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Straightforward Synthesis of Polyallylphosphazenes from Poly(dichlorophosphazene)

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In recent years one of the most rapidly expanding branches of materials science has been the area of inorganic polymers.[1] Phosphazene polymers are the most highly developed, surpassing the silicones in structural variety.[1,2] Their chemical and physical properties are due to their backbone of alternating phosphorus and nitrogen but are greatly influenced by the nature of the side groups.[1,2] The synthesis of high-polymeric phosphazenes with alkyl or aryl side groups is of primary importance since it is expected that the stability of the P–C bonds will enhance the thermal and chemical stability of the polymers, which would be isoelectronic/isostructural with polysiloxanes.[3] A few synthetic methods have been reported,[4] but none of them are effective from the only really available precursor, namely poly(dichlorophosphazene) (**1**). Here we report the synthesis, from poly(dichlorophosphazene), of polyphosphazenes bearing allyl groups; a preliminary study of the thermal properties is presented.

Although the most widely used method for preparing poly(dichlorophosphazene) (**1**) is the ring opening of hexachlorocyclotriphosphazene,[5] we prefer the polycondensation of *N*-(dichlorophosphoryl)-*P*,*P*,*P*-trichloromonophosphazene (**2**),[6] and thus we used this monomer to test the alkylation reaction. Tetraorganyltin derivatives, in the presence of zerovalent palladium complexes, are known to allow substitution of halogenated organic compounds,[7] and a very few transfer reactions of this type have been reported in phosphorus chemistry.[8] We chose allyltrimethyltin (**3a**) as a transferring reagent, but under the Pd(0)-catalyzed reaction conditions, no substitution of **2** occurred. In marked contrast, when **2** was photolyzed at 300 nm in the presence of 1.1 equiv of tin derivative **3a**, a 90/10 mixture of (*N*-dichlorophosphoryl)-*P*-allyl-*P*,*P*-dichloromonophosphazene (**4**) and *N*-(dichlorophosphoryl)-*P*,*P*-diallyl-*P*-chloromonophosphazene (**5**) was obtained. After distillation in the presence of Irganox, **4** was isolated in 81% yield.[9] In the same way, the use of 2.2 equiv of **3b** allowed the synthesis of the disubstituted derivative **5** in 85% isolated yield (Scheme I).[9] The radical mechanism of these reactions was clearly demonstrated, since no substitution occurred in the presence of a radical inhibitor (benzoquinone), whereas **4** and **5** were also obtained by heating the reaction mixture in the presence of azobis(isobutyronitrile).

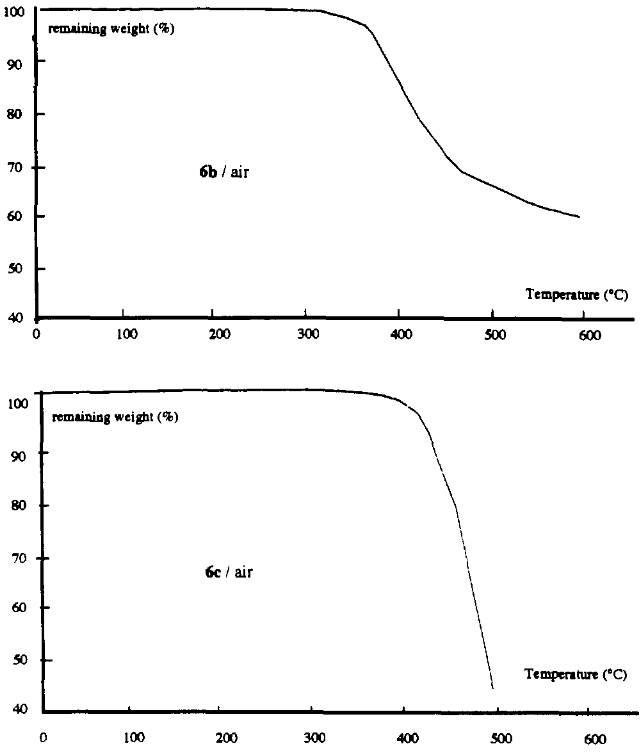

Figure 1. Thermograms of polymers **6b**,**c**.

These results prompted us to try the photochemical reaction of **3b** with poly(dichlorophosphazene) (**1**). It quickly appeared that 0.75 equiv of the tin reagent **3b**/equiv of chlorine atom was the maximum incorporation of allyl groups before cross-linking took place, affording an insoluble material. In a typical

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(1) For examples, see: *ACS Symp. Ser.* **1988**, 360. Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.

(2) Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147. Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351. Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.

(3) Allcock, H. R.; Patterson, D. B. *Inorg. Chem.* **1977**, *16*, 197. Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201. Allcock, H. R.; Desorcie, J. L.; Harris, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2814. Neilson, R. H.; Harris, R.; Wisian-Neilson, P.; Meister, J. J.; Rey, A. K.; Magnauer, G. L. *Macromolecules* **1987**, *20*, 910.

(4) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. Allcock, H. R.; Chu, C. T. *Macromolecules* **1979**, *12*, 551. Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814. Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119.

(5) Stokes, H. N. *Am. J. Chem.* **1897**, *19*, 782. Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(6) Heloui, M.; De Jaeger, R.; Puskaric, E.; Heubel, J. *Makromol. Chem.* **1982**, *183*, 113. Emsley, J.; Moore, J.; Udy, P. B. *J. Chem. Soc. A* **1971**, 2863.

(7) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(8) Bmagilov, R. K.; Razumov, A. I.; Yafavava, R. L. *Zh. Obshch. Khim.* **1972**, *42*, 1248. Vinokurava, G. M. *Zh. Obshch. Khim.* **1967**, *37*, 1652. Rolland, H.; Potin, P.; Majoral J.-P.; Bertrand, G. *Tetrahedron Lett.* **1992**, *33*, 8095. Novikova, Z. S.; Efimova, E. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1968**, *38*, 2345. Proskurina, M. V.; Novikova, Z. S.; Lutsenko, I. F. *Dokl. Akad. Nauk, SSSR* **1964**, *159*, 619. Hartman, H. *Justus Liebigs Ann. Chem.* **1968**, *714*, 1. Siebert, W.; Davidsohn, W. E.; Henry, M. C. *J. Organomet. Chem.* **1969**, *17*, 65. Ashe, A. J., III. *J. Am. Chem. Soc.* **1971**, *93*, 3293. Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748.

(9) **4**: bp 106 °C (10^{-3} mmHg); $^{31}P\{^1H\}$ NMR (C_6D_6) δ –8.8 (d) and 29.9 (d) (J_{PP} = 25.5 Hz); ^1H NMR (C_6D_6) δ 3.34 (dd, $^3J_{HH}$ = 5.2 Hz, $^2J_{HP}$ = 20.0 Hz, 2 H, CH_2), 5.11–5.82 (m, 3 H, $CH{=}CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 46.6 (dd, $^1J_{CP}$ = 105.0 Hz, $^3J_{CP}$ = 7.1 Hz, CH_2), 122.2 (d, $^2J_{CP}$ = 15.6 Hz, $=CH$), 126.5 (d, $^3J_{CP}$ 20.7 Hz, $=CH_2$); MS (EI) *m/e* 275. Anal. Calcd for $C_3H_5Cl_4NOP_2$: C, 13.11; H, 1.83; Cl, 51.60; N, 5.10. Found: C, 13.08; H, 1.82; Cl, 51.58; N, 5.08. **5**: bp 136 °C (10^{-3} mmHg); $^{31}P\{^1H\}$ NMR (C_6D_6) δ –7.3 (d) and 45.0 (d) (J_{PP} = 13 Hz); ^1H NMR (C_6D_6) δ 3.03 (dd, $^3J_{HH}$ = 6.4 Hz, $^2J_{HP}$ = 16.0 Hz, 2H, CH_2), 5.05–5.92 (m, 3 H, $CH{=}CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.0 (dd, $^1J_{CP}$ = 73.5 Hz, $^3J_{CP}$ = 5.0 Hz, CH_2), 123.7 (d, $^2J_{CP}$ = 11.3 Hz, $=CH$), 124.6 (d, $^3J_{CP}$ = 14.2 Hz, $=CH_2$); MS (EI) *m/e* 279. Anal. Calcd for $C_6H_{10}Cl_3NOP_2$: C, 25.70; H, 3.59; Cl, 37.92; N, 4.99. Found: C, 25.68; H, 3.56; Cl, 37.88; N, 4.97. **6b**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ –18.0 (m, $P(OC_6H_5)_2$), +8.1 (m, P(allyl)(OC_6H_5)), +18.0 (m, P(allyl)$_2$); ^1H NMR (C_6D_6) δ 2.35–2.85 (broad signal, CH_2), 4.68–5.10 (broad signal, $=CH_2$), 5.45–5.75 (broad signal, $=CH$), 6.60–7.20 (broad signal, C_6H_5); gel permeation chromatography M_n = 25 820, M_w = 80 000 (**1**: M_w = 61 000), $\overline{DP}_w$ = 400 (**1**: $\overline{DP}_w$ = 525). Experimental conditions used in the GPC analysis: column, 3 Polymer Laboratory Type 3PL gel, 300-mm length; solvent, THF stabilized with 2,6-di-*tert*-butylmethylphenol and LiBr; detector, LALLS *chromatix*.

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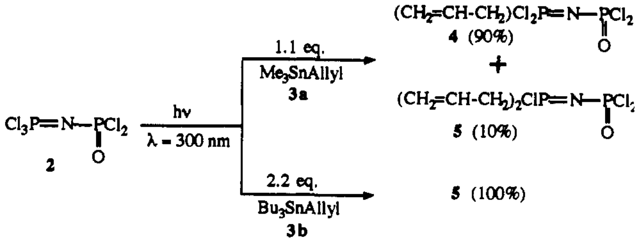
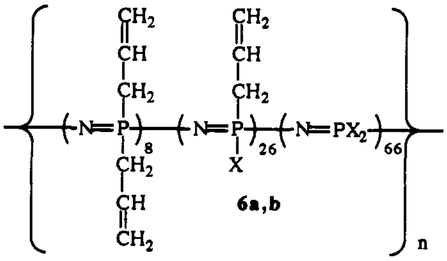
Scheme I



experiment, a stirred toluene solution (40 mL) of allyltributyltin (**3b**) (8.60 g, 25.9 mmol) and poly(dichlorophosphazene) (**1**) (2.01 g, 17.3 mmol, η = 14 mL/g) was irradiated at λ = 312 nm for 3 h, under argon. Three signals were present in the ^{31}P NMR spectrum at −19, +8, and +18 ppm in a 33/13/4 ratio. These signals can be assigned to PCl_2, (allyl)PCl and $(allyl)_2P$, respectively, and thus the structure of the polymer **6a** obtained is of type



6a,b

a : X = Cl

b : X = OPh

Of particular interest, the comparison of the value of the intrinsic viscosity of this partially allyl-substituted polymer **6a** (η = 27 mL/g) with that of the starting material **1** (η = 14 mL/g) shows that the skeleton has not been destroyed. The substitution of the remaining chlorine atoms of **6a** was carried out with sodium phenoxide in toluene at 110 °C, according to a procedure already reported[10] (the elemental analysis proves that less than 0.1% of chlorine remains). After treatment with concentrated sulfuric acid and filtration, the solution was concentrated under vacuum and added to methanol, precipitating an elastomeric material. After several washings with THF and drying in vacuo (0.1 mmHg), a light brown elastomeric material **6b**[10] was obtained (η = 18 mL/g).

Thermograms of polymers **6b**,**c** (**6c**: $[-(C_6H_5O)_2P{=}N-]_n$) are shown in Figure 1. The degradation of **6b** started at 360 °C instead of 400 °C as for **6c**. Nevertheless, 65% of the starting material or more likely of the resulting cross-link bulk was recovered after heating **6b** at 500 °C, while under the same experimental conditions only 35% of **6c** remained unchanged. Indeed, the incorporation of allylic groups into polyphosphazenes did not delay the beginning of the degradation but led to the formation of thermostable bulk probably because of allylic reticulation.

Studies aimed at improving the thermal stability of polyphosphazenes by incorporating various substituents are in progress.

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(10) Chambrette, J.-P.; Pagniez, G.; Potin, P. European Patent No. 0442 784 A1, 1991.