

# Synthesis of Polyphosphorinanes. 1. Homopolymerization and Telomerization of Allyl Ether Phosphite

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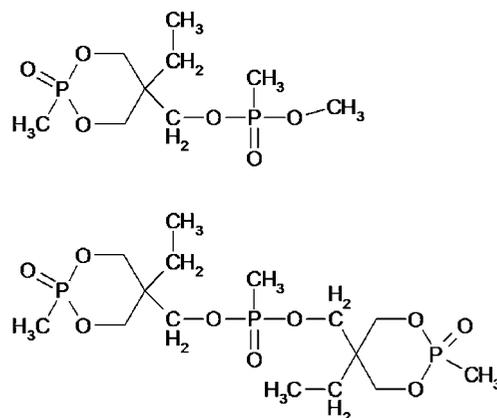
**ABSTRACT:** Cyclic allyl phosphonated monomers were synthesized by transesterification reaction between a glycol bearing a double bond and a hydrogenophosphonate and were fully characterized by NMR and IR spectroscopy. Radical homopolymerization of these monomers was carried out at 70 °C in the presence of  $\alpha,\alpha'$ -azoisobutyronitrile (AIBN) as initiator and acetonitrile as solvent. The thus-obtained polymers showed two SEC distributions, one composed of oligomers (with  $M_n \approx 800$  g/mol) and one composed of high-molecular-weight polymers (with  $M_n \approx 100\,000$  g/mol). The latter were hyperbranched polymers suffering from solubility limitations for future industrial applications. Therefore, telomerization of one phosphonated monomer using dimethyl hydrogenophosphonate (HP(O)(OMe)<sub>2</sub>) as a chain transfer agent (CTA) limited the hyperbranching through two concomitant mechanisms of polymerization, which are discussed. For  $R_0 = 2$  ( $R_0$  represents initial [CTA]<sub>0</sub>/[monomer]<sub>0</sub> molar ratio), the results showed a limited chain length, whereas monoadduct formation occurred for a  $R_0$  value of 10.

## I. Introduction

Polyphosphorinane products have found applications as fireproofing additives for textiles, particularly those of polyethylene-terephthalate-type. The commercially available product Antiblaze 19<sup>1</sup> marketed by the Mobil Company (Figure 1) is a mixture composed of two cyclic phosphite structures; its effectiveness as a flame retardant is ascribed to the phosphoric esters that entail transesterification reactions with PET.

Five- and six-membered cyclic phosphorous acid esters found much interest in the 1960s. They have been extensively investigated as potential pesticides,<sup>2,3</sup> plasticizers,<sup>4</sup> and fireproofing products,<sup>5</sup> as model substances for infrared structural and mechanical studies, and also as useful intermediates in organic and polymer chemistries.<sup>6</sup> There are several synthetic routes for preparing these compounds. The easiest method is the direct esterification (Figure 2a) of phosphites with 1,2- and 1,3-glycols.<sup>7,8</sup> Cyclic hydrogen phosphites with five-membered (dioxaphospholane) and six-membered (dioxaphosphorinane) ring structures are obtained by heating diethyl hydrogen phosphite with the appropriate alcohol. Besides alkylene phosphonates, synthesis methods developed so far are based on either the hydrolysis of the corresponding cyclic chlorophosphites<sup>2</sup> (Figure 2b) or the reaction of the corresponding cyclic ethers and phosphonic acid in the presence of acetic anhydride<sup>6</sup> (Figure 2c). From these reactions, various compounds can be prepared; some structures described in the open literature are listed in Table 1.

The dioxaphosphorinanes (six-membered cyclic product) bearing double bonds are particularly interesting because they easily polymerize. Phosphonated cyclic acrylates react promptly but cannot be synthesized in one step, for instance, by using a commercial diol bearing an allyl function at one end (2-(allyloxymethyl)-2-ethyl-1,3-propanediol), which is in contrast with allyl ones. Cyclic allyl phosphonated monomers were first synthesized and radical homopolymerized by Friedman<sup>9</sup> to improve the flame-retardant and flame-resistant properties of polymer material. They were prepared by Arbuzov rearrangement of the trimethylolpropane monoallyl ether phenyl phos-



**Figure 1.** Chemical structures of molecules comprising the industrial fireproofing agent Antiblaze 19 (Mobil).

phate<sup>9</sup> (Figure 2d). The polymer was obtained by heating pure bis(trimethylolpropane monoallyl ether) hydrogen phosphite in the presence of di-*tert*-butyl peroxide: it was a colorless, nonflammable resin. It is noteworthy that this type of allyl ether phosphate or phosphite monomer, containing several allyl linkages, was also photopolymerized by ultraviolet light initiation.<sup>9</sup> Starting from the diallylic monomers, hard, tough, colorless, and nonflammable materials were obtained as 3D networks. In addition, the dioxaphosphorinanes can be polymerized by ring-opening polymerization<sup>10–12</sup> (Figure 2e) in bulk or in solution in the presence of an anionic initiator (like potassium *tert*-butoxide, sodium ethoxide, triisobutyl aluminum, *n*-butyl lithium, and sodium acetate) between 0 and 100 °C. Polymers with molecular weights ranging from 10 000 to 100 000 g·mol<sup>-1</sup> generated a solid, highly elastic, and transparent material. Alternatively, poly(H-phosphonates) could also be formed by polycondensation between diols and phosphates.<sup>13</sup>

It is noteworthy that only a few articles deal with the polymerization of allyl ether monomers, probably because of the strong stability of allyl ether radicals, hence leading to longer radical polymerization time compared with that of the more reactive vinyl ethers. Thiol-allyl ether systems<sup>14,15</sup> have also been used for the formation of highly cross-linked networks

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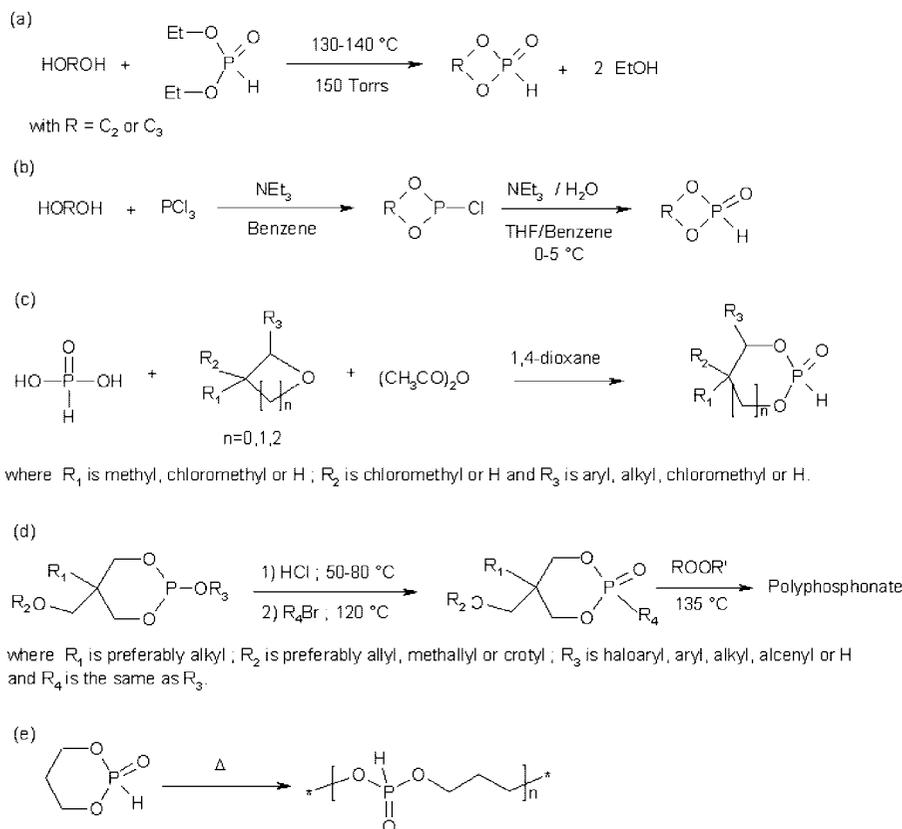
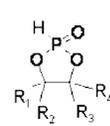
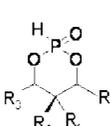


Figure 2. Main syntheses of dioxaphosphorinanes and their polymer derivatives.

Table 1. Dioxaphosphorinanes and Dioxaphosphorinanes Reported in the Open Literature

Molecules	Substituents	References
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =CH <sub>3</sub>	2, 6, 7
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =CH <sub>2</sub> CH <sub>3</sub>	6
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =CH <sub>2</sub> Cl	6, 7
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =C <sub>6</sub> H <sub>5</sub>	6
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =CH <sub>3</sub>	6
	R <sub>1</sub> , R <sub>3</sub> =H and R <sub>2</sub> , R <sub>4</sub> =CH <sub>3</sub>	2, 6, 7
	R <sub>1</sub> , R <sub>3</sub> =H and R <sub>2</sub> , R <sub>4</sub> =CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	6
	R <sub>1</sub> , R <sub>3</sub> =H and R <sub>2</sub> , R <sub>4</sub> =CH <sub>2</sub> OCH <sub>3</sub>	6
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> and R <sub>4</sub> =CH <sub>3</sub>	2, 6
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> =H and R <sub>4</sub> =CH <sub>2</sub> CH <sub>3</sub>	2
R <sub>1</sub> , R <sub>3</sub> =CH <sub>3</sub> and R <sub>2</sub> , R <sub>4</sub> =CH <sub>2</sub> CH <sub>3</sub>	2	
	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> , R <sub>4</sub> =H	2, 6, 7, 8
	R <sub>1</sub> , R <sub>2</sub> , R <sub>4</sub> =H and R <sub>3</sub> =CH <sub>3</sub>	2, 7
	R <sub>1</sub> , R <sub>2</sub> =CH <sub>3</sub> and R <sub>3</sub> , R <sub>4</sub> =H	2, 7, 8
	R <sub>1</sub> , R <sub>2</sub> =CH <sub>2</sub> Cl and R <sub>3</sub> , R <sub>4</sub> =H	6
	R <sub>1</sub> , R <sub>3</sub> =H, R <sub>2</sub> =C <sub>2</sub> H <sub>5</sub> and R <sub>4</sub> =C <sub>6</sub> H <sub>7</sub>	7
R <sub>1</sub> =CH <sub>2</sub> CH <sub>3</sub> , R <sub>2</sub> =CH <sub>2</sub> CHCH <sub>2</sub> OCH <sub>2</sub> and R <sub>3</sub> , R <sub>4</sub> =H	9	

with good physical and mechanical properties. The aim of this work thus concerns the synthesis of a macromolecular equivalent product starting from a similar cyclic structure that entails a fair content of phosphorus in the product and is compatible with PET. The presence of an allylic double bond should allow us, through polymerization, to increase the size of the fire-resistant agent. In this article, we describe the synthesis of the cyclic allyl phosphonated monomer and its telomerization and polymerization by radical means.

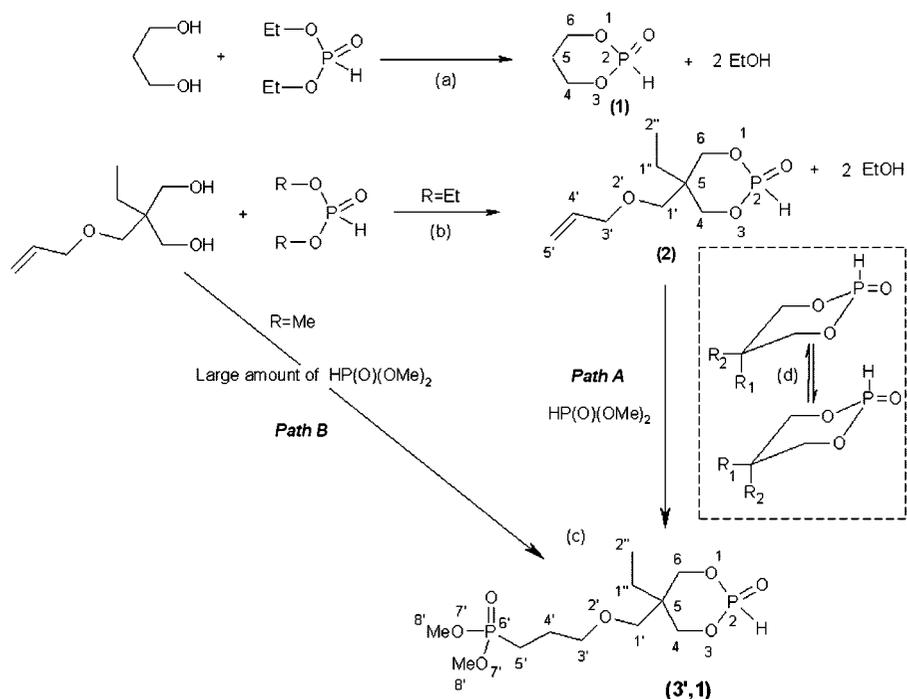
## II. Experimental Part

All of the solvents and reagents (Sigma-Aldrich or Fluka) were of 98 to 99% purity. 1,3-Propanediol, diethyl hydrogenophosphate, dimethyl hydrogenophosphate, 2-(allyloxymethyl)-2-ethyl-1,3-dioxanediol, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (VAR-OX), and *tert*-amyl peroxyphosphate (TAPPI) were used without purification.  $\alpha,\alpha'$ -Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol and dried under vacuum.

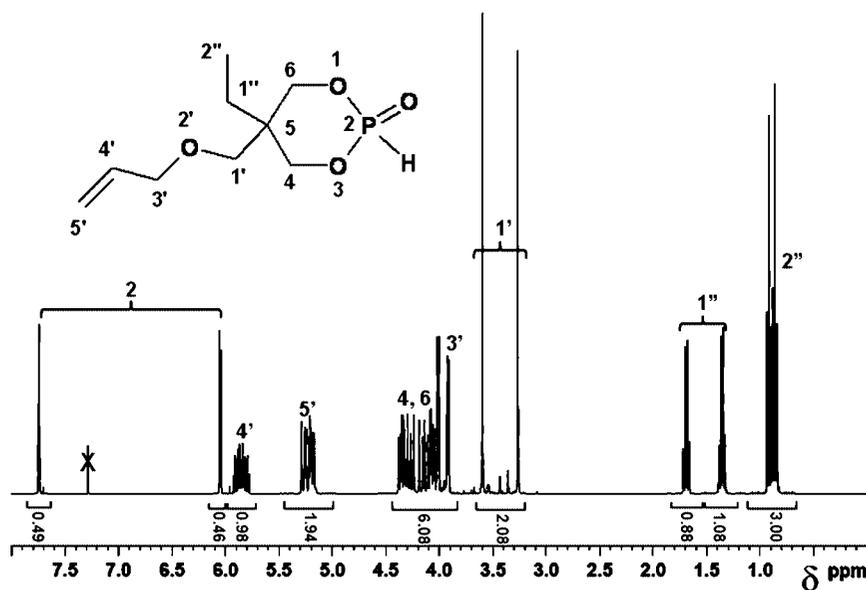
<sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded in CDCl<sub>3</sub> solutions on a Bruker AC 200 MHz or a Bruker Avance 400 MHz spectrometer. <sup>1</sup>H and <sup>31</sup>P chemical shifts are expressed in ppm/TMS and ppm/H<sub>3</sub>PO<sub>4</sub> external standard, respectively. HRMAS <sup>1</sup>H NMR spectrum was recorded on a Bruker Avance 500 MHz using 4 mm MAS probe head with deuterium lock. The polymer was swollen in DMSO-*d*<sub>6</sub> and put in a 100  $\mu$ L rotor. It was spun at 7000 Hz at the magic angle (MAS). All measurements were performed at ambient temperature.

Size exclusion chromatography (SEC) was performed on a Spectra-Physics apparatus equipped with an RI Shodex refractive index detector. Two PL-gel mix C columns were used at 70  $^\circ$ C with a 0.8 mL  $\cdot$ min<sup>-1</sup> flow rate of DMF, calibrated using polymethylmethacrylate standards. IR spectra were recorded on a Nicolet 510P FT-IR spectrometer with a band accuracy of 2 cm<sup>-1</sup> using the transmission mode. Liquid samples were analyzed using KBr disks.

**A. Synthesis of 2-Oxo-1,3,2-dioxaphosphorinane (1) (Figure 3a).** A mixture of 1,3-propanediol (15.0 g, 0.197 mol) and diethyl hydrogenophosphate (22.6 g, 0.164 mol) was poured in a round-bottomed flask equipped with a distillation apparatus. The mixture was heated to 130–140  $^\circ$ C under reduced pressure (160–200 mbars). Ethanol was distilled off all along the reaction, at the end of which the dioxaphosphorinane was distilled at 105–108  $^\circ$ C under vacuum ( $5 \times 10^{-2}$  mbars). A very viscous colorless liquid was obtained in 85% yield. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.80–2.25 (m, H<sub>5</sub>), 4.25 (m, H<sub>4</sub>, H<sub>6</sub>), 6.73 (d, H<sub>2</sub>, *J*<sub>P-H</sub> = 675.2 Hz). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.4 (P-H).



**Figure 3.** (a,b) Synthesis of dioxaphosphorinane (1) and (2), respectively, by transesterification of diethyl hydrogenophosphonate with the corresponding diols; (c) synthetic ways of generating the monoadduct (3',1); (d) two diastereoisomer forms of (2) with R<sub>1</sub>=CH<sub>2</sub>CH<sub>3</sub> and R<sub>2</sub>=CH<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>.

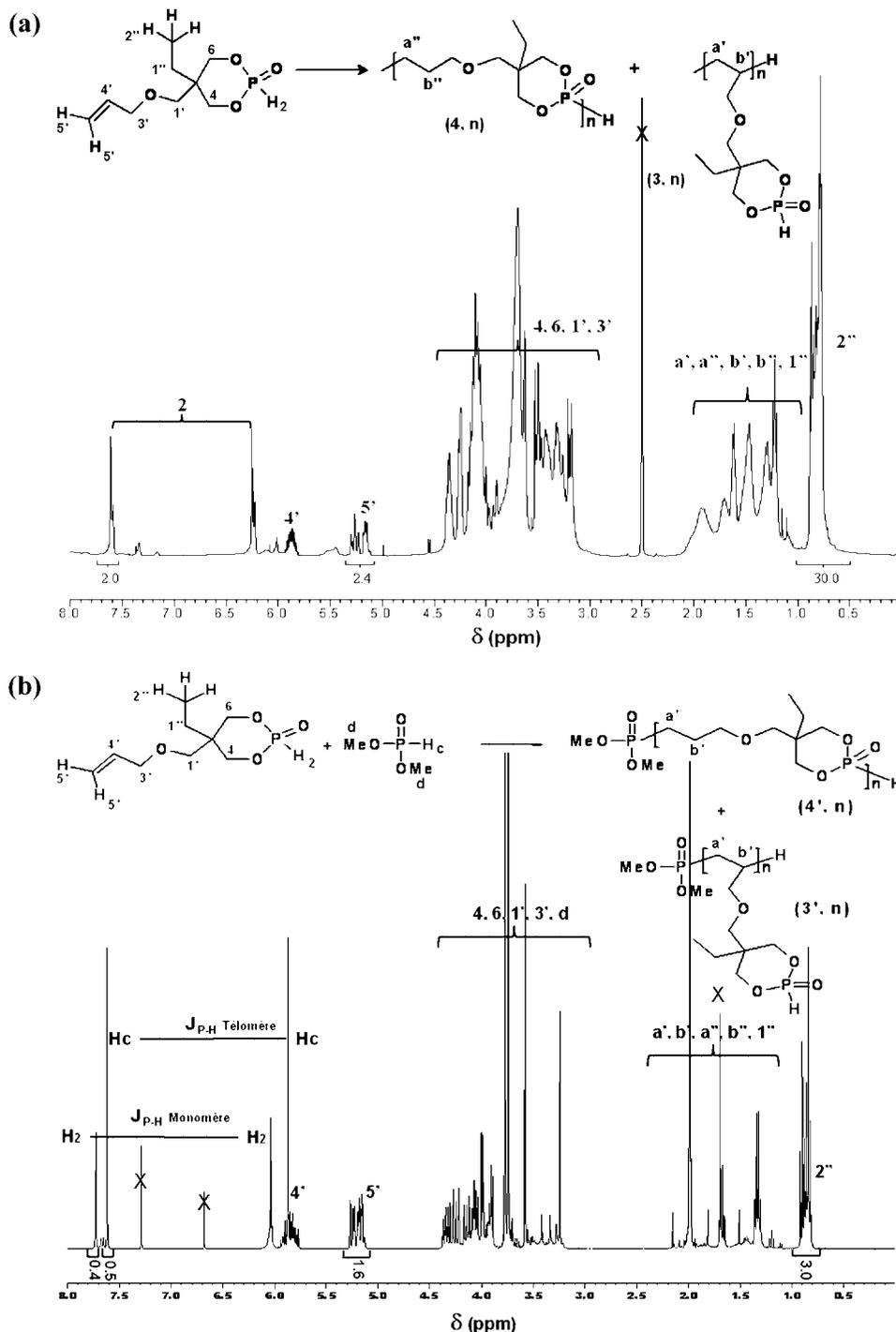


**Figure 4.** <sup>1</sup>H NMR spectrum of monomer (2) in CDCl<sub>3</sub>.

**B. Synthesis of 5-Ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (2) (Figures 3b and 4).** The procedure for the preparation of (2) is similar to that of model molecule (1), starting from a mixture of diethyl hydrogenophosphonate and 2-(allyloxymethyl)-2-ethyl-1,3-propanediol (20% molar excess). After distillation of ethanol, the transesterification product was distilled at 137–140 °C under  $7 \times 10^{-2}$  mbars, and a colorless liquid was obtained in 86% yield as a mixture of two diastereoisomers, **A** (55%) and **B** (45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.90 (t, H<sub>2'</sub>(**A**)), 0.84 (t, H<sub>2'</sub>(**B**)), 1.34 (q, H<sub>1'</sub>(**A**)), 1.67 (q, H<sub>1'</sub>(**B**)), 3.24 (s, H<sub>1'</sub>(**B**)), 3.57 (s, H<sub>1'</sub>(**A**)), 3.90 (d, H<sub>3'</sub>(**B**)), 4.00 (d, H<sub>3'</sub>(**A**)), 4.05–4.40 (m, H<sub>4'</sub>(**A** + **B**)–H<sub>6'</sub>(**A** + **B**)), 5.25 (m, H<sub>5'</sub>(**A** + **B**)), 5.85 (m, H<sub>4'</sub>(**A** + **B**)), 6.89 (2d, H<sub>2</sub>,  $J = 673.8$  and  $683.6$  Hz (**A**) and (**B**), respectively). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>, δ): 4.50 (**A**) and 4.04 (**B**) (P–H). IR  $\nu$  (cm<sup>-1</sup>): (C–Hsp<sup>2</sup>) = 3080, (C–Hsp<sup>3</sup>) =

2970–2885, (P–H) = 2400, (CH<sub>2</sub>=CH) = 1645, (CH<sub>2</sub>) = 1435, (P=O) = 1286, (C–O) = 1070, (P–O–C) = 1022 and 960.

**C. Example of Bulk Homopolymerization of 5-Ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (Entry 1, Table 2) (Figure 5a).** In a two-necked round-bottomed flask equipped with a condenser,  $1.5 \times 10^{-2}$  mol of allylic monomer (2) was stirred at 120 °C. The solution was degassed for 15 min with argon, and 3% molar (against monomer content) of initiator, VAROX, was added in three times. The mixture was stirred at 120 °C for 48 h, and a viscous, colorless gel was obtained. This sample swelled only in DMF or DMSO; HRMAS NMR analysis was performed in the latter. <sup>1</sup>H HRMAS NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ): 0.86 (t, H<sub>2'</sub>(**A**)), 0.80 (t, H<sub>2'</sub>(**B**)),  $1 \times 10^{-2}$ –2.00 (m, H<sub>4'</sub>(**A** + **B**)–H<sub>6'</sub>(**A** + **B**)–H<sub>4''</sub>(**A** + **B**)–H<sub>6''</sub>(**A** + **B**)–H<sub>1''</sub>(**A** + **B**)), 3.19 (m, H<sub>1'</sub>(**A** + **B**)–H<sub>3'</sub>(**A** + **B**)–H<sub>4'</sub>(**A** + **B**)–H<sub>6'</sub>(**A** + **B**)), 5.25 (m, H<sub>5'</sub>(**A** + **B**)), 5.88 (m, H<sub>4'</sub>(**A**



**Figure 5.** (a) HRMAS  $^1\text{H}$  NMR spectrum of the translucent elastomer prepared by bulk homopolymerization (entry 1, Table 1) in  $\text{DMSO-}d_6$  and (b)  $^1\text{H}$  NMR spectrum of total product mixture obtained from the telomerization of monomer (2) with dimethyl hydrogenophosphonate (entry 3, Table 3) in  $\text{CDCl}_3$ .

+ B)), 6.93 (2d,  $\text{H}_2$ ,  $J = 671.9$  and  $684.6$  Hz (A) and (B), respectively).

**D. Example of Solution Homopolymerization of 5-Ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (Entries 2 to 6, Table 2).** In a two-necked round-bottomed flask equipped with a condenser, 1.0 g of allylic monomer (2) was heated with acetonitrile at  $70^\circ\text{C}$ . The solution was degassed for 15 min with argon, and then 2,2'-azobis(isobutyronitrile) (AIBN) was added. The mixture was stirred for 24 h, and a yellow solution was obtained.

**E. Synthesis of Monoadduct (3',1) ( $R_0 = 10$ ) (Figure 3c).** 1. *Synthesis with 5-Ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (2).* A mixture of  $9 \times 10^{-3}$  mol of allylic monomer (2) and  $9 \times 10^{-2}$  mol of dimethyl hydrogenophosphonate was placed in a

round-bottomed flask equipped with a condenser and a bubbler. The solution was degassed for 20 min with argon and then stirred at  $110^\circ\text{C}$ . Another solution composed of 3% molar *tert*-amyl peroxyphosphate (TAPPI) and  $4 \times 10^{-3}$  mol of dimethyl hydrogenophosphonate was added dropwise to the reaction mixture for 1 h. It was stirred and heated continuously for 2 h. The excess dimethyl hydrogenophosphonate was distilled under reduced pressure ( $10^{-1}$  mbars) at  $40^\circ\text{C}$ . After a light water washing, the colorless liquid was dried at  $70^\circ\text{C}$  under  $10^{-2}$  mbars for 4 h, giving an A (55%) and B (45%) diastereoisomer mixture.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.78 (t,  $\text{H}_2$ '(A)), 0.82 (t,  $\text{H}_2$ '(B)), 1.26 (q,  $\text{H}_1$ '(A)), 1.60 (q,  $\text{H}_1$ '(B)), 1.76 (m,  $\text{H}_4$ '(A + B)– $\text{H}_5$ '(A + B)), 3.20–4.30 (m,  $\text{H}_4$ '(A + B)– $\text{H}_6$ '(A + B)– $\text{H}_1$ '(A + B)– $\text{H}_3$ '(A + B)), 3.67 (d,  $\text{H}_8$ '(A +

**Table 2. Radical Polymerization of Monomer (2): Ratios of Initiator and Solvent, Monomer Conversions, and Degrees of Polymerization<sup>a</sup>**

entry	C <sub>0</sub> (initiator) <sup>b</sup>	T (°C) <sup>c</sup>	S <sub>0</sub> <sup>d</sup>	α <sub>M</sub> <sup>e</sup>	α <sub>P-H</sub> <sup>f</sup>	DP <sub>n1</sub> (% area) <sup>g</sup>	DP <sub>n2</sub> (% area) <sup>g</sup>
1	0.03 (VAROX)	120	0	0.87 <sup>h</sup>	0.55 <sup>h</sup>		
2	0.010 (AIBN)	70	20.2	0	0		
3	0.012 (AIBN)	70	4.3	0.26	0.08		
4	0.050 (AIBN)	70	4.1	0.43	0.20	3.8 (60)	482 (40)
5	0.103 (AIBN)	70	3.8	0.57	0.20		

<sup>a</sup> VAROX: 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane; AIBN: 2,2'-azobis(isobutyronitrile). <sup>b</sup> C<sub>0</sub> = [initiator]<sub>0</sub>/[monomer]<sub>0</sub> (nature of initiator). <sup>c</sup> Temperature of polymerization. <sup>d</sup> S<sub>0</sub> = [solvent]<sub>0</sub>/[monomer]<sub>0</sub>. <sup>e</sup> Monomer conversion given by <sup>1</sup>H NMR. <sup>f</sup> P-H bond monomer conversion given by <sup>1</sup>H NMR. <sup>g</sup> Average degree of polymerization given by SEC (area in %). <sup>h</sup> Conversion determined by <sup>1</sup>H HRMAS NMR.

**Table 3. Radical Telomerization of Monomer (2) with HP(O)(OMe)<sub>2</sub>: Ratios of Initiator, Telogen, and Solvent, Monomer and Telogen Conversions, and Degrees of Polymerization<sup>a</sup>**

entry	C <sub>0</sub> (initiator) <sup>b</sup>	T (°C) <sup>c</sup>	R <sub>0</sub> <sup>d</sup>	S <sub>0</sub> <sup>e</sup>	α <sub>M</sub> <sup>f</sup>	α <sub>P-H</sub> <sup>g</sup>	α <sub>T</sub> <sup>h</sup>	DP <sub>n1</sub> (% area) <sup>i</sup>	DP <sub>n2</sub> (% area) <sup>i</sup>
1	0.03 (TAPPI)	110	10	monoadduct					
2	0.050 (VAROX)	120	0.5	0	0.58	0.25	0.20	2.3 (65)	60 (35)
3	0.052 (AIBN)	70	1.2	4.3	0.66	0.31	0.23	3.3 (73)	504 (27)
4	0.048 (AIBN)	70	2	3.8	0.75	0.32	0.32	3	
5	0.056 (AIBN)	70	6	4.6	0.64	0.28	0.20	2.2	

<sup>a</sup> TAPPI: *tert*-amyl peroxyvalate; VAROX: 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane; AIBN: 2,2'-azobis(isobutyronitrile). <sup>b</sup> C<sub>0</sub> = [initiator]<sub>0</sub>/[monomer]<sub>0</sub> (nature of initiator). <sup>c</sup> Temperature of polymerization. <sup>d</sup> R<sub>0</sub> = [telogen]<sub>0</sub>/[monomer]<sub>0</sub>. <sup>e</sup> S<sub>0</sub> = [solvent]<sub>0</sub>/[monomer]<sub>0</sub>. <sup>f</sup> Monomer conversion given by <sup>1</sup>H NMR. <sup>g</sup> P-H bond monomer conversion given by <sup>1</sup>H NMR. <sup>h</sup> Telogen conversion given by <sup>1</sup>H NMR. <sup>i</sup> Average degree of polymerization given by SEC (area in %).

B), *J* = 10.8 Hz), 6.83 (2d, H<sub>2</sub>, *J* = 673.0 and 683.2 Hz (A) and (B), respectively). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>, δ): 34.7 [A] and 34.5 [B] (P(OMe)), 4.4 [A] and 4.0 [B] (P-H).

2. *Synthesis with the 2-(Allyloxymethyl)-2-ethyl-1,3-propanediol in One Stage.* A mixture of 1.7 × 10<sup>-2</sup> mol of 2-(allyloxymethyl)-2-ethyl-1,3-propanediol and 5.2 × 10<sup>-2</sup> mol of dimethyl hydrogenophosphonate was stirred in a two-necked flask equipped with a condenser and a bubbler. The solution was degassed for 20 min with argon and then heated to 110 °C. TAPPI (3.5% molar) in dimethyl hydrogenophosphonate solution was added dropwise to the reaction mixture for 1 h. Stirring and heating were continuously performed for 1 h. The dimethyl hydrogenophosphonate excess was slowly distilled under reduced pressure (10<sup>-1</sup> mbars) at 70 °C for 8 h.

**F. Bulk Telomerization of Phosphonated Allyl Ether (R = 0.5) (Entry 2, Table 3).** A mixture of 2 × 10<sup>-2</sup> mol of allylic monomer (2) and 1 × 10<sup>-2</sup> mol of dimethyl hydrogenophosphonate was placed in a round-bottomed flask equipped with a condenser and a bubbler. The solution was heated to 120 °C, stirred and degassed with argon for 15 min. Then, the VAROX initiator was added in several shots (three times, every 24 h).

After 96 h, the mixture became viscous, heating was stopped, and the mixture was characterized by <sup>1</sup>H NMR. Only a partial conversion of the monomer into polymer was observed, however the solution obtained was analyzed in SEC.

**G. Solution Telomerization of 5-Ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane (2).** The same conditions as those used for homopolymerization in solution were applied. The chain transfer agent (CTA) (dimethyl hydrogenophosphonate) was added with the monomer at the beginning of the reaction before degassing with argon. The telomerization was stopped after 24 h of heating.

### III. Results and Discussion

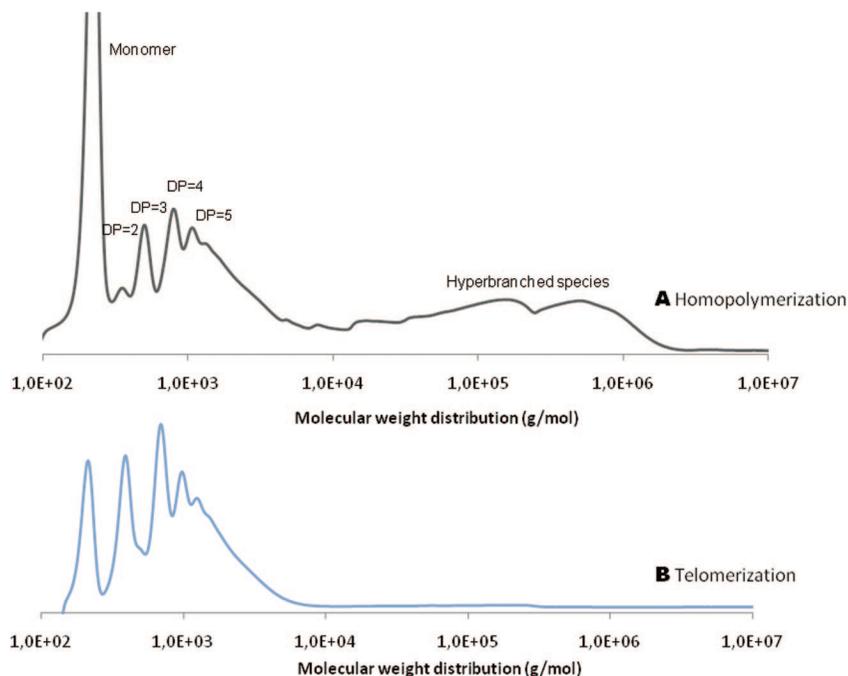
**A. Synthesis of Monomers.** The synthesis of phosphorinanes was first studied on a model molecule by condensing dialkyl hydrogenophosphonate with 1,3-propanediol. The 1,3-propanediol was chosen to be a model because it exhibits a structure and a reactivity in transesterification reaction close to those of 2-(allyloxymethyl)-2-ethyl-1,3-propanediol, whereas it is easier to characterize by <sup>1</sup>H NMR. During the transesterification reaction, the diol attacks the phosphorus atom in its trivalent form (minor product in the tautomeric equilibrium P<sup>III</sup>-P<sup>V</sup>).<sup>16</sup> On the contrary, a basic catalysis is then necessary, as for P-R (R ≠ H) phosphonates.<sup>17</sup> For this study, the 2-oxo-1,3,2-dioxaphosphorinane was synthesized (Figure 3a), as reported

in the literature,<sup>8</sup> by reaction at high temperature (130–140 °C) and under reduced pressure (200 mbars). Various operating conditions were tested, playing on the ratio [hydrogenophosphonate/1,3-propanediol], on the nature of hydrogenophosphonate, and on the time of reaction to reach a fair yield. The best parameters were a 20% excess of diol with diethyl hydrogenophosphonate and an 8 h reaction time. Compound (1), obtained by transesterification reaction under optimized conditions and purification by distillation, was further characterized by <sup>1</sup>H NMR spectroscopy (Figure 1' in the Supporting Information). This analysis perfectly confirmed the structure, as evidenced by the doublet of the P-H group with the high <sup>1</sup>J<sub>P-H</sub> coupling constant (675.2 Hz).

Then, the optimized conditions were applied to a diol bearing an allyl group (Figure 3b). Product (2) was obtained by distillation under reduced pressure with 86% yield. The <sup>1</sup>H NMR spectrum (Figure 4) confirmed the expected structure with the large H<sub>2</sub>-P coupling constants. <sup>1</sup>J(P-H) = 673.8 and 683.6 Hz. <sup>31</sup>P and <sup>1</sup>H NMR spectra both proved the presence of two diastereoisomers in almost equivalent quantities (55/45). A splitting of <sup>1</sup>H NMR or <sup>31</sup>P NMR peaks is observed for the groups situated in the para position of the phosphorus atom on the cycle. These para groups are *cis* or *trans* compared with the P=O bond (Figure 3d). Their conformations will be studied in a forthcoming paper.<sup>18</sup>

The IR spectrum (Figure 2' in the Supporting Information) confirmed the results observed by NMR: the hydrogenophosphonate function can be evidenced by the bands ν (P=O) = 1286 cm<sup>-1</sup>, ν (P-O-C) = 1022 to 960 cm<sup>-1</sup>, and ν (P-H) = 2400 cm<sup>-1</sup>, the ether function can be evidenced by ν (C-O) = 1070 cm<sup>-1</sup>, and the monosubstituted double bond can be evidenced by ν (CH<sub>2</sub>=CH) = 1645 cm<sup>-1</sup>.

**B. Radical Polymerization.** 1. *Homopolymerization in Bulk.* The bulk polymerization (Entry 1, Table 2), at 120 °C (to reach an acceptable viscosity allowing polymerization) initiated by VAROX was successful and led to a colorless and rather hard elastomeric material after 48 h of reaction. This polymer was insoluble in common organic solvents. The first assumption we made was that a cross-linking reaction takes place at high temperature, thus preventing liquid NMR spectroscopy analyses. Because the polymer swells in solvents such as DMSO or DMF, we used high-resolution magic angle spinning (HRMAS) <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (Figure 5a). The



**Figure 6.** SEC chromatograms of the total product mixture after (A) homopolymerization or (B) telomerization of monomer (2) with dimethyl hydrogenophosphate.

decrease in the  $^1\text{H}$  peaks integral with time, implied in the polymerization reaction and the branching polymerization ratio via P–H bond, gave two types of conversions, which were calculated according to eqs 1 and 2

$$\alpha_{\text{M}} = 1 - \frac{I(\text{H}_5)_T}{I(\text{H}_5)_0} \quad (1)$$

$$\alpha_{\text{PH}} = 1 - \frac{I(\text{H}_2)_T}{I(\text{H}_2)_0} \quad (2)$$

where  $\alpha_{\text{M}}$  and  $\alpha_{\text{P-H}}$  stand for the conversion of the monomer into polymer and the proportion of hyperbranching in the material, respectively.  $\text{CH}_3$ , noted  $\text{H}_2$ , was the group used as the internal standard in the course of the polymerization.  $\text{H}_5$  corresponds to both protons located on the  $\text{CH}_2$  of the allyl ether double bond, whereas  $\text{H}_2$  is the proton linked to P of the monomer. The NMR analysis of the product obtained from entry 1 (Table 2) showed that the polymerization of the double bond is of 87% yield and also that the consumption of P–H bond reached up to 55%. This result demonstrates that on the same molecule there are two functions reacting in a nonequivalent way, entailing a complex mechanism.

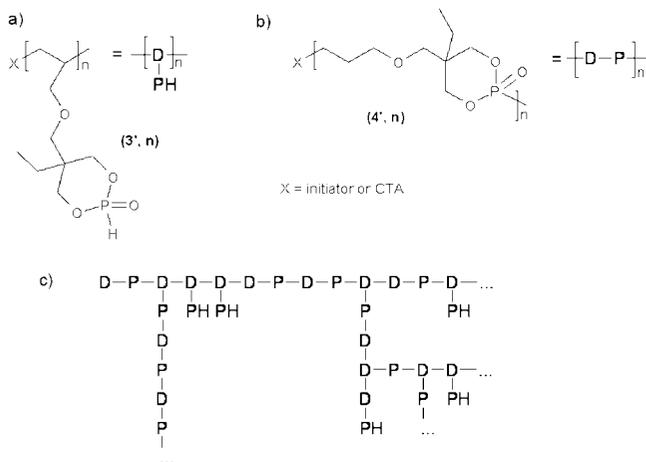
**2. Homopolymerization in Solution.** To avoid the problems of polymer solubility, solvent addition, shorter polymerization reaction times, and different temperatures (by changing the initiators) were tested. Various ratios of  $S_0$  ( $[\text{solvent}]_0/[\text{monomer}]_0$  molar ratio) and  $C_0$  ( $[\text{initiator}]_0/[\text{monomer}]_0$  molar ratio) were used (entries 2–5, Table 2).

The homopolymerization of (2) was tried in acetonitrile solution during 16 h at 70 °C in the presence of AIBN (entry 2, Table 2). Under these conditions, the polymerization did not start, as shown by the  $^1\text{H}$  NMR spectrum, where only the presence of the initial reactants is seen. The polymerization failed for  $S_0 = 20$  and  $C_0 = 0.01$ , that is, at an important dilution and low initiator concentration. By decreasing the solvent ratio monomer (entry 3) to  $S_0 = 4$ , the polymerization started, but the conversion remained weak even after 24 h of reaction (26% monomer consumption). The percentage of initiator was increased to 5% molar (entry 4), and the mixture of monomer

and initiator was concentrated to obtain a polymer conversion of 45%. With  $C_0 = 0.10$  (Entry 5), the monomer conversion further increased to 57%. These experiments illustrate that a reaction mixture that is not too diluted ( $S_0 = 4$ ) as well as a high  $C_0$  ( $\geq 0.05$ ) are required because allyl monomers are not prone to homopolymerize. The SEC profile of the product thus obtained (entry 4) displays a bimodal distribution containing 60% of oligomers ( $\text{DP}_n = 3.8$ ) and 40% of polymers of high molecular weight ( $\text{DP}_n = 480$ ) (Figure 6). This analysis shows that the formation of oligomers competes with the synthesis of more complex species of high molecular weight. Triple detection SEC analyses, using a refractometer, a light scattering detector, and a viscosity detector (Figure 4' in the Supporting Information), were carried out to better characterize the hyperbranched structures of polymers showing up in the high-molecular-weight region. Two hyperbranched species were clearly identified: The one with a lower hydrodynamic volume and lower viscosity but a strong scattering intensity corresponds to a dense, highly branched structure; the second one, of high viscosity and low scattering intensity, is the signature of a slightly branched, high-molecular-weight globular polymer.

The literature concerning the polymerization of allylic<sup>19</sup> monomers indicates that the maximum degree of polymerization ( $\text{DP}_n$ ) obtained in radical polymerization is rather low (about 50 units) because of a chain transfer phenomenon that limits the polymerization. Our allyl ether phosphonated monomer bears a double bond and a P–H group, which are both activated in the presence of radicals.<sup>20</sup> Two types of polymerization are likely to occur, which could partially explain this chromatographic distribution and the conversions,  $\alpha$ , deduced from  $^1\text{H}$  NMR peak integrations. (See eqs 1 and 2.) Besides the formation of a conventional polymeric chain via the double bonds (Figure 7a), the formation of a polyadduct (reaction of P–H bond on the double bond), according to the Figure 7b, may also take place.

In theory, the overlapping of both types of mechanisms, would lead to low-molecular-weight hyperbranched polymers.<sup>21</sup> (Their steric hindrance limits the propagation of the chains.) Let consider our monomer to be an entity having two reactive functions toward radical catalysis, such as D,



**Figure 7.** Two types of products resulting from the homopolymerization and telomerization of 5-ethyl-5-(allyloxymethyl)-2-oxo-1,3,2-dioxaphosphorinane monomer with the dimethyl hydrogenophosphonate: (a) through conventional double-bond reaction, (b) through vinyl/P-H addition, and (c) through both processes.

representing a double bond and PH, a P-H function. Such representation would give rise to the structures displayed in Figure 7, namely, linear polymer obtained by polymerization via the double bond (1) or polyaddition between the double bond and P<sup>o</sup> (D-P-D-P). If both mechanisms are taking place simultaneously, then the obtained structures can be of the hyperbranched type.

On one hand, if only polyaddition occurred [product (4', n)], then the monomer conversion,  $\alpha_M$ , would be equal to the P-H bond conversion,  $\alpha_{P-H}$ . On the other hand, if the mechanism implied only the polymerization on the double bond [product (3', n)], then  $\alpha_{P-H}$  would equal 0. In our case,  $\alpha_M$  was found to be higher than  $\alpha_{P-H}$  (with  $\alpha_{P-H} \neq 0$ ), so both mechanisms are concomitant. The (3', n) product ratio in the material can be estimated by the difference between  $\alpha_M$  and  $\alpha_{P-H}$ . For entry 5 (Table 2), this difference is 0.37, so the mechanism of polymerization on the double bond is favored. For the other entries (3 and 4), the difference is smaller, but the conclusion is identical. Triple detection SEC perfectly depicted the presence of high-molecular-weight (slightly branched) polymers, densely branched nanogels, and oligomers. Unfortunately, all of these three species show poor solubility in common organic solvents. To solubilize the phosphonated species, another synthetic strategy was used on the basis of the telomerization of phosphonated allyl ether involving HP(O)(OMe)<sub>2</sub> as the CTA. The advantage of the telomerization is to reduce the length of the chain and to introduce a chain-end function that can be useful for further applications.

**C. Radical Telomerization.** Many CTAs<sup>22</sup> can be involved in telomerization, such as thiols and halogenated or phosphorus products. Thiols have a strong nauseous smell, whereas the halogenated CTAs exhibit a high toxicity. Then, we focused only on hydrogenophosphonates as CTAs. As shown by Boulhana et al.,<sup>20</sup> these products exhibit a low transfer constant,  $C_T$ , on the styrenic monomers, whereas the production of monoadducts of vinyl acetate,<sup>23</sup> allyl acetate, or methyl 10-undecenoate<sup>24</sup> proved the high reactivity of those CTAs onto allyl monomers. In addition, the hydrogenophosphonate CTA introduces a phosphorus moiety at one chain end, which is interesting for future fireproofing applications.

**1. Synthesis of Monoadduct.** The telomerization of (2) with HP(O)(OMe)<sub>2</sub> as a CTA in various concentrations was carried out to obtain telomers of different chain lengths. With an excess of CTA ( $[CTA]_0/[monomer]_0$  molar ratio,  $R_0 = 10$ ), the monoadduct

was selectively obtained (3',1) (Figure 3c, path A). We could likely prepare this monoadduct by directly mixing the diol with dimethyl hydrogenophosphonate in a large amount according to the reaction (radical addition) (Figure 3c, path B). For each route, after 2 to 3 h of reaction, the unreacted dimethyl hydrogenophosphonate was evaporated under vacuum. The monoadduct was also characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, and the vanishing of the allyl protons and the presence of two methyl groups, P(OCH<sub>3</sub>)<sub>2</sub> (doublet centered at 3.67 ppm), was noted (Figure 3' in the Supporting Information). All other peaks were assigned similarly to those of monomer (2).

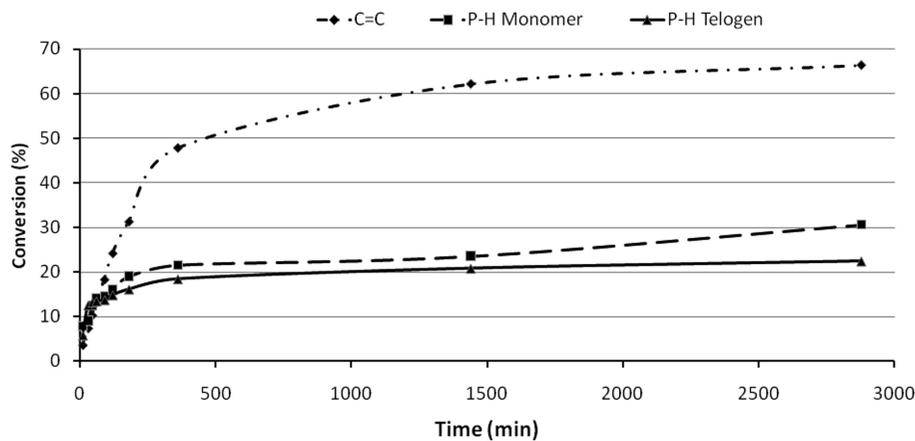
**2. Synthesis of Oligomers in Bulk or in Solution.** Taking into account the structure of (2), the mechanism of polymerization is more complex when the quantity of CTA is decreased; therefore, either the polyaddition of the monomer on itself to lead to (4', n) or a telomerization of the double allyl bond to lead to (3', n) (Figure 7a,b) could occur. To calculate the conversions in the polymer through double bonds or P-H bonds, eqs 1 and 2 were used in the first part. However, in telomerization, the CTA also reacts, as demonstrated by <sup>1</sup>H NMR where the P-H bond of CTA gave peaks other than those of the monomer (Figure 5b). Therefore, we introduced a new equation

$$\alpha_T = 1 - \frac{I(H_c)_T}{I(H_c)_0} \quad (3)$$

where  $\alpha_T$  stands for the conversion of the CTA into telomer.  $H_c$  corresponds to the proton linked to phosphorus atom on the CTA.

Various attempts of telomerization in bulk or in solution ( $[solvent]_0/[monomer]_0$  molar ratio:  $S_0 = 4$ ) were carried out while varying  $R_0$  (Table 3). Bulk telomerization (entry 2, Table 3) was efficient thanks to several additions of VAROX. SEC results on a sample with  $R_0 = 0.5$  (entry 2, Table 3) show the presence of two populations: the first peak arises from oligomers with  $DP_n = 2.3$ , whereas the second peak is assigned to polymers of higher molar mass ( $DP_n = 60$ ). This clearly confirms that both mechanisms occur simultaneously and that the products derived from (3', n) and from (4', n) are present in the reaction mixture. This is certainly due to the fact that both polymerization time and reaction temperature are rather large so that branching may take place. However, high-molecular-weight polymers have an average  $DP_n$  that is lower than that obtained in homopolymerization. This positive issue is ascribed to the telomerization process that decreases molecular weights and also to the high viscosity of the mixture, which prevents growing chains from meeting each other.

Then, several experiments of telomerization in solution were carried out under argon at 70 °C for 24 h with only one addition of AIBN at the beginning of the reaction. Optimum  $S_0$  and  $C_0$  ratios were selected thanks to the experiments made in conventional polymerization (Table 3). The CTA has been added to the reaction mixture with  $R_0$  ratios ranging between 1 and 6. Indeed, a higher CTA amount would exclusively provide the monoadduct (Entry 1). Conversions into polymer varied from 60 to 75%. Using the areas of SEC peaks for each species, a reduction in the (high-molecular-weight peak/oligomers peak) ratio for increasing values of  $R_0$  was evidenced. For the homopolymerization, that ratio was 0.67; then, it decreased to 0.37 for  $R_0 = 1$  and even to 0 for  $R_0 = 2$  (Figure 6). These results clearly demonstrate that the use of a CTA allows a decrease in the molar weight. For  $R_0 = 1$ , both high-molecular-weight hyperbranched polymer and oligomers were obtained, whereas for  $R_0 = 2$ , (entry 4, Table 3), SEC chromatograms show a homogeneous polymer population with  $DP_n = 3$  (Figure 6B). It should be noted that even under those



**Figure 8.** Kinetics of a model telomerization (entry 3, Table 3):  $\blacklozenge$ , double bond C=C conversion;  $\blacksquare$ , P–H bond of monomer conversion;  $\blacktriangle$ , P–H bond of telomer conversion.

optimum conditions, the P–H bond of the monomer was consumed at a content of up to 30% so that a polymerization with a double mechanism of chain propagation is expected. In the reaction mixture, two kinds of CTAs are in competition: the first one is the dimethyl hydrogenophosphonate (traditional telogen), whereas the second one is the monomer as a macrotelogen, of which reactivity in the mechanism of telomerization is unknown. To confirm that there are two telomerization mechanisms, the value of  $\alpha_M$  was compared with  $(\alpha_T + \alpha_{P-H})$ , where  $\alpha_T$  and  $\alpha_{P-H}$  represent the conversion ratios of the telogen and the monomer P–H bond, respectively. Because  $\alpha_M$  is slightly higher than  $(\alpha_T + \alpha_{P-H})$ , we can deduce that polymerization on the double bond is preponderant.

The kinetics were carried out to follow and to understand the implication of CTA as well as of the action of monomer P–H function in the mechanism of the telomerization of phosphonated allyl ether. The evolution of bond conversions versus time is represented in Figure 8. Conversion rates of both P–H bonds (present in the telogen and in the monomer) are close, even though it was expected that the P–H function of telogen would react faster than that of the monomer for steric hindrance issues. Finally, to check if the steric hindrance of the telogen agent modifies its reactivity in the radical reaction of polyaddition, a further experiment of telomerization was performed in the presence of diisopropyl hydrogenophosphonate ( $\alpha_{P-H}$  and  $\alpha_T$  are equal to 0.3) in place of the dimethyl hydrogenophosphonate. Under the same conditions ( $C_0 = 0.05$ ,  $R_0 = 1$ ,  $S_0 = 4$ ), the  $\alpha_T$  for the dimethyl hydrogenophosphonate was 0.2: this result confirms the equal reactivity of two previous P–H groups in telogen and in the cycle. The polymer is more soluble in usual solvents and then more useful for its industrial application as a fireproofing agent.

#### 4. Conclusions

This study described the synthesis and characterization of an oligomer carrying a phosphonated cycle in a view to manufacture a substitute for Antiblaze 19. Synthesis of cyclic allyl phosphonated monomer was carried out using a simple procedure, and it was in good yield. Characterization by NMR and IR confirmed the purity of the products and the presence of diastereoisomers. The originality of the polymerization mechanism of this monomer in thermal radical polymerization was demonstrated. First, both oligomers and high-molecular-weight polymers in hyperbranched forms were formed in bulk or solution reaction. These polymers thus present solubility difficulties for future industrial applications. Second, telomerization of this monomer with the dimethyl hydrogenophosphonate, for  $R_0 \leq 1$  ( $[\text{telogen}]_0/[\text{monomer}]_0$  molar ratio),

enabled us to limit the hyperbranching phenomenon. From  $R_0 = 2$ , the results show a limitation of the chain lengths to lead to the monoadduct with  $R_0 = 10$ . Fireproofing tests are now in progress.

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**Supporting Information Available:**  $^1\text{H}$  NMR spectrum of (1), IR spectrum of monomer (2),  $^1\text{H}$  NMR of product (3',1) in  $\text{CDCl}_3$ , and SEC chromatograms including triple detector traces of the total product mixture after homopolymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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