Phosphorus-Containing Renewable Polyester-Polyols via ADMET Polymerization: Synthesis, Functionalization, and Radical Crosslinking

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ABSTRACT: An α, ω -diene containing hydroxyl groups was prepared from plant oil-derived platform chemicals. The acyclic diene metathesis copolymerization (ADMET) of this monomer with a phosphorus-containing α, ω -diene (DOPO II), also plant oil derived, afforded a series of phosphorus containing linear polyesters, which have been fully characterized. The backbone hydroxyls of these polyesters have been acrylated and radically polymerized to produce crosslinked polymers. The thermomechanical and mechanical properties, the thermal stability, and the flame retardancy of these phosphorus-based thermosets have been studied. Moreover, methyl 10-undecenoate has been used as chain stopper in selected ADMET polymerizations to study the effect of the prepolymers' molecular weights on the different properties of the final materials. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1649–1660, 2010

KEYWORDS: ADMET; crosslinked polymer; crosslinking; flame retardance; metathesis; polyesters; renewable resources

INTRODUCTION Recently, the use of plant oils as renewable feedstock for the development of designed polymeric materials has received particular attention due to environmental concerns.¹ The main components of vegetable oils are triglycerides, consisting of glycerol and fatty acids. The chemical modification of their structure enables the synthesis of a wide variety of monomers for the development of polymers with specific properties,² which are now being used in an increasing number of industrial applications.

Synthetic polymer materials are used in many areas and thus the fire hazards associated with the use of these materials are of great concern for both consumers and manufacturers.³ Because of the composition of triglycerides, plant oil-based polymers are flammable, just like many other currently used polymeric materials. The flammability of these materials is a shortcoming in some applications. Therefore, the use of flame retardants to reduce the combustibility of polymers is an important part of the development of plant oil-based polymeric materials. In this way, the synthesis of flame-retardant polymers from bromoacrylated plant oil triglycerides was reported.⁴ However, it is known that bromine-containing flame-retardant resins release hydrogen bromide during combustion, which is toxic and corrosive.⁵ The concept of sustainable development requires fire-retardant technologies to be developed that have a minimum impact on health and the environment throughout the life cycle of the fire-resistant material: starting from its synthesis, via fabrication, use, and recycling to its final disposal. Therefore, the search for new environmentally friendly flame-retardant polymeric materials is of large current interest. Phosphorus-based polymers, for instance, are an effective and well-established class of flame-retardant materials.⁶ They have a good flame-retardant performance and are preferred to the widely applied halogenated flame retardants due to environmental and health reasons.⁷

Acyclic diene metathesis (ADMET) polymerization⁸ has proven to be a useful tool for the synthesis of polymers bearing a wide variety of functional groups.^{9,10} The ADMET polymerization of $\alpha_{,\omega}$ -dienes affords strictly linear, unsaturated polymers through a step-growth polycondensation, which is driven by the release of ethylene. In a previous study,¹¹ we synthesized a series of phosphorus-containing linear polyesters through ADMET copolymerization of a phosphorus-based α,ω -diene with different amounts of a castor oil-derived diene. These polymers showed good flame retardancy and potential application as flame-retardant coatings. However, the low T_{g} of these polymers can be a limiting factor for some applications. Taking into account the high functional group tolerance of the so-called 2nd generation Grubbs metathesis catalysts,^{12,13} ADMET polymerization enables the introduction of functional groups that can act as crosslinking points for the development of thermosets with improved mechanical properties.¹⁴ This work, thus, deals with the

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synthesis of plant oil-based linear polyesters containing phosphorus and alcohol functionalities via ADMET. Further crosslinking of these polymers has been achieved through acrylation of the hydroxyl groups and subsequent radical polymerization affording flame-retardant resins. The thermal and flame-retardant properties of the obtained materials are reported within this contribution.

EXPERIMENTAL

Materials

All chemicals were used as received unless otherwise specified. 10-undecenoic acid, 1,3-dichloro-2-propanol, ethyl vinyl ether, and dicumyl peroxide were purchased from Aldrich. Potassium carbonate and tetrabutylammonium hydrogen sulfate were purchased from Fluka, anhydrous magnesium sulfate and hydrochloric acid were purchased from Scharlab. Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (C1, Grubbs catalyst 1st generation), benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (C2, Grubbs catalyst 2nd generation), and [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxyphenylmethylene)ruthenium (C3, Hoveyda-Grubbs catalyst 2nd generation) were purchased from Aldrich. Hexane, ethyl acetate, and methanol were purchased from Scharlab. Tetrahydrofuran CHROMASOLV® Plus (HPLC) was purchased from Aldrich. Triethylamine (Aldrich) was dried by distillation over CaH₂ and acryloyl chloride (Aldrich) was distilled under vacuum before use. Dimethylformamide and dichloromethane (Scharlab) were dried over P₂O₅ and distilled immediately before use. Toluene was distilled from sodium/benzophenone. Thin layer chromatography (TLC) was performed on silica gel TLCcards (60 F₂₅₄, Merck). Compounds were visualized by spraying with sulfuric acid/anisaldehyde ethanol solution and heating at 200 °C. For column chromatography, silica gel 60 A.C.C. 40–63 μ m (SDS) was used. Methyl 10-undecenoate was prepared by esterification of 10-undecenoic acid with methanol according to standard procedures. 10-[2',5'-Bis(10-undecenoyloxy)phenyl]-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO II) was synthesized according to a previously published procedure.¹⁵

Synthesis of 1,3- and 1,2-Di-10-undecenoylglycerol Mixture (M1)

10-Undecenoic acid (7.14 g, 38.7 mmol), potassium carbonate (5.36 g, 38.7 mmol), and tetrabutylammonium hydrogen sulfate (0.26 g, 0.77 mmol) were mixed in a dry 250-mL two-necked flask under argon. The potassium carbonate was grinded and kept at 100 °C for 24 h prior to use. Anhydrous dimethylformamide (60 mL) and anhydrous toluene (60 mL) were added. The mixture was heated to reflux and stirred for 20 min. 1,3-Dichloro-2-propanol (1.85 mL, 19.4 mmol) was then added with vigorous stirring and the reaction was monitored with TLC (hexane/ethyl acetate 5/1). After completion of the reaction (approximately 4 h), the mixture was allowed to cool down under a constant flow of argon. The reaction mixture was diluted with 200 mL of toluene, washed twice with 300 mL of water, twice with 300 mL of HCl (5%), and once with 300 mL of brine. The organic layer was separated and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The reaction mixture was subjected to column chromatography (hexane/ethyl acetate 6/1) obtaining 4.53 g of a mixture of 1,3- and 1,2-di-10- undecenoylglycerol mixture (**M1**, 55% yield). Monoundecenoylglycerol (2.38 g) and triundecenoylglycerol (5.60 g) were obtained as by-products.

FTIR (cm⁻¹): 3475 (0–H), 3077 (=C–H), 1735 (C=O), 1638 (C=C), 1163 (C–O).

¹H NMR (CDCl₃, TMS, δ in ppm): 5.83–5.73 (m, CH₂=CH), 5.09–5.04 (m, CH–O of 1,2 isomer), 5.00 (d, CH₂=CH, J_{trans} = 17.2 Hz), 4.89 (d, CH₂=CH, J_{cis} = 10.4 Hz), 4.30 (dd, J = 12.00, 4.40 Hz, CH₂–CO of 1,2 isomer), 4.24–4.03 (m, O–CH₂–CHOH–CH₂–O of 1,3 isomer and CH₂–CO of 1,2 isomer), 3.70 (d, J = 5.20 Hz, CH₂–OH of 1,2 isomer), 2.65 (broad, OH), 2.33 (t, J = 7.60 Hz, CH₂–COOCH₂), 2.30 (t, J = 7.60 Hz, CH₂–COOCH), 2.01 (dt, J = 7.07 Hz, CH₂–CH=CH₂), 1.64–1.56 (m, CH₂–CH₂CO), 1.39–1.22 (m, CH₂).

¹³C NMR (CDCl₃, TMS, *δ* in ppm): 174.11 (COOR of 1,3 isomer), 173.98 (COOR of 1,2 isomer), 173.63 (COOR of 1,2 isomer), 139.32 (CH₂=*C*H), 114.34 (*C*H₂=CH), 72.23 (*C*H=O of 1,2 isomer), 68.43 (CH=OH of 1,3 isomer), 65.18 (*C*H₂=O of 1,3 isomer), 62.23 (*C*H₂=CO of 1,2 isomer), 61.60 (*C*H₂=OH of 1,2 isomer), 34.43 (*C*H₂=CO), 34.25 (*C*H₂=CH=CH₂), 33.95 (*C*H₂=CO), 29.46 (CH₂), 29.44 (CH₂), 29.37 (CH₂), 29.35 (CH₂), 29.25 (CH₂), 29.22 (CH₂), 29.21 (CH₂), 29.03 (CH₂), 29.07 (CH₂), 25.08 (*C*H₂=CH₂CO), 25.03 (*C*H₂=CH₂CO).

ADMET Polymerization of M1 to Give P1

M1 (3g, 7.07 mmol) and Hoveyda-Grubbs 2nd generation catalyst (22.1 mg, 0.035 mmol) were placed in a dry 10-mL round-bottom flask under nitrogen atmosphere. The mixture was stirred magnetically at 80 °C under a constant flow of nitrogen. After 12 h, the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 min at room temperature. **P1** was precipitated from methanol as a light brown sticky solid with 96% yield (2.86 g).

FTIR (cm⁻¹): 3540 (0–H), 1742 (C=O), 1142 (C–O).

¹H NMR (CDCl₃, TMS, δ in ppm): 5.42–5.30 (m, CH=CH), 5.10–5.05 (m, CH–O of 1,2 isomer), 4.31 (dd, J = 11.60, 4.40 Hz, CH₂–CO of 1,2 isomer), 4.24–4.04 (m, O–CH₂–CHOH–CH₂–O of 1,3 isomer and CH₂–CO of 1,2 isomer), 3.74–3.69 (m, CH₂–OH of 1,2 isomer), 2.65 (broad, OH), 2.35–2.29 (m, CH₂–CO), 2.04–1.90 (CH₂–CH=CH), 1.70–1.56 (m, CH₂–CH₂CO), 1.38–1.21 (m, CH₂).

¹³C NMR (CDCl₃, TMS, δ in ppm): 174.14 (COOR), 173.65 (COOR), 131.00–129.50 (*C*H=*C*H), 72.23 (*C*H=O of 1,2 isomer), 68.40 (CH=OH of 1,3 isomer), 65.19 (*C*H₂=O of 1,3 isomer), 62.24 (*C*H₂=CO of 1,2 isomer), 61.57 (*C*H₂=OH of 1,2 isomer), 34.44 (*C*H₂=CO), 34.26 (*C*H₂=CO), 32.76 (*C*H₂=CH=CH, *trans*), 29.77 (CH₂), 29.62 (CH₂), 29.41 (CH₂), 29.28 (CH₂), 29.14 (CH₂), 28.91 (CH₂), 28.76 (CH₂=CH=CH, *cis*), 25.04 (*C*H₂=CH₂CO), 24.90 (*C*H₂=CH₂CO).

TABLE 1 GPC, ¹H NMR, and Thermal Characterization of the Phosphorus-Containing ADMET Polyesters

Polymer (M1/M2) ^a	$\% P^{b}$	<i>M</i> _n ^c	PDI ^c	$T_{g} (^{\circ}C)^{d} / T_{m} (^{\circ}C)^{d}$
P1 (10.0/0.0)	0.0	5,300	2.18	-25.8/41.3
P2 (7.5/2.5)	1.6	3,700	2.20	-27.2/21.7
P3 (5.0/5.0)	2.9	5,200	2.56	-12.4
P4 (2.5/7.5)	3.9	7,300	3.13	5.9
P5 (2.5/7.5)	3.9	4,400	2.32	-16.6
P6 (2.5/7.5)	3.9	3,900	2.04	-19.1
^a Mol/mol ratio. ^b Weight/weight perce	ntages.	^с GP ^d DS	°C data. SC data.	

ADMET Copolymerization of M1 and DOPO II (M2)

M1 and **M2** were mixed (3 g scale) in the desired molar ratio (see Table 1) in a dry 10-mL round-bottom flask under nitrogen atmosphere. If required, the respective amount of end-capper (methyl 10-undecenoate) was added. Grubbs 2^{nd} generation catalyst (0.5% mol related to dienes) was added, and the mixture was stirred magnetically at 70 °C under a constant flow of nitrogen. After 12 h, the residue was dissolved in 10 mL of THF, and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 min at room temperature. **P2-P6** were precipitated from methanol with yields >95%. The spectroscopic data is essentially the same for all polymers.

FTIR (cm⁻¹): 3450 (0—H), 1764 (C=O, Ar COOR), 1735 (C=O, COOR), 1607, 1595, 1582 and 1560 (Ar C—C), 1165 (C—O), 1116 (P=O), 925 (P—O), 780, and 757 (Ar C—H).

¹H NMR (CDCl₃, TMS, *δ* in ppm, number assignations related to Scheme 2): 8.07–7.94 (m, H_{8,14,6}), 7.69 (t, J = 7.4 Hz, H₉), 7.57 (dd, J = 15.2, 7.6 Hz, H₁₁), 7.45–7.36 (m, H_{10,16,4}), 7.30–7.23 (m, H_{15,17}), 7.14 (dd, J = 8.6, 6.6 Hz, H₃), 5.43–5.31 (m, CH=CH), 5.10–5.06 (m, CH=O of 1,2 isomer), 4.31 (dd, J = 11.60, 4.40 Hz, CH₂—CO of 1,2 isomer), 4.23–4.03 (m, O—CH₂—CHOH—CH₂—O of 1,3 isomer and CH₂—CO of 1,2 isomer), 3.71 (d, J = 4.4 Hz, CH₂—OH of 1,2 isomer), 2.57 (t, J = 7.6 Hz, H₂₃), 2.35–2.29 (m, CH₂—CO), 2.04–1.90 (CH₂—CH=CH), 1.78–1.56 (m, H_{24,20} and CH₂—CH₂CO), 1.44–0.92 (m, H₂₁ and CH₂).

¹³C NMR (CDCl₃, TMS, *δ* in ppm, number assignations related to Scheme 2): 173.91 (COOR of 1,3 isomer), 173.76 (COOR of 1,2 isomer), 173.46 (COOR of 1,2 isomer), 171.94 (C₁₉), 170.85 (C₂₂), 149.71 (C₅), 149.22 (d, 9.15 Hz, C₂), 147.82 (d, 16.80 Hz, C₁₈), 135.09 (d, 5.33 Hz, C₁₂), 133.28 (C₉), 130.90 (C₁₁), 130.73 (C₁₆), 130.32 (*C*H=*C*H), 128.61 (d, *J* = 15.29 Hz, C₁₀), 128.31 (C₄), 128.01 (d, *J* = 8.35 Hz, C₆), 124.30 (d, *J* = 134.30 Hz, C₇), 124.80-124.61 (C₃, C₁₄, C₁₅), 123.21 (d, *J* = 9.87 Hz, C₈), 122.48 (d, *J* = 145.26 Hz, C₁), 121.02 (d, *J* = 11.47 Hz, C₁₃), 120.66 (d, *J* = 6.84 Hz, C₁₇), 72.04 (*C*H=O of 1,2 isomer), 67.91 (CH=OH of 1,3 isomer), 64.98 (*C*H₂=O of 1,3 isomer), 62.28 (*C*H₂=CO of 1,2 isomer), 61.16 (*C*H₂=OH of 1,2 isomer), 34.26 (*C*H₂=CO), 34.21 (C₂₃), 34.08 (CH₂—CO), 33.17 (C₂₀), 32.59 (CH₂—CH=CH, trans), 29.72 (CH₂), 29.59 (CH₂), 29.47 (CH₂), 29.32 (CH₂), 29.25 (CH₂), 29.12 (CH₂), 28.95 (CH₂), 28.79 (CH₂), 27.19 (CH₂—CH=CH, *cis*), 24.86 (CH₂—CH₂CO, C₂₄), 24.03 (C₂₁). ³¹P NMR (CDCl₃, 162 MHz, δ in ppm): 18.15.

Synthesis of Acrylated Polymers AP1-AP6

The acrylation of ADMET polymers **P1–P6** was carried out following a standard procedure: an anhydrous dichloromethane solution of an ADMET polymer (8 mL of DCM per gram of polymer) was placed in a round-bottom flask under argon. The solution was cooled to 0 °C and acryloyl chloride (1.5 mol-fold excess to hydroxyl groups), followed by triethylamine (3 mol-fold excess to hydroxyl groups) were added. The reaction mixture was allowed to reach room temperature and vigorous stirring was maintained for 2 h. The residue was added dropwise to stirring methanol, and the pure acrylated polymers (**AP1–AP6**) were obtained in yields between 60 and 96% as a light brown sticky solid precipitate.

Spectroscopic Data for AP1

FTIR (cm⁻¹): 1740 (C=0, COOR), 1637 (C=C, acrylate), 1173 (C=O), 808 (C=C-H).

¹H NMR (CDCl₃, TMS, δ in ppm): 6.43 (dd, J = 17.2, 1.2 Hz, COCH= CH_2), 6.41 (dd, J = 17.2, 1.2 Hz, COCH= CH'_2), 6.12 (dd, J = 17.2, 10.0 Hz, COCH= CH_2), 6.11 (dd, J = 17.2, 10.0 Hz, COCH= CH_2), 5.88 (dd, J = 10.0, 1.2 Hz, COCH= CH_2), 5.87 (dd, J = 10.0, 1.2 Hz, COCH= CH'_2), 5.87 (dd, J = 10.0, 1.2 Hz, COCH= CH'_2), 5.45–5.27 (m, CH=CH and CH=O of 1,2 isomer), 4.44–4.09 (m, $O-CH_2-CH-CH_2-O$ of 1,3 isomer, CH_2-CO of 1,2 isomer and CH_2-O of 1,2 isomer), 2.34–2.28 (m, CH_2-CO), 2.04–1.90 (m, $CH_2-CH=CH$), 1.72–1.59 (m, CH_2-CH_2CO), 1.44–1.20 (CH₂).

¹³C NMR (CDCl₃, TMS, δ in ppm): 173.50 (COOR), 165.31 (COOR acrylate), 132.06 (CH=*C*H₂ acrylate), 130.51 (*C*H=*C*H), 128.00 (*C*H=*C*H₂ acrylate), 69.47 (*C*H=OCOCH =CH₂), 68.95 (*C*H=OCOR), 62.59 (*C*H₂=OCOCH=*C*H₂), 62.22 (*C*H₂=OCOR), 34.19 (*C*H₂=CO), 32.79 (*C*H₂=CH=*C*H, *trans*), 29.82-28.98 (CH₂), 27.38 (*C*H₂=CH=*C*H, *cis*), 24.22 (*C*H₂=CH₂CO).

Spectroscopic Data for AP2-AP6

FTIR (cm⁻¹): 3066 (Ar C–H), 1764 (C=O, Ar COOR), 1736 (C=O, COOR), 1637 (C=C, acrylate), 1607, 1595, 1582, and 1560 (Ar C–C), 1180 (C–O), 1118 (P=O), 922 (P–O), 808 (C=C–H), 780 and 757 (Ar C–H).

¹H NMR (CDCl₃, TMS, δ in ppm, number assignations related to Scheme 2): 8.07–7.95 (m, H_{8,14,6}), 7.69 (t, J = 7.8 Hz, H₉), 7.60–7.55 (m, H₁₁), 7.45–7.36 (m, H_{10,16,4}), 7.30–7.23 (m, H_{15,17}), 7.15 (dd, J = 8.6, 6.6 Hz, H₃), 6.43 (dd, J = 17.2, 1.2 Hz, COCH = CH₂), 6.41 (dd, J = 17.2, 1.2 Hz, COCH = CH'₂), 6.12 (dd, J = 17.2, 10.0 Hz, COCH=CH₂), 6.11 (dd, J = 17.2, 10.0 Hz, COCH'=CH₂), 5.88 (dd, J = 10.0, 1.2 Hz, COCH=CH₂), 5.87 (dd, J = 10.0, 1.2 Hz, COCH=CH'₂), 5.45– 5.27 (m, CH=CH and CH=O of 1,2 isomer), 4.42–4.10 (m, O=CH₂=CH=CH₂=O of 1,3 isomer, CH₂=CO of 1,2 isomer and CH₂=O of 1,2 isomer), 2.57 (t, J = 7.6 Hz, H₂₃), 2.32– 2.28 (m, CH_2 —CO), 2.04–1.90 (CH_2 —CH=CH), 1.78–1.54 (m, $H_{24,20}$ and CH_2 —CH₂CO), 1.44–0.92 (m, H_{21} and CH₂).

¹³C NMR (CDCl₃, TMS, δ in ppm, number assignations related to Scheme 2): 173.47 (COOR), 172.08 (C19), 171.03 (C22), 165.29 (COOR acrylate), 149.85 (C₅), 149.45 (d, 9.20 Hz, C₂), 147.97 (d, 16.80 Hz, C18), 135.24 (C12), 133.32 (), 132.02 (CH=CH₂ acrylate), 131.03 (C₁₁), 130.83 (C₁₆), 130.48 (CH=CH), 128.72 (d, J = 14.48 Hz, C_{10}), 128.37 (C_4), 128.25 (d, J = 7.64 Hz, C₆), 127.96 (CH=CH₂ acrylate), 124.72 (d, J =135.00 Hz, C₇), 124.92–124.83 (C₃, C₁₄, C₁₅), 123.31 (d, J =9.86 Hz, C₈), 122.82 (d, J = 144.86 Hz, C₁), 121.23 (d, J =11.47 Hz, C_{13}), 120.88 (d, J = 6.04 Hz, C_{17}), 69.45 (CH-OCOCH=CH₂), 68.91 (CH-OCOR), 62.57 (CH₂-OCOCH =CH₂), 62.19 (CH₂-OCOR), 34.39 (CH₂-CO, C₂₃), 34.18 (CH₂-CO), 33.34 (CH₂-CO, C₂₀), 32.76 (CH₂-CH=CH, trans), 29.78–28.97 (CH₂), 27.37 (CH₂—CH=CH, cis), 24.99 (*C*H₂-CH₂CO, C₂₄), 24.19 (*C*H₂-CH₂CO, C₂₁).

Curing Reactions and Extraction of Soluble Parts

A dichloromethane solution (0.3 g/mL) of each acrylated polyester (**AP**s) and dicumyl peroxide (2 mol % related to acrylate groups) was cast on a glass plate of 7.5×2.5 cm². The samples were heated to 40 °C for 2 h to remove the solvent and then the temperature was raised to 150 °C at 1 °C/min and maintained for 12 h. All samples were subjected to soxhlet extraction with previously distilled dichloromethane to determine their soluble fractions. Each sample (0.5 g) was extracted with 125 mL of dichlorometane. Previously to extractions, the samples were grinded to maximize the extraction efficiency.

Instrumentation

¹H NMR 400 MHz and ¹³C NMR 100.6 MHz NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform. CDCl₃ was used as solvent and TMS as internal reference. Molecular weights were determined on a Shimadzu gel permeation chromatography (GPC) system equipped with a LC-20AD pump, RID-10A refractive index detector, SIL-20A autosampler, and a CTO-20A column oven set to 50 °C. A PLgel 5 μ m Mixed-D column from Polymerlabs in THF at a flow rate of 1 mL/min was used. Linear

poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany, Mp 102-981.000 Da) were used for calibration. The IR analyses were performed on a FTIR-680PLUS spectrophotometer with a resolution of 4 cm^{-1} in the transmittance mode. An attenuated-total-reflection accessory with thermal control and a diamond crystal was used to determine FTIR/ATR spectra. Calorimetric studies were carried out on a Mettler DSC822 differential scanning calorimeter using N₂ as a purge gas (20 mL/min). Dynamic mechanical thermal analysis (DMTA) and tensile tests were performed using a TA DMA 2928 in the controlled force-Tension Film mode with a preload force of 0.1 N, an amplitude of 10 μ m, and at a fixed frequency of 1 Hz in the -100 to 200 $^\circ$ C range and at a heating rate of 3 °C/min. Rectangular samples with dimensions $10 \times 5 \times 0.5 \text{ mm}^3$ were used. The tensile assays were performed by triplicate on rectangular samples $(10 \times 5 \times 0.5 \text{ mm}^3)$ measuring the strain while applying a ramp of 0.5 N/min at 30 °C. A preload force of 0.05 N and a soak time of 3 min were used. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as purge gas. The studies were performed in the 30-800 °C temperature range at a scan rate of 10 °C/min. The limiting oxygen index (LOI) is the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of materials. LOI values were measured in vertical tests on a Stanton Redcroft instrument provided with an oxygen analyzer. The dimensions of the polymer films were $100 \times 5 \times 0.5 \text{ mm}^3$.

RESULTS AND DISCUSSION

The versatility of ADMET polymerization enables the synthesis of linear polymers with functional groups that can be used as crosslinking points.^{14,16} Taking into account the good flame retardant properties obtained in our previous work with DOPO II (**M2**) as phosphorus containing comonomer,¹¹ we decided to use it for the preparation of flame-retardant thermosets. To introduce crosslinking points into the polymer backbone, a hydroxyl-containing α, ω -diene (**M1**, Scheme 1) was synthesized. **M1** and **M2** were copolymerized



SCHEME 1 Synthesis of 1,3- and 1,2-di-10-undecenoylglycerol mixture (M1) and ADMET polymerization in presence of Hoveyda-Grubbs 2nd generation catalyst (C3).



FIGURE 1 ¹H NMR spectra of (a) M1 (mixture of isomers), (b) P1, and (c) P3.

in different molar ratios via ADMET to give a series of linear polyesters with different phosphorus contents. The hydroxyl groups of these polyesters were then esterified with acryloyl chloride to introduce polymerizable groups, and finally, the resulting acrylated polyesters were crosslinked via radical polymerization to obtain a family of flame-retardant thermosets.

For the synthesis of M1, 1,3-dichloro-2-propanol was reacted with two equivalents of 10-undecenoic acid in presence of potassium carbonate and tetrabutylammonium hydrogen sulfate (TBAH) as phase-transfer catalyst (Scheme 1). It must be pointed out that 1,3-dichloro-2-propanol can be obtained directly from glycerol¹⁷ and 10-undecenoic acid is obtained from castor oil pyrolysis, thus, both reagents can be plant oil derived and M1 can be considered as 100% renewable. The ¹H NMR analysis of the reaction mixture revealed the presence of monoundecenoylglycerol, 1,3- and 1,2-diundecenoylglycerols and triundecenoylglycerol as byproducts. In the reaction conditions, glycidyl undecenoate is formed as intermediate (detected by ¹H NMR), and eventually, the epoxide is opened by another undecenoic acid molecule, leading to a mixture of both diacylglycerols. The crude reaction mixture was subjected to column chromatography and the resulting mixture of 1,3- and 1,2-di-10-undecenoylglycerol (60:40, as determined by ¹H NMR, see Fig. 1) was used in the ADMET polymerizations.

It is known that ADMET polymerizations can be carried out with heteroatom-containing dienes, if the heteroatom is not situated close to the double bonds.¹⁸ In both **M1** and **M2**, the terminal olefins are nine carbon atoms spaced from the functional groups. Moreover, previous work in Wagener's

group¹⁰ proved the viability of ADMET polymerization of alcohol-containing dienes using Grubbs 1st generation catalyst.

We first tested different metathesis catalysts in the polymerization of M1. The ADMET polymerizations were run in bulk while a continuous flow of nitrogen was passed through the reaction mixture to remove the ethylene, which is released during the metathesis reaction. When 1% mol Grubbs 1st generation catalyst (C1) was used, oligomerization and poor conversion (by GPC) at 80 °C after 24 h occurred, probably due to catalyst degradation in presence of the primary alcohol of 1,2-diundecenoylglycerol.¹⁹ On the other hand, when 1% mol Grubbs (C2) and Hoveyda-Grubbs (C3) 2nd generation catalysts were used at 80 °C, THF-insoluble products were obtained. Moreover, the polymerization products were not soluble in common organic solvents, suggesting that some kind of crosslinking reaction might have taken place. This poor solubility of hydroxyl-functionalized ADMET polymers was also observed by Valenti et al., and the only proposed reason for this behavior was the high molecular weight of the investigated polymers.¹⁰ However, when the catalyst load was lowered to 0.5% mol, THF soluble polymers were obtained at 80 °C with C1 and C2. Similar results were found in the bulk copolymerization of M1 and M2 at 80 °C in 1:1 molar ratio. C1 gave oligomerization, while C2 and C3 produced insoluble polymers with 1% mol catalyst. When the polymerizations were conducted at 70 °C with 0.5% mol of C2 and C3, soluble polymers were obtained with monomer conversions over 98% (by GPC).

On the basis of the results obtained in the initial experiments, we synthesized a series of polymers (P1-P4) with different M1/M2 molar ratios (Scheme 2) with the aim of



SCHEME 2 Synthesis of phosphorus-containing polyesters via ADMET copolymerization in presence of Grubbs 2nd generation catalyst (C2), with (bottom) and without (top) methyl 10-undecenoate as chain stopper.

determining the effect of the phosphorus content on the properties of the ADMET polymers and the final materials. We also wanted to study the effect of the molecular weight of the ADMET polymers on the flame retardant properties of the crosslinked materials. For this purpose, we performed ADMET polymerizations with 10 and 20% of methyl 10-undecenoate as chain stopper for the highest phosphorus content (**P5** and **P6**, Scheme 2). As reported previously, this procedure results in an efficient end-capping and reduction of the molecular weight.^{11,20} Thus, six polyesters (**P1–P6**) with different **M1/M2** molar ratios were synthesized (see Table 1).

Figure 1 shows the ¹H NMR spectra of **M1** [as a mixture of isomers; Fig. 1(a)], P1 [Fig. 1(b)], and P3 [Fig. 1(c)] as representative examples. The ADMET polymerizations could be confirmed by the disappearance of the terminal olefin signals at 5.8 and 4.9 ppm together with the appearance of a multiplet at 5.3 ppm in both P1 and P3. The molecular weights of the ADMET polyesters (P1-P6) were measured by GPC, using PMMA standards (Table 1). The Mn of the M1 ADMET polymer (P1) was 5300 Da, corresponding to a polymerization degree about 12. From P2 to P4, Mn increases as the content of comonomer M2 does. P5 and P6, with the same composition as P4, showed lower Mn according to the increasing percentage of chain stopper used in the copolymerization. The determination of the molecular weights by integration of the chain end group signals in the ¹H NMR spectrum was not reliable for most of these polymers due to the poor intensity of the terminal double bond signals. However, this fact indicates that the real molecular weights are probably higher than those obtained by GPC analysis.

The thermal characterization of the ADMET polyesters was carried out with differential scanning calorimetry (DSC). The DSC traces stemming from the second heating run (20 °C/min) of **P1–P4** are shown in Figure 2, and the data are collected in Table 1. The thermal analysis of **P1** showed a glass transition (T_g) at -25.8 °C and a melt followed by a cold crystallization and a second melt (T_m) at 41.3 °C. However,



FIGURE 2 DSC traces of the phosphorus-containing ADMET polyesters P1–P4.

			TGA (N ₂)		TGA (Air)			
Polymer	% P ^a	<i>T</i> _{5% loss} (°C)	T _{max} (°C) ^b	Char _{800 ∘C} (%)	<i>T</i> _{5% loss} (°C)	T _{max} (°C) ^b	Char _{800 ∘C} (%)	
P1	0.0	315	316/432	0.0	295	316/431/496	0.0	
P2	1.6	297	307/413/465	6.0	296	306/413/457/653	0.0	
P3	2.9	311	413/465	7.4	315	412/448/603	4.1	
P4	3.9	313	462	8.8	324	452/577	9.1	
P5	3.9	312	413/463	8.2	313	420/453/564	3.0	
P6	3.9	309	413/465	7.9	312	393/453/564	2.2	

TABLE 2 TGA Results of the Phosphorus-Containing ADMET Polyesters

^a Weight/weight percentages.

^b Temperature of maximum weight loss rate.

observations with a polarizing microscope did not reveal two different melting processes when using different heating rates or annealing conditions. As **M2** is added as comonomer, polymer crystallization becomes more difficult due to the bulky aromatic core of **M2**. Moreover, the increase in the aromatic content causes restrictions in the segmental mobility and an increase in the T_g occurs. The DSC trace of **P2**, with only a low content of **M2**, reveals a T_g of -27.2 °C and just one T_m of 21.7 °C. Finally, **P3** and **P4** show only glass transitions at -12.4 °C and 5.9 °C, respectively. As previously mentioned, the addition of methyl 10-undecenoate as chain stopper in the synthesis of **P4** affords lower molecular weights. As a result, the T_g s obtained for **P5** (-16.6 °C) and **P6** (-19.1 °C) are found below that of **P4**.

The thermal stability of the ADMET polyesters was studied by thermogravimetric analysis (TGA) under nitrogen and air atmospheres (data in Table 2). Good thermal stability is observed for P1-P6 under nitrogen [Fig. 3(a)] with 5% weight loss around 310 °C. For P1, the main degradation step takes place at 430 °C but as M2 is introduced, the thermal stability increases and a new degradation step appears around 460 °C. Moreover, an increase in the aromatic and phosphorus content carries an increase in the char obtained at 800 °C from P1 (0.0%) to P4 (8.8%). The thermal stability and char obtained at 800 °C of P5 and P6 is lowered with respect to P4 due to their lower molecular weight. A similar trend is observed in the thermal degradation behavior under air [Fig. 3(b)]. Five percent weight loss around 310 °C and two main degradation steps related with the M1/M2 composition at 430 and 450 °C were observed under these conditions. Under air, the residues at 800 $\,^\circ\text{C}$ increase with the phosphorus content reaching a maximum value of 9.1% for P4.

In the next step, the hydroxyl functionalized polyesters **P1** to **P6** were reacted with acryloyl chloride in the presence of triethylamine (Scheme 3). The acrylated polyesters (**AP1** to **AP6**) were isolated by slow addition of the reaction mixture to methanol in yields between 60 and 96%. Nonquantitative yields were probably due to the increased solubility of the polyesters in methanol after acrylation of the hydroxyl groups that led to partial fractionation. Two representative

¹H NMR spectra are shown in Figure 4, where the characteristic set of signals at 6.3, 6.1, and 5.7 ppm confirm the presence of the acrylate groups. Moreover, in the ¹³C NMR spectrum, the complete disappearance of the signals belonging to the non acrylated polymer **P3** and the appearance of the signals of **AP3** confirms full functionalization.



FIGURE 3 TGA measurements (a) under nitrogen and (b) under air of the phosphorus-containing ADMET polyesters P1–P6.



SCHEME 3 Synthesis of acrylated phosphorus-containing polyesters **AP1–AP6**.

Based on our previous experience in the crosslinking of acrylate derivatives,^{21,22} dicumyl peroxide was chosen as radical initiator for the crosslinking reaction of the acrylated ADMET polyesters. DSC curing runs between APs and dicumyl peroxide (2% molar to acrylate groups) showed similar exotherms with onsets about 150 °C for all the acrylated polyesters. Once the curing conditions were established, APs and dicumyl peroxide (2% mol) were dissolved in dichloromethane (0.3 g/mL) and the resulting solution was cast on a glass plate. The samples were heated at 40 $^\circ\text{C}$ for 2 h to remove the solvent and then the temperature was raised to 150 °C at 1 °C/min and maintained for 12 h. The cured materials (samples I to VI), were obtained as light brown transparent films. The curing extent of the crosslinking reactions was studied with FTIR spectroscopy by following the disappearance of the acrylate group bands. Figure 5 shows the FTIR spectra of AP3 and sample III as a representative example of the crosslinking reaction. The bands at 1637 cm^{-1} (C=C stretching), 1403 and 1294 cm^{-1} (=C-H in-

plane deformation) and 983 and 808 cm⁻¹ (=C-H out-ofplane deformation) completely disappear confirming the polymerization of the acrylate groups. The reactivity of nonconjugated internal double bonds toward radical polymerization is very low,^{23,24} thus, the double bonds of the polyester backbone were not expected to polymerize. This is confirmed in the ATR-FTIR spectrum after crosslinking by the presence of the band at 967 cm⁻¹, which is associated to the C=C-H out-of-plane deformation. The crosslink extent was also investigated by extracting the soluble fraction of samples I-VI. Sample I presents a soluble fraction of 0.9%. which indicates a very high crosslinking degree. The soluble fractions increase as the M2 content does reaching a value of 20.3% for sample IV due to the decreasing number of crosslink points available in the linear prepolymers. The soluble fractions of samples V (16.8%) and VI (17.7%) are similar to that of sample IV showing that similar crosslinking degrees were achieved independently of the prepolymers molecular weights.



FIGURE 4 ¹H NMR spectrum of AP3 and enlargement of the 75–60 ppm region of ¹³C NMR spectra of P3 and AP3.



FIGURE 5 FTIR-ATR spectra of (a) **AP3** and (b) sample **III**. The absorption bands associated to the acrylate group are indicated.

The soluble fractions were analyzed by ¹H and ³¹P NMR spectroscopy. ¹H NMR showed total reaction of the acrylate double bonds and the presence of a triplet \sim 2.4 ppm belonging to the methylene protons adjacent to the carbonyls of the polymerized acrylates. This clearly indicates that the soluble fractions are composed of low molecular weight polymers instead of non polymerized acrylates. However, the aromatic region showed little variations suggesting some change taking place in the DOPO moiety. This was further confirmed by examining the ³¹P NMR spectra, where a new singlet at 32.6 ppm appeared together with DOPO signal (18.2 ppm). This new signal matches with the opened DOPO form, having a phosphinic acid functionality (hydrolysis of the P-O bond). Although the DOPO ring was closed throughout the synthesis of M2, ADMET polymerizations and acrylation reactions, it is known that a certain amount of hydrated DOPO can be found when using DOPO as a reagent, and dehydration at temperatures over 200 °C under vacuum are usually necessary prior to use.²⁵ It is, thus, possible that part of the pendant DOPO moieties were hydrated by long exposure of the samples to air. As the DOPO P-O bond is cleaved in the early stages of thermal degradation (300 °C),²⁶ the flame retardant action of these materials will not be affected in any case and thus, the presence of the opened form of DOPO does not interfere with the aim of this study.

Figure 6 shows the dynamic thermomechanical analysis of samples I to VI as the tan delta plots from -100 to 150 °C. The main peak of the tan delta plots, that is the alpha relaxation, is related to the glass transition temperature. As expected, from sample I to sample IV, the maximum of the tan delta peak shifts to higher temperatures as M2 content increases due to the increasing aromatic fraction. On the other hand, an increase in M2 content means more space between acrylate groups, which is accompanied by a loss of crosslink density, and a decreased crosslink density is mani-

fested by a higher tan delta peak.²⁷ This fact is confirmed by the height of the tan delta peak, which increases from sample I to sample IV. The effect of the prepolymer molecular weight on the dynamic mechanical properties of the crosslinked materials is observed in samples IV, V, and VI. The $T_{\rm g}$ value drops from sample IV to samples V and VI as a consequence of the lower molecular weights of P5 and P6 with respect to P4.

The thermal degradation behavior of the crosslinked materials under nitrogen and air atmospheres is shown in Figure 7, and the data are collected in Table 3. Under nitrogen [Fig. 7(a)], all samples present good thermal stability with 5% weight loss around 340 °C. From the maxima of weight loss rate, it can be inferred that two general degradation mechanisms are taking place, which can be related to the prepolymer composition. Sample I contains the M1 homopolymer and degrades in one single step with the maximum weight loss rate around 430 °C. As M2 is added, a new maximum of weight loss rate appears around 460 $^\circ\text{C}$, which becomes the main degradation step as the M2 content increases. The char at 800 °C increases from sample I (5.0%) to sample IV (11.2%) as the phosphorus content does and slightly decreases for samples \boldsymbol{V} and $\boldsymbol{V}\boldsymbol{I}$ as a result of their lower crosslink density that causes a lower thermal stability. The thermal degradation behavior under air atmosphere is presented in Figure 7(b). 5% weight loss around 330 °C is observed for all samples followed by a main degradation process and an oxidative degradation step. Sample I presents a one-step degradation mechanism around 430 °C before the oxidative degradation. As explained above, the introduction of M2 as comonomer increases the thermal stability and a second degradation step appears at a higher temperature (~ 450 °C). For the M2 containing samples, the degradation rate is retarded over 500 °C with formation of an intermediate char. The amount of char formed at these temperatures, which increases proportionally to the phosphorus content, indicates how efficiently the burning surface would protect the rest of the polymer under real fire conditions. Moreover, the char at 800 °C increases with the phosphorus content from sample I to sample IV and decreases for samples V and VI for the



FIGURE 6 Tan delta plots of the crosslinked polymers I-VI.



FIGURE 7 TGA measurements (a) under nitrogen and (b) under air of the crosslinked polymers **I–VI**.

reasons explained earlier. These crosslinked systems show an increased thermal stability with onset degradation temperatures 30 $^{\circ}$ C above the non-crosslinked polymers, both under nitrogen and air atmospheres. The crosslinking retards the release of volatiles and favors char formation.

The mechanical properties of the crosslinked materials were investigated in tensile assays. The mechanical parameters obtained are collected in Table 4 and selected stress-strain curves of samples I to VI are compared in Figure 8. When examining the behavior of samples I to IV, two different factors must be taken into account. There is an increase in the aromatic content that leads to an increase of the network rigidity, but at the same time there is a decrease in the crosslink density. Because of the combination of both factors, the modulus decreases from sample I to sample IV as a result of the decreasing crosslink density, but at the same time, the tensile strength increases due to the increasing aromatic content. The decrease of crosslink density also determines the elongation at break, that increases from sample I to sample IV reaching a maximum value of 142% for sample IV. However, the variation of these parameters is not completely linear; the modulus increases for sample III, suggesting a higher influence of the aromatic fraction on mechanical behavior of this sample. Moreover, sample IV shows a decrease in tensile strength due to its lower crosslink density when compared with samples I-III, which is confirmed by the differences in soluble fractions. The effect of the prepolymer molecular weight on the mechanical properties is clearly observed when comparing the stress/strain curves of samples IV to VI. Although the aromatic content remains constant, the tensile strength and modulus decrease. Moreover, the elongation at break is reduced twofold.

The flame retardancy of the crosslinked materials was evaluated using the LOI vertical test with films of thickness between 0.4 and 0.5 mm. Table 3 contains the LOI values obtained for samples I to VI. The phosphorus-free sample I gave a LOI value of 18.4, a low index, which is related to its high aliphatic content. The LOI values clearly increase with the phosphorus content from sample II to sample IV reaching a value of 25.7 for the later. The effect of the prepolymer molecular weight at a constant phosphorus content on the flame retardancy can be observed by comparing samples IV, V, and VI. The LOI value drops from 25.7 in sample IV to 21.9 and 21.7 in samples V and VI, respectively. During combustion, the thermal scission of the polymer backbone leads to fragments of different sizes. In the case of low crosslink

TABLE 3 Dynamic Thermomed	chanical Characterization, T	ΓGA Results, and LOI Values α	of Crosslinked Polymers I-VI
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			TGA (N ₂)			TGA (Air)				
Sample	% P ^a	Т _g ^ь (°С)	Soluble Fraction (%) ^a	<i>T</i> _{5% loss} (°C)	T _{max} (°C) ^c	Char _{800 ∘C} (%)	<i>T</i> _{5% loss} (°C)	7 _{max} (°C) ^c	Char _{800 °C} (%)	LOI
I	0.0	35.4	0.9	343	434	5.0	331	428	0.0	18.4
II	1.5	47.0	4.1	328	423/462	9.8	324	418/452/564	0.1	21.8
III	2.7	47.3	8.9	346	425/463	10.9	328	418/449/619	2.6	24.0
IV	3.8	52.2	20.3	358	463	11.2	337	449/592	7.6	25.7
V	3.8	40.0	16.8	344	425/462	10.7	325	419/449/609	4.8	21.9
VI	3.8	47.9	17.7	337	425/462	10.2	329	419/452/631	6.0	21.7

^a Weight/weight percentages.

^b Maxima of the tan δ peak.

^c Temperatures of maximum weight loss rate.

TABLE 4 Mechanical Properties of the Crosslinked

 Polymers I–VI

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Sample	Modulus (MPa)	TS (MPa) ^a	Elongation (%) ⁵
I	65.8	2.37	5
II	31.5	3.07	15
ш	54.2	4.50	31
IV	16.8	2.16	142
V	10.3	1.46	64
VI	10.1	1.96	62
^a Tensile strength.		^b Elongation at	break.

density, small volatile fragments are rapidly produced and released to the flame, thus feeding it. As the prepolymer molecular weights decrease from sample **IV** to sample **VI**, the crosslink density also does and as a result lower LOI values are obtained. The effect of the crosslink density on the flame retardant properties is further confirmed when comparing the LOI values of samples **II** and **VI**. Despite its lower phosphorus content (1.5%), sample **II** gave the same LOI than sample **VI** (3.8%). The molecular weights of **P2** and **P6** are similar; however, the higher hydroxyl content of **P2** is responsible for the higher crosslink density of sample **II**. As a result, a similar flame retardant behavior is obtained for both samples.

CONCLUSIONS

A plant oil-based α, ω -diene containing hydroxyl groups (**M1**) has been successfully polymerized via ADMET polymerization with Hoveyda-Grubbs 2nd generation catalyst, reaching high molecular weights. This monomer has also been copolymerized with an α, ω -diene bearing a DOPO pendant group using Grubbs 2nd generation catalyst. In this way, phosphorus-containing polyesters with molecular weights up to 7000 Da have been obtained. Moreover, while maintaining a constant phosphorus content, the molecular weigh of the polyesters has been reduced using methyl 10-undecenoate as



FIGURE 8 Stress-strain curves of the crosslinked polymers I-VI.

renewable chain stopper. The crystallinity of these polyesters decreased as the amount of DOPO-based comonomer (M2) was increased and totally amorphous polymers were obtained for the higher M2 contents. Extensive acrylation of the hydroxyl groups in the polyesters backbone followed by radical polymerization afforded thermosetting polymers with high crosslinking degrees. These plant oil-based thermosets show glass transition temperatures ranging from 35 to 52 °C, good thermal stability, and relatively good flame retardancy despite their high aliphatic (fatty acid) content.

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