Synthesis and Characterization of Hindered Polyphosphazenes via Functionalized Intermediates: Exploratory Models for Electro-optical Materials

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ABSTRACT: Several cosubstituent polyphosphazenes were synthesized that incorporate the nonlinear optical chromophore, disperse red 1 (DR-1), linked covalently to the polymer backbone through spacer groups. These polymers have a high chromophore loading (one DR-1 per repeat unit), have glass transition temperatures near 100 °C, and are high refractive index materials ($n = \sim 1.71$). The syntheses were achieved via unconventional reactions that involve functionalized poly(organophosphazenes). Disperse red-1 was linked to the polymers by two different methods that generate either an ester- or an ether-linked system. Techniques such as ^{1}H, ^{13}C, and ^{31}P NMR, gel permeation chromatography, differential scanning calorimetry, UV−vis spectroscopy, and optical birefringence were used to monitor the structures.

Introduction

Considerable interest exists in the development of materials that are optically responsive and have the potential to be useful in photonics technology.[1−3] These materials have the ability to change inherent properties such as refractive index or the absorption or emission of light in response to incident electromagnetic radiation.[2] Such effects are seen in inorganic crystals, organic small molecule crystals, and polymers that contain NLO chromophores.[1,4] Polymer systems can either be "doped" with NLO chromophores or can contain chromophores covalently linked to the macromolecular structure. Such materials must be optically transparent and have a noncentrosymmetric structure.[5−7] More important for polymers, the materials should be homogeneous and have structural, photolytic, and thermo-oxidative stability at the temperatures produced by the heating effects of an incident laser light.[8]

Materials that have linear electrooptic (LEO) properties are species in which the refractive index of the medium can be changed through the application of a dc field.[9] This effect is very similar to the second harmonic generation (SHG), and its origin is related to the macroscopic polarization that arises in a material as a result of two distinct, propagating electric fields. The application of a dc field to an NLO material causes a change in the refractive index. A material that exhibits a LEO effect may or may not display the SHG effect. For a material to have a large LEO effect, it must have a high refractive index and a large Pockels coefficient. Generally, inorganic systems with high refractive indices generate larger LEO effects than organic systems.

To be an improvement over current inorganic systems, polymers must meet a set of rigorous constraints.[10] These are the polymer (1) must be a soluble, processable material with a high thermo-oxidative stability and a high glass transition temperature, (2) have good optical transparency, a high refractive index, and excellent photolytic stability, and (3) contain a high percentage of NLO active components (with large β values) to yield high values for the linear electrooptic coefficient (r_{33}).

Two of the main advantages of the polyphosphazene platform are (a) the photochemical stability and transparency of the backbone and (b) a synthesis method that allows many different side groups to be linked to the polymer skeleton. In this synthesis method a reactive macromolecular intermediate, poly(dichlorophosphazene), $(NPCl_2)_n$, is subjected to chlorine replacement reactions that link a wide variety of organic, organometallic, or inorganic side groups to the phosphorus atoms of the skeleton.[11] Typical reagents for these reactions are the sodium salts of alcohols or phenols. Different side groups or combinations of side groups generate different properties. This is particularly useful in view of the current trends in the synthesis of LEO polymers for photorefractive applications.[12−25]

Three sets of results from earlier work underly the present studies. First, preliminary studies in our laboratory have shown that NLO-active polyphosphazenes can be prepared.[26] These polymers contain NLO-active dye molecules such as disperse red-1 (DR-1) linked to the polyphosphazene backbone as side groups together with cosubstituent units such as trifluoroethoxy groups. However, the low solubility of the sodium salt of the DR-1 alcohol limited the extent of linkage of this side group to the phosphazene skeleton, and only a low loading (33%) of DR-1 molecules could be achieved. The resultant polymers had modest refractive index values and relatively low glass transition temperatures (44−58 °C). Even so, this system was NLO active and had a d_{33} value of 34 pm/V under an applied poling potential of 10 kV. A conclusion from this earlier work was that a better method was needed in order to raise the percentage of side groups that possessed electrooptical activity. An alternative approach, described in this paper, is the use of functionalized poly(organophosphazenes), which might react with a soluble form of DR-1 or other NLO chromophores to yield polymers with higher loadings of the electrooptical unit.

Second, a number of polyphosphazenes with high refractive indices have recently been synthesized in our program.[27,31] The highest refractive index value known for a polyphosphazene is $n = 1.75$. This is for the single-

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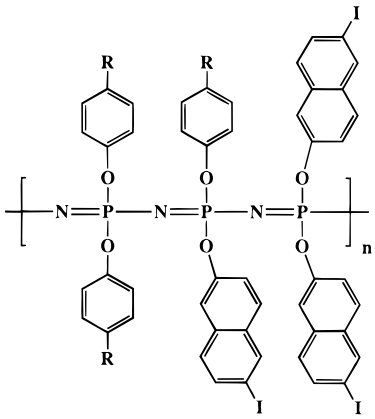
Chart 1. Polymers with 6-Iodo-2-naphthoxy Cosubstituents



Polymer	Side-group Structure (R)
4	$COOCH_2CH_2CH_3$
5	COOH
6	$COOCH_2CH_2N(CH_2CH_3)C_6H_4N{=}NC_6H_4NO_2$
7	$OSi(CH_3)_2C(CH_3)_3$
8	OH
9	$OCH_2CH_2N(CH_2CH_3)C_6H_4N{=}NC_6H_4NO_2$

substituent polymer, poly[bis(6-iodo-2-naphthoxy)phosphazene].[27] Thus, in this work, the use of 6-iodo-2-naphthol in a cosubstituent polyphosphazene was expected to result in high refractive index mixed-substituent polymers.

Third, it is known that relatively high glass transition temperatures (T_g's) can be obtained in polyphosphazene systems by the incorporation of bulky side groups that hinder backbone motions.[28−31]

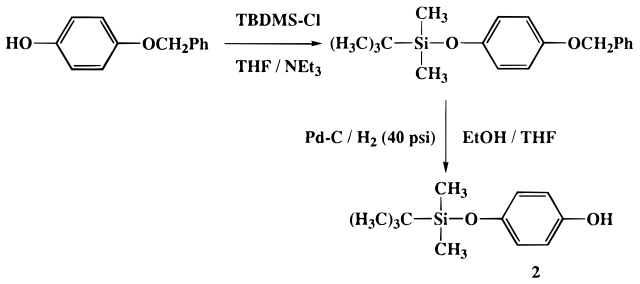
Thus, the earlier work demonstrated that polyphosphazenes with specific side groups have the potential to fulfill many of the requirements for LEO polymers if several different types of side groups can be combined in the same polymer. They also offer several advantages not found with organic-based polymers. The phosphorus−nitrogen backbone imparts a high thermooxidative and photolytic stability.[29,32] The backbone is optically transparent between 220 and 800 nm.[33] Finally, most polyphosphazenes have very high molecular weights (10^6). Mixed-substituent polyphosphazenes are usually amorphous, soluble materials.[29,34] Consequently, the synthesis of cosubstituent polyphosphazenes with carefully chosen side groups could yield polymers with both high refractive indices and interesting electrooptical behavior.

This present work comprises an exploration of synthetic methods to concentrate these various properties in a few model polymers. In later studies we plan to optimize specific properties by the control of different side groups and substituent ratios.

Results and Discussion

Synthesis. Two series of polyphosphazenes were synthesized. These polymers are shown in Chart 1. Species **4**−**6** comprise three polyphosphazenes with two

Scheme 1. Synthesis of *t*-BDMS-Protected Hydroquinone



different types of side groups in a ratio of 1:1. The first substituent is 6-iodo-2-naphthoxy, chosen for its ability to generate a high refractive index. The second side group moiety, propyl 4-hydroxybenzoate, was used as a functional unit for hydrolysis to the reactive intermediate polymer **5**, which was then esterified via the acid chloride to polymer **6**.

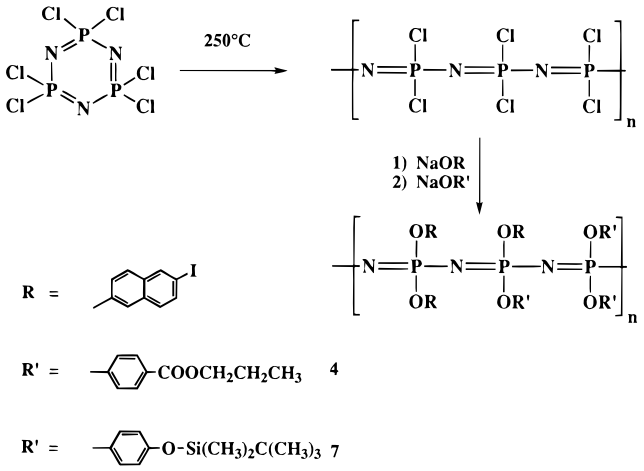
Similarly, the polymer series **7**−**9** consists of three cosubstituent polyphosphazenes with a theoretical side group ratio of 1:1. In this series also, polymer **7** was synthesized with one side group type to impart a high refractive index. However, in this case the second side group was a *tert*-butyldimethylsilyl (*t*-BDMS)-protected (aryloxy)siloxane as the functional unit. Once deprotected, this species was allowed to react through the pendent OH (polymer **8**), to yield the product polymer **9**. Thus, in both series of macromolecules, the DR-1 alcohol was incorporated as part of the functionalized polymer structure through covalent linkage of this alcohol to an existing side group moiety.

Some of the side group components were not available commercially and were synthesized. 6-Iodo-2-naphthol (**1**) was prepared from 6-bromo-2-naphthol using potassium iodide in the presence of $NiBr_2$ and P(*n*-Bu)$_3$. Side group **2** was prepared in a two-step reaction which involved *tert*-butyldimethylsilyl protection of 4-(benzyloxy)phenol, followed by selective removal of the benzyl moiety (Scheme 1). The *t*-BDMS ether protected 4-hydroxyphenol was chosen as a side group for use in the polymer synthesis because the deprotection reaction to **8** goes to 100% completion. Attempts to obtain polymer **8** by employing 4-(benzyloxy)phenoxy as the second side group resulted in incomplete deprotection of the benzyl-protecting functionality, which yielded only a limited number of free hydroxyl units.[35]

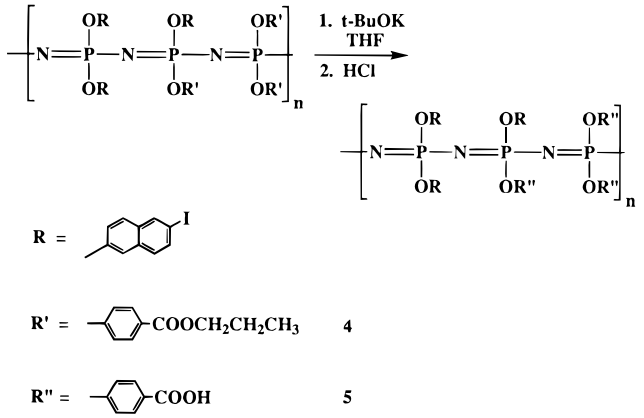
The overall synthesis of the two series of cosubstituent polyphosphazenes was carried out using the ring-opening polymerization−macromolecular substitution route.[33,36] outlined in Scheme 2. Subsequent deprotection conditions for the conversion of polymers **4** and **7** to polymers **5** and **8** are shown in Schemes 3 and 4. Coupling reactions were carried out on these deprotected polymers **5** and **8** to give the required DR-1-containing polymers. Scheme 5 depicts a standard acid to acid chloride conversion of polymer **5**, followed by reaction with DR-1 alcohol to yield the derivatized [DR-1] ester polymer **6**. Scheme 6 shows a Williamson ether type synthesis involving a reaction of DR-1 tosylate (**3**) with the hydroxy-functionalized polymer, **8**, to yield the derivatized [DR-1] ether polymer **9**. Both polymers **6** and **9** were dark red, soluble, noncrystalline materials.

An attempt was also made to prepare a polymer with two DR-1 units on every repeating unit. Polymers **10** and **11** were prepared according to a literature proce-

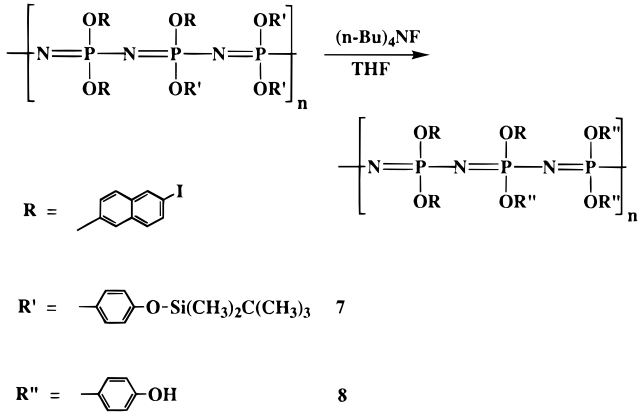
Scheme 2. Synthesis of Cosubstituent Polymers



Scheme 3. Deprotection of the Ester Polymers



Scheme 4. Deprotection of the Silyl Ether Polymers

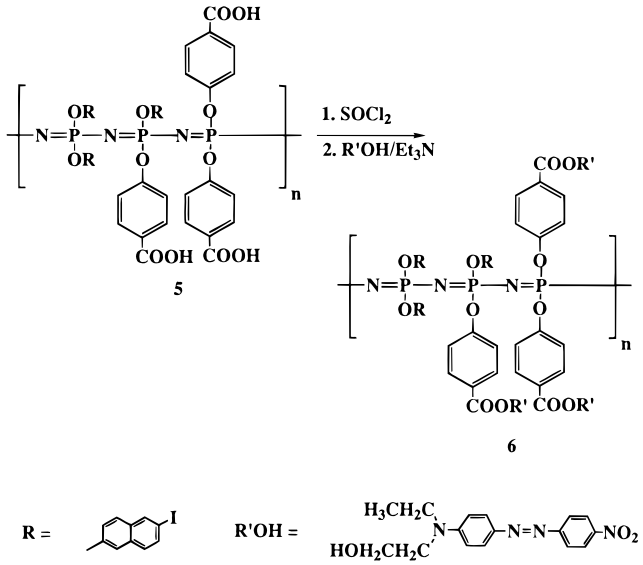


dure, as shown in Scheme 7,[35] and **11** was utilized for the synthesis of polymer **12** by the same method employed for polymer **9**. By using a limited amount of compound **3** (1.2 equiv per repeat unit), it was possible to obtain a soluble polymer that contained both 4-hydroxyphenoxy and DR-1 units. However, attempts to prepare a single-substituent polyphosphazene containing two DR-1 units per repeat unit via this route yielded an insoluble red material, which could not be characterized.

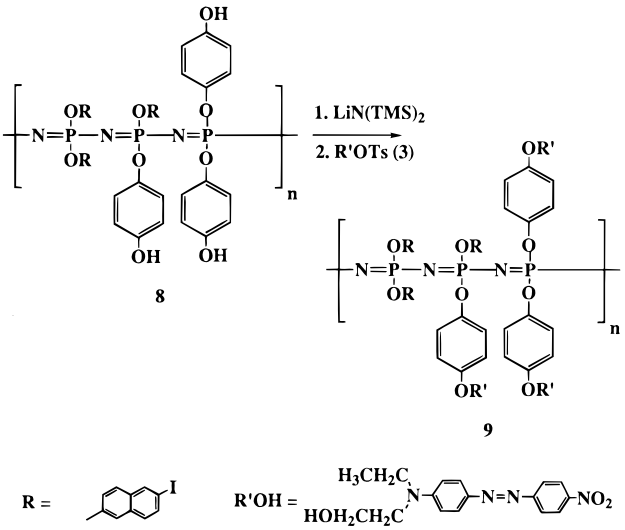
Characterization of the Polymers. Physical properties of the polymers are listed in Table 1.

Thermal Analysis. Glass transition temperatures (T_g's) of polymers **4**−**12** were measured using differential scanning calorimetry (DSC), and the data are

Scheme 5. Coupling of DR-1 Chromophore to Carboxylic Acid-Functionalized Polymers



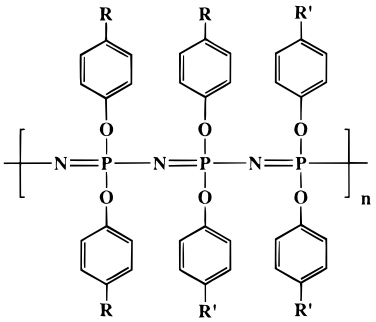
Scheme 6. Coupling of DR-1 Chromophore to Hydroxyl-Functionalized Polymers



shown in Table 1. The DR-1-derivatized polymers have some of the highest T_g's recorded for polyphosphazenes (98 °C for polymer **6** and 119 °C for polymer **9**), values that are significantly higher than those for previously reported NLO−polyphosphazene systems,[26] in which the maximum value was 58 °C. This brings polyphosphazenes into a useful range that is comparable with several other NLO−polymer systems.[12,15−20,22−24,37] However, these values are still well below those for polyimide-based NLO−polymer systems (over 300 °C).[21,38−40] Both of the intermediate polymers **4** and **7** had only moderate T_g's (27 and 44 °C). Thus, the steric influence by the DR-1 moiety raises the T_g significantly.[31] No melting transitions were detected in the DSC curves, and it appears that these polymers are amorphous.

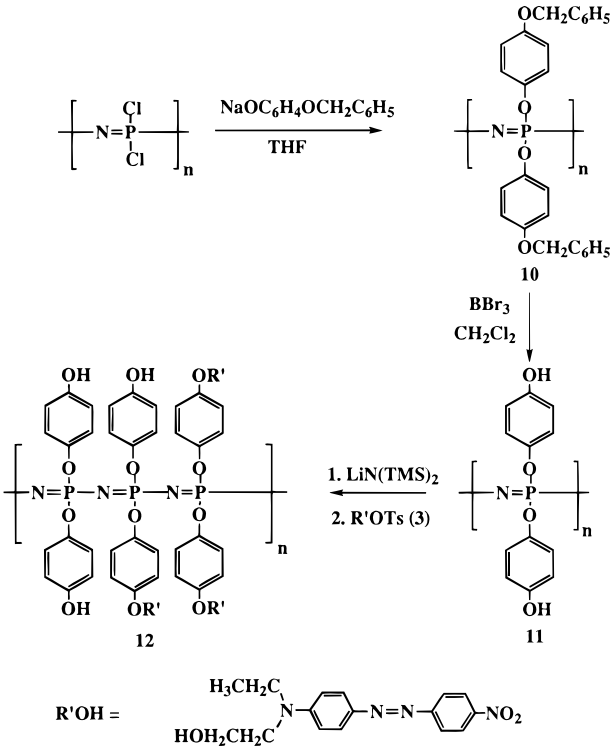
Attempts to measure the T_g of the cosubstituent, carboxylate−polymer (**5**) were unsuccessful because of an irreversible exothermic reaction that occurred at 161 °C. A similar exotherm at 200 °C has been detected in the DSC analysis of the closely related poly[bis(carboxyphenoxy)phosphazene].[41] This has been attributed to a condensation reaction between carboxylic acid units on neighboring side groups or different chains, which

Chart 2. Polymers without Iodonaphthoxy Side Groups



Polymer	Side-group Structures	
	R	R'
10	$OCH_2C_6H_5$	$OCH_2C_6H_5$
11	OH	OH
12	OH	$OCH_2CH_2N(CH_2CH_3)C_6H_4N{=}NC_6H_4NO_2$

Scheme 7. Synthesis and Deprotection of 4-Benzyloxyphenoxy Single-Substituent Polymer and Coupling to DR-1



generates cross-links with the production of H_2O and CO_2. An analogous condensation process probably accounts for the exotherm detected in the DSC analysis of polymer **5**.

The T_g of polymer **12** is lower than that of polymer **9**. This is surprising since the free OH functionalities should participate in hydrogen bonding. However, the deprotection reaction using boron tribromide is a severe process that causes chain cleavage and leads to a lower molecular weight for polymer **12**, and this may account for the low T_g.

Table 1. Polymer Characterization

polymer	T_g (°C)	M_n ($\times 10^5$)	M_w ($\times 10^5$)	PDI	loading[a]
4	27	4.2	12.1	2.9	*c*
5	161	*b*	*b*		*c*
6	98	0.3	0.6	1.7	0.9
7	44	6.2	17.6	2.9	*c*
8	111	*b*	*b*		*c*
9	119	0.4	0.7	1.5	0.9
10	31	8.8	16.2	1.8	*c*
11	43	*b*	*b*		*c*
12	91	*b*	*b*		1.2

[a] Loading indicates the average number of NLO chromophores per repeat unit. [b] Information not available because of insolubility of polymer. [c] Not applicable.

Molecular Weights. Analysis of the polymer molecular weights was carried out by using data from GPC experiments with the use of THF solvent. Although the precursor polymers **4** and **7** (Table 1) had M_n and M_w values in the 10^5 range, the DR-1-containing polymers had values in the 10^4 region, which is attributed to the severity of the conditions needed for the deprotection of the functional groups.[29,32,33,36,42−45] However, milder reaction conditions can probably be developed,[46,47] and this may provide access to higher molecular weight polymers if this feature is needed.

NLO Chromophore Loading. Integration analysis of the ^{1}H NMR spectra of polymers **6** and **9** was conducted to determine the mole percent ratio of DR-1 chromophore as a side group relative to 6-iodo-2-naphthoxy (**1**). A comparison of these to the ratio of reactive functional sites in the underivatized polymers **4** and **7** was also made. From this, an evaluation was made of the percent loading (listed in Table 1). To maintain consistency and to obtain accurate ratios, only comparisons of the integration values within the aromatic regions of the spectrum were made.

Analysis of the ^{1}H NMR data for polymer **6** indicated that an average of 0.9 DR-1 molecules existed per repeat unit. The evidence is as follows: The ratio of **1** to propyl 4-hydroxybenzoate as a side group was made for polymer **4** by comparison of the peak at 7.60 ppm, which corresponded to 1 H on **1**, with the remaining aromatic region (7.50−6.10 ppm), which corresponded to 9 H's (5 from **1**, 4 from propyl 4-hydroxybenzoate). This yielded a ratio of 1.12:1.0 of **1** to propyl 4-hydroxybenzoate. This means that approximately 53% of the side groups were 6-iodo-2-naphthol and 47% were propyl 4-hydroxybenzoate, which is close to the anticipated ratio of 50/50. The ratio of **1** to DR-1 in polymer **6** was estimated by comparison of the two peaks at 8.50 and 7.90 ppm, which correspond to a total of 6 H's from DR-1, with the remaining aromatic region (7.70−6.30 ppm), which corresponds to 12 H's (6 from **1**; 4 from propyl 4-hydroxybenzoate; 2 from DR-1). This yielded a ratio of 1.2:1.0 of **1** to DR-1, or a 45% DR-1 ester functionalization. This suggests that 97% of all the available acid sites present on polymer **5** had been connected to DR-1 through the acid chloride reaction.

Analysis of the ^{1}H NMR data for polymer **9**, indicated that, on the average, there were 0.95 DR-1 molecules per repeat unit. The ratio of **1** to the *t*-BDMS ether protected phenol (**2**) side-group in polymer **7** was estimated by comparison of the peak at 7.76 ppm, which corresponded to 1 H on **1**, to the remaining aromatic region (7.70−6.40), which corresponded to 9 H's (5 from **1**, 4 from **2**). This yielded a ratio of 1.2:1.0 of **1** to **2**, which means that approximately 55% of the side-groups

were 6-iodo-2-naphthol units and 45% were *t*-BDMS ether−phenol groups, which is close to the target ratio of 50/50. The ratio of **1** to DR-1 was made for polymer **9** in the same manner as described for polymer **6**. Here, two peaks at 8.25 and 7.90 ppm, which correspond to a total of 6 H's from DR-1, were compared with the remaining aromatic region (7.70−6.30 ppm), which corresponded to 12 H's (6 from **1**; 4 from **2**; 2 from DR-1). This yielded a ratio of 1.2:1.0 of **1** to DR-1, or a 45% DR-1 ether functionalization. This indicates that 100% of all the available phenolic sites present on polymer **8** were coupled to DR-1 through the reaction with DR-1 tosylate (**3**).

For both the ester-based and ether-based DR-1 polymers this analysis suggests an average of 46% loading. Thus, an average of 91% of the repeating units in these polymers contain at least one covalently linked DR-1 chromophore. This can be compared with the previously reported NLO polyphosphazene systems, where a maximum DR-1 loading of 33% was obtained,[26] which corresponds to an average of only 66% of the repeating units containing one covalently attached DR-1 chromophore. This is a significant increase in the percent loading and should increase the NLO response or χ'' values (d_{33} coefficients) for the resultant polymers relative to those reported previously.[48]

The disposition of the two types of side groups along the backbone is not clear. For the polymers in which 50% of the chlorine atoms were replaced first by 6-iodo-2-naphthoxide an argument can be made on steric grounds that the substitution pattern is probably nongeminal (i.e., one iodonaphthoxy and one chlorine per phosphorus). However, no control is possible yet over the cis or trans stereochemistry of substitution. Moreover, the possibility exists that the use of a slight excess of the first nucleophile will generate a few repeating units with two iodonaphthoxy units per phosphorus. The situation could be complicated further if the second nucleophile can displace some of the first organic groups from phosphorus. Most of the mixed-substituent polymers showed two ^{31}P NMR peaks or one broad resonance, and this is taken to be evidence that at least two different structural environments exist at the phosphorus atoms along the chain.

What is the maximum loading of NLO groups possible in these systems? The reaction of poly[bis(4-hydroxyphenoxy)phosphazene] with a limited amount of DR-1 tosylate (**3**) (Scheme 7),[18,20] yielded a polymer **12**, for which ^{1}H NMR data indicated a loading of up to 1.2 DR-1 chromophores per repeat unit (60%). In theory an ester- or ether-based DR-1-synthesized system could lead to 100% loading. Such polymers would bear two DR-1 moieties per repeat unit. However, attempts to synthesize such species yielded insoluble materials that could not be fully characterized. Insolubility in these polymers is attributed to the close packing or stacking of rigid aromatic side groups, which, although amorphous by normal detection techniques, nevertheless prevent the ingress of solvent molecules

Optical Properties. The UV−vis absorption spectra of polymers **6** and **9** were measured and were compared to the absorption spectra of the free-form constituent side-group moieties (**1**) and DR-1. These comparisons are shown in Figures 1 and 2. The absorptions can be attributed directly to the spectra of the constituent side-group components.[27,33] Both polymers **6** and **9** show a hypsochromic shift in their absorption spectra relative

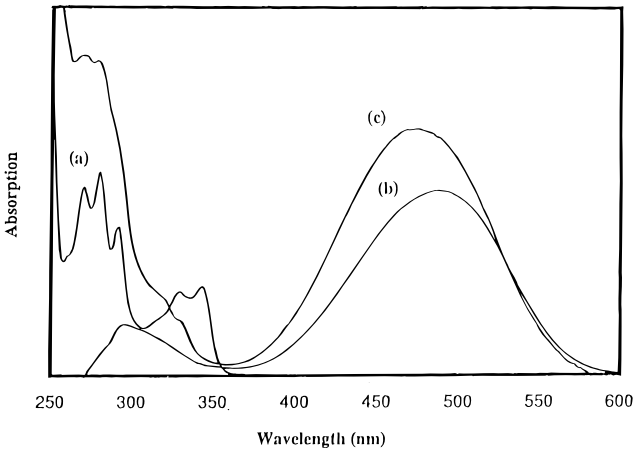


Figure 1. UV−vis absorption comparison in THF: (a) 6-iodo-2-naphthol; (b) DR-1; (c) polymer **6**.

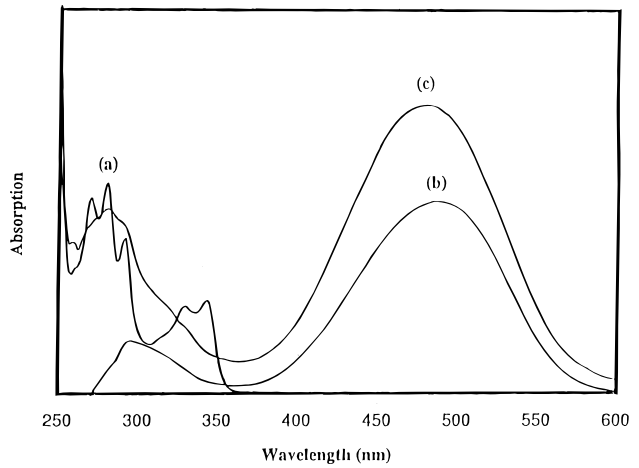


Figure 2. UV−vis absorption comparison in THF: (a) 6-iodo-2-naphthol; (b) DR-1; (c) polymer **9**.

to the side groups. This shift appears to be more pronounced for polymer **6** (Figure 1). Here, the λ_{max} for the absorption attributed to the DR-1-derivatized side group occurs at 474 nm in the ester-based polymer and 482 nm in the ether-based polymer, compared to an absorption maximum of 488 nm in the free alcohol form. The 6-iodo-2-naphthol side-groups show a similar hypsochromic shift, but one that is less pronounced than found for the DR-1 side-group moiety.

Electrooptic Properties. Birefringence measurements were carried out on polymers **6** and **9**. Thin films of the two polymers were spin coated on indium tin oxide (ITO) coated glass using *N*,*N*-dimethylformamide as the solvent. The chromophores were aligned by weak corona poling at 3 kV prior to birefringence measurements. The birefringence, *B*, of a sample caused by applied electric field, *E*, is related to the change in refractive index (Δn) by the following relationship: $B = (2\pi\Delta nD)/\lambda$, where λ is the wavelength of light used and *d* is the thickness of the polymer film. The change in the refractive index, in turn, is related to the Pockel's coefficient by $r = (2\Delta n)/(n^3E)$, where *n* is the refractive index of the polymer.

The refractive indices of polymers **6** and **9**, determined by ellipsometry, were 1.712 and 1.705, respectively. The thicknesses of the films spin coated on ITO glass, measured by stylus profilometry, were 0.10 and 0.13 μm, respectively. The birefringence values obtained for polymers **6** and **9** were 15.62×10^{-9} and 12.35×10^{-9},

respectively. These results suggest very approximate Pockel's coefficients in the range of 2.09 and 1.29 pm/V, respectively. These values are low and this is probably due to the low poling voltage, which was limited by the available apparatus. The ether-linked polymer **9** has a slightly lower value than polymer **6**, probably due to the faster relaxation of the ether-linked chromophores in **9**. Within 7 days the electrooptic coefficients had decreased to 1.45 and 0.81pm/V for polymers **6** and **9**, respectively. As a control to investigate the contributions from the backbone and the phenoxy groups to the birefringence effect, poly[bis(phenoxy)phosphazene], $[NP(OC_6H_5)_2]_n$, was spin coated on ITO glass and subjected to the same conditions as before. The birefringence for this polymer was negligible.

Conclusions

It is clear that polyphosphazenes can be designed and synthesized to generate NLO chromophore loadings that are higher than those reported previously.[26] Glass transition temperatures above 100 °C and NLO chromophore loadings of one per repeat unit have been achieved, making these polymers comparable to a number of other NLO polymer systems currently under investigation. In addition, the ease with which two or more different substituents can be introduced into each polymer molecule provides a synthetic advantage not available for many organic-backbone polymer systems.[11,29,34,36] The approximate electrooptic coefficients obtained are low, probably because of the low poling voltages used in this work. We presume that the stability of the electrooptic effect can be improved by using a cross-linking agent as a cosubstituent. However, certain applications exist for which a fast relaxation is needed to respond rapidly to induced changes in the electric field. None of the polyphosphazenes studied so far has a relaxation rate this fast, but the choice of highly flexible cosubstituent groups and spacers may provide opportunities in this area.

But the most important conclusion from this work is that synthetic methods have been developed that yield polyphosphazenes with higher loadings of very bulky side groups than can be achieved through direct macromolecular substitution on poly(dichlorophosphazene). The methods described here could be used for the linkage of many different alcohols, tosylates, or mesylates, which, because of the limited solubility of the corresponding side-group sodium salts, do not yield high levels of chlorine replacement through the classical macromolecular substitution technique.

Experimental Section

General Information. All chemical reagents were obtained from a commercial source (Aldrich) and were used without further purification, unless described differently. The organic solvents employed were distilled before use from sodium−benzophenone ketal or calcium hydride or were dried according to standard procedures.[49] All water used in the synthetic procedures was distilled and deionized before use. Propyl 4-hydroxybenzoate was recrystallized from dichloromethane before use.

Instrumentation. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker WM-360 spectrometer with $CDCl_3$, THF-d_8, acetone-d_6, D_2O, DMF-d_7, or DMSO-d_6 (MSD Isotopes or Cambridge Isotopes) as either the solvent or as an internal reference. UV−vis absorption spectra were recorded using a Hewlett-Packard 8452A Diode Array spectrophotometer and were analyzed with a HP Vectra ES/12 workstation. Gel permeation chromotography was performed with a HP 1090 liquid chromatograph equipped with two Phenominex Phengel linear 10 columns and a HP 1047A refractive index detector. A 0.01 M solution of $(n\text{-}Bu)_4N(NO_3)$ in THF was used as the eluting solvent. Analysis of the chromatographs was conducted on an HP Chemstation equipped with Polymer Laboratories software. Molecular weights were reported versus polystyrene standards. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 unit controlled by a PE 7500 computer with heating rates between 10 and 40 °C/min and sample sizes of 10−30 mg.

Purification of Disperse Red-1:[$HOCH_2CH_2N(CH_2CH_3)(C_6H_4N_2C_6H_4NO_2)$]. DR-1 was obtained by purification of 95% DR-1 (Aldrich). The impure material was dissolved in hot dichloromethane and the insoluble components were filtered off. The solvent was removed, and the solids were collected and recrystallized from 95% ethanol to yield dark red crystals of pure DR-1. The crystals were collected and dried in a vacuum oven at 40 °C for 24 h. The purity of these crystals was determined by comparison of ^{1}H and ^{13}C NMR spectra with literature references,[50] and by the mp of 159−162 °C.

Preparation of Poly(dichlorophosphazene). Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical) was recrystallized from heptane and was vacuum sublimed at 40 °C (0.02 mmHg). This was then placed in a clean, dry glass tube (200 g), which was sealed under vacuum. The sealed tube was placed in an oven fitted with a motorized rocking shelf (3 rocks/min) and heated at 250 °C for 18 h to induce polymerization. The tube was removed, cooled to room temperature, and then cooled in liquid nitrogen and was then warmed to room temperature three times before opening. The tube was opened under argon and the solids were removed and placed in a sublimator. Residual hexachlorocyclotriphosphazene was separated from the polymer through vacuum sublimation. The pure poly(dichlorophosphazene) was stored under an inert atmosphere prior to use. Yield: 38.39 g (18%). ^{31}P NMR ($CDCl_3$ internal reference), δ (ppm): −17.2 (s).

Synthesis of 6-Iodo-2-naphthol. This compound was prepared in a manner reported previously.[51,52] In an argon-charged reaction flask, 6-bromo-2-naphthol (10 g, 0.04 mol) and potassium iodide (50 g) in dry DMF (300 mL) were warmed gently. To this warm solution was added nickel bromide (1.5 g, 0.0068 mol) and 2 mL of tri(*n*-butyl)phosphine (1.62 g, 0.008 mol). The reaction mixture was stirred and heated to reflux for 12 h. After this time, the mixture was cooled to ambient temperature and a crude solid was isolated after removal of the DMF under vacuum. This solid was dissolved in 300 mL of a 1:1 petroleum ether and benzene mixture, and the solution was repeatedly extracted with several portions of excess water. The organic layer was collected and dried over $MgSO_4$, and the solvent was removed by rotoevaporation. A slightly brown-colored crude product remained, which was recrystallized from hot hexane. Yellow crystals were collected and sublimed at 105 °C/0.01 mmHg to yield white crystals, mp 134−136 °C. Yield: 73.0%, 7.80 g (0.0292 mol). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.10 (m, 2H), 7.40 (d, 1H), 7.60 (m, 2H), 8.10 (d, 1H). ^{13}C NMR, δ (ppm): 109.5, 153.7, 118.5, 128.8, 136.4, 88.2, 134.9, 128.0, 130.6, 133.3. MS calcd for $C_{10}H_7IO$: 270.0. Found: 270.0. Anal. Calcd: C, 44.44; H, 2.59; I, 47.04. Found: C, 44.03; H, 2.75; I, 49.44.

Synthesis of 4-(*tert*-Butyldimethylsiloxy)phenol: [$HOC_6H_4OSi(CH_3)_2C(CH_3)_3$] (2). The preparation of this compound involved a two-step reaction. Under argon, 4-(benzyloxy)phenol (21.0 g, 0.105 mol) was dissolved in dry THF (100 mL), and this solution was added dropwise to a mixture of *tert*-butyldimethylsilyl chloride (17.4 g, 0.116 mol) and dry triethylamine (21.9 mL, 0.157 mol) in dry THF (50 mL). The reaction mixture was stirred at room temperature for 8 h. The white, insoluble triethylamine hydrochloride was filtered from the solution. The THF solution was collected and the solvent was removed by rotoevaporation. A white solid remained, and this was dissolved in an ethanol/THF (5:1) mixture (150 mL). A catalyst of 10% activated palladium on carbon (2.0 g, 0.002 mol of Pd) was added to this solution. This mixture was placed

in a thick-walled, glass jar and fitted to a Parr hydrogenator. The reaction mixture was pressurized with H_2 (40 psi) and mechanically agitated for 5 h. After this time the reaction mixture was filtered through Celite to remove the palladium/carbon catalyst. The filtered solution was collected, and the solvents were removed under rotoevaporation. A light brown solid was obtained, and this was recrystallized from 95% ethanol to yield white crystals, mp 54−56 °C. Yield: 98.0%, 20.8 g (0.114 mol). ^{1}H NMR (acetone-d_6), δ (ppm): 6.68 (d, 2H), 6.65 (d, 2H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (acetone-d_6), δ (ppm). MS calcd for $C_{12}H_{20}O_2Si$: 224.0. Found: 224.0. Anal. Calcd: C, 59.34; H, 7.69. Found: C, 64.38; H, 8.29.

Synthesis of DR-1 Tosylate: [$CH_3C_6H_4SO_3CH_2CH_2N(CH_2CH_3)(C_6H_4N_2C_6H_4NO_2)$] (3). In an argon-charged reaction flask, a slurry was prepared from 4-toluenesulfonyl chloride (3.64 g, 0.0191 mol) in freshly distilled, dry pyridine (50 mL). This was maintained at 0 °C in an ice bath, and to this was added dropwise a solution of DR-1 (5.0 g, 0.016 mol) dissolved in 50 mL of dry pyridine. After the addition was complete, the reaction mixture was warmed to ambient temperature and was stirred for an additional 4 h. The reaction mixture was then poured into 500 mL of ice cold water in order to neutralize the excess 4-toluenesulfonyl chloride. The organic products were extracted from the pyridine/water mixture through repeated washings with excess dichloromethane. To remove the excess pyridine, the dichloromethane solution was extracted three times with excess quantities of aqueous, 5 N hydrochloric acid. The organic layer was dried over $MgSO_4$, and the solvent was removed by rotoevaporation. A red solid was obtained, which was recrystallized from 95% ethanol to yield red crystals. These crystals were collected and dried under vacuum, mp 132−136 °C. Yield: 47.8%, 3.56 g (0.0076 mol). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.31 (d, 2H), 7.90 (d, 2H), 7.81 (d, 2H), 7.71 (d, 2H), 7.25 (d, 2H), 6.61 (d, 2H), 4.19 (t, 2H), 3.69 (t, 2H), 3.43 (q, 2H), 2.37 (s, 3H), 1.17 (t, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 156.6, 150.5, 147.6, 145.1, 143.9, 132.5, 129.9, 127.8, 126.1, 124.7, 122.7, 111.4, 66.4, 49.1, 46.0, 21.7, 12.2. MS calcd for $C_{23}H_{24}N_4O_5S$: 468.1. Found: 468.0. Anal. Calcd: C, 58.97; H, 5.12; N, 11.97. Found: C, 58.17; H, 5.28; N: 11.45.

Synthesis of [$NP(OC_{10}H_6I)(OC_6H_4COOCH_2CH_2CH_3)]_n$ (4). Poly(dichlorophosphazene) (2 g: 1.22 g of Cl, 0.0344 mol) was dissolved in 250 mL of freshly distilled THF in a 2 L three-neck flask, charged with dry argon. To this was added 1 equiv per repeat unit of a solution of sodium 6-iodo-2-naphthoxide in dry THF (200 mL) prepared by the reaction of **1** (4.65 g, 0.0172 mol) with sodium metal (0.39 g, 0.017 mol) in dry THF (200 mL) over 24 h. Once the addition of this sodium salt was complete, the reaction mixture was heated at reflux for 24 h. The second sodium salt was synthesized in the following manner. Under argon, propyl 4-hydroxybenzoate (3.70 g, 0.021 mol) was dissolved in dry THF (100 mL), and this solution was added to a slurry of 95% NaH (0.5 g, 0.021 mol) in 50 mL of dry THF. The mixture was stirred at room temperature for 2 h and then warmed to 65 °C for an additional 2 h until a clear solution was obtained. This sodium salt solution was transferred into an argon-charged addition funnel, and the solution was added dropwise to the partially substituted polymer reaction mixture. The mixture was cooled before the addition of the second sodium salt. After the addition was complete, the total reaction mixture was heated to reflux for another 24 h. The reaction was monitored by ^{31}P NMR spectroscopy to confirm that both primary and secondary substitutions were complete. When no further change in the ^{31}P NMR spectrum was evident, the mixture was cooled to room temperature. The product was isolated by concentration of the solution to approximately one-fifth of its original volume through rotoevaporation of the solvent and then precipitation of this polymer solution into water. The solids were collected and further purified through repeated precipitations from THF into water, ethanol, diethyl ether, and hexane. The solid was then dried under vacuum to give a slightly off-white material, which was readily soluble in THF. Integration of the ^{1}H NMR spectrum indicated a side group ratio of 1.12:1.00, for **1** to propyl 4-hydroxybenzoate. ^{31}P NMR ($CDCl_3$), δ (ppm): −15.6, −19.3. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.60 (1H), 7.49−6.15 (9H), 4.05 (2H), 1.58 (2H), 0.90 (3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 165.3, 154.4, 148.4, 135.9, 134.5, 130.6, 128.5, 127.8, 127.3, 126.2, 120.1, 117.5, 116.9, 90.5, 66.3, 21.9, 10.4. Anal. Calcd: C, 48.15; H, 3.35; N, 2.81; P, 6.22. Found: C, 48.85; H, 3.30; N, 3.49; P, 6.81.

Synthesis of [$NP(OC_{10}H_6I)(OC_6H_4COOH)]_n$ (5). This polymer was obtained with the use of a deprotection method that has been reported previously.[53] A solution was obtained by dissolving polymer **4** (6.00 g, 0.0121 mol) in 200 mL of THF in a 1 L flask. This solution was added to a slurry of *t*-BuOK (15.0 g, 0.13 mol), 300 mL of THF, and 1 mL of water. After the addition was complete, the reaction mixture was stirred at room temperature for a period of 40 h. After this time, the mixture was poured onto 100 g of ice. When the ice had melted, the THF was allowed to evaporate and a 1 M solution of aqueous HCl was added to the reaction mixture until a pH of 4 was reached. A yellow solid precipitated from the solution and this was filtered off and collected as a powder. The solid was redissolved in a 1:1 solution mixture of aqueous NaOH (1 M) and THF. This solution was placed in 6000−8000 molecular weight cutoff dialysis tubing and was dialyzed against a 1:1 water/THF reservoir, which was changed continuously until a pH value of 7 for this reservoir was maintained. The solution was removed from the dialysis tubing, and some insoluble materials were filtered off. The soluble portion was acidified with a 1 M solution of aqueous HCl to a pH of 5, and a white solid precipitated out. This was filtered off, washed three times with water, and dried under vacuum. The product was a brittle, white solid. ^{31}P NMR (DMSO-d_6), δ (ppm): −18.6, −10.2. ^{1}H NMR (DMSO-d_6), δ (ppm): 12.57 (1H), 8.20−6.31 (10H). ^{13}C NMR (DMSO-d_6), δ (ppm): 167.0, 154.6, 148.9, 135.9, 134.4, 133.5, 131.9, 131.0, 129.3, 128.6, 127.7, 121.7, 120.4, 116.9, 91.0. Anal. Calcd: C, 44.92; H, 2.41; N, 3.05; P, 6.75. Found: C, 47.71; H, 2.68; N, 3.76; P, 7.89.

Synthesis of [$NP(OC_{10}H_6I)(OC_6H_4COOCH_2CH_2N(Et)(C_6H_4N_2C_6H_4NO_2))]_n$ (6). In an argon-charged flask, polymer **4** (1.10 g: 0.33 g of acid, 0.0024 mol) was dissolved in 20 mL of freshly distilled, dry $SOCl_2$ (12.26 g, 0.102 mol). This mixture was stirred and warmed to approximately 80 °C until the polymer was completely dissolved. The reaction mixture was then heated at this temperature for 1 h. During this time, the mixture remained clear but changed color and became progressively darker from light tan to dark orange. The mixture was then cooled to ambient temperature. ^{1}H NMR analysis of an aliquot indicated that the acid functionalities on polymer **4** (at 12.57 ppm) were completely converted to the acid chloride even though the ^{31}P NMR spectrum of polymer **5** showed no change from the spectrum of the starting polymer **4**. The excess $SOCl_2$ was removed from the mixture under vacuum to leave a light brown glassy solid. To this was added 100 mL of dry dioxane, and the solution was gradually heated. The solid dissolved readily in the warm dioxane, in contrast to the behavior of polymer **4**, which was insoluble even in refluxing dioxane. In a separate argon-charged reaction flask, a mixture of DR-1 (1.80 g, 0.0057 mol) and dry triethylamine (20 mL, 0.14 mol) was stirred in 100 mL of dry dioxane at 80 °C. The dioxane solution of acid chloride-functionalized polymer was transferred into an argon-charged addition funnel and added dropwise, very slowly, to the DR-1/NEt_3 solution. A white solid (presumed to be $HCl{\cdot}NEt_3$) precipitated. This was initially difficult to detect because of the dark color of the DR-1 solution. After the addition was complete, the polymer/DR-1 reaction mixture was heated to reflux for 24 h. After this time the reaction mixture was cooled to ambient temperature and the solvents were removed by rotoevaporation. The remaining red solids were washed three times with cold water, collected by centrifugation, and dissolved in 100 mL of dichloromethane. This solution was filtered to remove any insoluble material. The soluble mixture was collected, and the solvent was removed by rotoevaporation to leave a red powder. This powder was then adsorbed on silica gel, and column chromatography was carried out to remove unreacted DR-1 and small molecule byproducts. The excess DR-1 and byproducts were separated from the polymer by using consecutively diethyl

ether and dichloromethane eluting solvents. When all of the nonpolymeric products were removed, the polymer was eluted from SiO_2 with THF. This fraction was collected and the THF removed by rotoevaporation. A dark red, glassy material was obtained, which was very soluble in a variety of organic solvents. Integration of the ^{1}H NMR spectrum indicated a side-group ratio of 1.2:1.0, for **1** to DR-1, meaning a 96% substitution of the available ester-functionalized sites. ^{31}P NMR ($CDCl_3$), δ (ppm): −16.9, −13.1. ^{1}H NMR ($CDCl_3$), δ (ppm): 8.23 (2H), 7.84 (4H), 7.63−6.31 (12H), 4.38 (2H), 3.49 (2H), 3.32 (2H), 1.01 (3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 165.1, 156.6, 154.6, 151.5,148.5, 147.3, 143.8, 135.8, 134.0, 133.4, 131.8, 130.7, 128.2, 127.4, 125.5, 124.6, 122.6, 121.3, 120.5, 117.0, 115.0, 90.7, 61.6, 48.7, 45.7, 12.3. Anal. Calcd: C, 52.45; H, 3.54; N, 9.04; P, 4.21. Found: C, 54.80; H, 4.26; N, 9.35; P, 5.06.

Synthesis of $[NP(OC_{10}H_6I)(OC_6H_4OSi(CH_3)_2C(CH_3)_3)]_n$ (7). This cosubstituent polymer was synthesized in an analogous manner to that already described for **4**. For this copolymer, a sodium salt of the first substituent was synthesized from the reaction of **1** (4.65 g, 0.017 mol) with sodium (0.39 g, 0.017 mol) in 200 mL of dry THF. This sodium salt in THF was added to a solution containing poly(dichlorophosphazene) (2.0 g, 0.02 mol) in 250 mL of dry THF. The mixture was heated at reflux for 24 h. After this time, the second substituent sodium salt, made from the reaction of **2** (5.38 g, 0.02 mol) with sodium hydride (0.60 g, 0.02 mol) in 100 mL of dry THF, was added to the partially substituted poly(dichlorophosphazene) solution. The mixture was then heated at reflux for an additional 24 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. When the substitution was complete, the mixture was treated in an manner analogous to that described for **4**. Purification of this compound was achieved through repeated precipitations from THF into water, ether, and hexane. Integration of the ^{1}H NMR spectrum indicated a side-group ratio of 1.2:1.0, for **1** to **2**. ^{31}P NMR (THF-d_8), δ (ppm): −16.2, −13.2. ^{1}H NMR (THF-d_8), δ (ppm): 7.76 (1H), 7.70−6.65 (8H), 6.40 (1H), 0.86 (9H), −0.05 (6H). ^{13}C NMR (THF-d_8), δ (ppm): 153.4, 150.0, 146.2, 137.1, 135.6, 133.3, 129.9, 129.1, 128.4, 122.9, 121.1, 118.9, 118.3, 91.2, 30.7, 18.8, −4.2. Anal. Calcd: C, 47.90; H, 4.24; N, 2.57; P, 5.67. Found: C, 47.70; H, 4.30; N, 3.26; P, 7.09.

Synthesis of $[NP(OC_{10}H_6I)(OC_6H_4OH)]_n$ (8). This polymer was obtained through deprotection of polymer **7** in a manner analogous to the method used for *t*-BDMS-derivatized alcohols.[54] In an argon-charged reaction flask, polymer **7** (4.0 g: 1.66 g of side-group **2**, 0.007 45 mol) was dissolved in 100 mL of dry THF. To this was added dropwise a 1 M (n-Bu)$_4$NF (11.4 mL, 0.0114 mol) solution. After the addition was complete, the mixture was stirred at ambient temperature. After approximately 15 min, a solid precipitated from solution. The solids that were collected were found to be soluble in DMF. The material was precipitated three times from a concentrated DMF solution into ethanol. An adhesive, white solid was obtained. This was further purified by extensive washing with hexane, and it was then collected and dried under vacuum. The resultant polymer was a brittle powder that was insoluble in all common solvents except DMF. ^{31}P NMR (DMF-d_7), δ (ppm): −17.7, −12.6. ^{1}H NMR (DMF-d_7), δ (ppm): 9.48 (1H), 8.50−5.80 (14H). ^{13}C NMR (DMF-d_7), δ (ppm): 153.4, 150.1, 137.7, 135.0, 132.9, 129.8, 128.7, 128.1, 122.6, 118.0, 116.2, 90.8. Anal. Calcd: C, 39.30; H, 2.20; N, 2.76; P, 6.10. Found: C, 47.46; H, 3.48; N, 4.65; P, 9.20.

Synthesis of $[NP(OC_{10}H_6I)(OC_6H_4OCH_2CH_2N(Et)(C_6H_4N_2C_6H_4NO_2))]_n$ (9). This polymer was synthesized by a reaction of the lithium phenoxylate derivative of polymer **8** with **3**, in a manner analogous to a previously reported method.[18,20] In an argon-charged reaction vessel, polymer **8** (0.5 g: 0.13 g of phenol, 0.0012 mol) was dissolved into a solution with freshly distilled, dry DMF (30 mL). To this solution was slowly added dry $LiN(Si(CH_3)_3)_2$ (0.30 g, 0.0018 mol). The reaction mixture was warmed at 80 °C for 4 h. This mixture became turbid and developed a yellow color. In a separate argon-charged reaction flask compound **3** (1.20 g, 0.0026 mol) was dissolved in a solution of dry DMF. The lithium−polymer reaction mixture was transferred into an argon-charged addition funnel and added dropwise to the DMF solution of **3**. When the addition was complete, the reaction mixture was heated to 100 °C for 24 h. After this time, the reaction mixture was cooled to ambient temperature and the DMF solvent was removed under vacuum to yield a dark red solid. This solid was washed with 200 mL of benzene and filtered, and the solid was collected. The solid was washed three more times with excess diethyl ether. The solid was collected, dissolved in concentrated THF and precipitated into excess water. The precipitate was collected and washed again with excess diethyl ether to yield a red powdery substance. To remove unreacted **3** from this material, the powder was placed into a paper thimble and Soxhlet extracted with diethyl ether over 3 days. The extraction solvent reservoir was changed every 24 h until it did not show any further color change. The red powdery solid was then removed from the extraction apparatus and dried under vacuum. A material was obtained that was soluble in THF and DMF. Analysis of the integration of the ^{1}H NMR spectrum indicated a side-group ratio of 1.2:1.0, for **1** to DR-1, meaning complete or 100% substitution of the available ether-functionalized sites. ^{31}P NMR (THF-d_8), δ (ppm): −23.0 to −12.5 (broad peak). ^{1}H NMR (THF-d_8), δ (ppm): 8.25 (2H), 7.90 (4H), 7.70−6.30 (12H), 4.38 (2H), 3.49 (2H), 3.32 (2H), 1.01 (3H). ^{13}C NMR (THF-d_8), δ (ppm): 156.5, 155.5, 153.1, 148.6, 144.7, 137.1, 135.5, 134.0, 133.1, 132.8, 129.8, 128.4, 127.2, 127.0, 125.3, 123.4, 122.6, 121.1, 117.5, 115.4, 112.3, 91.0, 59.2, 50.4, 46.6, 12.5. Anal. Calcd: C, 63.00; H, 4.35; N, 10.98; P, 5.28. Found: C, 47.45; H, 3.44; N, 7.00; P, 5.51.

Synthesis of $[NP(OC_6H_4OCH_2C_6H_5)_2]_n$ (10). Polymer **10** was synthesized according to a method reported previously.[35] Spectral data match those in the literature.[35] ^{31}P NMR ($CDCl_3$), δ (ppm): −16.2 (broad peak). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.13 (5H), 6.61 (4H), 4.54 (2H). ^{13}C NMR ($CDCl_3$), δ (ppm): 154.6, 145.4, 136.6, 128.3, 127.5, 127.4, 122.3, 114.7, 69.9. Anal. Calcd: C, 70.40; H, 4.96; N, 3.16; P, 6.90; Cl, 0.0. Found: C, 67.62; H, 4.94; N, 3.02; P, 6.61; Cl, 0.43.

Synthesis of $[NP(OC_6H_4OH)_2]_n$ (11). Polymer **11** was synthesized from polymer **10** as reported in the literature.[35] The reagent used for the deprotection reaction was boron tribromide. Spectral data match those in the literature.[35] ^{31}P NMR (CD_3OD), δ (ppm): −17.1 (broad peak). ^{1}H NMR (CD_3OD), δ (ppm): 9.47 (1H), 6.62 (4H). ^{13}C NMR(CD_3OD), δ (ppm): 154.0, 146.2, 123.6, 116.3. Anal. Calcd: C, calcd. 54.75; H, 3.80; N, 5.33; P, 11.71. Found: C, 51.51; H, 4.30; N, 4.21; P, 9.28.

Synthesis of $[NP(OC_6H_4OH)_{0.8}(OC_6H_4OCH_2CH_2N(Et)(C_6H_4N_2C_6H_4NO_2))_{1.2}]_n$ (12). This polymer was synthsized in a manner similar to that for polymer **9**. The amounts of starting materials and reagents are as follows: polymer **11**, 0.5 g, 1.9 mmol; $LiN(Si(CH_3)_3)_2$, 0.41 g, 2.4 mmol; compound **3**, 1.15 g, 2.4 mmol. The product polymer **12** was soluble only in DMF. Analysis of the integration of ^{1}H NMR spectrum indicated that 60% of the alcohol groups on the polymer were converted to ether. ^{31}P NMR (DMF-d_7), δ (ppm): −16.9. ^{1}H NMR (DMF-d_7), δ (ppm): 9.42 (1H), 8.27 (2H), 7.78 (2H), 7.42−6.39 (8H), 4.40 (2H), 3.49 (2H), 3.30 (2H), 1.01 (3H). ^{13}C NMR (DMF-d_7), δ (ppm): 156.3, 154.6, 152.8, 147.9, 146.1, 144.8, 134.1, 130.4, 126.8, 125.3, 122.7, 116.0, 115.2, 58.9, 50.0, 46.1, 12.3. Anal. Calcd: C, 60.58; H, 4.72; N, 13.14; P, 5.01. Found: C, 55.33; H, 4.31; N, 10.15; P, 8.36.

Electrooptic Measurements. The polymers were spin coated onto ITO glass using a 3 wt % solution in *N*,*N*-dimethylformamide (DMF). The same solutions were also used to spin coat the polymers on silicon wafers. The samples were then heated to 60 °C in a vacuum oven to ensure complete removal of solvent. The samples on silicon wafers were used to determine the refractive indices and thicknesses of the films by ellipsometric measurements. The thicknesses of the films on ITO glass were further confirmed by stylus profilometry. Birefringence measurements were carried out as described by Kemp.[55] The alignment of chromophores was achieved by corona poling, with the source held about 1 cm from the surface of the film and the potential difference being 3 kV. During

poling the samples were maintained at 80 °C. After 1 h the samples were allowed to cool under the influence of the electric field before birefringence measurements were performed.

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