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high molecular weight end of the MWD, including the high molecular weight component detected by the LALLS detector, had greater UV absorbance per unit mass than those in the lower molecular weight region of the MWD. This heterogeneity with respect to UV absorbance further supports a branched chain structure since the increased absorbance at the high molecular weight end of the MWD is consistent with the greater availability of branching sites.

Although its detailed structure has not been established, the polymer is proposed to be composed primarily of linked borazine rings, analogous to those of the organic poly(phenylene) polymers.[20] Since small amounts of the N:B coupled dimer $1{:}2'\text{-}(B_3N_3H_5)_2$ are isolated in the volatile materials from the reaction, the polymer is likely to contain N–B linkages between the borazines. Consistent with this interpretation, the ^{11}B NMR spectrum has a broad peak centered in the borazine region at 31 ppm.[21] Also isolated in the volatiles were small amounts of borazanaphthalene; thus it is possible that the polymer also contains some degree of fused-ring structure.

The polymer prepared in the manner described above is soluble in polar solvents such as THF or glyme and appears to be stable for extended periods when stored as a solid at room temperature under vacuum. The polymer is sensitive to water and will decompose over several hours when exposed to moist air.

A number of chemical precursors[22] for the formation of boron nitride have now been reported;[23] however, because of its composition, high-yield synthesis, and solubility, poly(borazylene) would appear to be an almost ideal precursor system. Its ceramic conversion reactions were therefore investigated. Bulk pyrolyses of both the crude and recrystallized polymers were examined under either argon or ammonia to 1200 °C and were found to result in the formation of white boron nitride powders in excellent purities and ceramic yields (85–93%; theoretical ceramic yield, 95%):[24]

$$[B_3N_3H_4]_x \xrightarrow{25\text{–}1200\ ^\circ\text{C}} 3BN + 2H_2 \qquad (2)$$

The materials produced at 1200 °C exhibited diffuse reflectance IR spectra consistent with those previously reported for boron nitride[25] and densities (1.7–1.9 g/mL) and X-ray powder diffraction patterns characteristic of turbostratic boron nitride.[26]

Thermogravimetric analysis of the ceramic conversion reaction showed that the polymer follows a well-defined decomposition path in which an initial (2%) weight loss (probably resulting from polymer cross-linking) occurs in a narrow range between 125 and 300 °C, followed by a gradual 4% loss ending by 1100 °C. Thus, poly(borazylene) appears to be an excellent precursor to boron nitride, which, because of its solubility, low-temperature decomposition, and high ceramic and chemical yields, makes it an excellent candidate for the generation of, for example, coatings or fibers of boron nitride. We are presently exploring these possibilities.[27]

Acknowledgment. We thank the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, for the support of this research. We also thank Dr. Andrew McGhie and the National Science Foundation Materials Research Laboratory at the University of Pennsylvania for the thermogravimetric analysis results and Chris Albani for X-ray diffraction data. The Alcoa Foundation and Callery Chemical Co. provided additional support and are gratefully acknowledged.

Registry No. Borazine, 6569-51-3; polyborazylene, 39526-51-7; boron nitride, 10043-11-5.

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A Second-Order Nonlinear Optical Poly(organophosphazene)

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The development of polymeric nonlinear optical (NLO) materials is currently an area of intense investigation.[1] Polymeric systems that show second harmonic generation (SHG) have conjugated aromatic molecules with electron-donor and -acceptor moieties in a noncentrosymmetric array. These nonlinear optical molecules can be doped into a glassy polymer matrix[2] or can be covalently attached to

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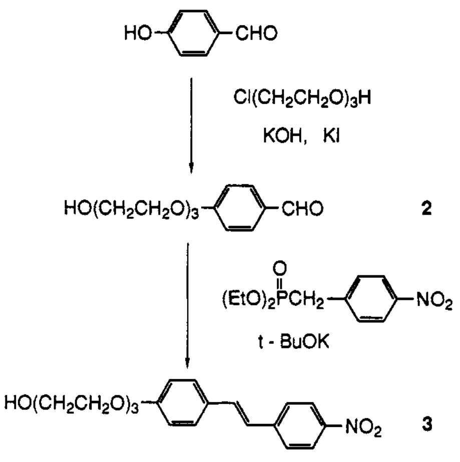
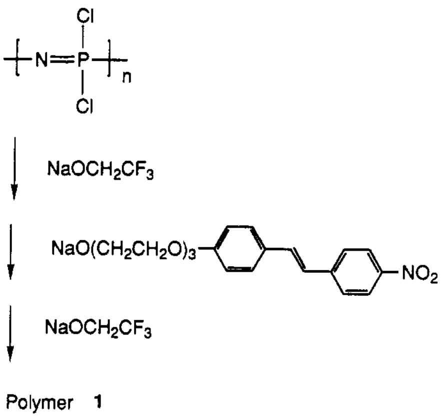
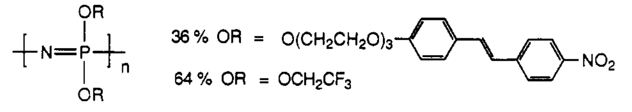
Scheme I



Scheme II



a polymer backbone.[3] Here we report the synthesis and second-order nonlinear optical response of polymer 1, a polyphosphazene in which a nitrostilbene unit is covalently linked to the polymer chain through a tris(ethylene oxide) spacer group. Phosphazene macromolecules offer a potential advantage in that the macroscopic properties of the polymer can be tailored by the incorporation of specific substituent groups.[4,5] Polymer 1 is therefore a prototype that offers many opportunities for further tailoring of the molecular structure to generate an optimum combination of nonlinear optical and physical properties.



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Our initial work involved the synthesis of a side chain for the polyphosphazene substrate that has molecular characteristics that are required for a nonlinear optical response. As outlined in Scheme I, 4-hydroxybenzaldehyde was allowed to react with 2-[2-(2-chloroethoxy)ethoxy]ethanol in basic ethanol containing potassium iodide for 15 h at reflux to yield 4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]benzaldehyde, **2**. Compound **2** was then allowed to react with diethyl (4-nitrobenzyl)phosphonate and potassium *tert*-butoxide in ethylene glycol dimethyl ether for 15 h at room temperature to give the desired *trans*-4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]-4′-nitrostilbene, **3**. Compound **3** was purified by column chromatography and was recrystallized from *n*-hexane/methylene chloride.[6]

Polymer 1 was synthesized by the procedure described in Scheme II. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of the cyclic trimer $(NPCl_2)_3$.[4] In the first step in the synthesis of 1, sodium trifluoroethoxide was added to poly(dichlorophosphazene) to replace approximately 50% of the P–Cl bonds. In the second step, a stoichiometric deficiency of *trans*-$NaO(CH_2CH_2O)_3C_6H_4CH{=}CHC_6H_4NO_2$ was allowed to react with the partially substituted polymer. In the final step, an excess of sodium trifluoroethoxide was added to replace the remaining P–Cl bonds in order to obtain a fully derivatized, hydrolytically stable polymer.[7] Polymer 1 was isolated by precipitation from tetrahydrofuran into water and was purified by dialysis against methanol/water (1:1 v/v) for 7 days. The polymer is a yellow elastomeric material that is soluble in common organic solvents such as tetrahydrofuran (THF) and methyl ethyl ketone (MEK). Characterization was achieved by ^{31}P and ^{1}H NMR spectroscopy,[8] infrared and UV/visible spectroscopy, elemental microanalysis, gel permeation chromatography, and differential scanning calorimetry.[9] ^{1}H NMR analysis of polymer 1 indicated a 36% incorporation of the nitrostilbene side chain.

Films of polyphosphazene 1 were cast onto indium–tin oxide coated glass from a concentrated solution in MEK. The solution was first filtered to remove particulate impurities and the films were dried in vacuum to remove all of the solvent. The NLO properties of the films were subsequently investigated by using second-harmonic generation. A Q-switched Nd:YAG laser ($\lambda = 1.064\ \mu m$) with a pulse width of 8 ns and a pulse energy of 10 mJ was used as the source of the fundamental, and a reference sample of Y-cut quartz ($d_{11} = 0.46$ pm/V) was used for calibration of the frequency-doubled signal. From measurements of the refractive index at both the fundamental and second-harmonic wavelengths, the coherence length of 1 was calculated to be 2.8 μm. The thin-film thicknesses used were always less than this coherence length, being typically ca. 0.5 μm.

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(6) For **3**: mp 66–67 °C; λ_{max} (THF) = 378 nm; *m/z* calcd 373, *m/z* found 373; IR (KBr) 3500–3100 (br, ν(OH)), 1340 cm^{-1} (s, $\nu(NO_2)$); ^{1}H NMR ($CDCl_3$) δ 8.21 (2 H, d, *J* = 8.8 Hz, Ar H), 7.61 (2 H, d, *J* = 8.7 Hz, Ar H), 7.49 (2 H, d, *J* = 8.7 Hz, Ar H), 7.23 (1 H, d, *J* = 16.3 Hz, CH), 7.01 (1 H, d, *J* = 16.3 Hz, CH), 6.95 (2 H, d, *J* = 8.8 Hz, Ar H), 4.18 (2 H, t, OCH_2), 3.90 (2 H, t, OCH_2), 3.75 (6 H, m, OCH_2), 3.65 (2 H, t, OCH_2), 2.20 (1 H, br s, OH); yield 40–55%. Anal. Calcd for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 63.96; H, 6.20; N, 3.72.

(7) This three-step synthetic procedure was necessary since the direct addition of *trans*-$NaO(CH_2CH_2O)_3C_6H_4CH{=}CHC_6H_4NO_2$ to poly(dichlorophosphazene) resulted in the formation of an insoluble, incompletely substituted polymeric precipitate.

(8) NMR spectra were recorded on a Bruker WP-360 spectrometer. Chemical shifts are relative to 85% H_3PO_4 (^{31}P) or tetramethylsilane (^{1}H).

(9) For 1: λ_{max} (THF) = 376 nm; ^{31}P NMR (THF/D_2O) δ −8.3; $M_n = 3.2 \times 10^5$, $M_w = 1.4 \times 10^6$, $M_w/M_n = 4$; IR (KBr) 1340 (s, $\nu(NO_2)$), 1280 cm^{-1} (s, $\nu(P{=}N)$); ^{1}H NMR (acetone-d_6) δ 8.3–6.9 (m, Ar H, CH), 4.5 (br s, OCH_2CF_3), 4.3–3.6 (m, OCH_2); T_g = 25 °C. Anal. Found: C, 43.01; H, 4.66; N, 5.13; Cl, <0.11. Analysis is consistent with a 30% incorporation of **3**.

Alignment of the NLO side groups in the layers was achieved by single-point corona poling, with the point source held at +10 kV, at a distance of 1.5 cm from the surface. Poling voltages greater than 10 kV sometimes resulted in damage to the film, manifested as a slight cloudiness. Note, however, that this voltage was still below the saturation point of the signal. The variation of the signal with poling voltages will be discussed more fully in a later publication. Due to the low glass transition temperature of 1 (T_g = 25 °C), the poling was carried out at room temperature while the SHG measurements were being made. Upon removal of the voltage, the second-harmonic signal decayed to zero within a few minutes.

The second-harmonic coefficient of the polymer film, d_{33}, was obtained from a Maker fringe analysis of the data,[10] giving d_{33} = 5.5 pm/V. This value of d_{33} was obtained by using the isotropic model for poled polymers, where d_{33}/d_{31} = 3.[2a] Singer et al.[3d] have found this model to be appropriate for analysis of their side-chain polymers. Recently, however, Eich et al.[3e] have observed deviations from this ratio, possible due to mesogenic interactions among the side groups. The applicability of the isotropic model to poly(organophosphazenes) is currently under investigation.

Given that the degree of alignment was not maximized in this experiment and that we are using a less efficient donor moiety than other studies of functionalized polymers,[2c,3d] this is a very promising value of d_{33}. Work to attach more efficient donors and to increase the glass transition temperature of the polymer is in progress.

Acknowledgment. The research at The Pennsylvania State University was supported by the U.S. Air Force Office of Scientific Research and the Office of Naval Research. The research at University of Southern California was supported by the U.S. Air Force Office of Scientific Research. We thank Y. Shi for the refractive index measurements.

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Molten Salt Synthesis of Low-Dimensional Ternary Chalcogenides. Novel Structure Types in the K/Hg/Q System (Q = S, Se)

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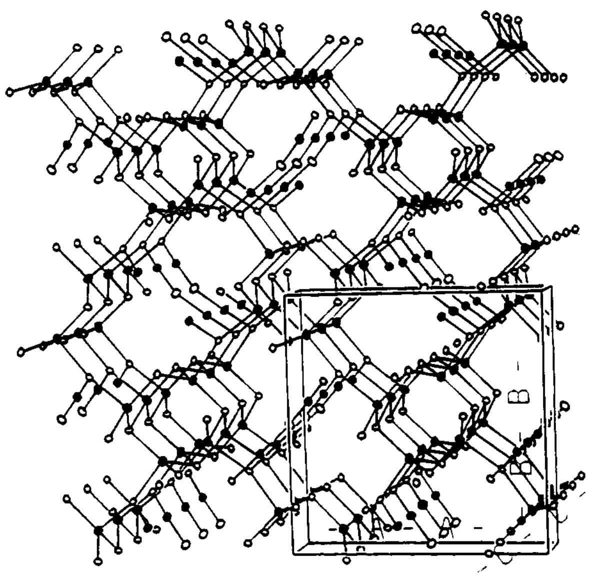

Figure 1. Three-dimensional structure of the $[Hg_6S_7]_n^{2n-}$ network.[17,18] The K atoms have been omitted for clarity. The Hg atoms are represented by black circles and the sulfur atoms by open circles. The S–Hg–S angle about the two-coordinate Hg atom is 172.4 (4)°.

Recently we demonstrated that by using alkali-metal polysulfide melts as solvents at intermediate temperatures (i.e., 150–350 °C), novel, low-dimensional solid-state compounds can be isolated in crystalline form.[1] This intermediate temperature regime has not been explored as a synthetically useful area.[2] It has been regarded by molecular coordination chemists as too hot for any normal solvents to be stable and stay in liquid form and by classical solid-state chemists as too cold for most reactions to proceed. This is particularly true in chalcogenide chemistry.[3] We believe that an enormous number of interesting and perhaps metastable compounds occur at these temperatures and could be crystallized, provided suitable solvents are available. Molten salts have been well studied[4] and can be prepared to exhibit a wide range of temperatures at which they remain liquid and thus are appropriate media for synthetic applications. Indeed they have been used as such at high temperatures.[5] Alkali-metal polychalcogenide melts in particular are very interesting because melting points as low as ~150 °C can be achieved[6] and can serve as solvents as well as reagents (i.e., chalcogen and alkali-metal donors). Recrystallizations of binary sulfides have been accomplished in these melts at high (>700 °C) temperatures.[7] The purposeful use of these systems for synthesis of new materials has not been seriously pursued. Low-dimensional chalcogenides are of intense interest due to their useful electronic[8] and catalytic[9]

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(2) This does not include the hydrothermal synthesis technique which also involves solvents in high pressures (supercritical state). However, chalcogenide synthesis under these conditions is also a relatively unexplored area. For examples of such synthesis, see: (a) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23–30. (b) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 98–104. (c) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105–111.

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