. Monodispersed polystyrene standards were purchased from Polymer Laboratories for instrument calibration.

The densities of the materials were measured with a Micromeritics Accu-pyc 1330 TC gas pycnometer at 30 °C.

LOIs were measured on a Fire Testing Technology flammability unit in conformance with ASTM D 2863 for samples measuring 100 mm x 6 mm x 3 mm and supported on glass fibers.

Monomer Synthesis

Synthesis of 2-Bromomethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-Br)⁶

Epibromohydrin (50 g, 0.36 mol) was added dropwise over a period of 15 min at a temperature below 10 °C in an argon atmosphere to a mixture of 180 g (2.09 mol) of γ -BL and 1.5 mL (11.8 mmol) of $\text{BF}_3 \cdot \text{OEt}_2$ as a catalyst. After the addition was completed, the mixture was stirred for 60 min at the same temperature. The reaction was quenched by the addition of 1.9 mL (13.5 mmol) of triethylamine. The solvent was removed under reduced pressure, and the residue was fractionally distilled to yield 60.4 g (74 %) of a transparent, colorless liquid.

¹H NMR (CDCl_3 , two diastereomers): δ (ppm) = 4.54-4.48 (m, 1H, -O-CH-), 4.43-4.37 (m, 1H, -O-CH-), 4.21-4.17 (dd, 2H, -O-CH₂-), 3.98-3.87 (m, 6H, -O-CH₂-), 3.91-3.31 (m, 4H, Br-CH₂-), 2.20-2.11 (m, 4H, -CH₂-), 2.05-1.98 (m, 4H, -CH₂-).

¹³C NMR (CDCl_3 , two diastereomers): δ (ppm) = 129.98 (s, spiranic C), 129.88 (s, spiranic C), 75.48 (s, -O-CH-), 74.74 (s, -O-CH-

), 68.72 (s, -O-CH₂-), 67.68 (s, -O-CH₂-), 67.40 (s, -O-CH₂-), 67.38 (s, -O-CH₂-), 32.87 (s, -CH₂-), 32.81 (s, -CH₂-), 32.74 (s, Br-CH₂-), 32.28 (s, Br-CH₂-), 24.20 (s, -CH₂-), 24.05 (s, -CH₂-).

Synthesis of 1,4,6-Trioxaspiro [4,4]-2-nonylmethyl Acrylate (SOE-AC)¹⁴

SOE-Br (10 g, 45.0 mmol) in 10 mL of anhydrous dimethyl sulfoxide (DMSO) was added slowly to a mixture of 3.24 g (45.0 mmol) of acrylic acid and 6.84 g (45.0 mmol) of DBU in 20 mL of anhydrous DMSO and stored under an argon atmosphere in a three-necked flask in a bath at 65 °C. This mixture was stirred vigorously for a period of 30 min during the addition. After the addition was complete, the mixture was stirred for an additional 5 h at the same temperature. The radical inhibitor, 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (8 mg), was added when the reaction had reached completion. The desired product was taken out of DMSO with several extractions with CH_2Cl_2 (4 x 30 mL). The product was purified through washing with a dilute solution of HCl and was then neutralized with a solution of NaOH. The dichloromethane solution was dried over MgSO_4 and evaporated. After the removal of the SOE-Br impurities under reduced pressure, 7.27 g (76%) of a transparent liquid was yielded.

^1H NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm}) = 6.46\text{--}6.41$ (dd, 1H, $J_{\text{trans}} = 16.8$ Hz, $J_{\text{cis}} = 1.6$ Hz, C=CH), $6.44\text{--}6.40$ (dd, 1H, $J_{\text{trans}} = 17.2$ Hz, $J_{\text{cis}} = 1.6$ Hz, C=CH), $6.17\text{--}6.01$ (m, 2H, C=CH₂), $5.87\text{--}5.84$ (dd, 1H, $J_{\text{cis}} = 9.6$ Hz, $J_{\text{gem}} = 1.2$ Hz, C=CH₂), $5.86\text{--}5.83$ (dd, 1H, $J_{\text{cis}} = 10.8$ Hz, $J_{\text{gem}} = 1.6$ Hz, C=CH₂), $4.35\text{--}3.50$ (m, 1H, -O-CH-), $4.38\text{--}4.32$ (m, 1H, -O-CH-), $4.38\text{--}4.01$ (m, 6H, -O-CH₂-), $3.96\text{--}3.89$ (m, 4H, -O-CH₂-), $3.84\text{--}3.77$ (m, 2H, -O-CH₂-), $2.16\text{--}2.10$ (m, 4H, -CH₂-), $2.04\text{--}1.99$ (m, 4H, -CH₂-).

^{13}C NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm}) = 166.04$ (s, C=O), 131.73 (s, C=CH₂), 129.98 (s, spiranic carbon), 128.11 (s, C=CH), 74.32 (s, -O-CH-), 73.47 (s, -O-CH-), 67.58 (s, -O-CH₂-), 66.29 (s, -O-CH₂-), 66.16 (s, -O-CH₂-), 65.32 (s, -O-CH₂-), 64.41 (s, -O-CH₂-), 32.89 (s, -CH₂-), 24.41 (s, -CH₂-), 24.22 (s, -CH₂-).

Synthesis of Diethyl(methacryloyloxymethyl)phosphonate (DEMMP)^{15,16}

A mixture of 16.8 g (0.10 mol) of diethyl (hydroxymethyl)phosphonate and 12 g (0.12 mol) of triethylamine was dissolved in anhydrous dichloro-methane (100 mL), cooled in an iced bath, and purged with argon. To this solution was added, dropwise with stirring, an argon-purged solution of 11.5 g (0.11 mol) of methacryloyl chloride in anhydrous dichloro-methane (30

mL). The mixture was then warmed to room temperature and stirred for 18 h more. The precipitated triethylamine hydrochloride was removed by filtration. The solution was then evaporated to remove the solvent, cooled overnight in a freezer, filtered again, and washed with deionised water to leave yield a brown oil. 3-*tert*-Butyl-4-hydroxy-5-methylphenyl sulphide (8 mg) was added to serve as polymerization inhibitor, and the oil was distilled under reduced pressure to yield 16.9 g (72%) of a colorless, viscous liquid (bp = 109 °C at 0.6 mmHg).

^1H NMR (CDCl_3): $\delta(\text{ppm}) = 6.23$ (d, 1H, vinyl), 5.72 (d, 1H, vinyl), 4.51 (d, 2H, -O-CH₂-P), 4.23 (m, 4H, P-O-CH₂-), 2.04 (s, 3H, =C-CH₃), 1.45 (t, 6H, -CH₃).

^{13}C NMR (CDCl_3): $\delta(\text{ppm}) = 166.41$ (d, C=O, $J_{\text{C-P}} = 8.4$ Hz), 135.40 (s, C=), 127.14 (s, =CH₂), 62.91 (d, -O-CH₂-P, $J_{\text{C-P}} = 6.1$ Hz), 57.13 (d, -O-CH₂-, $J_{\text{C-P}} = 169.4$ Hz), 18.48 (s, α -CH₃), 16.55 (d, CH₃, $J_{\text{C-P}} = 5.3$ Hz).

^{31}P NMR (CDCl_3): $\delta(\text{ppm}) = 19.7$.

Polymer Synthesis

Homopolymerization of SOE-AC

A solution of 3 g (14.0 mmol) of SOE-AC and 69.1 mg (0.42 mmol) of AIBN in benzene (20 mL) in a sealed ampule was heated in a water bath at 65 °C for 40 h. The reaction mixture was added

dropwise into *n*-hexane to precipitate the polymer as a white powder. The polymer was further purified by reprecipitation of the dissolved polymer from dry dichloromethane into *n*-hexane. The yield was 2.0 g (66%).

^1H NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm})$ 4.45 (br, -O-CH-), 4.31 (br, -O-CH-), 4.12 (br, -O-CH₂-), 3.93 (br, -O-CH₂-), 3.74 (br, -O-CH₂-), 2.30 (br, main chain -CH-), 2.10 (br, -CH₂-), 1.97 (br, -CH₂-), 1.64 (br, main chain -CH₂-).

^{13}C NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm})$ 174.33 (s, C=O), 129.98 (s, spiranic C), 129.86 (s, spiranic C), 74.07 (s, -O-CH-), 73.28 (s, -O-CH-), 67.46 (s, -O-CH₂-), 67.40 (s, -O-CH₂-), 66.60 (s, -O-CH₂-), 66.21 (s, -O-CH₂-), 65.76 (s, -O-CH₂-), 64.64 (s, -O-CH₂-), 41.45 (s, main chain -CH₂-), 35.28 (s, main chain -CH-), 32.87 (s, -CH₂-), 24.47 (s, -CH₂-), 24.28 (s, -CH₂-).

Copolymerization of SOE-AC with Phosphorus-Containing Monomers

Copolymerizations of the phosphorus-containing monomers with SOE-AC were carried out in benzene with a procedure similar to that for the homopolymerization of SOE-AC. The initiator used was AIBN, and the reaction was performed at 65 °C. The initiator concentrations were 3 mol % in all cases. All the copolymers were

recovered by precipitation in *n*-hexane. The purification of DEVP- and DEMMP-based copolymers was carried out by the reprecipitation of the dissolved polymer from dry dichloromethane into *n*-hexane. The purification of ADPPO-based copolymers was performed as follows: the polymer was washed twice with methanol (to remove any unreacted ADPPO), and then the dissolved polymer was reprecipitated from dry dichloromethane into *n*-hexane.

SOE-AC/DEVP.

^1H NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm})$ 4.45 (br, -O-CH-), 4.32 (br, -O-CH-), 4.14 (br, -O-CH₂-), 3.89 (br, -O-CH₂-), 3.78 (br, -O-CH₂-), 3.62 (br, main chain -CH-P-), 2.37 (br, main chain -CH-), 2.12 (br, -CH₂-), 1.96 (br, -CH₂-), 1.86 (br, -CH₂-), 1.83 (br, main chain -CH₂-), 1.64 (br, main chain -CH₂-), 1.27 (br, -CH₃-).

^{31}P NMR (CDCl_3): $\delta(\text{ppm})$ = 31.3 (br).

SOE-AC/ADPPO.

^1H NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm})$ 7.74 (br, Ar-H), 7.50 (br, Ar-H), 4.51 (br, -O-CH-), 4.39 (br, -O-CH-), 4.12 (br, -O-CH₂-), 3.90 (br, -O-CH₂-), 3.79 (br, -O-CH₂-), 3.52 (br, -P-CH₂-), 2.40 (br, main chain -CH-), 2.15 (br, -CH₂-), 2.01 (br, -CH₂-), 1.89 (br, main chain -CH₂-), 1.71 (br, main chain -CH₂-).

^{31}P NMR (CDCl_3): $\delta(\text{ppm})$ 32.1 (br).

SOE-AC/DEMMP.

^1H NMR (CDCl_3 , two diastereomers): $\delta(\text{ppm})$ = 4.49 (br, -O-CH), 4.38 (br, -O-CH-), 4.21 (br, -O-CH₂-, -P-O-CH₂-), 3.98 (br, -O-CH₂-), 3.84 (br, -O-CH₂-), 3.67 (br, -O-CH₂-P-), 2.42 (br, main chain -CH-), 2.17 (br, -CH₂-), 2.02 (br, -CH₂-), 1.91 (br, main chain -CH₂-), 1.71 (br, main chain -CH₂-), 1.38 (br, -CH₃), 1.21 (br, -C-CH₃).

^{31}P NMR (CDCl_3): $\delta(\text{ppm})$ 20.5 (br)

Crosslinking Reactions

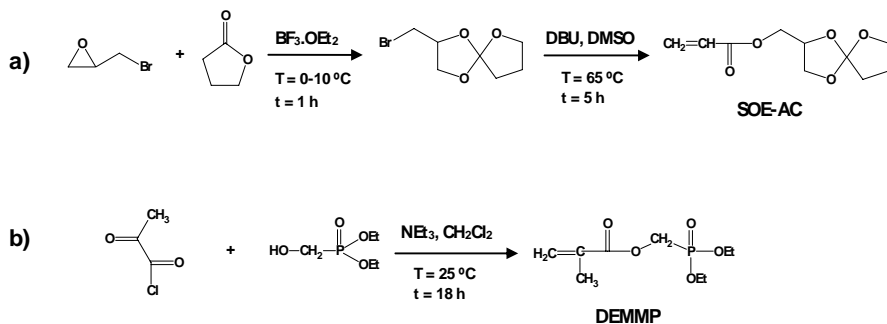
The cationic crosslinking reactions of SOE-containing copolymers were carried out via the mixing of the corresponding copolymer with 1phr ytterbium triflate, and after suitable

homogeneization, the mixture was heated at 80 °C for 5 h.

RESULTS AND DISCUSSION

A novel SOE-containing monomer, SOE-AC, was synthesized via the reported procedure for the ester synthesis by direct C-O bond formation between carboxylic acids and halides in the presence of a strong base such as DBU.¹⁷ SOE-AC was prepared by the reaction of SOE-Br with acrylic acid in the presence of DBU under mild conditions [(Scheme 1(a)]. SOE-Br was obtained from epibromohydrin and γ -BL in a $\text{BF}_3 \cdot \text{OEt}_2$ catalyzed reaction.⁶

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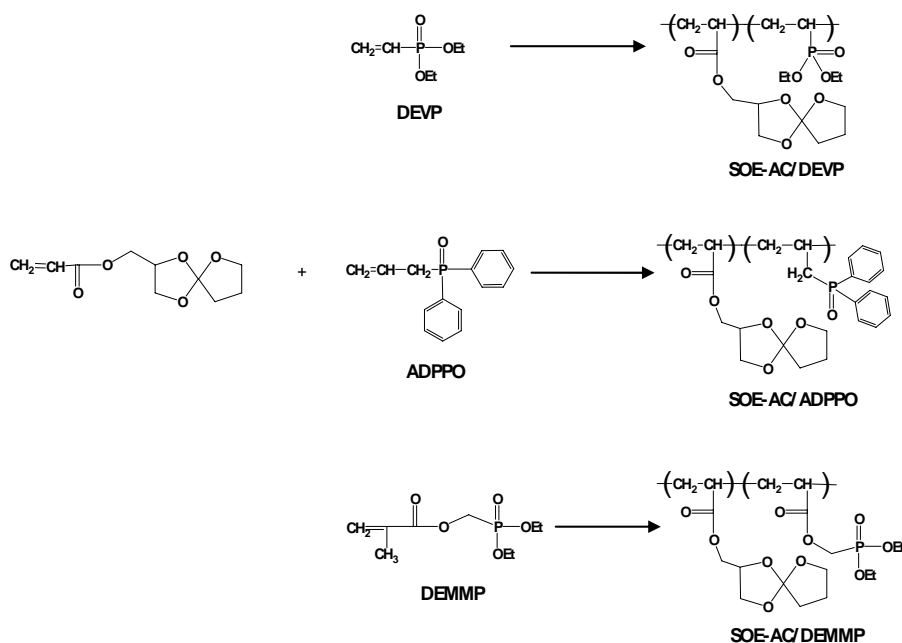


Scheme 1

A series of phosphorus-containing, unsaturated comonomers were used: DEVP; ADPPO and DEMMP (Scheme 2). DEVP and ADPPO are commercial materials, whereas DEMMP was synthesized by the esterification of methacryloyl

chloride and diethylhydroxymethyl phosphonate as shown in Scheme 1(b).

The homopolymerization of SOE-AC and the copolymerization of SOE-AC with the phosphorus-



Scheme 2

^a Estimated by ¹H NMR

^b Weight-average molecular weight estimated by GPC (based on polystyrene standards).

Polymer	Monomer Feed Ratio (mol %) SOE: monomer P (wt% P)	Copolymer Composition (mol %) SOE: monomer P (wt% P) ^a	Yield (%)	M _w × 10 ⁴ ^b	T _g (°C)
SOE-AC	100:0 (0%)	100:0 (0%)	66	2.5	32
SOEAC/DEV	80:20 (3%)	80:20 (3.1%)	54	2.9	24
	62:38 (6%)	63:37 (5.8%)	47	2.1	22
SOE-	79:21 (3%)	81:19 (2.7%)	41	1.0	47
AC/ADPPO	56:44 (6%)	77:23 (3.2%)	35	1.3	48
SOE-	79:21 (3%)	72:28 (3.9%)	61	2.9	25
AC/DEMMP	57:43 (6%)	52:48 (6.6%)	53	0.9	20

containing un-saturated comonomers, via a radical polymerization using AIBN as the initiator, were carried out in sealed tubes at 65 °C in benzene for 36-44 h (Scheme 2). In all cases, two different ratios of the comonomers were used to obtain phosphorus content of either 3 or 6% (Table 1). The unimodal, but broad gel permeation chromatography (GPC) curves of the obtained copolymers supported the successful copolymerizations. The structures of the polymers were confirmed with ¹H, ¹³C, and ³¹P NMR and IR spectroscopy. The composition of the copolymers was determined by the integration ratios of the following signals in ¹H NMR: for SOE-AC/DEV, 4.6-3.7 ppm (7 H_{SOE} + 4H_{DEV}) and 1.4-1.2 ppm (6H_{DEV}); for SOE-AC/ADPPO, 8-7.3 ppm (10H_{ADPPO}) and 4.6-3.4 ppm (7H_{SOE} + 2H_{ADPPO}); and for SOE-AC/DEMMP, 4.6-3.5 ppm (7H_{SOE} +

6H_{DEMMP}) and 1.5-1.3 ppm (6H_{DEMMP}).

In Figure 1, the ¹H NMR spectrum of the homopolymer and ¹H and ³¹P NMR spectra of the SOE-AC/DEV copolymer are shown. In the ¹H NMR spectrum of SOE-AC/DEV [Fig.1(b)] the signals corresponding to the phosphorus-containing comonomer are clearly identifiable. The ³¹P NMR spectrum is shown [Fig.1(c)]; the single ³¹P signal is split due to the presence of different diastereomers and the sequential distribution of the comonomers. For the same reason, in the ¹H NMR spectra, some signals are also split.

The IR spectra of the copolymers show absorption bands in the region 1200-1000 cm⁻¹ assignable to the SOE moieties, as well as absorptions at 1732 cm⁻¹ due to the carbonyl ester group and at 1242

and 1163 cm^{-1} due to $\text{P}=\text{O}$ absorption and corresponding to the phosphonate and phosphine oxide moieties, respectively.

weights, determined by size exclusion chromatography are shown in Table 1 within a range of 0.9×10^4 to 2.9×10^4 g/mol. The T_g values of the copolymers are also

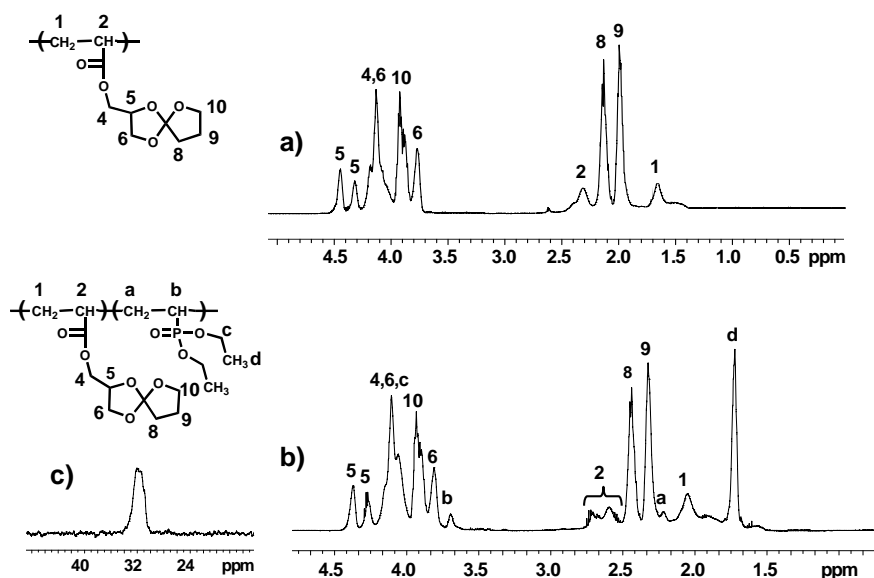


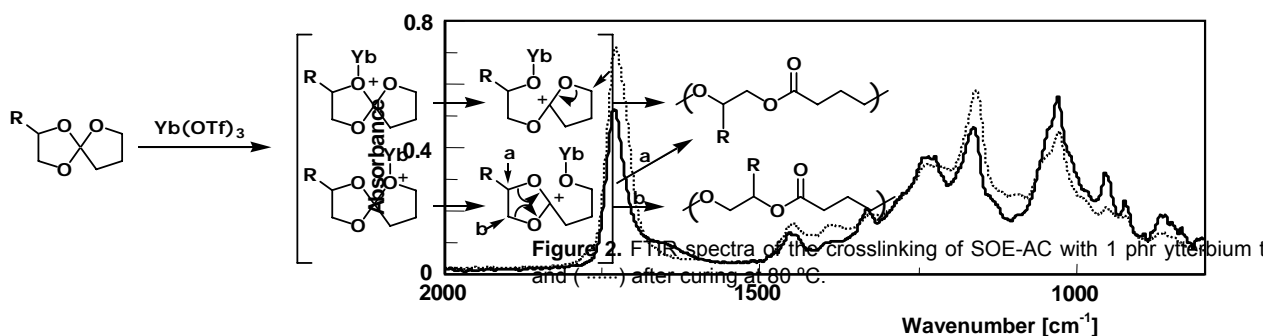
Figure 1. (a) ^1H NMR spectrum of homopolymer SOE-AC, (b) ^1H NMR spectrum of copolymer SOE-AC/DEVP (80/20), and (c) ^{31}P NMR spectrum of copolymer SOE-AC/DEVP (80/20).

In the copolymerizations, the initial feed ratios and the copolymer compositions observed were in excellent agreement for SOE-AC/DEVP and SOE-AC/DEMMP. However, the SOE-AC/ADPPO copolymers showed a lower than expected incorporation of the phosphorus-containing comonomer, with a more pronounced decreased incorporation at higher phosphorus feed ratio (Table 1). These results seem to indicate that the ADPPO monomer is less reactive than the other comonomers. The molecular

shown in Table 1. T_g in the DEVP and DEMMP copolymers decreased as the amount of the phosphorus-containing monomer increased. This was probably due to a decrease in the bulky and rigid SOE moieties. Upon the addition of the DEVP and DEMMP comonomers to SOE, there was an apparent decrease in T_g . This decrease may have been due to the ethylene units from the comonomer breaking up the stacking of the SOE. This was supported by the observation of reduced T_g values as the concentration of the phosphorus-

containing comonomers was further increased. When the comonomer ADPPO was added, an increase in T_g appeared. This may have been due to the aromatic units stabilizing the SOE stacking. However, upon further addition of ADPPO comonomer, there appears to be little additional effect.

The crosslinking reaction was monitored by FTIR/ATR spectroscopy in isothermal experiments at 80 °C. This technique allowed us to monitor the evolution of the groups involved in the reaction by means of the variations in the corresponding absorptions. Figure 2 shows the FTIR spectra of the SOE-AC



Scheme 3

The cationic crosslinking of all the synthesized polymers was performed with ytterbium triflate as the cationic initiator. This reaction occurs through the double ring-opening of pendant SOEs moieties, the mechanism of which has previously been reported.¹⁸⁻²⁰ This process occurs through an intermediate carbocation, stabilized by the adjacent oxygens, which gives rise to a poly(ether-ester) chain (Scheme 3). In the case of the SOE used in this paper, the reaction yielded crosslinking materials that were insoluble in common organic solvents.

homopolymer before and after isothermal crosslinking with 1 phr Yb(OTf)₃. The double ring opening of the SOE gave rise to the formation of a linear poly(ether-ester) moiety, which exhibit a typical carbonyl ester band²¹ at about 1735-1750 cm⁻¹. The acrylate derivatives used in this article contained an ester group that had a carbonyl band at 1732 cm⁻¹ and therefore overlapped the band observed during crosslinking. Therefore, only an increase in the intensity of this band could be observed during polymerization.

Table 2. T_g Values, Thermogravimetric Data in N_2 and Air, and LOIs of the Crosslinked

Polymer	T_g (°C)	$T_{5\%}^a$ (°C)		T_{max}^b (°C)		Char Yield at 800°C (wt%)		LOI
		N_2	Air	N_2	Air	N_2	Air	
SOE-AC	-12	185	144	219/384	212/380/555	13.3	0	23.5
SOE-AC/DEVP								
80/20	-13	185	210	231/365	266/362	25.0	5.2	26.7
63/37	-12	196	178	215/229/344	221/232/341	21.0	2.7	26.9
SOE-								
AC/ADPPO	4	199	222	251/399	310/400	11.5	3.7	26.7
81/19	4	210	228	244/400	295/398	10.6	5.3	26.8
77/23								
SOE-								
AC/DEMMP	-13	190	175	211/323	250/400	27.5	3.4	28.6
72/28	-14	170	158	203/301	202/297	27.6	6.3	28.9

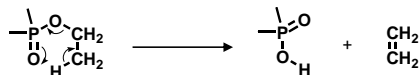
^a Temperature of 5% weight loss

^b Temperature of the maximum rate of degradation

The crosslinking of all linear copolymers was studied by differential scanning calorimetry (DSC). In the initial experiment performed, only a weak and broad exotherm was observed in all cases, and this did not allow an accurate determination of the reaction enthalpies. These low enthalpy values were in accordance with the low ring tension of SOEs and were in agreement with other reported data.²² Further DSC experiments were performed to evaluate T_g for the crosslinked copolymers (Table 2). The T_g 's of the crosslinking materials were lower than those of the linear precursors. This is an

unusual behaviour and can be explained if we take into account that, in the crosslinking, the bulky and rigid ring SOE becomes an aliphatic, linear chain and the decrease can be attributed to the highly flexible nature of the subsequent network.

The decomposition behaviour of the copolymers was studied with TGA under nitrogen and air atmospheres (Table 2). In the presence of a nitrogen atmosphere, the degradation of all the copolymers occurred at similar temperatures. However, in air, the degradation of SOE-AC/ADPPO started at a



Scheme 4

slightly higher temperature. It has been reported^{16,23} that polymers with alkyl phosphonate moieties can undergo an elimination of alkene, and a phosphorus acid derivative is produced, as shown in scheme 4. This phosphorus acid ester, or similar derivative, is capable of thermally decomposing at relatively low temperatures to give intermediates that can modify the degradation mechanism, such as transesterifications, anhydride group formation, and other reactions, to finally lead to a carbonaceous char. Thus, the DEVP and DEMMP copolymers could follow this mechanism. However, this was not the case for the phenyl-containing ADPPO copolymers. In addition, these materials showed several degradation steps at higher temperatures, and this was indicative of a more complex mechanism. The derivatives of the thermogravimetric plots showed various maxima (Table 2) that could be attributed to different degradation processes.

For the phosphorus-free resin, thermooxidative degradation took place at temperatures higher than 500 °C, whereas for the phosphorus-containing resins, it does not take place. This behaviour

is in accordance with the mechanism of actuation of phosphorus for improving fire resistance, in which the phosphorus forms an insulating, protective layer.

The LOI values, which can be taken as indicators for evaluating the flame retardancy of the phosphorus-modified polymers, were also measured and are shown in Table 2. The value for the SOE-AC homopolymer without phosphorus was the lowest, and the incorporation of phosphorus in the copolymers increased the LOI values; this was indicative of an improvement in the flame retardancy of the materials. However, the percentage of phosphorus used seemed to have little effect on any further increase in the LOI value, and this seems to indicate that the lowest phosphorus contents are enough to confer the flammability improvement.

Conventional wisdom in flame retardancy is when more char is produced upon burning, the flame-retardancy effect will be better. Because LOI value is an empirical measure of flame retardancy, we can expect there to be a strong correlation between the LOI and the char yield. However, in this case, the difference in the LOI values does not correspond to the char yields. Similar behaviour has been reported for other phosphorus-containing acrylates.

It has been reported that cationically double ring opened SOE-based materials exhibit almost no shrinkage and that copolymers having SOE moieties will also crosslink without shrinkage. Therefore, the volume changes in the crosslinking reaction of the copolymers containing SOE moieties were evaluated by density measurements with a Micromeritics gas pycnometer before and after

polymer. Thus, negative values indicate expansion.

In all cases, the observed values of the volume change were negative, and therefore the crosslinking process shows an expansion, although typical crosslinking reactions are generally accompanied by significant volume shrinkage.²⁴ In Table 3, it can be seen that the greater the SOE ratio

Table 3. Densities of the Copolymers before and after Crosslinking and Volume Changes upon Crosslinking.

Polymer	Density (d^{30} , g/cm ³)		Volume Change (%)
	Linear	Crosslinked	
SOE-AC	1.145	1.110	-3
SOE-AC/DEVP			
80/20	1.122	1.098	-2.1
63/37	1.119	1.097	-1.9
SOE-AC/ADPPO			
81/19	1.121	1.092	-2.6
77/23	1.120	1.092	-2.5
SOEAC-DEMMP			
72/28	1.128	1.098	-2.6
52/48	1.115	1.096	-1.7

crosslinking (Table 3). The volume change (Δ) was calculated from the following equation:

$$\Delta V (\%) = \frac{d_{\text{crosslinked polymer}} - d_{\text{linear polymer}}}{d_{\text{linear polymer}}} \times 100$$

where $d_{\text{crosslinked polymer}}$ is the density of the crosslinked polymer and $d_{\text{linear polymer}}$ is the density of the linear

polymer. The greater the expansion coefficient is. Therefore, it can be concluded that the SOEs moieties used here proved to be effective monomers for obtaining crosslinkable copolymers that do not shrink, regardless of the copolymer composition.

CONCLUSIONS

An SOE-containing monomer, SOE-AC, was radically homopolymerized and copolymerized with three phosphorus-containing monomers in various ratios. With ytterbium triflate as the cationic initiator, the crosslinking of the SOE moieties was achieved. SOE-AC/ADPPO, the only phosphorus-containing copolymer without alkyl phosphonate units, degraded at higher temperatures than the copolymers with alkyl phosphonate moieties. This indicated that the degradation followed a different mechanism. The incorporation of phosphorus into the copolymers increased the LOI values, thus improving the flame retardancy of the materials, regardless of the percentage of phosphorus used. All the crosslinked polymers showed expansion after crosslinking, regardless of their composition.

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