Novel Dialkyl Vinyl Ether Phosphonate Monomers: Their Synthesis and Alternated Radical Copolymerizations with Electron-Accepting Monomers

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ABSTRACT: Three new vinyl ether monomers containing phosphonate moieties were synthesized from transetherification reaction. We showed that the yield was dependent on the spacer length between the vinyl oxy group and the phosphonate moieties: when the spacer is a single methylene side reaction may occur, leading to the formation of acetal compounds. Free-radical copolymerizations of phosphonate-containing vinyl ether monomers with maleic anhydride were carried out, leading to alternated copolymers of rather low molecular weights (from 1000 to 7000 g/mol). Both gel permeation chromatography and ³¹P NMR analyses enhanced possible intramolecular transfer reactions occurring from the phosphonate moieties. Kinetic investigation showed that the electron-withdrawing character of the phosphonate moieties tends to decrease the rate of copolymerization. Nevertheless,

INTRODUCTION Phosphorus-containing polymers functionalized either at the main chain (e.g., polyphosphazene and polyphosphoesters) or at the side chain found applications in many fields. Dental adhesives, ion-exchange resins, and flame retardants are just some of the more common applications.¹⁻⁴ Compounds containing phosphorus are also excellent promoters with respect to adhesion,5-9 and thus anticorrosion. Only few phosphorus-containing monomers are so far commercially available, and most of them are phosphate-type monomers.^{10,11} Recently, we have published a reviewing paper¹² gathering the syntheses and radical (co)polymerizations of phosphonate-containing vinyl monomers, ranging from allyl-type to (meth)acrylic-type monomers. This article shows that the phosphonate group weakly changes the double bond reactivity, despite its electrondonating character with the exception of *p*-benzyl phosphonate monomers, where the phosphonate group enhances the reactivity of the styryl monomer in free-radical polymerization.¹³ Considering specifically both phosphonate allyl-type and vinyl-type monomers, we showed that their radical homopolymerization led to oligomers with expected poor almost complete monomers conversion was reached after 30 min of reaction with dimethyl vinyloxyethylphosphonate (VEC₂PMe). Then, radical copolymerization of VEC₂PMe with a series of electron-accepting monomers, that is, dibutyl maleate, dibutylitaconate, itaconic anhydride, butyl maleimide, and methyl maleimide, led to a series of alternated copolymers. From kinetic investigation, we showed that the higher the electron-accepting effect, the faster the vinyl ether consumption and the higher the molecular weights. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

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yields.^{14,15} In contrast, their radical copolymerization with electron-accepting monomers was deeply investigated. For instance, radical copolymerization of diethyl vinyl phosphonate (DEVP) with styrene carried out at 100 °C resulted in copolymers of high molecular weight values;16 the incorporation of DEVP units lowered the T_{g} value of polystyrene due to the steric hindrance of phosphonate group. In this article, we focus on dialkyl vinyl ether phosphonate monomers. Vinyl ether monomers are good candidates to reach high molecular weights polymers either by cationic homopolymerization¹⁷ or by radical copolymerization^{18,19} (when associated to an electron-accepting monomer). To the author's knowledge, only Kohli et al.²⁰⁻²² performed the radical copolymerization of diisopropyl 2-vinyloxyethylphosphonate with a series of maleimide monomers to modify selective surfaces.

We develop herein the synthesis through transetherification of a series of novel dialkyl vinyl ether phosphonate monomers as well as their radical copolymerization with a series of electron-accepting monomer.

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SCHEME 1 Synthetic pathway to provide dialkyl vinyl ether phosphonate monomers.

RESULTS AND DISCUSSION

Synthesis of Dialkyl Vinyl Ether Phosphonate Monomers

Several attempts were made to efficiently perform the synthesis of dialkyl vinyl ether phosphonate monomers. The first ones were made through the Arbusov reaction by reaction of chloro ethyl vinylether with triethylphosphite.²³ Diethyl vinyloxy phosphonate was obtained in good yield; however, ethyl diethylphosphonate is always obtained in non-negligible amounts, despite drastic reaction conditions. More interestingly, transetherification reaction was also used between hydroxyl compound and vinyl ether. Transetherification efficiently occurs when catalyzed by mercury or palladium salts.²⁴⁻²⁶ Furthermore, acetals may be also formed, depending on both the efficiency and the stability of the catalyst. The rather complex mechanism of transetherification, catalyzed by palladium salts, was recently discussed by Muzart.²⁷ Despite the expected catalyst complexation from phosphorus, we have investigated this reaction to obtain a series of novel dialkyl vinyl ether phosphonate monomers. The synthetic strategy, given in Scheme 1, is based on a twostep reaction.

The first one is the synthesis of phosphonate-containing hydroxyl compounds from dialkyl phosphite. The reaction of dialkyl phosphite with paraformaldehyde leads to phosphonate-containing primary alcohol with one methylene spacer in between.²⁸ Furthermore, the radical addition of dialkylphosphite onto vinyl acetate, followed by the acetate group cleavage in basic medium, leads to phosphonate-containing primary alcohol with two methylene spacers in between.^{29,30} This first-step reaction was already deeply described in other papers and leads to alcohols with good yields and high purity. The second-step reaction is the transetherification reaction between ethyl vinyl ether and phosphonate-containing primary alcohols in the presence of palladium catalyst and 1,10-phenantrolin, which is expected to avoid the formation of acetal side products. This synthetic strategy allowed performing the synthesis of four different phosphonate-containing vinyl ethers, noted VEC_xPR, by varying both the spacer length x and the R group of the phosphonate moieties (Table 1).

We can note that the final yields, obtained after purification by column, are rather low (about 30%) and do not vary with the R group. Nevertheless, with two methylene spacers, the final yield is increased up to 80%. This behavior was ascribed to the acetal formation during the transetherification reaction. Indeed, the ³¹P NMR (Fig. 1) of VEC₂PMe crude product reveals the presence of two acetal compounds: tetramethyl((ethane-1,1-diylbis(oxy))bis(ethane-2,1diyl))bisphosphonate in high yield and dimethyl(2-(1ethoxyethoxy)ethyl)phosphonate in lower yield. The ³¹P NMR of the crude also shows the unreacted hydroxyl compound as well as the expected vinyl ether monomer.

Despite the presence of 1,10-phenantrolin, acetals were formed, which demonstrates the negative effect of phosphorus complexation toward the catalyst. We decreased the temperature down to ambient temperature to lower the amount of acetals. Nevertheless, column purification with dichloromethane/ethyl acetate as eluent was required and vinyl ether monomers were obtained with high purity. Figure 2 shows both the ³¹P and ¹H NMR of VEC₂PMe.

TABLE 1	Yield	and ³	¹ P NMR	for New	Phosphonate	-Containing
Vinyl Eth	er Mo	nome	ers			

Monomer	Structure	Yield (%)	³¹ P NMR Chemical Shift
VEC ₁ PMe	$H \xrightarrow{H} O_{-CH_2-P-OCH_3}$	20	22.00
VEC ₁ PEt	$H \xrightarrow[H]{} O = CH_2 - P = OCH_2CH_3$	30	19.69
VEC ₂ PMe	$H \xrightarrow[H]{0-CH_2-CH_2-P} O \xrightarrow[H]{0-CH_3} O \cap O $	85	30.57



FIGURE 1 ³¹P NMR spectrum of the crude product for the reaction between ethyl vinyl ether and phosphonate-containing primary alcohol.

The ³¹P NMR shows a single peak centered at 30.57 ppm, characterizing the phosphonate moieties of the monomer. From ¹H NMR, the vinyl protons are clearly identified at 6.4, 4.2, and 4.06 ppm. The OCH_2 methylene group shows a peak centered at 3.88 ppm as triplet of doublets. Similarly, the signal of CH₂P methylene group appears at 2.2 ppm as a triplet of doublets due to the α -position of the phosphorus atom. Finally, the signal of the methyl groups for phosphonate moieties is clearly identified as a doublet at 3.75 ppm. Figure 3 shows both the ³¹P and ¹H NMR of VEC₁PEt. A single peak is also observed from ³¹P NMR centered at 19.69 ppm. This signal is downshifted, compared with that of dimethyl vinyloxyethylphosphonate (VEC₂PMe), as the phosphonate moieties is situated in β -position of the vinyl-oxy group. From ¹H NMR, we can especially observe the signal at 3.9 ppm of the methylene CH_2P that appears as a doublet.

Radical Copolymerization of Dialkyl Vinyl Ether Phosphonate Monomers with Maleic Anhydride

Vinyl ether monomers are good electron-donating monomers, and their radical copolymerizations with electronaccepting 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 to estimate the copolymer structures, that is, statistical or alternated structures. If the polar-

izing 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,^{31–33} vinyl ether monomers usually exhibit negative values for e parameter, which enhances the electron-donating character of allyl monomers. Maleic anhydride (MA)34-36 shows positive e value of about 2.3. Furthermore, MA and vinyl ethers show Q values of about 0.2 and 0.1, respectively (0.1 is an average value as the Q value of the vinyl ethers)may vary with the substituent). Thus, the Alfrey-Price parameters of vinyl ethers and MA clearly support behavior of alternated radical copolymerization. Furthermore, Fujimori³⁷ performed a kinetic investigation of the radical copolymerization between MA and isobutyl vinyl ether and stated on the formation of charge transfer complex (CTC) with a complexation constant value of 0.033 L/mol. The formation of the CTC enhances the formation of alternated structure. Hao et al.³⁸ also showed that the cis-conformation of MA was obtained in the copolymer, due to the CTC formation and participation to the radical polymerization.

Hence, in this study, the radical copolymerizations of dialkyl vinyl ether phosphonate monomers were investigated with MA as electron-accepting monomer to perform alternated copolymers bearing phosphonate moieties (Scheme 2). For each radical copolymerization, the reaction conditions were





the following: chloroform as solvent with a molar ratio concentration S_0 of 4 ($S_0 = [\text{solvent}]_0/[\text{monomers}]_0$), 2,2'-azobis(isobutyronitrile) (AIBN) as initiator with a molar ratio concentration C_0 of 0.05 ($C_0 = [\text{initiator}]_0/[\text{monomers}]_0$). All radical copolymerizations were carried out at 70 °C with a MA/vinyl ether monomer molar ratio of 1/1.

Quantitative conversion for both MA and vinyl ethers was observed after 24 h. Three alternated copolymers were synthesized (Scheme 2) and purified from diethyl ether precipitation. As an example, Figure 4 shows the ¹³C NMR of poly(VEC₂PMe-*alt*-MA) and proves the good purity of the obtained copolymers.



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The ³¹P NMR shows a single peak shifted at 31 ppm. Similar result was obtained for poly(VEC₁PMe-*alt*-MA), where a single peak was also obtained at 26 ppm from ³¹P NMR. When radical copolymerization is carried out with VEC₁PEt, two peaks are nevertheless observed from ³¹P NMR (Fig. 5): a

broad peak at 18.6 ppm characterizes the phosphonate moieties of $poly(VEC_1PEt-alt-MA)$, whereas the second peak at 15 ppm enhances possible side reaction.

Bingöl et al.³⁹ have demonstrated, especially by means of electrospray ionization-mass spectroscopy, that polymerization of







vinyl phosphonate is mainly dominated by transfer reaction; the predominant transfer occurs by intramolecular hydrogen transfer of phosphonate ester groups, which in consequence creates a P—O—C bond in the main chain. Nevertheless, these authors mentioned that this reaction was predominant mainly with isopropyl as alkyl group (Scheme 3, reaction 1), thus leading to a tertiary radical that promotes fast initiation. Shulyndin et al.⁴⁰ proposed another mechanism also based on radical transfer reaction (Scheme 3, reaction 2). They claimed that intracyclization occurred between the growing radical and the phosphonate moieties, leading to the generation of an alkyl radical species and of the creation of five-member cycle. As alternated copolymerization between MA and phosphonate-bearing vinyl ethers is expected, it is rather difficult to state on the mechanism leading to side reaction.

Gel permeation chromatography (GPC) was also conducted on different copolymers and molecular weight values were evaluated by using PMMA standards. GPC traces of copolymers show shoulder in the low molecular weight region, especially for poly(VEC₁PEt-*alt*-MA) copolymer (Fig. 6). This shoulder confirms the presence of side reactions by chain transfer reaction, as mentioned above, leading to low molecular weight oligomers. This shoulder is increased when the vinyl ether alkyl group is ethyl group, which again confirms the previous observed data (Fig. 5). The M_w values are rather low for poly (VEC₁PEt-*alt*-MA) and poly(VEC₁PMe-*alt*-MA), about 900 and



SCHEME 3 Side reactions occurring by intramolecular transfer reaction.



FIGURE 6 GPC traces of poly(VEC1PEt-alt-MA), poly(EVC1Me-alt-MA) copolymers (left), and poly(EVC1Me-alt-MA) copolymer (right).

1100 g/mol, respectively (Table 2). Poly(VEC₂PMe-*alt*-MA) shows higher M_w value of about 7000 g/mol.

No shoulder was observed from the GPC trace, which may support that the spacer length has an influence on the chain transfer reaction mechanism (Scheme 3).

Kinetic investigation of the radical copolymerizations was carried out by means of Fourier Transform Infra Red (FTIR), and especially by following the disappearance of the vinyl ether double-bond characteristic vibration bands at 1623 and 1638 cm⁻¹. Thus, the vinyl ether consumption was plotted versus time (Fig. 7) for the radical copolymerizations of VEC₁PMe/MA and VEC₂PMe/MA. For comparison, model radical copolymerizations of butyl vinyl ether (BVE) with MA and of 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether (FAVE-8) with MA were also followed by FTIR (Fig. 7).

We can note that the rate of polymerization for phosphonatebearing VEs is generally lower than that of model systems. This may be attributed first to the electron-withdrawing character of the phosphonate moieties. Nevertheless, the perfluorodecyl group of FAVE-8 shows a stronger electron-withdrawing character than the phosphonate moieties for a faster FAVE-8 copolymerization as compared to phosphonate-bearing VEs. Thus, another factor has to be taken into account, relating to phosphonate moieties acting as radical inhibitor. Indeed, phosphorus compounds are known to act as radical scavenger, especially in the gas phase when used as flame retardant;⁴¹ furthermore, retardation is often observed during the controlled radical polymerization of phosphonate-containing monomers due to radical initiator inhibition.⁴² Finally, if the polymerization rates for both VEC₁PMe/MA and VEC₂PMe/MA copolymerizations are fairly similar, VEC₂PMe reaches 100% conversion after 30 min, whereas for VEC₁PMe, the maximum conversion is 78%. This result enhances the negative effect of the spacer length: the lower the spacer length the higher the electron-withdrawing effect of the phosphonate group.

Radical Copolymerization of VEC₂PMe with a Series of Electron-Accepting Monomers

As VEC₂PMe provides both the higher M_w and monomer conversion when copolymerized with MA, it was copolymerized with a series of electron-accepting monomers, such as dibutyl maleate (DBM), dibutylitaconate (DBI), itaconic anhydride

TABLE 2 Monomer Conversion and Molecular Weight of Copolymers Obtained by Radical Copolymerization of Phosphonate-Bearing VE with Electron-Accepting Monomers

Copolymer	VE Conversion ^a	Comonomer Conversion ^a	$M_{ m w}~({ m g/mol})^{ m b}$	PDI
Poly(VEC ₁ PMe- <i>alt</i> -MA)	0.99	0.98	1,100	1.10
Poly(VEC ₂ PMe- <i>alt</i> -MA)	0.98	0.98	7,000	1.06
Poly(VEC ₁ PEt- <i>alt</i> -MA)	0.97	0.85	900	1.10
Poly(VEC ₂ PMe- <i>alt</i> -DBMA)	0.65	0.70	4,600	1.54
Poly(VEC ₂ PMe- <i>alt</i> -DBI)	0.74	0.93	3,200	1.25
Poly(VEC ₂ PMe- <i>alt</i> -IA)	0.90	0.93	1,700	1.24
Poly(VEC ₂ PMe- <i>alt</i> -BM)	0.97	0.99	3,100	1.69
Poly(VEC ₂ PMe- <i>alt</i> -MM)	0.98	0.90	5,000	1.90

^a Calculated from ¹H NMR.

^b From GPC by using PMMA standards.





FIGURE 7 Vinyl ether conversion versus time for the radical copolymerizations with MA.

(IA), butyl maleimide (BM), and methyl maleimide (MM) (Scheme 4).

After 24 h reaction, conversion of monomers was determined from 1 H NMR (Table 2). The conversion of VEC₂PMe

and the comonomer (i.e., electron-accepting monomer) is close for each copolymerization, which may depict alternating copolymerization as VE does not homopolymerize. Copolymers were purified by precipitation. As an example,



SCHEME 4 Radical copolymerizations of VEC₂PMe with a series of electron-accepting monomers.



¹³C NMR (Fig. 8) of poly(VEC₂PMe-*alt*-BM) is given to prove the good purity of the obtained copolymers. The purified copolymers were analyzed by means of GPC and M_w values were obtained from PMMA standards (Table 2). The GPC traces, given in Figure 9, do not show any shoulder in the low molecular weight region, which is in agreement with the result obtained from the copolymerization of VEC₂PMe with MA. Interestingly, we can also remark that both M_w and polydispersity index (PDI) values are dependent on the type of electron-accepting monomer. Indeed electron-poor monomers, such as MA or maleimides, lead to copolymers of higher M_w and higher PDIs values. In contrary, monomers

Poly(VEC_PMe-alt-Al) Poly(VEC_PMe-alt-DBMA) Poly(VEC_PMe-alt-DBI) Poly(VEC_PMe-alt-BM) Poly(VEC_PMe-alt-BM) Poly(VEC_PMe-alt-MM) Poly(VEC_PMe-alt-AM) Poly(VEC_PMe-alt-AM) Molecular weight distribution (g.mol¹)

Decrease of electron-accepting effect

FIGURE 9 Molecular weight distribution of copolymers obtained from radical copolymerization of VEC₂PMe.

showing a lower electron-accepting effect, such as dibutyl itaconate or IA, lead to copolymers of low M_w and PDIs values. Furthermore, these monomers show a strong polarizing effect unlike vinyl ether monomers. These opposite effects are detrimental for efficient radical copolymerizations, as expressed from the lower monomer conversions (Table 2).

Kinetic investigation of the radical copolymerizations of VEC₂PMe with the electron-accepting monomers was carried out by means of FTIR and VE conversion was plotted versus time (Fig. 10). This figure evidences the positive effect of strong electron-accepting monomers on the polymerization rate. Indeed, the higher the electron-accepting effect, the faster the VE consumption, as expected. We can also observe an inhibition period during the copolymerizations of



FIGURE 10 VEC₂PMe conversion versus time for the radical copolymerizations with a series of electron-accepting monomers.

VEC₂PMe with IA and dibutyl maleate (DBMA). Unexpectedly, after this inhibition period, the VE consumption is very fast with IA. Regarding the polarizing and electron-accepting effects of IA, this result remains unexplained.

EXPERIMENTAL

Materials

All the solvents and reagents (Sigma-Aldrich, Fluka or Unimatec) were used with a purity of 98–99%. Diethyl vinyl ether, palladium(II)acetate, 1-10 phenanthroline, paraformaldehyde, dimethyl phosphonate, diethyl phosphonate, diisopropyl phosphonate, BVE, FAVE-8, tert-amylperoxipivalate, potassium hydroxide, potassium carbonate, vinyl acetate, itaconate anhydride, dibutyl itaconate, dibutyl maleate, methyl maleimide, and butyl maleimide were used without purification. MA and AIBN were purified by recrystallization from dichloromethane and methanol, respectively, and dried under vacuum.

¹H, ¹³C, ³¹P, and ¹⁹F NMR spectra were recorded in CDCl₃, acetone d_6 solutions, dimethyl sulfoxide- d_6 , or MeOH- d_4 (between 5 and 100 mg of each compound dissolved in 0.6 mL of solvent) on a Bruker Avance 400 MHz spectrometer. ¹H, ¹³C, ³¹P, and ¹⁹F chemical shifts are expressed in ppm/tetramethylsilane, ppm/H₃PO₄, and CFCl₃ external standard, respectively. All non-first-order spectra were calculated with g-NMR. Size exclusion chromatography 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 flow rate of DMF, calibrated using polymethylmethacrylate standards, and two PL-gel mix C columns were used at 35 °C with 1 mL/min flow rate of THF, calibrated using polystyrene. FTIR spectra were recorded on Nicolet 6700 FTIR spectrometer coupled with thermo spectra tech.

Monomers and Polymers Syntheses Synthesis of Dialkyl-α-Hydroxymethylphosphonate

Dialkyl- α -hydroxyalkylphosphonate compounds were synthesized from Pudovik reaction by reacting equimolar amounts of dialkyl hydrogenophosphonate and paraformaldehyde in the presence of anhydrous potassium carbonate and methanol at room temperature.

For example: 10 g (0.09 mol) of dimethyl hydrogenophosphonate, 2.73 g (0.09 mol) of paraformaldehyde, 30 mL of methanol, and 0.62 g of anhydrous K_2CO_3 were introduced in a two-necked flask. The solution was vigorously stirred under methanol during 1 h. Dimethyl- α -hydroxymethyl-phosphonate is obtained under high vacuum with 98% yield.

¹H NMR (400 MHz, CDCl₃, δ): 3.6 (d, 6H,PO(OCH₃); 3.9 (d, 2H, CH₂P); 5.3 (sl, 1H, OH). ³¹P NMR (CDCl₃), ³¹P NMR (400 MHz, CDCl₃), δ): 28.2, ¹³C NMR (400 MHz, CDCl₃): 56 (d, Cb), 53 (d, Cc).

Diethyl-α-Hydroxymethylphosphonate

¹H NMR (400 MHz, CDCl₃, δ): 5.17 (sl, 1H, OH), 3.8 (d, 2H, CH₂—P), 4.1 (m, 4H, CH₂—O), 1.24 (t, 6H, CH₃). ¹³C NMR (400 MHz, CDCl₃, δ): 56.55 (sd, 1C, CH₂-P), 62.55 (d, 2C,

<u>C</u>H₂-O), 16.33 (d, 2C, <u>C</u>H₃). ³¹P NMR (162 MHz, CDCl₃, δ): 24,72.

Synthesis of Dimethyl- α -Hydroxyethylphosphonate

A mixture of 3.92 g (0.02 mol) 2-(dimethoxyphosphoryl) ethyl acetate, (previously synthesized from telomerization of vinylacetate with dimethyl phosphonate and tert-amylperoxipivalate at 70 °C), KOH 3% (0.0672, 12.10^{-4} mol), and 20 mL of methanol was stirred at 60 °C for 24 h. Dimethyl- α -hydroxyethylphosphonate is obtained under high vacuum with 90% yield.

¹H NMR (400 MHz, CDCl₃, δ), ppm: 4.36 (s, 1H, O<u>H</u>); 3.64 (td, H₂,O-C<u>H</u>₂); 3.48 (d, H₆, PO(OC<u>H</u>₃)₂); 1.84 (td, H₂, C<u>H</u>₂P). ³¹P NMR (162 MHz, CDCl₃, δ): 32.62.

Synthesis of Dialkyl Vinyl Ether Phosphonate

The dialkyl vinyl ether phosphonate was obtained from transetherification of hydroxyl-alkylphosphonate.

For example, a solution of 1,10 phenanthrolin (0.210 g, 0.03 mol) in 15 mL of dichloromethane was added dropwise to a flask already containing palladium acetate catalyst (11.0 g, 5 mmol) in dichloromethane (15 mL). The reaction mixture was left under magnetic stirring for 20 min to form a complex. Then a mixture 6.1 g (0.04 mol) of dimethyl 2-hydroxyethylphosphonate, 28.05 g (0.4 mol) of ethyl vinyl ether, and 15mL of CH_2Cl_2 was added to the complex. The reaction mixture was left under stirring at room temperature during 48 h. Then the reaction mixture was filtered on celite (dicalite 4158) to eliminate the complex and followed by vacuum distillation to remove the excess of ethyl vinyl ether and solvent. The crude product was purified by silica gel column chromatography by using a mixture of 20 acetate/80 CH_2Cl_2 to obtain a monomer as a colorless oil.

¹H NMR (400 MHz, CDCl₃, δ): 6.4 (q, 1H, CH), 4.06, and 4.22 (dd, 2H, H₂C=), 3.88 (td, 2H, O-CH₂), 1.84 (sd, 6H, CH₃), 2.2 (td, 2H, CH₂-). ¹³C NMR (400 MHz, CDCl₃, δ): 150.8 (s, CH), 87.18 (s, H₂C=), 61.55(s, O-CH₂), 52.23 (s, CH₃), 25.31 (d, CH₂-P). ³¹P NMR (400 MHz, CDCl₃, δ): 30.57.

Dimethyl Vinyloxymethylphosphonate

¹H NMR (400 MHz, CDCl₃, δ): 6.4 (q, 1H, C<u>H</u>), 4.06 et 4.22 (dd, 2H, =C<u>H</u>₂), 3.88 (td, 2H, C<u>H</u>₂—P), 1.84 (sd, 6H, C<u>H</u>₃). ¹³C NMR (400 MHz, CDCl₃, δ): 151 (d, 1C, <u>C</u>H), 87.8 (s,1C, =<u>C</u>H₂), 59 and 61 (d, 1C, <u>C</u>H₂-Pc), 52.8 (d, 2C, <u>C</u>H₃). ³¹P NMR (162 MHz, CDCl₃, δ): 22.

Diethyl Vinyloxymethylphosphonate

¹H NMR (400 MHz, CDCl₃, δ): 6.4 (q, 1H, C<u>H</u>), 4.06 et 4.22 (dd, 2H, =C<u>H</u>₂), 3.88 (td, 2H, P–C<u>H</u>₂), 1.84 (sd, 6H, C<u>H</u>₃). ¹³C NMR (400 MHz, CDCl₃, δ): 150 (d, 1C, CH), 88 (s, 1C, =CH₂), 60, 62 (d, 1C, P–CH₂), 62 (s, 2C, OCH₂), 16 (d, 2C, CH₃). ³¹P NMR (162 MHz, CDCl₃, δ): 19.69.

Radical copolymerizations of dialkyl vinyl ether phosphonate monomers with electron-accepting monomers.

The copolymers were synthesized by reacting equimolar amounts of vinyl ethers and MA, and of VEC_2PMe with a series of electron-accepting monomers (IA, DBM, DBI, MM, and BM).

As an example, in a two-necked round-bottomed flask equipped with a condenser, a solution of 2 g $(1.11 \times 10^{-2} \text{ mol})$ of VEC₂PMe and 1.09 g $(1.11 \times 10^{-2} \text{ mol})$ of MA, 3% (0.110 g) of AIBN, and 7.15 mL of chloroform (S = 4) was degassed for 20 min with argon and then stirred at 70 °C. After 20 h, poly (VEC₂PMe-*alt*-MA) was precipitated from diethyl ether.

¹H NMR (400 MHz, d-CDCl₃, δ): 3.5–3.7 (6H, CH₃), 1.9–2.2 (2H,CH₂—P), 4.0–4.4 (2H, CH₂—O), 2.2–3.1 (2H,CH, MA ring and CH—O), 1.2–1.6 (2H, CH₂ from ethyl group). ¹³C NMR (400 MHz, *d*₆-DMSO, δ): 170–175 (2C, C=O), 55–65 (3C, CH₂ from ethyl group and CH of MA ring), 72–80 (2C, CH₂—O and CH from VEC₂PMe), 52 (2C, CH₃), 25(1C, P—CH₂). ³¹P NMR (162 MHz, *d*₆-DMSO, δ): 24.72.

Poly(VEC₁PMe-alt-MA)

¹H NMR (400 MHz, d_4 -CH₃OH, δ): 3.5-4.3(6H, CH₃, O-CH, CH₂-P), 1.9-2.2 (2H, CH₂-P), 4.0-4.4 (2H, CH₂-O), 2.5-2.9 (2H, CH, MA ring). 1.1-1.3 (2H, CH₂ from ethyl group). ³¹P NMR (162 MHz, d_4 -CH₃OH, δ): 26.

Poly(VEC₁PEt-alt-MA)

¹H NMR (400 MHz, d_6 -DMSO, δ): 1–1.5(8H, CH₃, CH₂ from ethyl group), 3.7 (2H,CH₂—P), 3.9–4.3 (3H, O—CH₂, O—CH), 2.5–2.9 (2H,CH, MA ring). ¹³C NMR (400 MHz, d_6 -DMSO, δ): 170–175 (2C, C=O) 52–65 (6C, CH₂ from ethyl group and CH of MA ring, O—CH₂—P and O—CH from VEC₂PMe), 15 (2C, CH₃). ³¹P NMR (162 MHz, d_6 -DMSO, δ): 18.5 and 15.

Poly(BVE-alt-MA)

¹H NMR (400 MHz, d_6 -acetone, δ): 0.8 (3H, CH₃ from BVE), 1.2–1.7 (6H, -CH₂ and CH₂ from ethyl group), 1.8–2.6 (2H, -CH, 2.8–4.2 (6H, O-CH₂, O-CH, O-CH₃ from acetate group), 7–9.5 (1H, OH from acid group).

Poly(FAVE-8-alt-MA)

>¹⁹F NMR (377 MHz, d_6 -acetone, δ): -81 (3F, CF₃), -113.6 (2F, CF₂-CF₃), -126.3 (2F, CH₂-CF₂), (-121.8)-(-123.7) (10 F, -CF₂).

Poly(VEC₂PMe-alt-IA)

¹H NMR (400 MHz, d_6 -DMSO, δ): 3.5–3.7 (6H, CH₃), 4.0–4.3 (2H, CH₂-O), 1.2–3.1 (9H, CH₂ from IA, O—CH, CH₂—P, and CH₂ from VEC₂PMe). ¹³C NMR (400 MHz, d_6 -DMSO, δ): 170–175 (3C, C, and C=O) 20–30 (3C, P-CH₂, and CH₂ of IA), 55–70 (3C, O—CH₂, O—CH, and —CH₂ from VEC₂PMe), 52 (2C, CH₃), ³¹P NMR (162 MHz, d_6 -DMSO, δ): 27.28.

Poly(VEC₂PMe-alt-BM)

¹H NMR (400 MHz, d_6 -acetone, δ): 0.7–1.7 (7H, CH₃ and CH₂ from BM), 1.7–2.5 (4H, P-CH₂ and CH₂ from ethyl group), 4.0–4.7 (2H, O–CH, and N–CH₂), 3.0–3.6 (4H, O–CH₂, and 2CH from succinimide ring). ¹³C NMR (400 MHz, d_6 -acetone, δ): 175–180 (2C, C=O) 14–35 (4C, P–CH₂, 2CH₂, and CH₃ from BM), 55–70 (3C, O–CH₂, O–CH, and –CH₂ from VEC₂PMe), 50–63 (4C, O–CH₃, N–CH₂, and CH succinimide ring), 64–80 (2C, O–CH and O–CH₂). ³¹P NMR (162 MHz, d_6 -acetone, δ): 31.0.

Poly(VEC₂PMe-alt-MM)

¹H NMR (400 MHz, d_6 -DMSO, δ): 1.7–2.5 (4H, P–CH₂ and CH₂ from ethyl group), 4.0–4.4 (1H, O–CH), 3.2–3.9 (11H,



0–CH₂, 2(0–CH₃), N–CH₃), 2.1–3.1 (2H, CH from succinimide ring). ¹³C NMR (400 MHz, d_6 -DMSO, δ): 175–180 (2C, C=0) 21–29 (2C, P–CH₂, N–CH₃), 52 (2C, 0–CH₃), 53–66 (4C, –CH₂ ethyl group and CH succinimide ring), 70–78 (2C, 0–CH and 0–CH₂). ³¹P NMR (162 MHz, d_6 -DMSO, δ): 31.2.

Poly(VEC₂PMe-alt-DBM)

¹H NMR (400 MHz, d-CHCl₃, δ): 0.7–1.0 (6H, CH₃ from DBM), 1.1–2.3 (12H, P–CH₂, CH₂ from ethyl group, CH₂ from DBM), 2.5–3.1(2H, CH), 3.1–4.4 (15H, 0–CH₂, 0–CH, and CH, 0–CH₃). ¹³C NMR (400 MHz, d-CDCl₃, δ): 168–175 (2C, C=0) 14–28 (4C, CH₂ and CH₃, P–CH₂), 52 (2C, 0–CH₃), 54–67 (3C, 0–CH₂, 0–CH), 32–45 (4C, 0–CH and 0–CH₂). ³¹P NMR (162 MHz, d-CDCl₃, δ): 31.0.

Poly(VEC₂PMe-alt-DBI)

¹H NMR (400 MHz, d-CHCl₃, δ): 0.7–1.0 (6H, CH₃ from DBI), 1.7–2.4 (6H, P–CH₂, CH₂ from ethyl group), 2.5–3.2 (3H, CH CH₂–C=O), 3.5–4.2 (12H, O–CH₂, O–CH₃). ¹³C NMR (400 MHz, d-CDCl₃, δ): 165–175 (3C, CH₂–C, C=O) 12–21 (4C, CH₂ and CH₃), 22–48 (6C, P–CH₂, CH₂–C=O, CH₂), 53 (2C, O–CH₃), 54–67 (4C, O–CH₂, O–CH). ³¹P NMR (162 MHz, d-CDCl₃, δ): 31.0.

CONCLUSIONS

A series of three new vinyl ether monomers containing phosphonate moieties was developed from transetherification reaction, in the presence of catalytic system, that is, palladium acetate/phenanthrolin. Their radical copolymerizations with MA afforded alternated copolymers, bearing phosphonate moieties. Unexpected intramolecular chain transfer reactions, occurring from phosphonate moieties, led to low molecular weight copolymers, depending on the spacer length between the vinyl oxy group and the phosphonate moieties. Finally, we developed a range of phosphonatecontaining alternated copolymers by free-radical copolymerization of VEC₂PMe with a series of electron-accepting monomers, such as DBMA, DBI, IA, BM, and MM. From kinetic investigation, we demonstrated the positive effect of the strong electron-withdrawing effect of maleimide monomers on both the molecular weight and the vinyl ether conversion. Interestingly, fast rate of free-radical copolymerization was observed when VEC₂PMe was polymerized with IA, a bio-based monomer. In conclusion, we were able to provide a wide range of alternated copolymers bearing phosphonate moieties, these compounds may be investigated for different applications such as anticorrosive coatings or even as flame retardant.

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