Synthesis of Novel Copolymers Obtained from Acceptor/Donor Radical Copolymerization of Phosphonated Allyl Monomers and Maleic Anhydride

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ABSTRACT: A series of four phosphonated-bearing allyl monomers, that is, diethyl-1-allylphosphonate (**AP**), dimethyl-1-allyloxymethylphosphonate (**AOP**), 5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (**AEDPH**), and 2-benzyl-5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (**AEDPBn**) were synthesized. These monomers were then copolymerized by free radical polymerization in the presence of maleic anhydride, thus leading to alternated copolymers with phosphonate moieties. It was shown that both monomer conversion and reaction rate were dependent on the phosphonate moieties carried out by the

INTRODUCTION Flame retardants (FR) for textiles^{1,2} have never had so much interest as the recent introduction of a strict legislation, especially focusing on halogenated compounds. Then, phosphorus atoms containing FR progressively came to replace halogenated ones.³⁻⁷ These phosphorusbased flame retardants additives are generally incorporated into polymeric materials as additives in melted polymers. These FR additives usually have low molecular weight, which may undergo migration to the surface of polymeric materials, in time and uses. This exudation sometimes creates a change in the mechanical properties as well as in the FR behavior of the material. Hence FR additives having higher $M_{\rm w}$ should allow reducing this phenomenon. A wide range of phosphorus-containing polymers were synthesized and used as FR additives of polymeric materials.⁸⁻¹⁰ Phosphorus-containing allyl monomers have also attracted much interest. We have recently developed^{11,12} the synthesis of polymers from radical polymerization of 2-R-5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (Scheme 1).

We also showed that, depending on both the reaction conditions and of the *R* substituent, the resulting polymeric species could have either hyperbranched (with high M_w values) or linear structure (with low M_w values). Indeed, it is wellknown that the radical homopolymerization of allyl monoallyl monomer: the bulkier the phosphonate group, the higher the polymerization rate. Thermogravimetric analysis of the copolymers revealed a high content of residue, also varying with the nature of the phosphonate moieties. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3905–3910, 2011

KEYWORDS: AD copolymerization; allyl monomer; copolymerization; dioxaphosphorinane; flame retardance; heteroatomcontaining polymers; kinetics (polym.); maleic anhydride; radical polymerization; thermogravimetric analysis

mers usually results in low M_w oligomers, mainly due to degradative chain transfer.^{13–15} The weakness of the allyl C—H bond arises from the high resonance stability of the allyl radical, which is too stable to reinitiate polymerization and undergoes termination by reaction with a propagating radical.¹¹

However, if allyl monomers poorly homopolymerized, they are good candidates in radical copolymerizations. Indeed, allyl monomers, as electron-donating monomers, are able to efficiently copolymerize with high electron-accepting monomers, leading to high M_w copolymers. As an example, Nippon Oils and Fats Corporation¹⁶ performed the radical copolymerization of allyl ether, containing (oxyalkylenes) side groups of M_w ranging from 400 to 5000 g mol⁻¹, with maleic anhydride (Scheme 2). The resulting copolymer was sold under the MALIALIM[®] trademark.

Furthermore, the radical copolymerizations of vinyl monomers can be carried out either by heating or under UV light, with or without photoinitiator.¹⁷

To our knowledge, no study was achieved, so far, on the radical copolymerization of phosphonated-containing allyl monomers with electron-accepting monomers. The purpose of this work is first to prepare a series of phosphonated allyl

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SCHEME 1 Polymerization of 2-*R*-5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane by radical solution procedure (CTA stands for Chain Transfer Agent).

monomers, which then will be used as electron-donating monomers in radical copolymerizations with electron-accepting monomers (such as maleic anhydride). Kinetics of radical copolymerizations were investigated as well as the thermal properties of the resulting copolymers.

RESULTS AND DISCUSSION

Synthesis of Phosphonate-Bearing Allyl Monomers

Four phosphonated-bearing allyl monomers were selected for this study. Scheme 3 gathers the structures of the monomers: diethyl-1-allylphosphonate (**AP**), dimethyl-1-allyloxymethylphosphonate (**AOP**), 5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (**AEDPH**) and 2-benzyl-5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (**AEDPBn**).

We can note that **AOP**, **AEDPH**, and **AEDPBn** are allyl-oxy monomers. Both **AP** and **AOP** contain a dialkylphosphonate group, whereas both **AEDPH** and **AEDPBn** have a dioxaphosphorinane group. None of them is commercially available and, hence, need to be synthesized. **AEDPH** and **AEDPBn** syntheses, described in a recently published paper,¹² consist on a direct transesterification of a diol with hydrogen or arylphosphonate.

As mentioned in the literature, diethyl-1-allylphosphonate (**AP**) monomer was obtained by reaction of allyl bromide (Scheme 4) with triethylphosphite, according to Arbusov rearrangement,^{18–21} that is, isomerization of $P(OR)_3$ into $(RO)_2P(=O)R'$ (where R' corresponds to allyl group). The Arbuzov reaction of triethyl phosphite with commercial allyl bromide afforded **AP** with 95% yield. The structure was con-

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SCHEME 2 MALIALIM structures obtained by radical copolymerization of maleic anhydride with allyl ether.

firmed by ¹H NMR (Fig. 1), especially by considering the peak centered at 2.34 ppm, characterizing the methylene adjacent to the phosphonate group. ³¹P NMR showed only one peak at 26.8 ppm for the phosphonate group.

To the author's knowledge, the synthesis of **AOP** has never so far been described. **AOP** was obtained by nucleophilic substitution of allyl bromide by a primary alcohol bearing a phosphonate group (Scheme 4).

This reaction requires an equimolar amount of allyl bromide and primary alcohol. The functional alcohol, that is, dimethyl hydroxymethylphosphonate, was previously synthesized from reaction of dimethylhydrogenophosphonate with paraformaldehyde using anhydrous potassium carbonate, as described elsewhere.^{22,23} Following this procedure, **AOP** was obtained in quantitative yield. The high purity of **AOP** was evidenced from ³¹P NMR as a single peak in 24 ppm was observed (Fig. 2). ¹H NMR (Fig. 2) also allows to perfectly characterizing AOP: allyl protons signal is shown at δ = 5.8-5.2 ppm, the signal of CH₂ in α -position is centered at δ = 4.03 ppm and the 8 others protons show a broad signal centered at δ = 3.75 ppm.

Free Radical Copolymerization

It is widely recognized that conventional radical homopolymerization of allyl monomers usually leads to low molecular weights oligomers (DP_n less than 50 units); this behavior is generally ascribed to chain transfer process occurring onto the methylene group of allyl monomers, then limiting the



SCHEME 3 Structures of phosphonated-bearing allyl monomers AP, AOP, AEDPH, and AEDPBn.



SCHEME 4 Synthesis of dimethyl-1-allyloxymethylphosphonate (AOP) and of diethyl-1-allylphosphonate (AP).

propagation reaction.14,15,24 As already mentioned in the introduction part, allyl monomers are good electron-donating monomers, and their radical copolymerizations with electron-accepting monomers mainly afford alternated copolymers. The capability of monomers to efficiently copolymerize is connected to both their polarizing effect and their ability to accept/give electrons. These Alfrey-Price parameters, noted Q (for polarizing effect) and *e* (for the ability to give/accept electrons), must be known in order to estimate the copolymer structures, that is, statistical or alternated structures. If the polarizing effects are similar for both monomers (i.e., values of Q very close), then the polymerization will turn into alternated radical copolymerization. Besides, if two monomers show opposite values for *e* parameter, then expected alternated copolymer should be also obtained. According to the literature, allyl monomers usually exhibit negative values for e parameter, which enhances the electron-donating character of allyl monomers. For instance, allyl butyl ether and allyl alcohol show e values of -2.53 and -1.48, respectively. When involved in radical copolymerizations with maleic anhydride, maleimides or maleates (showing e values of 3.69, 3.3, and 1, respectively), it turned to alternated structures.²⁵ Some others papers also described the radical copolymerization between alkyl allyl ethers and monomers such as vinyl acetate,²⁶ maleic anhydride (MA),²⁷ maleates,^{28,29} maleimides or fluorinated olefins.³⁰⁻³² In all cases, alternated copolymers were obtained. Noteworthy, if the radical copolymerization of allyl ethers usually leads to alternated copolymers, the final conversion is lowered by using



FIGURE 2 ¹H and ³¹P NMR spectrum of dimethyl-1-allyloxymethylphosphonate (AOP).

different electron-accepting monomers, that is, butyl acrylate, dialkyl maleate or fumarate. Among all electron-accepting monomers, maleic anhydride (MA) appears to be the most efficient to obtain alternated copolymers by radical copolymerizations with allyl monomers, according to its Q and e parameters (0.86 and 3.69, respectively).³³ As mentioned earlier, the radical copolymerization of allyl ether, containing (oxyalkylenes) side groups, with MA afforded alternated copolymer produced and sold under the MALIALIM® trademark.

Hence, in this study, the radical copolymerizations of phosphonate-bearing allyl monomers (**AP**, **AOP**, **AEDPH**, and **AEDPBn**) were investigated with MA as electron-accepting monomer. For each radical copolymerization involving phosphonate-bearing allyl ether/MA, the reaction conditions were the following: acetonitrile as solvent with a molar ratio concentration S_0 of 4 (S_0 = [solvent]₀/[monomers]₀), AIBN as initiator with a molar ratio concentration C_0 of 0.05 (C_0 = [initiator]₀/[monomers]₀). All radical copolymerizations were carried out at 70 °C with a MA/allyl monomer molar ratio of 1/1 (Scheme 5).



FIGURE 1 ¹H and ³¹P NMR spectrum of dimethyl-1-allylphosphonate (AP).



SCHEME 5 Radical copolymerizations of maleic anhydride with phosphonate-bearing allyl monomers. MA/ABE (allyl butyl ether) radical copolymerization was used as model reaction.

ARTICLE



FIGURE 3 Kinetic plots of allyl monomer conversion vs reaction time for the radical copolymerizations of MA with a series of phosphonate-bearing allyl monomers (AP, AOP and AEDPBn) carried out at 70 °C in acetonitrile in the presence of AIBN. Radical copolymerization of MA with allyl butyl ether (ABE) is also given for comparison.

Allyl butyl ether (ABE)/MA radical copolymerization was carried out as a model reaction by using the aforementioned reaction conditions. Kinetic plots of allyl monomer conversion were reported (Fig. 3) against reaction time for each radical copolymerization.

Kinetic plots of allyl monomer conversion vs reaction time for the radical copolymerizations of MA with a series of phosphonate-bearing allyl monomers (AP, AOP, and AEDPBn) carried out at 70 $^{\circ}$ C in acetonitrile in the presence of AIBN. Radical copolymerization of MA with allyl butyl ether (ABE) is also given for comparison.

We can note that, expectedly, reaction completion was observed after only few hours for MA/ABE radical copolymerization. The copolymers were precipitated into methanol and molecular weights were evaluated by means of SEC. Monomer conversions obtained after 24 hr of reaction as well as molecular weight values and PDI are also given (Table 1).

Free radical copolymerization of MA/ABE affords low molecular weights oligomers with rather low polydispersity values.



FIGURE 4 TGA thermograms of MA/ADEPBn, MA/AOP and MA/ AP copolymers recorded in nitrogen atmosphere 10 °C·min⁻¹.

TABLE 1 Monomer Conversions, Molecular Weight, andPolydispersity Index Obtained for the RadicalCopolymerizations of Phosphonate-Bearing Allyl Monomerswith MA Carried Out at 70 °C in Acetonitrile in the Presence ofAIBN and Stopped after 24 h

Copolymer	α _{Allyl} ^a	α _{MA} ^a	M _n (g/mol) ^b	PDI ^b
MA/ABE	0.99	0.98	2.500	1.9
MA/AP	0.49	0.68	1.700	2.3
MA/AOP	0.45	0.78	1.600	2.9
MA/AEDPBn	0.80	0.97	8.300	1.8

Results for radical copolymerization of MA with allyl butyl ether are also given for comparison.

^a Monomer conversions obtained from ¹H NMR after 24 hrs of reaction.

^b Calculated from SEC analysis in DMF by using PMMA standards.

This behavior is ascribed to predominant radical transfer onto ABE, referred to as "degradative monomer chain transfer." Inoue et al.¹⁴ have therefore estimated the chain transfer constant $C_{\rm m}$ of allyl acetate of about 3.7 imes 10⁻² at 80 °C. The MA/phosphonate allyl monomers free radical copolymerizations show different trend, as compared to MA/ABE copolymerization. First the polymerization rates are lowered, according to monomers conversion, which highlights the decrease of the electron-donating character for phosphonatebearing allyl monomers. Such decrease was already observed by Skwarski and Wodka^{34,35} during the free radical copolymerization of acrylonitrile with phosphonate-bearing allyl monomer. This decrease was indeed denoted by the Q and evalues of 0.02 and -0.15, respectively for the phosphonatebearing allyl monomer. Nevertheless, we can note distinct behaviors between phosphonate-allyl type monomers. Concerning MA/AEDPBn free radical copolymerization, after 24 hrs of reaction ¹H NMR of the crude reaction mixture gave allyl conversions (α_{AEDPBn}) of 80%, the maleic anhydride conversion (α_{AM}) increased further up to 97%. AEDPBn conversion shows a two-step kinetic; a first-order kinetic is observed with a sharp increase until 60% of conversion after 1 hr, followed by a slow-down of the monomer conversion. The sharp increase may be explained by the affinity of maleic anhydride radical towards allyloxy monomer, that is, acceptor-donor (AD) free radical copolymerization. This also demonstrates that the electron-donating character of AEDPBn is not lowered by the phosphonate moities, situated far from the allyl double bond. The slowdown of the polymerization may be explained either by the benzyl-dioxaphosphorinane group or by occurrence of termination reaction (contribution of both phenomena is not excluded). MA/ AEDPH free radical copolymerization was also performed in the same experimental conditions but a gelification of the reaction mixture was observed. This gel was insoluble in conventional organic solvents such as THF, dichloromethane, acetone or even in DMF... Despite the presence of MA, hyperbranched species were indeed growing due to the reactivity of the P-H bond, as already mentioned in a previous article.11 MA/AP and MA/AOP free radical copolymerizations proceed similarly (Fig. 3). Indeed, the conversion profiles of

TABLE 2 Thermal	Stability	y of	Copoly	ymers
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Copolymer	P Content (%) ^a	T Onset (°C) ^b	<i>T</i> _{10%} (°C) ^c	<i>T</i> _{50%} (°C) ^c	Residue at 600 °C (%)	τ _g (°C) ^d
MA/ABE	/	285	303	399	13	79
MA/AEDPBn	7.5	180	260	440	23	118
MA/AOP	10.5	150	240	430	41	85
MA/AP	10.5	140	165	310	36	105

^a *P* content is the phosphorus content in the copolymer.

^b *T* onset corresponds to the temperature of the decomposition onset.

 $^{\rm c}$ $T_{\rm 10\%}$ and $T_{\rm 50\%}$ are the temperatures at 10% and 50% weight loss, respectively.

both AP and AOP are identical, that is, denoting a very slow polymerization rate. The resulting copolymers show low molecular weight values (ca. 1600 g/mol) for high PDI (Table 1). This behavior can be explained by the close proximity of the phosphonate moieties to the allyl double bond, thus lowering the electron-donating effect of the allyl group. The high polydispersity associated to the low molecular weights values is probably the result of either occurrence of termination process or radical transfer.

Thermal Behavior

DSC curves of copolymers were operated at 20 °C/min heating rate. As shown in Table 2, only one glass transition was observed for each copolymer. The $T_{\rm g}$ value increases with the steric hindrance of the lateral group (i.e., phosphonate or dioxaphosphorinane). Recently, organo-phosphorus compounds have demonstrated good ability in imparting flame retardancy to polymers and some researchers reported that they work either in both condensed and gas phase.³⁶ They degrade at a relatively low temperature and form a protective layer of char rather than yielding to radicals capturing volatiles during decomposition. Thermogravimetric analyses (TGA) of copolymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min, from 50 to 600 °C. Detailed TGA data including initial decomposition temperature (T_{onset}), the temperatures at 10 and 50% weight loss (T_{10} and T_{50}) and the fraction of residue at 600 °C, are summarized in Table 2.

First, the initial decomposition temperature was rather low for the three copolymers, according to the progressive loss of solvent (i.e., water). Then, MA/AEDPBn copolymer shows a better thermal behavior until about 450 °C. The benzyl group attached to the phosphonate moieties enhances the thermal stability of MA/AEDPBn copolymer, as compared to alkyl ester groups. The better resistance of benzyl groups was already mentioned in the literature.^{3,4,37,38} Furthermore, Hoang et al.^{3,4} showed that the thermal degradation behavior of phosphonate-bearing (co)polymers is mainly dependant on the nature of pendant groups directly linked to the phosphorus atom. The sharp decrease of the thermal stability until about 350 °C for both MA/AP and MA/AOP, corresponding to about 35% weight loss, was attributed to the cleavage of ester group from phosphonate moieties. Nevertheless, the content of residue for both MA/AP and MA/AOP is rather high (ca. 36-40%) and more important than for MA/AEDPBn copolymer. Indeed, after the loss of alkyl

^d Glass transition temperature obtained from DSC analysis.

groups, MA/AP and MA/AOP copolymers easily form P-O-P anhydride bonds highly thermally stable.²⁰ In the other way, MA/AEDPBn copolymer has a lower phosphorous content, which explains the lower content of residue. Finally, we can note that MA/AOP copolymer, having the same phosphorous content and the same M_w value than MA/AP, gives both a better stability and a higher content of residue. MA/ABE copolymer shows a starting thermal degradation at 250 °C but low residue content (ca. 13%) was obtained at 600 °C, which enhances the contribution of phosphonate groups in the condensed phase. Finally, MA/AOP copolymer is probably a good candidate as flame retardant additive; this will be studied in a forthcoming paper.

EXPERIMENTAL

All the solvents and reagents (Sigma-Aldrich, Fluka or Acros) were used with a purity of 98–99%. 1,3-propanediol, diethyl hydrogenophosphonate, dimethyl hydrogenophosphonate, allyl butyl ether, 2-(allyloxymethyl)-2-ethyl-1,3-propanediol, allyl bromide, benzyl bromide, sodium hydride (60% in oil), triethyl phosphite, potassium *tert*-butoxide were used without purification. 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recristallization from methanol and dried under vacuum.

¹H and ³¹P NMR spectra were recorded in CDCl₃ solutions on a Bruker Avance 400 MHz spectrometer. ¹H and ³¹P chemical shifts are expressed in ppm/TMS and ppm/H₃PO₄ external standard, respectively. Size exclusion chromatography (SEC) was performed on a Varian apparatus equipped with a RI Shodex refractive index detector. Two PL-gel mix D columns were used at 70 °C with a 0.8 mL min⁻¹ flow rate of DMF, calibrated using poly(methyl methacrylate) or PMMA standards. TGA experiments were conducted on a Pyris 1 TGA by Perkin–Elmer. They were performed on 2–10 mg samples under nitrogen at a heating rate of 10 °C min⁻¹. Differential scanning calorimeter analyses were recorded with a Netzsch 200 Maïa DSC at a heating rate of 20 °C/min under nitrogen atmosphere.

Synthesis of Dimethyl-1-allyloxymethylphosphonate (AOP)

To a solution of NaH (0.99 g, 4×10^{-2} mol) in dry THF (40 mL), under inert gas at 0 °C, was added dropwise a mixture of 4.2×10^{-2} mol (5.0 g) of allyl bromide and 4.2×10^{-2} mol (4.6 g) of dimethyl hydroxymethylphosphonate. The reaction mixture was stirred at room temperature during 24 hrs. The precipitated NaBr was removed by filtration and the



solvent was evaporated. The dimethyl allyloxymethylphosphonate was obtained in quantitative yield.

¹H NMR (400 MHz, CDCl₃, δ): 3.72 (s, H₅); 3.75 (d, H₇); 4.03 (s, H₃); 5.18-5.27 (dd, H₁) and 5.82 (m, H₂). ³¹P NMR (400 MHz, CDCl₃, δ): 24.03 (P-C).

Synthesis of Diethyl-1-allylphosphonate (AP)

Into a flask equipped with a dean-starck, 6×10^{-2} mol (9.95 g) of triethyl phosphite was added to 9×10^{-2} mol (10.8 g) of allyl bromide under nitrogen. The resulting solution was stirred for 14 hrs at 80 °C. The product was distilled under reduced pressure (5 mmHg) with a yield of 95%.

¹H NMR (400 MHz, CDCl₃, δ): 1.05 (m, H₇); 2.34 (m, H₃); 3.83 (m, H₆); 4.94 (m, H₁) and 5.53 (m, H₂). ³¹P NMR (400 MHz, CDCl₃, δ): 26.76 (P-C). Bp = 102 °C (11 mmHg).³⁹

Radical Copolymerization of Phosphonated-Bearing Allyl

Monomer with Maleic Anhydride or Dimethyl Maleate Allyl monomer (3 \times 10⁻³ mol) and 3 \times 10⁻³ mol of acceptor monomer (maleic anhydride or dimethyl maleate) was added in acetonitrile (2.4 \times 10⁻² mol). The reaction mixture was stirred at 70 °C under nitrogen for 20 min. Then, 5 mol % of AIBN initiator was added in several shots (3 times, every 24 hrs). After 24 hrs, the product was precipitated in water to obtain a powder.

CONCLUSIONS

The free radical copolymerization of maleic anhydride was successfully carried out in the presence of allyl monomers carrying phosphonate moieties, that is, diethyl phosphonate or dioxaphosphorinane group. The free radical copolymerization resulted in alternated copolymers with rather low molecular weights values. Interestingly, the kinetics of copolymerization were influenced by the phosphonate group of the allyl monomers: the bulkier the phosphonate moieties, the faster the polymerization rate and the higher the monomer conversion. Furthermore, the close proximity between the phosphonate moieties and the allyl double bond led to a decrease of the electron-donating character of allyl monomer. We also showed the occurrence of allyl transfer, by comparison with model free radical copolymerization, thus explaining the low molecular weight values. Finally, the high content of residue obtained from thermo gravimetric analysis proves the potential efficiency of such copolymers as flame retardant additives.

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