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## Second-Order Nonlinear Optical Poly(organophosphazenes): Synthesis and Nonlinear Optical Characterization

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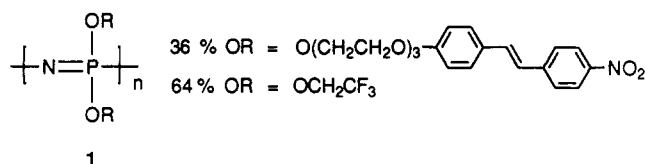
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**ABSTRACT:** The synthesis and second-order nonlinear optical properties of a series of mixed-substituent poly(organophosphazenes) that possess covalently attached donor-acceptor-substituted, conjugated moieties are reported. The mixed-substituent polymers have the general structure  $[\text{NP}(\text{OCH}_2\text{CF}_3)_x(\text{OR})_y]_n$ , where  $\text{OR} = \text{O}(\text{CH}_2\text{CH}_2\text{O})_k\text{C}_6\text{H}_4(\text{CH}=\text{CH})_m\text{C}_6\text{H}_4\text{NO}_2$ , where  $k = 1-3$  and  $m = 1-3$ ,  $\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CN}$ ,  $\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{NO}_2$ , and  $\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$  and  $x + y = 100\%$ . Model compound studies were carried out with the cyclic trimers  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_3$  and  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_3$ , where  $\text{OR} = \text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$ . Molecular structural characterization for the high polymers was achieved by  $^1\text{H}$  and  $^{31}\text{P}$  NMR, infrared, and UV-visible spectroscopy, gel permeation chromatography, and thermal analysis. The second-order nonlinear optical properties of polymer films were evaluated by second-harmonic generation. Alignment of the nonlinear optical groups was achieved by application of an electric field by a corona discharge. The second-order nonlinear coefficients,  $d_{33}$ , of the polymer films were in the range  $d_{33} = 4.1-34 \text{ pm/V}$  and were determined by a Maker fringe analysis of the data. The second-harmonic generation behavior decayed following removal of the electric field. The variation in the  $d_{33}$  values was correlated to the molecular structure and the percent incorporation of the chromophores.

Considerable interest exists in the development of new nonlinear optical (NLO) polymeric materials with large electrooptic coefficients for use in the field of optoelectronics.<sup>1</sup> The occurrence of second-order effects in organic materials has been found to be associated with a large intramolecular charge transfer along a conjugated framework from a donor to an acceptor moiety.<sup>1</sup> In a polymeric nonlinear optical material, the polymer can function either as a simple host matrix into which the nonlinear optical molecule is doped<sup>2</sup> or as a carrier backbone to which the molecule is covalently attached.<sup>3</sup> The noncentrosymmetric and unidirectional alignment of the nonlinear optical molecules in both approaches is achieved by heating the polymer to its glass transition temperature where the chains have reorientational mobility, followed by the application of a strong electric field. Of the two, the second approach is the preferred, due to the enhanced stability of the molecular alignment and the high concentrations of the nonlinear optical chromophore which can be achieved. This present work involves the synthesis and nonlinear optical properties of phosphazene macromolecules that possess covalently attached donor-acceptor-substituted, conjugated moieties.

Polyphosphazenes comprise a broad class of macromolecules with the general formula  $(\text{NPR}_2)_n$ .<sup>4,5</sup> The specific physical or chemical properties of these polymers are imposed by the structure of the organic, inorganic, or organometallic side group. Recently we reported the synthesis and second-order nonlinear optical response of polymer 1, a polyphosphazene with a nitrostilbene unit covalently linked to the polymer backbone through a tris(ethyleneoxy) spacer group.<sup>6</sup> Polymer 1 was a prototype which offered many opportunities for further tailoring of the molecular structure to generate an optimum combi-



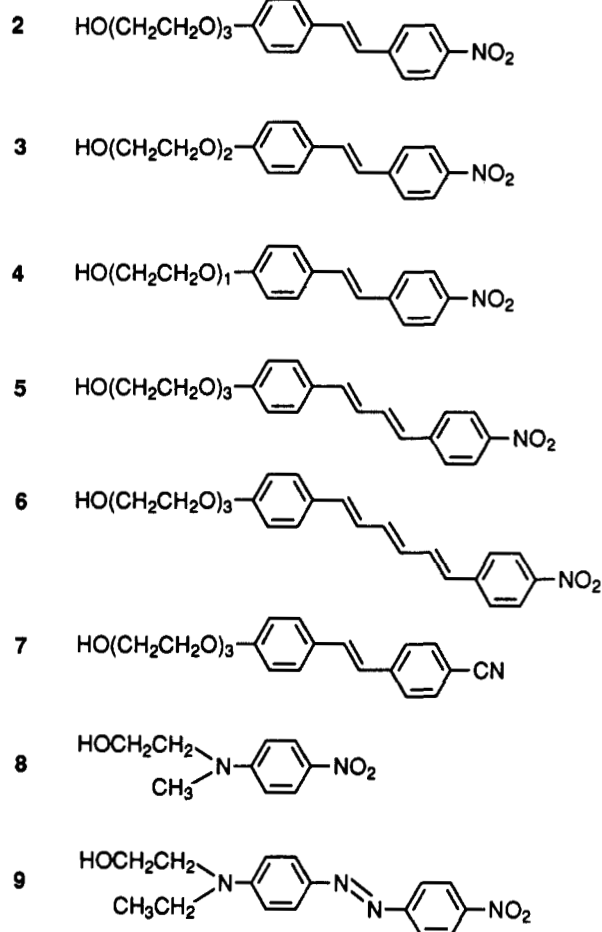
nation of nonlinear optical and physical properties.

In this paper we discuss the synthesis of mixed-substituent poly(organophosphazenes) that bear chromophores 2-9 (Chart I) as pendent side chains. Variations in the molecular structure of the chromophores were explored to include changes in the extent of  $\pi$ -conjugation, the donor and acceptor substituents, and the length of the connecting ethyleneoxy spacer group. The nonlinear optical properties of these poly(organophosphazenes) were investigated by using second-harmonic generation measurements, and the polymers' electrooptic properties were evaluated. The discussion will address the relationship between the nonlinear optical behavior of the polymers and both the percent incorporation and the molecular structure of the chromophores.

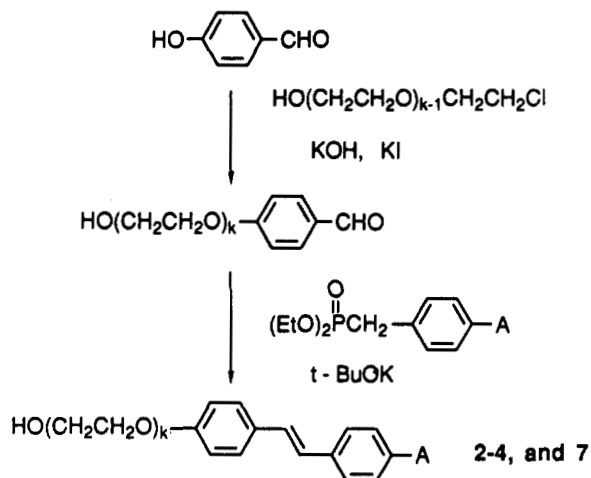
### Results and Discussion

**Synthesis and Characterization of Side-Group Units.** The synthesis of 2-8 is illustrated in Schemes I-IV. Compound 9, 4-[ethyl(2-hydroxyethyl)amino]-4'-nitroazobenzene, was commercially available as the dye Disperse Red 1. Compounds 2-7 were prepared by the use of Wittig and Horner-Emmons-Wadsworth Wittig methodologies.<sup>7</sup> The first step in the synthesis of 2-7, as shown in Scheme I, involves the reaction of 4-hydroxybenzaldehyde with chloroethanol derivatives. The benzaldehyde product was then allowed to react with diethyl

Chart I



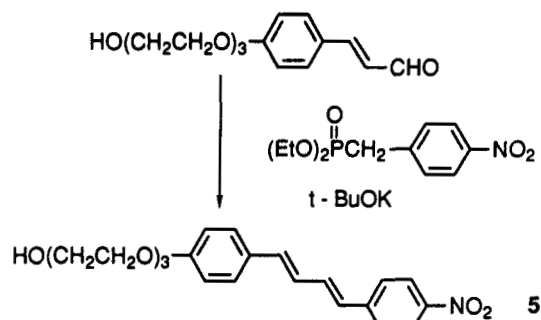
Scheme I



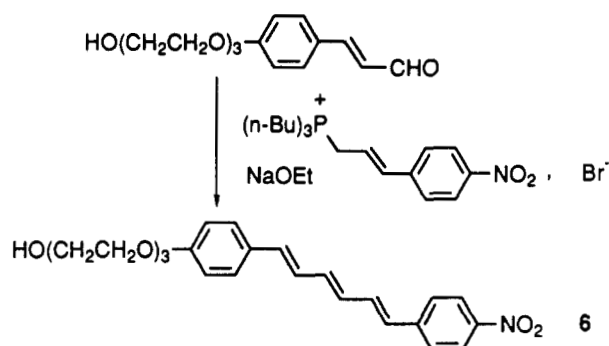
- 2  $k = 3, \text{A} = \text{NO}_2$
- 3  $k = 2, \text{A} = \text{NO}_2$
- 4  $k = 1, \text{A} = \text{NO}_2$
- 7  $k = 3, \text{A} = \text{CN}$

(4-substituted benzyl)phosphonate in the presence of potassium *tert*-butoxide to yield the stilbene side groups 2-4 and 7. For compounds 2-4 the para substituent was a nitro group, while in 7 the para substituent was a cyano group. The diene 5 was prepared by the reaction of the analogous cinnamaldehyde derivative<sup>8</sup> with diethyl (4-

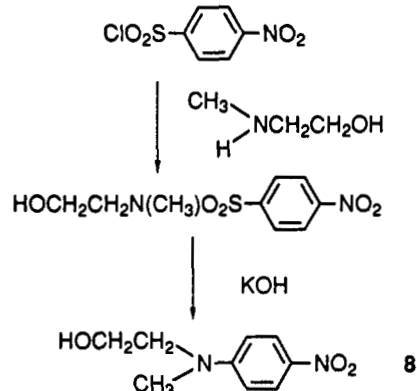
Scheme II



Scheme III

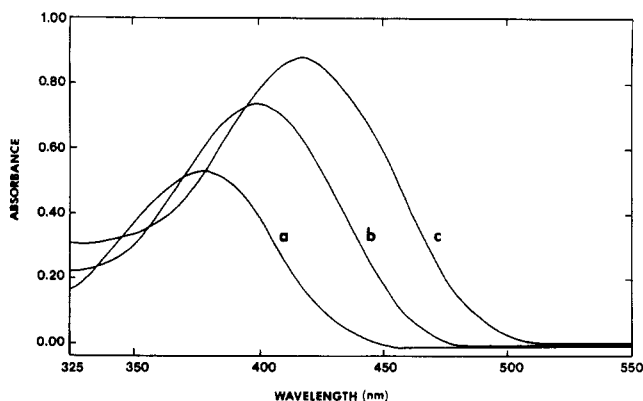


Scheme IV

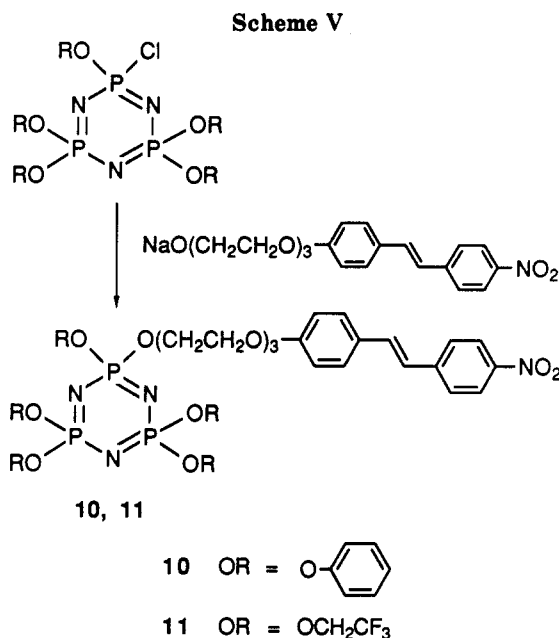


nitrobenzyl)phosphonate in the presence of potassium *tert*-butoxide (Scheme II), while synthesis of the corresponding triene 6 involved the reaction of the cinnamaldehyde derivative<sup>9</sup> in the presence of sodium ethoxide (Scheme III). Compound 8, *N*-methyl-*N*-(2-hydroxyethyl)-4-nitroaniline, was prepared by means of a literature procedure for a double-Smiles rearrangement (Scheme IV).<sup>10</sup>

Characterization of 2-9 was achieved by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectrometry, melting point, UV-visible and infrared spectroscopy, and elemental microanalysis. The characterization data are summarized in the Experimental Section. The *trans* conformation of the double bond in the stilbene compounds 2-4 and 7 was confirmed by  $^1\text{H}$  NMR analysis. For example, in the  $^1\text{H}$  NMR spectrum of 2, the coupling constant for the olefinic protons was 16.3 Hz, which is within the typical range of 12-18 Hz for *trans* coupling constants.<sup>11</sup> (Note that a typical range for *cis* coupling constants is 6-12 Hz.<sup>11</sup>) The *trans* conformation of all the double bonds in the diene 5 and the triene 6 was established by 500-MHz  $^1\text{H}$  NMR. The olefinic protons showed *trans* coupling constants in the range of 14.8-15.5 Hz and *s-trans* coupling constants in the range of 10.0-10.7 Hz.<sup>11</sup> In addition, the  $^{13}\text{C}$  NMR spectra of the stilbene and polyene compounds indicated



**Figure 1.** UV-visible spectra of side-group compounds measured in tetrahydrofuran: (a) stilbene compound 2; (b) diene compound 5; (c) triene compound 6.



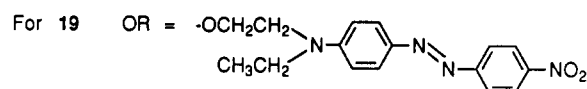
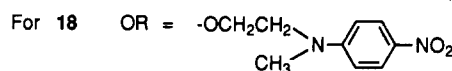
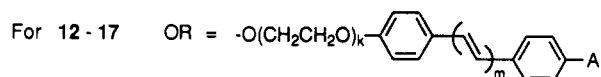
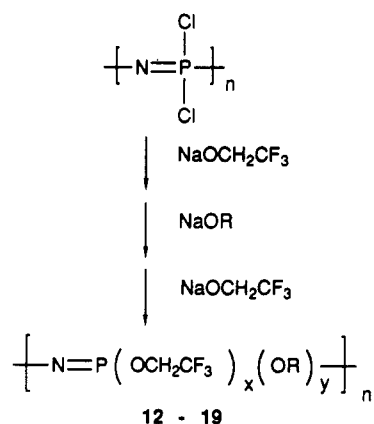
the presence of a single isomer that was consistent with the desired structures.

The UV-visible spectra of the alcohols were recorded with tetrahydrofuran as the solvent. Figure 1 shows the UV-visible spectra of 2 ( $\lambda_{\max}$  378 nm,  $\epsilon$   $2.6 \times 10^4$ ), 5 ( $\lambda_{\max}$  400 nm,  $\epsilon$   $3.9 \times 10^4$ ), and 6 ( $\lambda_{\max}$  418 nm,  $\epsilon$   $4.7 \times 10^4$ ). The bathochromic shift in the  $\lambda_{\max}$  value paralleled the increase in the conjugation length of the donor-acceptor-substituted chromophore. A change in the electron-withdrawing substituent, from the nitro group in 2 to the cyano group in 7, shifted the  $\lambda_{\max}$  value from 378 to 342 nm ( $\epsilon$   $3.7 \times 10^4$ ). The UV-visible spectrum of compound 9, which has a dialkylamino electron-donating substituent and a nitro electron-withdrawing substituent connected by an azo linkage, showed the highest  $\lambda_{\max}$  value of 490 nm ( $\epsilon$   $3.1 \times 10^4$ ).

**Synthesis and Characterization of Cyclic Phosphazene Model Compounds.** Cyclic trimeric phosphazenes were used as reaction models for the linear high polymer.<sup>12</sup> The model system was simplified by use of the monofunctional trimers  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$  and  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{Cl}$ . As outlined in Scheme V, the sodium salt of 2 was allowed to react with the remaining P-Cl bond in  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$  and  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{Cl}$  to yield 10 and 11, respectively.

The structures of 10 and 11 were confirmed by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy, mass spectrometry, UV-visible

**Scheme VI**



and infrared spectroscopy, and elemental microanalysis. The characterization data are summarized in the Experimental Section. The  $^{31}\text{P}$  NMR spectrum of 10 was that of an  $\text{AB}_2$  spin system and showed a doublet of doublets resonance at 12.6 ppm, which was assigned to the phosphorus atom bearing the chromophore side chain and a phenoxy group, and a doublet of doublets resonance at 8.9 ppm, assigned to the phosphorus atoms that bear two phenoxy groups. The  $^{31}\text{P}$  NMR spectrum of 11 was consistent with a second-order  $\text{B}_2\text{A}$  spin system, with  $\nu_{\text{B}} = 17.1$  ppm and  $\nu_{\text{A}} = 16.3$  ppm.<sup>11</sup> The second-order spectrum arises from the similar nature of the alkoxy substituents on the phosphorus atoms.

The  $^1\text{H}$  NMR spectra of 10 and 11 were consistent with the target structures. In addition, for trimer 11, the olefinic protons were detected as a doublet of doublets resonance at 7.23 and 7.01 ppm, with a coupling constant of 16.4 Hz. This supported the unchanged trans conformation of the double bond. The UV-visible spectra in tetrahydrofuran of 10 and 11 both showed  $\lambda_{\max}$  at 376 nm. The results of these model reactions suggested that the corresponding substitution reactions at the phosphazene high-polymeric level should be possible and could proceed without olefin isomerization.

**Synthesis of High-Polymeric Phosphazenes.** The overall synthetic pathway to mixed-substituent polyphosphazenes 12-19 is described in Scheme VI, and the corresponding polymer structures and composition ratios are listed in Table I. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of the cyclic trimer  $(\text{NPCl}_2)_3$ , as described in earlier papers.<sup>4</sup> The substitution reactions of poly(dichlorophosphazene) were carried out in three steps. The synthesis and purification of polymer 12d will be discussed as a representative example. In the first step, sodium trifluoroethoxide was added to poly(dichlorophosphazene) to replace approximately 50% of the P-Cl bonds. In the second step, a stoichiometric deficiency of the sodium salt of 2 was allowed to react with the partially substituted polymer. In the final step, an excess of sodium trifluoroethoxide

**Table I**  
**Polyphosphazene Structures and Composition Ratios**

compd <sup>a</sup>	side-group structure <sup>b</sup>	y, <sup>c</sup> %
12a	$k = 3, m = 1, A = \text{NO}_2$	4
12b		10
12c		26
12d		36
13a	$k = 2, m = 1, A = \text{NO}_2$	4
13b		39
14a	$k = 1, m = 1, A = \text{NO}_2$	5
14b		24
14c	$k = 3, m = 2, A = \text{NO}_2$	31
15a		6
15b		19
15c		32
16	$k = 3, m = 3, A = \text{NO}_2$	17
17a	$k = 3, m = 1, A = \text{CN}$	12
17b		51
17c	—	62
18		11
19a		26
19b		33

<sup>a</sup> See Scheme VI for general polymer structure. <sup>b</sup> See Scheme VI for general side-group structure. <sup>c</sup>  $x + y = 100\%$ ;  $x/50\% + y/50\% = 2$  side groups per repeat unit.

was added to replace the remaining chlorine atoms in order to obtain a fully derivatized, hydrolytically stable polymer. This three-step synthetic procedure was necessary to generate *soluble* polymers. Polymer 12d was isolated by precipitation from the concentrated tetrahydrofuran reaction mixture into water and was purified by dialysis against methanol/water for 7–10 days.

The major hurdle in this work was the difficulty of preparation of soluble, single-substituent polyphosphazenes that contained species 2–9 only as side groups. For example, the direct addition of the sodium salt of 2 to poly(dichlorophosphazene) resulted in the formation of an insoluble, incompletely substituted polymeric precipitate. The precipitates were insoluble in refluxing tetrahydrofuran as well as warm dioxane, *N,N*-dimethylformamide, dimethyl sulfoxide, nitrobenzene, and *N*-methylpyrrolidinone. This insolubility was attributed to both the extended rigid structure and the intrinsically high polarity of the donor–acceptor-substituted conjugated side chains. Both factors may induce extensive side-group stacking<sup>13,14</sup> in the solid state and thus lead to the formation of insoluble solids. In our previous research on the synthesis of side-chain liquid crystalline polyphosphazenes, similar insolubility was found for polymers that possessed a donor–acceptor substitution pattern within the mesogenic group.<sup>14</sup> For example, the incorporation of a phenylazophenoxy mesogen that bears a nitro or cyano para substituent yielded insoluble polymeric solids. Interestingly, replacement of the nitro terminal unit by a methoxy unit, which represents replacement of an acceptor by a donor group, allowed the preparation of *soluble* liquid crystalline polymers. These results indicate that electronic factors play a dominant role in controlling the solubility of the polymeric system.

It was clear that nonlinear optical polymers that were soluble enough to permit solution fabrication into films would be accessible only by the introduction of cosubstituent groups. Thus, the preparation of soluble polymers containing species 2–9 was accomplished by the use of the polar trifluoroethoxy group as a cosubstituent. The partially substituted trifluoroethoxy polymer, prepared in the first step of the polymer synthesis (see Scheme VI), provided a polar environment for the incorporation of the chromophoric side chains. However, the maximum loading of chromophores 2–9 was limited by the solubility of the

polymeric products, as illustrated in the following examples.

First, in the series of polymers 12a–d, which contained the nitrostilbene side group 2, a soluble polymer could be prepared if the incorporation of 2 did not exceed ca. 36% (12d). Attempts to synthesize polyphosphazenes with loadings of ca. 45% resulted in the formation of incompletely substituted polymers which precipitated from the reaction mixture after the addition of the sodium salt of 2 and remained insoluble, even after the addition of the final trifluoroethoxide nucleophile. Second, a series of polymers that contained a 15–30% incorporation of the nitroanilino side group 8 was synthesized. The polymer did not precipitate from the reaction mixture. However, after isolation by precipitation techniques, the solid polymer was only sparingly soluble in tetrahydrofuran, dioxane, *N,N*-dimethylformamide, dimethyl sulfoxide, and *N*-methylpyrrolidinone. We attribute this behavior to the enhanced opportunities for side-group stacking once the polymer is in the solid state.

Thus, soluble polyphosphazenes could be prepared only by limiting the loading of the nonlinear optical side group. Hence, the side-group ratios for polymers 12d, 13b, 14c, 15c, 16, 17c, 18, and 19b represent an upper limit for the incorporation of the chromophoric side group by the use of this synthetic scheme. Note that the maximum loading of the nitro-substituted stilbene is lower than that of the analogous cyano compound, presumably a consequence of the stronger electron-withdrawing character of the nitro unit.

The effect was explored of variations in the length of the ethyleneoxy spacer group on both the loading of the chromophore and the solubility of the resultant polymer. The spacer group was needed in order to decouple the electron-withdrawing characteristics of the phosphazene backbone from those of the donor–acceptor-substituted, conjugated side chain. In our previous studies of liquid crystalline polyphosphazenes, the length of the ethyleneoxy spacer group was found to be an important factor in controlling the solubility of the polymer.<sup>14</sup> As the spacer length decreased from three to one ethyleneoxy units or, in the limiting case, to no spacer group at all, the solubility of the polymer decreased dramatically. On the basis of these results, we anticipated that the solubility of the polymer and the concentration of the nonlinear optical side group might be maximized with the use of the tris-(ethyleneoxy) spacer group. However, a comparison of polymers 12d, 13b, and 14c illustrated that the length of the spacer group had no significant effect on the maximum loading of the chromophore side group that could be achieved in a soluble polyphosphazene. Note that the spacer group length did influence the glass transition temperature, and this will be discussed in a later section.

The preparation of mixed-substituent polymers that contained cosubstituents other than trifluoroethoxy groups was also explored. This part of the investigation was carried out in an attempt to tailor the macromolecular properties, for example, glass transition temperature, solubility behavior, morphology, and film-forming ability, in order to optimize the nonlinear optical behavior.<sup>15</sup> However, the use of aryloxy cosubstituents, such as phenoxy, 4-methylphenoxy, and 3-ethylphenoxy, as well as (methoxyethoxy)ethoxy side groups yielded polymers that were insoluble or only partially soluble, thus preventing effective purification and complete characterization. These results suggest that (surprisingly) the highly polar trifluoroethoxy group is a necessary cosubstituent for the preparation of soluble polymers that contain cosubstit-

uents 2–9 as side units. Recent investigations have shown that soluble polymers can be obtained from three-substituent systems that contain trifluoroethoxy, phenoxy, and the chromophoric side groups. This synthetic modification should allow the preparation of polymers with a broader range of properties.

**Structural Proof and Properties of Polyphosphazenes.** Characterization of polymers 12–19 was achieved by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, UV–visible and infrared spectroscopy, and elemental microanalysis. The characterization data are summarized in Tables II and III. All the polymers were soluble in common organic media, such as tetrahydrofuran, acetone, or methyl ethyl ketone.

A typical  $^{31}\text{P}$  (36.23 MHz) NMR spectrum consisted of a sharp, singlet resonance at  $-8$  ppm, presumably a consequence of the similar environment at the trifluoroethoxy and ethoxy ether substituted phosphorus atoms in the mixed-substituent system. In addition, the singlet resonance indicated a high degree of chlorine replacement. This was supported by the elemental microanalysis data.

The substituent ratios of the polymers were determined by  $^1\text{H}$  NMR analysis. For polymers 12–19, the side-group ratios were estimated by a comparison of the integration of the combined aromatic and vinyl resonances, which were generally between 8.4 and 6.8 ppm, with the trifluoroethoxy resonance at 4.5 ppm.

The molecular weights of polymers 12–19 were estimated by gel permeation chromatography to be in the range  $M_n = 9.4 \times 10^4$  to  $3.2 \times 10^5$ ,  $M_w > 8.2 \times 10^5$ , with  $M_w/M_n$  values in the region of 4–14. The broad, bimodal molecular weight distribution is typical of polyphosphazenes. UV–visible spectroscopy in tetrahydrofuran showed the same trends as in the corresponding side-group compounds 2–9, with  $\lambda_{\text{max}}$  values in the range 338 (for 17a) to 468 nm (for 19b). Infrared spectroscopy of thin films cast on KBr for all of the polymers showed an intense  $\text{P}=\text{N}$  stretching vibration at  $1250$ – $1200\text{ cm}^{-1}$ . In addition, the absorbances for the  $\text{NO}_2$  unit at ca.  $1345\text{ cm}^{-1}$  (in 12–16, 18, and 19) and the  $\text{CN}$  unit at  $2222\text{ cm}^{-1}$  (in 17) were detected.

The glass transition temperature ( $T_g$ ) of the mixed-substituent polyphosphazenes 12–19 varied with both the loading of the chromophoric side chain and the length of the connecting ethyleneoxy spacer group. Species with one ethyleneoxy unit as the spacer generated the highest glass transition temperature.<sup>14</sup> The  $T_g$  values were in the range from  $-60^\circ\text{C}$  for 12a to  $+58^\circ\text{C}$  for 19a. The low  $T_g$  values are primarily a consequence of the highly flexible character of the phosphazene backbone coupled with the small steric size and high flexibility of the trifluoroethoxy cosubstituent.<sup>13</sup> The single-substituent polymer  $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$  has a  $T_g$  at  $-66^\circ\text{C}$ .<sup>16</sup> Since a high  $T_g$  is desired in order to maintain the noncentrosymmetric alignment of the side groups and the nonlinear optical character of the polymer matrix,<sup>1</sup> cosubstituents other than the trifluoroethoxy group were also studied. Sterically hindered cosubstituents, such as phenoxy or 4-phenylphenoxy groups, would be expected to raise the  $T_g$  significantly.<sup>13</sup> However, as discussed previously, the presence of these units decreases the polymer solubility. Other strategies for increasing the  $T_g$  by the incorporation of a third cosubstituent are currently underway.

In addition to a  $T_g$  transition, polymers 12a, 15c, 17b, and 17c showed a  $T(1)$  transition in the range  $40$ – $86^\circ\text{C}$ . For polymer 12a, the low loading (4%) of a nonlinear optical side chain 2 may have been insufficient to disrupt the microcrystallinity that is typical of  $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ ,

which has a  $T(1)$  between  $60$  and  $90^\circ\text{C}$  and a  $T_m$  at  $240^\circ\text{C}$ .<sup>16</sup> In a similar manner, the high loading of the nonlinear optical side chain 7 in polymers 17b and 17c (51% and 62%, respectively) may allow extensive side-group stacking<sup>13</sup> and thus induce mesomorphic behavior.<sup>14</sup> No evidence of a  $T_m$  transition was detected in any of the polymer systems.

The colors of all the polyphosphazenes corresponded to those of the chromophores employed. Thus, those polymers based on compound 7 were colorless, compounds 2–5 and 8 were yellow, compound 6 were orange, and compound 9 were red.

**Second-Order Nonlinear Optical Properties of Polyphosphazenes. Analysis of the Second-Harmonic Coefficients,  $d_{33}$ .** The second-order nonlinear optical behavior<sup>1–3</sup> of polyphosphazenes 12c, 12d, 13b, 14c, and 19b was examined. Thin films of the polymers were spin cast onto indium tin oxide (ITO) coated glass, the nonlinear optical side groups in the polymer films were aligned by corona poling, and the nonlinear optical properties were investigated by using second-harmonic generation, which is the conversion of light of frequency  $\omega$  to light of frequency  $2\omega$ . The details of the film preparation, poling conditions, second-harmonic generation measurements, and calculation of the second-harmonic coefficients are described in the Experimental Section.

The second-harmonic coefficients,  $d_{33}$ , for polyphosphazenes 12c, 12d, 13b, 14c, and 19b are listed in Table IV. These polymer samples were amenable to nonlinear optical analysis because of their amorphous morphology, which was supported by the absence of a  $T(1)$  or a  $T_m$  transition, the ability to prepare optical-quality thin films, and the ability to obtain a consistent set of refractive index and thickness data. Attempts were made to obtain  $d$  coefficients for polymers 12a, 12b, 13a, and 14a, which had lower chromophore incorporations (4–15%). However, a consistent set of refractive index data and film thicknesses could not be obtained from ellipsometric studies for these polymer samples. The reason for this is unclear at the present time and is under investigation.

The  $d_{33}$  coefficients for the nitrostilbene-substituted polymers 12c, 12d, 13b, and 14c were in the range  $4.1$ – $5.0\text{ pm/V}$ , and the  $d_{33}$  value for the nitroazobenzene-substituted polymer, 19b, was  $34\text{ pm/V}$ . For the nitrostilbene-substituted polymers, the trend in  $d_{33}$  versus loading of the chromophoric side group was well reproduced. Note that the increase in the spacer length, from one to three ethyleneoxy units, appeared to have no significant effect on the  $d_{33}$  value. For all the polymer samples, removal of the electric field was followed by a decay in the second-harmonic signal to zero within several minutes. Strategies to delay the signal decay, for example, by cross-linking the poled polymer matrix, are currently being investigated and will be discussed in a future publication.

The  $d_{33}$  coefficient for  $[\text{NP}(\text{OCH}_2\text{CF}_3)_{86\%}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_{14\%}]_n$  (20) was examined in order to investigate the contributions of the phosphazene backbone and the trifluoroethoxy side groups to the second-harmonic signal. This mixed-substituent polyphosphazene was selected for study because of its amorphous morphology, as opposed to the single-substituent polymer  $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ , which is microcrystalline.<sup>16</sup> The  $d_{33}$  coefficient of 20 was less than that of quartz. Therefore, the contributions to  $d_{33}$  from the phosphazene skeleton and the trifluoroethoxy side groups were negligible in comparison to the contribution from the chromophoric side chain.<sup>17</sup>

**Table II**  
**Polyphosphazene Characterization Data (Part 1)**

compd <sup>a</sup>	<sup>31</sup> P NMR, <sup>b</sup> ppm	<sup>1</sup> H NMR, <sup>c</sup> ppm	elem anal.		
				calcd	found
<b>12a</b>	-8.5 (s)	8.3-6.9 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	24.66	24.06
			H	2.13	2.01
			N	5.71	6.01
			Cl	0.00	<0.11
<b>12b</b>	-8.5 (s)	8.3-6.9 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	30.66	29.92
			H	2.71	2.36
			N	5.65	5.68
			Cl	0.00	<0.11
<b>12c</b>	-8.1 (s)	8.2-6.8 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	41.66	37.01
			H	3.77	3.44
			N	5.53	5.72
			Cl	0.00	0.12
<b>12d</b>	-8.3 (s)	8.3-6.9 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	46.31	43.01
			H	4.22	4.66
			N	5.48	5.13
			Cl	0.00	<0.11
<b>13a</b>	-8.5 (s)	8.3-6.9 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.7 (m, OCH <sub>2</sub> )	C	24.26	24.63
			H	2.04	1.99
			N	5.76	5.89
			Cl	0.00	<0.09
<b>13b</b>	-8.2 (s)	8.2-6.6 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.7 (m, OCH <sub>2</sub> )	C	42.39	41.07
			H	3.56	2.61
			N	8.34	6.01
			Cl	0.00	<0.24
<b>14a</b>	-8.5 (s)	8.2-6.7 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	24.79	25.25
			H	2.00	1.97
			N	5.89	6.14
			Cl	0.00	<0.09
<b>14b</b>	-8.2 (s)	8.2-6.6 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.4-4.0 (m, OCH <sub>2</sub> )	C	34.15	36.52
			H	2.61	2.60
			N	9.22	6.41
			Cl	0.00	0.08
<b>14c</b>	-8.2 (s)	8.3-6.6 (m, Ar, H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.4-4.0 (m, OCH <sub>2</sub> )	C	37.80	37.78
			H	2.86	1.90
			N	9.11	8.44
			Cl	0.00	<0.34
<b>15a</b>	-8.5 (s)	8.2-6.7 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	27.55	26.84
			H	2.40	2.20
			N	5.62	5.68
			Cl	0.00	<0.13
<b>15b</b>	-8.2 (s)	8.2-6.6 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.5 (m, OCH <sub>2</sub> )	C	34.67	35.06
			H	3.10	3.06
			N	8.30	5.64
			Cl	0.00	0.06
<b>15c</b>	-8.0 (s)	8.2-6.7 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	46.42	47.40
			H	4.19	3.96
			N	5.29	5.33
			Cl	0.00	0.03
<b>16</b>	-8.2 (s)	8.2-6.2 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	34.58	35.74
			H	3.07	3.02
			N	8.22	5.45
			Cl	0.00	0.26
<b>17a</b>	-8.5 (s)	7.8-6.9 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	33.83	32.58
			H	2.92	2.64
			N	5.72	5.69
			Cl	0.00	<0.10
<b>17b</b>	-8.2 (s)	7.8-6.7 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.5 (m, OCH <sub>2</sub> )	C	51.38	48.52
			H	4.50	3.64
			N	7.74	5.75
			Cl	0.00	0.02
<b>17c</b>	-8.1 (s)	7.7-6.7 (m, Ar H, vinyl), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3-3.6 (m, OCH <sub>2</sub> )	C	54.96	57.59
			H	4.82	3.20
			N	7.54	5.58
			Cl	0.00	<0.12
<b>18</b>	-8.3 (s)	8.0 (d, Ar H), 6.8, (s, Ar H), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.3 (m, OCH <sub>2</sub> ), 3.9 (m, NCH <sub>2</sub> ), 3.2 (s, NCH <sub>3</sub> )	C	25.18	25.07
			H	2.28	2.35
			N	7.64	7.44
			Cl	0.00	<0.12
<b>19a</b>	-8.2 (s)	8.4-6.6 (m, Ar H), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.4-3.4 (m, OCH <sub>2</sub> , NCH <sub>2</sub> ), 1.3 (br s, CH <sub>3</sub> )	C	33.91	33.95
			H	2.98	2.87
			N	14.31	10.37
			Cl	0.00	0.37
<b>19b</b>	-8.5 (s)	8.4-6.6 (m, Ar H), 4.5 (br s, OCH <sub>2</sub> CF <sub>3</sub> ), 4.4-3.3 (m, OCH <sub>2</sub> , NCH <sub>2</sub> ), 1.3 (br s, CH <sub>3</sub> )	C	37.03	36.31
			H	3.26	2.70
			N	15.14	11.70
			Cl	0.00	0.06

<sup>a</sup> See Scheme VI and Table I for structure. <sup>b</sup> In THF (locked by D<sub>2</sub>O). <sup>c</sup> In acetone-*d*<sub>6</sub>.

**Table III**  
Polyphosphazene Characterization Data (Part 2)

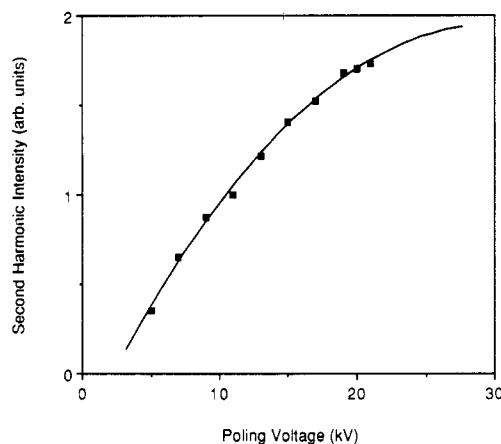
compd <sup>a</sup>	$T_g$ (T(1)), <sup>b</sup> °C	$\lambda_{max}$ , <sup>c</sup> nm	mol wt (GPC)		$M_w/M_n$ (GPC)
			$M_w$	$M_n$	
12a	-60 (40)	378	$1.1 \times 10^6$	$1.5 \times 10^5$	7
12b	-12	378	$1.2 \times 10^6$	$1.7 \times 10^5$	7
12c	19	378	$6.0 \times 10^6$	$9.4 \times 10^4$	6
12d	25	376	$1.4 \times 10^6$	$3.2 \times 10^5$	4
13a	-53	376	$1.4 \times 10^6$	$2.1 \times 10^5$	7
13b	25	371	$1.3 \times 10^6$	$2.0 \times 10^5$	6
14a	-46	373	$1.2 \times 10^6$	$1.8 \times 10^5$	7
14b	48	374	$9.2 \times 10^5$	$1.2 \times 10^5$	7
14c	54	369	$9.3 \times 10^5$	$1.4 \times 10^5$	7
15a	-45	398	$1.5 \times 10^6$	$1.9 \times 10^5$	8
15b	12	396	$1.2 \times 10^6$	$1.0 \times 10^5$	11
15c	26 (86)	396	$9.6 \times 10^5$	$1.4 \times 10^5$	7
16	25	416	$9.8 \times 10^5$	$1.2 \times 10^5$	8
17a	-1	338	$1.6 \times 10^6$	$2.5 \times 10^5$	6
17b	20 (80)	340	$1.5 \times 10^6$	$1.4 \times 10^5$	11
17c	17 (83)	339	$1.7 \times 10^6$	$1.2 \times 10^5$	14
18	-32	376	$1.7 \times 10^6$	$1.7 \times 10^5$	10
19a	58	464	$8.2 \times 10^5$	$1.2 \times 10^5$	7
19b	44	468	$1.3 \times 10^6$	$2.0 \times 10^5$	6

<sup>a</sup> See Scheme VI and Table I for structure. <sup>b</sup> Value for T(1) in parentheses. <sup>c</sup> In THF solution.

**Table IV**  
Second-Harmonic Coefficients,  $d_{33}$ , for Polyphosphazenes

compd <sup>a</sup>	$d_{33}$ , <sup>b</sup> pm/V
12c ( $y = 26\%$ )	4.1
14c ( $y = 31\%$ )	4.7
12d ( $y = 36\%$ )	5.0
13b ( $y = 39\%$ )	5.0
19b ( $y = 33\%$ )	34.0 <sup>c</sup>

<sup>a</sup> See Scheme VI and Table I for structures; polymers 12–14 arranged in order of increasing value of  $y$ . <sup>b</sup> Measurements were obtained at 10 kV. <sup>c</sup>  $d_{33}$  value was 46 pm/V at 21 kV.



**Figure 2.** Plot of  $I_{2\omega}$  versus poling voltage for polymer 19b.

The value of  $d_{33}$  for the azo-substituted polymer 19b is significantly higher than for the stilbene-substituted polymers (12c, 12d, 13b, and 14c). This is due to three factors: (1) the azo chromophore has a greater resonant enhancement due to the lower transition energy, (2) this chromophore has a larger zero-frequency second-order hyperpolarizability,  $\beta_0$ , and (3) the azo chromophore has a larger ground-state dipole moment,  $\mu$ , and, hence, a greater alignment can be achieved under the poling field.

In order to separate the contributions from each of these factors, the stilbene-substituted polymer 14c was compared with the azo-substituted polymer 19b, which had a similar concentration of the nonlinear optical side group (31% for 14c and 33% for 19b). The resonant enhancement was considered first. The spin-cast films of 14c and 19b had absorption peaks at 362 and 416 nm, respectively.

Use of these values in the two-level model<sup>2d</sup> gave second-harmonic resonant enhancements of 2.1 for 14c and 3.1 for 19b, at a fundamental wavelength of 1064 nm. Thus, a factor of 1.5 was accounted for.

In order to explain the remaining difference in the  $d_{33}$  value, it was necessary to rely on published values of  $\mu$  and  $\beta_0$  for the two chromophores, i.e., 4,4'-methoxynitrostilbene (MONS) for 14c and Disperse Red 1 (DR1) for 19b. For this comparison, three recent electric field induced second-harmonic generation (EFISH) studies of donor-acceptor-substituted chromophores were used.<sup>18</sup> However, since only ref 18a considered DR1, while MONS was discussed only in ref 18b, a cross comparison was difficult. Such cross comparison is important due to the large variations in the values of  $\mu$  and  $\beta_0$  from the different studies.

In order to obtain the ratio  $\mu^{DR1}/\mu^{MONS}$ , we have used  $\mu^{DR1}$  from ref 18a (8.7 D) and  $\mu^{MONS}$  from ref 18b (5.7 D), which gave a ratio of 1.5. The remaining factor must be accounted for by the difference in  $\beta_0$ . If the  $\beta_0$  values from refs 18a and 18b are used, the value of  $\beta_0^{DR1}/\beta_0^{MONS} = 1.2$ . However, this was a much smaller enhancement than would be expected following substitution of a dialkylamino donor for a methoxy donor. This was supported by the data in ref 18c, where an enhancement of  $\beta_0$  by about 2.3 is typically found for such a substitution. Therefore, we have used the latter ratio in our comparison.

Multiplication of all the above factors by that due to the different concentrations leads to an expected ratio of  $d_{33}(19b)/d_{33}(14c) = 5.5$ . This compares with an experimental value of 7.2. Thus, the agreement is well within the expected uncertainty limits.

The maximum attainable second-harmonic signal from sample 19b was examined. A plot of  $I_{2\omega}$  versus poling voltage for this sample is shown in Figure 2. The form of the curve is slightly different from that obtained by Eich et al.,<sup>3e</sup> with a more gentle onset of saturation. The maximum voltage applied (21 kV) was limited by the onset of arcing. The signal at this voltage corresponds to  $d_{33} = 46$  pm/V, a value that is comparable to those of other functionalized polymers reported in the literature.<sup>3d,19</sup>

The value of  $d_{33}$  for a poled polymer is given by

$$d_{33} = (1/2)N\beta f_{\omega}^2 f_{2\omega} \langle \cos^3 \theta \rangle \quad (1)$$

where  $N$  is the number density of the chromophore,  $f_{\omega}$  and  $f_{2\omega}$  are Lorentz-Lorentz local field factors, and  $\langle \cos^3 \theta \rangle$  is the polar order factor. Using the measured density of ca.  $1.4 \text{ g cm}^{-3}$  for 19b, we obtained  $N \approx 3.9 \times 10^{27} \text{ m}^{-3}$ . The local field factors were calculated by using the measured refractive indices. However, the choice of  $\beta$  was more difficult. Singer et al.<sup>18a</sup> obtained  $\beta_0^{DR1} \approx \beta_0^{DANS} \approx 2.1 \times 10^{-40} \text{ m}^4/\text{V}$ , while Spangler et al.<sup>18c</sup> obtained  $\beta_0^{DANS} \approx 4.8 \times 10^{-40} \text{ m}^4/\text{V}$ , where DANS is 4-(dimethylamino)-4'-nitrostilbene. We therefore assumed  $\beta_0$  to be similar for DANS and DR1 and used these two values in the present calculations. Using the resonant enhancement of 3.1 determined earlier, we have calculated  $\langle \cos^3 \theta \rangle$  for  $\beta$  values of  $6.5 \times 10^{-38}$  and  $14.3 \times 10^{-38} \text{ m}^4/\text{V}$ , obtaining  $\langle \cos^3 \theta \rangle = 0.11$  and 0.05, respectively. These values are consistent with theoretical studies of alignment discussed in the literature.<sup>2d,20</sup>

Finally, we have calculated the electrooptic coefficient,  $r_{33}$ , for 19b by use of the two-level model for the dispersion, as discussed by Singer et al.<sup>2d</sup> The Onsager local field factor was calculated assuming  $\epsilon_0 = 4$ , where  $\epsilon_0$  is the static dielectric constant. Using this value, we obtained  $r_{33} = 18 \text{ pm/V}$  at a wavelength of  $0.83 \text{ }\mu\text{m}$ . Once again, this value is comparable to those obtained for similar polymers in the literature.<sup>3d,19</sup>



## Future Developments

The synthetic versatility offered by the phosphazene system has allowed the preparation of polymers that contain a high loading of donor-acceptor-substituted, conjugated moieties as pendent side chains. Our future research on second-order nonlinear optical polyphosphazenes will focus on tailoring the macromolecular system to generate higher glass transition temperatures. This, and the stabilized alignment of the chromophoric side groups, should be attainable by the incorporation of a third cosubstituent that contains a cross-linkable moiety. Thus, cross-linking of the polymeric matrix during the application of an electric field should stabilize the nonlinear optical character.

## Experimental Section

**Materials.** Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by vacuum sublimation ( $40\text{ }^{\circ}\text{C}/10^{-2}$  Torr) before use. Poly(dichlorophosphazene) was prepared according to the previously published procedure.<sup>4</sup> Tetrahydrofuran (THF) was dried over and distilled from sodium benzophenone ketyl under an atmosphere of dry argon. 2,2,2-Trifluoroethanol (Halocarbon) and 2-(2-methoxyethoxy)ethanol were distilled from  $\text{CaH}_2$ . All other reagents (Aldrich, Eastman) were used as received. Pentaphenoxymonochlorocyclotriphosphazene<sup>21</sup> and pentakis(trifluoroethoxy)monochlorocyclotriphosphazene<sup>22</sup> were prepared by procedures reported in the literature. All manipulations of chlorophosphazene reagents before the substitution reaction were carried out under an atmosphere of dry argon by using standard Schlenk and drybox techniques. Column chromatography was carried out with the use of silica gel (60–200 mesh, Fisher) as packing material. Dialysis was accomplished with Spectra/Por cellulose membranes (MW cutoff 6000–8000, VWR).

**Equipment.**  $^{31}\text{P}$  (36.23 MHz) NMR spectra were recorded with a JEOL FX90Q NMR spectrometer.  $^{31}\text{P}$  (145.8 MHz),  $^1\text{H}$  (360.0 MHz), and  $^{13}\text{C}$  (90.0 MHz) NMR spectra were recorded with a Bruker WM360 spectrometer.  $^1\text{H}$  (500.0 MHz) NMR spectra were recorded with a Bruker AM500 spectrometer. Chemical shifts are relative to external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) or tetramethylsilane ( $^1\text{H}$  and  $^{13}\text{C}$ ). All heteronuclear NMR spectra were proton decoupled. Electron-impact mass spectra were obtained with a Kratos MS9/50 spectrometer. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1037A refractive index detector and a Polymer Laboratories PL gel 10- $\mu\text{m}$  column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. UV-visible spectra of all compounds as solutions in spectroscopic grade THF were obtained by means of a Hewlett-Packard Model HP8450A UV-visible spectrometer. The spectra were recorded in quartz cells (1-cm path length). 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  $10\text{--}25\text{ }^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere were used. Sample sizes were between 10 and 30 mg. Infrared spectra were recorded in a Perkin-Elmer 1710 FTIR instrument interfaced with a Perkin-Elmer 3600 Data Station. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Indium tin oxide coated glass was obtained from Delta Technologies, Limited. Polymer film thicknesses and refractive indices were obtained by using a Rudolph ellipsometer. Second-harmonic generation measurements were carried out by using a Quanta-Ray DCR11 Q-switched Nd:YAG laser ( $\lambda = 1064\text{ nm}$ ).

**Synthesis of  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$  (2).** To a solution of 4-hydroxybenzaldehyde (15.0 g, 0.123 mol), potassium hydroxide (6.89 g, 0.123 mol), and potassium iodide (2.03 g, 0.012 mol) in ethanol (300 mL) was added a solution of 2-[2-(2-chloroethoxy)ethoxy]ethanol (2.48 g, 0.147 mol) in eth-

anol (20 mL). The reaction mixture was heated at  $78\text{ }^{\circ}\text{C}$  for 16 h, cooled to room temperature, and neutralized with dilute hydrochloric acid. After evaporation of the solvent, the crude mixture was redissolved in methylene chloride (400 mL), and the solution was washed with water ( $2 \times 200\text{ mL}$ ) and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed to isolate 4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]benzaldehyde. To a solution of this aldehyde (15.0 g, 0.059 mol) and diethyl (4-nitrobenzyl)phosphonate (16.1 g, 0.059 mol) in ethylene glycol dimethyl ether (250 mL) was added a solution of potassium *tert*-butoxide (7.3 g, 0.065 mol) in ethylene glycol dimethyl ether (60 mL). The reaction mixture was stirred at room temperature for 16 h and was heated at  $85\text{ }^{\circ}\text{C}$  for 1 h. The reaction mixture was poured into water (400 mL), neutralized with dilute hydrochloric acid, extracted with diethyl ether ( $3 \times 400\text{ mL}$ ), washed with saturated aqueous sodium chloride ( $2 \times 200\text{ mL}$ ), and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product 2 was isolated by column chromatography on silica gel and was further purified by recrystallization from *n*-hexane/methylene chloride.

For 2: mp  $65\text{--}67\text{ }^{\circ}\text{C}$ ; yield 40–55%; MS  $m/z$  calcd 373,  $m/z$  found 373;  $\lambda_{\text{max}}$  (THF) 378 nm ( $\epsilon\ 2.6 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.61 (d,  $J = 8.7\text{ Hz}$ , 2 H, Ar H), 7.49 (d,  $J = 8.7\text{ Hz}$ , 2 H, Ar H), 7.23 (d,  $J_{\text{trans}} = 16.3\text{ Hz}$ , 1 H, vinyl), 7.01 (d,  $J_{\text{trans}} = 16.3\text{ Hz}$ , 1 H, vinyl), 6.95 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 4.18 (t, 2 H,  $\text{OCH}_2$ ), 3.90 (t, 2 H,  $\text{OCH}_2$ ), 3.75 (m, 6 H,  $\text{OCH}_2$ ), 3.65 (t, 2 H,  $\text{OCH}_2$ ), 2.20 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.33, 146.36, 144.22, 132.81, 129.14, 128.36, 126.46, 124.13, 124.09, 114.95; IR (KBr)  $\nu$  1343 (s,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_6$ : C, 64.33; H, 6.21; N, 3.75. Found: C, 63.96; H, 6.20; N, 3.72.

**Synthesis of  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$  (3).** Compound 3 was prepared from 2-(2-chloroethoxy)ethanol by following the same procedure described for 2.

For 3: mp  $99\text{--}101\text{ }^{\circ}\text{C}$ ; yield 40–55%; MS  $m/z$  calcd 329,  $m/z$  found 329;  $\lambda_{\text{max}}$  (THF) 378 nm ( $\epsilon\ 2.6 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.60 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.49 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.23 (d,  $J_{\text{trans}} = 16.4\text{ Hz}$ , 1 H, vinyl), 7.01 (d,  $J_{\text{trans}} = 16.4\text{ Hz}$ , 1 H, vinyl), 6.95 (d,  $J = 8.7\text{ Hz}$ , 2 H, Ar H), 4.18 (t, 2 H,  $\text{OCH}_2$ ), 3.90 (t, 2 H,  $\text{OCH}_2$ ), 3.76 (t, 2 H,  $\text{OCH}_2$ ), 3.69 (t, 2 H,  $\text{OCH}_2$ ), 2.11 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.28, 146.40, 144.18, 132.76, 129.24, 128.38, 126.47, 124.22, 124.09, 114.95; IR (KBr)  $\nu$  1333 (s,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{19}\text{NO}_5$ : C, 65.64; H, 5.82; N, 4.25. Found: C, 65.81; H, 5.83; N, 3.99.

**Synthesis of  $\text{HOCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$  (4).** Compound 4 was prepared from 2-bromoethanol by following the same procedure described for 2.

For 4: mp  $140\text{--}142\text{ }^{\circ}\text{C}$ ; yield 45–60%; MS  $m/z$  calcd 285,  $m/z$  found 285;  $\lambda_{\text{max}}$  (THF) 378 nm ( $\epsilon\ 2.6 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.22 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.61 (d,  $J = 8.9\text{ Hz}$ , 2 H, Ar H), 7.51 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.23 (d,  $J_{\text{trans}} = 16.4\text{ Hz}$ , 1 H, vinyl), 7.01 (d,  $J_{\text{trans}} = 16.4\text{ Hz}$ , 1 H, vinyl), 6.96 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 4.14 (t, 2 H,  $\text{OCH}_2$ ), 4.01 (m, 2 H,  $\text{OCH}_2$ ), 1.99 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.25, 146.40, 144.19, 132.75, 129.39, 128.46, 126.54, 124.36, 124.16, 114.94; IR (KBr)  $\nu$  1338 (s,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}_4$ : C, 67.36; H, 5.30; N, 4.91. Found: C, 67.45; H, 5.28; N, 4.46.

**Synthesis of  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4(\text{CH}=\text{CH})_2\text{C}_6\text{H}_4\text{NO}_2$  (5).** Compound 5 was prepared from 4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]cinnamaldehyde<sup>8</sup> by following the same procedure described for 2.

For 5: mp  $75\text{--}77\text{ }^{\circ}\text{C}$ ; yield 40–45%; MS  $m/z$  calcd 399,  $m/z$  found 399;  $\lambda_{\text{max}}$  (THF) 400 nm ( $\epsilon\ 3.9 \times 10^4$ );  $^1\text{H}$  NMR (500 MHz) ( $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 8.9\text{ Hz}$ , 2 H, Ar H), 7.51 (d,  $J = 8.9\text{ Hz}$ , 2 H, Ar H), 7.39 (d,  $J = 8.8\text{ Hz}$ , 2 H, Ar H), 7.08 (dd,  $J_{\text{trans}} = 15.5\text{ Hz}$ ,  $J_{\text{trans}} = 10.4\text{ Hz}$ , 1 H, vinyl), 6.91 (d,  $J = 8.7\text{ Hz}$ , 2 H, Ar H), 6.84 (dd,  $J_{\text{trans}} = 15.5\text{ Hz}$ ,  $J_{\text{trans}} = 10.4\text{ Hz}$ , 1 H, vinyl), 6.74 (d,  $J_{\text{trans}} = 15.5\text{ Hz}$ , 1 H, vinyl), 6.63 (d,  $J_{\text{trans}} = 15.5\text{ Hz}$ , 1 H, vinyl), 4.16 (t, 2 H,  $\text{OCH}_2$ ), 3.88 (t, 2 H,  $\text{OCH}_2$ ), 3.75 (m, 6 H,  $\text{OCH}_2$ ), 3.64 (t, 2 H,  $\text{OCH}_2$ ), 1.74 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.00, 146.33, 144.13, 135.71, 134.08, 129.71, 128.94, 128.05, 124.41, 126.31, 124.09, 114.90; IR (KBr)  $\nu$  1337 (s,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{25}\text{NO}_6$ : C, 66.15; H, 6.31; N, 3.51. Found: C, 66.00; H, 6.23; N, 3.40.

**Synthesis of  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4(\text{CH}=\text{CH})_3\text{C}_6\text{H}_4\text{NO}_2$  (6).** To a solution of 4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]cinnamaldehyde<sup>8</sup> (10.0 g, 0.036 mol) and (4-nitrocinnamyl)tri-*n*-butylphosphonium bromide<sup>9</sup> (5.82 mL of a 0.614 M solution in absolute ethanol, 0.036 mol) in absolute ethanol (300 mL) was added an ethanol solution (50 mL) of a sodium ethoxide, prepared from sodium metal (0.98 g, 0.043 mol) and absolute ethanol (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 h and was heated at 78 °C for 1 h. The reaction mixture was poured into water (300 mL), neutralized with dilute hydrochloric acid, extracted with methylene chloride (3 × 300 mL), washed with saturated aqueous sodium chloride (2 × 200 mL), and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product 6 was isolated by column chromatography on silica gel and was further purified by recrystallization from *n*-hexane/methylene chloride.

For 6: mp 101–102 °C; yield 30–40%; MS  $m/z$  calcd 425,  $m/z$  found 425;  $\lambda_{\text{max}}$  (THF) 418 nm ( $\epsilon$   $4.7 \times 10^4$ );  $^1\text{H}$  NMR (500 MHz) ( $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J$  = 8.9 Hz, 2 H, Ar H), 7.50 (d,  $J$  = 8.9 Hz, 2 H, Ar H), 7.36 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 7.03 (dd,  $^1J_{\text{trans}} = 15.4$  Hz,  $^1J_{\text{a-trans}} = 10.7$  Hz, 1 H, vinyl), 6.89 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 6.78 (dd,  $^1J_{\text{trans}} = 15.5$  Hz,  $^1J_{\text{a-trans}} = 10.0$  Hz, 1 H, vinyl), 6.63 (d,  $^1J_{\text{trans}} = 15.4$  Hz, 1 H, vinyl), 6.62 (dd,  $^1J_{\text{trans}} = 14.8$  Hz,  $^1J_{\text{a-trans}} = 10.0$  Hz, 1 H, vinyl), 6.60 (d,  $^1J_{\text{trans}} = 15.5$  Hz, 1 H, vinyl), 6.49 (dd,  $^1J_{\text{trans}} = 14.8$  Hz,  $^1J_{\text{a-trans}} = 10.7$  Hz, 1 H, vinyl), 4.19 (t, 2 H,  $\text{OCH}_2$ ), 3.90 (t, 2 H,  $\text{OCH}_2$ ), 3.75 (m, 6 H,  $\text{OCH}_2$ ), 3.67 (t, 2 H,  $\text{OCH}_2$ ), 2.15 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  158.81, 146.39, 144.10, 137.13, 134.38, 133.84, 131.45, 129.23, 128.69, 127.93, 126.70, 126.46, 124.12, 114.92; IR (KBr)  $\nu$  1335 (s,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{27}\text{NO}_6$ : C, 67.75; H, 6.40; N, 3.29. Found: C, 67.77; H, 6.47; N, 3.27.

**Synthesis of  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CN}$  (7).** Compound 7 was prepared from diethyl (4-cyanobenzyl)phosphonate by following the same procedure described for 2.

For 7: mp 74–76 °C; yield 45–60%; MS  $m/z$  calcd 353,  $m/z$  found 353;  $\lambda_{\text{max}}$  (THF) 342 nm ( $\epsilon$   $3.7 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J$  = 8.3 Hz, 2 H, Ar H), 7.55 (d,  $J$  = 8.3 Hz, 2 H, Ar H), 7.47 (d,  $J$  = 8.6 Hz, 2 H, Ar H), 7.17 (d,  $J_{\text{trans}} = 16.3$  Hz, 1 H, vinyl), 6.96 (d,  $J_{\text{trans}} = 16.3$  Hz, 1 H, vinyl), 6.94 (d,  $J$  = 8.4 Hz, 2 H, Ar H), 4.18 (t, 2 H,  $\text{OCH}_2$ ), 3.89 (t, 2 H,  $\text{OCH}_2$ ), 3.73 (m, 6 H,  $\text{OCH}_2$ ), 3.63 (t, 2 H,  $\text{OCH}_2$ ), 2.39 (br s, 1 H, OH); selected  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.19, 142.18, 132.43, 131.90, 129.29, 128.24, 126.55, 124.64, 119.12, 114.95, 110.05; IR (KBr)  $\nu$  2223 (s, CN)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_4$ : C, 71.37; H, 6.56; N, 3.96. Found: C, 70.86; H, 6.54; N, 3.89.

**Synthesis of  $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{NO}_2$  (8).** Compound 8 was prepared by following a modified literature procedure.<sup>10</sup> To a solution of 4-nitrobenzenesulfonyl chloride (37.7 g, 0.17 mol) in dioxane (300 mL) was added a solution of *N*-methyl-ethanolamine (25.5 g, 0.34 mol) in dioxane (50 mL). The reaction mixture was heated at 100 °C for 5 h and was stirred at room temperature for 16 h. The dioxane layer was decanted, and the oily residue was dissolved in methylene chloride (300 mL) and extracted with water (2 × 300 mL). The organic layer was combined with the dioxane layer, extracted with water (2 × 300 mL), and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the yellow solid was washed with pentane to yield *N*-(2-hydroxyethyl)-4-nitrobenzenesulfonamide. A solution of the sulfonamide in dilute sodium hydroxide (6%, 500 mL) was heated at 100 °C for 0.5 h. The reaction mixture was extracted with methylene chloride (2 × 300 mL) and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the yellow solid was recrystallized from methanol to yield 8.

For 8: mp 101–102 °C (lit.<sup>10</sup> mp 104 °C); yield 45–55%; MS  $m/z$  calcd 196,  $m/z$  found 196;  $\lambda_{\text{max}}$  (THF) 390 nm ( $\epsilon$   $2.5 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J$  = 9.4 Hz, 2 H, Ar H), 6.68 (d,  $J$  = 9.4 Hz, 2 H, Ar H), 3.89 (t, 2 H,  $\text{OCH}_2$ ), 3.64 (t, 2 H,  $\text{NCH}_2$ ), 3.15 (s, 3 H,  $\text{CH}_3$ ), 1.7 (br s, 1 H, OH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  126.18, 110.50, 60.10, 54.48, 39.87; IR (KBr)  $\nu$  1300 (w,  $\text{NO}_2$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_3$ : C, 55.09; H, 6.16; N, 14.28. Found: C, 54.91; H, 6.07; N, 14.48.

**Purification of  $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$  (9).** Compound 9 was commercially available (Aldrich) as the dye Disperse Red 1 and was purified by

column chromatography followed by recrystallization from *n*-hexane/methylene chloride.

For 9:  $\lambda_{\text{max}}$  (THF) 490 nm ( $\epsilon$   $4.1 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.33 (d, 2 H, Ar H), 7.94 (m, 4 H, Ar H), 6.85 (d, 2 H, Ar H), 3.95 (t, 2 H,  $\text{OCH}_2$ ), 3.66–3.57 (m, 4 H,  $\text{NCH}_2$ ), 1.57 (br s, 1 H, OH), 1.27 (t, 3 H,  $\text{NCH}_3$ ).

**Synthesis of  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2\}$  (10).** To a suspension of sodium hydride (8.2 mg, 0.21 mmol) in THF (25 mL) was added a solution of 2 (0.084 g, 0.23 mmol) in THF (5 mL). After 5 h at room temperature, a solution of  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$  (0.10 g, 0.16 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 24 h, after which the solvent was removed by rotary evaporation. The product was purified by column chromatography to yield 10 as a yellow oil (yield 0.11 g, 72%).

For 10: MS  $m/z$  calcd 972,  $m/z$  found 972;  $\lambda_{\text{max}}$  (THF) 376 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.20 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 7.58 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 7.46 (d,  $J$  = 8.7 Hz, 2 H, Ar H), 7.27–6.91 (m, 29 H, Ar H, vinyl and  $\text{OC}_6\text{H}_5$ ), 4.15–3.43 (m, 12 H,  $\text{OCH}_2$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) (145.8 MHz)  $\delta$  12.5 (dd,  $^2J_{\text{PNP}} = 88.1$  Hz), 9.0 (dd,  $^2J_{\text{PNP}} = 88.1$  Hz); IR (KBr)  $\nu$  1339 (s,  $\text{NO}_2$ ), 1178 (vs, b,  $\text{P}=\text{N}$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{50}\text{H}_{47}\text{N}_4\text{O}_{11}\text{P}_3$ : C, 61.73; H, 4.87; N, 5.76. Found: C, 62.12; H, 5.19; N, 5.33.

**Synthesis of  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2\}$  (11).** To a suspension of sodium hydride (7.3 mg, 0.19 mmol) in THF (30 mL) was added a solution of 2 (0.80 g, 0.22 mmol) in THF (5 mL). After 5 h at room temperature, a solution of  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{Cl}$  (0.10 g, 0.15 mmol) in THF (5 mL) was added. The reaction mixture was stirred at room temperature for 24 h, after which the solvent was removed by rotary evaporation. The product was purified by column chromatography to yield 11 as a yellow oil (yield 0.13 g, 84%).

For 11: MS  $m/z$  calcd 1002,  $m/z$  found 1002;  $\lambda_{\text{max}}$  (THF) 376 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J$  = 8.9 Hz, 2 H, Ar H), 7.60 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 7.50 (d,  $J$  = 8.7 Hz, 2 H, Ar H), 7.23 (d,  $J_{\text{trans}} = 16.4$  Hz, 1 H, vinyl), 7.01 (d,  $J_{\text{trans}} = 16.4$  Hz, 1 H, vinyl), 6.94 (d,  $J$  = 8.8 Hz, 2 H, Ar H), 4.33–4.22 (m, 10 H,  $\text{OCH}_2\text{CF}_3$ ), 4.20–3.69 (m, 12 H,  $\text{OCH}_2$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) (145.8 MHz)  $\delta$   $\nu_{\text{B}} = 17.1$ ,  $\nu_{\text{A}} = 16.3$  ppm,  $^2J_{\text{PNP}} = 88.6$  Hz; IR (KBr)  $\nu$  1343 (s,  $\text{NO}_2$ ), 1175 (vs, br,  $\text{P}=\text{N}$ ), 1082 (s, CF)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{32}\text{N}_4\text{O}_{11}\text{P}_3\text{F}_{15}$ : C, 35.94; H, 3.22; N, 5.59. Found: C, 36.93; H, 3.72; N, 5.02.

**Synthesis of Polymers 12–19.** The polymer structures and composition ratios are listed in Table I and Scheme VI. Polymers 12–19 were prepared in the same manner. The following procedure for the preparation of 12d is typical. A solution of sodium trifluoroethoxide was prepared from trifluoroethanol (0.16 g, 1.55 mmol) and an excess of sodium (0.04 g, 1.71 mmol) in THF (25 mL). The solution was filtered and was then added slowly to a solution of poly(dichlorophosphazene) (0.18 g, 1.55 mmol) in THF (75 mL). The reaction mixture was stirred at room temperature for 24 h. A solution of the sodium salt of 2 was prepared from the reaction of 2 (0.52 g, 1.37 mmol) and sodium hydride (0.05 g, 1.24 mmol) in THF (50 mL) at room temperature for 5 h. The sodium salt of 2 was added slowly to the polymer reaction mixture, and the solution was warmed at 40–45 °C for 24 h. A solution of sodium trifluoroethoxide was prepared from trifluoroethanol (0.43 g, 4.26 mmol) and sodium (0.09 g, 3.88 mmol) in THF (40 mL). The sodium salt was added to the polymer reaction mixture, and the solution was warmed at 40–45 °C for 24 h. The reaction mixture was concentrated by rotary evaporation, and the polymer was isolated by precipitation into water. The polymer was purified by dialysis against methanol/water (1:1 (v/v)) for 7–10 days. Note: The polymer was shielded from direct sunlight during the preparation and purification stages in order to minimize the photoisomerization process. The characterization data for 12–19 are listed in Tables II and III.

**Synthesis of  $[\text{NP}(\text{OCH}_2\text{CF}_3)_{3.66}(\text{OCH}_2\text{CH}_2-\text{OCH}_2\text{CH}_2\text{OCH}_3)_{1.44}]_n$  (20).** To a solution of poly(dichlorophosphazene) (10.0 g, 86.3 mmol) in THF (500 mL) was added slowly a solution of sodium 2-(2-methoxyethoxy)ethoxide, which was prepared from sodium (0.40 g, 17.3 mmol) and 2-(2-methoxyethoxy)ethanol (2.28 g, 19.0 mmol) in THF (100 mL). The reaction mixture was stirred at room temperature for 24 h. A solution of sodium trifluoroethoxide was prepared from sodium (7.14 g, 0.031 mol) and trifluoroethanol (34.2 g, 0.034

mol) in THF (250 mL). The sodium salt was added to the polymer reaction mixture, and the mixture was warmed at 40–45 °C for 48 h. The reaction mixture was concentrated by rotary evaporation, and the polymer was isolated by precipitation into water and was purified by successive precipitation from THF into water (four times) and pentane (twice).

For 20:  $^{31}\text{P}$  NMR (THF/locked by  $\text{D}_2\text{O}$ )  $\delta$  -8.1 (s);  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.8 (br s,  $\text{OCH}_2\text{CF}_3$ ), 3.6–2.9 (m,  $\text{OCH}_2$ );  $M_w = 1.4 \times 10^6$ ,  $M_n = 2.0 \times 10^5$ ,  $M_w/M_n = 7$ ;  $T_g = -56$  °C. Anal. Calcd: C, 23.25; H, 2.61; N, 5.64; Cl, 0.00. Found: C, 22.82; H, 2.39; N, 6.02; Cl, <0.12.

**Measurement of the Second-Order Nonlinear Optical Properties of Polyphosphazenes.** Films of the polymers were spin cast onto indium tin oxide coated conductive glass from concentrated solutions in methyl ethyl ketone and were then heated at 80–85 °C to remove all the solvent. The thicknesses and refractive indices of the polymers were obtained from ellipsometric measurements on calibration layers, which were spun on BK7 glass substrates. Because of the low glass transition temperature of the polymer samples, the measurement of film thickness was found to be more accurate and reliable by use of an ellipsometer, as opposed to using a stylus profilometer. Measurements on each sample were obtained at four different wavelengths (634.8, 753.0, 802.0, and 852.0 nm) in order to minimize the errors in the extrapolated values at 532 and 1064 nm. The thicknesses of the layers examined ranged from 70 to 250 nm and were always much less than the coherence lengths as determined from the refractive index measurements. The coherence lengths of the polymer films were in the range 1.5–3.0  $\mu\text{m}$ .

The nonlinear optical properties of the polymer films were subsequently investigated by using second-harmonic generation (SHG).<sup>1–3</sup> A Q-switched Nd:YAG laser ( $\lambda = 1064$  nm) 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. A photomultiplier was employed for detection, and the intensity of the signal was obtained from a boxcar averager.

Alignment of the nonlinear optical side groups in the polymer films 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.<sup>3</sup> Increasing the poling voltage led to an increase in the harmonic intensity; i.e., maximum alignment was not achieved at this voltage. However, higher voltages occasionally resulted in damage to the sample surface. Hence, for comparison purposes, the voltage was limited to +10 kV. Because of the low glass transition temperature of these polymers, the poling was carried out at room temperature, concurrent with the SHG measurements. This arrangement had the advantage of reproducibility of the measurement conditions for each layer.

The second-harmonic coefficients of the polymer films,  $d_{33}$ , were obtained by using the analysis of Jerphagnon and Kurtz.<sup>23</sup> The values of  $d_{33}$  were calculated with the assumption that the degree of alignment of the nonlinear optical chromophores can be described by use of the isotropic model, with the assumption that  $d_{33} = 3d_{31}$ .<sup>2d</sup> In this case the value of  $d_{33}$  relative to the  $d_{11}$  of quartz is given by

$$\frac{d^p}{d^q} = \frac{(n_{2\omega}^p)^2 - (n_{\omega}^p)^2 (t_{\omega}^q)^2 (T_{2\omega}^q)^{1/2} P_q(\phi) \sin(\psi_q) \left( \frac{I_p^{2\omega}}{I_q^{2\omega}} \right)^{1/2}}{(n_{2\omega}^q)^2 - (n_{\omega}^q)^2 (t_{\omega}^p)^2 (T_{2\omega}^p)^{1/2} P_p(\phi) \sin(\psi_p) \left( \frac{I_p^{2\omega}}{I_q^{2\omega}} \right)} \quad (2)$$

where p and q signify the polymer and quartz, respectively,  $n_{2\omega}$  and  $n_{\omega}$  are the refractive indices at the second harmonic and fundamental, respectively,  $t_{\omega}$  and  $T_{2\omega}$  are transmission factors,  $P(\phi)$  is a projection factor, and  $I^{2\omega}$  is the measured second-harmonic intensity. The oscillating factor  $\sin(\psi)$  is determined by the optical path length ( $l$ ) of the sample relative to the coherence length ( $l_c$ ) through

$$\psi = \pi l / (2l_c) \quad (3)$$

with the coherence length given by

$$l_c = \frac{\lambda}{4(n_{2\omega} \cos \phi_{2\omega} - n_{\omega} \cos \phi_{\omega})} \quad (4)$$

where  $\lambda$  is the wavelength of the fundamental and  $\phi_{\omega}$  and  $\phi_{2\omega}$  are respectively, the angles of propagation (measured from the surface normal) of the fundamental and harmonic within the polymer thin film. The transmission and projection factors are discussed in detail in ref 23. Note that the form of the projection factor is determined in the present case by the foregoing assumption of  $d_{33} = 3d_{31}$ .

The accuracy of the refractive index measurements was  $\pm 0.01$ , which may lead to a potential uncertainty of about  $\pm 20\%$  in the  $d_{33}$  value, due to the  $n_{2\omega} - n_{\omega}$  factor contained in the first term in eq 2. However, the thicknesses of the polymer films were much smaller than the coherence length. Hence,  $\sin \psi \approx \psi$ , and the error was greatly reduced by the presence of  $n_{2\omega} \cos \phi_{2\omega} - n_{\omega} \cos \phi_{\omega}$  in the expression for the coherence length (eq 4). An additional uncertainty was the accuracy of the thickness measurements of the polymer films, which was estimated to be  $\pm 5\%$ . Note also the uncertainty in the absolute values, due to the  $\pm 10\%$  accuracy in the value of  $d_{11}$  for quartz.

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## References and Notes

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**Registry No.** 2, 131684-59-8; 3, 131684-60-1; 4, 131684-61-2; 5, 131684-62-3; 6, 131684-64-5; 7, 131684-66-7; 8, 18226-16-9; 10, 131684-67-8; 11, 131684-68-9; Br(CH<sub>2</sub>)<sub>2</sub>OH, 540-51-2; (E)-HO(CH<sub>2</sub>-CH<sub>2</sub>O)<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-p-CH=CHCHO, 131684-63-4; (E)-(Bu)<sub>3</sub>P<sup>+</sup>CH<sub>2</sub>-CH=CHC<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub>, 131684-65-6; N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Cl, 5032-39-3; N<sub>3</sub>P<sub>3</sub>(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>Cl, 55975-53-6; (EtO)<sub>2</sub>POCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub>, 2609-49-6; 2-[2-(2-chloroethoxy)ethoxy]ethanol, 5197-62-6; hydroxybenzaldehyde, 123-08-0; 2-(2-chloroethoxy)ethanol, 628-89-7; diethyl (4-cyanobenzyl)phosphonate, 1552-41-6; 4-nitrobenzene-sulfonyl chloride, 98-74-8; N-methylethanolamine, 109-83-1.