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Surandar Nath Kaul and Jack E. Fernandez*
Chemistry Department and Center for Materials Development
University of South Florida, Tampa, Florida 33620

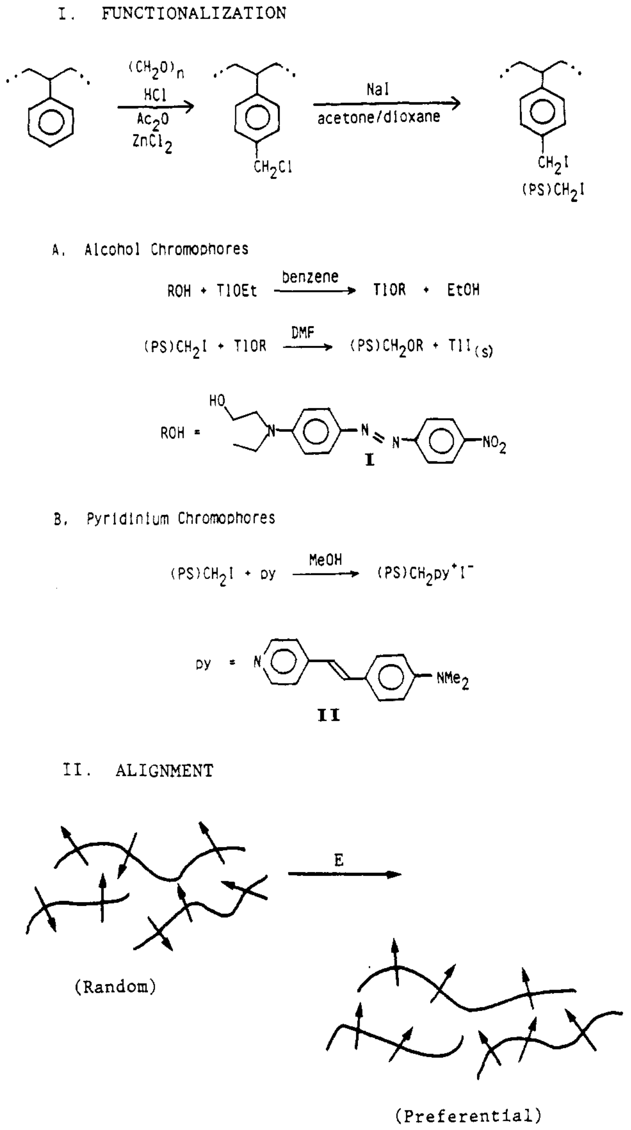
Received April 29, 1986

Synthesis of Molecular Arrays with Nonlinear Optical Properties. Second-Harmonic Generation by Covalently Functionalized Glassy Polymers

Current interest in organic (π-electron) nonlinear optical (NLO) materials derives from the attraction of large nonresonant susceptibilities, ultrafast response times, low dielectric constants, high damage thresholds, and the intrinsic tailorability of organic structures.[1] For second-harmonic generation (SHG), a major synthetic challenge is to construct *necessarily noncentrosymmetric* molecular assemblies having high structural integrity and suitable processability. We report here an approach[2] in which nonlinear chromophores are covalently linked to a glassy, film-forming macromolecule to produce, after alignment in an electric field, a new class of single-component polymeric frequency-doubling materials.[3-5]

Polystyrene was chosen as backbone because of its excellent transparency,[6,7] low dielectric constant,[7] relatively high T_g (to help stabilize chromophore alignment),[7] and amenability to varying kinds/levels of functionalization and processing. Polystyrene ($\bar{M}_w \approx 22\,000$) was chloromethylated,[8] followed by conversion to the more reactive iodomethyl derivative,[9] as shown in Scheme I. These and subsequent steps are conveniently monitored by 400-MHz ^{1}H NMR.[10] Introduction of high-β chromophores I and II[11,12] was effected by thallium-mediated etherification[13] or quaternization,[14] respectively. The new polymers were characterized by standard spectroscopic/analytical techniques and by DSC.[15] Most experiments have been carried out with polymers having 4.5-12.5% (by elemental analysis and NMR) of the benzene rings functionalized.

Scheme I



Solutions of $(PS)CH_2$-I (12.5% functionalization, in dioxane) and $(PS)CH_2$-II (4.5% functionalization, in $ClCH_2CH_2Cl$) were multiply suction filtered through a 5-μm frit and were spin coated[16] onto pieces of ITO-coated conductive glass in a class 100 laminar-flow clean hood (to minimize contamination by dust). After they were dried under vacuum, the 0.3-7.0-μm thick[17] films were covered with a second ITO electrode and were then poled in an electric field[18] (0.040-0.500 MV cm^{-1}) for 20 min at 115 °C. The films were then cooled in the presence of the electric field.

Second harmonic coefficients of the poled films were measured in the p-polarized geometry at 1.064 μm by using the Q-switched Nd:YAG laser-based instrumentation described previously.[19] Verification of the second-harmonic character was provided by measurement of the spectral purity with a 0.5-m monochromator and by the quadratic dependence of the intensity on the fundamental beam intensity (Figure 1). In Figure 2, the dependence of the second harmonic intensity on the incident angle of the fundamental beam is shown for a typical film. This angular dependence can be analyzed by using the theoretical expression of Jerphagnon and Kurtz[20] for uniaxial materials and by assuming that the five nonzero second-harmonic coefficients are interrelated by $d_{31} = d_{21} = d_{24} = d_{15} = {}^1/_3 d_{33}$,[3a,21] where 3 refers to the unique axis of the uniaxial material. By calibrating against d_{11} of quartz, the d_{33} of $(PS)CH_2$-I is determined to be 2.7 (3) $\times 10^{-9}$ esu at a poling field of 0.300 MV cm^{-1}. This value exceeds the analogous parameter for KDP where $d_{36} = 1.1 \times 10^{-9}$ esu and is comparable to the d_{33} of PMMA films doped with similar concentrations of I and poled at comparable fields.[3a,b] For the $(PS)CH_2$-I films, the magnitude of d_{33} is found to be linearly proportional to the strength of the

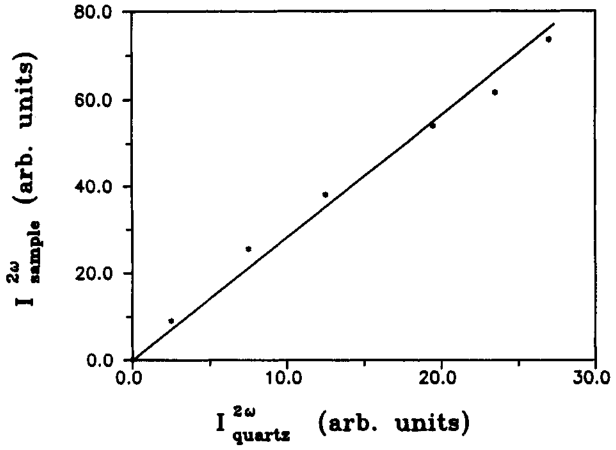


Figure 1. Second-harmonic intensity of a typical film of (PS)-CH_2-I versus that from a quartz reference crystal for 1.064-μm incident laser light. The linear relationship demonstrates that $I^{2\omega}$ depends quadratically upon I^{ω}.

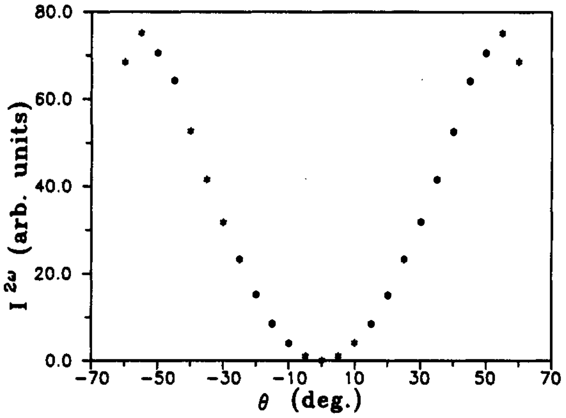


Figure 2. Second-harmonic intensity of a typical film of (PS)-CH_2-II as a function of incident laser beam angle.

poling field (up to 0.500 mV cm^{-1}—the highest field employed), in accord with simple Langevin descriptions of the orientation process.[3a,b,22] In regard to stability, the (PS)CH_2-I films exhibit negligible diminution in SHG efficiency on storage for several days at room temperature. However, heating to 115 °C in the absence of the electric field immediately destroys the frequency-doubling capacity.

The behavior of (PS)CH_2-II films is somewhat different from that of the (PS)CH_2-I films. At ca. 40% of the chromophore concentration and comparable poling fields, d_{33} values of the former material (e.g., 1.2 (1) × 10^{-10} esu for poling at 0.300 MV cm^{-1}) are invariably ca. 1 order of magnitude lower than that of the latter, although the calculated[11a] $\mu\beta_{vec}$ is approximately the same for both chromophores. Furthermore, d_{33} for (PS)CH_2-II is only linearly dependent on poling field up to ca. 0.300 MV cm^{-1} (Figure 3). At higher fields, saturation is observed, accompanied by a significant transient current (only above T_g). We suggest that these effects are related to the ionic nature of (PS)CH_2-II and phenomena accompanying ion mobility.[23] Nevertheless, the present SHG results evidence significant nonrandom chromophore alignment in this ionic polymer.

The results of this study indicate that a processable, glassy polymer can be converted into a relatively robust and efficient frequency-doubling material by covalent functionalization with high-β NLO chromophores. The scope of the synthetic chemistry possible and the conditions under which maximum persistent noncentrosymmetry can be achieved are under continuing exploration.

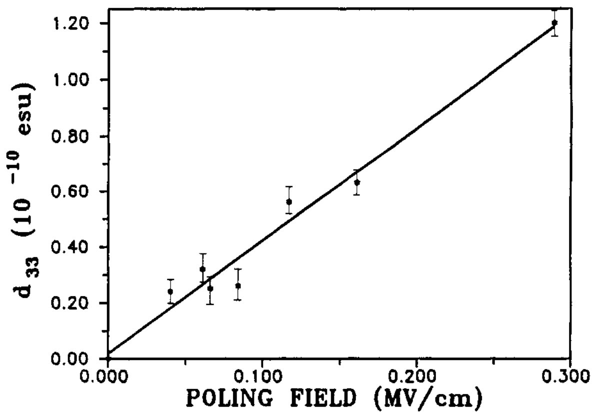


Figure 3. d_{33} values of (PS)CH_2-II films as a function of poling field.

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(11) (a) From perturbation theory and the PPP formalism,[11b–d] we estimate $\beta_{vec}(I) = 142 \times 10^{-30}$ cm^5 esu^{-1} ($\hbar\omega = 0.656$ eV), μ = 10.4 D, and $\beta_{vec}(CH_3\text{-}II^+) = 191 \times 10^{-30}$ cm^5 esu^{-1} ($\hbar\omega = 1.17$ eV), μ = 8.1 D. (b) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370–375. (c) Li, D.; Yang, J.; Ye, C.; Ratner, M. A.; Wong, G.; Marks, T. J. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum: New York, in press. (d) Li, D.; Marks, T. J.; Ratner, M. A., submitted for publication.

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(14) Model chromophore from II + benzyl chloride: ^{1}H NMR (CDCl$_3$) δ 9.079 (2 H, d, J = 7.0 Hz), 7.724 (2 H, d, J = 7.0 Hz), 7.528 (1 H, d, J = 16 Hz), 7.477 (2 H, d, J = 8.8 Hz), 7.365–7.529 (5 H, m), 6.780 (1 H, d, J = 16 Hz), 6.666 (2 H, d, J = 9.0 Hz), 5.980 (2 H, s), 3.053 (6 H, s); λ_{max} = 529 nm (ClCH$_2$CH$_2$Cl). Anal. Calcd for C$_{22}$H$_{23}$N$_2$Cl: C, 75.31; H, 6.61; N, 7.98; Cl, 10.10. Found: C, 75.18; H, 6.73; N, 7.74; Cl, 10.35.

(15) (PS)CH$_2$-I: ^{1}H NMR (CDCl$_3$) δ((PS)CH$_2$O) 4.51, bound chromophore signals at δ 8.31 (2 H, d, J = 9.0 Hz), 7.89 (4 H, m), 6.81 (2 H, d, J = 9.0 Hz), 3.88 (2 H, t, J = 6.0 Hz), 3.62 (2 H, t, J = 6.0 Hz), 3.55 (2 H, q, J = 7.0 Hz), 1.24 (3 H, t, J = 7.0 Hz); λ_{max} = 483 nm (film); T_g = 105–109 °C. Anal. (prepared from PS having 12.5% of rings iodomethylated). Calcd: C, 87.33; H, 7.43; N, 2.81. Found: C, 86.52; H, 7.42; N, 2.65. (PS)CH$_2$-II: ^{1}H NMR (CDCl$_3$) δ ((PS)CH$_2$) 5.63 (2 H, br), bound chromophore signals at δ 8.62 (2 H, br), 7.72 (2 H, br), 7.50 (3 H, br), 5.63 (2 H, br), 3.00 (6 H, s); λ_{max} = 480 nm (film); T_g = 103–107 °C. Anal. (prepared from PS having 4.5% of rings iodomethylated). Calcd: C, 89.35; H, 7.51; N, 0.56; I, 2.56. Found: C, 88.85; H, 7.45; N, 0.57; I, 2.53.

(16) Headway Research Inc. photoresist spinner.

(17) Measured after poling and SHG experiments with a Tencore Alpha-Step 200 surface profiler.

(18) Toyoseki 650 electret thermal analyzer.

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C. Ye and T. J. Marks*

Department of Chemistry and the
Materials Research Center, Northwestern University
Evanston, Illinois 60201

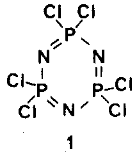
J. Yang and G. K. Wong*

Department of Physics and the
Materials Research Center, Northwestern University
Evanston, Illinois 60201

Received June 24, 1987

Magic-Angle Spinning NMR of Polyphosphazenes

Polyphosphazenes are inorganic polymers based on chains of alternating phosphorus and nitrogen atoms.[1,2] The key steps in the development of these materials were the discoveries by Allcock and co-workers of methods for converting the phosphonitrilic chloride cyclic trimer **1** into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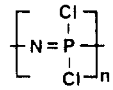
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the soluble, linear chloropolymer **2** and substitution reactions to convert **2** into a wide variety of hydrolytically stable polymers with diverse properties. These polymers are of considerable interest because of their mechanical and thermal properties, solvent resistance, and potential for providing biocompatible materials.

We are using high-resolution solid-state NMR techniques such as magic-angle spinning (MAS)[3] to study the synthesis, structure, reactivity, and dynamics of polyphosphazenes. This is the first high-resolution solid-state NMR study of polyphosphazenes, although wide-line studies of these materials have been previously reported.[4,5] In this paper we report preliminary results on the hydrolytic cross-linking of **2** and molecular dynamics in two solid elastomeric phosphazene polymers, poly(diethoxyphosphazene) (PBEP) and poly(dimethoxyphosphazene) (PBMP). This report also demonstrates the potential of MAS NMR for the study of a number of other problems in polyphosphazene chemistry.

The linear chloropolymer was synthesized by using a BCl$_3$-catalyzed melt polymerization reaction.[6] PBMP and PBEP were synthesized from the chloropolymer and purified by the methods described by Allcock and co-workers.[7] Solid-state NMR spectra were obtained by using a Chemagnetics M-100S NMR spectrometer operating at a magnetic field strength of 2.35 T. The ^{13}C spectra were obtained by using cross polarization with magic-angle spinning (CP/MAS)[8], whereas the ^{31}P spectra were obtained by using single-pulse excitation and MAS. High-power proton decoupling was used for all spectra. All ^{31}P chemical shifts are reported with respect to external 85% H$_3$PO$_4$; more positive shifts represent deshielding.

^{31}P MAS NMR has been used to examine hydrolysis and cross-linking in **2**. Figure 1a, which is a spectrum of crystalline **1**, is extremely broad and shows multiplicity patterns that appear to be consistent with heteronuclear dipole–dipole couplings to quadrupolar nuclei (i.e., ^{14}N, ^{35}Cl, and ^{37}Cl).[9] Figure 1b is the ^{31}P MAS spectrum of a solid sample of linear **2**. The chemical shift (−18 ppm) is very similar to the value reported in solution.[7] Notice that the breadth of the line has been greatly reduced with respect to that in Figure 1a. This is due to averaging of the dipolar couplings by molecular motion, consistent with the elastomeric nature of this material.[7] One of the most important problems in polyphosphazene chemistry is maximizing the yield of soluble, linear **2** and minimizing that of insoluble, cross-linked **2**, which cannot be converted to hydrolytically stable polymers.[10] The ^{31}P spectrum of a sample of the cross-linked polymer, which formed during the uncatalyzed thermal polymerization of **1**, is shown in Figure 1c. This spectrum does not show any additional peaks that can be attributed to cross-linking sites. We believe that such sites are not observed in Figure 1c because of their low concentration and the relatively modest number of scans taken (24).

An important cross-linking mechanism in the synthesis of **2** is thought to involve water—either as an impurity in **1** or abstracted from the glass reaction tube. In order to investigate this hypothesis and to assess the potential of solid-state NMR to identify reaction pathways in polyphosphazenes, we performed the following experiment: A sample of insoluble **2** was swollen in benzene and approximately 0.1 equiv (on a per Cl basis) of water was added. After the mixture was refluxed for several hours, the polymer was isolated, and the ^{31}P MAS spectrum shown in Figure 1d was obtained. This spectrum differs markedly from Figure 1c in that there is a peak at −11 ppm in Figure 1d. The partially hydrolyzed sample of insoluble **2** was then heated for 14 h in a closed container at 230 °C, and a friable residue was obtained. The spectrum of this residue is shown in Figure 1e. As can be seen in Figure 1e, heating produces a new peak at −29 ppm and essentially eliminates the peak at −11 ppm, which was observed prior

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