UNIVERSITAT ROVIRA I VIRGILI
SYNTHESIS OF POLYMERS WITH COMBINED FLAME RETARDANCE AND LOW SHRINKAGE PROPERTIES.
Judit Canadell Ayats
ISBN: T.1300-2007 / DL: T.1300-2007

SYNTHESIS OF A NOVEL BIS-SPIROORTHOESTER CONTAINING 9,10-DIHYDRO-9-OXA-10-PHOSPHAPHENANTRENE-10-OXIDE AS A SUBSTITUENT: HOMOPOLYMERIZATION AND COPOLYMERIZATION WITH DIGLYCIDYL ETHER OF BISPHENOL A

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Abstract

A new bis-spiroorthoester-containing monomer, bis[(1,4,6-trioxaspiro [4,4] nonan-2-yl)-methyl] 2-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide-10-yl)] maleate (SOE-DOPOMA), was synthesized with good yields by an esterification reaction with a hydroxylated spiroorthoester (2-hydroxymethyl-1,4,6-trioxaspiro-[4,4]-nonane) and a phosphorus-containing diacid (2-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide-10-yl)] maleic acid), both of which were previously synthesized. SOE-DOPOMA was characterized with ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. This new spiroorthoester was crosslinked with ytterbium triflate as a cationic initiator. A mixture of SOE-DOPOMA and diglycidyl ether of bisphenol A was also crosslinked under the same conditions. The curing was studied with differential scanning calorimetry and monitored with Fourier transform infrared spectroscopy. The materials were characterized with differential scanning calorimetry, termogravimetric analysis, and thermodynamomechanical analysis. The shrinkage effect on cationic crosslinking was assessed with gas pycnometry, and the flame retardant properties were determined with limiting oxygen index measurements.

Keywords: cationic polymerization; curing of polymers; epoxy resins; flame retardancy; ring opening

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INTRODUCTION

Epoxy networks are very versatile materials that can be used in a wide number of applications. Each application has some requirements that include a combination of physical, mechanical, and other specific properties. In many industrial applica-tions such as industrial casting, coatings, and microelectronics, shrin-kage during curing is a major problem because it leads to poor adhesion to the substrate, delamination, and microvoids and microcracks, which reduce the durability of the material.[1] Another disadvantage of epoxy resins is that they are more flammable than similar thermosets, because they have a reduced tendency to carbonize. To reduce this flamma-bility, both halogenated and inorganic flame retardants have been used.[2] The generation and release of toxic, corrosive, and halogenated gases in the combustion of polymers when halogen flame retardants are used might be avoided with a halogen-free flame retardant in polymeric materials. Therefore, phosphorus-containing polymers, which have been reported to have great flame retardancy, have been widely investigated in recent years.[3] Polyme-rization with phosphorus monomers and polymer modification with phosphorus compounds have both been used to obtain phosphorus-containing polymers, the former method having the advantages of convenience in molecular design, synthesis diversity, and polymer property modulation, which can allow the modification of various properties simultaneously.

The goal of this work is to develop a new phosphorus-containing mono-mer bearing spiroorthoester (SOE) groups. SOEs are considered *expanding monomers*,[1] a term that refers to monomers that lead to zero shrinkage or even positive expansion during polymerization. Some kinds of cyclic monomers have been reported to maintain their volume or actually expand during double ring-opening polymerization.[4-6] SOEs can be synthesized from epoxides and lactones[7,8] and undergo cationic ring-opening polymerization by Lewis acid catalysts. Moreover, SOEs can copolymerize with epoxides and therefore can be used to modify epoxy resins, reducing their shrinkage during curing, which leads to significant change in the volume.

In a previous work,[9] we synthesized a phosphorus-containing SOE from 9,10- dihydro-9-oxa-10-phosphaphe-nantrene-10-oxide (DOPO), which was

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homopolymerized and copolymerized with phenyl glycidyl ether, using as a cationic initiator ytterbium triflate, a Lewis acid, that can cure epoxy resins.[10,11] Lanthanide triflates are commercially available and have many advantages over BF_3 derivatives and alkylating agents because they maintain their catalytic activity even in the presence of water.[12]

In this work, we synthesized a bis-spiroorthoester (bis-SOE) monomer from DOPO: bis[(1,4,6-trioxaspiro-[4,4]-nonan-2-yl)-methyl] 2-[10-(9,10-dihydro-9-oxa-10-phosphaphenan-trene-10-oxide-10-yl)] maleate (SOE-DOPOMA). DOPO with an active hydrogen can react with electron-deficient compounds such as maleic acid[13] and subsequently with an hydroxylic compound bearing an SOE moiety. The incorporation of the rigid and bulky phosphorus-containing DOPO confers good flame-retardant properties to materials. This approach allows both flame retardancy and expanding properties in the bis-SOE monomer, which can be crosslinked by a double ring-opening using ytterbium triflate as cationic initiator. This bis-SOE was also copolymerized with diglycidylether of bisphenol A (DGEBA) to obtain modified epoxy resins with lower shrinkage and flame- retardant properties than conventional epoxy resins.

The curing was studied with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The materials were characterized with DSC, thermo-gravimetric analysis (TGA), and thermodynamomechanical analysis (DMTA). The shrinkage effects during the cationic crosslinking were assessed with gas pycnometry. The flame-retardant properties were determined with limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

Commercial DOPO was kindly supplied by Aismalibar and purified before use via heating at 130 ºC in vacuo for 2 h and then gradual heating to 150 ºC. The purified product was cooled to room temperature under an argon atmosphere. Maleic acid (Merck); epibromo-hydrin (Fluka); glycidol (Aldrich); γ-butirolactone (γ-BL; Aldrich), boron trifluoride diethyl etherate ($BF_3.OEt_2$; Aldrich), triethylamine (Fluka), 1,8-diazabicyclo[5.4.0]-undec-7-en (DBU; Aldrich), N-(3-dimethylaminopropyl)-N'-ethyl-carbodiimide hydrochloride (EDC; Fluka), 4-(dimethylamino)py-ridine (DMAP; Fluka), DGEBA (Epikote Resin 827, Shell Chemicals; epoxy equivalent = 182.08 g/equiv), ytterbium(III) trifluoromethanesulfonate [($Yb(OTf)_3$; Aldrich] were used as received. All solvents were purified by standard procedures.

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Instrumentation

The microwave-irradiated reaction was carried out in a 10-mL reactor vial with a CEM Discover monomodal microwave reactor and an IR temperature sensor at a maximum power of 300 W.

NMR spectra (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; and ^{31}P, 161.9 MHz) were obtained with a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ or DMSO as the solvent, and with tetramethylsilane or phosphoric acid as the internal standard.

Calorimetric studies (DSC) were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at scanning rates of 10 ºC/min in the first scan and 20 ºC/min in the second. The samples weighed approximately 8 mg.

The isothermal crosslinking process at 120 ºC was monitored with a 680 Plus FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with a thermal control and a diamond crystal was used to determine the FTIR/ATR spectra.

TGAs were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 10 mg were degraded between 30 and 800 ºC at a heating rate of 10 ºC/min in an atmosphere of N_2 or air.

DMTA were carried out with TA DMA 2928 working with a three-point bending clamp from 30 to 200 ºC at a heating rate of 3 ºC/min.

The densities of the materials were measured with a Micromeritics Accupyc 1330 TC gas pycnometer at 30 ºC.

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

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

Epibromohydrin (50 g, 0.36 mol) was added dropwise over a period of 15 min at a temperature below 10 ºC in an argon atmosphere to a mixture of 180 g (2.09 mol) of γ-BL and 1.5 mL (11.8 mmol) of $BF_3.OEt_2$ 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. After the solvent was removed under reduced pressure, the residue was distilled fractionally to yield 60.4 g (74 %) of a transparent, colorless liquid.

^{1}H 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-CH_2-), 3.98-3.87 (m, 6H, -O-CH_2-), 3.91-3.31 (m, 4H, Br-CH_2-), 2.20-2.11

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(m, 4H, -CH_2-), 2.05-1.98 (m, 4H, -CH_2-).

^{13}C 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-CH_2-), 67.68 (s, -O-CH_2-), 67.40 (s, -O-CH_2-), 67.38 (s, -O-CH_2-), 32.87 (s, -CH_2-), 32.81 (s, -CH_2-), 32.74 (s, Br-CH_2-), 32.28 (s, Br-CH_2-), 24.20 (s, -CH_2-), 24.05 (s, -CH_2-).

Synthesis of 2-hydroxymethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-OH)

Glycidol (30 g, 0.40 mol) was added dropwise over a period of 15 min at a temperature below 10 ºC in an argon atmosphere to a mixture of 200 g (2.3 mol) of γ-BL and 1.0 mL (7.9 mmol) of BF_3.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 1.4 mL (10 mmol) of triethylamine. After the solvent was removed under reduced pressure, the residue was distilled fractionally to yield 11.2 g (17%) of a transparent, colorless liquid.

^{1}H NMR ($CDCl_3$, two diastereomers): δ(ppm) = 4.41-4.32 (m, 2H, -O-CH-), 4.14-4.03 (m, 2H, -O-CH_2-), 3.99-3.89 (m, 4H, -O-CH_2-), 3.85-3.80 (m, 2H, -O-CH_2-), 3.73-3.54 (m, 4H, -CH_2-OH), 2.89 (br, 2H, OH), 2.18-2.12 (m, 4H, -CH_2-), 2.05-1.97 (m, 4H, -CH_2-).

^{13}C NMR ($CDCl_3$, two diastereomers): δ(ppm) = 129.60 (s, spiranic C), 129.32 (s, spiranic C), 75.99 (s, -O-CH-), 67.42 (s, -O-CH_2-), 65.69 (s, HO-CH_2-), 64.92 (s, HO-CH_2-), 62.81 (s, -O-CH_2-), 62.54 (s, -O-CH_2-), 32.67 (s, -CH_2-), 32.50 (s, -CH_2-), 24.51 (s, -CH_2-), 24.35 (s, -CH_2-).

Synthesis of 2-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxi-de-10-yl)] Maleic Acid (DOPOMA)

Into a 250-mL, round-bottom flask equipped with a condenser, 20 g (92.5 mmol) of DOPO, 30 mL of xylene, and 30 mL of THF were introduced. The flask was heated to 80 ºC under an argon atmosphere with vigorous stirring. After the complete dissolution of DOPO, 10.74 g (92.5 mmol) of maleic acid was added for 1 h, and the reaction mixture was maintained at that temperature for 20 h. After cooling to room temperature, the reaction product was filtered, washed with a mixture of xylene and THF (1/1) three times, and then dried in an oven at 120 ºC to yield 24.7 g (80%) of a white powder (mp = 222 ºC, DSC).

^{1}H NMR (DMSO, two diastereomers): δ(ppm) = 12.63 (br, 4H, -OH), 8.24-8.15 (m, 4H, Ar-H), 8.05-7.79 (m, 4H, Ar-H), 7.65-7.59 (m, 2H, Ar-H), 7.47-7.44 (m, 2H, Ar-H), 7.34-7.24 (m, 4H, Ar-H), 3.72-3.64 (m, 1H, -CH-), 3.52-3.43 (m,

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1H, -CH-), 2.92-2.82 (m, 2H, -CH_2-), 2.70-2.61 (m, 2H, -CH_2-).

^{13}C NMR (DMSO, two diastereomers): δ(ppm) = 172.06 (d, J_{C-P} = 18.3 Hz, C=O), 171.89 (d, J_{C-P} = 18.3 Hz, C=O), 168.62 (d, J_{C-P} = 4.6 Hz, C=O), 148.74 (d, J_{C-P} = 8.3 Hz, Ar-C), 135.21 (d, J_{C-P} = 6.1 Hz, Ar-C), 134.29 (s, Ar-CH), 134.12 (s, Ar-CH), 131.25 (s, Ar-CH), 131.13 (d, J_{C-P} = 10.7 Hz, Ar-CH), 128.85 (d, J_{C-P} = 13.9 Hz, Ar-CH),125.93 (s, Ar-CH), 125.78 (s, Ar-CH), 125.28 (s, Ar-CH), 125.08 (s, Ar-CH), 124.42 (d, J_{C-P} = 9.9 Hz, Ar-CH), 124.28 (d, J_{C-P} = 9.9 Hz, Ar-CH), 122.71 (d, J_{C-P} = 124.3 Hz, Ar-C), 122.62 (d, J_{C-P} = 124.5 Hz, Ar-C), 121.68 (d, J_{C-P} = 10.8 Hz, Ar-C), 121.37 (d, J_{C-P} = 10.6 Hz, Ar-C), 120.28 (d, J_{C-P} = 6.1 Hz, Ar-CH), 120.21 (d, J_{C-P} = 6.1 Hz, Ar-CH), 43.82 (d, J_{C-P} = 83.9 Hz, -CH-), 42.97 (d, J_{C-P} = 86.2 Hz, -CH-), 30.13 (d, J_{C-P} = 22.1 Hz, -CH_2-).

^{31}P NMR (DMSO, two diastereomers): δ(ppm) = 31.25 (s); 30.72 (s)

Synthesis of SOE-DOPOMA

Way A

Conventional Heating. Into a three-necked, 100 mL, round-bottom flask equipped with an argon inlet, a condenser and a magnetic stirrer, 0.5 g (1.5 mmol) of DOPOMA was dissolved in 10 mL of anhydrous DMSO. After the complete dissolution, 0.45 mL (3.0 mmol) of DBU was added. The brown solution was heated to 50 ºC; then 0.67 g (3.0 mmol) of SOE-Br with 10 mL of DMSO was added slowly. After the complete addition of SOE-Br, the reaction mixture was maintained at that temperature for 12 h to ensure completion of the reaction. After it cooled at room temperature, water was added, and then the product was obtained by several extractions with CH_2Cl_2 (4 x 30 mL). The product was purified by several washes with dilute solution of HCl and then was neutralized with a solution of NaOH. The dichloromethane solution was dried over $MgSO_4$ and the solvent was evaporated to yield a brown, viscous oil that was a complex mixture where (1,4,6-trioxaspiro[4,4]nonan-2-yl)-me-thyl 3-[10-(9,10-dihydro-9-oxa-9-phosphaphenantrene-10-oxide-10-yl)]-propanoate (SOE-P) was detected.

Microwave irradiation. In a microwave reactor vial (10 mL) equipped with a magnetic stirring bar, 0.1 g (0.3 mmol) of DOPOMA was dissolved in 1.5 mL of anhydrous DMSO. After the complete dissolution, 90 μl (0.6 mmol) of DBU and 0.135 g (0.6 mmol) of SOE-Br were added. The vial was purged with argon.

The maximum power setting of 50 W was maintained until the desired temperature (130 ºC) was reached (160 s). The power was reduced to 27 W for the remainder of the reaction time to maintain 130 ºC.

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After 60 min, the reaction mixture was cooled to room temperature. The purification was performed in the same way that in conventional heating to yield a yellowish, viscous oil that corresponds to SOE-P.

Other microwave assays were performed with a similar procedure at different temperatures: 100 ºC (12 W), 80 ºC (8 W) and 65 ºC (5 W) leading in all cases to the same result.

Table 1. Compositions (wt % P), DSC Data, and Curing Conditions of the

Assay	Sample	P	ΔH (J/g)[a]	ΔH (KJ/ee)[b]	T_{max} wt(%) (ºC)[d]	Tg (ºC)	Curing Conditions	
							Temperature (ºC)	Time (h)
1	SOE-DOPOMA	5.0	31.1	9.7[c]	207	94	180	5
2	DGEBA/SOE-DOPOMA	2.7	141.7	106.0	165/184	103	140 160	3 2
3	DGEBA	0	54.24	70.2	215	130	150	5

[a] Enthalpies per gram of mixture.
[b] Enthalpies expressed by equivalent epoxy.
[c] Enthalpy expressed by equivalent SOE.
[d] Temperature of the maximum heat release rate.

Way B

Under an argon atmosphere, an oven-dried 100 mL, round-bottom flask containing 20 mL of anhydrous dichloromethane was charged with 0.50 g (1.5 mmol) of DOPOMA, 0.53 g (3.3 mmol) of SOE-OH, 0.60 g (3.1 mmol) of EDC, and 0.38 g (3.1 mmol) of DMAP. The brown solution was stirred and heated at 40 ºC for 4 h. After cooling to room temperature, the solution was washed with two 30-mL portions of a 10% citric acid solution, twice with 30-mL portions of a 10% sodium bicarbonate solution, and twice with brine. The organic solution was dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation to give 0.66 g (71%) of a white solid (mp= 58-60 ºC).

^{1}H NMR ($CDCl_3$, diastereomers mixture): δ(ppm) = 7.98-7.87 (m, 3H, Ar-H); 7.74 (m, 1H, Ar-H); 7.55 (m, 1H, Ar-H); 7.38 (m, 1H, Ar-H); 7.27-7.22 (m, 2H, Ar-H); 4.42-3.17 (m, 15H, -O-CH-, -COO-CH_2-, -O-CH_2-, -P-CH-); 2.99-2.95 (m, 2H, CH_2-CO-); 2.93-1.60 (m, 8H, -CH_2-).

^{13}C NMR ($CDCl_3$, diastereomers mixture): δ(ppm) = 170.82 (d, J_{C-P} = 17.68 Hz, -C=O); 170.77 (d, J_{C-P} = 17.50 Hz, C=O), 170.48 (d, J_{C-P} = 16.80 Hz, C=O); 170.65 (d, J_{C-P} = 17.50 Hz, C=O); 170.60 (d, J_{C-P} = 16.80 Hz, C=O); 170.54 (d, J_{C-P} = 16.80 Hz, C=O); 167.29 (br, C=O); 167.00 (d, J_{C-P} = 4.12 Hz, C=O); 166.97 (d, J_{C-P} = 4.12 Hz, C=O), 149.06 (d, J_{C-P} = 9.15 Hz, Ar-C); 136.11 (d, J_{C-P} = 6.13 Hz, Ar-C); 134.19 (br, Ar-CH); 131.36 (br, Ar-CH); 131.97 (br, Ar-CH); 129.79 (s, spiranic C); 129.67 (s, spiranic C); 129.61 (s, spiranic C); 129.49 (s, spriranic C); 128.68 (d, J_{C-P} = 13.78 Hz, Ar-CH); 125.16 (s, Ar-CH); 125.06 (s, Ar-CH); 123.81 (s, Ar-CH); 122.56 (br, Ar-CH-); 121.51 (d, J_{C-P} = 125.07 Hz, Ar-C); 121.43 (d, J_{C-P} = 125.67 Hz, Ar-C); 121.34 (d, J_{C-P} = 10.70 Hz, Ar-C); 120.48 (d,

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J_{C-P} = 6.23 Hz, Ar-CH); 120.24 (d, J_{C-P} = 6.33 Hz, Ar-CH); 73.83 (s, -O-CH-); 73.17 (s, -O-CH-); 73.11 (s, -O-CH-); 73.00 (s, -O-CH-); 72.96 (s, -O-CH-); 72.48 (s, -O-CH-); 67.34 (s, -O-CH_2-); 67.28 (s, -O-CH_2-); 67.18 (s, -O-CH_2-); 66.48 (s, -O-CH_2-); 66.38 (s, -O-CH_2-); 66.18 (s, -O-CH_2-); 66.13 (s, -O-CH_2-); 65.78 (s, -O-CH_2-); 65.62 (s, -O-CH_2-); 65.04 (s, -COO-CH_2-); 64.89 (s, -COO-CH_2-); 44.49 (d, J_{C-P} = 85.53 Hz, -P-CH-); 44.45 (d, J_{C-P} = 85.12 Hz, -P-CH-); 44.41 (d, J_{C-P} = 86.94 Hz, -P-CH-); 43.48 (d, J_{C-P} = 87.04 Hz, -P-CH-); 32.61 (s, -CH_2-); 30.39 (br, -CH_2-CO-); 29.85 (br, -CH_2-COO-); 24.19 (s, -CH_2-); 24.26 (s, -CH_2-); 24.01 (s, -CH_2-).

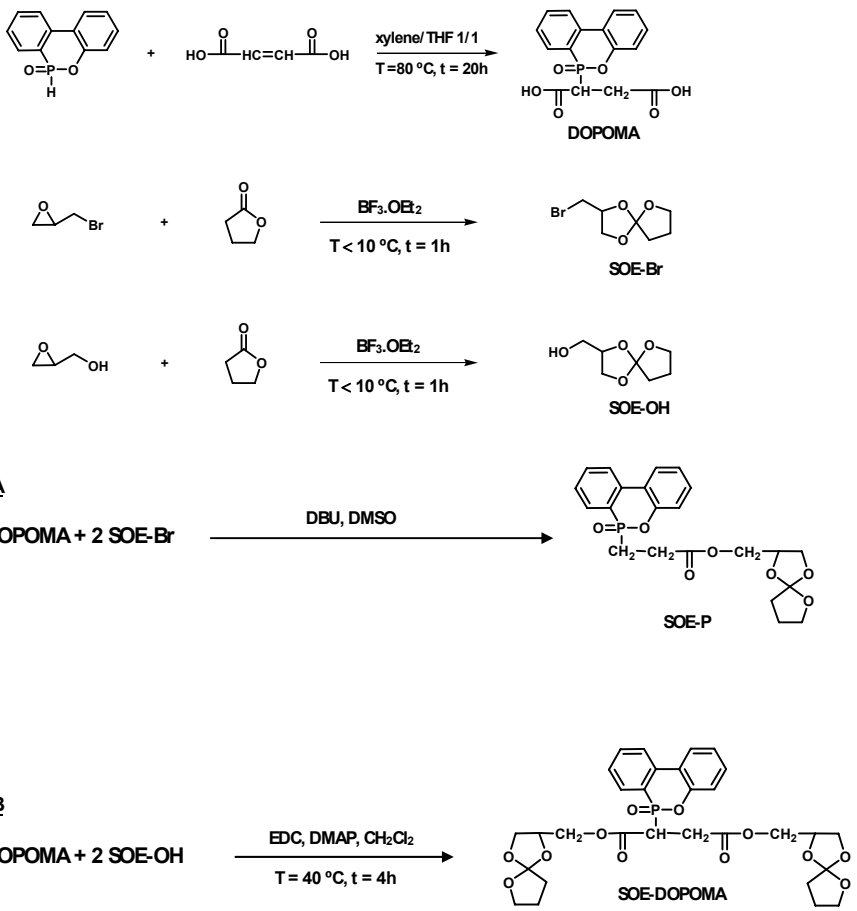
^{31}P NMR ($CDCl_3$, diastereomers mixture): δ(ppm) = 29.68 (s); 29.66 (s); 29.53 (s); 29.50 (s); 29.48 (s); 29.47 (s); 29.43 (s); 29.41 (s); 29.35 (s); 29.31 (s); 29.28 (s); 29.26 (s); 29.23 (s); 29.18 (s); 29.12 (s); 29.01 (s).

Crosslinking Reaction

The cationic crosslinking reactions were carried out through the mixing of the corresponding monomers with 1.5 phr ytterbium triflate (1 phr = 1 part per 100 parts of the monomer mixture weight/weight). The molar ratio used in the copolymerization of DGEBA and SOE-DOPOMA was 2:1. The sample bars used for dynamo-mechanical analysis, TGA, and burn tests were cured in aluminium molds by heating in an oven. The curing conditions were determined from DSC data and are listed in Table 1.

RESULTS AND DISCUSSION

The synthesis of SOE-DOPOMA was carried out with the two



Scheme 1

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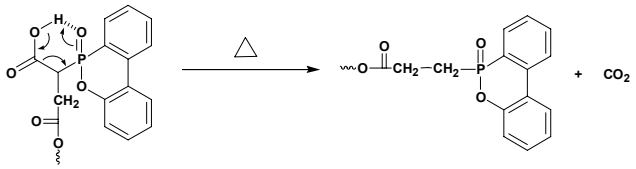
synthetic pathways shown in Scheme 1. First, we synthesized the substituted maleic acid, DOPOMA, as previously described.[13] This synthetic step consisted of the incorporation of DOPO by means of a conjugated addition reaction to the α,β-unsaturated dicarboxylic acid. When DOPO reacts with a double-bond-containing compound, the structures of the double-bond-containing compounds have a significant influence on the reaction rate. For example, when DOPO reacts with a compound with only one electron-withdrawing carbonyl group next to the double bond, such as itaconic acid, the reaction is very slow, even at 140 ºC,[13] whereas the reaction with two electron-withdrawing carbonyl groups next to the double bond, such as maleic acid or benzoquinone,[14] occurs at about 70-90 ºC. The second intermediate synthesized was SOE-Br. This compound was prepared from epibromohydrin and γ-BL[15] with $BF_3{\cdot}OEt_2$ as a catalyst, and its structure was confirmed by spectroscopic experiments. The reaction of SOE-Br with DOPOMA to obtain SOE-DOPOMA was initially carried out in the presence of DBU in DMSO at different temperatures under an argon atmosphere (way A). Direct ester formation from a primary halide and a carboxylic acid using DBU is a useful method that has been used by several authors.[15,16] This method also leads to good results in polymer modification.[17-19] However, in this case, after 12 h of reaction, we obtained a complex mixture which SOE-P was detected. The presence of this compound could be confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra.[9] The formation of SOE-P can be explained by a thermal decarboxylation reac-tion similar to β-keto acid decar-boxylations, as shown in Scheme 2. This decarboxylation takes place in the monosubstituted compound in C-1 because the other possible product of monosubstitution (in C-4) cannot undergo thermal β-decarboxylation.



Scheme 2

One way to avoid this and other undesirable transformations of the organophosphorus compounds is to reduce the reaction time. One promising approach to reducing the reaction time is the application of microwaves energy. Microwave irradiation offers a number of advantages over conventional hea-

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ting, such as noncontact heating, which for many organophosphorus compounds is very important, and rapid and highly specific heating.[20,21]

Thus, the reaction was carried out in a microwave reactor with anhydrous DMSO as solvent and DBU as a catalyst. Initially, a power of 27 W at 130 ºC was applied. After 1 h of reaction and further purification, an oil was obtained, which was identified as SOE-P by NMR spectroscopy. To avoid this undesired reaction, lower temperatures: 100 ºC (12W), 80 ºC (8W) and 65 ºC (5W) were tested. In this way, SOE-DOPOMA was obtained but always together with SOE-P.

To improve these results, another synthetic way was followed. Pathway B uses the esterification reaction of DOPOMA with SOE-OH in the presence of EDC and DMAP.[22] We use water soluble EDC as an alternative to dicyclohexylcarbodiimide because its

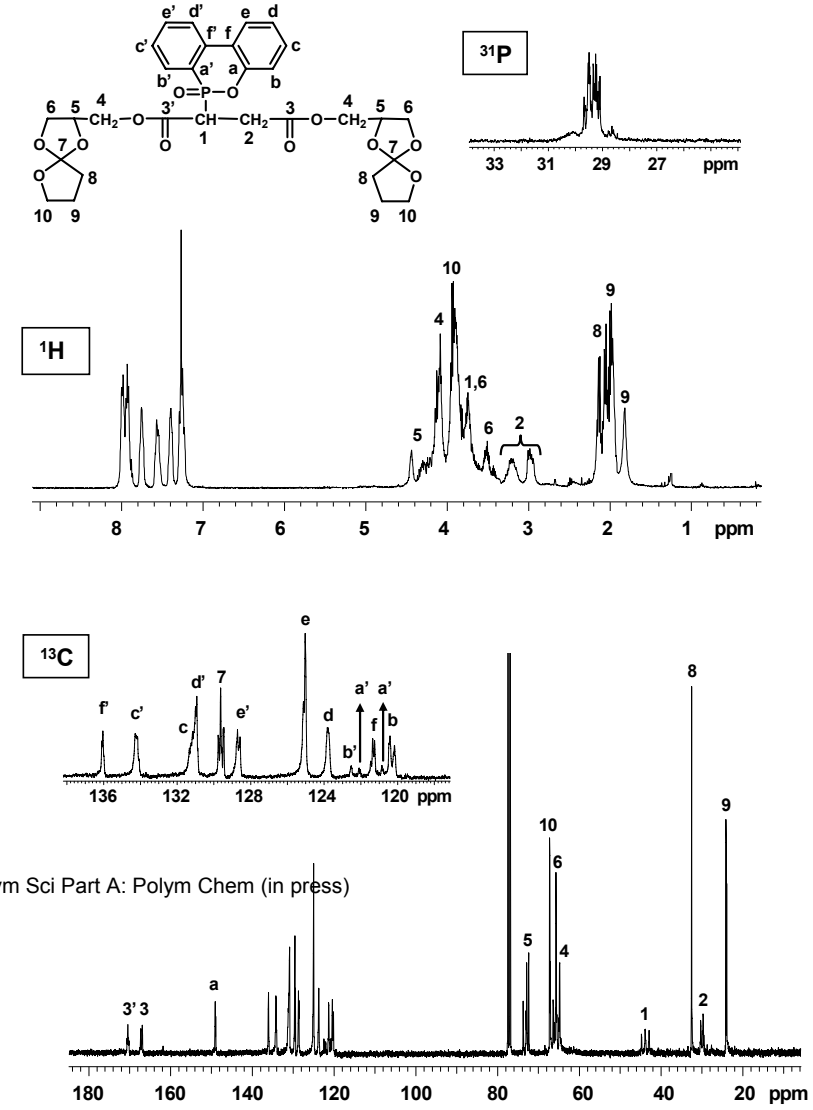

Figure 1. ^{31}P, ^{1}H, and ^{13}C NMR spectra of SOE-DOPOMA.

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elimination was easier and we obtained better yields. SOE-OH was synthesized from γ-BL and glycidol by a procedure similar to that described by Nishida et al.[6] for other hydroxylic SOEs. By this procedure, a solid product was obtained with a good yield.

This novel phosphorus-containing bifunctional SOE, SOE-DOPOMA, was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Because of the several chiral centers in the molecule, a mixture of diastereomers was formed. Figure 1 shows the ^{31}P, ^{1}H, and ^{13}C NMR spectra, with all assignments. The single ^{31}P signal is split because of the presence of the different diastereomers. In ^{1}H and ^{13}C NMR spectra, some signals are also split for the same reason. The SOE ring and aromatic protons and carbon signals could be assigned unequivocally by means of gHSQC and COSY experiments and by comparison with the DOPOMA and SOE-P spectra.[9] Although the two SOEs and the methylene directly attached to them are nonequivalent, their signals in both ^{1}H, ^{13}C spectra are not different. However, carbonylic carbons appear as two different signals.

As we previously mentioned, we are interested in using this phosphorus-containing monomer to modify epoxy resins. In the cationic copolymer-ryzation of DGEBA and SOE-DOPOMA, three simultaneous processes are expected (Scheme 3): (a) the reaction of SOE with epoxy groups, (b) the homopolymerization of SOE, and (c) the homopolymerization of epoxy groups. Processes a and b lead to the formation of linear ether-ester moieties, whereas reaction c leads only to ether linkages. The homo-polymerization of SOE-DOPOMA and its copolymerization with DGEBA were carried out with 1.5 phr ytterbium triflate as a cationic initiator. Figure 2 shows the dynamic DSC plots of these reactions. For comparison, the corresponding DGEBA curve is also included in the figure. The enthalpy of the SOE-DOPOMA homopolyme-rization is very low, corresponding to the ring opening of a nontensionated spiroorthoesther.[23] The maximum of the exotherm of both homopolyme-rizations (SOE-DOPOMA and DGEBA) appears at a higher temperature than that of the copolymerization. Howe-ver, this copolymerization shows two maxima, indicating that more than one process occurs. From these dynamic experiments, the

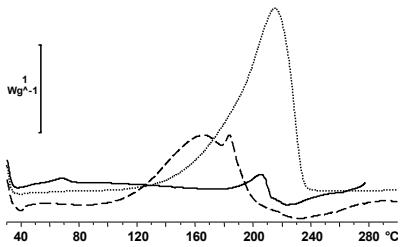

Figure 2. Dynamic DSC plots of (⟶) SOE-DOPOMA; (⊢ ⊣) 2/1 (mol/mol) DGEBA/SOE-DOPOMA, (·····) DGEBA initiated by 1.5 phr $Yb(OTf)_3$ obtained at a 10 ºC/min heating rate.

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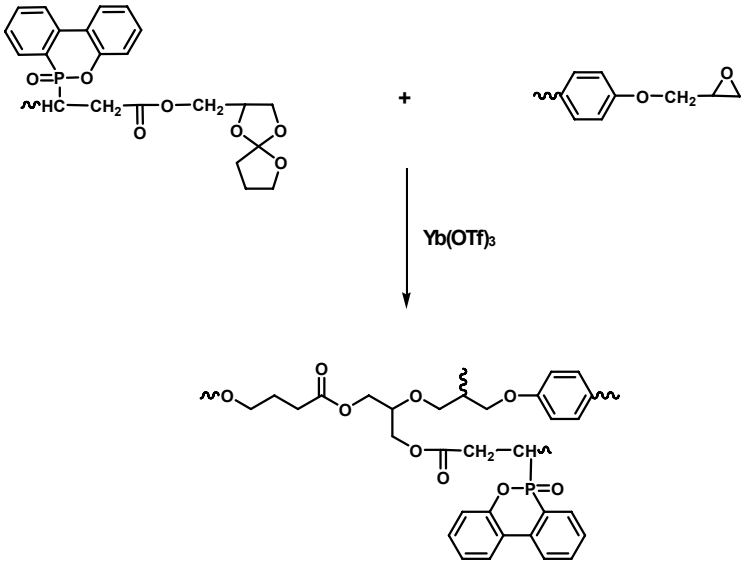
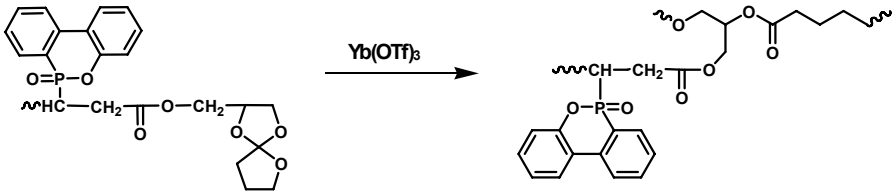
isothermal curing conditions were established. For the copolymerization of 2/1 (mol/mol) DGEBA/SOE-DOPOMA mix-ture, the curing conditions were 140 ºC for 3 h and then 160 ºC for 2 h. The

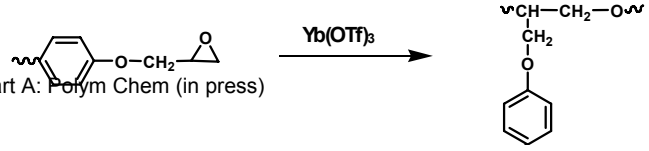
a) Reaction of SOE-DOPOMA with DGEBA



b) Homopolymerization of SOE-DOPOMA



c) Homopolymerization of DGEBA



Scheme 3

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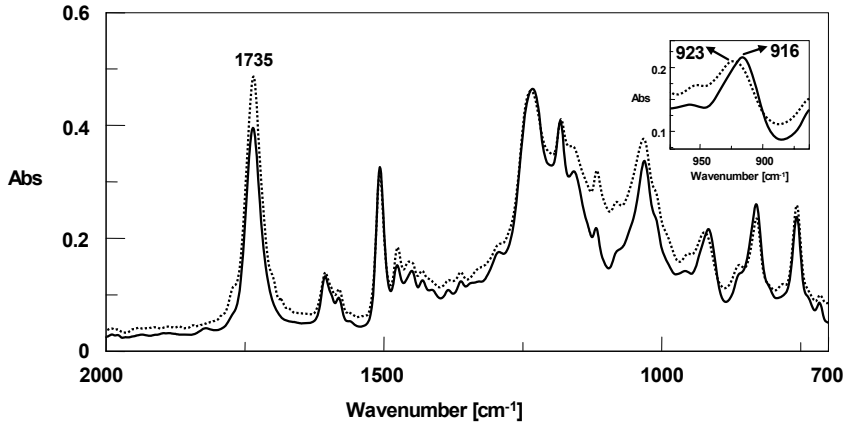

Figure 3. FTIR spectra of 2/1 (mol/mol) DGEBA/SOE-DOPOMA with 1.5 phr $Yb(OTf)_3$ before (──) and after (·····) polymerization at 120 ºC.

enthalpy values, temperatures of the maximum of the exotherms, phos-phorus contents, and curing condi-tions are collected in Table 1. A dynamic run for the cured samples allowed us to calculate the glass transition temperature (T_g) values (Table 1). The copolymer T_g is between the T_g values of the two homo-polymers.

The copolymerization reaction was monitorized by FTIR-ATR spectros-copy in isothermal experiments at 120 ºC. This technique allowed us to follow the evolution of the groups involved in the process by means of the variations in the corresponding absorptions. Figure 3 shows the FTIR spectra of the DGEBA/SOE-DOPOMA mixture with 1.5 phr $Yb(OTf)_3$ before and after polymerization. The double ring-opening of SOE that took place during the polymerization led to a linear poly(ether-ester) group forma-tion; thus, a typical band of carbonyl ester group must appear[24] around 1735-1750 cm^{-1}. SOE-DOPOMA con-tains ester groups that appear at 1735 cm^{-1} in the initial spectrum, and therefore in this zone only an increase in this band was observed upon polymerization. Unfortunately, the disappearance of the typical epoxy band at 916 cm^{-1} could not be confirmed by FTIR because the initial SOE presented absorptions in the same zone. Therefore, we confirmed the total epoxy reaction by DSC. A dynamic scan of the sample cured in FTIR did not show any residual enthalpy.

To study the different processes that occur during crosslinking, we calcu-lated the conversion of SOE groups by calculating the increase of the band at 1735 cm^{-1}. The band at 916 cm^{-1}

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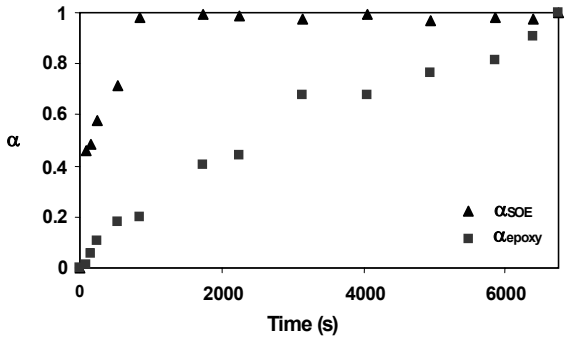

Figure 4. α_{SOE} and α_{epoxy} versus time for the 2/1 (mol/mol) DGEBA/SOE-DOPOMA reaction system with 1.5 phr $Yb(OTf)_3$ cured in an FTIR spectrometer at 120 ºC.

overlaps the band associated with the O-P-Ph moiety of SOE-DOPOMA, which appears at about 920 cm^{-1}.[25] As the intensity of this band must not change during the reaction, the diminution observed in this zone during the crosslinking may be attributed to the reaction of the epoxy groups. Therefore, the conversion of the epoxy group was calculated by this difference. During the crosslinking the maximum of this band was shifted to 923 cm^{-1}.

The absorbances were calculated in terms of the peak areas. The conver-sions of the epoxy and SOE groups (α_{epoxy} and α_{SOE}, respectively) were determined by the Lambert-Beer law from the normalized changes in the absorbance with respect to the band at 1507 cm^{-1} corresponding to the phenyl group in DGEBA, and the conversions were calculated with the following equations:

$$\alpha_{SOE} = \left(\frac{\overline{A}^{t}_{1735}}{\overline{A}^{\infty}_{1735}} \right)$$

$$\overline{A}^{t}_{1735} = \frac{A^{t}_{1735}}{A^{t}_{1507}} - \frac{A^{0}_{1735}}{A^{0}_{1507}} \qquad \overline{A}^{\infty}_{1735} = \frac{A^{\infty}_{1735}}{A^{\infty}_{1507}} - \frac{A^{0}_{1735}}{A^{0}_{1507}}$$

Figure 4 shows the conversions against the time. As we can see, the SOE group reacts very fast in the beginning of the process up to a conversion of about 0.5 and reaches its maximum conversion below 1000 s. On the other hand,

$$\alpha_{epoxy} = 1 - \left(\frac{\overline{A}^{t}_{916}}{\overline{A}^{0}_{916}} \right)$$

$$\overline{A}^{t}_{916} = \frac{A^{t}_{916}}{A^{t}_{1507}} - \frac{A^{\infty}_{923}}{A^{\infty}_{1507}} \qquad \overline{A}^{0}_{916} = \frac{A^{0}_{916}}{A^{0}_{1507}} - \frac{A^{\infty}_{923}}{A^{\infty}_{1507}}$$

the evolution of epoxy group steadily progresses up to the complete reaction. It must be noted that the epoxy/SOE group ratio is 2:1 in the initial mixture. In the first

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stages of the crosslinking, when SOE is present in the mixture reaction, processes a and b in Scheme 3 must be more significant, and then, when SOE is run out, process c predomi-nantly occurs.

The dynamic mechanical behavior of the crosslinked materials was obtained as a function of the temperature from the glassy state to the rubbery plateau of each material. The crosslinking density of a polymer can be estimated from the plateau of the elastic modulus in the rubbery state.[26] However, this theory is strictly valid only for slightly crosslinked materials and is therefore used only to make qualitative comparisons of the level of crosslinking among the various polymers. As can be seen in Figure 5, the incorporation of SOEs reduces the crosslinking density. Therefore, samples 1 and 2 show a lower storage modulus in the rubbery state. This is due to the greater distance between knots produced by the linear ether-ester moieties introduced in the network by SOEs.

Figure 6 shows tan δ versus tem-perature for the crosslinked materials. The highest T_g value corresponds to the more aromatic DEGBA homo-polymer. As the height of the tan δ peak is associated with the crosslin-king density, the lowest density of crosslinking corresponds to the SOE-homopolymer. The peak width at half-height broadens as the number of branching modes increases, and this produces a wider distribution of structures. The copolymer shows a broad curve in which, moreover, it is possible to detect two maxima indi-cating the non-homogeneity of the material.

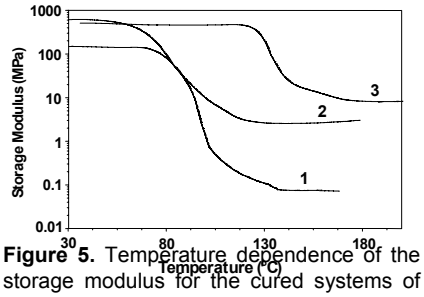

Figure 5. Temperature dependence of the storage modulus for the cured systems of **(1)** SOE-DOPOMA, **(2)** 2/1 (mol/mol) DGEBA/SOE-DOPOMA, and **(3)** DGEBA.

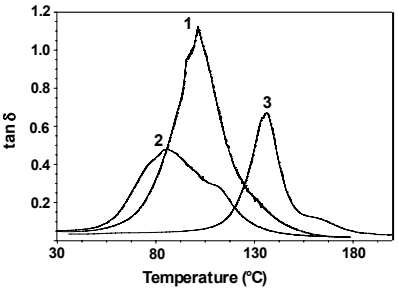

Figure 6. Temperature dependence of tan δ for the cured systems of **(1)** SOE-DOPOMA, **(2)** 2/1 (mol/mol) DGEBA/SOE-DOPOMA, and **(3)** DGEBA.

It has been reported that cationic double ring-opened SOE-based mate-rials exhibit almost no shrinkage and that copolymers having SOE moieties will also crosslink without shrinkage.

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Therefore, the volume changes (Δ) in the crosslinking reaction of the copolymers containing SOE moieties were evaluated by density measure-ments with a Micromeritics gas pyc-nometer before and after crosslinking (Table 2). Δ was calculated from the following equation:

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

where d is the density. Thus, negative values indicate expansion.

In SOE-containing samples 1 and 2, the observed values of Δ were negative, and therefore the cross-linking process shows an expansion greater for sample 1, which corres-ponds to pure SOE. Sample 3, corresponding to pure DGEBA, shows the typical volume shrinkage that generally accompanies crosslinking reactions.[27] Therefore, it can be concluded that the SOE moieties are effective monomers to obtain crosslinkable copolymers that do not shrink.

Table 2. Volume change upon

Assay	density (d^{30}, g/cm^3)		Volume Change (%)[a]
	Mixture	Crosslinked	
1	1.422	1.381	-2.9
2	1.294	1.282	-0.9
3	1.158	1.192	2.9

[a] Calculed with the following equation: Volume change (%) = [(Density of the crosslinked polymer) – (Density of initial mixture)] / (Density of initial mixture) x 100.

To examine the effect of the phosphorus content on the thermal stability and the decomposition behaviour, TGA data under nitrogen and air atmospheres were deter-mined and analysed. Figures 7 and 8 show the weight loss with the temperature for the three samples as well as the derivative curves under nitrogen an air respectively. Table 3 summarizes the thermogravimetric data.

In both nitrogen and air atmospheres, only the sample of pure DGEBA has a single major break in their decom-position curve, indicating a single decomposition step. However, the other two samples show a more complex decomposition processes. The temperatures of 5% weight loss are, in both atmospheres, above 300 ºC for pure DGEBA but about 250 ºC for SOE-containing samples, probably due to the ester linkage break.

In air, a second stage of weight loss for sample 3, without phosphorus, corresponds to thermooxidative degradation. This behaviour is in accordance with the mechanism of improved fire performance via phosphorous modification. In this retarded-degradation phenomenon, the phosphorous groups form an insulating protective layer, which prevents the combustible gases from transferring to the surface of the materials, increases the thermal stability at higher temperatures, and improves the fire resistance.

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The char yields under nitrogen is nor-mally correlated with the polymer's flame retardance,[28] but it should be pointed out that, in our case, the experimental char yields of the phosphorus-containing resins and the phosphorus-free resins are not significantly different under nitrogen. However, under air, the char yield is significantly lower in sample 3 without phosphorus, and sample 1 with a higher phosphorus content has the greater char yield.

The LOI values, which can be taken as an indicator to evaluate the polymer's flame retardancy for the phosphorus-containing resins, were measured and are shown in Table 3. The presence of phosphorus slightly increases the LOI values for the phosphorus-containing samples, but no significant increase can be observed when the phos-phorus content increases; this indica-tes that low amounts of phosphorus are sufficient to obtain improvements in the flame retardancy.

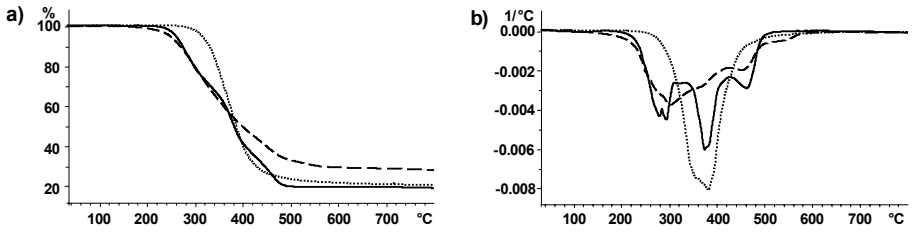

Figure 7. (a) TGA thermograms of ( ) SOE-DOPOMA, ( ) 2/1(mol/mol) DGEBA/SOE-DOPOMA, and ( ) DGEBA and (b) first derivatives under N_2.

CONCLUSIONS

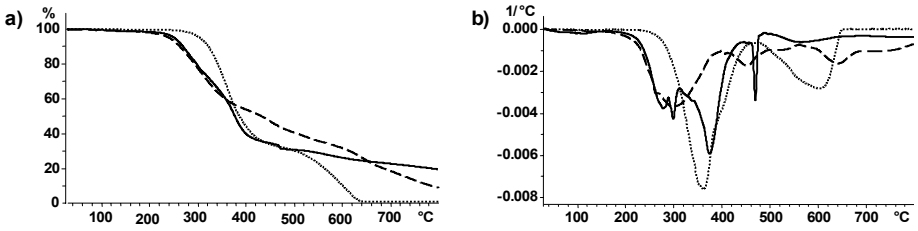

Figure 8. (a) TGA thermograms of ( ) SOE-DOPOMA, ( ) 2/1(mol/mol) DGEBA/SOE-DOPOMA, and ( ) DGEBA and (b) first derivatives under air.

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Assay	N_2 Atmosphere			Air Atmosphere			LOI
	$T_{5\%}$[a] (ºC)	T_{max}[b] (ºC)	Char yield at 800 ºC (wt%)	$T_{5\%}$[a] (ºC)	T_{max}[b] (ºC)	Char yield at 800 ºC (wt%)	
1	258	278/293/373/461	18,6	250	278/299/373/469	19,3	25.6
2	247	303/450	27,9	242	298/451/640	9,1	25.1
3	314	381	20,4	303	360/602	0,5	24.0

Table 3. TGA and LOI results of cured polymers.

[a] Temperature of 5% of weight loss.
[b] Temperatures of the maximum degradation rate.

A new bis-SOE-containing monomer, SOE-DOPOMA, was synthesized with good yields by an esterification reaction with SOE-OH and a phosphorus-containing diacid, both of which were previously synthesized. This method avoids the undesirable decarboxylation of the diacid precursor, which leads to a mono-SOE compound. This new SOE was crosslinked with ytterbium triflate as a cationic initiator. A mixture of SOE-DOPOMA and DEGBA was also crosslinked under the same condi-tions. These two curing processes occurred with expansion, which was higher for pure SOE-DOPOMA. The incorporation of phosphorus into the materials produced an increase in the char yields and a slight increase in the LOI values; thus, the flame retardancy of the materials was increased.

The authors thank the Comisión Interminesterial de Ciencia y Tecnología (MAT2005-01593) and (MAT2005-01806) for providing financial support for this work.

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