Molecular Motion of Phosphazene-Bound Nonlinear Optical Chromophores

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Received April 4, 1995[⊗]

ABSTRACT: The behavior of nonlinear optical (NLO) groups linked to a polyphosphazene chain was studied by solid-state NMR spectroscopy. A series of poly(organophosphazenes) was prepared with the general structure $[NP(RN(CH_3)C_6H_4NO_2)_x\{O(CH_2CH_2O)_2CH_3\}_{2-x}]_n$, where $x < 0.5$ and the spacer group R = $O(CH_2)_2$, $O(CH_2)_6$, or OCH_2(2-pyrrolidino), in addition to the stilbene-containing polyphosphazene $[NP\{O(CH_2)_2N(CH_3)C_6H_4CH{=}CHC_6H_4NO_2\}_{0.4}\{O(CH_2CH_2O)_2CH_3\}_{1.6}]_n$. Structural characterization for the above polymers was achieved by ^{31}P NMR spectroscopy, differential scanning calorimetry, and elemental microanalysis. (Methoxyethoxy)ethoxy (MEE) cosubstituent poly(organophosphazenes) bearing $O(CH_2)_2N(CH_3)C_6H_4NO_2$ and $O(CH_2)_6N(CH_3)C_6H_4NO_2$ side groups were selected for study by room-temperature and variable-temperature solid-state ^{31}P and ^{13}C NMR spectroscopy. The variable-temperature solid-state ^{13}C NMR spectra indicated that the use of a longer spacer group between the polymer backbone and the aromatic portion of the NLO side group lowers the temperature at which chromophore motion is quenched. This implied that the use of such structures may accelerate the randomization of NLO side group orientation at ambient temperatures following poling. This behavior was mirrored in the solid-state variable-temperature ^{31}P NMR spectra, which suggested that side chain and polymer backbone motion may be coupled.

Introduction

A growing interest exists in the design and synthesis of polymeric materials for use in nonlinear optical (NLO) applications.[1] The synthesis of such materials has been accomplished in two ways. First, a small-molecule chromophore may be dissolved in a glassy[2,3] or crystalline polymer.[4] Second, NLO-active groups can be covalently linked to macromolecules by either radiative cross-linking[5] to a host polymer, derivatization of a functionalized polymer,[6,7] or macromolecular substitution reactions.[8] The occurrence of NLO effects is associated with an intramolecular charge transfer process which can exist in organic molecules with a donor−acceptor moiety. For second harmonic generation (SHG), or the conversion of light of frequency ν to light of frequency 2ν, noncentrosymmetric alignment of the donor−acceptor moieties (usually by electric field poling) is required. In the absence of a method of stabilization of the alignment, SHG is lost quickly as orientational randomization of the donor−acceptor moieties occurs.[8] The rate of orientational randomization is a function of the quasi liquidity in the polymeric material, which in turn is connected with macromolecular flexibility and the free volume. Randomization of the NLO components is normally considered to be a detrimental property unless the material forms part of a device in which electric field generated alignment forms part of a working component.[1e]

Methods used to stabilize SHG in host−guest systems and in polymers that incorporate NLO groups as side chains include both a "freezing in" of the alignment by cooling of the polymer or by radiative cross-linking, but these approaches generate additional challenges. An example of the first technique exists when the chromophore is poled in a host polymer above its T_g. "Flash cooling" to below the T_g is then carried out in an attempt to maintain the chromophore orientation. This method yields only modest success. For example, when 4-(dimethylamino)-4′-nitrostilbene is dissolved in poly(methyl methacrylate) and poled at 383 K, the system loses 80% of the SHG in 12 h after the material is allowed to cool to 298 K.[2] Radiative cross-linking has been applied to polymers that contain side group NLO chromophores. For example, Tripathy et al.[5] reported considerable success in stabilizing cinnamate-derivatized NLO chromophores by irradiation with UV light while poling.

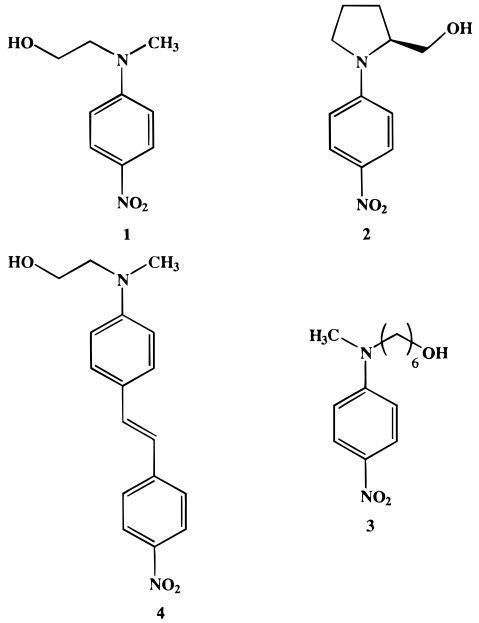
Thus, an understanding of chromophore motions in unpoled systems in the region of the T_g should yield insights into the molecular motions of poled polymers. In this work, we have attempted to obtain an insight into this phenomenon through the synthesis and solid-state NMR characterization of polyphosphazenes that bear pendent NLO chromophore side groups.

Polyphosphazenes have several advantages for the study of chromophore motion in polymeric materials. These include the following: (1) different cosubstituent groups can be readily incorporated into polyphosphazenes by macromolecular substitution, and this allows properties such as the T_g to be tailored over a broad range; (2) the relative ease of side group incorporation allows a wide variety of NLO chromophores to be covalently linked to the polymer backbone and provides a vehicle for the products to be examined by solid-state NMR; (3) the phosphorus−nitrogen backbone contains no carbon atoms; hence, ^{13}C NMR studies of pendent side chains are not complicated by the backbone elements; (4) the polymer backbone motion can be studied unambiguously by solid-state ^{31}P NMR spectroscopy. In this paper, we discuss the synthesis of mixed-substituent poly(organophosphazenes) that bear chromophores **1**−**4** (see Chart 1) and analyze the chromophore motion of polymers **8** and **9** (see Scheme 1) by solid-state variable-temperature NMR.

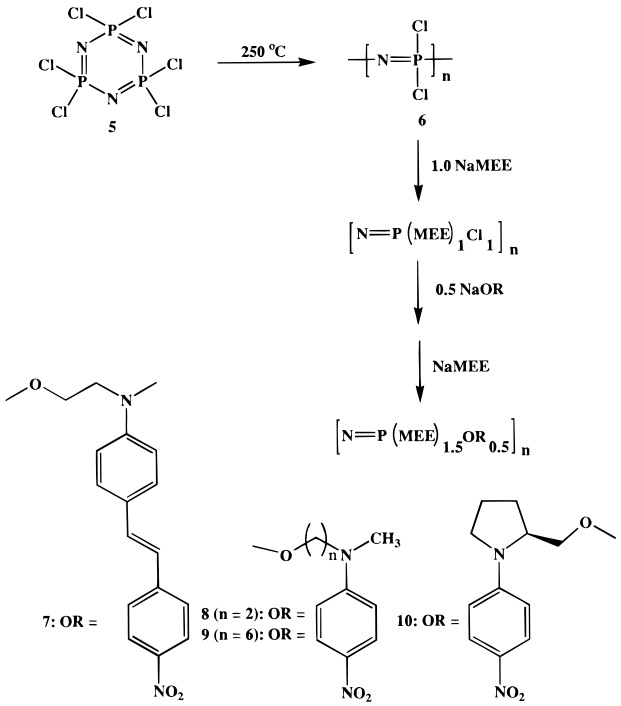
[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

0024-9297/96/2229-0233$12.00/0

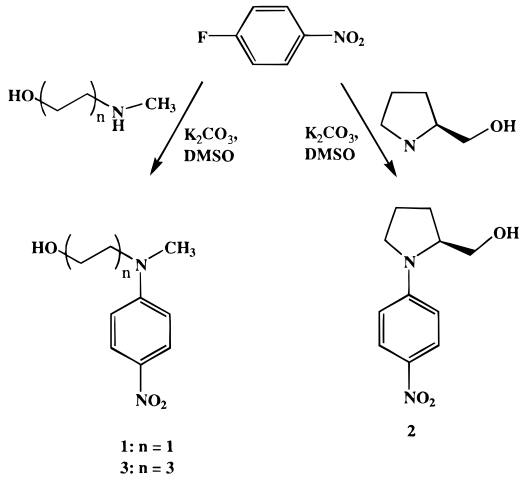
Chart 1



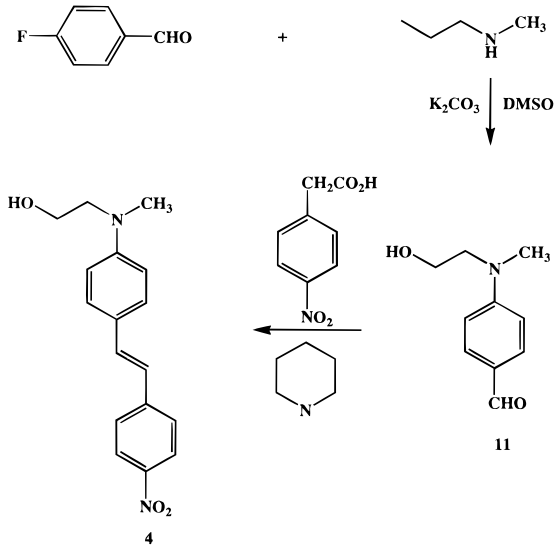
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

Side Group Synthesis. Chromophores **1**−**3** were prepared[7,9−11] by the reaction between 4-fluoronitrobenzene and the appropriate amine in DMSO solvent in the presence of K_2CO_3 as a hydrofluoride acceptor (see Scheme 2). Chromophore **4** was synthesized in two steps (see Scheme 3). First, 4-fluorobenzaldehyde was allowed to react with (*N*-methylamino)ethanol under the above conditions to give intermediate aldehyde **11**. Stilbene **4** was obtained by the condensation of **11** with 4-nitrophenylacetic acid. Chromophores **1**−**4** were characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see Experimental Section).

Polymer Synthesis. The synthetic route to high-polymeric phosphazenes **7**−**10** is shown in Scheme 1. Poly(dichlorophosphazene) (**6**) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (**5**).[12−14] The substitution reactions of **6** were carried out in three steps. The synthesis and purification of polymer **8** will be given as a representative example. Polymer **8** was prepared by allowing 1 equiv of sodium (methoxyethoxy)ethoxide to react with **6** to form a partially substituted polymer with the idealized structure $[NPCl\{O(CH_2CH_2O)_2CH_3\}]_n$. This macromolecular intermediate was then treated with 0.5 equiv of the sodium salt of **1** to replace approximately 50% of the remaining chlorine atoms. Lastly, a fully substituted, chlorine-free polymer was obtained by allowing an excess of $Na(OCH_2CH_2)_2OCH_3$ to replace all the remaining chlorine atoms to give a polymer with the idealized structure $[NP(OCH_2CH_2N(CH_3)C_6H_4\text{-}p\text{-}NO_2)_{0.5}\{(OCH_2CH_2)_2OCH_3\}_{1.5}]_n$. Total chlorine replacement and side group loadings were confirmed by the elemental analytical data (see Table 1).

This synthetic route was used for several reasons: (1) The initial addition of the sodium salt of the chromophores to poly(dichlorophosphazene) in THF resulted in the formation of an insoluble precipitate which could not be induced to undergo further reaction. (2) The use of 2,2,2-trifluoroethoxy cosubstituents (side groups that were used in earlier phases of our NLO work[8] and were found to generate soluble NLO polyphosphazenes) may bring about the displacement of NLO side groups during the second step of the substitution reaction. (3) The ^{13}C resonance of the CF_3 carbon in the trifluoroethoxy side group is a quartet centered at ca. 115 ppm, which overlaps the ^{13}C resonances of the aromatic ring in the

Table 1. Characterization Data for Polymers 7−10

polymer	cosubstituent	T_g (K)	cosubstituent loading (%)	exptl elem anal. % C	% H	% N	% Cl
7	**4**	201	20	52.14	7.26	7.04	0.008
8	**1**	211	20	43.95	6.97	7.86	0.014
9	**3**	201	20	47.55	8.43	5.29	0.031
10	**2**	209	20	49.37	7.75	7.37	0.016

NLO cosubstituent. (4) The glass transitions of (methoxyethoxy)ethoxy cosubstituent polymers **7**−**10** are easily detected by DSC. These data are essential for the study of the molecular dynamics of polymers near the glass transition temperature.

Although the (methoxyethoxy)ethoxy cosubstituent facilitates solid-state NMR characterization, polymers **7**−**10** were insoluble in common organic solvents after isolation from the THF dialysis. This insolubility is attributed to the high polarity of the donor−acceptor side chains, which may result in stacking of the NLO groups in the solid state.[15,16] This behavior is similar to that found in side chain liquid crystalline polyphosphazenes.

Solid-State NMR Studies

Room-Temperature ^{13}C NMR Spectroscopy. Polymers **8** and **9** were selected for detailed characterization by variable-temperature ^{13}C and ^{31}P magic angle spinning (MAS) NMR. Since chromophore orientation is a requirement for second-order NLO polymers, the focus of this investigation was on qualitative studies of side chain and main chain dynamics. Polymers **8** and **9** were very similar, with the exception of the number of carbon atoms in the spacer unit that connects the chromophore to the main chain (2 CH_2's for **8** vs 6 CH_2's for **9**). At a given temperature, the chromophore with the longer spacer would be expected to be the more mobile species. This expectation was confirmed, but the room-temperature and variable-temperature ^{31}P NMR results indicated an additional effect. The NMR results are reported below in detail for polymer **8**. The results for polymer **9** are then explained briefly, with emphasis on the differences between the two materials.

The ^{13}C MAS NMR spectra obtained at room temperature for polymer **8** and crystalline chromophore **1** are compared in Figure 1. Peaks in the spectra of chromophores **1** and **3** were identified by comparison with solution spectra as well as by acquisition of interrupted decoupling spectra (not shown). The MAS spectrum of solid chromophore **1** showed two clear characteristics of a rigid molecule. The pairs C_3,C_5 and C_2,C_6 had different isotropic shifts due to their inequivalent locations in the unit cell. Secondly, the chemical shift anisotropy of the aromatic carbon atoms was unaveraged, as reflected by the intensities of the spinning sidebands. These features were absent from the ^{13}C MAS spectrum of polymer **8** at 298 K (Figure 1). Note that each pair C_3,C_5 and C_2,C_6 in the polymer collapsed to a single line and that the sideband intensity is negligible. These results demonstrate that reorientation of the aromatic group in the macromolecular system with respect to its local chemical environment was rapid on a time scale of ca. 5 ms and that its reorientation with respect to the direction of the applied magnetic field was rapid on a time scale of ca. 200 μs. These time scales are the reciprocals of the resonance frequency differences for the 2 and 6 carbons and the MAS spinning speeds, respectively.

Variable-Temperature ^{13}C NMR Spectroscopy. Variable-temperature ^{13}C MAS spectra of polymer **8**

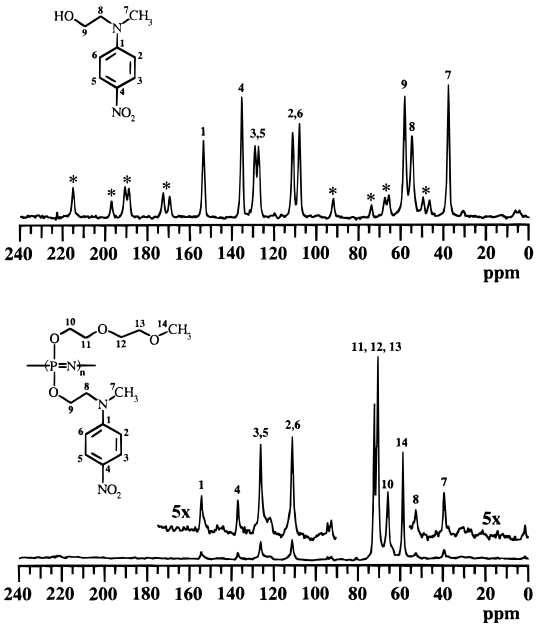


Figure 1. Assigned ^{13}C MAS NMR of chromophore **1** and the chromophore-incorporated polymer **8** at room temperature. Asterisks denote spinning sidebands.

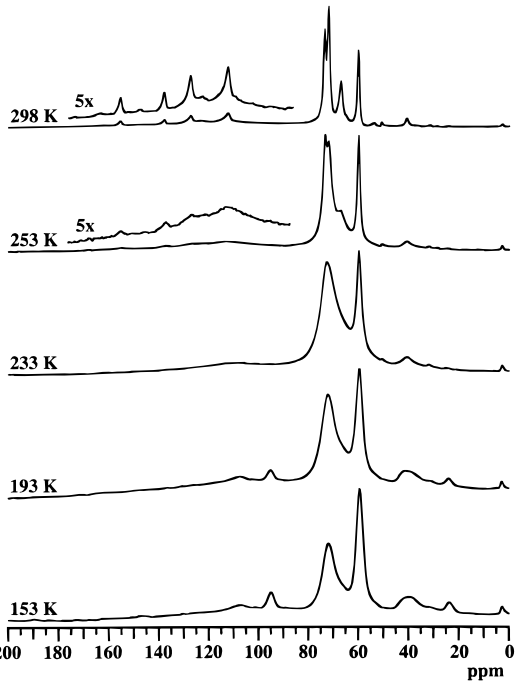


Figure 2. Variable-temperature ^{13}C Bloch decay MAS NMR spectra of polymer **8** (4 s pulse delay, 400 transients). The expanded region shows the broadening of the aromatic chromophore signals with decreasing temperature.

were obtained using both Bloch decay and cross polarization[17] over a temperature range of 153−298 K and are reported in Figures 2 and 3, respectively. These two different types of spectra should be regarded as complementary. At lower temperatures, where the chromophore is immobile, the ^{13}C T_1's of the aromatic carbon atoms were longer than the pulse delay used in the

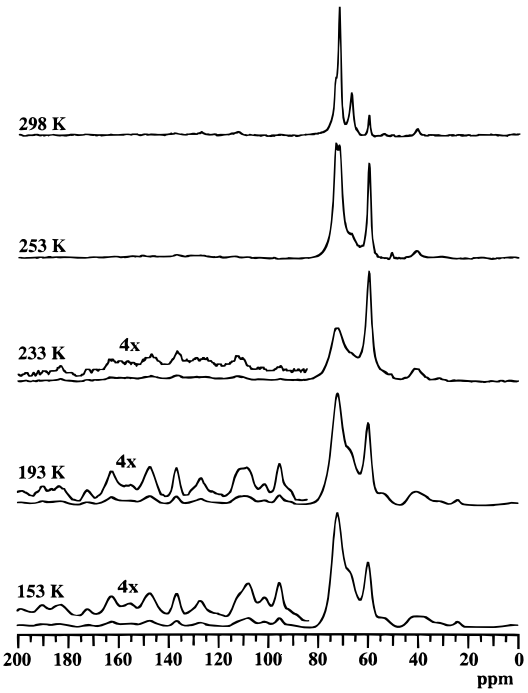


Figure 3. Variable-temperature ^{13}C CP-MAS NMR spectra of polymer **8** (4 ms contact time, 2 s pulse delay, 800 transients). The expanded region shows a reappearance of the aromatic chromophore signal at 193 K.

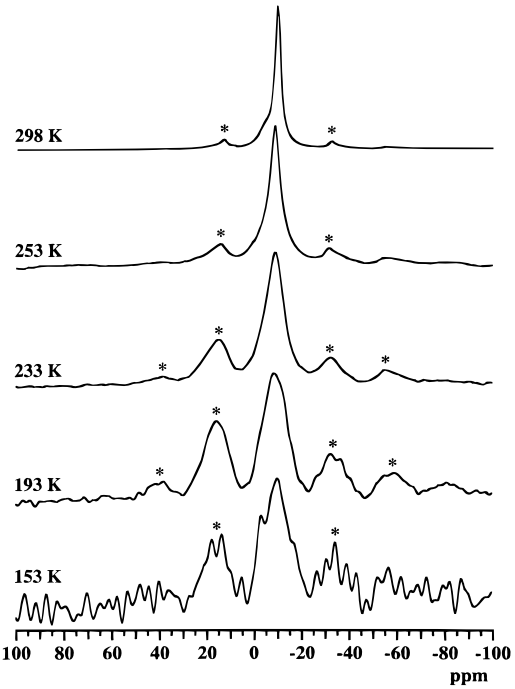


Figure 4. Variable-temperature ^{31}P Bloch decay MAS NMR spectra of polymer **8** (10 s pulse delay, 64 transients). Spinning sidebands are denoted by asterisks.

Bloch decay spectra, and the signals from these carbon atoms were absent because of saturation (see Figure 2). At higher temperatures, the mobility of the chromophore precluded efficient cross polarization of the aromatic carbons, but aromatic isotropic peaks and spinning sidebands were seen clearly at lower temperatures in the cross polarization spectra (see Figure 3). The signals from the aromatic carbon atoms were very broad at intermediate temperatures in both types of spectra. In the Bloch decay spectrum at 253 K, the aromatic signals were barely recognizable, and they were broad in CP spectra above ca. 193 K. This

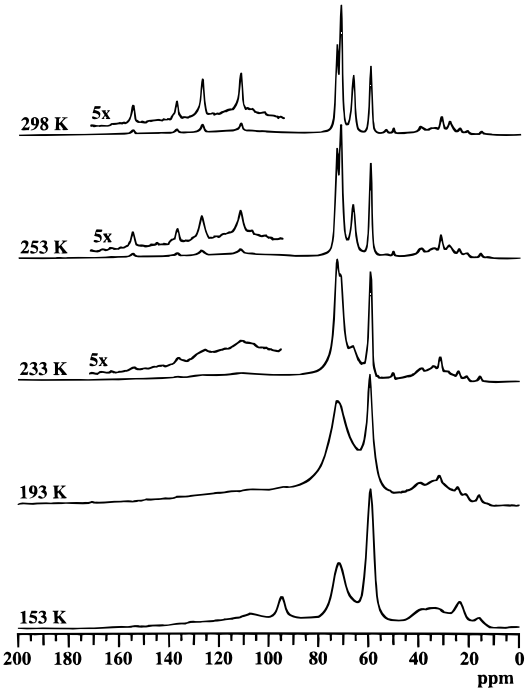


Figure 5. Variable-temperature ^{13}C Bloch decay MAS NMR spectra of polymer **9**. Broadening of the aromatic chromophore signals was seen at a lower temperature than for polymer **8**.

behavior is well known in MAS NMR studies of mobile materials,[18,19] and it was used previously to characterize the time scale of chromophore reorientation for a simple small-molecule doped polymer system.[20] Magic angle spinning provides coherent averaging of chemical shift anisotropy, while molecular motion is an incoherent averaging process. When both effects are present and operate at similar time scales, a conflict arises such that line narrowing does not occur. The aromatic ring in polymer **8** underwent large-amplitude motion on a time scale of ca. 200 μs in the vicinity of 233 K. The broadening of the 65−75 ppm signals from the MEE side chains at 233 K and below was attributed to a freezing in of conformational inequivalence.

Variable-Temperature ^{31}P NMR Spectroscopy. The variable-temperature ^{31}P MAS spectra of polymer **8** (Figure 4) were readily assigned based on previous studies of phosphazene polymers in solution and in the solid phase.[21−23] Most of the ^{31}P nuclei resonated at an isotropic shift of −8.0 ppm, but those with one MEE side chain and one chromophore side chain provided the downfield shoulder at −2.9 ppm. Careful line fitting indicated that the chromophore content is 8% of all side groups or 16% of all main chain units. Small spinning sidebands were evident at 298 K, but these became much more pronounced when the sample was cooled to 233 K and lower temperatures, which indicated that the polymer backbone became rigid at this temperature.

The corresponding ^{13}C and ^{31}P spectra for polymer **9** (Figures 5−7) showed the same overall behavior. The notable difference was that the longer spacer group lowered by 30−40 deg the temperature at which chromophore and main chain motion were quenched relative to the counterpart with a shorter spacer. Again, good correlation existed between the temperature profiles observed for the ^{13}C and ^{31}P spectra, and this suggested that the chromophore and main chain motions may be coupled processes.

Conclusions

Several conclusions can be drawn from the room-temperature and variable-temperature solid-state ^{31}P

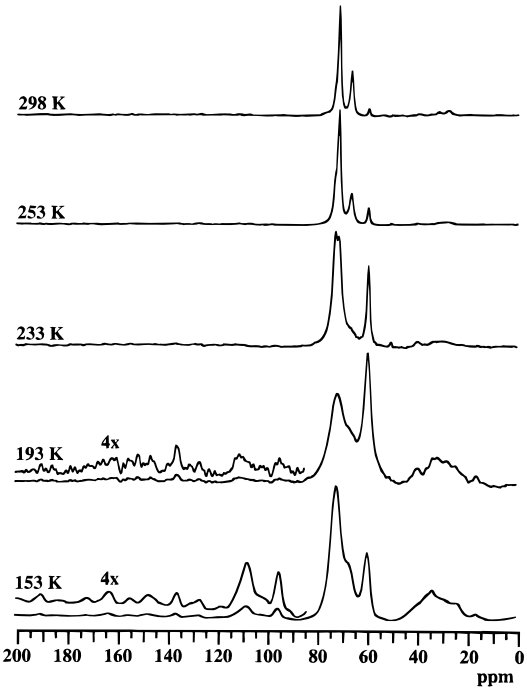


Figure 6. Variable-temperature ^{13}C CP-MAS NMR spectra of polymer **9**. The expanded region shows a reappearance of the aromatic chromophore signal at a temperature 20 deg lower (153 K) than for polymer **8**.

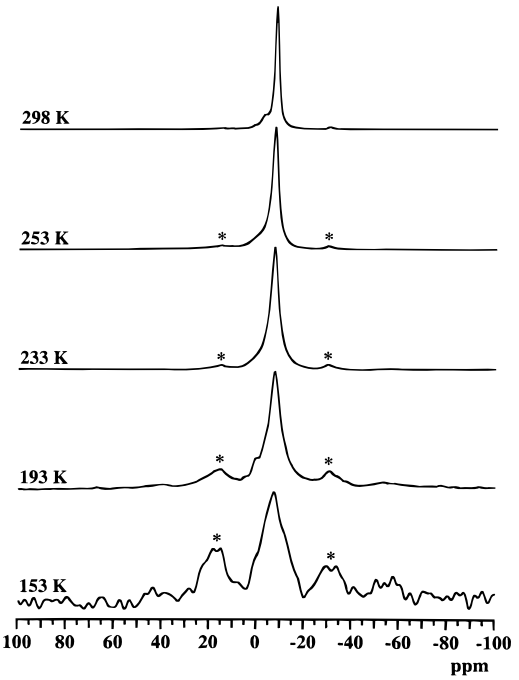


Figure 7. Variable-temperature ^{31}P Bloch decay MAS NMR spectra of polymer **9**. The spinning sidebands, denoted by asterisks, appear at a lower temperature (193 K) than for polymer **8**.

and ^{13}C NMR spectra. The room-temperature CP/MAS NMR spectrum of free chromophore **1** showed features characteristic of a rigid molecule, such as spinning sidebands and different isotropic shifts of carbon atom pairs C_3,C_5 and C_2,C_6. When chromophore **1** was attached to a flexible polyphosphazene backbone as in polymer **8**, all the characteristics of a rigid molecule are lost and the aromatic group was found to be undergoing reorientation with respect to its local chemical environment on a time scale of ca. 5 ms. Moreover, chromophore reorientation with respect to the direction of the applied magnetic field is rapid, being on a time scale of 200 μs.

Variable-temperature solid-state ^{31}P and ^{13}C NMR of polymer **8** yielded additional insights into the backbone and side chain motions, respectively. The use of Bloch decay in the solid-state variable-temperature ^{13}C NMR spectra showed that the aromatic chromophore motion was quenched at ca. 233 K, which was confirmed by the complementary technique of cross-polarized ^{13}C NMR. A similar effect of temperature on the polymer backbone was noted at ca. 233 K when polymer **8** was subjected to solid-state variable-temperature ^{31}P NMR.

Lastly, when polymer **9** was analyzed under the same conditions, both backbone and side chain motion were found to be quenched at ca. 30−40 deg lower than for polymer **8**. This behavior was attributed to the more flexible spacer group in polymer **9**. However, because both chromophore and polymer backbone motion are affected at the same temperature in polymers **8** and **9**, chromophore and backbone motion may be a coupled process.

From the viewpoint of retention of NLO group orientation following poling, the results suggest the following: As expected, a polymer which possesses a longer spacer unit between the aromatic portion of the NLO side group and the backbone gives a material in which the NLO side groups are more mobile than when a shorter spacer group is present. Second, because polymer backbone and side group motions may be coupled, the use of a flexible skeletal system and mobile side groups to solubilize the polymer may be counterproductive with respect to the retention of NLO properties after poling. Thus, for the polymers studied, polymer **8** must be cooled to below 233 K and polymer **9** below 193 K before rapid chromophore randomization is eliminated, which implies a higher room-temperature mobility for the NLO groups of polymer **9**. Of course, the more flexible, and more rapidly randomized system may, in fact, be more appropriate for use in applications where the switching on and off of the poling field is an integral feature of the device.

Experimental Section

Hexachlorocyclotriphosphazene **5** (provided by Ethyl Corp.) was recrystallized from heptane and sublimed (60 °C, 0.05 mmHg) before use. Poly(dichlorophosphazene) (**6**) was prepared according to a previously published procedure.[6−8] Tetrahydrofuran was distilled from sodium benzophenone under an atmosphere of dry argon. (Methoxyethoxy)ethanol was distilled from calcium hydride before use. The other reagents (Aldrich, Lancaster, and Pfaltz & Bauer) were used as received. All manipulations of chlorophosphazene reagents before substitution reactions were carried out under an inert atmosphere of dry argon by using standard Schlenk and drybox techniques. Dialysis was accomplished with Spectra-Por cellulose membranes (MW cutoff 12 000−14 000, VWR).

Solution-state high-field ^{31}P (146 MHz), ^{13}C (90 MHz,) and ^{1}H (360 MHz) NMR spectra were obtained with a Bruker WM360 spectrometer. High-field solution-state ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained with a Bruker AM300 spectrometer. Solution-state ^{13}C (50 MHz) and ^{1}H (200 MHz) NMR spectra were also obtained with a Bruker WP200 spectrometer or a Bruker ACE200 spectrometer. Both ^{13}C and ^{31}P NMR spectra were proton decoupled unless otherwise specified. Liquid-state ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. Solution-state ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane.

Elemental analyses were by Galbraith Laboratories (Knoxville, TN). Chemical ionization (CI) mass spectra were obtained with a Kratos MS-25 spectrometer. Electron-impact (EI) mass spectra were obtained with the use of a Kratos MS-

9/50 spectrometer. Glass transition temperatures were determined by differential scanning calorimetry using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Heating rates of 10−40 °C/min under a nitrogen atmosphere were used.

Room-temperature ^{13}C MAS NMR spectra of polymers **8** and **9** and chromophores **1** and **3** were acquired on a Chemagnetics CMX-360 spectrometer operating at 90.5 MHz for ^{13}C. Single-pulse (Bloch decay) excitation experiments were performed on the polymer samples while spinning at 2000 Hz. Cross polarization experiments were carried out with the chromophore samples spinning near 5000 Hz. ^{13}C and ^{31}P variable-temperature studies on polymers **8** and **9** were performed on a Chemagnetics CMX-300 instrument with the samples spun at a controlled rate of 2700 Hz. The samples were cooled to −120 °C and were then incrementally raised in temperature with at least 5 min of equilibration time before the first experiment. Reproducible results without any detectable hysteresis were obtained from multiple temperature cycles. Both single-pulse (10 s recycle delay) and CP experiments (4 ms contact time, 1 s recycle delay) were acquired in the variable-temperature study. Reduction of background signal from the Vespel MAS spinning module was accomplished by the use of composite excitation pulse sequences[24] in all CP and Bloch decay experiments.

Synthesis of 4-[(2-Hydroxyethyl)methylamino]nitrobenzene (1). Compound **1** was prepared by a modified literature procedure.[7,9−11] 4-Fluoronitrobenzene (10.0 g, 70.9 mmol) and K_2CO_3 (10.0 g, 70.9 mmol) were added to DMSO (100 mL). (*N*-Methylamino)ethanol (6.0 g, 80 mmol) was added over 10 min with stirring. The reaction mixture was warmed to 60 °C for 12 h, after which it was poured into water (500 mL). The yellow precipitate was collected by vacuum filtration, washed with water (500 mL), and recrystallized from toluene. ^1H NMR ($CDCl_3$, 200 MHz) 8.1 (d, 2H), 6.6 (d, 2H), 3.85 (q, 2H), 3.6 (t, 2H), 3.1 (s, 3H), 2.0 ppm (t, 1H). ^{13}C NMR ($CDCl_3$) 153.8, 137.0, 126.2, 110.4, 60.0, 54.4, 39.4 ppm. MS *m*/*z* calcd 196, *m*/*z* found 197 (CI, MH^+). Yield 89%. Mp 101.5−102.5 °C.

Synthesis of 1-(4-Nitrophenyl)-2-pyrrolidinemethanol (2)[25] and 4-[(6-Hydroxyhexyl)methylamino]nitrobenzene (3). Compounds **2** and **3** were prepared in a manner similar to compound **1**, with the use of (S)-(+)-pyrrolidine-2-methanol for **2** and 6-(methylamino)hexanol for **3**. Characterization for **2**: Yield 53%. ^1H NMR (300 MHz, $CDCl_3$) 8.1 (2H, d, $J = 9$ Hz), 6.6 (2H, d, $J = 9$ Hz), 4.0 (1H, q, br), 3.7 (1H, m), 3.6 (2H, m), 2.1 (4H, m), 1.5 ppm (1H, t, $J = 6$ Hz). ^{13}C NMR (DMSO-d_6) 151.8, 135.2, 125.9, 111.2, 60.5, 60.3, 48.3, 27.7, 22.4 ppm. Mp 114−116 °C (lit. mp, 116 °C). MS *m*/*z* calcd 222, *m*/*z* found 222 (EI, M^+). Characterization for **3**: ^1H NMR (300 MHz, $CDCl_3$) 8.1 (2H, d, $J = 8$ Hz), 6.6 (2H, d, $J = 8$ Hz), 3.6 (2H, q, $J = 6$ Hz), 3.4 (2H, t, $J = 7$ Hz), 3.1 (3H, s), 1.7 (4H, m), 1.6 (4H, m), 1.2 ppm (1H, t, $J = 5$ Hz). ^{13}C NMR (90 MHz, $CDCl_3$) 153.5, 145.7, 126.3, 110.1, 62.7, 52.6, 38.7, 32.6, 26.9, 26.8, 25.6 ppm. MS *m*/*z* calcd 252, *m*/*z* found 252 (EI). Anal. Calcd: C, 61.90; H, 7.94; N, 11.11. Found: C, 62.01; H, 8.19; N, 10.88.

Synthesis of 2-[Methyl[4-[2-(4-nitrophenyl)ethenyl]-phenyl]amino]ethanol (4). Stilbene **4** was synthesized according to a literature procedure.[26] ^1H NMR ($CDCl_3$, 300 MHz) 8.2 (2H, d, $J = 9$ Hz), 7.6 (2H, d, $J = 9$ Hz), 7.4 (2H, d, $J = 9$ Hz), 7.2 (1H, d, $J = 16$ Hz), 6.9 (1H, d, $J = 16$ Hz), 6.8 (2H, d, $J = 9$ Hz), 3.9 (2H, q, $J = 6$ Hz), 3.6 (2H, t, $J = 6$ Hz), 3.1 (3H, s), 1.65 ppm (1H, t, $J = 6$ Hz). ^{13}C NMR (DMSO-d_6) 145.2, 145.0, 128.6, 126.2, 124.0, 123.4, 120.7, 111.6, 58.1, 54.0, 38.5 ppm. MS *m*/*z* calcd 298.1317, *m*/*z* found 298.1321.

Synthesis of 4-[(2-Hydroxyethyl)methylamino]benzaldehyde (11). Aldehyde **11** was prepared according to a literature procedure.[26] ^1H NMR ($CDCl_3$, 300 MHz) 9.7 (1H, s), 7.7 (2H, d, $J = 8$ Hz), 6.8 (2H, d, $J = 9$ Hz), 3.9 (2H, d, $J = 6$ Hz), 3.6 (2H, d, $J = 6$ Hz), 3.1 (3H, s), 1.6 ppm (1H, br). ^{13}C NMR ($CDCl_3$, 75 MHz). MS *m*/*z* calcd 196, *m*/*z* found 196 (EI).

Synthesis of Polymers 7−10. The synthesis of polymer **8** will be given as a representative example. Fifty milliliters of a solution of sodium (methoxyethoxy)ethoxide (prepared from (methoxyethyl)ethanol (2.06 g, 17.2 mmol) and sodium hydride (0.41 g, 17.2 mmol)) in THF (100 mL) was added over 2 min to a warm solution of poly(dichlorophosphazene) (1.0 g, 8.6 mmol) in THF (500 mL), and the solution was stirred at 40 °C for 2 h. Then the sodium salt of **1** (prepared from alcohol **1** (1.68 g, 4.3 mmol) and NaH (0.10 g, 4.3 mmol) in THF (50 mL)) was added over 2 min, and the solution was again stirred at 40 °C for an additional 2 h. Finally, 50 mL of the solution of sodium (methoxyethoxy)ethoxide was added, and the solution was stirred overnight at room temperature. The entire reaction mixture was dialyzed against water for 4 days and then against THF for 7 days. The polymer was isolated by rotary evaporation followed by vacuum drying at 50 °C overnight.

Acknowledgment. H.R.A. and C.G.C. thank the Office of Naval Research for the support of this work through Grant No. N00014-91J-1194. T.W.S., S.T.-M., and J.F.H. thank the Office of Naval Research for Grant No. N00014-91-J-1475.

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MA950452+