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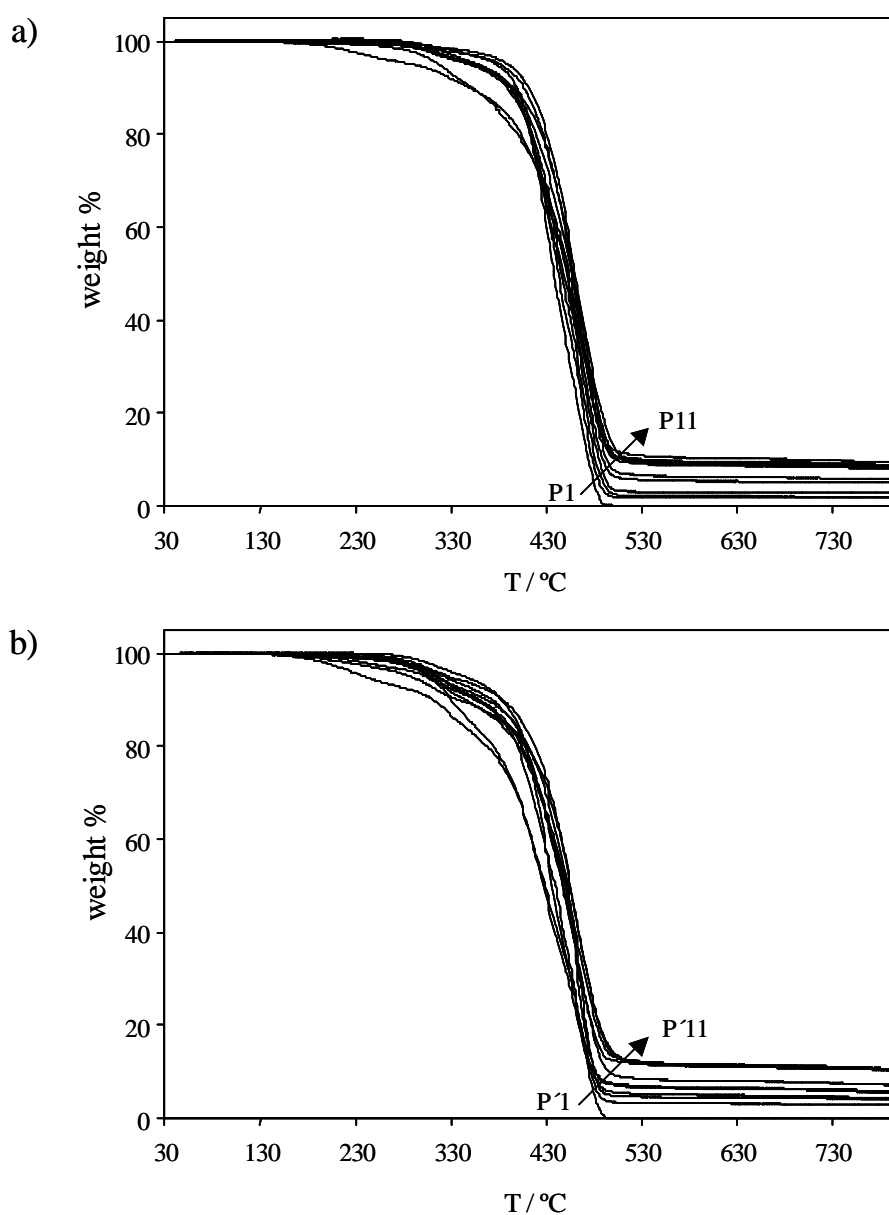
**Table 5.** Thermal stability data and flame retardant characterization of copolymers prepared at 80 °C

Sample (M1 / M2) <sup>a</sup>	% P <sup>b</sup>	TGA (N <sub>2</sub> )			TGA (Air)			LOI
		T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%) <sup>b</sup>	T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%) <sup>b</sup>	
P1 (10 / 0)	4.72	317	327 / 464	9.3	317	441 / 550 / 746	8.4	22.8
P2 (9 / 1)	4.46	348	316 / 460	8.9	356	438 / 480 / 568 / 713	4.2	22.1
P3 (8 / 2)	4.18	390	460	8.8	356	452 / 595 / 705	5.2	22.4
P4 (7 / 3)	3.87	381	462	8.4	359	440 / 555	1.8	22.6
P5 (6 / 4)	3.52	290	232 / 332 / 464	7.8	310	427 / 461 / 533	1.4	22.7
P6 (5 / 5)	3.12	357	310 / 470	5.7	336	418 / 541 / 665 / 693	1.6	23.5
P7 (4 / 6)	2.67	353	465	4.9	330	343 / 460 / 544 / 680	1.1	22.1
P8 (3 / 7)	2.15	350	311 / 470	2.8	336	413 / 535 / 678	0.9	21.6
P9 (2 / 8)	1.54	356	314 / 438 / 466	1.8	338	421 / 460 / 548 / 619	0.5	21.3
P10 (1 / 9)	0.84	358	326 / 437 / 467	1.8	322	396 / 424 / 512	0.0	20.9
P11 (0 / 10)	0.00	378	433 / 462	0.0	330	421 / 509	0.0	19.0

<sup>a</sup> mol/mol ratio, <sup>b</sup> weight/weight percentages, <sup>c</sup> temperatures of maximum weight loss rate.

loss rates were found between 433 and 470 °C for the 80 °C series and between 422 and 469 °C for the 100 °C series. The typical bond energies of P-C, C-C, C-O and C-H bonds are 260, 349, 286 and 370 KJ/mol, respectively. This means that the thermal stability of a polymer should be lowered by addition of a phosphorus-containing comonomer. However, **M1** contains phosphorus as a pendant group and it has been demonstrated that the presence of phosphorus as a pendant group does not affect the thermal stability as it does when it is part of the main chain.<sup>28</sup> Moreover, Wang and Lin

reported the unusual high thermal stability of the P-O-C bond in a similar DOPO-derived polyester, which could be attributed to the three phenylene groups protection.<sup>29</sup> The thermal degradation of the pendant group leads to the formation of the phosphorus-containing char, which acts as a protective layer for the polymer surface. Therefore, the residues obtained at 800 °C increase as the phosphorus content does, reaching a maximum around 10% in both copolymer series. The TGA measurements in air atmosphere (Figure 5) show a main degradation step followed by a complex degradation process for both copolymer series.



**Figure 4.** TGA measurements of copolymers obtained at 80 °C (a) and 100 °C (b) under nitrogen atmosphere.

In all samples, the weight loss rate is lowered around 500 °C by formation of an intermediate residue. The thermal behavior of the polymers at this temperature is representative of the polymer surface behavior under flame conditions. Thus, a high amount of char at 500 °C would mean a better protection of the non-burned polymer. The general tendency observed in both copolymer series is a direct relationship between

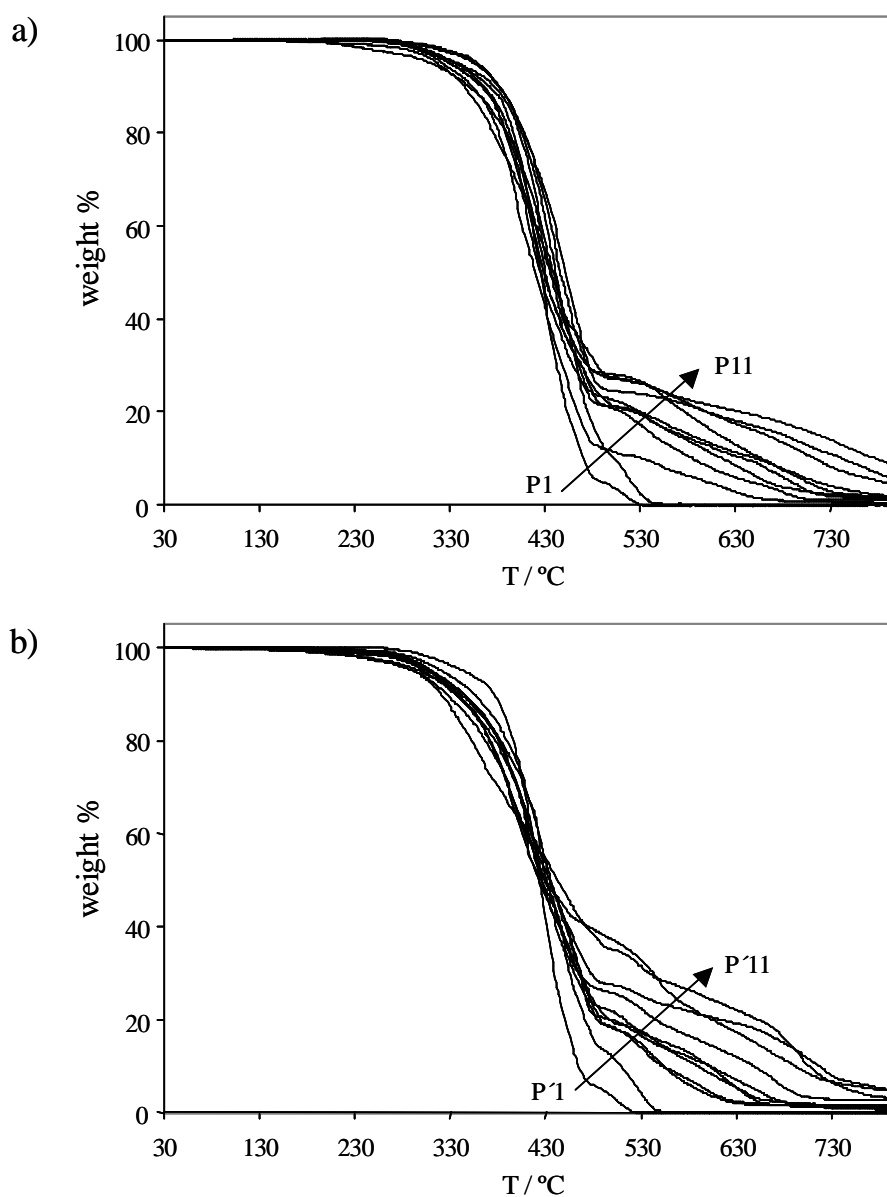
**Table 6.** Thermal stability data and flame retardant characterization of copolymers prepared at 100 °C

Sample (M1 / M2) <sup>a</sup>	% P <sup>b</sup>	TGA (N <sub>2</sub> )			TGA (Air)		
		T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%) <sup>b</sup>	T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%) <sup>b</sup>
P'1 (10 / 0)	4.72	288	310 / 460	10.4	297	410 / 543 / 656	4.7
P'2 (9 / 1)	4.46	307	316 / 456	10.3	302	409 / 445 / 529 / 692	3.1
P'3 (8 / 2)	4.18	328	308 / 460	10.3	320	424 / 528 / 714	4.6
P'4 (7 / 3)	3.87	315	316 / 457	10.5	310	406 / 456 / 531 / 668	2.7
P'5 (6 / 4)	3.52	310	311 / 462	7.0	306	425 / 540 / 624	0.7
P'6 (5 / 5)	3.12	314	314 / 466	5.7	310	417 / 442 / 519 / 617	1.1
P'7 (4 / 6)	2.67	322	431 / 468	5.4	308	392 / 465 / 523 / 586	1.5
P'8 (3 / 7)	2.15	316	325 / 422 / 454	4.2	308	400 / 448 / 544	1.4
P'9 (2 / 8)	1.54	242	229 / 327 / 427 / 463	4.0	291	413 / 464 / 531 / 593	1.1
P'10 (1 / 9)	0.84	304	330 / 424 / 464	2.8	290	360 / 430 / 453 / 525	0.1
P'11 (0 / 10)	0.00	344	431 / 469	0.0	344	425 / 506	0.0

<sup>a</sup> mol/mol ratio, <sup>b</sup> weight/weight percentages, <sup>c</sup> temperatures of maximum weight loss rate.

the phosphorus content and the amount of char formed at 500 °C. As a consequence, the subsequent oxidative degradation is retarded proportionally to the phosphorus content. Thus, the char residues found at 800 °C in air atmosphere range from 0.0 to 8.4 % in the 80 °C copolymer series and from 0.0 to 4.7 % in the 100 °C copolymer series. These observations clearly indicate the advantages of defined polymer libraries in polymer

science.<sup>30</sup> Here, the systematic variation of the phosphorous content allowed us a straightforward correlation of material properties with molecular characteristics.



**Figure 5.** TGA measurements of copolymers obtained at 80 °C (a) and 100 °C (b) under air atmosphere.

The flame retardancy properties of the copolymer series synthesized at 80 °C were evaluated using the limiting oxygen index (LOI) test. The LOI is the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of a certain material. For the preparation of the samples, concentrated solutions of each polymer in THF were used to impregnate glass fiber probes (50 x 10 x 1 mm<sup>3</sup>). We used these probes instead of standard ones due to

the lack of consistence of the obtained polymers. The LOI values obtained are shown in Table 2. **P11** gave a LOI of 19.0, which indicates that it has not flame retardant properties. However, the introduction of **M1** as comonomer causes a clear and steady increase of the LOI with the increasing P content reaching a maximum value of 23.5 for a phosphorus content of 3.12 % (**P6**). Interestingly, higher phosphorus contents did not give an increase in the LOI values but a slight decrease from 23.5 (**P6**) to 22.1 (**P2**). It is known that low phosphorus contents are sufficient to infer flame retardant properties to polymers and that high contents do not usually give better results.<sup>31,32</sup> However, in this case a decrease in the LOI values is observed when the phosphorus content is increased. A possible explanation to this fact may be found in the thermal properties of the copolymers. As mentioned above, **P11** is crystalline with a melting point of 54.6 °C. The incorporation of increasing amounts of **M2** comonomer causes a gradual decrease of  $T_m$  until amorphous copolymers are obtained. In polymers, the amount of energy required to initiate combustion varies as a function of the physical characteristics of the material. During the heating of semi-crystalline thermoplastics, the polymer softens, melts and drips. As a consequence, depending on the heat-storage capacity and the enthalpy of fusion of the polymer, part of the energy involved in the combustion process is consumed.<sup>33</sup> For this reason, the LOI values found for the copolymers **P10-P6** could be affected not only by the presence of phosphorus, but also by its crystalline fraction. The polymers **P5-P1** are essentially amorphous and thus, no endothermic processes can be added to the effect of phosphorus resulting in lower LOI values.

## CONCLUSIONS

A phosphorus-containing  $\alpha,\omega$ -diene bearing two 10-undecenoic acid moieties has been homopolymerized via acyclic diene metathesis (ADMET) using Grubbs 2<sup>nd</sup> generation metathesis catalyst. This monomer was also copolymerized with undecylenyl undecenoate leading to a series of copolymers with different phosphorus contents. Moreover, the molecular weight of the prepared polyesters could be controlled by addition of methyl 10-undecenoate as chain stopper. The presence of phosphorus in the structure of the monomer did not affect the activity of the catalyst and high molecular weight polyesters could be obtained. The polymerizations were carried out at two different temperatures. When working at 80 °C, inhomogeneous molecular weight distributions were obtained for intermediate comonomer ratios. When the temperature

was increased to 100 °C the catalyst lost activity, as observed by somewhat lower molecular weights, but homogeneous molecular weight distributions were found in all polymers. LOI values up to 23.5 were obtained for the phosphorus-containing polyesters **P1-P10**. These values show an increase in the flame retardant properties of the polyesters compared to the phosphorous-free sample **P11**. Both studies monomers have a high percentage of renewable resources, in this case a castor oil derived platform chemical, and thus the studied polymers can be considered as renewable flame retardant materials.

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# Phosphorus-Containing Renewable Polyester-Polyols via ADMET Polymerization. Synthesis, Functionalization and Radical Cross-Linking.

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**ABSTRACT.** An  $\alpha,\omega$ -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  $\alpha,\omega$ -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 cross-linked 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 in order to study the effect of the prepolymers molecular weights on the different properties of the final materials.

**Keywords:** polyester, renewable resources, ADMET, flame retardant, cross-linked polymer.

## 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.<sup>1</sup> The main components of vegetable oils are triglycerides, consisting of glycerol and fatty acids. The chemical modification of their structure enables the synthesis a wide variety

of monomers for the development of polymers with specific properties,<sup>2</sup> that 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.<sup>3</sup> Due to 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.<sup>4</sup> However, it is known that bromine-containing flame-retardant resins release hydrogen bromide during combustion, which is toxic and corrosive.<sup>5</sup> 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.<sup>6</sup> They have a good flame retardant performance and are preferred to the widely applied halogenated flame retardants due to environmental and health reasons.<sup>7</sup>

Acyclic diene metathesis (ADMET) polymerization has proven to be a useful tool for the synthesis of polymers bearing a wide variety of functional groups.<sup>8,9</sup> 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,<sup>10</sup> we synthesized a series of phosphorus-containing linear polyesters through ADMET copolymerization of a phosphorus based  $\alpha,\omega$ -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 second generation Grubbs metathesis catalysts,<sup>11,12</sup> ADMET polymerization enables the introduction of functional groups that can act as cross-linking points for the development of thermosets with improved mechanical properties.<sup>13</sup> This work thus deals with the synthesis of plant oil based linear polyesters containing phosphorus and alcohol functionalities via ADMET. Further

cross-linking 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 SECTION

### 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 1<sup>st</sup> generation), benzylidene[1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (C2, Grubbs catalyst 2<sup>nd</sup> generation) and [1,3-*Bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(*o*-isopropoxyphenylmethylene)ruthenium (C3, Hoveyda-Grubbs catalyst 2<sup>nd</sup> generation) were purchased from Aldrich. Hexane, ethyl acetate and methanol were purchased from Scharlab. Tetrahydrofuran CHROMASOLV<sup>®</sup> Plus (HPLC) was purchased from Aldrich. Triethylamine (Aldrich) was dried by distillation over CaH<sub>2</sub> and acryloyl chloride (Aldrich) was distilled under vacuum before use. Dimethylformamide and dichloromethane (Scharlab) were dried over P<sub>2</sub>O<sub>5</sub> and distilled immediately before use. Toluene was distilled from sodium/benzophenone. Thin layer chromatography (TLC) was performed on silica gel TLC-cards (60 F<sub>254</sub>, Merck). Compounds were visualized by spraying with sulphuric acid/anisaldehyde ethanol solution and heating at 200 °C. For column chromatography, silica gel 60 A.C.C. 40-63 μm (SDS) was used. Methyl 10-undecenoate was prepared by esterification with methanol from corresponding 10-undecenoic acid 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.<sup>14</sup>

**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 toluene, washed twice with water, twice with HCl (5%) and once with brine. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The 1,3- and 1,2-di-10-undecenoylglycerol mixture (**M1**) was obtained in 55 % yield after column chromatography with hexane/ethyl acetate 6/1.

FTIR (cm<sup>-1</sup>): 3475 (O-H), 3077 (=C-H), 1735 (C=O), 1638 (C=C), 1163 (C-O).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ in ppm): 5.83-5.73 (m, CH<sub>2</sub>=CH), 5.09-5.04 (m, CH-O of 1,2 isomer), 5.00-4.89 (m, CH<sub>2</sub>=CH), 4.30 (dd, *J* = 12.00, 4.40 Hz, CH<sub>2</sub>-CO of 1,2 isomer), 4.24-4.03 (m, O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-O of 1,3 isomer and CH<sub>2</sub>-CO of 1,2 isomer), 3.70 (d, *J* = 5.20 Hz, CH<sub>2</sub>-OH of 1,2 isomer), 2.65 (broad, OH), 2.33 (t, *J* = 7.60 Hz, CH<sub>2</sub>-COOCH<sub>2</sub>), 2.30 (t, *J* = 7.60 Hz, CH<sub>2</sub>-COOCH), 2.01 (q, *J* = 7.07 Hz, CH<sub>2</sub>-CH=CH<sub>2</sub>), 1.64-1.56 (m, CH<sub>2</sub>-CH<sub>2</sub>CO), 1.39-1.22 (m, CH<sub>2</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 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 (CH<sub>2</sub>=CH), 114.34 (CH<sub>2</sub>=CH), 72.23 (CH-O of 1,2 isomer), 68.43 (CH-OH of 1,3 isomer), 65.18 (CH<sub>2</sub>-O of 1,3 isomer), 62.23 (CH<sub>2</sub>-CO of 1,2 isomer), 61.60 (CH<sub>2</sub>-OH of 1,2 isomer), 34.43 (CH<sub>2</sub>-CO), 34.25 (CH<sub>2</sub>-CH=CH<sub>2</sub>), 33.95 (CH<sub>2</sub>-CO), 29.46 (CH<sub>2</sub>), 29.44 (CH<sub>2</sub>), 29.37 (CH<sub>2</sub>), 29.35 (CH<sub>2</sub>), 29.25 (CH<sub>2</sub>), 29.22 (CH<sub>2</sub>), 29.21 (CH<sub>2</sub>), 29.03 (CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 25.08 (CH<sub>2</sub>-CH<sub>2</sub>CO), 25.03 (CH<sub>2</sub>-CH<sub>2</sub>CO).

**ADMET polymerization of M1.** **M1** (3g, 7.07 mmol) and Hoveyda-Grubbs 2<sup>nd</sup> 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.

FTIR (cm<sup>-1</sup>): 3540 (O-H), 1742 (C=O), 1142 (C-O).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm): 5.42-5.30 (m,  $\text{CH}=\text{CH}$ ), 5.10-5.05 (m,  $\text{CH}-\text{O}$  of 1,2 isomer), 4.31 (dd,  $J = 11.60, 4.40$  Hz,  $\text{CH}_2-\text{CO}$  of 1,2 isomer), 4.24-4.04 (m,  $\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O}$  of 1,3 isomer and  $\text{CH}_2-\text{CO}$  of 1,2 isomer), 3.74-3.69 (m,  $\text{CH}_2-\text{OH}$  of 1,2 isomer), 2.65 (broad, OH), 2.35-2.29 (m,  $\text{CH}_2-\text{CO}$ ), 2.04-1.90 ( $\text{CH}_2-\text{CH}=\text{CH}$ ), 1.70-1.56 (m,  $\text{CH}_2-\text{CH}_2\text{CO}$ ), 1.38-1.21 (m,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm): 174.14 (COOR), 173.65 (COOR), 131.00-129.50 ( $\text{CH}=\text{CH}$ ), 72.23 ( $\text{CH}-\text{O}$  of 1,2 isomer), 68.40 ( $\text{CH}-\text{OH}$  of 1,3 isomer), 65.19 ( $\text{CH}_2-\text{O}$  of 1,3 isomer), 62.24 ( $\text{CH}_2-\text{CO}$  of 1,2 isomer), 61.57 ( $\text{CH}_2-\text{OH}$  of 1,2 isomer), 34.44 ( $\text{CH}_2-\text{CO}$ ), 34.26 ( $\text{CH}_2-\text{CO}$ ), 32.76 ( $\text{CH}_2-\text{CH}=\text{CH}$ , *trans*), 29.77 ( $\text{CH}_2$ ), 29.62 ( $\text{CH}_2$ ), 29.41 ( $\text{CH}_2$ ), 29.28 ( $\text{CH}_2$ ), 29.14 ( $\text{CH}_2$ ), 28.91 ( $\text{CH}_2$ ), 28.76 ( $\text{CH}_2$ ), 27.35 ( $\text{CH}_2-\text{CH}=\text{CH}$ , *cis*), 25.04 ( $\text{CH}_2-\text{CH}_2\text{CO}$ ), 24.90 ( $\text{CH}_2-\text{CH}_2\text{CO}$ ).

**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<sup>nd</sup> 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 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 ( $\text{cm}^{-1}$ ): 3450 (O-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).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm, number assignments related to scheme 2): 8.07-7.94 (m,  $\text{H}_{8,14,6}$ ), 7.69 (t,  $J = 7.4$  Hz,  $\text{H}_9$ ), 7.57 (dd,  $J = 15.2, 7.6$  Hz,  $\text{H}_{11}$ ), 7.45-7.36 (m,  $\text{H}_{10,16,4}$ ), 7.30-7.23 (m,  $\text{H}_{15,17}$ ), 7.14 (dd,  $J = 8.6, 6.6$  Hz,  $\text{H}_3$ ), 5.43-5.31 (m,  $\text{CH}=\text{CH}$ ), 5.10-5.06 (m,  $\text{CH}-\text{O}$  of 1,2 isomer), 4.31 (dd,  $J = 11.60, 4.40$  Hz,  $\text{CH}_2-\text{CO}$  of 1,2 isomer), 4.23-4.03 (m,  $\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O}$  of 1,3 isomer and  $\text{CH}_2-\text{CO}$  of 1,2 isomer), 3.71 (d,  $J = 4.4$  Hz,  $\text{CH}_2-\text{OH}$  of 1,2 isomer), 2.57 (t,  $J = 7.6$  Hz,  $\text{H}_{23}$ ), 2.35-2.29 (m,  $\text{CH}_2-\text{CO}$ ), 2.04-1.90 ( $\text{CH}_2-\text{CH}=\text{CH}$ ), 1.78-1.56 (m,  $\text{H}_{24,20}$  and  $\text{CH}_2-\text{CH}_2\text{CO}$ ), 1.44-0.92 (m,  $\text{H}_{21}$  and  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm, number assignments 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 (C<sub>19</sub>), 170.85 (C<sub>22</sub>), 149.71 (C<sub>5</sub>), 149.22 (d, 9.15 Hz, C<sub>2</sub>), 147.82 (d, 16.80 Hz, C<sub>18</sub>), 135.09 (d, 5.33 Hz, C<sub>12</sub>), 133.28 (C<sub>9</sub>), 130.90 (C<sub>11</sub>), 130.73 (C<sub>16</sub>), 130.32 (CH=CH), 128.61 (d,  $J = 15.29$  Hz, C<sub>10</sub>), 128.31 (C<sub>4</sub>), 128.01 (d,  $J = 8.35$  Hz, C<sub>6</sub>), 124.30 (d,  $J = 134.30$  Hz, C<sub>7</sub>), 124.80-124.61 (C<sub>3</sub>, C<sub>14</sub>, C<sub>15</sub>), 123.21 (d,  $J = 9.87$  Hz, C<sub>8</sub>), 122.48 (d,  $J = 145.26$  Hz, C<sub>1</sub>), 121.02 (d,  $J = 11.47$  Hz, C<sub>13</sub>), 120.66 (d,  $J = 6.84$  Hz, C<sub>17</sub>), 72.04 (CH-O of 1,2 isomer), 67.91 (CH-OH of 1,3 isomer), 64.98 (CH<sub>2</sub>-O of 1,3 isomer), 62.28 (CH<sub>2</sub>-CO of 1,2 isomer), 61.16 (CH<sub>2</sub>-OH of 1,2 isomer), 34.26 (CH<sub>2</sub>-CO), 34.21 (C<sub>23</sub>), 34.08 (CH<sub>2</sub>-CO), 33.17 (C<sub>20</sub>), 32.59 (CH<sub>2</sub>-CH=CH, *trans*), 29.72 (CH<sub>2</sub>), 29.59 (CH<sub>2</sub>), 29.47 (CH<sub>2</sub>), 29.32 (CH<sub>2</sub>), 29.25 (CH<sub>2</sub>), 29.12 (CH<sub>2</sub>), 28.95 (CH<sub>2</sub>), 28.79 (CH<sub>2</sub>), 27.19 (CH<sub>2</sub>-CH=CH, *cis*), 24.86 (CH<sub>2</sub>-CH<sub>2</sub>CO, C<sub>24</sub>), 24.03 (C<sub>21</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz,  $\delta$  in ppm): 18.15.

**Acrylation of ADMET polymers P1-P6.** In a standard procedure, an anhydrous dichloromethane solution of an ADMET polymer (8 mL of DCM per g 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<sup>-1</sup>): 1740 (C=O, COOR), 1637 (C=C, acrylate), 1173 (C-O), 808 (C=C-H).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$  in ppm): 6.43 (dd,  $J = 17.2$ , 1.2 Hz, COCH=CH<sub>2</sub>), 6.41 (dd,  $J = 17.2$ , 1.2 Hz, COCH=CH<sub>2</sub>), 6.12 (dd,  $J = 17.2$ , 10.0 Hz, COCH=CH<sub>2</sub>), 6.11 (dd,  $J = 17.2$ , 10.0 Hz, COCH=CH<sub>2</sub>), 5.88 (dd,  $J = 10.0$ , 1.2 Hz, COCH=CH<sub>2</sub>), 5.87 (dd,  $J = 10.0$ , 1.2 Hz, COCH=CH<sub>2</sub>), 5.45-5.27 (m, CH=CH and CH-O of 1,2 isomer), 4.44-4.09 (m, O-CH<sub>2</sub>-CH-CH<sub>2</sub>-O of 1,3 isomer, CH<sub>2</sub>-CO of 1,2 isomer and CH<sub>2</sub>-O of 1,2 isomer), 2.34-2.28 (m, CH<sub>2</sub>-CO), 2.04-1.90 (m, CH<sub>2</sub>-CH=CH), 1.72-1.59 (m, CH<sub>2</sub>-CH<sub>2</sub>CO), 1.44-1.20 (CH<sub>2</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS,  $\delta$  in ppm): 173.50 (COOR), 165.31 (COOR acrylate), 132.06 (CH=CH<sub>2</sub> acrylate), 130.51 (CH=CH), 128.00 (CH=CH<sub>2</sub> acrylate), 69.47 (CH-OCOCH=CH<sub>2</sub>), 68.95 (CH-OCOR), 62.59 (CH<sub>2</sub>-OCOCH=CH<sub>2</sub>), 62.22 (CH<sub>2</sub>-OCOR),

34.19 ( $\text{CH}_2\text{-CO}$ ), 32.79 ( $\text{CH}_2\text{-CH=CH}$ , *trans*), 29.82-28.98 ( $\text{CH}_2$ ), 27.38 ( $\text{CH}_2\text{-CH=CH}$ , *cis*), 24.22 ( $\text{CH}_2\text{-CH}_2\text{CO}$ ).

Spectroscopic data for **AP2-AP6**:

FTIR ( $\text{cm}^{-1}$ ): 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).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm, number assignments related to scheme 2): 8.07-7.95 (m,  $\text{H}_{8,14,6}$ ), 7.69 (t,  $J = 7.8$  Hz,  $\text{H}_9$ ), 7.60-7.55 (m,  $\text{H}_{11}$ ), 7.45-7.36 (m,  $\text{H}_{10,16,4}$ ), 7.30-7.23 (m,  $\text{H}_{15,17}$ ), 7.15 (dd,  $J = 8.6, 6.6$  Hz,  $\text{H}_3$ ), 6.43 (dd,  $J = 17.2, 1.2$  Hz,  $\text{COCH=CH}_2$ ), 6.41 (dd,  $J = 17.2, 1.2$  Hz,  $\text{COCH=CH}'_2$ ), 6.12 (dd,  $J = 17.2, 10.0$  Hz,  $\text{COCH=CH}_2$ ), 6.11 (dd,  $J = 17.2, 10.0$  Hz,  $\text{COCH}'=\text{CH}_2$ ), 5.88 (dd,  $J = 10.0, 1.2$  Hz,  $\text{COCH=CH}_2$ ), 5.87 (dd,  $J = 10.0, 1.2$  Hz,  $\text{COCH=CH}'_2$ ), 5.45-5.27 (m,  $\text{CH=CH}$  and  $\text{CH-O}$  of 1,2 isomer), 4.42-4.10 (m,  $\text{O-CH}_2\text{-CH-CH}_2\text{-O}$  of 1,3 isomer,  $\text{CH}_2\text{-CO}$  of 1,2 isomer and  $\text{CH}_2\text{-O}$  of 1,2 isomer), 2.57 (t,  $J = 7.6$  Hz,  $\text{H}_{23}$ ), 2.32-2.28 (m,  $\text{CH}_2\text{-CO}$ ), 2.04-1.90 ( $\text{CH}_2\text{-CH=CH}$ ), 1.78-1.54 (m,  $\text{H}_{24,20}$  and  $\text{CH}_2\text{-CH}_2\text{CO}$ ), 1.44-0.92 (m,  $\text{H}_{21}$  and  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$  in ppm, number assignments related to scheme 2): 173.47 (COOR), 172.08 ( $\text{C}_{19}$ ), 171.03 ( $\text{C}_{22}$ ), 165.29 (COOR acrylate), 149.85 ( $\text{C}_5$ ), 149.45 (d, 9.20 Hz,  $\text{C}_2$ ), 147.97 (d, 16.80 Hz,  $\text{C}_{18}$ ), 135.24 ( $\text{C}_{12}$ ), 133.32 ( ), 132.02 ( $\text{CH=CH}_2$  acrylate), 131.03 ( $\text{C}_{11}$ ), 130.83 ( $\text{C}_{16}$ ), 130.48 ( $\text{CH=CH}$ ), 128.72 (d,  $J = 14.48$  Hz,  $\text{C}_{10}$ ), 128.37 ( $\text{C}_4$ ), 128.25 (d,  $J = 7.64$  Hz,  $\text{C}_6$ ), 127.96 ( $\text{CH=CH}_2$  acrylate), 124.72 (d,  $J = 135.00$  Hz,  $\text{C}_7$ ), 124.92-124.83 ( $\text{C}_3, \text{C}_{14}, \text{C}_{15}$ ), 123.31 (d,  $J = 9.86$  Hz,  $\text{C}_8$ ), 122.82 (d,  $J = 144.86$  Hz,  $\text{C}_1$ ), 121.23 (d,  $J = 11.47$  Hz,  $\text{C}_{13}$ ), 120.88 (d,  $J = 6.04$  Hz,  $\text{C}_{17}$ ), 69.45 ( $\text{CH-OCOCH=CH}_2$ ), 68.91 ( $\text{CH-OCOR}$ ), 62.57 ( $\text{CH}_2\text{-OCOCH=CH}_2$ ), 62.19 ( $\text{CH}_2\text{-OCOR}$ ), 34.39 ( $\text{CH}_2\text{-CO}$ ,  $\text{C}_{23}$ ), 34.18 ( $\text{CH}_2\text{-CO}$ ), 33.34 ( $\text{CH}_2\text{-CO}$ ,  $\text{C}_{20}$ ), 32.76 ( $\text{CH}_2\text{-CH=CH}$ , *trans*), 29.78-28.97 ( $\text{CH}_2$ ), 27.37 ( $\text{CH}_2\text{-CH=CH}$ , *cis*), 24.99 ( $\text{CH}_2\text{-CH}_2\text{CO}$ ,  $\text{C}_{24}$ ), 24.19 ( $\text{CH}_2\text{-CH}_2\text{CO}$ ,  $\text{C}_{21}$ ).

### Curing reactions and extraction of soluble parts

A dichloromethane solution (0.3 g/mL) of each acrylated polyester (**APs**) and dicumyl peroxide (2% mol related to acrylate groups) was cast on a glass plates of  $7.5 \times 2.5 \text{ cm}^2$ . The samples were heated to 40 °C for 2h in order to remove the solvent and then the temperature was raised to 150 °C at 1 °C/min and maintained for 12h. All samples were subjected to soxhlet extraction with previously distilled dichloromethane to determine

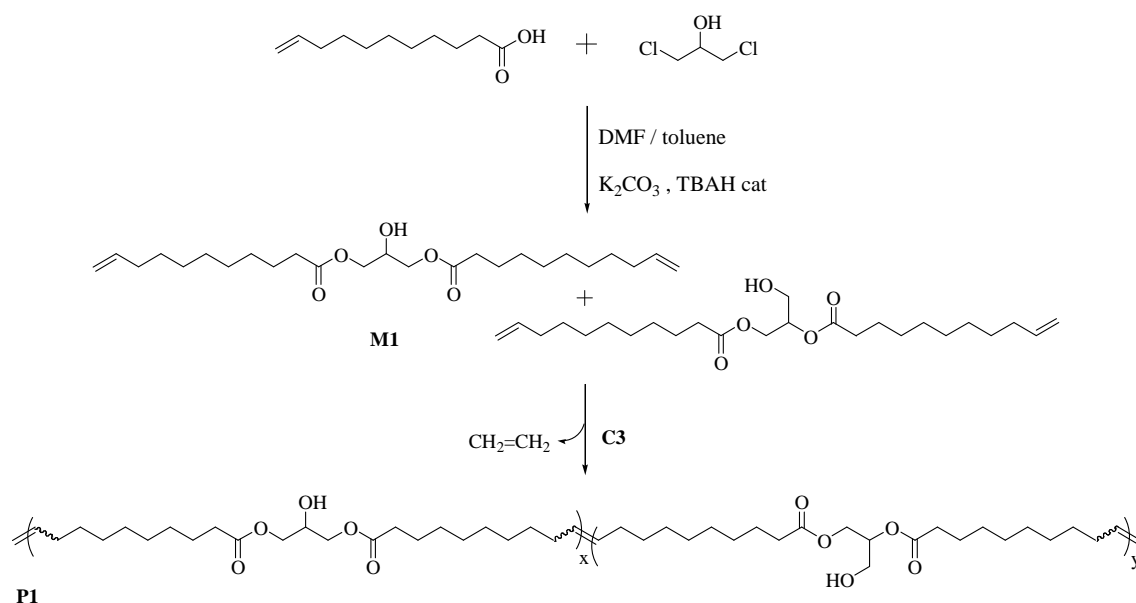
their soluble fractions. 0.5g of each sample were extracted with 125 mL of dichlorometane. Previously to extractions, the samples were grinded to maximize the extraction efficiency.

### **Instrumentation**

$^1\text{H}$  NMR 400 MHz and  $^{13}\text{C}$  NMR 100.6 MHz NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform.  $\text{CDCl}_3$  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  $\mu\text{m}$  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  $\text{cm}^{-1}$  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  $\text{N}_2$  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  $\mu\text{m}$  and at a fixed frequency of 1 Hz in the -100 to 200 °C range and at a heating rate of 3 °C/min. Rectangular samples with dimensions 10 x 5 x 0.5  $\text{mm}^3$  were used. The tensile assays were performed by triplicate on rectangular samples (10 x 5 x 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  $\text{N}_2$  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 analyser. The dimensions of the polymer films were 100 x 5 x 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 cross-linking points.<sup>13,15</sup> Taking into account the good flame retardant properties obtained in our previous work with DOPO II (**M2**) as phosphorus containing comonomer,<sup>10</sup> we decided to use it for the preparation of flame retardant thermosets. To introduce cross-linking points into the polymer backbone, a hydroxyl containing  $\alpha,\omega$ -diene (**M1**, scheme 1) was synthesized. **M1** and **M2** were copolymerized 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 cross-linked *via* radical polymerization to obtain a family of flame retardant thermosets.



**Scheme 1.** Synthesis of 1,3- and 1,2-di-10-undecenylglycerol mixture and ADMET polymerization in presence of Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst.

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

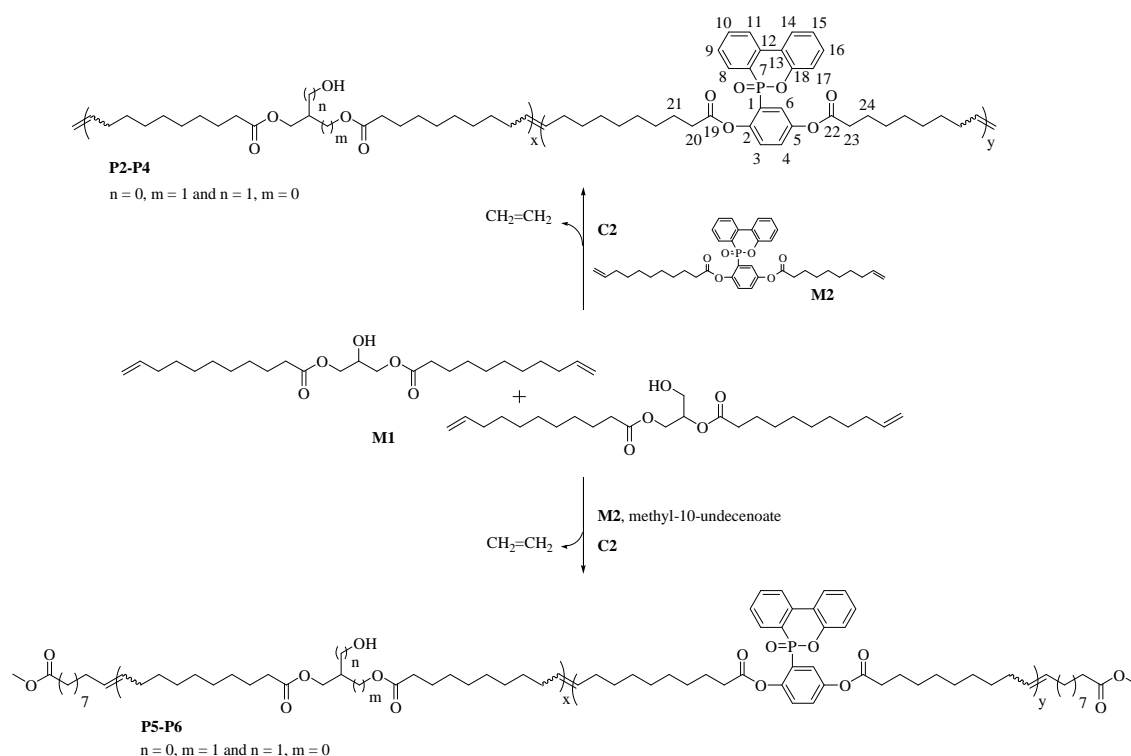
must be pointed out that 1,3-dichloro-2-propanol can be obtained directly from glycerol<sup>16</sup> and 10-undecenoic acid is obtained from castor oil pyrolysis, thus, both reagents can be plant oil derived and **M1** can be considered as 100% renewable. The <sup>1</sup>H-NMR analysis of the reaction mixture revealed the presence of 1,3-diundecenoylglycerol together with 1,2-diundecenoylglycerol and triundecenoylglycerol as byproducts. In the reaction conditions, glycidyl undecenoate is formed as intermediate (detected by <sup>1</sup>H-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 <sup>1</sup>H-NMR, see figure 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.<sup>17</sup> In both **M1** and **M2**, the terminal olefins are nine carbon atoms spaced from the functional groups. Moreover, previous work in Wagener's group<sup>9</sup> proved the viability of ADMET polymerization of alcohol containing dienes using Grubbs 1<sup>st</sup> 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 in order to remove the ethylene, which is released during the metathesis reaction. When 1% mol Grubbs 1<sup>st</sup> 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.<sup>18</sup> On the other hand, when 1% mol Grubbs (**C2**) and Hoveyda-Grubbs (**C3**) 2<sup>nd</sup> 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 cross-linking 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.<sup>9</sup> 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).

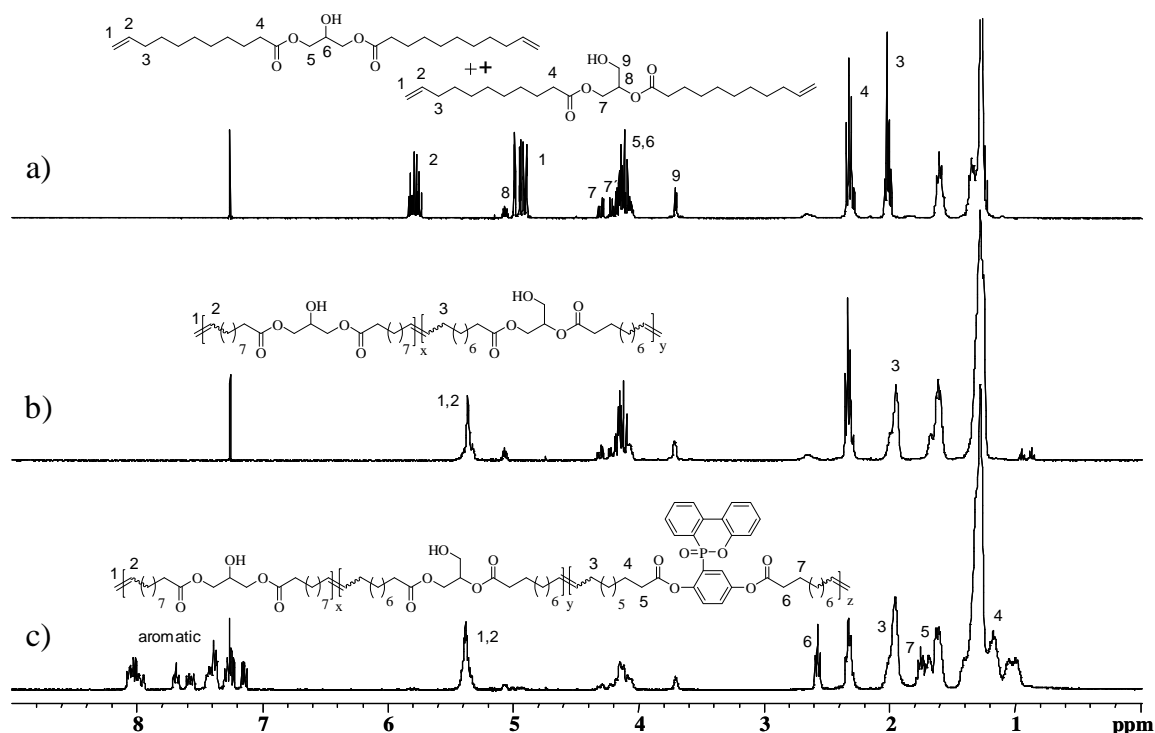
On the basis of the results obtained in the initial experiments, we synthesized a series of polymers (**P1-P4**) with different **M1/M2** molar ratios (Scheme 2) with the aim of determining the effect of the phosphorus content on the properties of the ADMET polymers and the final materials. We also wanted to study the effect of the molecular weight of the ADMET polymers on the flame retardant properties of the cross-linked 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.<sup>10,19</sup> Thus, six polyesters (**P1-P6**) with different **M1/M2** molar ratios were synthesized (see table 1).



**Scheme 2.** Synthesis of phosphorous containing polyesters via ADMET copolymerization with (bottom) and without (top) chain stopper.

Figure 1 shows the <sup>1</sup>H-NMR spectra of **M1** (as a mixture of isomers) (Fig. 1a), **P1** (Fig. 1b) and **P3** (Fig. 1c) 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**. Although not possible in all cases, the analysis of the integrations of the chain end olefins revealed a  $M_n$  of 24,600 Da for **P2** and 18,400 Da for **P3**. These values are significantly higher than the ones obtained by GPC (3,700 and 5,200 Da, respectively). However, there is no direct correlation between GPC and NMR  $M_n$  values due to the different **M1/M2** contents of **P2** and **P3**, which cause different hydrodynamic volumes. For **P1** and **P4**, the chain end signals were too small for reliable integration indicating that high molecular weight polymers were obtained. In the cases of **P5** and **P6**, the  $M_n$  could not be determined as the end-capping was not completely efficient and both terminal olefins and methyl ester signals were observed. Nevertheless, the objective of obtaining two polyesters with the same phosphorus content as **P4**, but lower molecular weights was achieved. Furthermore, these results indicate that high molecular weight hydroxyl-containing polyesters could be synthesized *via* ADMET polymerization.



**Figure 1.**  $^1\text{H}$  NMR spectra of a) **M1** (mixture of isomers), b) **P1** and c) **P3**.

**Table 1.** GPC, <sup>1</sup>H-NMR and thermal characterization of the phosphorus-containing ADMET polyesters.

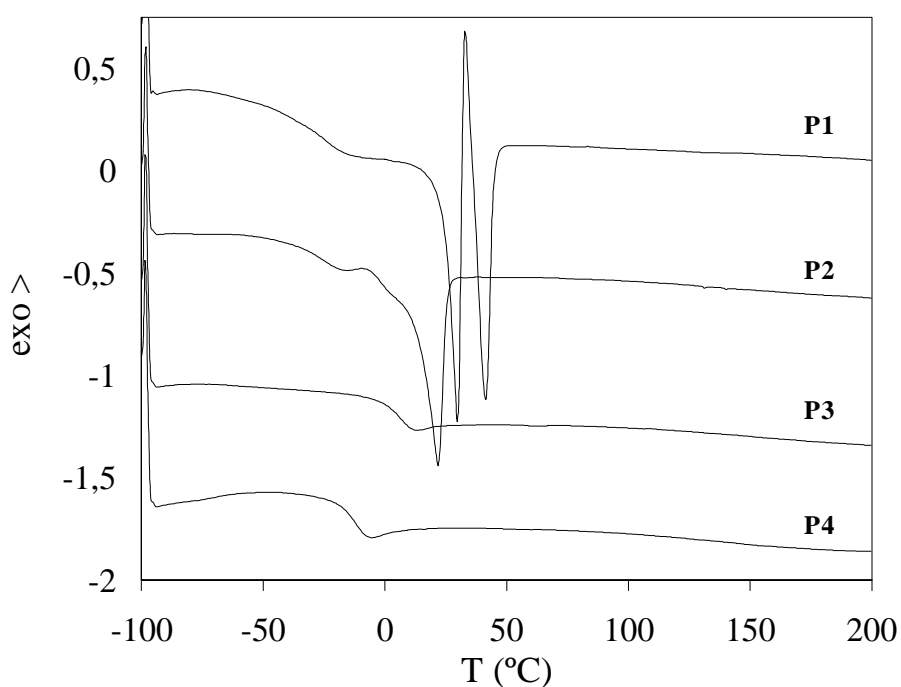
Polymer (M1 / M2) <sup>a</sup>	% P <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	M <sub>n</sub> (NMR)	PDI <sup>c</sup>	T <sub>g</sub> (°C) <sup>d</sup> / T <sub>m</sub> (°C) <sup>d</sup>
P1 (10.0 / 0.0)	0.0	5,300	- <sup>d</sup>	2.18	-25.8 / 41.3
P2 (7.5 / 2.5)	1.6	3,700	24,600	2.20	-27.2 / 21.7
P3 (5.0 / 5.0)	2.9	5,200	18,400	2.56	-12.4
P4 (2.5 / 7.5)	3.9	7,300	- <sup>d</sup>	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

<sup>a</sup> mol/mol ratio, <sup>b</sup> weight/weight percentages, <sup>c</sup> GPC data,

<sup>d</sup> end group signals not detectable, <sup>e</sup> DSC data.

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 is collected in table 1. The thermal analysis of **P1** showed a glass transition (T<sub>g</sub>) at -25.8 °C and a melt followed by a cold crystallization and a second melt (T<sub>m</sub>) at 41.3 °C. However, 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<sub>g</sub> occurs. The DSC trace of **P2**, with only a low content of **M2**, reveals a T<sub>g</sub> of -27.2 °C and just one T<sub>m</sub> 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**.



**Figure 2.** DSC traces of the phosphorus-containing ADMET polyesters **P1-P4**.

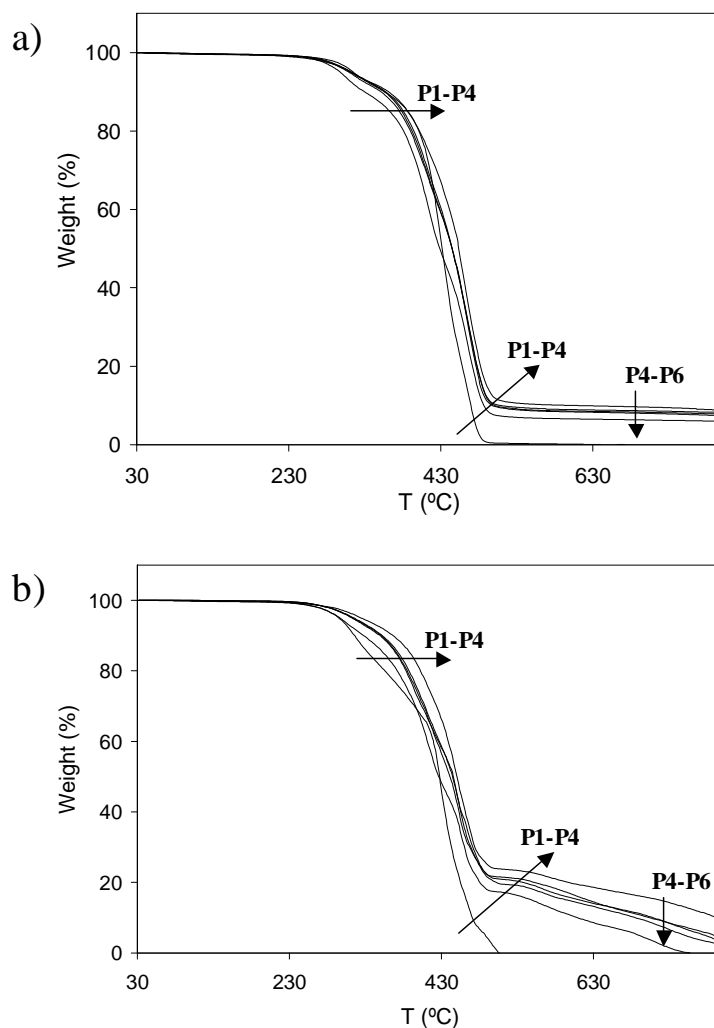
The thermal stability of the ADMET polyesters was studied by thermogravimetric analysis (TGA) under nitrogen and air atmospheres (data in table 2). Good thermal stability is observed for **P1-P6** under nitrogen (Fig 3a) with 5% weight loss around 310 °C. For **P1**, the main degradation step takes place 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 behaviour under air (Fig 3b). 5% 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 °C increase with the phosphorus content reaching a maximum value of 9.1% for **P4**.

**Table 2.** TGA results of the phosphorus-containing ADMET polyesters.

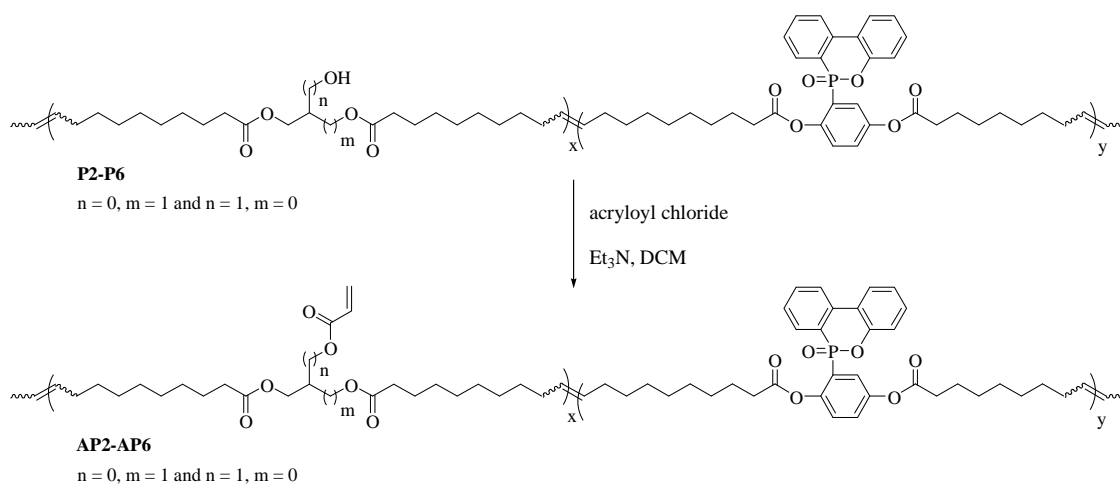
Polymer	% P <sup>a</sup>	TGA (N <sub>2</sub> )			TGA (Air)		
		T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>b</sup>	Char <sub>800°C</sub> (%)	T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>b</sup>	Char <sub>800°C</sub> (%)
P1	0.0	315	316 / 432	0.0	295	316 / 431 / 496	0.0
P2	1.6	297	307 / 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

<sup>a</sup> weight/weight percentages, <sup>b</sup> temperature of maximum weight loss rate.

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 %. Non quantitative 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 <sup>1</sup>H-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 <sup>13</sup>C-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.

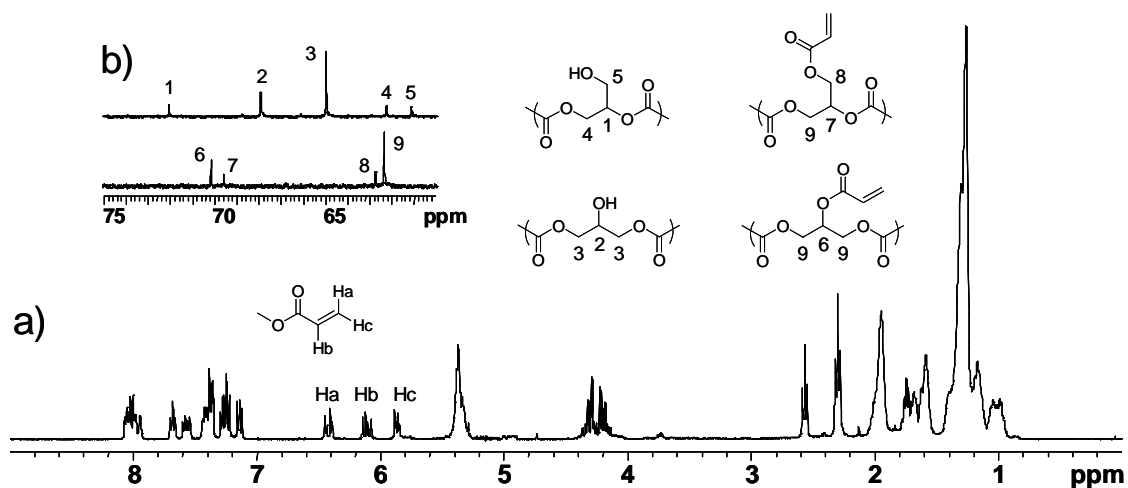


**Figure 3.** TGA measurements a) under nitrogen, and b) under air of the phosphorus-containing ADMET polyesters **P1-P6**.



**Scheme 3.** Synthesis of acrylated phosphorous-containing polyesters **AP1-AP6**.

Based on our previous experience in the cross-linking of acrylate derivatives,<sup>20,21</sup> dicumyl peroxide was chosen as radical initiator for the cross-linking reaction of the acrylated ADMET polyesters. DSC curing runs between **APs** and dicumyl peroxide (2% molar to acrylate groups) showed similar exotherms with onsets ca. 150 °C for all the acrylated polyesters. Once the curing conditions were established, **APs** and dicumyl

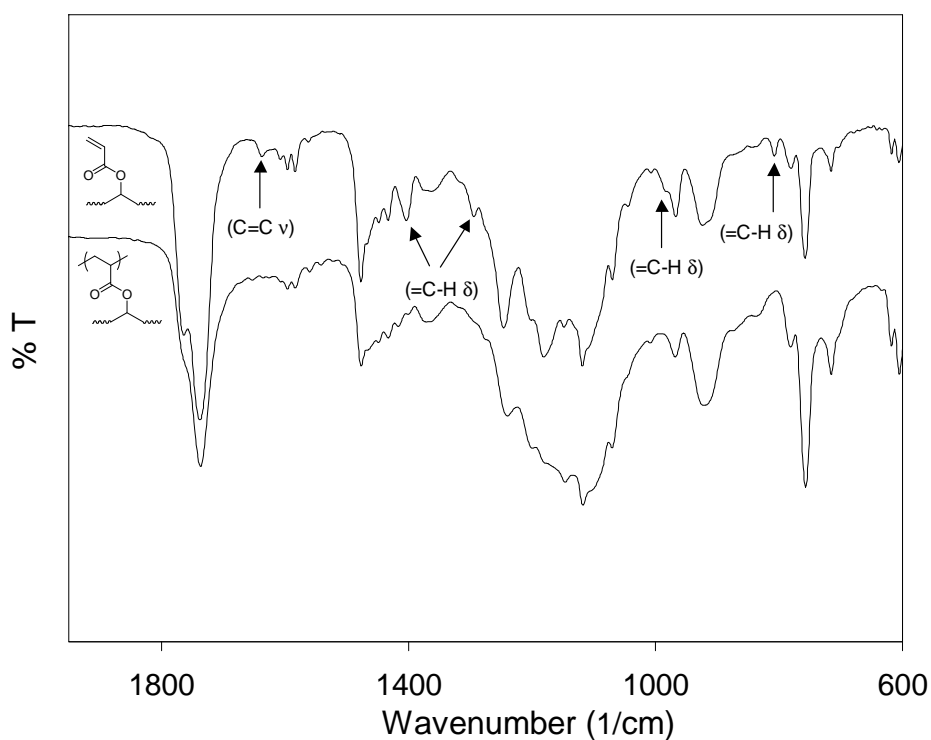


**Figure 4.** <sup>1</sup>H-NMR spectrum of **AP3** and enlargement of the 75-60 ppm region of <sup>13</sup>C-NMR spectra of **P3** and **AP3**.

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 °C for 2h to remove the solvent and then the temperature was raised to 150 °C at 1 °C/min and maintained for 12h. The cured materials (samples **I** to **VI**), were obtained as light brown transparent films. The curing extent of the cross-linking 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 cross-linking reaction. The bands at 1637 cm<sup>-1</sup> (C=C stretching), 1403 and 1294 cm<sup>-1</sup> (=C-H in-plane deformation) and 983 and 808 cm<sup>-1</sup> (=C-H out-of-plane deformation) completely disappear confirming the polymerization of the acrylate groups. The reactivity of non-conjugated internal double bonds towards radical polymerization is very low,<sup>22,23</sup> thus, the double bonds of the polyester backbone were not expected to polymerize. This is confirmed in the ATR-FTIR spectrum after cross-linking by the presence of the band at 967 cm<sup>-1</sup>, which is associated to the C=C-H out-of-plane

deformation. The cross-link extent was also investigated by extracting the soluble fraction of samples **I-VI**. Sample **I** presents a soluble fraction of 0.9 %, that indicates a very high cross-linking 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 cross-link 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 cross-linking degrees were achieved independently of the prepolymers molecular weights.

The soluble fractions were analyzed by  $^1\text{H}$  and  $^{31}\text{P}$ -NMR spectroscopy.  $^1\text{H}$ -NMR showed total reaction of the acrylate double bonds and the presence of a triplet ca. 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  $^{31}\text{P}$ -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.<sup>24</sup> It is thus possible that part of the pendant DOPO moieties were hydrated by long exposure of the samples to air. Since the DOPO P-O bond is cleaved in the early stages of thermal degradation (300 °C),<sup>25</sup> 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.



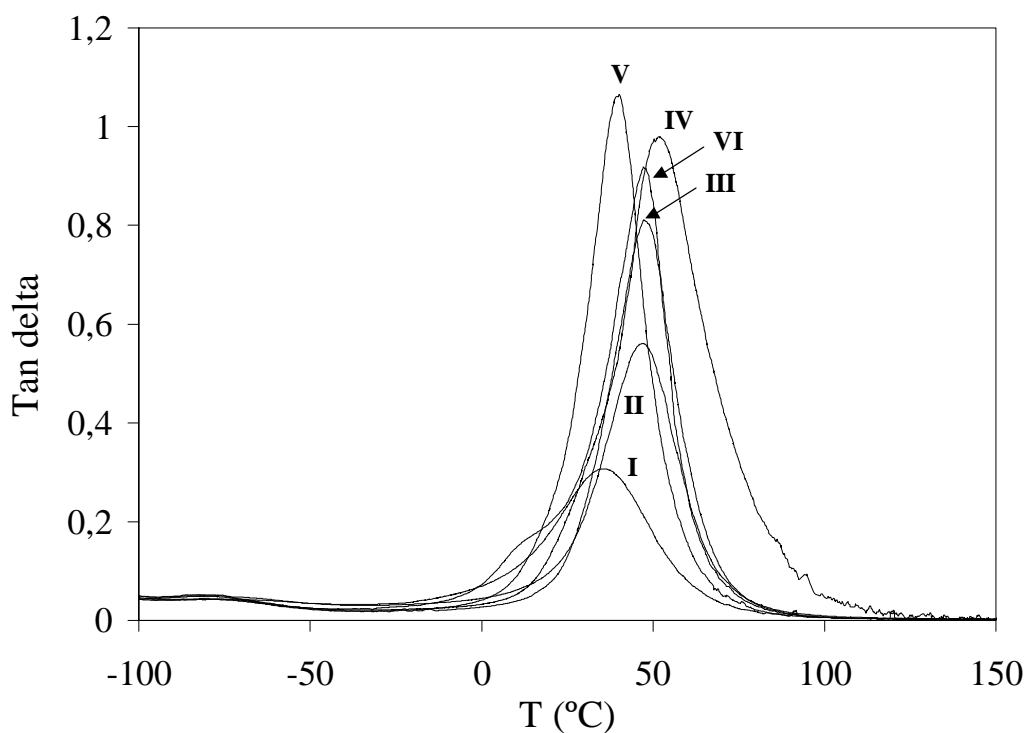
**Figure 5.** FTIR-ATR spectra of a) **AP3** and b) sample **III**. The absorption bands associated to the acrylate group are indicated.

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, that is accompanied by a loss of crosslink density, and a decreased cross-link density is manifested by a smaller tan delta peak.<sup>26</sup> 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 cross-linked materials is observed in samples **IV**, **V** and **VI**. The  $T_g$  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**.

**Table 3.** Dynamic thermomechanical characterization, TGA results and LOI values of cross-linked polymers I-VI.

Sample	% P <sup>a</sup>	T <sub>g</sub> <sup>b</sup> (°C)	Soluble fraction (%) <sup>a</sup>	TGA (N <sub>2</sub> )			TGA (Air)			LOI
				T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%)	T <sub>5% loss</sub> (°C)	T <sub>max</sub> (°C) <sup>c</sup>	Char <sub>800°C</sub> (%)	
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

<sup>a</sup> Weight/weight percentages, <sup>b</sup> Maxima of the tan delta peak, <sup>d</sup> Temperatures of maximum weight loss rate.

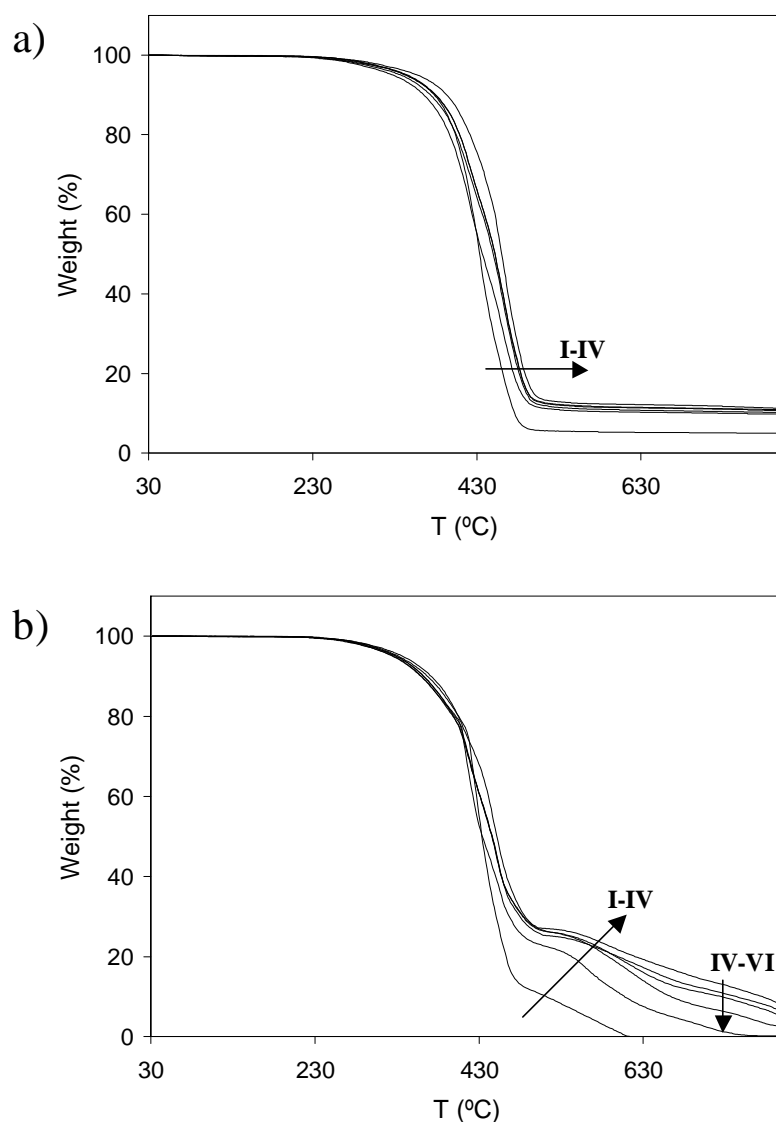


**Figure 6.** Tan delta plots of the cross-linked polymers I-VI.

The thermal degradation behaviour of the cross-linked materials under nitrogen and air atmospheres is shown in figure 7 and the data is collected in table 3. Under nitrogen (Fig. 7a), 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 °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 **V** and **VI** as a result of their lower crosslink density that causes a lower thermal stability. The thermal degradation behaviour under air atmosphere is presented in figure 7b. 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 (ca. 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, that 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 reasons explained above. These cross-linked systems show an increased thermal stability with onset degradation temperatures 30 °C above the non-cross-linked polymers, both under nitrogen and air atmospheres. The cross-linking retards the release of volatiles and favours char formation.

The mechanical properties of the cross-linked 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 behaviour 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 cross-link density. Due to the combination of

both factors, the modulus decreases from sample **I** to sample **IV** as a result of the decreasing cross-link density, but as the same time, the tensile strength increases due to



**Figure 7.** TGA measurements a) under nitrogen, and b) under air of the cross-linked polymers **I-VI**.

the increasing aromatic content. The decrease of cross-link 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 behaviour of this sample. Moreover, sample **IV** shows a decrease in tensile strength due to its lower cross-link density compared to samples **I-III**, that 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 cross-linked materials was evaluated using the limiting oxygen index (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

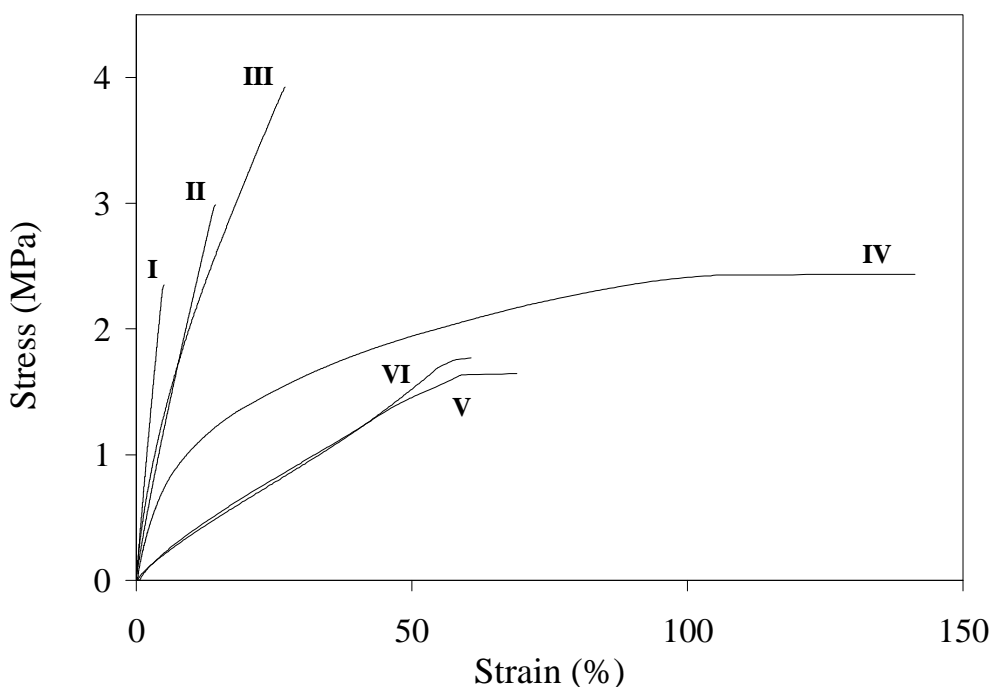
**Table 4.** Mechanical properties of the cross-linked polymers **I-VI**.

Sample	Modulus (MPa)	TS (MPa)	Elongation (%)
I	65.8	2.37	5
II	31.5	3.07	15
III	54.2	4.50	31
IV	16.8	2.16	142
V	10.3	1.46	64
VI	10.1	1.96	62

<sup>a</sup> Tensile strength, <sup>b</sup> Elongation at break.

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 density, small volatile fragments are rapidly produced and released to the flame, thus feeding it. Since 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 cross-link density of sample **II**. As a result, a similar flame retardant behaviour is obtained for both samples.



**Figure 8.** Stress/strain curves of the cross-linked polymers **I-VI**.

## CONCLUSIONS

A plant oil-based  $\alpha,\omega$ -diene containing hydroxyl groups (**M1**) has been successfully polymerized via acyclic diene metathesis (ADMET) polymerization with Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst, reaching high molecular weights. This monomer has also been copolymerized with an  $\alpha,\omega$ -diene bearing a DOPO pendant group using Grubbs 2<sup>nd</sup> generation catalyst. In this way, phosphorus containing polyesters with molecular weights over 18,000 Da have been obtained. Moreover, while maintaining a constant phosphorus content, the molecular weight of the polyesters has been reduced using methyl 10-undecenoate as 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 cross-linking 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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## GENERAL CONCLUSIONS

- High oleic sunflower oil has been used as renewable starting material for the synthesis of two monomers as precursors of plant oil-based cross-linked polymers.
- The photoperoxidation of high oleic sunflower oil with singlet oxygen has been used as an efficient reaction for the synthesis of functionalized triglyceride derivatives. In this reaction, high oleic sunflower oil and oxygen are the only reactants, making this transformation very attractive from an environmental point of view.
- A triglyceride derivative containing  $\alpha,\beta$ -unsaturated ketones has been synthesized and cross-linked *via* aza-Michael addition with an aromatic diamine. The high reactivity of this monomer and the properties of the final materials make this curing system a good alternative to the conventional plant oil-based epoxy-amine systems.
- The effects of the reaction conditions on the mentioned aza-Michael cross-linking reaction have been studied. High temperatures and the presence of a Lewis acid promote the formation of substituted quinolines as cross-link points. On the basis of these findings, new plant oil-based quinoline-containing thermosets have been synthesized.
- A triglyceride derivative containing allylic alcohol groups has been synthesized, acrylated, and cross-linked *via* radical polymerization. The extensive hydrogenation of this derivative, prior to acrylation and radical polymerisation, has led to an improvement of the thermal stability of the cross-linked polymers. In both cases, highly cross-linked thermosets have been obtained.
- High oleic sunflower oil and 10-undecenoic acid have been used as renewable starting materials for the synthesis of plant oil-based flame retardant polymers.

- A series of new high oleic sunflower oil-based monomers containing phosphine oxide and acrylate groups have been synthesized and cross-linked *via* radical polymerization. These cross-linked materials have shown improved thermal stability and flame retardancy. Phosphorus compounds have been found among the pyrolysis products in the gas-phase suggesting a gas-phase mechanism of flame inhibition. Finally, a thermal degradation mechanism has been proposed.
- Acyclic diene metathesis (ADMET) polymerization has been proven to be an efficient tool for the synthesis of phosphorus-containing plant oil-based linear polyesters.
- A series of new phosphorus-containing castor oil-derived polyesters have been synthesized *via* ADMET polymerization. Some of these linear polyesters have shown good flame retardant properties.
- A series of new castor oil-derived polyesters containing hydroxyl and phosphine oxide groups have been synthesized *via* ADMET polymerization. Acrylation of the backbone hydroxyls followed by radical polymerization has led to a family of flame retardant cross-linked polymers.

## APENDIXES

### Appendix A. List of abbreviations

$^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ -NMR	Proton, carbon and phosphorus nuclear magnetic resonance
ADMET	Acyclic diene metathesis
ASO	Acrylated high oleic sunflower oil
ASO[H]	Acrylated hydrogenated high oleic sunflower oil
BF <sub>3</sub> ·MEA	Boron trifluoride-ethylamine complex
CDPP	Chlorodiphenylphosphine
DCM	Dichloromethane
DCP	Dicumyl peroxide
DDM	4,4'-Diaminodiphenylmethane
DMTA	Dynamomechanical thermal analysis
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DSC	Differential scanning calorimetry
EDX	Energy-dispersive X-ray spectroscopy
EMO	Epoxidized methyl oleate
FR	Flame retardant
FTIR/ATR	Fourier transform infrared spectroscopy
gHSQC	Gradient-selected heteronuclear single quantum correlation
gCOSY	Gradient-selected correlation spectroscopy
GC/MS	Gas chromatography coupled with mass spectrometry
GPC	Gel permeation chromatography
hr-MAS NMR	High resolution magic angle spinning nuclear magnetic resonance
HSO	Hydrogenated high oleic sunflower oil
HSO[H]	Acrylated hydrogenated high oleic sunflower oil
LOI	Limiting oxygen index
$M_n$	Number average molecular weight
$M_w$	Weight average molecular weight

P-ASO	Tertiary phosphine oxide containing acrylated high oleic sunflower oil
PDI	Polydispersity index ( $M_w/M_n$ )
PETA	Pentaerithritol tetraacrylate
P-SO	Tertiary phosphine oxide containing high oleic sunflower oil
SEM	Scanning electron microscopy
SO	High oleic sunflower oil
$T_{5\% \text{ loss}}$	Temperature of 5 % weight loss
$T_g$	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
$T_m$	Melting temperature
$T_{\text{max}}$	Temperature of maximum weight loss
TMS	Tetramethylsilane
TPP	Tetraphenylporphyrine
UV-vis	Ultraviolet-visible spectroscopy

## Appendix B. List of publications

A New Enone-Containing Triglyceride Derivative as Precursor of Thermosets from Renewable Resources.

Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. *J Polym Sci Part A: Polym Chem* 2008, 46, 6843-6850.

Quinoline-Containing Networks from Enone and Aldehyde Triglyceride Derivatives.

Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. Submitted to *J Polym Sci Part A: Polym Chem*.

A New Route To Acrylated Oils. Crosslinking And Properties Of Acrylated Triglycerides From High Oleic Sunflower Oil.

Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz V. *J Polym Sci Part A: Polym Chem* 2009, 47, 1159-1167.

A Straightforward Strategy For The Efficient Synthesis Of Acrylate And Phosphine Oxide-Containing Vegetable Oils And Their Crosslinked Materials

Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. *J Polym Sci Part A: Polym Chem* 2009, 47, 4051–4063.

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Vegetable oil-based thermosetting polymers.

Galià, M.; Montero de Espinosa, L.; Ronda, J. C.; Lligadas, G.; Cádiz, V. *Eur. J. Lipid Sci Technol* 2009, 111, DOI 10.1002/ejlt.200900096, in press.

## **Appendix C. Stages and meeting contributions**

### **Stages**

Three months stay (1<sup>st</sup> September - 1<sup>st</sup> December 2008) at the University of Applied Sciences Oldenburg / Ostfriesland / Wilhelmshaven, Faculty of Technology, Emden (Germany) under the supervision of Prof. Dr. Michael A. R. Meier.

Two weeks stay (July 2009) at the University of Applied Sciences Oldenburg / Ostfriesland / Wilhelmshaven, Faculty of Technology, Emden (Germany) under the supervision of Prof. Dr. Michael A. R. Meier.

### **Meeting contributions**

Flame Retardant Vegetable Oil-based Thermosetting Polymers.

L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz.

Oral communication.

11th European Meeting on Fire Retardant Polymers, Bolton, Manchester (UK), 03-06 July, 2007.

Polímeros retardantes a la llama derivados de ésteres del ácido oléico modificados con óxidos de fosfina.

L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz.

Oral communication.

X Reunión Del Grupo Especializado De Polímeros (RSEQ y RSEF), Sevilla (Spain), 16-20 September, 2007.

Vegetable oil-based thermosetting polymers.

V. Cádiz, L. Montero de Espinosa, J. C. Ronda, M. Galià.

Poster.

International Workshop On Biomacromolecules 2008, Stockholm (Sweden), 1-4 June, 2008.

Flame retardant polyesters from renewable resources *via* ADMET.

L. Montero de Espinosa, J. C. Ronda, V. Cádiz, M. A. R. Meier.

Poster.

2nd Workshop On Fats And Oils As Renewable Feedstock For The Chemical Industry,  
Emden (Germany), 22-24 March, 2009.

A new route to phosphorus-containing vegetable oils. Crosslinking and properties of  
phosphorus-containing acrylate triglycerides from high oleic sunflower oil.

L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz.

Poster.

Frontiers In Polymer Science International Symposium, Mainz (Germany), 7-9 June,  
2009.

Synthesis of plant oil derived polyester-polyols *via* ADMET as precursors of flame  
retardant materials.

L. Montero de Espinosa, M. A. R. Meier, J. C. Ronda, V. Cádiz.

Poster.

XI Reunión Del Grupo Especializado De Polímeros (RSEQ y RSEF), Valladolid  
(Spain), 20-24 September, 2009.

Crosslinking of enone-containing triglycerides with aromatic amines.

L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz.

Poster.

XI Reunión Del Grupo Especializado De Polímeros (RSEQ y RSEF), Valladolid  
(Spain), 20-24 September, 2009.