

Polyalkoxyphosphazenes by Room-Temperature Polymerization of an Electronegative Phosphoranimine Monomer

Robert D. Chapman,^{1,2} Mark F. Welker,¹ and Charles B. Kreutzberger^{1,3}

Received July 18, 1996; revised October 29, 1996

A new electronegative alkoxyphosphazene monomer, tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)phosphoranimine, has been prepared. The anionic polymerization of this monomer occurs even at room temperature, in contrast to that of previous trialkoxy-*N*-(trimethylsilyl)phosphoranimines, which require elevated temperatures for efficient polymerization. The new polymerizations occur via catalysis by tetra-*n*-butylammonium fluoride or even by adventitious moisture.

KEY WORDS: Polyphosphazenes; polyalkoxyphosphazenes; room temperature; anionic polymerization; phosphoranimines; dinitropropanol.

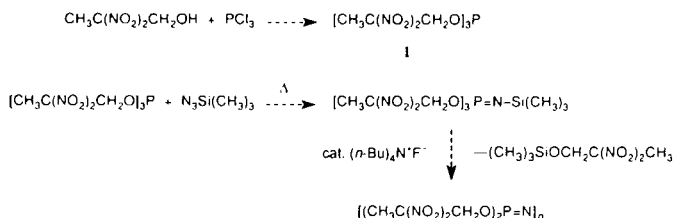
INTRODUCTION

The feasibility of *P*-trialkoxo-*N*-(trimethylsilyl)phosphoranimines as precursors to poly(alkoxyphosphazenes) was demonstrated in the 1970s by Flindt and Rose [1]: thermal degradation of *P*-tris(2,2,2-trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine at 200 °C for 48 h resulted in polymerization to poly[bis(2,2,2-trifluoroethoxy)phosphazene]. Matyjaszewski *et al.* made a significant advancement in this utility by demonstrating catalyzed anionic polymerization of *N*-silylphosphoranimines [2]: conditions required to polymerize this monomer were made much gentler by the use of catalytic tetrabutylammonium fluoride, whose anion served as a nucleophile with a high affinity for silicon. Thus, thermal treatment at 95 °C

¹ TPI, Inc., Albuquerque, New Mexico 87109.

² To whom correspondence should be addressed at Research & Technology Group (Code 4B2200D), Naval Air Warfare Center Weapons Division, China Lake, California 93555.

³ Present address: PPG Industries, Inc., Monroeville, Pennsylvania 15146.



Scheme 1. Proposed synthetic sequence toward an energetic polyphosphazene.

for only 1.5 h resulted in a 45 % yield of poly[bis(2,2,2-trifluoroethoxy)-phosphazene], and heating in diglyme solvent at 125°C for 4 h resulted in nearly 100 % conversion.

Because of potential interest in phosphazene-based energetic materials, such as nitramine-substituted derivatives [3], we undertook the preparation of a (polynitroalkoxy)phosphazene polymer as another example of such a material. We also sought to demonstrate the feasibility of preparing pure, tailorable phosphazene polymers containing energetic (e.g., polynitroaliphatic) substituents. The system to be investigated would employ the sequence shown in Scheme 1.

The requisite tris(2,2-dinitropropyl) phosphite intermediate (**1**) might be made by esterification of the alcohol with phosphorus trichloride. This ester would react with azidotrimethylsilane to make the corresponding *P*-tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)phosphoranimine monomer; then the monomer would be polymerized by catalysis with a suitable nucleophile (tetrabutylammonium fluoride [2] or *N*-methylimidazole [4]) to yield an energetic linear polymer, poly[bis(2,2-dinitropropoxy)phosphazene].

RESULTS AND DISCUSSION

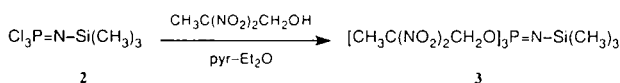
Tris(2,2-dinitropropyl) phosphite (**1**), a new compound, was prepared by conditions based on those reported for tris(2-methyl-2-nitro-1-propyl) phosphite [5]. In the first attempt, the reaction of 2,2-dinitropropanol (DNPOH) with phosphorus trichloride produced--along with significant unreacted DNPOH--phosphorus acid esters identifiable by ¹H and ³¹P NMR as the desired phosphite ester plus four *phosphate* species. The esters were separated from the unreacted alcohol by chromatography. The phosphates are the expected by-products of *deoxygenation* of nitro compounds by phosphorus(III) species, a phenomenon previously observed in nitroorganic compounds [6]. Although the phosphate species were not isolated for specific identification, their number is consistent with the various degrees of deoxygenation likely on a tris(2,2-dinitropropyl) ester (0–3 nitroalkoxy groups deoxygenated); the multiple products are also consistent with different modes of deoxygenation of nitroaliphatics [7]. In

the next run of this reaction, carefully dried DNPOH, upon reaction with PCl_3 in diethyl ether containing pyridine, produced the desired phosphite ester in an 87% yield with a minor amount of phosphate ester by-product. However, spontaneous exothermic decomposition of the product indicates inherent instability of the material, which should be regarded as hazardous and unstable in the solid state.

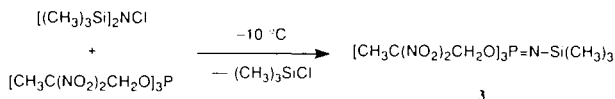
Based on evidence of its instability, it seemed unlikely that the reaction of **1** with azidotrimethylsilane at elevated temperature—a conventional method to prepare trialkoxy-*N*-(trimethylsilyl)phosphoranimines—would be a viable approach to this required intermediate. Therefore, alternative routes to the required trialkoxy-*N*-(trimethylsilyl)phosphoranimine were considered. The most attractive of these initially appeared to be via the known [8] trichloro-*N*-(trimethylsilyl)phosphoranimine, $\text{Cl}_3\text{P}=\text{N}-\text{Si}-(\text{CH}_3)_3$ (**2**). It may be expected that nucleophilic substitution of **2** by DNPOH could be conducted under mild conditions, as in the preparation of **1**, producing the corresponding trialkoxy-*N*-(trimethylsilyl)phosphoranimine (**3**). The phosphorus(V) species **2** would have less tendency than did **1** to deoxygenate the nitroalkoxy substituents.

The nucleophilic substitution of **2** was attempted with DNPOH under the conditions previously used for the phosphite ester (Scheme 2). After 2 days at ambient temperature, **2** had been consumed (according to ^{31}P NMR) and pyridinium salts had deposited on the flask wall. Analysis of the pyridinium salt residue by ^{31}P NMR revealed the likely presence of the desired product (**3**) in this separated phase, but the spectrum was also complex, indicating numerous by-products or degradation products.

Still another alternative approach to trialkoxy-*N*-(trimethylsilyl)phosphoranimines has been reported to be via the reaction of *N*-chlorohexamethyldisilazane, $[(\text{CH}_3)_3\text{Si}]_2\text{NCl}$, with the corresponding phosphite of a desired phosphoranimine: this reaction produced tripropoxy-*N*-(trimethylsilyl)phosphoranimine in a 34% yield [9]. Although this reaction would require the less desirable phosphite of the energetic alcohol, it need not be isolated for this reaction, and the conditions appear to be mild enough ($0-10^\circ\text{C}$) to avoid several degradation of the phosphite. *N*-Chlorohexamethyldisilazane is made by chlorination of hexamethyldisilazane with chlorine in dichloromethane or *t*-butyl hypochlorite in diethyl ether [10].

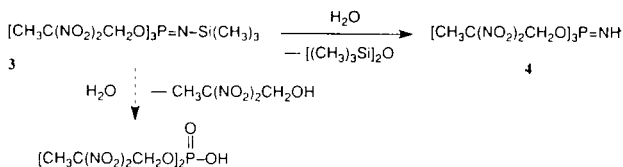


Scheme 2. Formation of tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)phosphoranimine (**3**).



Scheme 3. Alternative preparation of tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)-phosphoranimine.

The reaction of tris(2,2-dinitropropyl) phosphite (**1**) with excess *N*-chlorohexamethyldisilazane in diethyl ether at -10°C produced the desired product, **3** (Scheme 3), with $\sim 80\%$ conversion based on phosphite reactant according to ^{31}P NMR analysis of the ether-soluble components, but the isolated yield was only $\sim 30\%$. The synthesis of **3** was repeated with modification by using dichloromethane, a better solvent for **1**. The modified reaction of **1** with excess $[(\text{CH}_3)_3\text{Si}]_2\text{NCl}$ led to complete consumption of **1** in 6 days. During the course of this reaction, tris(2,2-dinitropropyl) phosphate was formed as a by-product (identified by ^{31}P NMR), presumably by the competing deoxygenation of nitroalkyl groups by **1**. The crude reaction mixture at this time comprised a mixture of phosphoranimine **3** (39 mol%) in the presence of by-products. Purification by extraction between ether and water produced an ether layer containing **3** (50 mol%), phosphate (35 mol%), and a new species (10 mol%) with a ^{31}P NMR absorption at δ 9.4 (vs δ -15.2 for **3**); the balance was unidentified minor by-products. Recrystallization reduced the content of the inert phosphate constituent to ~ 25 mol% and removed the unidentified by-products. After observation that the new species (δ 9.4) disappears concomitantly with monomer **3** during polymerization of the latter (*vide infra*), we speculate that this compound is the corresponding free phosphoranimine **4**, formed by hydrolysis of the *N*-trimethylsilyl derivative (Scheme 4), which is also amenable to anionic polymerization via its relatively stable conjugate base. The same behavior has been reported by Matyjaszewski *et al.* from studies of the effects of water on the polymerization of tris(2,2,2-trifluoroethoxy)phosphoranimines [11]. Phosphate ester(s) might also be formed by the nucleophilic attack of water on phosphorus.

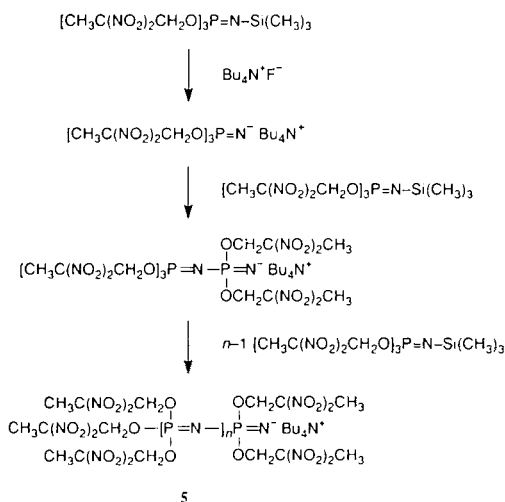


Scheme 4. Hydrolysis of tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)phosphoranimine.

The polymerization of tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)-phosphoranimine (**3**) was carried out by the anionic mechanism (Scheme 5). Catalysis by tetra-*n*-butylammonium fluoride in tetrahydrofuran (5 mol% relative to **3** + **4**) caused polymerization of **3** and **4** at room temperature to >99% completion in 2 h. This facile polymerization of **3** is consistent with the nature of polynitroalkoxy as an efficient leaving group relative to traditional alkoxy substituents. Phosphate ester impurity apparently did not interfere with progress of the anionic polymerization and was removed from polymer product in subsequent purifications.

The product polymer is a light-brown solid which could be purified by multiple successive precipitations from THF into diethyl ether and water. It shows ^{31}P NMR absorptions at δ -11.6 (25 mol%) and two broad absorptions at δ -3.8 and -2.8 comprising the balance of ^{31}P signals. The two downfield peaks are slightly broadened and overlap, but the δ -2.8 peak is larger. The ^1H NMR spectrum shows absorptions for tetrabutylammonium in addition to those expected for 2,2-dinitropropoxy. The relatively large proportion of absorption at δ -11.6 in the ^{31}P NMR indicates a relatively high content of the tris(2,2-dinitropropoxy) phosphoranimine end cap in the expected polymer **5**. The 3:1 mole ratio of downfield absorptions to upfield absorptions in the ^{31}P NMR spectrum indicates that $n \approx 3$ in this product.

A later, modified workup of the remainder of crude product from the main preparation of **3** produced a tacky, light-colored solid that was



Scheme 5. Catalyzed anionic polymerization of tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)-phosphoranimine.

insoluble but swelled like a cross-linked polymer in some solvents; it was soluble in dimethyl sulfoxide. ^{31}P NMR analysis indicated a degree of polymerization of ~ 22 . Also, as this polymerization was initiated without catalysis by tetrabutylammonium fluoride, this cation is absent in the ^1H NMR spectrum. We surmise that dissociation of **4**, expected to be a relatively strong acid compared to most trialkoxyphosphoranimines, is sufficiently facile to produce the same phosphoranimine anion that is the initial intermediate in the anionic polymerization. In this case, the anion-terminated oligomer appears (according to ^1H NMR) to be associated with an ammonium (NH_4^+) species presumably derived from hexamethyl-disilazane by-products.

EXPERIMENTAL

2,2-Dinitropropanol (DNPOH) was a gift of the Propulsion Division of GenCorp Aerojet (Sacramento, CA). It was purified by passing its solution in 1,2-dichloroethane through silica gel followed by azeotropically drying the isolated product with benzene. NMR spectra were obtained on a 300-MHz Bruker AC-300 (IBM NR 300) spectrometer with multinuclear capabilities.

Tris(2,2-dinitropropyl) Phosphite (1). A solution of DNPOH (19.58 g, 0.130 mol) and pyridine (9.10 g, 0.115 mol) in 300 ml dry ether was cooled to 0 °C. A solution of phosphorus trichloride (5.27 g, 0.038 mol) in 100 ml ether was added over 1.5 h at 0 °C. The solution was stirred at 0 °C for another 0.5 h. Salts were filtered from the solution, and the crude product was concentrated to a yellow solid and stored in a freezer overnight. The impure product was chromatographed (80:20 hexane dichloromethane) on silica gel to yield 16 g (87%) of white solid, **1**. ^1H NMR (CDCl_3): δ 2.13 [s, $\text{CH}_3\text{C}(\text{NO}_2)_2$], 4.53 (d, $J_{\text{HP}} = 5.6$ Hz, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 139.5. *Warning:* About 20 min after isolation as a pure solid and containment in a glass bottle, the sealed tris(2,2-dinitropropyl) phosphite sample blew off its screw cap, with a concomitant flame which extinguished itself upon depressurization. This behavior indicates inherent instability of the material. Most of the phosphite material survived as a residue, presumably with combustion product contaminants; but the sample did not appear to undergo detonation, based on this evidence. This material should be regarded as hazardous and unstable in the solid state.

Tris(2,2-dinitropropoxy)-N-(trimethylsilyl)phosphoranimine (3). To a solution of tris(2,2-dinitropropyl) phosphite (**1**; 2.01 g, 4.20 mmol) in

80 ml dichloromethane, maintained under anhydrous, airless conditions with dry argon and covered with aluminum foil to exclude light, was added freshly distilled *N*-chlorohexamethyldisilazane [10] (0.92 g, 4.7 mmol) at 0 °C with stirring. After 3 h at 0 °C, the cooling bath was removed, and the reaction was maintained at ambient temperature. Additional aliquots of *N*-chlorohexamethyldisilazane were added intermittently (when ^{31}P NMR analysis still showed residual starting material) in order to replenish this unstable reagent: 1.25 g (6.38 mmol) at 48 h, 1.65 g (8.42 mmol) at 72 h, and 0.83 g (4.24 mol) at 5 days. After 6 days, ^{31}P NMR spectroscopy indicated no residual starting material. Solvent was removed from half of the reaction product mixture at reduced pressure. The resulting solids were redissolved in 100 ml diethyl ether and washed with 1 L of water. After removal of the ether at reduced pressure, the product consisted of **3** (50 mol%), phosphate (35 mol%), and **4** (10 mol%), with a weight of 0.974 g (crude yield of **3** + **4** being ~52%). Recrystallization with dichloromethane hexanes led to partial precipitation of the phosphate and unknowns, and the recovered product was comprised of **3** (40 mol%), phosphate (25 mol%), and **4** (35 mol%). Yield, 0.671 g (43% based on **3** + **4**). Compound **3**: ^1H NMR (CDCl_3): δ 0.1 (CH_3Si), 2.05 [s, $\text{CH}_3\text{C}(\text{NO}_2)_2$], 4.86 (d, $J_{\text{HP}} = 5.6$ Hz, CH_2); ^{31}P NMR (CDCl_3): δ -15.2. Compound **4**: ^{31}P NMR (CDCl_3): δ 9.4.

Bis(2,2-dinitropropoxy)phosphazene Oligomer, Tetrabutylammonium Salt (5). To the crude product above (0.671 g), containing **3** + **4**, was added 1.0 ml of 0.05 *M* anhydrous tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran, prepared from 1.0 *M* TBAF in THF (Lancaster Synthesis), at room temperature, maintaining air-free, anhydrous conditions. After 2 h, ^{31}P NMR indicated that <1% of **3** remained, and the resonance assigned to **4** had concomitantly disappeared. After 20 h, the spectrum was essentially unchanged except for complete disappearance of **3**. The reaction mixture was precipitated into 200 ml diethyl ether. The recovered oil was successively reprecipitated into diethyl ether, hexanes, water, and ethanol, yielding <100 mg of purified **5**. ^1H NMR ($\text{DMSO}-d_6$): δ 1.01 (CH_3CH_2), 1.46 (CH_2CH_2), 1.69 ($\text{CH}_2\text{CH}_2\text{N}$), 2.37 [s, $\text{CH}_3\text{C}(\text{NO}_2)_2$], 3.38 (CH_2N), 4.84 [d, $J_{\text{HP}} = 5.6$ Hz, $\text{C}(\text{NO}_2)_2\text{CH}_2$]; ^{31}P NMR ($\text{DMSO}-d_6$): δ -11.6 ([$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}$] $_3\text{P}=\text{N}$), -3.8 ([$\text{CH}_3\text{C}(\text{NO}_2)_2\text{-CH}_2\text{O}$] $_2\text{P}=\text{N}-\text{Bu}_4\text{N}^+$), -2.8 ([$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}$] $_2\text{P}=\text{N}$).

Alternative Preparation of Bis(2,2-dinitropropoxy)phosphazene Polymer. One-half of the crude reaction product from the preparation of **3** above was dissolved in 100 ml dichloromethane. Washing this solution

with 1 L water, followed by evaporation of the dichloromethane layer, redissolution into dimethyl sulfoxide, and addition to THF, resulted only in precipitation of ammonium chloride, a by-product of *N*-chlorohexamethyldisilazane hydrolysis. Removal of THF from the filtered solution yielded a viscous oil. Reprecipitation from DMSO into diethyl ether produced a yellow solid that was insoluble in chloroform, THF, toluene, and water. ^{31}P NMR is similar to that of **5** prepared via catalysis by TBAF. ^{31}P NMR ($\text{DMSO}-d_6$): δ -12.0 ($[\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}]_3\text{P}=\text{N}$), -4.0 ($[\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}]_3\text{P}=\text{N}$), -2.6 ($[\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}]_3\text{P}=\text{N}$). Integration of these peaks indicates a degree of polymerization of approximately 22.

CONCLUSIONS

The unusual electronegative character of the polynitroaliphatic group in the new phosphazene monomer tris(2,2-dinitropropoxy)-*N*-(trimethylsilyl)phosphoranimine (**3**) has been discovered to facilitate the anionic polymerization mechanism of the energetic phosphoranimine. The (polynitroalkoxy)phosphazene intermediates are sufficiently acidic, due to inductive effects, that free phosphoranimine **4** is observable upon hydrolysis of **3** and undergoes anionic polymerization even without powerful catalysts. The polymerization of **3** occurs even at room temperature in contrast to previous trialkoxy-*N*-(trimethylsilyl)phosphoranimines, which required $\geq 95^\circ\text{C}$ for efficient polymerization [2]. As Matyjaszewski *et al.* have noted previously [11], this reaction's efficiency (e.g., degree of polymerization) is greatly affected by conditions such as the catalyst and solvent (for example, their anhydrous nature). The product from our initial (fluoride-catalyzed) polymerization of phosphoranimine **3** appear to be approximately a tetramer, but it is expected that conditions can be modified to achieve higher molecular weights as desired for practical applications. Our alternative product formed from "uncatalyzed" polymerization of **3** (presumably by adventitious hydrolysis), after a longer polymerization time *without* fluoride catalyst, has a degree of polymerization of ~ 22 .

In the course of conduct of our work, the discovery by the collaboration of Manners and Allcock of the similarly facile polymerization of trichloro-*N*-(trimethylsilyl)phosphoranimine (**2**) to poly(dichlorophosphazene), catalyzed by PCl_5 , was made and reported [12].

The facile polymerization of *N*-silylphosphoranimines with electronegative, good leaving groups may offer technical advantages in the preparation of polyphosphazenes for other applications. In theory, the propensity to polymerize is dictated by the best leaving group in a phosphoranimine monomer. It should therefore be possible to prepare

mixed-alkoxy monomers (phosphoranimines) involving only one poly-nitroaliphatic group, with two other conventional functionalities for other purposes. This variation may allow preparation of even bis(trifluoroethoxy)phosphazene polymers, for example, under milder conditions than previously observed.

ACKNOWLEDGMENT

The financial support of this work by the Naval Surface Warfare Center (White Oak), Silver Spring, MD, under Small Business Innovation Research Contract N60921-93-C-0123, is gratefully acknowledged.

REFERENCES

1. (a) E.-P. Hündt and H. Rose, *Z. Anorg. Allgem. Chem.* **428**, 204 (1977); (b) E.-P. Hündt, H. Rose, and H. C. Marsmann, *Z. Anorg. Allgem. Chem.* **430**, 155 (1977).
2. (a) R. A. Montague and K. Matyjaszewski, *J. Am. Chem. Soc.* **112**, 6721 (1990); (b) K. Matyjaszewski, *J. Inorg. Organomet. Polym.* **2**, 5 (1992); (c) K. Matyjaszewski, M. Cypryk, J. Dauth, R. Montague, and M. White, *Makromol. Chem. Macromol. Symp.* **54/55**, 13 (1992); (d) K. Matyjaszewski, U. Franz, R. A. Montague, and M. L. White, *Polymer* **35**, 5005 (1994).
3. (a) P. R. Dave, F. Forohar, T. Avenrod, C. D. Bedford, M. Chaykovsky, M.-K. Rho, R. Gilardi, J. Hippen-Anderson, and C. George, Joint International Symposium on Energetic Materials Technology [Proceedings], New Orleans, LA, Oct. (1992), p. 306; American Defense Preparedness Association, Arlington, VA. (b) P. R. Dave, F. Forohar, T. Avenrod, C. D. Bedford, M. Chaykovsky, M.-K. Rho, R. Gilardi, and C. George, *Phosphorus Sulfur Silicon Relat. Elem.* **90**, 175 (1994).
4. K. Matyjaszewski, J. Dauth, R. Montague, C. Reddick, and M. White, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **32**(1), 305 (1991).
5. W. Shelver, M. E. Blake, and C. E. Miller, *J. Am. Pharm. Assoc.* **47**, 72 (1958); *Chem. Abstr.* **52**, 9945f (1958).
6. (a) J. I. G. Cadogan, *Q. Rev.* **22**, 222 (1968); (b) P. A. Wehrli and B. Schaer, *J. Org. Chem.* **42**, 3956 (1977).
7. (a) I. Neda and R. Vileanu, *Rev. Chim. (Bucharest)* **31**, 1053 (1980); *Chem. Abstr.* **95**, 6415x (1980); (b) E. Uprir and J. Vilarrasa, *Tetrahedron Lett.* **31**, 7497 (1990).
8. (a) E. Neecke and W. Bitter, *Inorg. Nucl. Chem. Lett.* **9**, 127 (1973); (b) C. H. Honeyman, A. J. Lough, and I. Manners, *Inorg. Chem.* **33**, 2988 (1994).
9. A. M. Pinchuk, M. G. Suleimanova, and I. P. Filonenko, *Zh. Obshch. Khim.* **42**, 2115 (1972).
10. N. Wiberg and F. Raschig, *J. Organomet. Chem.* **10**, 15 (1967).
11. K. Matyjaszewski, J. B. Green, and R. A. Montague, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **33**(1), 174 (1992).
12. C. H. Honeyman, I. Manners, C. T. Morrissey, and H. R. Allcock, *J. Am. Chem. Soc.* **117**, 7035 (1995).