UNIVERSITAT ROVIRA I VIRGILI
SYNTHESIS OF POLYMERS WITH COMBINED FLAME RETARDANCE AND LOW SHRINKAGE PROPERTIES.
Judit Canadell Ayats
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NOVEL SILICON-CONTAINING SPIROORTHOESTER WITH COMBINED FLAME RETARDANCY AND LOW SHRINKAGE PROPERTIES TO MODIFY EPOXY RESINS

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Abstract

A new silicon-containing spiroorthoester, 1,4,6-trioxaspiro[4,4]-2-nonylmethyl 3-trimethylsilyl propionate (SOE-Si), was synthesized with good yields by an esterification reaction with a previously synthesized 2-hydroxymethyl-1,4,6-trioxaspiro [4,4] nonane and trimethylsilyl propionic acid. The structure of the new SOE-Si was confirmed by ^{1}H, and ^{13}C NMR spectroscopy. The SOE-Si was homopolymerized with ytterbium triflate as a cationic initiator. A mixture of SOE-Si and diglycidyl ether of bisphenol A was also polymerized under the same conditions. The curing was studied with differential scanning calorimetry and monitored by Fourier transform infrared spectroscopy. The materials were characterized with differential scanning calorimetry, thermogravimetric analysis and thermodyna-momechanical analysis. The volume change was evaluated with a Micromeritics gas pycnometry, and the flame retardancy was tested by the limiting oxygen index measurements.

Keywords: cationic polymerization; epoxy resins; ring opening; flame retardance; heteroatom-containing polymers; spiroorthoester; ytterbium triflate

INTRODUCTION

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Epoxy resins are widely used in casting, coating, adhesion, and com-posite applications. They have many attractive properties: they are easy to cure and process, are resistant to moisture, solvents, and chemicals and they have good mechanical and electrical properties.[1] However, in some applications, epoxy resins require special functions, such as low flammability and low shrinkage.

Traditionally, halogen-containing mo-nomers such as diglydicylether of tetrabromobisphenol A have been used to render effective flame retardant properties, although their uses are limited because of their productions of toxic and corrosive gases as well as carcinogenic chemicals during combustion. On the contrary, the halogen-free flame retardants are environmentally fri-endly because they generate less toxic and corrosive substances during fire. The common halogen-free flame retardants are mainly organophos-phorus[2-3] and organosilicon[4-5] com-pounds. Both elements are described that can function in the condensed phase or vapor phase, and possibly concurrently in both phases.[6]

Phosphorus-containing polymers mainly act changing the chemical reactions of decomposition, in favor of reactions yielding carbonaceous char rather than CO and CO_2. They form a surface layer of protective char during fire before the unburned material begins to decompose. The char layer acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air.[3,7,8]

Silicon-containing polymers have also a flame retardant effect, arising partly from the property that such com-pounds dilute the more combustible gases and partly from the barrier that silicaceous residues can form to an advancing flame.[4,9]

Another problem of the epoxy resins is their shrinkage during curing, which can lead to internal compressive stress in the material, poor adhesion of coatings to the substrate, and the appearance of microvoids and micro-cracks, which reduce the durability of materials.[10] One of the best solutions to solve the shrinkage is the use of monomers that show no volume shrinkage in their polymerization, such as spiroorthoesters (SOEs)[11,12], spiroorthocarbonates (SOCs)[13,14], and bicyclicorthoesters (BOEs).[15]

We recently reported the synthesis of phosphorus-containing spiroortho-esters[16,17] and their homopolymeriza-tion and copolymerization with epoxy resins to obtain materials with enhanced flame retardancy and with low shrinkage during curing.

The aim of the present study is to use silicon instead of phosphorus to solve the above mentioned disadvantages of epoxy resins, by

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means of the cationic crosslinking of a new silicon-containing spiroorthoester with mix-tures of DGEBA.

The cationic crosslinking was carried out using ytterbium triflate as a cationic initiator, which has shown to be effective to polymerize glycidyl compounds and spiroorthoesters.[18] This crosslinking was studied with differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The materials were characterized by DSC, ther-mogravimetric analysis (TGA), and thermodynamomechanical analysis (DMTA). The volume change was evaluated with a Micromeritics gas pycnometry and the flame retardancy was tested by the limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

Glycidol (Aldrich), γ-butirolactone (γ-BL; Aldrich), boron trifluoride diethyl etherate ($BF_3.OEt_2$; Aldrich), triethyl-amine (Fluka), trimethylsilyl acetic acid (Aldrich), trimethylsilylpropionic acid (Fluorochem), N-(3-Dimethylamino-propyl)-N'-ethyl-carbodiimide hydro-chloride (EDC; Fluka), 4-(dimethyl-amino)pyridine (DMAP; Fluka), DGEBA (Epikote Resin 827, Shell Chemicals; epoxy equivalent = 182.08 g/eq), ytterbium(III) trifluoromethanesulfo-nate [$Yb(OTf)_3$; Aldrich] were used as received. All solvents were purified by standard procedures.

Instrumentation

NMR spectra (^1H 400 MHz; ^{13}C 100.6 MHz) were obtained with a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ as the solvent. ^{29}Si MAS NMR spectra were performed, with finely ground samples, on a Varian Gemini 400 MHz spectrometer at a 79 MHz resonance frequency, MAS being applied with a 20-s delay time.

Polymerization and crosslinking studies were performed on a Mettler DSC-821e thermal analyzer in covered Al pans under nitrogen at scan rates of 10 ºC/min. The determination of glass transition temperatures (T_g's) were carried out on a Mettler DSC-822e thermal analyzer in covered Al pans under N_2 at scan rates at 20 ºC/min. The samples weighed approximately 8 mg.

The isothermal crosslinking process at 140 ºC was monitored with a 680 Plus FTIR spectrophotometer with a reso-lution 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 ºC and

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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 180 ºC at a heating rate of 5 ºC/min.

The molecular weight distribution of the polymers was determined with a Waters gel permeation chroma-tograph equipped with the 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 tetrahy-drofuran as the solvent. Monodisper-sed 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 ºC.

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.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 scanning electron microscope at an activation voltage of 8 kV. For the atomic mapping, an Oxford INCA energy-dispersive X-Ray microana-lyzer was used.

XRD measurements were made using a Siemens D 5000 diffractometer (Bragg-Brentano parafocusing geo-metry and vertical θ-θ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06º receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 5 and 70º. Sample was tested on to a low background Si(510) sample holder. The data were collected with an angular step of 0.05º at 3 s per step and sample rotation. $Cu_{k\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

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.

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^{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, OH-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-).

Reaction of trimethylsilyl acetic acid with SOE-OH

Under an argon atmosphere, an oven-dried 100 mL round-bottom flask containing 20 mL of anhydrous dichloromethane was charged with 1.0 g (7.5 mmol) of trimethylsilyl acetic acid, 1.20 g (7.5 mmol) of SOE-OH, 1.59 g (8.3 mmol) of EDC, and 1.01 g (8.3 mmol) of DMAP. The solution was stirred and heated at 40 ºC for 2 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 1.04 g of transparent colorless liquid, which corresponds to a mixture of 1,4,6-trioxaspiro [4,4]-2-nonylmethyl acetate (SOE-Ac) and 1,4,6-trioxaspiro [4,4]-2-nonylmethyl trimethylsilyl ether (SOE-OSi). The mixture of SOEs was separated by flash chroma-tography with a silica gel neutralized with triethylamine and ethyl aceta-te/hexane (8:2) containing 1% of triethylamine as eluent.

SOE-Ac.

^{1}H NMR ($CDCl_3$, two diastereomers): δ(ppm) = 4.49-4.42 (m, 1H, -O-CH-), 4.35-4.28 (m, 1H, -O-CH-), 4.25-4.19 (m, 2H, -O-CH_2-), 4.16-4.03 (m, 4H, -O-CH_2-), 3.94-3.81 (m, 4H, -O-CH_2-), 3.77-3.70 (m, 2H, -O-CH_2-), 2.16- 2.09 (m, 4H, -CH_2-), 2.15-2.12 (d, 6H, -CH_3), 2.10-1.94 (m, 4H, -CH_2-).

^{13}C NMR ($CDCl_3$, two diastereomers): δ(ppm) = 170.84 (s, -COO-), 129.82 (s, spiranic C), 74.28 (s, -O-CH-), 73.40 (s, -O-CH-), 67.47 (s, -O-CH_2-), 67.40 (s, -O-CH_2-), 66.13 (s, -O-CH_2-), 66.05 (s, -COO-CH_2-), 65.20 (s, -O-CH_2-), 64.30 (s, -COO-CH_2-), 32.78 (s, -CH_2-), 24.32 (s, -CH_2-), 24.14 (s, -CH_2-), 20.97 (s, -CH_3), 20.76 (s, -CH_3).

SOE-OSi.

^{1}H NMR ($CDCl_3$, two diastereomers): δ(ppm) = 4.29-4.26 (m, 1H, -O-CH-), 4.17-4.09 (m, 1H, -O-CH-), 4.08-4.03 (m, 2H, -O-CH_2-), 3.91-3.84 (m, 4H, -O-CH_2-), 3.77-3.73 (m, 2H, -O-CH_2-), 3.66-3.47

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(br, 4H, -O-CH_2-), 2.11-2.05 (m, 4H, -CH_2-), 1.99-1.92 (m, 4H, -CH_2-), 0.06 (d, 18H, -CH_3).

^{13}C NMR ($CDCl_3$, two diastereomers): δ(ppm) = 129.78 (s, spiranic C), 129.60 (s, spiranic C), 76.79 (s, -O-CH-), 75.90 (s, -O-CH-), 67.38 (s, -O-CH_2-), 67.26 (s, -O-CH_2-), 66.39 (s, -O-CH_2-), 64.41 (s, -O-CH_2-), 63.03 (s, -O-CH_2-), 33.02 (s, -CH_2-), 32.80 (s, -CH_2-), 24.36 (s, -CH_2-), 24.29 (s, -CH_2-), 1.11 (s, -CH_3), -0.46 (s, -CH_3).

Synthesis of *1,4,6-trioxaspiro[4,4]-2-nonylmethyl 3-trimethylsilyl propio-nate (SOE-Si)*

Under an argon atmosphere, an oven-dried 100 mL round-bottom flask containing 20 mL of anhydrous dichloromethane was charged with 1.0 g (6.8 mmol) of trimethylsilyl propionic acid, 1.09 g (6.8 mmol) of SOE-OH, 1.44 g (7.5 mmol) of EDC, and 0.91 g (7.5 mmol) of DMAP. The solution was stirred and heated at 40 ºC for 3 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 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 1.97 g (90%) of a transparent, colorless liquid.

^{1}H NMR ($CDCl_3$, two diastereomers): δ(ppm) = 4.37-4.34 (m, 1H, -O-CH-), 4.24-4.21 (m, 1H, -O-CH-), 4.15-4.13 (m, 2H, -O-CH_2-), 4.12-3.96 (m, 4H, -CH_2-OCO-), 3.86-3.75 (m, 4H, -O-CH_2-), 3.69-3.64 (m, 2H, -O-CH_2-), 3.63-2.14 (m, 4H, -CH_2-COO-), 2.08-1.99 (m, 4H, -CH_2-), 1.91-1.85 (m, 4H, -CH_2-), 1.19-0.69 (m, 4H, -Si-CH_2-), -0.08 (s, 8H, -CH_3).

^{13}C NMR ($CDCl_3$, two diastereomers): δ(ppm) = 174.63 (s, -COO-), 129.69 (s, spiranic C), 129.61 (s, spiranic C), 74.20 (s, -O-CH-), 73.32 (s, -O-CH-), 67.21 (s, -O-CH_2-), 67.14 (s, -O-CH_2-), 65.99 (s, -O-CH_2-), 65.89 (s, -CH_2-OCO-), 64.95 (s, -CH_2-O-), 64.05 (s, -O-CH_2-), 32.61 (s, -CH_2-), 28.56 (s, -CH_2-COO-), 24.17 (s, -CH_2-), 23.98 (s, -CH_2-), 11.47 (s, -Si-CH_2-), -2.03 (s, -CH_3).

Polymerization of SOE-Si

A mixture of 0.5 g of SOE-Si with 1 phr (1 part per 100 of monomer mixture weight/weight) of ytterbium triflate was heated in an oven for 4 h at 180 ºC to obtain SOE-Si homopolymer (SOE-Si hom)

Crosslinking reactions

The cationic crosslinking reaction was carried out through the mixing DGEBA/SOE-Si in (mol/mol) ratio 2:1, with 1 phr of ytterbium triflate. The sample bars used for dynamo-mechanical and thermogravimetric

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analysis and burn tests were cured in aluminum molds by heating in an oven. The curing conditions were determined from DSC.

RESULTS AND DISCUSSION

The synthesis of a silicon-containing spiroorthoester was assayed with two different substrates. The synthetic pathway consisted in the esteri-fication reaction of two commercially available silicon-containing acids and a hydroxyl-containing spiroorthoester (SOE-OH) in presence of EDC and DMAP. Direct ester formation from acids and alcohols or phenols using a carbodiimide coupling agent is a useful method which has been utilized by several authors.[19,20] In a previous work we synthesized a phosphorus-containing spiroorthoes-ter using this synthetic method[17] but with the water soluble EDC as alternative to dicyclohexylcarbo-diimide (DCC) because its elimination result easier and we obtained better yields. The SOE-OH was synthesized, as previously described,[17] from glycidol and γ-BL.

First, the esterification of the trimethylsilyl acetic acid with SOE-OH [scheme 1(a)] was assayed, not obtaining the desired product but yielding a mixture of two products: SOE-OSi and SOE-Ac. The formation of these compounds could be confirmed with ^{1}H and ^{13}C NMR spectroscopy.

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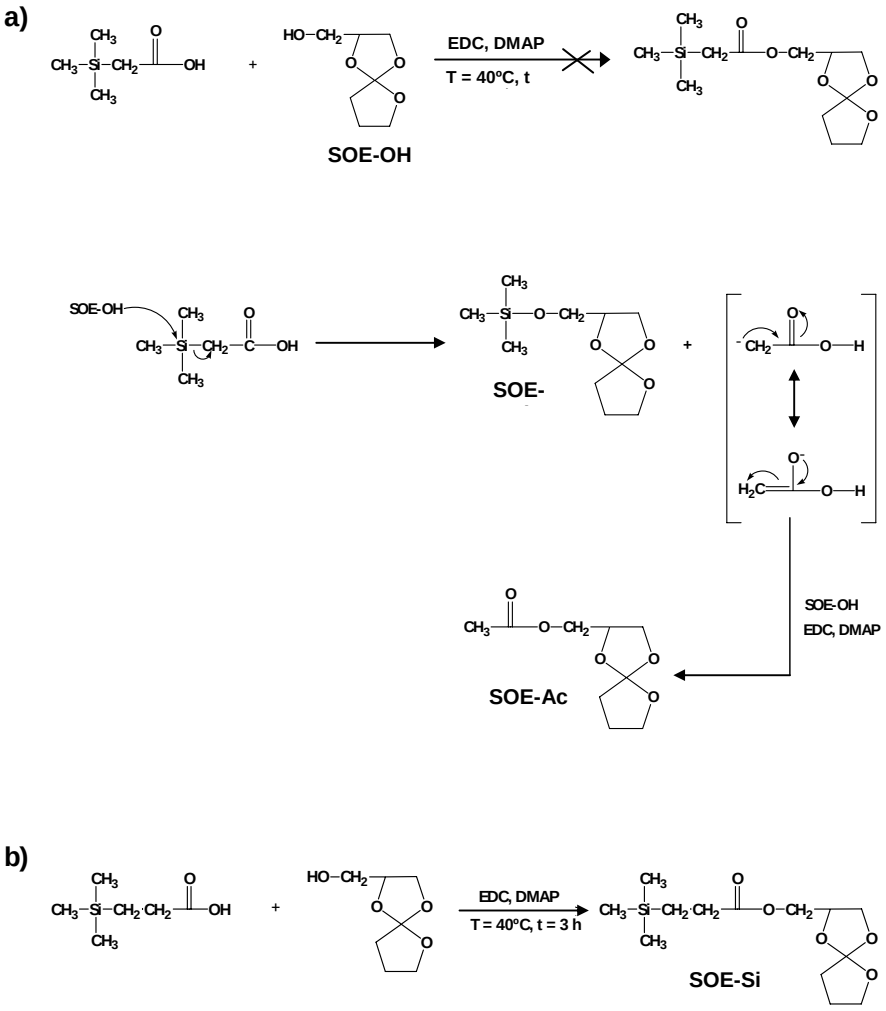

Scheme 1

The formation of SOE-OSi could be explained by a nucleophilic attack of SOE-OH to silicon centre. Different factors facilitate this process: a) the unique nature of silicon in comparison to carbon that arises from the longer bond between silicon and carbon (Si-C = 1.89 Å) in comparison to the corresponding system involving only carbon (C-C = 1.54 Å) and the vacant d-orbitals of silicon which facilitates nucleophilic attacks[21,22] and b) the enolate leaving group is stabilized by resonance. The forma-tion of SOE-Ac could be explained for the further

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esterification of the acetate with SOE-OH in presence of EDC/DMAP.

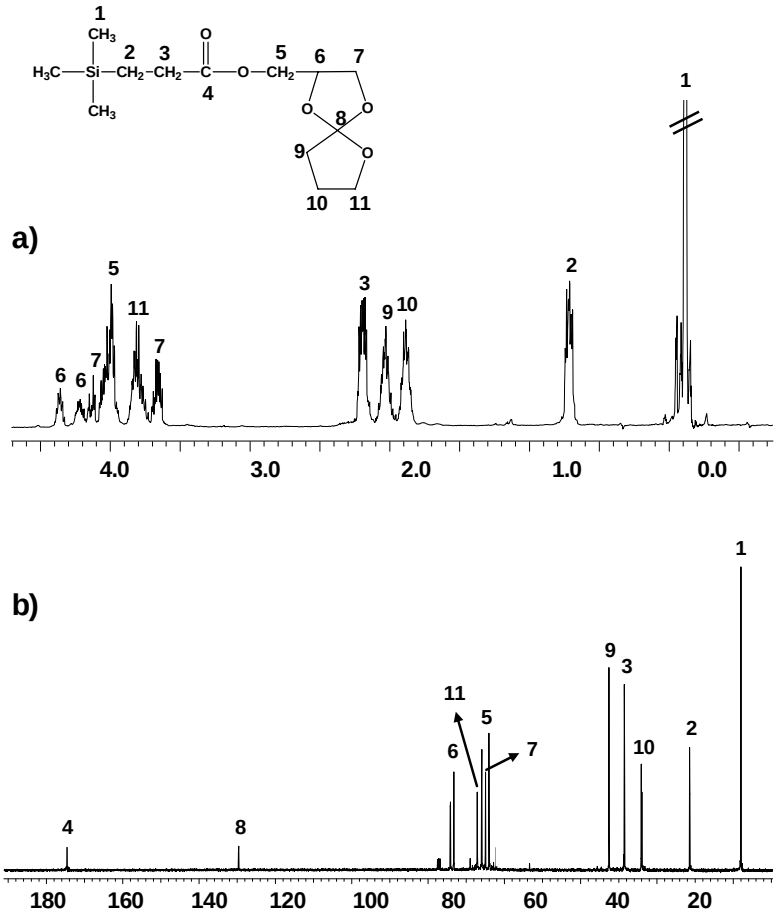

Figure 1. NMR spectra of SOE-Si; ^{1}H (a) and ^{13}C (b).

The ratio 68%:32% for SOE-OSi/SOE-Ac was determined by means of ^{1}H NMR, by the integration ratios of the following signals of ^{1}H NMR spectra: 0 ppm (9 $H_{SOE\text{-}OSi}$) and 2.2-1.8 (4 $H_{SOE\text{-}OSi}$ + 7 $H_{SOE\text{-}Ac}$). This SOE-OSi was not tested as monomer because its tedious work-up and the low yield reached in its formation.

We assayed the synthesis of another silicon-containing acid without a possible leaving group. Thus, the esterification of trimethylsilyl propio-nic acid with

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SOE-OH [(scheme 1(b)] allows a silicon-containing spiro-orthoester (SOE-Si) to be obtained with a good

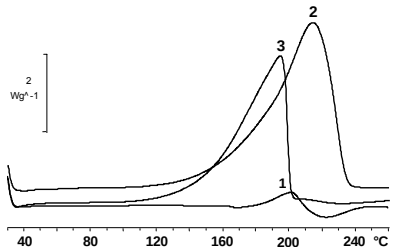
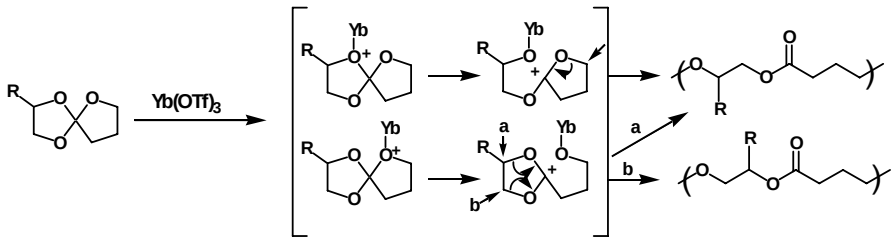


Figure 2. Dynamic DSC plots of (1) SOE-Si; (2) DGEBA and; (3) 2/1 (mol/mol) DGEBA/SOE-Si initiated by 1 phr $Yb(OTf)_3$ obtained at 10 ºC/min heating rate.

yield (90 %). This novel SOE-Si was characterized by means of ^{1}H, ^{13}C, COSY, and HSQC expe-riments. Figure 1 shows the ^{1}H (a), and ^{13}C (b) NMR spectra, with all the assignments. Because the spiroortho-ester has two chiral carbons, the presence of two diastereomers was detected through some split signals in ^{1}H and ^{13}C NMR spectra.

The homopolymerization of SOE-Si with ytterbium triflate as a cationic initiator was first studied by DSC. Scheme 2 summarizes the different ring-opening polymerization path-ways to form linear poly(ether-ester) structures. The dynamic DSC plot of this reaction (Figure 2, curve 1) shows a small exotherm with a maximum at 202 ºC. The enthalpy of this SOE-Si homopolymerization is very low (ΔH



Scheme 2

= 10.5 KJ/SOE equiv.) as observed for ring opening of a non-tensionated spiroorthoester.[18] In a second scan, the T_g of the polymer at -51 º C was observed.

Figure 3 shows the ^{1}H (a) and ^{13}C (b) spectra of the poly(ether-ester), obtained after heating at 180 ºC for 4 h in an oven. In the ^{1}H NMR spectrum, the broadness of protons signals is characteristic of polymeric com-pounds due to the different environ-ment. The methylene and methyl attached to the silicon atom appears at 0.8 ppm and -0.1 ppm respectively. In the ^{13}C NMR spectrum the spiranic carbon does not appear, which indicates the successful polyme-rization of the SOE yielding a poly(ether-ester). Moreover, two different carbonyl signals appear, attributed to the main chain and side chain ester groups. The various aliphatic carbons appear below 80 ppm. The

Figure 3. NMR spectra of homopolymer SOE-Si obtained by cationic polymerization; ^{1}H (a) and ^{13}C (b)

methylene and methine carbons attached to the oxygen atom appear between 80 and 60 ppm. The methylene and methyl groups attached to the silicon atom appear at about 16 ppm and 0.8 ppm, respectively. The complexity of

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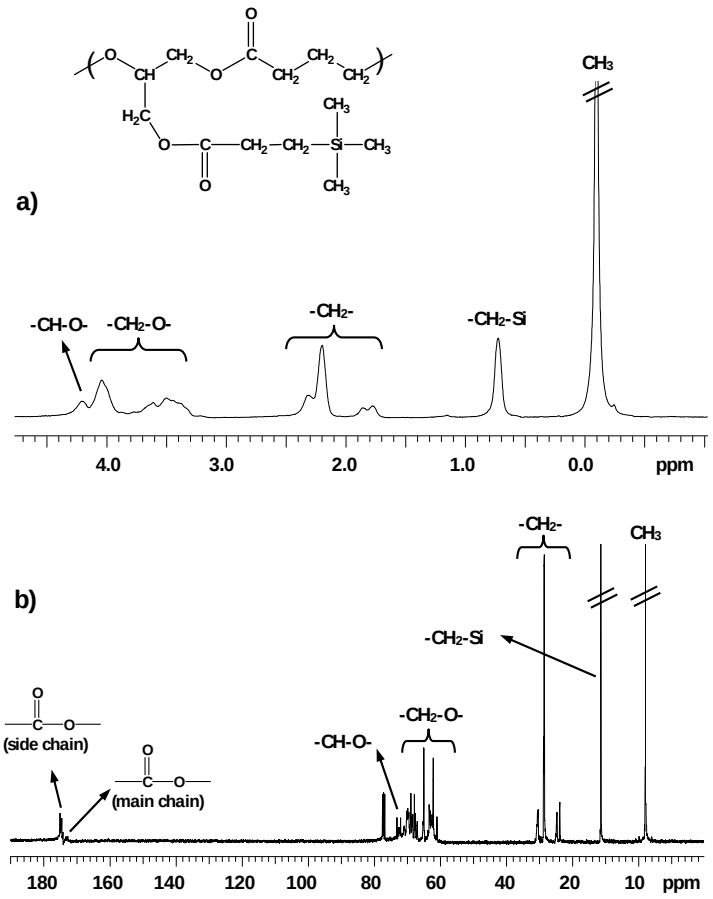

these signals could be attributed to the regioirregularity of the main chain, which are the result of different polymerization pathways and the presence of diastereomers.

The molecular weight of the homopolymer, determined by size exclusion chromatography, was about 3 $x10^3$ g/mol and a polydispersity of 2.5. The unimodal but broad curve of the polymer denotes the different path-ways of polymerization.

As earlier mentioned, our first interest is focused on the modification of epoxy resins with this silicon-containing SOE monomer. In the cationic copolymerization of epoxy resins with spiroorthoesters three simultaneous processes are expected (Scheme 3): a) reaction of SOE with epoxy groups, b) homopolymerization of SOE and c) homopolymerization of epoxy groups. Both a) and b) processes lead to the formation of linear ether

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ester moieties, whereas c) reaction only lead to ether linkages. The copolymerization of DGEBA with SOE-Si (molar ratio 2:1) was monitorized by FTIR/ATR spectroscopy in isothermal experiments at 140 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 4 shows the FTIR spectra of the DGEBA/SOE-Si mixture with 1 phr of $Yb(OTf)_3$ before and after polymerization. The ring opening of spiroorthoester that takes place during the polymerization led to a linear poly(ether-ester) moieties, thus a typical band of carbonyl ester group must appear about 1735-1750 cm^{-1}.[23] SOE-Si contains ester groups which appear at 1737 cm^{-1} in the initial spectrum, and therefore in this zone only an increase in this band was observed on polymerizing. We can see the disappearance of the absorption at 912 cm^{-1} due to the oxirane ring, thus confirming that the glycidylic compound has completely reacted. The Si-C absorption, seen in the SOE-Si homopolymer spectrum at 829 cm^{-1}, in this case appears overlapped with the aromatic CH absorption of DGEBA.

Figure 2 shows the dynamic DSC plot corresponding to this copolymeriza-tion of DGEBA/SOE-Si (curve 3) with an exotherm at 195 ºC. To compare, the corresponding DGEBA polymerization curve is also included in the same figure (curve 2). The maximum of the exotherm of both homopolymeri-zations (SOE-Si and DGEBA) appears at higher temperature than that of the copolymerization. From these dynamic experiments the isothermal

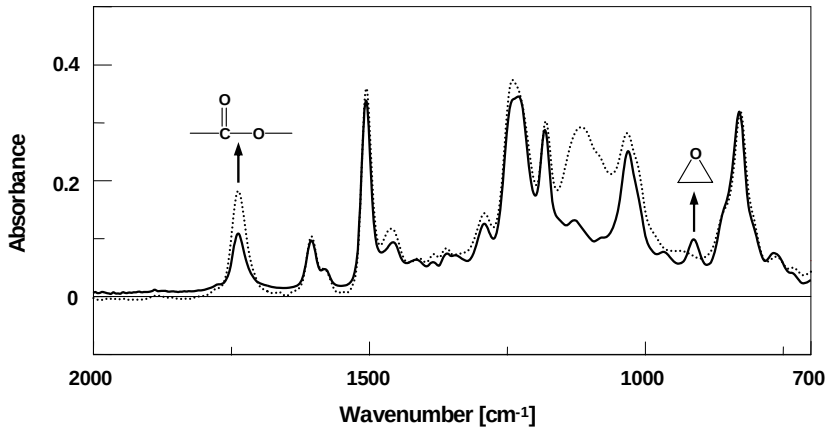

Figure 4. FTIR spectra of 2/1 (mol/mol) DGEBA/SOE-Si with 1 phr of $Yb(OTf)_3$ before (——) and after (·····) polymerization at 140 ºC.

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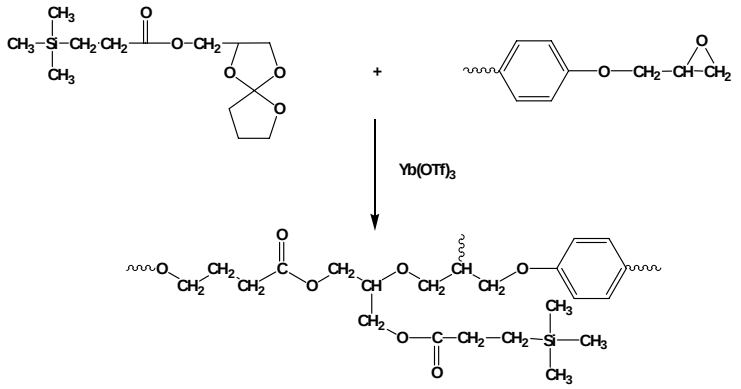
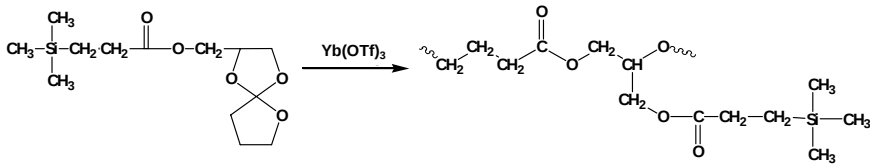
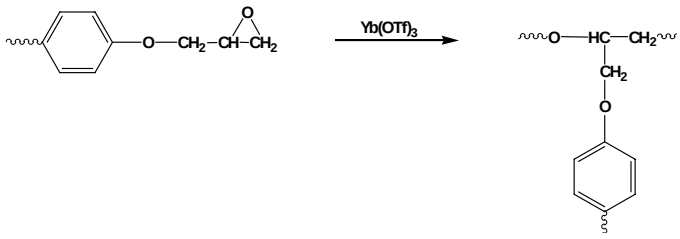
a) Copolymerization of DGEBA with SOE-Si



b) Homopolymerization of SOE-Si



c) Homopolymerization of DGEBA



Scheme 3

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curing conditions were established.

For the copolymerization of DGEBA/SOE-Si the curing conditions were: 150 ºC for 3 h and then 175 ºC for 3 h. The enthalpy values of DGEBA and DGEBA/SOE-Si polymerizations are very similar, 98.1 and 94.8 KJ/epoxy equiv respectively. A dyna-mic run for cured samples allows the calculation of T_g values, which are 139 ºC for DEGBA and 73 ºC for DGEBA/SOE-Si copolymer. The T_g of copolymer is between the T_g values of the two homopolymers.

The dynamic mechanical behaviour of the silicon-modified epoxy resin was obtained as a function of the temperature beginning in the glassy state to the rubbery plateau.[24] Figure 5 (a) shows the storage modulus plots versus the temperature for the DGEBA/SOE-Si copolymer, and the DGEBA homopolymer plot is also included for comparison. The dynamic mechanical properties for the SOE-Si homopolymer, due to its low T_g, was not tested. The crosslinking density of a polymer can be estimated from the plateau of the elastic modulus in the rubbery state. This theory is strictly valid only for lightly crosslinked materials and was therefore used to make qualitative comparisons of the crosslinky density among the two polymers. As can be seen, the incorporation of SOE reduces the crosslinking density. This is due to the greater distance between knots

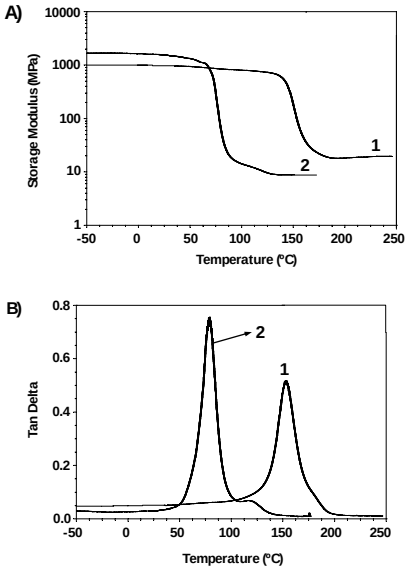

Figure 5. Temperature dependence of (a) Storage Modulus and, (b) Tan Delta for the cured systems of: **(1)** DGEBA; and **(2)** 2/1 (mol/mol) DGEBA/SOE-Si.

produced by the linear ether-ester moieties introduced into the network by the SOE.

The plots of loss factor versus temperature show the α relaxation peak, which is associated with the T_g of the material. Figure 5 (b) shows the Tan δ versus temperature for the crosslinked materials. The highest T_g value corresponds to the more aromatic DGEBA homopolymer. As the height of the Tan δ peak is associated with the crosslinking density, the plots show a lower crosslinking density for the copo-

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lymer. Moreover, the analysis of the width of the Tan δ shows trends in the network homogeneities, and because there are not significant differences among the homopolymer and the copolymer, the branching distribution for the two samples must be similar.

It has been reported that cationic double ring opened SOE based materials exhibit almost no shrinkage and that copolymers having SOE moieties will also crosslink without shrinkage. 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 1). 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-Si sample, the observed value was negative and therefore the polymerization process shows an expansion. The copolymerization of SOE-Si with DGEBA show a positive value, but SOE-Si is much lower than those observed in the crosslinking of pure DGEBA, which shows the typical volume shrinkage that generally accompanied the crosslinking reac-tions.[25] Therefore, it can be conclu-ded that the SOE moieties are effective monomers to obtain crosslinkable copolymers which do not shrink.

Table 1. Volume Change on Crossinking.

Assay	Density (d^{30}, g/cm^3)		Volum Chang (%)
	Mixture	Crosslinked	
SOE-Si	1.005	0.976	-3
DGEBA/ SOE-Si	1.186	1.197	0.9
DGEBA	1.158	1.193	3

To examine the effect of silicon content on the thermal stability and decomposition behaviour, TGA data under nitrogen and air atmospheres were determined and analyzed. Figure 6 and 7 show the weight loss with the temperature and the derivative curves under N_2 and air respectively. Table 2 summarizes the thermogravimetric data.

Table 2. Thermogravimetric Data in N_2 and Air and LOIs of the Polymers.

Assay	Temperature of 5% Weight Loss (ºC)		T_{max}[a] (ºC)		Char yield at 800 ºC (% wt)		LOI
	N_2	Air	N_2	Air	N_2	Air	
SOE-Si	224	222	288	290	3.6	0.0	—
DGEBA/SOE-Si	266	260	332	321/635	18.0	0.0	20.9
DGEBA	314	303	381	360/602	20.4	0.5	20.0

[a] Temperature of the maximum weight loss rate.

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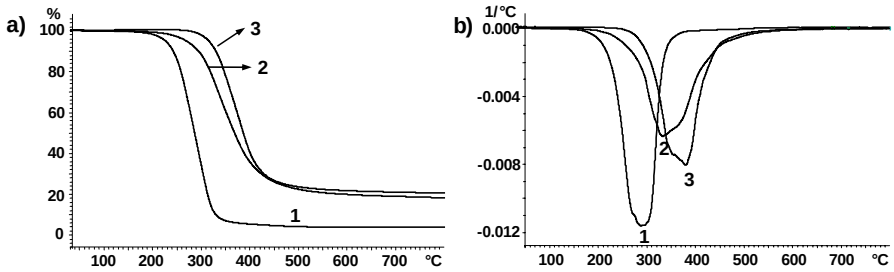

Figure 6. (a) TGA thermograms and (b) first derivative of: (1) SOE-Si homopolymer; (2) DGEBA/SOE-Si copolymer; and (3) DGEBA homopolymer under N_2 atmosphere.

In nitrogen, only one-stage degradation was observed for the three materials. The polymers with SOE-Si degrade at lower temperatures than pure DGEBA, due to the presence of ester moieties in the structure. Under air, the polymers exhibited similar weight loss behaviour as they did under nitrogen atmosphere at temperatures below 400 ºC. A second weight loss at temperatures above 500 ºC occurs in the crosslinked materials. This second stage takes place at higher temperatures when silicon is incorporated into the epoxy resin. This behaviour indicates that the introduction of silicon has slightly improved the thermal stability of the char formed in the first degradation stage. It has been reported that silicon-containing thermosets exhibit significant char formation on heating under air.[5] In this case, the DGEBA/SOE-Si copolymer does not form char residue at temperatures above 700 ºC, what could be explained by its low silicon content (2.75 wt %).[26]

The LOI values, which can be taken as indicators to evaluate the polymer's flame retardancy for the silicon-containing resins, were measured and are shown in Table

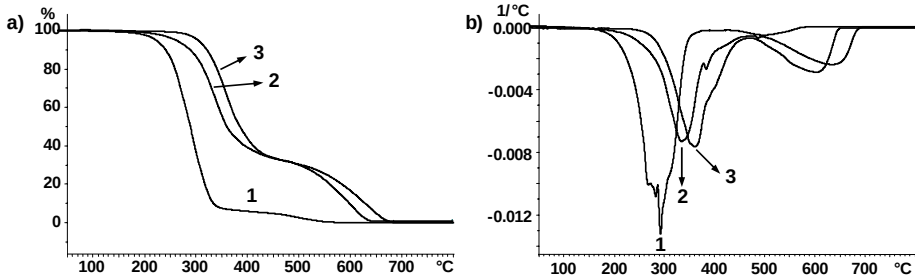

Figure 7. (a) TGA thermograms and (b) first derivative of: (1) SOE-Si homopolymer; (2) DGEBA/SOE-Si copolymer; and (3) DGEBA homopolymer under air atmosphere.

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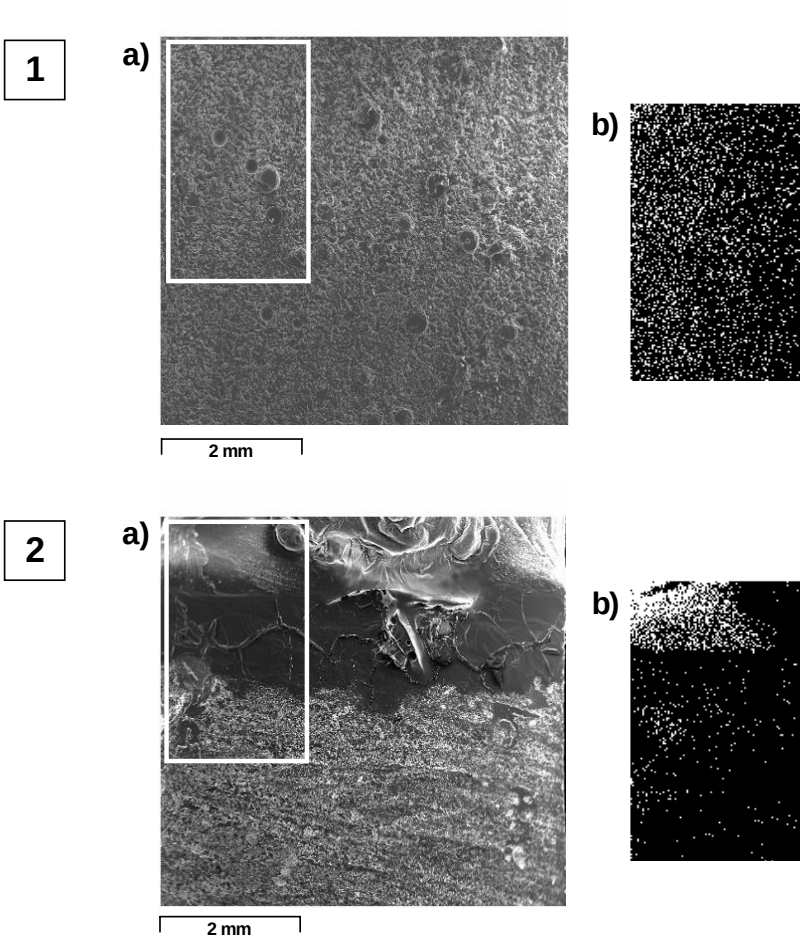

Figure 8. SEM (a) and SEM-EDX Si mapping (b) micrographs of DGEBA/SOE-Si copolymer before (1) and after (2) LOI test.

2. The SOE-Si homopolymer could not be determi-ned because its low T_g. The presence of silicon only slightly increases the LOI value, indicating that a higher silicon content is necessary to achieve a significant flame retardan-cy. However, in this case, an increase of SOE-Si in the final materials should lead to materials with poor mecha-nical properties.

To better understand the role of silicon in the flame retardant properties of the polymer, the ele-ment mapping was performed with energy-dispersive X-ray spectroscopy (EDX) on the surfaces of the initial sample and the sample

after the LOI test. The Si mapping of the initial sample of the DGEBA/SOE-Si copoly-mer indicated a homogeneous distri-bution of this element, as can be observed in the micrograph of Figure 8 (1b). The white points in the figure denote Si atoms. Figure 8 (2a) shows the SEM micrograph of the top surface view of the sample after the LOI test. The burned zone has the appearance of a black and charred material. The Si distribution, in Figure 8 (2b), shows that the silicon density increased toward the top burned surface and that a silicon-rich layer formed. This result could be explained to the low surface energy of silicon renders it to migrate to the surface of the material and to form a protective layer. Incorporating silicon into the polymers enhanced flame retardancy because it produced a continuous layer of silica that retarded the oxidation of the char.[27]

The solid-state ^{29}Si MAS NMR allowed to detect the presence of the SiO_2, at –71 ppm, in the char produced in the LOI test of DGEBA/SOE-Si copolymer. A pure SiO_2 spectrum was recorded in the same conditions to confirm this signal assignation. By Ray-X diffract-tion a crystalline fraction was obser-ved, which can be attributed to the presence of SiO_2.

CONCLUSIONS

A new silicon-containing spiroortho-ester, SOE-Si, was synthesized with good yield by an esterification reaction with a previously synthesized SOE-OH and the commercially available trimethylsilyl propionic acid. This new SOE and a mixture of DGEBA/SOE-Si were polymerized with ytterbium triflate as a cationic initiator. The homopolymerization occurred with expansion and the copolymerization occurred with slight shrinkage which is lower than that observed in conventional epoxy resins. The incorporation of silicon into the epoxy resin improved the thermal stability of the formed char but only slightly increased the LOI values.

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REFERENCES AND NOTES

1. Epoxy Resins: Chemistry and Technology; May, C. A. Ed.; Marcel Dekker, New York, 1988.
2. Jain, P.; Choudhary, V.; Varma, I. K. J Macromol Sci Polym Rev 2002, C42(2), 139.
3. Lu, S-Y.; Hamerton, I. Prog Polym Sci 2002, 27, 1661.
4. Hsuie, G-H.; Wang, W-J.; Chang, F-C. J Appl Polym Sci 1999, 73, 1231.
5. Wang, W-J.; Perng, L. H.; Hsiue, G-H.; Chang, F-C. Polymer 2000, 41, 6113.

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6. Levchik, S.; Weil, E. Polym Int 2004, 53, 1901.
7. Liu, Y. L. Polymer 2001, 42, 3445.
8. Ebdon, J. R.; Jones, M. S. In Polymeric Materials Encyclopedia; J.C. Salomone, Ed., CRC Press, Boca Raton, FL, 1996.
9. Hsuie, G-H.; Liu, Y-L.; Tsiao, J. J Appl Polym Sci 2000, 78, 1.
10. Expanding monomers: Synthesis, Characterization and Applica-tions; Shadir, R. K.; Luck, R. M. Ed.; CRC Press: Boca Raton, FL, 1992.
11. Nishida, H.; Morikawa, H.; Nakahara, T.; Ogata, T.; Kusumoto, K.; Endo, T. Polymer 2005, 46, 2531.
12. Kume, M.; Hirano, T.; Ochiai, B., Endo, T. J Polym Sci Part A: Polym Chem 2006, 44, 3666.
13. Kume, M.; Maki, Y, Ochiai, B, Endo, T. J Polym Sci Part A: Polym Chem 2006, 44, 7040.
14. Zhou, Z.; Jin, B.; He, P. J Appl Polym Sci 2002, 84, 1457.
15. Saigo, K.; Bailey, W. J.; Ento, T.; Okawara, M. J Polym Sci Part A: Polym Chem 1983, 21, 1435.
16. Canadell, J.; Mantecón, A.; Cádiz, V. J Polym Sci Part A: Polym Chem 2006, 44, 4722.
17. Canadell, J.; Mantecón, A.; Cádiz, V. J Polym Sci Part A: Polym Chem (in press).
18. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2003, 41, 2794.
19. Bringmann, G.; Breuning, M.; Henschel, P.; Hinrichs, J. Org Synt Coll 2002, 79, 72.
20. Neises, B.; Steglich, W. Org Synt Coll 1990, 7, 93.
21. Organic Synthesis: The Roles of Boron and Silicon. Thomas, S.E. Oxford University Press, 1992.
22. Silicon Reagents in Organic Chemistry. Colvin, E.W. Academic Press Limited, 1988.
23. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos. Spanish Edition, Springer-Verlag Ibérica, Barcelona, 1998.
24. Tobolsky, A. V.; Carlson, D. W.; Indictor, N. J. J Polym Sci 1961, 54, 175.
25. Chung, K.; Takata, T.; Endo, T. Macromolecules 1997, 30, 2532.
26. Liu, Y-L.; Chiu, Y-C.; Wu, C-S. J Polym Sci Part A: Polym Chem 2003, 87, 404.
27. Kambour, R. P.; Lignon, W. V.; Russell, R. R. J Polym Sci Part C: Polym Lett 1978, 16, 327.

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