

Phosphorus-Containing Soybean-Oil Copolymers: Cross-Metathesis of Fatty Acid Derivatives as an Alternative to Phosphorus-Containing Reactive Flame Retardants

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ABSTRACT: Two different approaches to the creation of phosphorus-containing soybean-oil copolymers were investigated. First, two phosphorus-containing styrene (ST) derivatives, diphenyl styryl phosphine oxide and dimethyl-*p*-vinylbenzylphosphonate (STP2), were tested as comonomers in the cationic copolymerization of soybean oil (SOY), ST, and divinylbenzene (DVB), to obtain heterogeneous systems in all cases. To overcome this drawback, the cross-metathesis reaction of methyl 10-undecenoate and STP2 was carried out to link the phosphorus moiety to the vegetable-oil derivative. This second approach permitted the synthesis of a new reactive phosphorus-containing plant-oil derivative, which was incorporated into the soybean oil, ST, and DVB system. The cationic copolymerization was

investigated, and the structure, thermal stability, and mechanical and flame-retardant properties of the resulting copolymers were studied. Thermosets with moderate glass-transition temperatures were obtained; this showed that the cross-metathesis reaction is a convenient way to produce oil-compatible monomers able to undergo homogeneous polymerization reactions. The resulting thermosets with 1% phosphorus had limiting oxygen index values about 24.0; this indicated an improvement in the fire-retardant properties of the soybean-oil-based copolymers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1649–1658, 2011

Key words: flame retardance, metathesis; renewable resources

INTRODUCTION

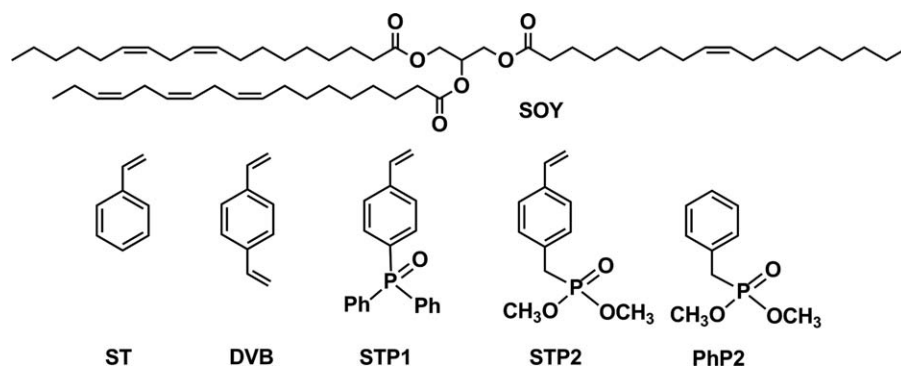
One of the biggest challenges in polymer science is to find replacements for the rapidly decreasing fossil feedstocks. The utilization of renewable resources as raw materials for the production of monomers and polymers can contribute to sustainable development, not only because it decreases CO₂ emissions and prevents contributions to greenhouse effects but also because it can meet other advantages, such as biodegradability and low toxicity. Polymers from renewable resources will play an increasing role because of economical and environmental benefits and the new property profiles that renewable resource polymers can exhibit, such as biocompatibility and biodegradability.¹

Vegetable oils are one of the cheapest and most abundant annually renewable natural resources. They are available in large quantities from various

oilseeds and are now being used in an increasing number of industrial applications. Recently, there have been many attempts to convert vegetable oils and fatty acids to useful polymers.² One of the more stimulating facets of this field is the search for new applications of vegetable oils on the basis of enhancing their specific reactivity in a given type of polymerization process. Vegetable oils are triglycerides of different fatty acids with varying degrees of unsaturation, with the C=C double bonds capable of undergoing cationic polymerization. Among the Lewis acids capable of initiating the polymerization, boron trifluoride diethyl etherate (BF₃·OEt₂) has proven to be the most efficient initiator.³ However, the cationic homopolymerization of regular vegetable oils or the corresponding conjugated oils affords only low-molecular-weight viscous oils or soft rubbery materials of limited utility. Thus, olefinic monomers, such as styrene (ST), divinylbenzene (DVB), norbornadiene, and dicyclopentadiene, are usually copolymerized with vegetable oils to overcome these drawbacks.⁴ Moreover, like other organic polymers, a factor limiting the use of oil-based polymers is their flammability. The synthesis and characterization of flame-retardant polymers from bromoacrylated plant-oil triglycerides has been reported,⁵ but resins

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Scheme 1 Structures of the comonomers.

that contain bromine release hydrogen bromide during combustion, which causes corrosion and toxicity. For these reasons, the search is now on for new environmentally friendly flame-retardant polymeric materials. Phosphorus- and silicon-containing polymers are well recognized for their flame-retardant properties,⁶ and they are increasingly becoming more popular than their halogen counterparts, as they generally give off nontoxic combustion products. In a previous article, we described the incorporation of an organo-silicon functionality to soybean-oil-based polymers.⁷ Their properties suggest that the resulting materials may prove to be useful alternatives for current non-renewable-based thermosets and that the flame-retardant properties of vegetable-oil-based thermosets can be improved by the addition of covalently bonded silicon to the polymer.

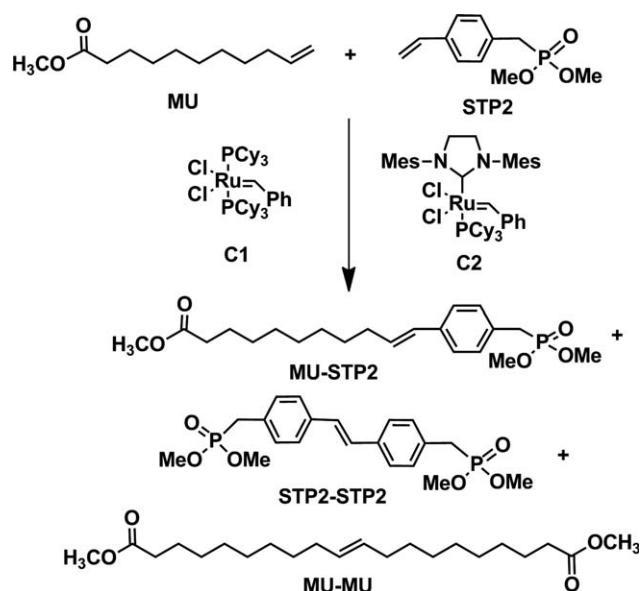
The aim of this work was to extend the application possibilities of vegetable oil-based thermosets through the improvement of their flame retardance and to preserve the environmentally friendly charac-

ter of these materials with a phosphorus-based system instead of a halogen-based system. We investigated the influence of two phosphorus-containing ST derivatives, diphenyl styryl phosphine oxide (STP1) and dimethyl-*p*-vinylbenzylphosphonate (STP2; Scheme 1), on the cationic copolymerization of soybean oil, ST, and DVB, and obtained heterogeneous systems in all cases. Then, we carried out the cross-metathesis reaction of methyl 10-undecenoate (MU) and STP2 (Scheme 2) to attach the phosphorus moiety to the vegetable-oil derivative and incorporated this reactive phosphorus derivative into the soybean oil, ST, and DVB system. The cationic copolymerization of this curing system was investigated, and the structure, thermal stability, and mechanical and flame-retardant properties of the resulting copolymers were studied.

EXPERIMENTAL

Materials

The soybean oil used in this study was supplied by Sigma-Aldrich Chemie GmbH Steinheim (Germany) and was used without further purification. It was primarily composed of unsaturated linoleic (C18 : 2), oleic (C18 : 1), and linolenic (C18 : 3) acids and saturated stearic (C18 : 0) and palmitic (C16 : 0) fatty acids. The content of other saturated and unsaturated fatty acids was negligible. The ¹H-NMR spectrum of soybean oil shows signals at 5.4–5.2 ppm (characteristic of olefinic hydrogens and the methyne protons of the glycerin backbone), 4.2 and 4.1 ppm (corresponding to the diastereotopic protons of the glycerin methylene units), 2.7 ppm (attributed to the methylene protons between two carbon–carbon double bonds), 2.3 ppm (assigned to the methylene protons adjacent to the carbonyl groups), and 2.1 ppm (characteristic of the methylene protons adjacent to the carbon–carbon double bonds). The degrees of unsaturation, expressed as the numbers of carbon–carbon double bonds per triglyceride, were 4.7, as obtained from the iodine index value, and 4.5, as obtained from ¹H-NMR



Scheme 2 Reaction of MU with STP2 with C1 or C2 catalysts.

spectroscopy (calculated from the area of the signal at 5.4–5.2 ppm and the area of the signal at 4.2–4.1 ppm).

ST and DVB were purchased from Fluka and were washed with an NaOH 10% solution and then with water before use. The distilled-grade $\text{BF}_3 \cdot \text{OEt}_2$ used to initiate the cationic polymerizations of the soybean oil was supplied by Sigma-Aldrich Chemie GmbH Steinheim (Germany). Methyl oleate (MeOL; 75%) was purchased from Alfa Aesar GmbH & Co Karlsruhe (Germany) and was used to modify the original initiator, $\text{BF}_3 \cdot \text{OEt}_2$. 4-Bromostyrene, 4-vinylbenzylchloride, 10-undecenoic acid, butyllithium (2.5M in hexane), chlorodiphenylphosphine, sodium hydride (60% in mineral oil), dimethyl phosphite, oxone, benzylidene-*bis*(tricyclohexylphosphine) dichlororuthenium [Grubbs catalyst first generation (C1)], and benzylidene [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium [Grubbs catalyst second generation (C2)] were purchased from Aldrich. MU was synthesized from 10-undecenoic acid by a standard method.⁸ Tetrahydrofuran (THF) and dichloromethane (DCM) were dried over sodium/benzophenone and P_2O_5 , respectively, and were freshly distilled before use. Thin-layer chromatography (TLC) was performed on silica-gel TLC cards (layer thickness = 0.20 mm, Fluka: Sigma-Aldrich Chemie GmbH Steinheim (Germany)). For column chromatography, silica 60 (0.035–0.070 mm, Fluka) was used.

Synthesis of STP1 (Scheme 1)^{9,10}

A dry, two-necked, 250-mL, round-bottom flask equipped with a magnetic stirrer was purged with N_2 , and anhydrous THF (65 mL) was added. The flask was cooled to -78°C , and BuLi (54.6 mmol) was added. 4-Bromostyrene (54.6 mmol) was added dropwise, and the reaction was stirred for 2 h at -78°C . After that, chlorodiphenylphosphine (54.6 mmol) was added dropwise at -78°C , and the reaction was allowed to reach room temperature and was stirred overnight. At the end of the reaction, the mixture was washed twice with a saturated solution of NH_4Cl and twice with brine. The aqueous layer was extracted with diethyl ether. The organic layer was dried over MgSO_4 , and the solvent was removed under reduced pressure. Diphenyl styryl phosphine was dissolved in dichloroethane (40 mL) and oxidized with a saturated aqueous solution of oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) maintaining the temperature below 30°C . The reaction was followed by TLC (methanol/ethyl acetate = 2 : 3) until the disappearance of the starting material (1 h). A solution of $\text{Na}_2\text{S}_2\text{O}_5$ was added until the oxidant reagent was consumed. A large excess of water was added, and the layers separated. The product was extracted with DCM, and the organic phase was dried over

MgSO_4 . The solvent was removed under reduced pressure obtaining a solid that was dissolved in DCM and precipitated in hexane. The product was obtained in a 65% yield.

$^1\text{H-NMR}$ (CDCl_3 , Tetra methylsilane (TMS), δ , ppm): 5.38 (dd, $J_{\text{cis}} = 11.2$ Hz, $J_{\text{gem}} = 0.8$ Hz, $\text{CH}=\text{CH}_2$), 5.86 (dd, $J_{\text{trans}} = 17.6$ Hz, $J_{\text{gem}} = 0.8$ Hz, $\text{CH}=\text{CH}_2$), 6.74 (dd, $J_{\text{trans}} = 17.6$ Hz, $J_{\text{cis}} = 10.8$ Hz, $\text{CH}=\text{CH}_2$), 7.44–7.69 (m, H_{ar}). $^{13}\text{C-NMR}$ (CDCl_3 , TMS, δ , ppm): 116.73 (s, $\text{CH}=\text{CH}_2$), 126.31 (d, $\text{C}_{\text{ar,orto}}$, $J = 12.2$ Hz), 128.62 (d, $\text{C}_{\text{ar,meta}}$, $J = 12.3$ Hz), 132.10–132.40 ($\text{C}_{\text{ar,meta}}$, C_{ipso} , $\text{C}_{\text{ar,orto}}$), 132.51 (s, C_{ipsoP}), 132.98 (C_{ipsoP}), 135.94 ($\text{CH}=\text{CH}_2$), 141.12 (C_{ipso}). ^{31}P (CDCl_3 , H_3PO_4 , δ , ppm): 29.76.

Synthesis of STP2 (Scheme 2)^{11,12}

A two-necked, round-bottom flask equipped with a condenser and a magnetic stirrer was charged under an inert atmosphere with 170 mL of anhydrous THF and 5.04 g (0.246 mol) of sodium hydride. The whitish suspension was cooled to 0°C under magnetic stirring. To this solution, 19.0 g of dimethyl phosphite (0.172 mol) was added slowly. Hydrogen evolution was observed. At the end of the addition, the mixture was taken to room temperature. Sodium iodide (2.46 g; 16.4 mmol) were added, and the mixture was cooled to 0°C . Next, a solution of 28.50 g of 4-vinylbenzyl chloride (0.259 mol) in anhydrous THF was added dropwise to the mixture at 0°C . After addition, the mixture was allowed to reach room temperature and was stirred overnight. The salt formed was removed by precipitation from ethyl acetate and filtration. The filtrate was concentrated, and the product obtained was purified by column chromatography with 1 : 2 hexane–ethyl acetate and then ethyl acetate as an eluent. The yield was 80%.

$^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 3.16 (d, $J = 21.6$ Hz, $\text{CH}_2\text{-P}$), 3.67 (d, $J = 10.4$ Hz, OCH_3), 5.24 (dd, $J_{\text{cis}} = 10$ Hz, $J_{\text{gem}} = 0.8$ Hz, $\text{CH}=\text{CH}_2$), 5.73 (dd, $J_{\text{trans}} = 17.2$ Hz, $J_{\text{gem}} = 0.8$ Hz, $\text{CH}=\text{CH}_2$), 6.69 (dd, $J_{\text{trans}} = 17.6$ Hz, $J_{\text{cis}} = 11.2$ Hz, $\text{CH}=\text{CH}_2$), 7.25 (d, $J = 8$ Hz, $\text{H}_{\text{ar,meta}}$), 7.36 (d, $J = 7.6$ Hz, $\text{H}_{\text{ar,orto}}$). $^{13}\text{C-NMR}$ (CDCl_3 , TMS, δ , ppm): 32.72 (d, $J = 138.0$ Hz, $\text{CH}_2\text{-P}$), 53.05 (d, $J = 6.9$ Hz, OCH_3), 113.97 (s, $\text{CH}=\text{CH}_2$), 126.60 (d, $J = 3.0$ Hz, $\text{C}_{\text{ar,orto}}$), 129.97 (d, $J = 6.9$ Hz, $\text{C}_{\text{ar,meta}}$), 130.77 (s, C_{ipso}), 130.87 (s, C_{ipso}), 136.45 (s, $\text{CH}=\text{CH}_2$). ^{31}P (CDCl_3 , H_3PO_4 , δ , ppm): 29.30.

Synthesis of dimethylbenzylphosphonate (PhP2; Scheme 1)¹¹

A two-necked, round-bottom flask equipped with a condenser and a magnetic stirrer was charged, under an inert atmosphere, with 80 mL of anhydrous THF and 2.1 g (0.088 mol) of sodium hydride. The whitish suspension was cooled to 0°C under

TABLE I
Self- and Cross-Metathesis Results in the Reaction of MU with STP2 in the Presence of C1 and C2

| Catalyst | Molar ratio (STP2/MU) | Conversion of MU (%) ^d | CM ^e (%) | SM ^f (%) |
|-------------------|-----------------------|-----------------------------------|---------------------|---------------------|
| C1 | 2.0 | 36.8 | 28.5 | 8.3 |
| C1 ^a | 2.0 | 46.4 | 38.0 | 8.4 |
| C1 ^b | 1.4 | 55.4 | 43.9 | 11.5 |
| C1 | 1.0 | 53.7 | 38.0 | 15.7 |
| C2 ^{a,c} | 1.0 | 70.9 | 42.6 | 28.3 |
| C2 ^a | 1.0 | 90.4 | 60.4 | 30.0 |
| C2 | 2.0 | 98.6 | 40.6 | 58.0 |

Reaction conditions: [MU+STP2] = 1M in DCM, [C] = 2 mol %, temperature = 40°C, time = 12 h.

^a Without solvent.

^b Reaction performed for 24 h. MU (0.4 mol) was added at 12 h of reaction.

^c Catalyst concentration = 1 mol %.

^d Estimated by ¹H-NMR.

^e Yield of cross-metathesis products estimated by ¹H-NMR.

^f Yield of self-metathesis products estimated by ¹H-NMR.

magnetic stirring. To this solution, 10.5 g of dimethyl phosphite (0.095 mol) was added slowly. Hydrogen evolution was observed. At the end of the addition, the mixture was taken to room temperature, and 2.46 g of sodium iodide (16.4 mmol) was added. Next, a solution of 15.0 g of benzyl chloride (0.088 mol) in anhydrous THF was added dropwise to the mixture at 0°C. After addition, the mixture was allowed to reach room temperature and was stirred overnight. The salt formed was removed by precipitation from ethyl acetate and filtration. The filtrate was concentrated, and the product obtained was purified by silica gel column chromatography with 1 : 2 hexane–ethyl acetate and then ethyl acetate as an eluent. The yield was 80%.

¹H-NMR (CDCl₃, TMS, δ , ppm): 3.14 (d, J = 21.6 Hz, CH₂–P), 3.63 (d, J = 10.8 Hz, OCH₃), 7.21–7.33 (m, 5H). ¹³C-NMR (CDCl₃, TMS, δ , ppm): 32.89 (d, J = 138.8 Hz, CH₂–P), 52.95 (d, J = 6.8 Hz, OCH₃), 127.07 (d, J = 3.8 Hz, C_{ar,para}), 129.71 (d, J = 3.8 Hz, C_{ar,meta}), 129.77 (d, J = 6.8 Hz, C_{ar,orto}), 131.26 (d, J = 9.1 Hz, C_{ipso}). ³¹P (CDCl₃, H₃PO₄, δ , ppm): 29.49.

Cross-metathesis reactions (Scheme 2)

A mixture of MU and STP2 in anhydrous DCM was placed in a two-necked, round-bottom flask equipped with a reflux condenser. The required amount of the metathesis catalyst was then added. The resulting mixture was stirred at 40°C for 12 h under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the unreacted MU and STP2 were removed by distillation *in vacuo* (0.1 mmHg). Then, the products of self-metathesis were separated by

gradual elution through a short pad of silica with hexane followed by ethyl acetate as eluents. The solvent was removed under reduced pressure.

MU–STP2: ¹H-NMR (CDCl₃, TMS, δ , ppm): 1.18–1.31 (m, 4H), 1.34–1.42 (m, 2H), 1.50–1.61 (m, 2H), 2.07–2.17 (m, 2H), 2.18–2.26 (t, 2H), 6.10–6.19 (m, 1H), 6.32 (d, 1H), 7.11–7.18 (m, 2H), 7.18–7.26 (m, 2H). ¹³C-NMR (CDCl₃, TMS, δ , ppm): 25.14, (s, CH₂CH₂COOCH₃), 27.05 (s, CH₂CH=CH_{cis}), 29.34–29.50 (5C, CH₂), 32.78 (d, J = 137.8 Hz, CH₂–P), 33.23 (s, CH₂CH=CH_{trans}), 34.30 (s, CH₂COOCH₃), 51.68 (s, OCH₃), 53.15 (d, J = 6.8 Hz, POCH₃), 126.37 (d, J = 3.12 Hz, C_{meta}–P), 129.42 (d, J = 2.31 Hz, =CH–Ph), 129.67 (d, J = 9.96 Hz, C_{ipso}–CH₂), 130.01 (d, J = 6.84 Hz, C_{orto}–P), 131.50 (s, CH=CH–Ph), 136.25 (s, C_{ipso}–CH), 174.50 (s, C=O). ³¹P (CDCl₃, H₃PO₄, δ , ppm): 29.41.

STP2–STP2: ¹H-NMR (CDCl₃, TMS, δ , ppm): 3.2 (d, 4H, J = 22 Hz), 3.7 (d, 12H, J = 10.8 Hz), 7.1 (s, 2H), 7.3 (d, 4H, J = 8.0 Hz), 7.5 (d, 4H, J = 8.0 Hz). ¹³C-NMR (CDCl₃, TMS, δ , ppm): 32.89 (d, J = 138.8 Hz, CH₂P), 53.16 (d, J = 6.8 Hz, OCH₃), 126.96 (d, J = 3.0 Hz, C_{ipso}–CH₂), 128.37 (s, CH=CH), 130.24 (d, J = 6.8 Hz), 130.79 (d, J = 9.9 Hz, Car), 136.25 (s, C_{ipso}–CH). ³¹P (CDCl₃, H₃PO₄, δ , ppm): 29.24.

MU–MU: ¹H-NMR (CDCl₃, TMS, δ , ppm): 1.20–1.37 (m, 20H), 1.55–1.69 (m, 4H), 1.90–2.05 (m, 4H), 2.30 (t, J = 7.2 Hz), 3.66 (s, 6H), 5.32–5.42 (m, 2H). ¹³C-NMR (CDCl₃, TMS, δ , ppm): 25.17 (CH₂), 27.05 (CH_{2,cis}), 29.30 (CH₂), 29.36 (CH₂), 29.44 (CH₂), 29.51 (CH₂), 29.81 (CH₂), 32.79 (CH_{2,trans}), 34.33 (CH₂), 51.68 (CH₃), 130.55 (CH=CH), 174.50 (C=O).

Cationic copolymerization

The following reaction procedure was usually employed. The desired amounts of monomers were added to the soybean oil (Tables I and II). The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of initiator (3 mol % BF₃·OEt₂ on the basis of the total number of C=C double bonds in the polymerization mixture). The initiator was prepared by the mixture of BF₃·OEt₂ with MeOL (BF₃·OEt₂/MeOL molar ratio = 1.1 : 1.0). The reaction mixture was then poured into aluminum molds and heated for a given time at the appropriate temperatures, usually for 12 h at 80°C and 12 h 140°C. To determine the soluble and insoluble fractions, a 0.5-g sample of the bulk polymer finely ground was extracted for 24 h with 200 mL of methylene chloride with a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation. The soluble substances and the insoluble solid were dried *in vacuo* until a constant weight was reached and isolated for further characterization.

TABLE II
Composition of the Copolymerization Mixtures, Curing Data, and Composition of the Copolymers

| Sample | P (wt %) | Molar ratio | | | | T_{onset} (°C) ^{a,b} | T_{max} (°C) ^{a,c} | Soluble fraction (%) | Insoluble fraction (%) | P (%) soluble fraction |
|--------|-------------|-------------|---------|------|------|---|---|-------------------------|---------------------------|---------------------------|
| | | SOY | MU/STP2 | ST | DVB | | | | | |
| A | — | 1.00 | — | 6.00 | 2.25 | 52 | 74 | 8 | 92 | — |
| B | 1 | 1.00 | 0.69 | 5.30 | 2.25 | 41 | 68 | 41 | 59 | 0.5 |
| C | 1 | 0.83 | 0.75 | 6.00 | 2.25 | 54 | 75 | 22 | 78 | 0.2 |

^a From DSC.

^b Temperature of onset of the crosslinking exotherm.

^c Temperature of the maximum of the crosslinking exotherm.

Instrumentation

The NMR spectra of the samples were recorded on a Varian Gemini 400-MHz spectrometer (400 MHz for ¹H, 100.57 for ¹³C, and 161.9 MHz for ³¹P). The samples were dissolved in deuterated chloroform, and the spectra were obtained at room temperature with TMS or H₃PO₄ as an internal standard.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer with N₂ as the purge gas. The heating rate was 10°C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N₂ as the purge gas at a scanning rate of 10°C/min. The mechanical properties were measured with a dynamic mechanical thermal analyzer (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three-point bending configuration. The various thermal transitions were studied between -100 and 100°C at a heating rate of 3°C/min and a fixed frequency of 1 Hz. The limiting oxygen index (LOI) values were measured on a Stanton Redcroft instrument provided with an oxygen analyzer on polymer bars that measured 70 × 6 × 3 mm³.

RESULTS AND DISCUSSION

The cationic polymerization of soybean oil with BF₃ as an initiator produced viscous oils. Its reactivity toward cationic homopolymerization was rather low, and the initiator was found to be immiscible with the oil;¹³ thus, the conversion to high-molecular-weight polymers has proven relatively difficult. The copolymerization of soybean oil, ST, and DVB with BF₃·OEt₂ was also heterogeneous, with the poor miscibility between the soybean oil and the initiator being the main reason for the heterogeneity rather than the difference in the reactivity between the oil and the styrenic monomers. However, completely homogeneous reaction media can be obtained when the initiator is modified with fish-oil ethyl esters.^{3,13} In our case,⁷ the initiator system was obtained by the mixture of MeOL with BF₃·OEt₂ (BF₃·OEt₂/MeOL molar ratio = 1.1 : 1.0), and homogeneous reactions were generated from a mixture of soybean oil, ST,

and DVB in a molar ratio of 1.00 : 6.00 : 2.25. This composition was chosen because it approximated the composition of the maximum oil incorporated into the polymer, as described in the literature for this system.¹³ The amount of BF₃·OEt₂ was kept constant at 3 mol % on the basis of the total number of C=C double bonds in the polymerization mixture.

The copolymerization of ST with a variety of comonomers containing covalently bound phosphorus, including vinylphosphonic acid, several dialkyl vinylphosphonates, and various vinyl and allyl phosphine oxides, was described earlier.¹² All of these phosphorus-containing copolymers show flame-retardant properties, but their behavior indicates that the phosphorus environment plays an important role. Indeed, the P—C bond is more stable to hydrolysis than the P—O—C bond and is broken just before the C—C bond because of its lower bond energy.¹⁴ In our search for phosphorus-containing comonomers with high thermal and chemical stability, we considered phosphine oxides. In this way, we used ST and STP1 as major comonomers and DVB as a crosslinking agent for the cationic-initiated polymerization of soybean oil (Scheme 1). STP1 was obtained from 4-bromostyrene by reaction with BuLi and further addition of Ph₂PCl, followed by oxidation, according to the reported procedure.^{9,10}

To obtain phosphorus-containing soybean-oil based thermosets, a set of copolymerization mixtures were prepared. The DVB amount was kept constant as was the ST + STP1 amount, whereas the content of ST was decreased as STP1 was increased to obtain thermosets with different phosphorus contents. Samples were prepared by the addition of the desired amounts of ST, STP1, and DVB to the soybean oil, and the mixture was vigorously stirred. For all of the compositions, the solid STP1 remained insoluble even when it was heated to 50°C. The reaction procedure was modified by mixture of the phosphorus-containing monomer in the mixture of ST and DVB and further addition to the soybean oil. In another approach, soybean oil was mixed with DVB, STP1 was mixed with ST, and one mixture was slowly added to the other with stirring. These experiments led to the formation of translucent mixtures with a

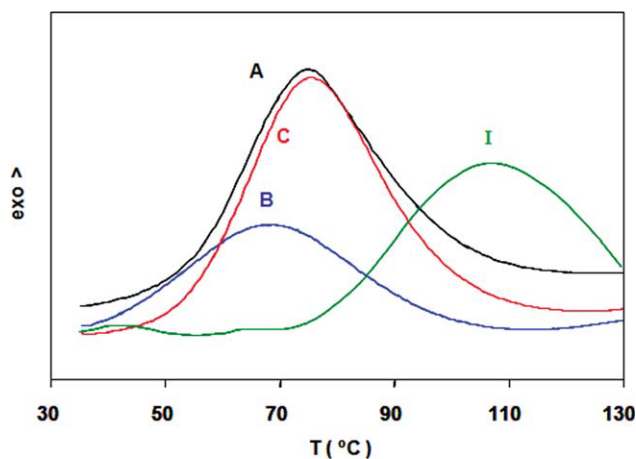


Figure 1 DSC thermograms (10°C/min) of the (I) SOY/STP2/ST/DVB curing mixtures and (A,B,C) mixtures of SOY/MU-STP2/ST/DVB (see Table II for the compositions; T = temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suspension of fine particles in some cases. Although the mixtures seemed to not be completely homogeneous, $\text{BF}_3 \cdot \text{OEt}_2/\text{MeOL}$ was added as a cationic initiator to carry out the copolymerization. In all cases, a large number of small, solid particles appeared in the early stages of the reaction and precipitated. The obtained products were dark brown and heterogeneous.

Heterogeneous reactions are difficult to control experimentally. As a result, the densities are not identical in the final bulk polymers, and the mechanical properties are different in various parts of the material. In our case, the phosphorus-containing monomer was found to be immiscible with soybean oil, and therefore, the cationic-initiated copolymerization was difficult. If so, an improvement in the miscibility of this system should solve the heterogeneity problem. For this reason, we decided to use a different phosphorus-containing monomer, STP2 (Scheme 2). This compound, which is a liquid at room temperature and has a lower aromatic content than STP1, was obtained from vinylbenzyl chloride and dimethyl phosphite by a reported procedure.^{11,12} Polymerization mixtures were prepared as previously described, and in all cases, homogeneous samples were obtained. $\text{BF}_3 \cdot \text{OEt}_2/\text{MeOL}$ (3 mol % on the basis of the total $\text{C}=\text{C}$) as an initiator was added, and a broad exotherm with $T_{\text{onset}} = 83^\circ\text{C}$ and $T_{\text{max}} = 107^\circ\text{C}$ was observed in the differential scanning calorimetry (DSC) plot (Fig. 1, sample I). From these data and according to previous results,⁷ the mixtures were heated at 110°C . However, again, a large number of white particles appeared, and a brownish liquid product was recovered; this showed that the copolymerization did not produce solid polymers. Further attempts to carry out the copoly-

merization of the SOY/STP2/ST/DVB system at higher reaction temperatures or with increasing amounts of catalyst gave similar results in all cases.

There are different possible reasons for the heterogeneous nature of these copolymerizations. The first was the difference in the reactivity of soybean oil and styrenic monomers, which seemed to increase in the presence of STP2 because homogeneous copolymers were obtained in the absence of this monomer. With this taken into account, the white particles should have been crosslinked copolymers of the ST derivatives, which contained the highly polar $\text{P}=\text{O}$ moiety from the STP2 monomer and which showed poor miscibility with soybean oil. In fact, when the reaction mixture was extracted with methylene chloride, a soluble fraction was obtained that did not contain styrenic $\text{C}=\text{C}$ bonds, as revealed by the $^1\text{H-NMR}$ spectrum. The amount of this soluble fraction ranged from 37 to 43 wt %; this matched the soybean-oil content of the initial polymerization mixture.

Another disadvantage to be considered was that the cationic initiator, $\text{BF}_3 \cdot \text{OEt}_2$, was a strong Lewis acid that could interact with the basic $\text{P}=\text{O}$ moieties. The strong coordination of the catalyst to the phosphoryl groups impeded the polymerization of the internal double bonds of the oil, favoring the homopolymerization of the more reactive styrenic monomers. Moreover, the Lewis acid could have promoted the hydrolysis of the methoxy groups, leading to the phosphonic acid that substantially decreased the miscibility of the systems.

To better understand the cause of the heterogeneity in these reaction mixtures, we carried out several experiments. We started by investigating the possible interactions between the catalyst and the phosphoryl moiety. For this purpose, we synthesized PhP2 (Scheme 1) as a model compound containing a $\text{P}=\text{O}$ group but not a styrenic $\text{C}=\text{C}$. When this compound was mixed with the $\text{BF}_3 \cdot \text{OEt}_2/\text{MeOL}$ initiator system, a homogeneous solution was obtained. The analysis by $^{31}\text{P-NMR}$ revealed the presence of two different signals: a singlet at 29.4 ppm, which belonged to the free $\text{P}=\text{O}$ group of PhP2, and a new singlet at 30.3 ppm due to the Lewis acid–base interaction between part of the phosphoryl groups and the initiator, which took place at room temperature.

Another factor causing heterogeneity could have been the hydrolysis of the phosphonate groups during the curing reaction. To determine whether the hydrolysis occurred, PhP2 was mixed with the $\text{BF}_3 \cdot \text{OEt}_2/\text{MeOL}$ initiator system and heated at 90°C for 12 h. The $^1\text{H-NMR}$ analysis of the resulting mixture showed that the signals at 3.6 ppm, attributed to the methoxy groups, remained unaltered, as well as the signals corresponding to the $\text{P}=\text{O}$ in the $^{31}\text{P-NMR}$ spectrum, which still appeared at 29.4 and

30.3 ppm. These results confirmed that the hydrolysis of the phosphonate groups did not take place and that the acid–base Lewis complex was stable at high temperatures. To check that the coordinated catalyst was able to initiate the polymerization of the styrenic monomers, the same experiments were carried out with the STP2 monomer. At room temperature, two signals corresponding to the initial monomer and the coordinated species appeared in the ^{31}P -NMR spectrum (29.9 and 32.7 ppm, respectively). When the mixture was heated at 90°C for 2 h, the polymerization took place as confirmed by the appearance of the polymer backbone signals between 1.2 and 2.0 ppm and the disappearance of the vinyl signals at 5.0, 5.6, and 6.5 ppm in the ^1H -NMR spectrum of the final material. This indicated that the acid–base Lewis complex gave the active species for the cationic polymerization. In a similar way, the cationic copolymerization between STP2, ST, and DVB took place with 3 mol % $\text{BF}_3\cdot\text{OEt}_2/\text{MeOL}$.

From the previous discussion, it can be concluded that in the SOY/STP2/ST/DVB systems, the styrenic monomers were first copolymerized to give the observed particles, which precipitated from the polymerization mixture and were not able to serve as active polymerization centers. Therefore, most of the styrenic monomers were consumed before copolymerization with the oil took place, and oil homopolymerization happened solely on the residual solution. In this way, the difference in the reactivities between the oil and the styrenic monomers under the previously described reaction conditions was the main reason for the heterogeneous copolymerization reactions.

Other attempts to obtain SOY/STP2/ST/DVB homogeneous materials were carried out. We previously described the cationic copolymerization of SOY, ST, and DVB under microwave irradiation with $\text{BF}_3\cdot\text{OEt}_2/\text{MeOL}$ as an initiator, and a comparison with conventional heating showed a great enhancement in the reaction rates.¹⁵ In this way, the cationic copolymerization of the previous P-containing system was carried out under microwave irradiation with different power inputs and reaction times. Solid materials of an extremely fragile nature and poor mechanical integrity were obtained in all cases; the materials also contained high loadings of soluble fractions. Finally, we attempted to use other Lewis acid initiators, such as HBF_4 and $\text{Yb}(\text{OTf})_3$, to carry out the polymerization, and in all cases, no improvements in the homogeneity of the materials were observed.

In view of these results, the development of a miscible phosphorus-containing monomer with similar reactivity to the oil was necessary to incorporate a phosphorus derivative into the soybean-oil copolymers. For this purpose, we chose olefin cross-

metathesis as a synthetic method to chemically attach a phosphorus moiety to a vegetable-oil derivative. Olefin metathesis with oleochemicals allows for a versatile introduction of many different functional groups and takes advantage of the double-bond functionality of fatty-acid derivatives. We carried out the metathesis of MU, which could be obtained from the pyrolysis of castor oil, and STP2 with C1 and C2. (Scheme 2).

Olefin cross-metathesis is a convenient route to functionalized olefins from simple alkene precursors.¹⁶ The cross-metathesis of MU with terminal¹⁷ or internal olefins¹⁸ has been described. Because of the higher reactivity of terminal olefins, when compared to the internal double bonds, even C1 is able to catalyze the cross-metathesis of this compound, although the self-metathesis product dominates. Better results have been described for C2 with almost full conversion for lower catalyst loading without large amounts of byproducts. On the other hand, STs represent one of the classes of olefins used in cross-metathesis because of the slow dimerization of ST to stilbene, which allows for selective cross coupling. Thus, the cross-metathesis products are usually obtained in moderate yields, and only terminal olefins are employable in cross-metathesis with C1. However, the *N*-heterocyclic carbene-based ruthenium complex C2 efficiently catalyzes the cross coupling of STs with a variety of substituted olefins.¹⁹

We examined the reaction of MU with STP2 (Scheme 2) with C1 and C2 and DCM as a solvent at reflux temperature for 12 h, and Table I summarizes the results. As shown, lower conversions in a clean reaction without large amounts of self-metathesis were obtained when we used C1. When C2 was employed, a significantly higher conversion was observed, but the yield of self-metathesis also significantly increased. The highest cross-metathesis yield was obtained with stoichiometric amounts of MU and STP2 and 2% C2. The cross-metathesis product (MU–STP2) was isolated and characterized by ^1H -, ^{13}C -, and ^{31}P -NMR spectroscopy. The ^1H - and ^{13}C -NMR spectra showed characteristic signals for C=C double bonds at 6.10–6.19 and 6.32 ppm and at 129.42 and 131.50 ppm, respectively.

MU–STP2 was mixed with soybean oil, ST, and DVB with the compositions shown in Table II. The amount of DVB was kept constant, and the amounts of MU–STP2, ST, and SOY were varied to obtain thermosets with a phosphorus content of 1 wt %. In all cases, homogeneous mixtures were obtained, and the curing reactions were studied by dynamic DSC (Fig. 1). The plots showed a broad exotherm that shifted slightly at lower temperatures when ST was substituted by MU–STP2 (sample B). However, no significant differences were observed when SOY was substituted by MU–STP2 (sample C). Curing and

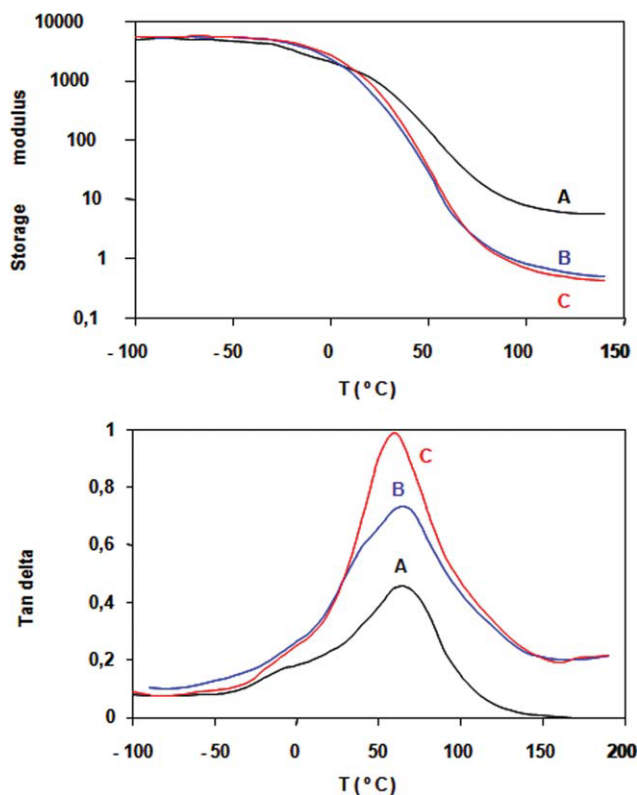


Figure 2 Storage modulus and Tan δ of the (A,B,C) copolymers of SOY/MU-STP2/ST/DVB (see Table II for the compositions; T = temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

postcuring conditions were established as 12 h at 80°C, 24 h at 140°C, and 12 h at 160°C according to previously reported studies.^{7,15}

The copolymers were obtained in essentially quantitative yields and appeared as dark brown rubbery materials at room temperature; they ranged from tough to very soft rubbers. The composition of the copolymers was studied by analysis of the results of overnight Soxhlet extractions with DCM as the solvent. An amount of 59 wt % insoluble materials was retained from the bulk materials when ST was substituted by MU-STP2 (sample B), which contained a less reactive C=C. A higher amount of insoluble fraction was obtained when part of SOY was substituted by MU-STP2 (sample C), according to the higher reactivity of this compound. The soluble fractions were characterized by ¹H-NMR spectroscopy. The presence of signals at 3.6 and 3.1 ppm, corresponding to the CH₃-O and CH₂-P protons, and a broad signal centered at 7.0 ppm, corresponding to the aromatic and C=C protons of MU-STP2, confirmed the presence of this compound. Moreover, signals at 4.2, 2.7, and 2.0 ppm, attributable to the soybean oil, were observed. These results indicate that the soluble fractions were composed of oligo-

meric fractions and unreacted moieties. The P content of the soluble fraction (Table II) was calculated from the ³¹P-NMR spectra with triphenylphosphine as an internal standard (-4.9 ppm) by integration of the signal at 29.4 ppm. As can be seen, the reactive phosphorus-containing flame retardant was mainly incorporated into the network and retained in the insoluble fraction.

DMA was used to investigate the dynamic mechanical behavior of the copolymers. Figure 2 shows the storage moduli and the Tan δ values of the samples. The storage modulus of the phosphorus-containing copolymers was lower than the one of the phosphorus-free sample at temperatures higher than the temperature range corresponding to the primary relaxation process. Moreover, the crosslinking density of sample A was much higher than those of the phosphorus-containing samples because of their higher soluble fraction content. From the Tan δ plots, the presence of a shoulder indicated that the copolymers had two glass-transition temperatures, which merged into a very broad transition. The copolymers appeared to be complex heterogeneous systems composed of hard, aromatic-rich phases and soft, oil-rich phases, with a certain amount of oligomers that acted as plasticizers. The high-temperature transition (ca. 60°C) corresponded to the glass-transition temperature of the plasticized aromatic-rich phase, whereas the low-temperature transition (-10°C) was attributed to the plasticized oil-rich phase. The height of the Tan δ peaks increased for samples B and C; this indicated a lower crosslinking density.

The thermal stability of the copolymers was analyzed by TGA (Fig. 3). Both in nitrogen and in air atmospheres, the decomposition temperatures ($T_{5\%}$'s) for the phosphorus-containing copolymers were lower than for the phosphorus-free resin (Table III). This weight loss at low temperatures should have been attributed to the decomposition of the low-molecular-weight oligomers. Under a nitrogen atmosphere, the degradation took place in one step, and in air, a three-stage weight loss could be seen for the three samples. The first stage was attributed to the decomposition of soluble fractions, whereas the second corresponded to the crosslinked polymer degradation, which took place at a faster rate. The thermooxidative degradation was observed at temperatures higher than 500°C and took place at a lower weight loss rate and at higher temperatures for the phosphorus-containing polymers. This behavior was in accordance with the mechanism of improved fire performance via phosphorus modification. In this retarded-degradation phenomenon, the phosphorus groups formed an insulating protective layer, which prevented the combustible gases from transferring to the surface of the materials,

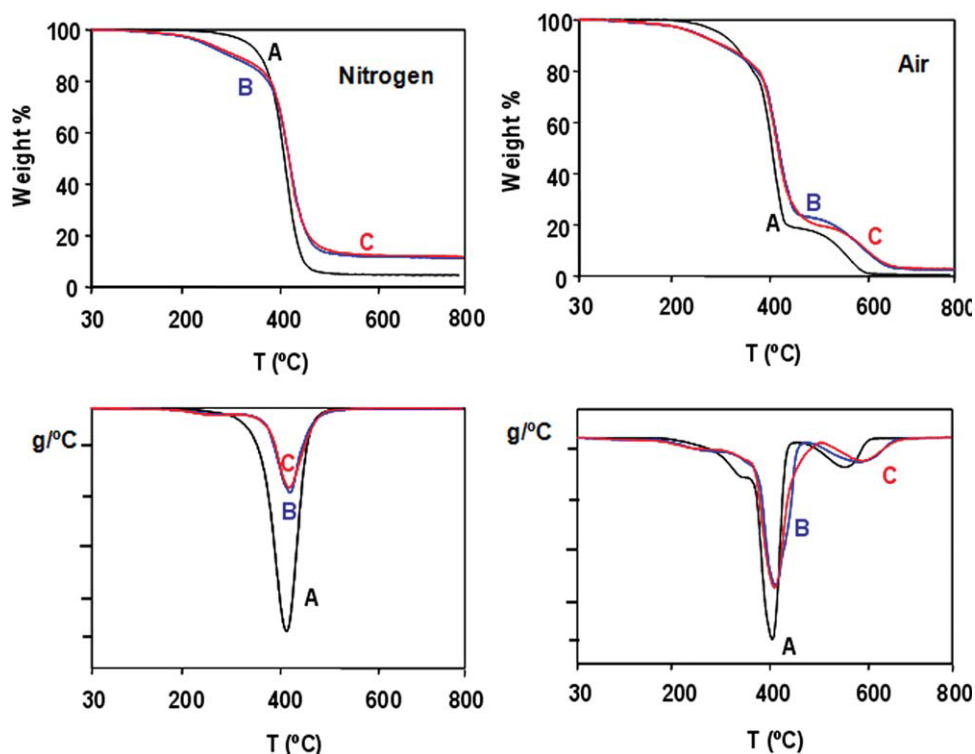


Figure 3 TGA plots (10°C/min) and first derivative curves of the (A,B,C) copolymers of SOY/MU-STP2/ST/DVB (see Table II for the compositions; T = temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased the thermal stability at higher temperatures, and improved the fire resistance. Char yields under nitrogen and air increased slightly for the phosphorus-containing copolymers.

To test the fire resistance, LOI measurements were carried out. LOI values increased from 19.2 for the phosphorus-free system to 23.1 and 24.0 for copolymers B and C, according to the expected behavior for fire-retarded phosphorus-containing materials. Previous work on silicon⁷ and boron²⁰ containing soybean-oil copolymers showed similar LOI values for similar heteroatom percentages (22.6 for Si and 23.7 for B). These results show that the phosphorus-containing copolymers no longer burned in ambient air without complementary oxygen, which suggests that these biobased materials are very interesting for applications that require fire resistance.

CONCLUSIONS

To extend the application possibilities of vegetable oil-based thermosets by improving their flame retardance, we investigated the influence of two phosphorus-containing ST derivatives, STP1 and STP2, in the cationic copolymerization of soybean oil, ST, and DVB, obtaining heterogeneous systems in both cases. We carried out the cross-metathesis reaction of MU and STP2 to attach the phosphorus moiety to the vegetable-oil derivative and incorpo-

rated this reactive phosphorus derivative (MU-STP2) into the soybean oil, ST, and DVB system. The cationic copolymerization was investigated, and homogeneous thermosets were obtained. Dynamic mechanical analysis indicated that the crosslinking density decreased, and no significant differences in the glass-transition temperature were observed. Thermogravimetric analysis showed that the thermal stability decreased, and LOI measurements showed that the phosphorus-containing copolymers no longer burned in ambient air without complementary oxygen.

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