MICROWAVE-ASSISTED SYNTHESIS OF A NOVEL PHOSPHORUS-CONTAINING SPIROORTHOESTER, CHARACTERIZATION AND CATIONIC POLYMERIZATION

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Abstract

A new phosphorus-containing spiroorthoester, (1,4,6-trioxaspiro [4,4] nonan-2-yl)-methyl 3-[10-(9,10-dihydro-9-oxa-9-phosphaphenantrene-10-oxide-10-yl)]-propa-noate (SOE-P), was synthesized under microwave irradiation with a short reaction time (1h), because classical thermal heating did not lead to the desired product. The structure of the new monomer was confirmed by ^{1}H, ^{13}C, and [31]P. SOE-P was homopolymerized and copolymerized with phenyl glycidyl ether with ytterbium triflate as a cationic initiator in DSC experiments. These reactions were monitored by FTIR/ATR, and the formation of poly(ether-ester)s with a pendant bulky phosphorylated group was shown.

Keywords: cationic polymerization; flame retardance; heteroatom-containing polymers; microwave synthesis; spiroorthoester; ytterbium triflate

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INTRODUCTION

Epoxy resins have a good combination of attractive properties such as moisture, solvent and chemical resistance, toughness, superior elec-trical and mechanical properties, and good adhesion to many substrates.[1] However, one of their disadvantages is that they are more flammable than similar thermosets, because they have a
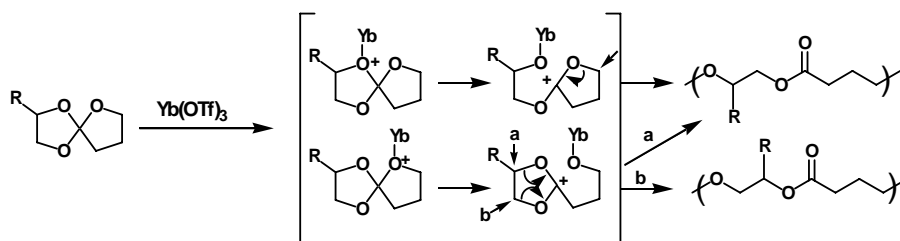
Scheme 1. Cationic polymerization of SOE.

reduced tendency to carboni-ze. In recent years, the modification of epoxy resins has received increasing attention in an attempt to improve their flame resistance, particularly through halogen-free flame-retardant intumescent-based technology, which is an alternative to both halogenated and inorganic flame retardants.[2-4] One way of retarding polymer combustion is to block the source of fuel by covering the outer layer of the material with a nonflammable coating, such as a phosphorous con-taining compound. Reactive organic phosphorous compounds are power-ful flame retardants, and thus attract more attention.[3]

Another disadvantage of epoxy resins is that they shrink during curing, which leads to a significant change in volume. This shrinkage is a major problem in such industrial appli-cations as industrial castings, coatings, mold replication, and microelectronics, because it leads to poor adhesion to the substrate, delamination, and microvoids and microcracks, which reduce the durability of the materials. One way of solving this problem is to copoly-merize the epoxy resins with the so-called "expanding monomers",[5] which are monomers that lead to zero shrinkage or even positive expansion during polymerization. Some kinds of cyclic monomers such as spiroorthoesters (SOEs), spiroortho-carbonates (SOCs), and bicycloortho-esters (BOEs) have been reported to maintain their volume or actually expand during the double ring-opening polymerization.[5-8] SOEs can be readily synthesized from epoxides and lactones[9,10] and undergo cationic ring-opening polymerization by Lewis acid catalysts.

In this study, we synthesized a new phosphorus-containing spiroorthoes-ter, (1,4,6-trioxaspiro[4,4] nonan-2-yl)-methyl 3-[10-(9,10-dihydro-9-oxa-9-phosphaphenanthrene-10-oxide-10-yl)] propanoate (SOE-P), derived from 9,10-dihydro-9-oxa-10-phos-phaphenantrene-10-oxide (DOPO), in an attempt to combine both their flame retardance and expanding properties. The incorporation of this rigid and bulky phosphorus-containing moiety confers good flame retardant properties on epoxy resins.[11] SOEs polymerize with cationic initiators to afford linear poly(ether-ester)s[12-14] (Scheme 1). They can also be used to modify epoxy resins.[15,16] Thus, we tested the ability of this phosphorus-containing spiroorthoester to homopolymerize and to copolymerize with epoxide, in this case with phenyl glycidyl ether as a model compound.

In the polymerization reactions of SOE-P, we used ytterbium triflate as the cationic initiator. In previous studies, our research group demonstrated that lanthanide trifla-tes are Lewis acids that can cure epoxy resins.[17,18] Lanthanide triflates are commercially available and have many advantages over BF_3 deriva-tives and alkylating agents, because they maintain their catalytic activity even in the presence of water.[19] The strong electron-withdrawing capacity of the trifluoromethanesulfonate anion enhances the Lewis acid character of the initiator. Moreover, lanthanide cations have low electronegativities, strong oxophili-cities, and large ionic radii, and they coordinate to the oxygen atoms of monomers to create the active species.[20]

EXPERIMENTAL

Materials

Commercial DOPO was kindly supplied by Aismalibar and it was purified before use by heating at 130 ºC under vacuum for 2 h and then gradually heated to 150 ºC. The purified product was cooled to room temperature under argon atmos- phere. Phenylglycidyl ether (PGE; Aldrich), epibromohydrin (Fluka), γ-butyrolactone (γ-BL; Aldrich), boron trifluoride diethyl etherate ($BF_3.OEt_2$; Aldrich), triethylamine (Fluka), acrylic acid (Aldrich), 1,8-diazabicyclo[5.4.0]-undec-7-en (DBU; Aldrich), 3-*tert*-butyl-4-hidroxy-5-methylphenyl sul-fide (Aldrich), hydrogen hexachloro-platine (IV) (H_2PtCl_6, Aldrich) were used as received. All solvents were purified by standard procedures. The poly-merization catalyst, ytterbium (III) trifluoromethanesulfonate [Yb(OTf)$_3$], was purchased from Aldrich and used without purification.

Instrumentation

The microwave irradiated reaction was carried out in a 10-mL reactor vial, using a CEM Discover mono-

modal microwave reactor and an IR temperature sensor and operating 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 using a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ as the solvent, and tetra-methylsilane (TMS) or phosphoric acid as internal standards.

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

The isothermal polymerization process at 180 ºC was monitored with a FTIR-680PLUS spectrophotometer at a resolution of 4 cm^{-1} in the absorbance mode. An attenuated-total-reflection accessory with ther-mal control and a diamond crystal was used to determine FTIR/ATR spectra.

Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 and air as a purge gas at scan rates of 10 ºC/min.

Modified UL-94 Burn Test: three sample bars (30 x 20 x 0.5 mm^3) were used for this test. The height of the Bunsen burner flame was 25 mm and the height from the top of the Bunsen burner to the bottom of the test bar was 10 mm. All test bars underwent two trials and each

trial consisted of ignition for 10 s, after which the flame was removed and the time for self-extinguishing and dripping characte- ristics were recorded.

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

A total of 50 g (0.36 mol) of epibromohydrin was added dropwise for 15 min at a temperature below 10 ºC in argon atmosphere to a mixture of 180 g of (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 complete, 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 had been removed under reduced pressure, the residue was distilled fractionally to yield 60.4 g (74 %) of transparent 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 (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 SOE-acrylate

A total of 10 g (45.0 mmol) of SOE-Br with 10 mL of anhydrous 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, stored under argon atmosphere in a three-necked flask in a bath at 65 ºC. 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. When the reaction had finished, 8 mg of a radical inhibitor, 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide, was added. The desired product was removed from DMSO by several extractions with CH$_2$Cl$_2$. The product was purified by 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 SOE-Br impurities had been removed under reduced pressure, 7.27 g (76%) of transparent liquid was afforded.

^{1}H NMR (CDCl$_3$, two diastereomers): δ(ppm) = 6.46-6.41 (dd, 1H, J_{trans} = 16.8 Hz, J_{cis} = 1.6 Hz, C=CH), 6.44-6.40 (dd, 1H, J_{trans} = 17.2 Hz, J_{cis} = 1.6 Hz, C=CH), 6.17-6.01 (m, 2H, C=CH$_2$), 5.87-5.84 (dd, 1H, J_{cis} = 9.6 Hz, J_{gem} = 1.2 Hz, C=CH$_2$), 5.86-5.83 (dd, 1H, J_{cis} = 10.8 Hz, J_{gem} = 1.6 Hz, C=CH$_2$), 4.35-3.50 (m, 1H, -O-CH-), 4.38-4.32 (m, 1H, -O-CH-), 4.38-4.01 (m, 6H, -O-CH$_2$-), 3.96-3.89 (m, 4H, -O-CH$_2$-), 3.84-3.77 (m, 2H, -O-CH$_2$-), 2.16-2.10 (m, 4H, -CH$_2$-), 2.04-1.99 (m, 4H, -CH$_2$-).

^{13}CNMR (CDCl$_3$, two diastereomers): δ(ppm)= 166.04 (s, C=O), 131.73 (s, C=CH$_2$), 129.98 (s, spiranic carbon), 128.11 (s, C=CH), 74.32 (s, -O-CH-), 73.47 (s, -O-CH-), 67.58 (s, -O-CH$_2$-), 66.29 (s, -O-CH$_2$-), 66.16 (s, -O-CH$_2$-), 65.32 (s, -O-CH$_2$-), 64.41 (s, -O-CH$_2$-), 32.89 (s, -CH$_2$-), 24.41(s, -CH$_2$-), 24.22 (s,-CH$_2$-).

Synthesis of SOE-P

Microwave Irradiation

A microwave reactor vial (10 mL) was charged in air with 0.1 g (0.46 mmol) of DOPO and 0.108g (0.50 mmol) of SOE-acrylate and a new magnetic stirring bar. The vial was purged with nitrogen.

The maximum power setting of 50 W was maintained until the desired temperature (130 ºC) had been reached (160 s). The power was reduced to 11 W for the remainder of the reaction time to maintain 130 ºC. After 60 min, the mixture reaction was cooled to room temperature.

The product was purified by flash chromatography with silica gel neutralized with triethylamine and using acetone with 1% triethylamine

as eluent. A yellowish viscous oil (0.184 g , 93%) was afforded.

^{1}H NMR (CDCl$_3$, four diastereomers): δ(ppm)= 7.93-7.80 (m, 12H, Ar-H), 7.66 (t, 4H, J$_o$ = 7.6 Hz, Ar-H), 7.47 (t, 4H, J$_o$ = 7.6 Hz, Ar-H), 7.33 (dt, 4H, J$_o$ = 8.4 Hz, J$_m$ = 1.2 Hz, Ar-H), 7.22-7.15 (m, 8H, Ar-H), 4.38 (m, 2H, -O-CH-), 4.29-4.17 (m, 4H, -O-CH-, -O-CH$_2$-), 4.10-4.00 (m, 10H, -O-CH$_2$-), 3.90-3.84 (m, 8H, -O-CH$_2$-), 3.73-3.65 (m, 4H, -O-CH$_2$-), 2.67-2.57 (m, 8H, -CH$_2$-), 2.40-2.30 (m, 8H, -P-CH$_2$-), 2.12-2.05 (m, 8H, -CH$_2$-), 1.97-1.90 (m, 8H, -CH$_2$-).

^{13}C NMR (CDCl$_3$, four diastereomers): δ(ppm)= 171.29 (d, J$_{C-P}$ = 17.5 Hz, C=O), 171.28 (d, J$_{C-P}$ = 17.5 Hz, C=O), 148.78 (d, J$_{C-P}$ = 7.9 Hz, Ar-C), 148.77 (d, J$_{C-P}$ = 7.9 Hz, Ar-C), 135.52 (d, J$_{C-P}$ = 6.1 Hz, Ar-C), 135.51 (d, J$_{C-P}$ = 6.0 Hz, Ar-C), 135.50 (d, J$_{C-P}$ = 6.1 Hz, Ar-C), 133.45 (d, J$_{C-P}$ = 2.3 Hz, Ar-CH), 133.42 (d, J$_{C-P}$ = 2.2 Hz, Ar-CH), 130.59 (s, Ar-CH), 130.60 (s, Ar-CH), 129.93 (d, J$_{C-P}$ = 11.1 Hz, Ar-CH), 129.92 (d, J$_{C-P}$ = 11.1 Hz, Ar-CH), 129.62 (s, spiranic C), 129.60 (s, spiranic C), 129.50 (s, spiranic C), 128.50 (d, J$_{C-P}$ = 13.5 Hz, Ar-CH), 128.49 (d, J$_{C-P}$ = 13.4 Hz, Ar-CH), 125.11 (s, Ar-CH), 125.10 (s, Ar-CH), 125.09 (s, Ar-CH), 125.08 (s, Ar-CH), 124.66 (s, Ar-CH), 124.64 (s, Ar-CH), 123.91 (d, J$_{C-P}$ = 9.5 Hz, Ar-CH), 123.90 (d, J$_{C-P}$ = 9.5 Hz, Ar-CH), 123.88 (d, J$_{C-P}$ = 9.5 Hz, Ar-CH), 124.10 (d, J$_{C-P}$ = 121.3 Hz, Ar-C), 124.09 (d, J$_{C-P}$ = 121.2 Hz, Ar-C), 124.08 (d, J$_{C-P}$ = 121.2 Hz, Ar-C), 124.07 (d, J$_{C-P}$ = 121.3 Hz, Ar-C), 121.88 (d, J$_{C-P}$ = 11.1 Hz, Ar-C), 121.86 (d, J$_{C-P}$ = 11.1 Hz, Ar-C), 120.19 (d, J$_{C-P}$ = 6.1 Hz, Ar-CH), 73.79 (s, -CH-) 73.77 (s, -CH-), 72.92 (s, -CH-), 67.16 (s, -O-CH$_2$-), 67.07 (s, -O-CH$_2$-), 65.64 (s, -O-CH$_2$-), 65.63 (s, -O-CH$_2$-), 65.61 (s, -O-CH$_2$-), 65.59 (s, -O-CH$_2$-), 65.21 (s, -O-CH$_2$-), 65.17 (s, -O-CH$_2$-), 64.56 (s, -O-CH$_2$-), 64.51 (s, -O-CH$_2$-), 32.48 (s, -CH$_2$-), 32.45 (s, -CH$_2$-), 26.38 (d, J$_{C-P}$ = 6.1 Hz, -CH$_2$-), 26.37 (d, J$_{C-P}$ = 6.5 Hz, -CH$_2$-), 26.36 (d, J$_{C-P}$ = 6.1 Hz, -CH$_2$-), 26.35 (d, J$_{C-P}$ = 6.4 Hz, -CH$_2$-), 24.13 (d, J$_{C-P}$ = 99.1 Hz, -CH$_2$-), 24.05 (s, -CH$_2$-), 24.03 (s, -CH$_2$-), 23.88 (-CH$_2$-), 23.85 (s, -CH$_2$-).

^{31}P NMR (CDCl$_3$, four diastereomers) δ(ppm)= 37.02 (s), 37.01 (s), 36.93 (s), 36.90 (s).

Conventional Heating

In a 25-mL round-bottom flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer, 0.5 g (2.31 mmol) of DOPO and drops of 5% H$_2$PtCl$_6$ catalyst in isopropyl alchohol were dissolved in 2.5 mL of xylene. The flask was heated to 125 ºC and then 0.5 g (2.33 mmol) SOE-acrylate with 3 mL of xylene was added slowly for 20 min. After the complete addition of SOE-acrylate, the reaction was maintained at that temperature for 150 min. After cooling to room temperature, the reaction product was filtered, washed with acetone several times, and then dried in an

oven at 120 ºC for 4 h. The recovered solid was a complex mixture in which the desired product was not detected.

Polymerization Reactions

About 10 mg of pure spiroorthoester or spiroorthoester/PGE mixture was put into an aluminium pan and the polymerization was monitored in a dynamic DSC experiment.

Polymerization of SOE-P. The sample was prepared by mixing SOE-P (0.1 g, 0.23 mmol) with 1 mol % of ytterbium triflate (1.45 mg, 0.00234 mmol).

Copolymerization of SOE-P with PGE. The sample was prepared by mixing SOE-P (0.1 g, 0.23 mmol) and PGE (0.0349 g, 0.23 mmol) with 1 mol % of ytterbium triflate (2.9 mg, 0.00468 mmol).

RESULTS AND DISCUSSION

SOE-P was synthesized following the synthetic pathway shown in Scheme 2. First, we synthesized 2-bromomethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-Br). This was prepared from epibromohydrin and γ-butyrolactone,[9] using $BF_3 \cdot OEt_2$ as catalyst and its structure was confirmed by spectroscopic experiments. The reaction of SOE-Br with acrylic acid in the presence of DBU in DMSO, to obtain SOE-acrylate, was carried out under mild conditions. Direct ester formation from a primary halide and a carboxylic acid using DBU is a useful method that has been
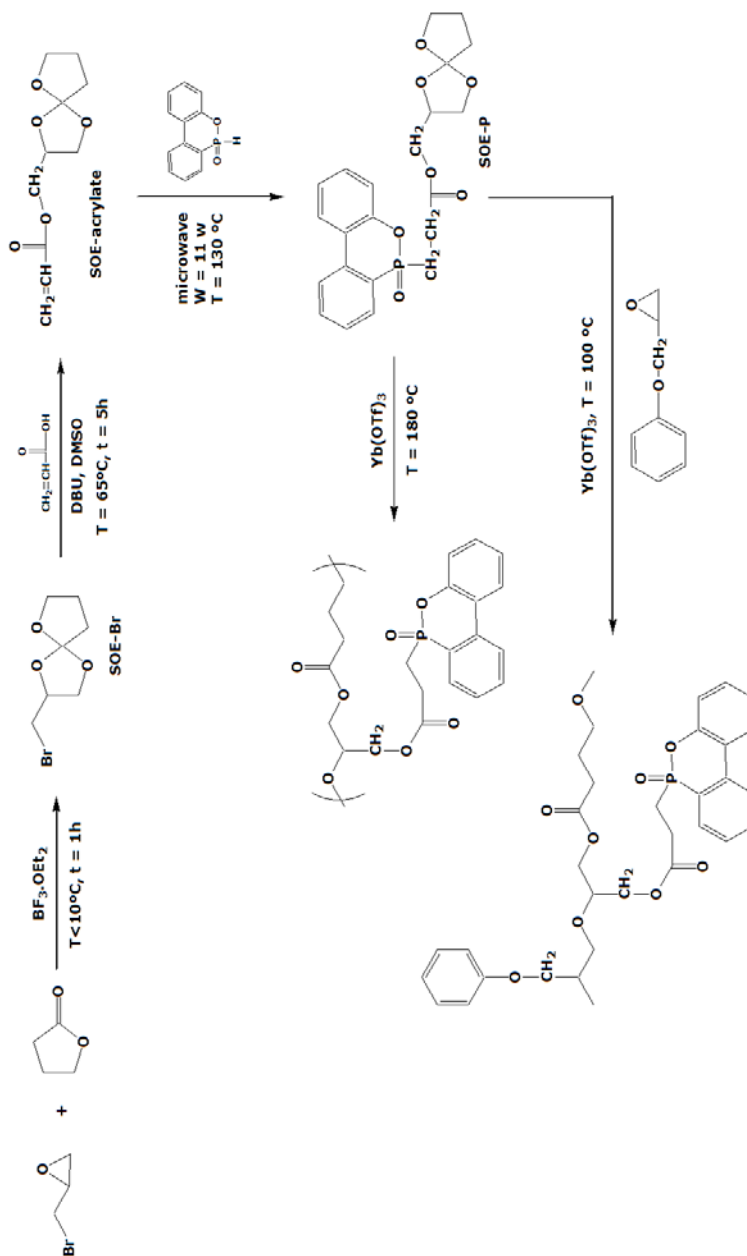
Scheme 2. Synthesis of SOE-P and its homo and copolymerization.

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used by several authors.[21,22] This method also leads to good results in polymer modification.[23-25] The following synthetic step consisted in the incorporation of DOPO by means a conjugated addition reaction to the α,β-unsaturated SOE-acrylate. When DOPO reacts with a double-bond-containing compound, the structures of double-bond-containing com-pounds have a significant influence on the reaction rate. For example, when DOPO reacts with benzoquinone[26] or maleic acid,[27] with two electron-withdrawing carbonyl groups next to the double bond, the reaction temperature is about 70-90 ºC. However, when DOPO reacts with itaconic acid,[27] with only one electron-withdrawing carbonyl group next to the double bond, the reaction is very slow, even at 140 ºC. Thus, the addition of the H_2PtCl_6 catalyst is necessary to facilitate the reaction. The electron density of double bonds in the double-bond-containing compound is responsible for this. In the case of itaconic acid, because one carbonyl group is not next to the double bond, the double bond can only resonate with one carbonyl group, and the inductive effect of carbonyl decreases because of the considerable distance between the carbonyl group and the double bond. In our case, the SOE-acrylate should exhibit almost the same reactivity towards DOPO as itaconic acid. Thus, SOE-acrylate was reacted with DOPO at 125 ºC in a xylene solution and with H_2PtCl_6 as catalyst in reaction conditions that were similar to those of DOPO-itaconic acid. However, the reaction did not lead to the desired compound but a complex mixture in which the presence of SOE-P was not detected.

Although this addition of hydrogen phosphinate to alkenes can take place thermally, one way to avoid the undesirable transformations of the organophosphorus compounds is to reduce the reaction time. One promising way of doing this is to apply microwave energy. Microwave irradiation has a number of advantages over conventional hea-ting, such as noncontact heating, which for many organophosphorus compounds is very important, and rapid and highly specific heating.[28,29] Thus, the hydrogen phosphinate was added to the unsaturated spiroortho- ester under microwave irradiation and SOE-P was obtained in a significantly short reaction time and in a good yield.[30]

This novel phosphorus-containing spiroorthoester was characterized by means of ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Since the phosphorus center in DOPO is chiral and the spiroorthoester has two chiral carbons, the product of the addition reaction produced a mixture of diastereomers. Figure 1 shows the ^{31}P (a), ^1H (b), and ^{13}C (c) NMR spectra, with all the assignments. The single ^{31}P signal is split because of the presence of the four diastereomers. In ^1H and ^{13}C NMR spectra, some signals are

also split because of the four diastereomers. The inset in Figure 1 (c) shows, as an example, the ampli-fication of the C-2 next to

the ester

group, where the C-P

T_gs (by DSC) of SOE-P (a), SOE-P/PGE copolymer homopolymer (c).
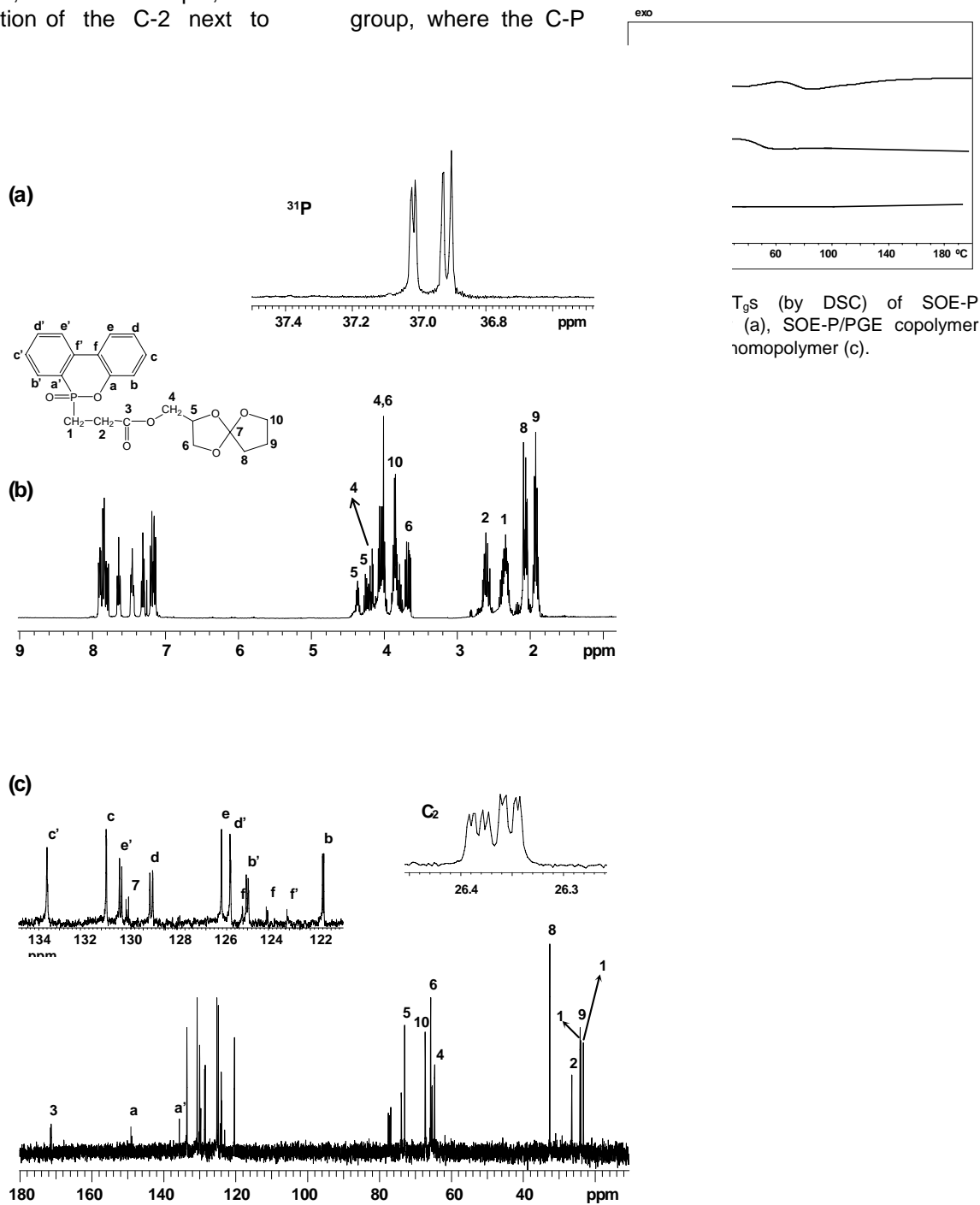
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Figure 1. NMR spectra of SOE-P; [31]P (a), [1]H (b), and [13]C (c).

coupling can also be observed. The spiroorthoester rings, aromatic proton, and carbon signals were assigned unequivocally by means of DEPT, HSQC, and COSY experiments.

As mentioned earlier, we are interested in testing the ability of the phosphorus-containing monomer SOE-P to modify epoxy resins. The polymerization of SOE-P, using 1 mol % of ytterbium triflate as cationic initiator was studied by DSC. Figure 2 (a) shows the dynamic DSC plot of this reaction in which there is a broad exotherm with a maximum at 245 ºC, attributed to the polymerization. In a second scan, the T_g of the polymer at 74 ºC was observed (Fig. 3a). TGA experiments in air showed that the 5% weight loss occurred at 202 ºC. The derivative curve showed that the temperature of maximum rate of degradation was 390 ºC and a second step was observed at 455

Figure 2. DSC plots of homopolymerization of SOE-P (a) and copolymerization of SOE-P/PGE 1:1 mol/mol (b) with 1% mol of Yb(OTf)$_3$.
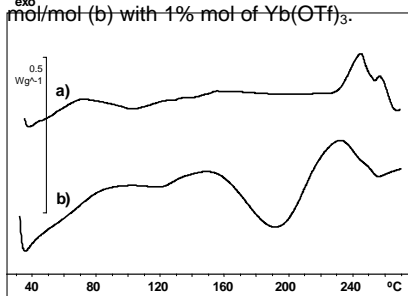
ºC. The char yield at 750 ºC was 20%.

This polymerization reaction was monitored by FTIR/ATR spectroscopy in isothermal experiment at 180 ºC. 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 4 shows the FTIR spectra of SOE-P with 1 mol % of Yb(OTf)$_3$ before and after polymerization. The double ring-opening of the spiroorthoester that took place during the polymerization led to a linear poly(ether-ester) formation, so a typical band of carbonyl ester group must appear[31] at about 1735-1750 cm^{-1}. Our acrylate derivative initially contains an ester group, which appears at 1734 cm^{-1}, and therefore in this zone, only an increase in this band was observed on polymerizing.

Figure 5 shows the ^{31}P and ^{13}C NMR spectra of the obtained polymer. The broadness of P signal is characteristic of polymeric compounds because of the different environment. The ^{13}C NMR spectrum shows two different carbonyl signals, attributed to the main chain and side chain ester groups, and the aromatic carbons between 150 and 120 ppm. The various aliphatic carbons appear below 80 ppm. The methylene and methine carbons attached to the oxygen atom appear between 80 and 60 ppm. The methylene group attached to the phosphorus atom appears at about 30 ppm and the other methylene
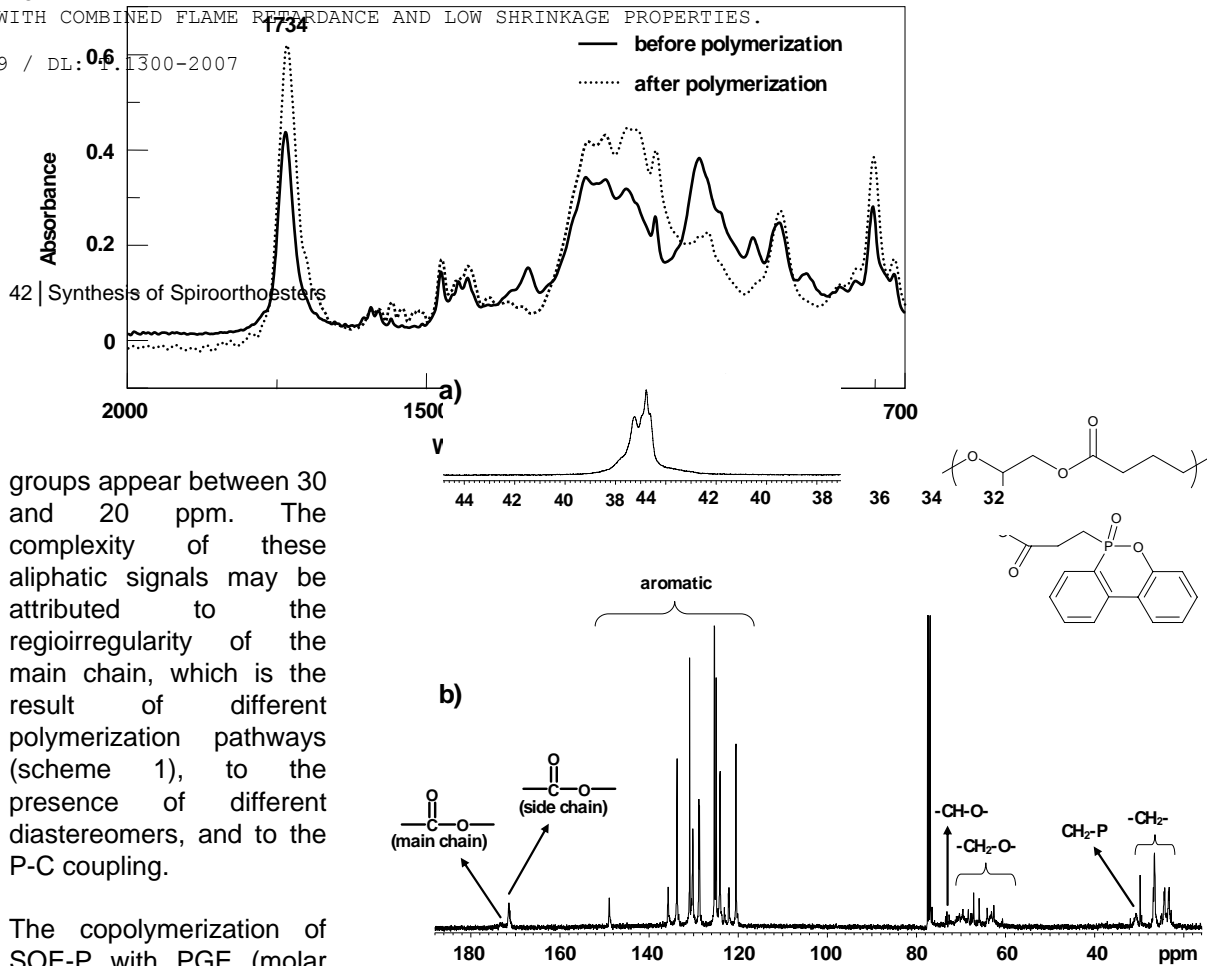
Figure 4. FTIR spectra of SOE-P with 1% molar of Yb(OTf)$_3$ before and after polymerization at 180 ºC.

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Figure 5. ^{31}P (a) and ^{13}C (b) NMR spectra of the polymer obtained by cationic polymerization of SOE-P.

groups appear between 30 and 20 ppm. The complexity of these aliphatic signals may be attributed to the regioirregularity of the main chain, which is the result of different polymerization pathways (scheme 1), to the presence of different diastereomers, and to the P-C coupling.

The copolymerization of SOE-P with PGE (molar ratio 1:1), using 1 mol % of ytterbium triflate as cationic initiator was studied by DSC. Figure 2 (b) shows the first broad exotherm attributed to the copolymerization of the two comonomers. The second exotherm, with a maximum at 230 ºC, was attributed to the remaining spiroorthoester, which homopolyme- rizes in the last stage of the process. It must be noted that PGE homopoly- merization exotherm, the maximum of which is at 170 ºC, is not observed. Figure 3 plots the T_gs obtained in a second scan of SOE-P homopolymer (a), PGE homopolymer (c) and copolymer (b). As can be seen, the T_g value of the copolymer is between both homopolymer values, which indicates that a random copolymer was obtained. The fact that a single T_g was observed indicates that the homopolymerization of the remaining SOE-P takes place only to a small extent.

This copolymerization reaction was monitored by FTIR/ATR spectroscopy in isothermal experiments at 100 ºC. The carbonyl band was observed to increase, which indicates that the spiroorthoester opening took place. Unfortunately, the disappearance of the typical epoxy band at 913 cm^{-1} could not be confirmed, because the initial spiroorthoester presented ab-sorptions in the same zone.

The ^{31}P spectrum of the copolymer showed a signal at 36.5-37.5 ppm in the same range as the homopolymer. The ^{13}C NMR spectrum of the obtained copolymer showed a pattern similar to that of the SOE-P homopolymer but with a greater complexity in the aliphatic zone.

We did the flame retardant testing of the synthesized homopolymer (no test of the copolymer was made because its low T_g), using a modified UL-94 flame test, in which the sample was suspended above cotton.[32] The sample was subjected to two 10-s ignitions with a calibrated methane-fueled flame in a controlled-size unit that was free of passing air currents. After the first ignition, the flame was removed and the time for the polymer to self-extinguish was recorded. The second ignition was then performed on the same sample and the self-extinguishing time/dripping charac-teristics were recorded. If the sample self-extinguished in less than 10 s with no dripping, we considered it to be a V-0 material, which is an industry standard for flame retardancy. According to the UL-94 test, the homopolymer sample produced a V-0 result as we expected from phosphorus-containing polymers.

CONCLUSIONS

The microwave irradiation method was used to synthesize a phosphorylated spiroorthoester (SOE-P). This method avoids the undesirable transformations of the organophosphorus compounds that take place with conventional heating, which failed in the case of the synthesis of SOE-P. This new spiroorthoester was polymerized and copolymerized using an epoxy compound by a cationic mechanism with ytterbium triflate as initiator. Therefore, this spiroorthoester can be used to modify epoxy resins and even to form thermosets with improved properties.

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