

FLAME RETARDANCE AND SHRINKAGE REDUCTION OF POLYSTYRENE MODIFIED WITH ACRYLATE CONTAINING- PHOSPHORUS AND CROSSLINKABLE SPIROORTHOESTER MOIETIES

J. Canadell¹, B. J. Hunt², A. G. Cook², A. Mantecón¹, V. Cádiz¹

¹ Departament de Química Analítica i Química Orgànica. Universitat Rovira i Virgili.
Marcel·lí Domingo s/n, 43007 Tarragona, Spain

² Polymer Centre, Department of Chemistry, University of Sheffield, Sheffield S3 7HF,
United Kingdom

Abstract

Styrene was radically copolymerized with a spiroorthoester with an acrylate group (SOE-AC), and terpolymerized with SOE-AC and diethyl(methacryloyloxymethyl)-phosphonate (DEMMP). This was done for several different feed ratios, to obtain polymers with spiroorthoesters moieties in the side chain. These polymers were then crosslinked with ytterbium triflate, as cationic initiator, via the double ring-opening polymerization. The thermal stability and fire retardance properties of these materials were evaluated by TGA and LOI. The DEMMP-containing polymers give materials which were significantly more flame retarded than the non phosphorus-containing materials, as indicated by the LOI measurements. The volume changes measured upon crosslinking of the polymers were evaluated by density measurements with a gas pycnometry. In all the cases, expansion was observed. This indicates that SOE-AC is an effective monomer for crosslinkable polymers without volume changes.

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

INTRODUCTION

Typical polymerizations of vinyl and monocyclic monomers (e.g., styrene, methyl methacrylate, and epoxy resins) and curing of materials are accompanied by some degree of shrinkage, which can lead to internal compressive stress in the material producing poor adhesion of coatings to the substrate, delamination, and the appearance of microvoids and microcracks, which reduce the durability of the materials.¹ The most common way of reducing this shrinkage is to use inert fillers. In some applications such as encapsulating, potting, and impregnating this is not possible due to the significant increase of the viscosity, which restricts material flow, and mold filling properties. Another problem inherent to the use of fillers is their tendency to settle out, giving rise to inhomogeneous systems.²

The most effective method of solving this problem is to use so-called "expanding monomers", which can polymerize without shrinkage or even show some expansion. A number of spirobicyclic monomers have been reported as an effective way of reducing shrinkage during the double ring-opening polymerization.^{1,3,4} Amongst these are the spiroortho-esters (SOEs),

which can be prepared from epoxides and lactones and exhibit a wide variety of structures.⁵ The introduction of vinyl or acrylate functionalities into the SOE structure allows the free-radical polymerization to yield soluble polymer with intact spiroorthoester functionality. These can be crosslinked, without significant shrinkage, by cationic double ring-opening polymerization using a Lewis acid initiators.⁶⁻⁸

Considerable attention has been made in the last decade to controlling the inherent flammability of organic polymers by the physical incorporation of fire retardant additives. However, the incorporation of additives has several disadvantages. These additives are often required in high loadings to be effective, leading to concomitant undesirable changes in physical and mechanical properties. Also, additives may leach from the polymer through normal service and ageing. An alternative approach is the chemical incorporation into the structure of the polymer via copolymerization or some chemical modifications. Fire retardant polymers generally contain heteroelements such as halogen, phosphorus, silicon or boron. Although halogen-containing flame-

retardants are exceptionally efficient, they have clear disadvantages, as they generate toxic and corrosive gases during thermal degradation. In recent years, phosphorylation has been considered to be one of the most efficient means of conferring flame retardancy on synthetic polymer materials.⁹⁻¹¹

In a previous work⁶ we studied the free-radical copolymerization of a SOE-containing monomer, 1,4,6-trioxaspiro[4,4]-2-nonylmethyl acrylate (SOE-AC), with different phosphorus-containing comonomers, yielding linear polymers with spiro-orthoester moieties as side pendant groups and phosphorus in their structure. These polymers were crosslinked cationically with ytterbium triflate as initiator. In all cases, expansion was observed and the incorporation of phosphorus increased LOI values improving the flame retardancy of materials. However, they presented glass transition (T_g s) below room temperature limiting the applications of these materials.

Encouraged by these findings, we have embarked on improving T_g s of these crosslinked polymers without detriment of flame retardancy and expansion, by introducing rigid structures into the polymer. Thus, this work presents the radical terpolymerization of styrene, SOE-AC and diethyl (methacryloyloxymethyl)-phosphonate (DEMMP). The volume change observed during the

cationic crosslinking was calculated by gas pycnometry. Finally, flame retardancy properties of the polymers were investigated by limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

Styrene (ST; Aldrich) was freshly distilled before use. Ytterbium (III) trifluoromethanesulfonate [$\text{Yb}(\text{OTf})_3$; Aldrich] was used as received. 2,2'-azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from methanol before use. All solvents were purified by standard procedures.

Instrumentation

^1H NMR (400 MHz), ^{13}C NMR (100.6 MHz), and ^{31}P NMR (161.9 MHz) spectra were obtained with a Varian Gemini 400-MHz Fourier transform spectrometer with tetrachloroethane- d_2 or CDCl_3 as the solvent and tetramethylsilane and phosphoric acid as internal standards.

Crosslinking studies were performed on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at a scanning rate of 10 $^\circ\text{C}/\text{min}$. The determination of the glass transition temperatures (T_g 's) was carried out on a Mettler DSC-822e thermal analyzer in covered Al

pans under N₂ at scanning rate of 20 °C/min.

The isothermal polymerization process at 80 °C was monitored with an FTIR-680 Plus spectrophotometer with a resolution of 4 cm⁻¹ in the absorbance mode. An attenuated-total-reflection accessory with thermal control and a diamond crystal was used to obtain Fourier transform infrared/attenuated total reflection (FTIR-ATR) spectra.

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

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

The densities of the materials were measured with a Micromeritics

Accu-pyc 1330 TC helium pycnometer at 30 °C.

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

Monomer Synthesis

Synthesis of 2-bromomethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-Br)⁵

Epibromohydrin (Fluka), γ -butirolactone (γ -BL; Aldrich), boron trifluoride diethyl etherate (BF₃.OEt₂; Aldrich), triethylamine (Fluka).

Synthesis of 1,4,6-trioxaspiro[4,4]-2-nonylmethyl acrylate (SOE-AC)¹²

Acrylic acid (Aldrich), SOE-Br, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; Aldrich), 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (Aldrich).

Synthesis of Diethyl(methacryloyloxymethyl)phosphonate (DEMMP)^{13,14}

Methacryloyl chloride (Aldrich), diethylhydroxymethylphosphonate (Aldrich), triethylamine (Fluka).

All these materials were used as received.

Polymer Synthesis

Copolymerization of ST with SOE-AC (ST/SOE-AC)

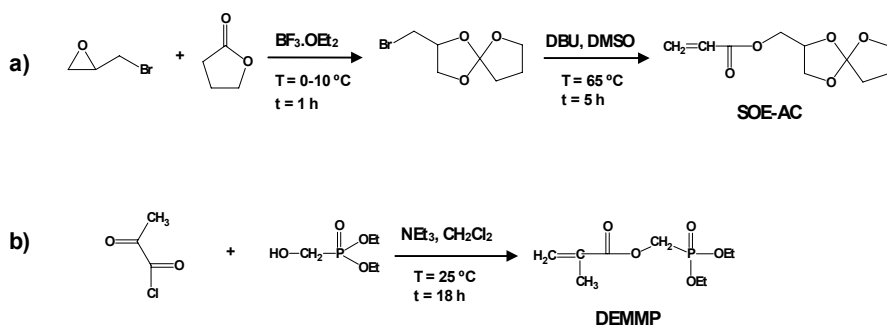
In a typical procedure, a solution of 0.99 g (9.5 mmol) of ST, 2.05 g (9.5 mmol) of SOE-AC, and 93 mg (0.56 mmol) of AIBN in benzene (20 mL) in a sealed ampoule was heated in a water bath at 65 °C for 40 h. The reaction mixture was added dropwise into n-hexane to precipitate the polymer as a white powder. The polymer was further purified by reprecipitation of the dissolved polymer from dry dichloromethane into n-hexane.

^1H NMR (tetrachloroethane- d_2):
 $\delta(\text{ppm}) = 7.4\text{--}6.2$ (br, Ar-H), 4.2-3.2 (br, -O-CH₂-, -O-CH-), 2.4-1.2 (br, -CH₂-, main chain -CH-, main chain -CH₂-).

Terpolymers containing ST, SOE-AC, and DEMMP were obtained in benzene by a similar procedure described before. The initiator used was AIBN and the reaction was performed at 65 °C. The initiator concentration was 3% molar in all cases. All the terpolymers were recovered by precipitation in n-hexane and the purification was carried out by the reprecipitation of the dissolved polymer from dry dichloromethane into n-hexane.

^1H NMR (tetrachloroethane- d_2):
 $\delta(\text{ppm}) = 7.6\text{--}6.4$ (br, Ar-H), 4.4-3.7 (br, -O-CH₂-, -O-CH-, -O-CH₂-P-), 3.7-3.4 (br, -P-O-CH₂-), 2.4-2.2 (br, -C-CH₃), 2.0-1.7 (br, -CH₂-, main chain -CH-, main chain -CH₂-), 1.4-1.0 (br, -CH₃).

^{31}P NMR (tetrachloroethane- d_2):
 $\delta(\text{ppm}) = 20.3$ (br).



Scheme 1

Terpolymerization of ST with SOE-AC and DEMMP (ST/SOE-AC/DEMMP)

Crosslinking Reactions

ST/SOE-AC/DEMMP: 7.6-6.2 (5 H_{ST}), 4.4-3.5 (7 H_{SOE-AC} + 6 H_{DEMMP}), and 1.2-1.0 (6 H_{DEMMP}); 3) ST/DEMMP: 7.6-6.2 (5 H_{ST}) and 4.4-3.8 (6 H_{DEMMP}); 4) SOE-AC/DEMMP: 4.6-3.5 ppm (7 H_{SOE-AC} + 6 H_{DEMMP}) and 1.5-1.3 ppm (6 H_{DEMMP}). These two last signals correspond to the spectra of the copolymers ST/DEMMP and SOE-AC/DEMMP, not shown in the figures. For the copolymer ST/SOE-AC system, signals of the five aromatic protons of the styrene units appear at 7.6-6.4 ppm. The signals at 4.2-3.2 ppm correspond to the $-O-CH_2-$ and $-O-CH-$ of SOE unit. Between 2.4-1.2 ppm the rest of SOE and main chain protons appear. In Figure (1b) the signals corresponding to the phosphorus-containing comonomer are clearly identifiable. In Figure (1c) the single ^{31}P signal is broad due to the presence of different diastereomers and the sequential distribution of the comonomers. For the same reason, in the 1H NMR spectra some signals are split.

The IR spectra of the copolymers show characteristic bands of the

carbonyl ester group at 1731 cm^{-1} , aromatic ring of styrene unit at 1493 cm^{-1} and between 1200 and 1000 cm^{-1} C-O-C vibrations assignable to the SOE moieties. Moreover, in the terpolymer, absorptions at 1247 cm^{-1} corresponding to P=O of phosphonate moieties appear.

In the copolymerizations of ST/SOE-AC the initial feed ratios and the copolymer compositions are in close agreement with the initial feed ratios. Unfortunately, the phosphorus-containing terpolymers showed a lower incorporation of SOE-AC. When the initial feed ratio of SOE-AC was 22% molar, no incorporation of SOE-AC into the structure of the copolymer was detected (table 1). These results would seem to indicate that the DEMMP monomer is more reactive than the other monomers, especially the SOE-AC. Table 1 shows the molecular weights, determined by SEC, which are moderate, for these materials and range between 0.9×10^4 and $2.9 \times 10^4\text{ g/mol}$. The T_g s values, obtained from DSC measurements, are also presented in Table 1 and

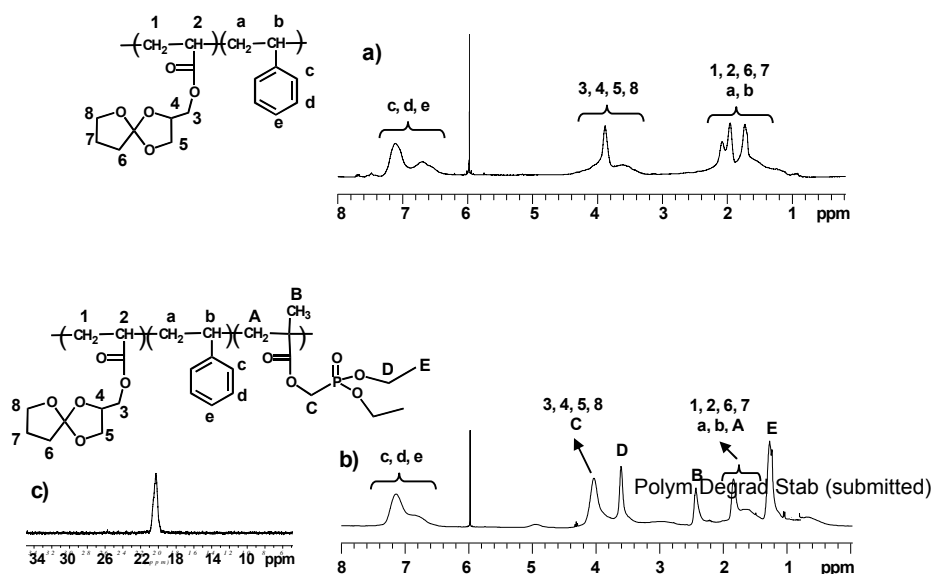


Figure 1. a) 1H NMR of copolymer ST/SOE-AC: 56/44, b) 1H NMR of terpolymer ST/SOE-AC/DEMMP: 42/18/40, c) ^{31}P NMR of terpolymer ST/SOE-AC/DEMMP: 42/18/40.

range, between 19 and 98 °C. Figure 2 shows the DSC curves of polystyrene (1), SOE-AC homopolymer (5) and the ST/SOE-AC copolymers (2-4). As can be seen, the T_g s values of the copolymers are between those of both homopolymers, which would indicate that random copolymers were obtained. The fact that a single T_g was observed indicates that block polymerization does not

using ytterbium triflate as a cationic initiator (Scheme 3). This reaction takes place by a double ring-opening of the pendant SOEs moieties to yield a poly(ether-ester) chain.¹⁶⁻¹⁸ In the case of the SOE used in this work, the reaction yielded crosslinking materials which were insoluble in common organic solvents.

Table 1. Radical copolymerization of ST with SOE-AC and radical terpolymerization of ST with SOE-AC and DEMMP.

Entry	Polymer	Monomer Feed Ratio (mol %) ST : SOE-AC : DEMMP (wt% P)	Copolymer Composition (mol %) ST : SOE-AC : DEMMP (wt% P) ^a	Yield (%)	Mw x 10 ⁴ (g/mol) ^b	T _g (°C)
1	SOE-AC	0 : 100 : 0 (0)	0 : 100 : 0 (0)	66	2.5	32
2	ST/SOE-AC	75 : 25 : 0 (0)	77 : 23 : 0 (0)	53	1.0	73
3		50 : 50 : 0 (0)	56 : 44 : 0 (0)	61	1.1	57
4		25 : 75 : 0 (0)	39 : 61 : 0 (0)	54	1.4	47
5	ST	100 : 0 : 0 (0)	100 : 0 : 0 (0)	82	0.9	98
6	SOE- AC/DEMMP	0 : 79 : 21 (3)	0 : 72 : 28 (3.9)	61	2.9	25
7	ST/SOE- AC/DEMMP	64 : 22 : 14 (3)	66 : 0 : 34 (7.0)	38	1.4	40
8		42 : 42 : 16 (3)	42 : 18 : 40 (8.9)	51	1.2	27
9		20 : 61 : 19 (3)	26 : 46 : 28 (6.3)	48	1.3	19
10	ST/DEMMP	88 : 0 : 11 (3)	90 : 0 : 10 (2.6)	73	0.9	75

^a Estimated by ¹H NMR

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

occur. As expected, an increase in amount of styrene in the copolymers increases the T_g of the materials, due to the rigid and bulky phenyl groups.

The cationic crosslinking of all SOE-containing polymers was performed

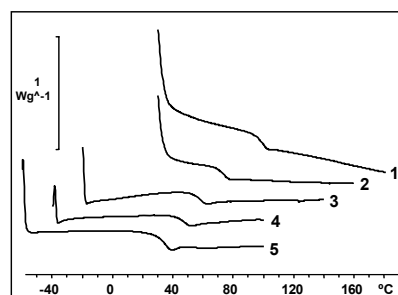
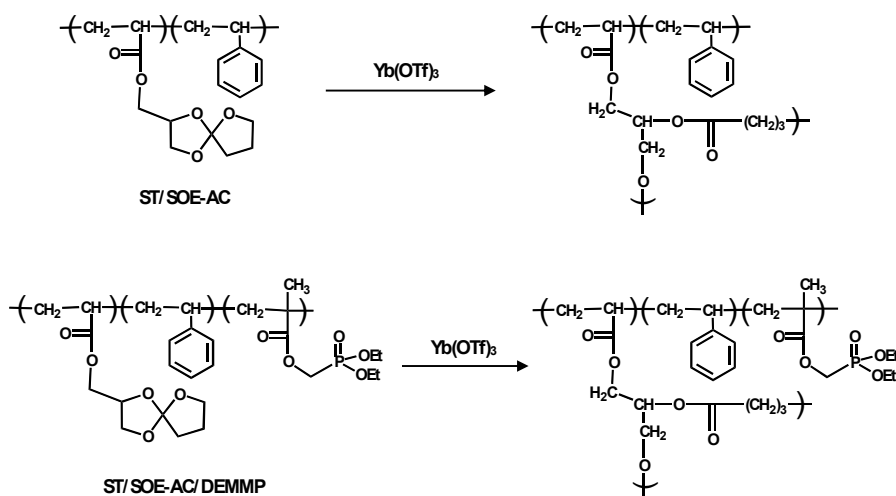


Figure 2. T_g s of polystyrene (1), copolymers ST/SOE-AC: 77/23 (2); 56/44 (3); 39/61 (4); and SOE-AC homopolymer (5).

polymers were studied by DSC. The experiments showed a weak and broad exotherm, which does not allow an accurate determination of the reaction enthalpies to be made. These low enthalpy values can be associated to the low ring tension of SOEs and are in agreement with

assessed by dynamic thermogravimetric analysis (TGA) under nitrogen and in air atmosphere (Table 2). The TGA curves and derivative TGA curves are given in Figures 3 and 4. Under both atmospheres, the temperature for 5% weight loss ($T_{5\%}$) of the



other reported data.¹⁹ A second scan was performed to evaluate the T_g of the crosslinked polymers (Table 2). As can be seen, T_g s for the crosslinked polymers are lower than the linear precursors. This unusual result can be rationalized in terms of differing flexibility of the chain. The rigid and bulky ring SOE becomes an aliphatic and more flexible linear chain in the network, decreasing the T_g of materials.

The thermal degradation behaviours of the crosslinked polymers were

copolymers lay between those the homopolymers and decreases as the SOE content increases. Under nitrogen, the presence of styrene into a copolymer with SOE-AC has a dramatic effect on char formation, with a drop from 14 to 0.7% char being observed on increasing the styrene content from 0 mol% to 100 mol% (Table 2 and Figure 3a). This can be rationalized in terms of the differing degradation mechanisms of the two base polymers: Polystyrene proceeds by a chain scissoring mechanism followed by a

depolymerization and the formation of volatiles, styrene monomer and oligomers,²⁰⁻²² whereas crosslinked SOE-AC does not depolymerize and promotes carbonaceous char. Similarly, under air atmosphere the char formation at 500 °C decreases as styrene content increases (Table 2 and Figure 4a).

In all cases, the char yield under air at 800 °C is zero.

It can be seen from Table 2 and Figure 3a, that the thermal degradation of the copolymers starts at lower temperatures with increasing SOE-AC content, due to the labile linear ester groups in the network. Also, we observe from derivatives of

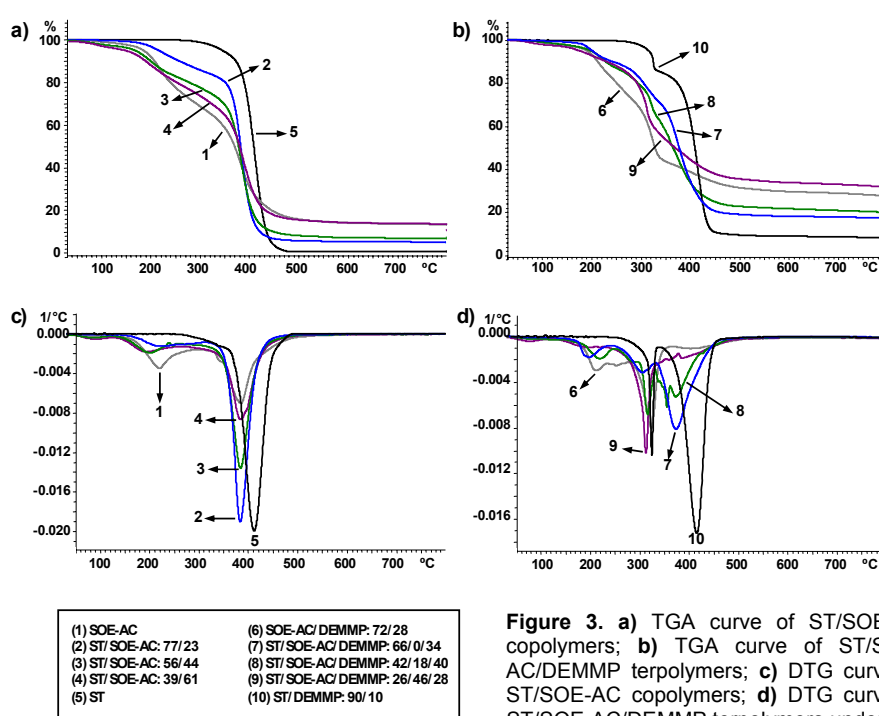


Figure 3. a) TGA curve of ST/SOE-AC copolymers; b) TGA curve of ST/SOE-AC/DEMMP terpolymers; c) DTG curve of ST/SOE-AC copolymers; d) DTG curve of ST/SOE-AC/DEMMP terpolymers under N₂.

However, the char yield of SOE-AC homopolymer is lower than some ST/SOE-AC copolymers. This result suggests a barrier effect of the SOE-AC, so the radicals which are produced through chain scission of polystyrene have more opportunity to undergo recombination reactions.

the thermogravimetric plots (Figure 3c and Figure 4c) that the mechanism of thermal degradation of copolymers is not affected by replacing nitrogen by an oxidative atmosphere with the exception of the oxidation of the char, that takes

ST/SOE-AC	ST/SOE-AC/DEMMP
(1) ST	(6) SOE-AC/DEMMP: 72/28
(2) ST/SOE-AC: 77/23	(7) ST/SOE-AC/DEMMP: 66/0/34
(3) ST/SOE-AC: 56/44	(8) ST/SOE-AC/DEMMP: 42/18/40
(4) ST/SOE-AC: 39/61	(9) ST/SOE-AC/DEMMP: 26/46/28
(5) ST	(10) ST/DEMMP: 90/10

place at temperatures higher than 500 °C.

The TGA char yields of DEMMP-containing terpolymers presented in Table 2 show an increase in the percentages of residual material at 800 °C under nitrogen and seems to be independent of phosphorus content. For example, the copolymer 8 that contains 8.9 % of phosphorus, presents lower char than copolymer

the phosphorus-unmodified copolymers, independently of the atmosphere. However, the derivate curves of the thermogravimetric plots (Fig. 3d) showed a new maximum that appears close to 310 °C, under nitrogen atmosphere. This maximum could be attributed to DEMMP degradation. A small peak, at around

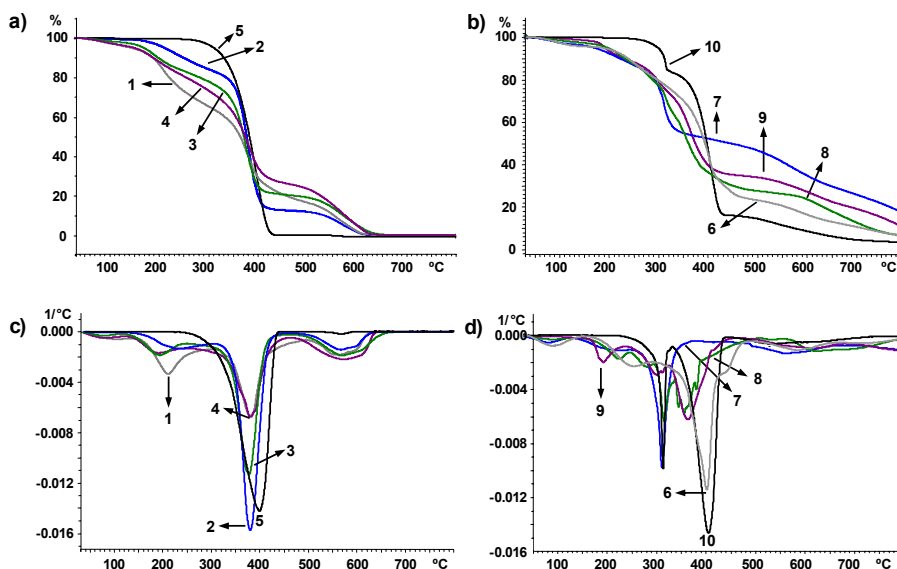


Figure 4. a) TGA curve of ST/SOE-AC copolymers; b) TGA curve of ST/SOE-AC/DEMMP terpolymers; c) DTG curve of ST/SOE-AC copolymers; d) DTG curve of ST/SOE-AC/DEMMP terpolymers under air.

9, which contains 6.3 % of phosphorus. This can be attributed to the effect of increasing SOE-AC content, which also promotes char formation. Similarly results were observed under an air atmosphere.

The terpolymers started the pyrolysis at similar temperatures to

200 °C, could be assigned to the degradation of SOE-AC, as it does not appear in either the polystyrene or styrene/DEMMP polymers. At higher temperatures, between 370 and 380 °C another peak appears, associated with the styrene and the SOE-AC degradations. In addition,

for the phosphorus-free resin, thermooxidative degradation takes place at temperatures higher than 500 °C, while for the phosphorus containing resins it does not take place. This behavior may be in accordance with the mechanism of activation of phosphorus in improving fire resistance, in which the phosphorus forms an insulating protective layer.

flame retardancy of the materials. However, only the % of phosphorus no justify these results and seems to be that SOE-AC content also contributes to LOI values.

The char produced in the LOI test of DEMMP-containing polymers was characterized by solid-state ^{31}P MAS NMR (Figure 6). The sharp signal at 0 ppm corresponds to the

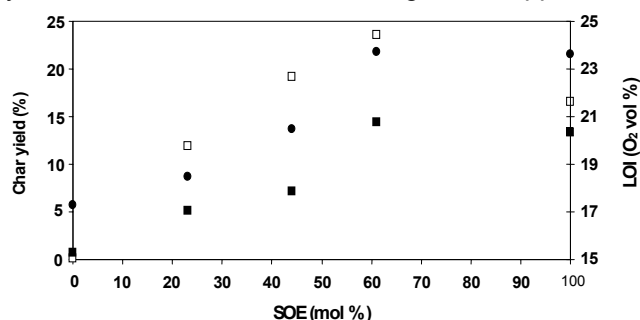


Figure 5. Char Yields (wt%) under nitrogen at 800 °C, under air at 500 °C and LOIs (O₂ vol %) for ST/SOE-AC varying levels of SOE-AC. Left abscissa: Char Yields (■) under N₂ and (□) under air; right abscissa: LOI (●)

The limiting oxygen index (LOI) values, which can be taken as indicators for evaluating the flame retardancy of the phosphorus-modified polymers, were also measured and are shown in Table 2. The LOI values of copolymers SOE-AC/ST increase with the SOE-AC content. Char yield is correlated to the polymer's flame retardancy.²³ In Figure 5 we can observe a good correlation between the amount of SOE-AC in the copolymer and the char yields and LOI values. All phosphorus-containing terpolymers showed higher LOI values, indicative of an improvement in the

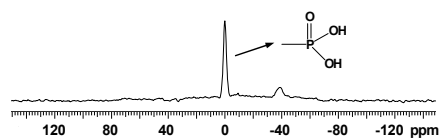


Figure 6. Solid-state ^{31}P NMR spectra of char residue (from the LOI test) of ST/SOE-AC/DEMMP : 26/46/28 terpolymer.

known monophosphoric acid.²⁰

It has been reported that cationic double ring-opening of SOEs takes place without shrinkage or even with expansion.^{1,24} Therefore, the volume changes in the crosslinking reaction of the polymers containing SOE moieties were evaluated by

density measurements with a Micromeritics helium pycnometer at 30 °C before and after crosslinking (Table 3). The volume change was calculated with the following equation:

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

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

Polymer	Density at 30 °C (g/cm ³)		ΔV (%)
	Linear	Crosslinked	
SOE-AC	1.145	1.110	-3
ST/SOE-AC			
77 : 23	1.112	1.105	-0.6
56 : 44	1.127	1.111	-1.4
39 : 61	1.135	1.108	-2.3
SOE-AC/DEMMP	1.128	1.098	-2.6
ST/SOE- AC/DEMMP			
42 : 18 : 40	1.110	1.105	-0.45
26 : 46 : 28	1.123	1.106	-1.5

d_{linear} is the density of the linear polymer. Thus, negative values indicate expansion.

Although typical crosslinking reactions are generally observed significant volume shrinkage,²⁵ in all cases, negative values of the volume change were observed, and therefore the crosslinking process is accompanied by expansion. It can be seen that increasing the amount of SOE-AC gives rise to a greater expansion of the materials.

Therefore, it can be concluded that the SOE moieties used here proved to be effective mo-nomers for obtaining crosslinkable materials.

CONCLUSIONS

Styrene was copolymerized radically with a SOE-containing monomer, SOE-AC, previously synthesized, and terpolymerized with both SOE-AC and diethyl(methacryloyloxymethyl)phos-phonate. The structure of linear polymers was confirmed by ¹H and ³¹P NMR and as well as IR spectroscopy. These polymers were crosslinked through the SOE moieties to yield a poly(ether-ester) network using ytterbium triflate as cationic initiator. A correlation of SOE-AC content in ST/SOE-AC copolymers with LOI values and char yields was detected. Furthermore, phosphorus-containing polymers showed higher LOI and char yields values compared with free-phosphorus polymers, indicating an improvement in the flame retardancy of the materials. All the polymers undergo expansion during crosslinking, increasing with SOE-AC content.

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