Synthesis of Poly(phenyl-*o*-tolylphosphazene) via Reaction of Trimethylsilyl Azide with 2,2,2-Trifluoroethyl Phenyl-*o*-tolylphosphinite

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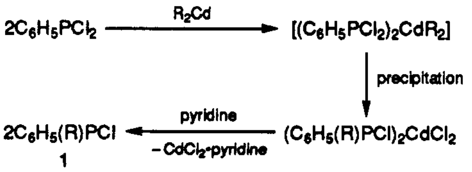
Introduction. Polyphosphazenes are commercially prepared by either ring-opening polymerization of halogenated cyclotriphosphazenes[1] or condensation of *P,P,P*-trichloro-*N*-(dichlorophosphoryl)monophosphazene.[2] Subsequently, hydrolytically unstable P–X groups are replaced by various –OR and –NHR substituents. Another approach employs thermal[3] and catalyzed[4] polymerization of *N*-(trimethylsilyl)phosphoranimines and decomposition of phosphine azides.[5,6] In these methods substituents at phosphorus are introduced at the stage of monomer rather than polymer. Attempts to synthesize poly(diarylphosphazenes) by substitution method or by the corresponding phosphoranimines were reported.[7,8] In addition, perphenylated polyphosphazenes could be prepared via phosphine azide intermediates.[5,9] Poly(diarylphosphazenes) are potentially interesting materials which might exhibit greater thermal and chemical stability due to a direct P–C bond. We have previously reported the modified synthesis and some characterization of poly(diphenylphosphazene), prepared via *in situ* decomposition of diphenylphosphine azide.[9,10] Unfortunately, poly(diphenylphosphazene) is poorly soluble and intractable due to high crystallinity. Linear poly(diphenylphosphazene) with a degree of polymerization DP > 10 is soluble only at elevated temperatures. It was, however, previously reported that a polymer with DP ≈ 200 prepared by substitution of poly(difluorophosphazene) with phenyllithium was soluble, at least enough to perform GPC analysis.[11] The reason for the enhanced solubility is unknown and may involve either incomplete substitution or branching of the polymer chains. Both effects could suppress crystallinity of the polymer.

We now report the synthesis of poly(phenyl-*o*-tolylphosphazene) via thermal decomposition of phenyl-*o*-tolylphosphine azide, formed in the reaction of asymmetrically substituted 2,2,2-trifluoroethyl phenyl-*o*-tolylphosphinite and trimethylsilyl azide. This is an alternative approach to soluble poly(diarylphosphazenes) which enables control of the substituents at each P atom.

Results and Discussion. Asymmetrically substituted phosphorus(III) compounds (R_1R_2PX) with a reactive group X such as halogen or alkoxy are difficult to synthesize. Common literature procedures lead to low yields and are very complicated.[12] Modifying the method developed by Chodkiewicz *et al.*,[13] we prepared 2,2,2-trifluoroethyl phenyl-*o*-tolylphosphinite (**2**) in 60% yield from dichlorophenylphosphine and di-*o*-tolylcadmium.



(1)

R = *o*-tolyl (i.e., 2-methylphenyl)

In order to obtain the desired monomer **2**, the initially synthesized phenyl-*o*-tolylchlorophosphine (**1**) is reacted with 2,2,2-trifluoroethanol in the presence of triethylamine.

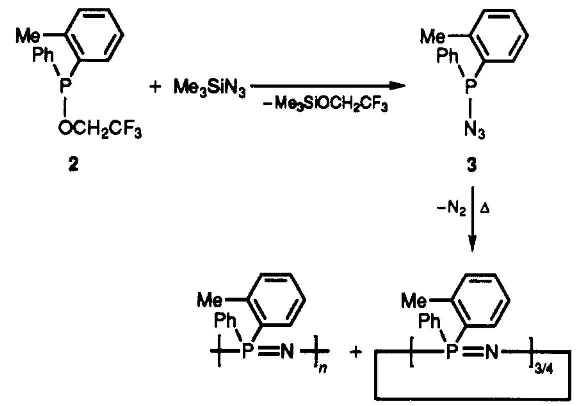
$$\underset{\mathbf{1}}{C_6H_5(R)PCl} + CF_3CH_2OH \xrightarrow[-Et_3NH^+Cl^-]{Et_3N} \underset{\mathbf{2}}{C_6H_5(R)POCH_2CF_3} \quad (2)$$

R = *o*-tolyl

The exchange reaction with trimethylsilyl azide leads to the formation of phenyl-*o*-tolylphosphine azide, which can be obtained in nearly quantitative yields at low temperatures. This reaction intermediate slowly decomposes even at –20 °C. The azide exchange reaction is strongly catalyzed by fluoride and chloride anions, which may be present as impurities or may be intentionally added as ammonium salts:

$$\underset{\mathbf{2}}{Ph(o\text{-tolyl})POCH_2CF_3} + Me_3SiN_3 \xrightleftharpoons{[Bu_4N^+F^-]} \underset{\mathbf{3}}{Ph(o\text{-tolyl})PN_3} + Me_3SiOCH_2CF_3 \quad (3)$$

Highly purified compound **2** does not react with trimethylsilyl azide in a dry diglyme solution even after stirring for 1 day at ambient temperature. Addition of 0.1 mol % of tetrabutylammonium fluoride catalyzes the formation of phosphine azide which is formed in >95% yield after <20 min. Subsequently, nitrogen evolution can be observed. The decomposition of compound **3** results in the formation of poly(phenyl-*o*-tolylphosphazene) and variable amounts of cyclic trimer and tetramer:



(4)

Higher concentrations of salt (1–5 mol %) accelerate the azide exchange reaction dramatically. Unfortunately the use of higher salt concentrations leads to lower molecular weight products.

Figure 1 shows the ^{31}P NMR spectra obtained during a typical polymerization experiment. **2** (1 mol/L) was mixed with trimethylsilyl azide (1 mol/L) in a diglyme solution at 25 °C in the presence of 0.1 mol % of tetrabutylammonium fluoride. Spectrum 1a, obtained 5 min after the addition of trimethylsilyl azide, shows unreacted phosphinite at 121 ppm ($^4J_{PF}$ = 6.1 Hz) and phenyl-*o*-tolylphosphine azide (**3**) at 71 ppm. Spectrum 1b recorded after 25 min reveals complete conversion of **2**, the presence of unreacted **3**, and the products of thermal decomposition. The signals could be assigned in analogy with the diphenyl system[14] as follows: cyclic trimer **4** at 13.5 ppm and oligomeric/polymeric product **5** in the range of 0 to –10 ppm. An unidentified impurity gives rise to

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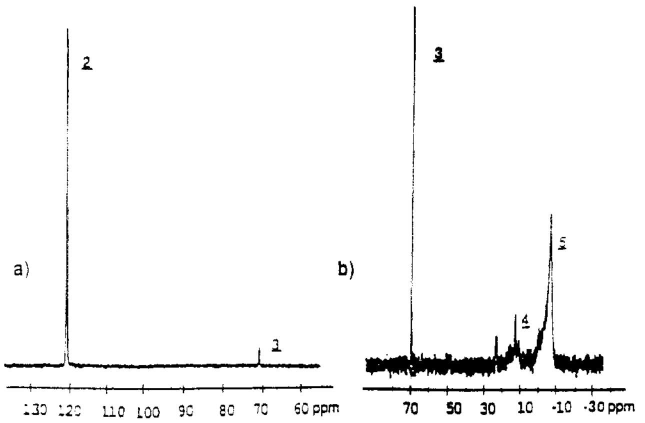

Figure 1. ^{31}P NMR spectra of the reaction mixture of 2 (1 mol/L) with trimethylsilyl azide (1 mol/L) in diglyme at 25 °C in the presence of 0.1 mol % of tetrabutylammonium fluoride after 5 min (a) and after 25 min (b).

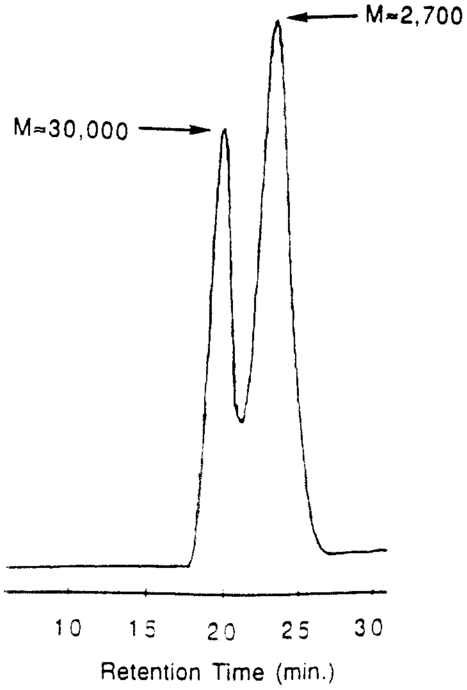

Figure 2. GPC traces of poly(phenyl-*o*-tolylphosphazene) prepared via reaction of 2 (1 mol/L) with trimethylsilyl azide (1 mol/L) in diglyme at 90 °C.

a signal at 25 ppm. In some spectra cyclic tetramer is also present at 7 ppm.

Although the reaction of compound 1 with trimethylsilyl azide leads to the same azide intermediate 3, the *in situ* polymerization in the presence of the reaction byproduct trimethylchlorosilane predominantly results in the formation of cyclic trimer and tetramer rather than polymer. When the leaving group is trifluoroethoxy, as discussed in this paper, the *in situ* polymerization of compound 3 leads to linear polymer and smaller amounts of cyclics (<30%).

The obtained cyclic trimers and tetramers can be separated from the high molecular weight products by extraction with acetone. GPC (Figure 2) of the remaining slightly yellow solid indicates a bimodal molecular weight distribution with a high polymer in the range of 30 000 to 40 000 and low molecular weight polymer in the range of 3000 to 4000, based on polystyrene standards. The reason for the bimodality and the mechanistic aspects of the polymerization is under investigation in our laboratories.

In contrast to the symmetrically substituted poly(diphenylphosphazene),[9,10] poly(phenyl-*o*-tolylphosphazene) is completely amorphous and does not exhibit any mesophase or melting. A glass transition temperature is detected at 120 °C. TGA experimnts in air show thermal stability up to 380 °C (10% decomposition) and a surprisingly high 35% yield of a char (Figure 3).

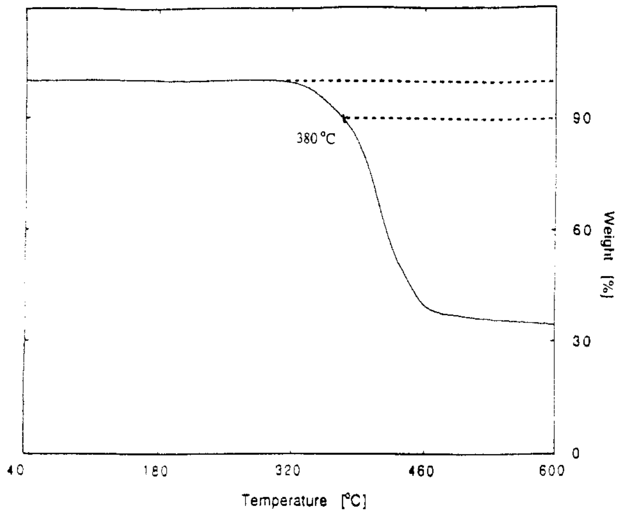

Figure 3. TGA traces of poly(phenyl-*o*-tolylphosphazene) prepared as in Figure 2.

Experimental Section. All reactions were carried out under an atmosphere of dry argon with exclusion of moisture and oxygen. Solvents were dried using common literature procedures[15] and stored under an argon atmosphere. The trivalent phosphorus compounds were freshly distilled before use. NMR spectra were recorded on a 300-MHz IBM/NR. Trimethyl phosphite (141 ppm) was used as the external standard for ^{31}P NMR studies. Thermal analysis was performed using Perkin-Elmer DSC7 and Seiko DSC and TGA instruments.

GPC data were obtained using Ultrastyragel columns (linear, 100 Å, and 1000 Å) equipped with a Waters 410 RI detector at 35 °C with a flow rate of 1 mL/min. To avoid the interaction of the polyphosphazenes with the column, a 0.1% by weight solution of tetrabutylammonium bromide in THF was used. Calibration is based on polystyrene standards.

Phenyl-*o*-tolylchlorophosphine (1). The synthesis of 1 follows the literature procedure.[13] A clear, slightly yellow liquid monomer distilled at 125 °C (0.2 Torr). Yield: 60%. ^{1}H NMR (benzene-d_6): δ 8–6.9 (m, 9 H); 2.3 (s, 3 H). ^{31}P NMR (CDCl$_3$): δ 77.

2,2,2-Trifluoroethyl Phenyl-*o*-tolylphosphinite (2). A total of 40 g (0.17 mol) of compound 1 is added to 600 mL of benzene and 19 g (0.19 mole) of triethylamine in a 1-L two-neck flask equipped with an addition funnel and a magnetic stirrer. A total of 18.6 g (0.19 mol) of 2,2,2-trifluoroethanol is added dropwise at 0 °C under stirring. The suspension is stirred for 8 h at ambient temperature. The formed triethylamine hydrochloride is separated by filtration. After removal of benzene the colorless oil is distilled at 0.2 Torr showing a boiling point of 110 °C. Yield: 48 g (95% on the basis of compound 1). ^{1}H NMR (benzene-d_6): δ 8–6.9 (m, 9 H); 3.8 (q, 2 H); 2.4 (s, 3 H). ^{31}P NMR (CDCl$_3$): δ 121.

In Situ Polymerization of 2,2,2-Trifluoroethyl Phenyl-*o*-tolylphosphinite (2) with Trimethylsilyl Azide. The polymerization is carried out in a flame-dried 50-mL two-neck flask equipped with a reflux condenser and an argon inlet/outlet. To 2 g (6.7 mmole) of compound 2 dissolved in 7 mL of diglyme is added at room temperature 0.9 mL of trimethylsilyl azide. The reaction mixture is stirred for 1 h at ambient temperature and then heated to 90 °C, at which point a vigorous evolution of nitrogen takes place. After the evolution is finished (1–2 min) the homogeneous reaction mixture is heated for 2 h at 90 °C. The mixture is allowed to cool down to room temperature and poured into cyclohexane. The precipitated oligomeric/polymeric materials are collected on a filter. The low molecular weight products (predominantly cyclic trimer and tetramer) are extracted with acetone.

This reaction carried out in bulk might be explosive and special cautions should be undertaken; on the other hand, it can be mediated in solution.

Yield of polymer: 73% on the basis of compound **2**. ^{1}H NMR (benzene-d_6): δ 9–6.5 (m, 9 H); 2.5–1.9 (s, 3 H). ^{31}P NMR ($CDCl_3$): δ 0–10.

The polymerization (oligomerization) of compound **1** was studied in the same manner.

Polymerization experiments of **2** with trimethylsilyl azide in the presence of tetrabutylammonium fluoride are studied as described above. The catalyst for the azide exchange reaction is added in a THF solution (1 mol/L) to the mixture of **2** and trimethylsilyl azide. The reaction mixture is heated to 90 °C immediately after the nitrogen evolution starts. The following steps are the same as those for the uncatalyzed system.

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