Polyphosphazenes with High Refractive Indices: Synthesis, Characterization, and Optical Properties

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Received February 13, 1995; Revised Manuscript Received June 2, 1995[⊗]

ABSTRACT: This work was carried out in order to demonstrate that polymers with tunable, high refractive index values can be designed and synthesized to fit a variety of optical applications. A series of polyphosphazenes bearing conjugated, organic side groups were synthesized and their refractive indices were measured. Refractive index values ranging from 1.60 to 1.75 were obtained. A systematic approach to tailoring various polymer properties such as refractive index, optical absorption, solubility, and glass transition temperature was utilized in the synthesis of these polymers. Control over the extent of conjugation of the side group, side group molecular symmetry, and the use of a molecular spacer group were employed to achieve this goal. These polymers can be cast from solution and used in applications that require optically transparent films.

Introduction

A considerable amount of literature exists on the synthesis of organic-based polymers with high refractive indices.[1-11] Such polymers are used as replacements for heavier, more brittle and more expensive inorganic glasses. The advantage of using polymers lies in their relative ease of processing, better impact resistance, and lightness of weight compared to their inorganic glass counterparts.[12] The use of synthetic polymers allows a wider versatility with respect to the design and synthesis of materials with properties that suit specific device-use parameters. This broad versatility is only rarely available with inorganic materials. Examples are found in optical communications technology, especially with the use of thin films as optical interconnections or wave guides which require precise refractive index matching.[13] However, one disadvantage of classical organic polymeric materials is their sensitivity to prolonged exposure to intense light: They may discolor over long periods of time and are susceptible to free-radical chain cleavage and cross-linking processes. In addition, typical organic polymers are limited to refractive index values between 1.3 and 1.7.[12,14-16] This has prevented the use of many such polymers for critical optical applications in preference to high refractive index inorganic glasses.[12-14] Efforts are underway to develop isotropic polymers with refractive indices that exceed 1.7. Essentially, three classes of polymeric materials have been described in the literature in an attempt to address this need.

The first class of polymers makes use of composite type systems. This approach involves the formation of blends or alloys of organic with inorganic components to give hybrid materials with properties derived from both components. Generally, a sol–gel synthesis is used to incorporate domains of inorganic glass into a polymer matrix. The resultant materials are lightweight relative to true inorganic glasses and have refractive index values up to 1.8.[2,3,5,6,17-19] The second class of high refractive index polymers are similar to those described above but utilize a host–guest type arrangement that involves a polymer matrix with dissolved organic dyes, inorganic salts, or colloidal particulates. The refractive index values for these systems range from 1.55 to 2.9.[1,7,11] The third approach involves the synthesis of rigid, rodlike polymers that contain a high π-electron density in the backbone structure. Several reports[4,9,10,20-25] have demonstrated the preference for these polymers to be wholly aromatic polyamides and aromatic heterocyclic ring backbone polymers. The range of refractive index values for these systems is from 1.7 to 2.0. The principal underlying quality sought for all of these systems is the formation of colorless, noncrystalline, isotropic films by fabrication from solution.

The refractive index of a homogeneous polymer is a result of many factors. For polymers with molecular weights of 10^5 Da or less, two of these factors are the degree of polymerization of the polymer and the molar refraction of the polymer repeat unit.[15,16] The molar refraction per repeat unit is considered to be the sum of the refraction contributions of all the bonds or groups that make up the repeat unit. Polyphosphazenes, which contain an inorganic phosphorus–nitrogen backbone, have the potential to generate high refractive index values because of the relatively high electron density in the backbone structure.[27-30] Moreover, polyphosphazenes typically have high degrees of polymerization.[31] Consequently, the refractive indices should be at a maximum and therefore be independent of the molecular weight for these polymers. In addition, polyphosphazenes can be designed and synthesized with a variety of side group structures (Scheme 1). The $-P{=}N-$ backbone is optically transparent in the region between 220 and 800 nm,[32] and the physical properties of the resultant polymer depend significantly on the choice of the side groups, R.[33] Therefore, the design of usable, optically transparent polymers that exhibit high refractive index values from polyphosphazenes seems reasonable. In earlier work, Allcock, Wynne, and coworkers[34] found that a specific, fully substituted, biphenyl-based polyphosphazene had a refractive index value of 1.686 (measured at 632 nm, He–Ne laser, critical angle method). This value is high compared to values for typical organic polymers.

A more detailed examination of polyphosphazenes was conducted in order to explore the tuneability of the refractive index by the choice of the side group structure

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

0024-9297/95/2228-6188$09.00/0

Scheme 1. Synthesis of Polyphosphazenes

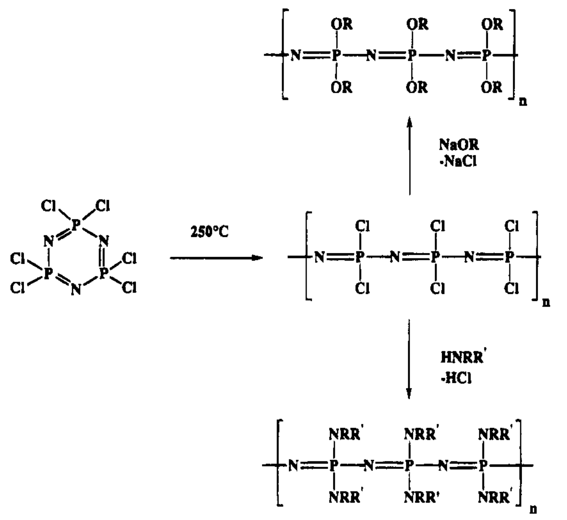
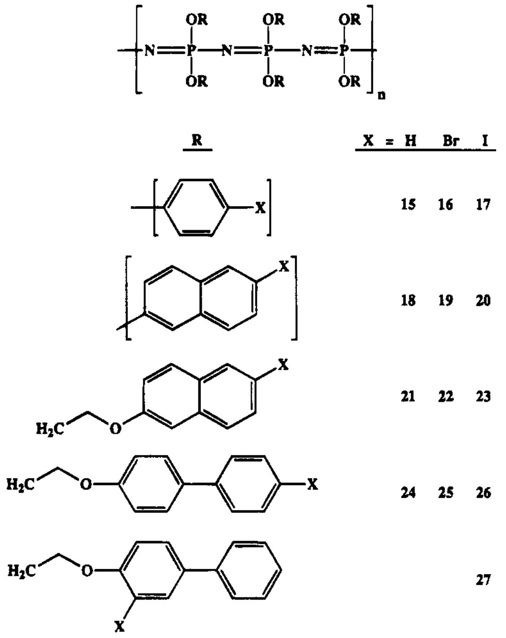


Chart 1. Polymer Systems Studied

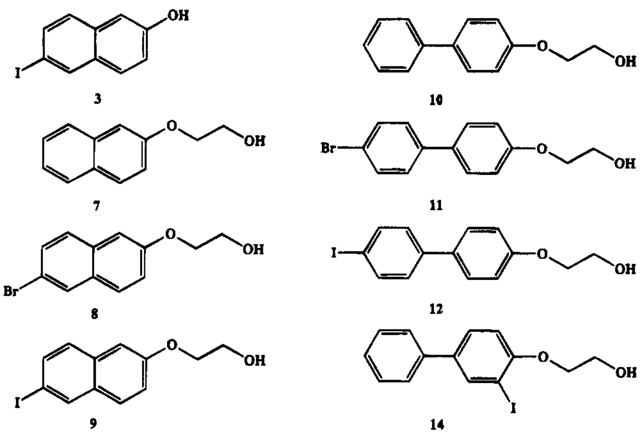


and by the chemical modifications of the substituents on these side groups. In this work, the synthesis of a series of polymers was undertaken, and the effects on thermal properties, molecular weight, and solubility as well as the optical properties of such polymers were investigated. Attempts were made to maximize the refractive index, glass transition temperature, and optical transparency while maintaining a soluble and therefore processable polymer system.

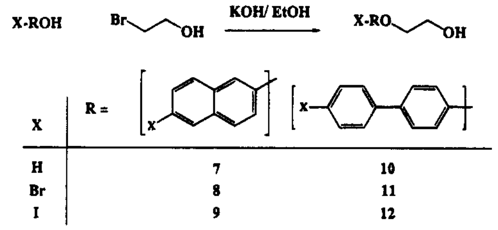
In a second work currently in progress, a thorough study of the optical dispersion and molar refractivity calculations for these polymers is being conducted. A comparison of measured values of the refractive indices with calculated values for the polymers will be made in a forthcoming paper.

Four series of structures were investigated as shown in Chart 1. Several parameters were investigated which included (a) the number of π-electrons and extent of conjugation[47] within the side group, (b) the effect of heavy-element substitution on the side group structure as well as its positioning on the side chain, and (c) the influence of a short-chain, molecular spacer between the side group structure and the inorganic polymer backbone. The influence of these factors on both the optical and morphological behavior of the resultant polymers is described below.

Chart 2. Side Group Alcohols Synthesized



Scheme 2. Williamson Ether Synthesis of Side Group Structures with Attached Spacers

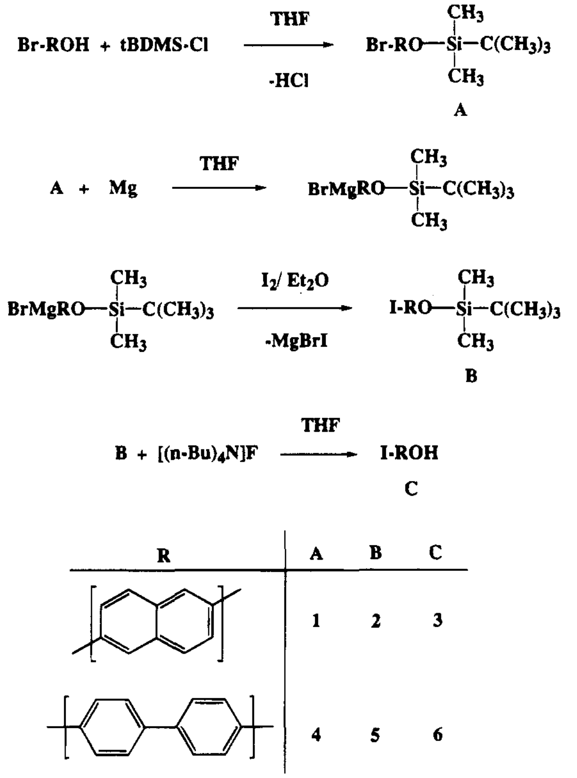


Results and Discussion

Side Group Synthesis. Not all the side group units used in these polymers were available commercially. Those side groups that had to be synthesized are listed in Chart 2. The reaction protocols shown in Schemes 2–4 illustrate the preparation of specific side groups. Scheme 2 shows the linkage of an aliphatic spacer unit to the aryl alcohol by a Williamson ether synthesis. Scheme 3 illustrates the synthesis of the iodinated species. An initial step in this reaction involved the protection of the alcohol functionality by treatment with *tert*-butyldimethylsilyl chloride (TBDMS chloride).[35] This product was then used in the preparation of a Grignard reagent, which provided a vehicle for halogen exchange of iodine for bromine in the presence of excess iodine. The alcohol site was then deprotected in a standard manner[36] to yield the appropriate iodinated alcohol. Scheme 4 shows the treatment of the tetrahydropyran (THP)[37] protected, bromo-substituted alcohol with *n*-butyllithium to induce a metal–halogen exchange reaction. This was followed by a corresponding shift in the positioning of the lithium on the aromatic ring following warming. This shift is due to a complex-induced proximity effect[38] which stabilizes the migration of the lithium ion to the position ortho to the etheric linkage. Subsequent treatment of this lithium salt with iodine, followed by isolation and deprotection[37] of the desired isomer, gave the substituted alcohol shown.

Polymer Synthesis. The general synthesis of these high molecular weight polymers follows previously described methods[39] which involve the nucleophilic reaction of an appropriate side unit sodium salt with poly(dichlorophosphazene). The reactions took place by the addition of a solution of poly(dichlorophosphazene) in either dry THF or dry dioxane to a more than 2 molar excess of the sodium salt nucleophile of the corresponding side group alcohol. The reaction mixtures were then

Scheme 3. Grignard Reagent Formation for Halogen Exchange Reaction



Scheme 4. THP Protection of Alcohol and Metal–Lithium Exchange

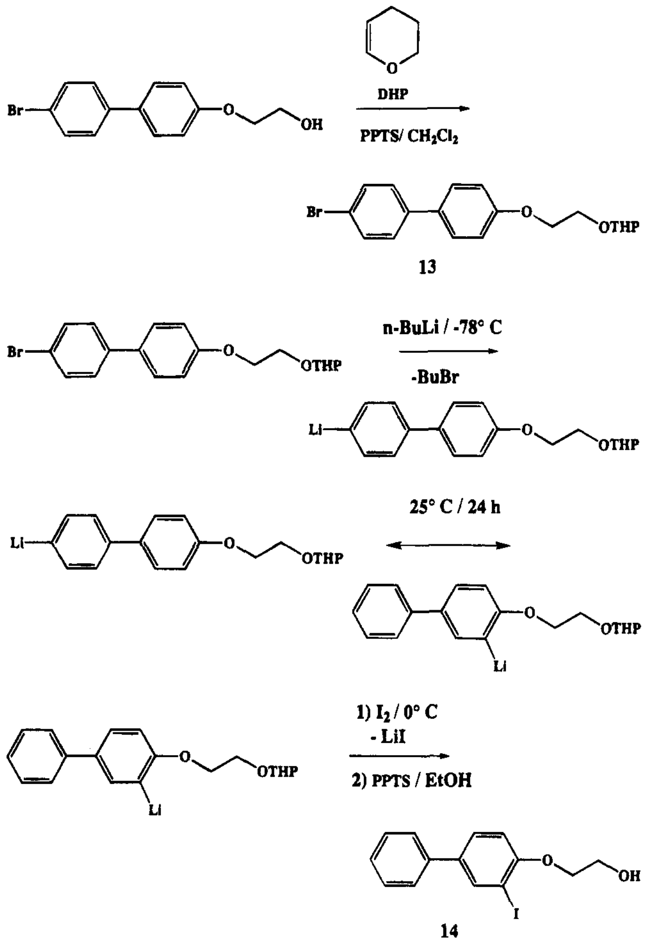


Table 1. UV–Visible Absorption of Small-Molecule Side Group Alcohols

structure	solvent	ϵ_{max} (L/(mol·cm))	λ_{max} (nm)	λ_{onset} (nm)
phenol	THF	1 887	274.5	290.5
4-bromophenol	THF	1 555	284.5	303.0
4-iodophenol	THF	1 501	275.0	317.0
2-naphthol	THF	4 584	275.5	347.5
6-bromo-2-naphthol	THF	5 528	277.5	358.0
3	THF	6 286	279.5	359.5
7	THF	4 009	273.5	343.5
8	THF	6 310	275.0	345.5
9	THF	7 575	276.5	349.0
10	THF	18 936	263.5	308.5
11	THF	23 842	273.0	315.0
12	THF	25 379	275.0	320.5
14	THF	18 330	264.0	342.0

refluxed for periods of time from several days to 1 week, and the progress of each reaction was monitored by ^{31}P NMR spectroscopy. The excess of nucleophile was necessary to achieve full displacement of the chlorine atoms and to overcome the retarding influence of the steric bulk of some of the nucleophiles.[34] The relative molecular weights of the resultant polymers were measured by gel permeation chromatography (GPC) methods. This molecular weight monitoring was necessary to ensure that the conditions used for polymer synthesis (i.e., high temperatures for extended periods of time) did not cleave the inorganic polymer backbone (see GPC results in a later section).

Thin-Film Formation. The polymers listed in Table 2 were fabricated into thin films by a hot press technique. Each polymer was placed on a glass slide, which was gently warmed on a hot plate. A few drops of a strongly solvating, high-boiling solvent, such as 1-methyl-2-pyrrolidinone (NMP) or dimethylformamide (DMF), was added until the polymer had partially dissolved. Another glass slide was then placed on top, and the polymer was sandwiched into a film between the two slides. The sandwich was cooled to room temperature while maintained under pressure. After cooling, the sandwich structure was dried thoroughly in a vacuum oven (30 °C, 48 h). After this step, the top slide was removed. This technique worked well enough to give transparent, thin films of the polymers appropriate for refractive index measurements.

Optical Measurements. UV–Visible Spectroscopy. An examination of the absorption onset for the polymers and side group units listed in Tables 1 and 2 indicated that nearly all the polymers are optically transparent in the visible region of the spectrum (350–700 nm). The naphthyl-bearing polymers **22** and **23** start to absorb at this shorter wavelength cutoff, and this may limit their utility in this region of the spectrum. The biphenyl polymers **24**–**27** showed very short-wavelength cutoffs, which makes them especially useful for purposes that require complete transparency in the visible region.

A comparison of the absorption of the free side units to those of the polymers indicated that the optical absorption of all of the polymers described here can be attributed directly to the corresponding side group absorption. The extinction coefficients for the biphenyl systems are the highest of all the polymer systems studied. Similarly, the extinction coefficients of the corresponding biphenyl side groups are higher than those of the other listed side group molecules.

Refractive Index Measurements. Refractive index measurements were carried out at ambient temperature (25 °C) using the immersion oil method[45] in which an optical microscope fitted with a conical focusing con-

Table 2. UV–Visible Absorption of Polymer Systems

polymer	solvent	ϵ_{max} (L/(g · cm))	λ_{max} (nm)	λ_{onset} (nm)
15	THF	3.749	253.5	290.5
16	THF	2.980	271.5	301.5
17	NMP	2.483	275.0	308.5
18	THF	13.618	276.0	342.0
19	NMP	insol	278.5	340.0
20	NMP	insol	280.5	339.0
21	THF	17.025	273.5	345.5
22	THF	17.317	276.0	358.0
23	THF	18.658	278.5	351.0
24	THF	60.788	260.0	309.5
25	NMP	60.022	267.5	319.0
26	NMP	55.155	273.0	322.5
27	THF	37.984	262.5	324.5

denser is employed to conduct Becke line analysis. A tungsten lamp producing an optical spectrum centered around 550 nm, located sufficiently distant from the microscope condenser to ensure substantially parallel rays of light, was used as the light source. The refractive indices indicated are measured at this wavelength. Each immersion oil comparison was done quickly and with a fresh sample of polymer to ensure no imbibition of the immersion oils.

The results of the refractive index measurements indicated relatively high values for the refractive indices of the polymers. These high refractive index values arise from additive contributions from (1) the large electron density on the side group substituents and (2) a contribution from the inorganic polymer backbone. This can be seen by comparing the refractive indices of the liquids benzene (n = 1.5010), bromobenzene (n = 1.5590), and iodobenzene (n = 1.6161) with polymers that have the corresponding side group structures, **15** (n = 1.620), **16** (n = 1.646), and **17** (n = 1.715). On average, the polymeric species have a refractive index value 0.1 unit higher than those of their corresponding free side group structures, and this can be correlated with the relatively high electron density of the polymer backbone. Currently, work is under way to compare these measured values with calculated values obtained using tabulated bond molar refractivity contributions.

In general, the refractive index value of a polymer should increase as the number of π-electrons increases within the side group structures.[4,10,21,22,25] This is demonstrated by the comparison of the series **15–17** with the series **18–20**. In all cases, it appears that the refractive index increases when the side group structure contains heavier elements (H to Br to I). This same effect is seen for small molecules (benzene < bromobenzene < iodobenzene) and is expected, since refractive index increases with increasing electron density. However, it appears that this effect is diluted, and is smaller with the biphenyl series **24–27** than for every other series. In addition, comparison of the polymers **26** and **27** indicates that the positioning of the iodine on the aromatic ring structure has a very small effect on the refractive index. Presumably different side group molecular symmetries result in different side group packing in the solid state. However, this comparison may not be representative of a true molecular symmetry effect since it is clear that, within the biphenyl system, the effects that influence refractive index (i.e., halogen replacement) have been diluted.

A decrease in the refractive index was evident following the incorporation of an aliphatic spacer group. This can be seen by comparing the series **18–20** with **21–23**.

Table 3. Refractive Index Values of Polymers (Immersion Oil Technique)

polymer	refractive index	polymer	refractive index
15	1.618–1.620	**21**	1.632–1.634
16	1.644–1.646	**22**	1.646–1.648
17	1.710–1.715	**23**	1.682–1.684
18	1.662–1.664	**24**	1.650–1.652
19	1.686–1.688	**25**	1.660–1.662
20	1.750–1.755	**26**	1.664–1.666
		27	1.662–1.664

Table 4. Physical Data for Polymers: Molecular Weights, Glass Transitions (T_g), and Melting Temperatures (T_1)

polymer	M_n[a]	M_w[a]	M_n/M_w	T_g (°C)	T_1 (°C)
15	1.5	3.4	2.3	−6.9	123.3
16	2.2	3.9	1.8	17.3	129.8
17	2.5	4.7	1.9	43.1	196.7
18	2.6	3.4	1.3	33.4	136.6
19		*0.4*		71.0	187.0
20		*0.2*		90.3	211.7
21	0.3	1.0	3.4	30.6	none
22	4.7	5.7	1.2	43.5	none
23	4.1	5.0	1.2	64.8	none
24	1.9	3.2	1.7	56.2	107.8, 133.7
25	3.8	4.7	1.2	89.7	167.4, 176.3
26	1.3	2.4	1.8	111.4	201.4, 212.7
27	4.3	5.2	1.2	69.5	decomp

[a] M_n and M_w values are 10^6.

Polymer Characterization. Gel Permeation Chromatography. Table 4 shows the relative molecular weights of the polymers, as compared to a calibration curve obtained using reference polystyrene samples of varying molecular weights. Typical MW values of approximately 1 × 10^6 or higher are expected for polyphosphazene systems.[31] Most of the molecular weights listed are in agreement with this expectation and show no evidence of degradation during synthesis or isolation. Polymer systems **19** and **20** had relatively lower molecular weight values than the other polymer systems described. Indeed these values are quite low for polyphosphazenes in general. A reason for this may be the insolubility of polymers **19** and **20** in all solvents tested except for hot NMP. Consequently, in the filtration of these samples, before carrying out the GPC experiments, the higher molecular weight components of the samples may have been removed. In fact, the GPC chromatogram revealed trace amounts of species with molecular weights that exceed 1.2 × 10^6 for **19** and 0.2 × 10^6 for **20**. Therefore it is reasonable to assume these polymer samples actually consist of molecular weights in a similar range.

The attachment of a molecular spacer to the side group structure increased the polymer solubility dramatically. Because of this effect, naphthyl polymers **21–23** were very soluble, while the counterpart polymers **18–20** were not. This effect was not as marked for the biphenyl polymers. The solubilities of samples **17**, **25** and **26** in THF were too low to allow a GPC experiment to be conducted. These polymers had to be first dissolved in a minimum amount of hot NMP and then diluted to a standard concentration (2.5 wt %) with THF before injection into the GPC chromatograph. Surprisingly, once these polymers were dissolved in NMP, they remained soluble even after dilution with excess THF.

It is interesting to note that the positioning of an iodine atom within the side group structure has a dramatic effect on the solubility of the resultant polymer. Comparison of polymers **26** with **27** demonstrates this effect. Polymer **26** with iodine in the 4 position of the aromatic ring of the side group is insoluble in THF. However, polymer **27**, with iodine in the 2 position of the aromatic ring, is completely soluble in THF. A similar effect has also been observed for rigid-rod polyamides that contain biphenyl repeat units. Thus, for such polymers, the use of asymmetric molecular monomers increases the solubility of the resultant polymer.[40] Note also that the molecular weight of polymer **27** is, on the average, higher than that of polymer **26**. Polymer **27** would prove easier for processing due to this enhanced solubility.

Thermal Analysis. The results of the thermal analysis of several of the polymers are also listed in Table 4. Several scans were obtained for each polymer sample as the ramp of the temperature was varied from 10 to 40 °C/min. This was carried out to enhance the features of the transitions. All samples were initially ramp-heated up to 100 °C and were then cooled quickly to −30 °C in an attempt to establish a more uniform thermal history for all the polymer systems.

Comparisons of the thermal data for the naphthalene systems (series **18**−**20** and **21**−**23**) showed that the attachment of a spacer group between the naphthyl unit and the main chain decreased the crystallinity of the polymers, presumably by decoupling the motions of the side group from those of the main chain.[27] No T_1 transitions were detected. This decrease in crystallinity could also explain the increased solubility of polymers that contained spacer groups compared to those without. Glass transition values for the biphenyl systems **24**−**27** were high (in the region of 55−110 °C) even when the spacer groups were present. This spacer group effect was not significant enough in the biphenyl systems to remove all the crystallinity. Consequently, the biphenyl-containing polymers were less soluble and showed several T_1 type transitions.

Crystalline regions may exist within biphenyl-bearing polymers that are responsible for the effects on solubility and for the observed T_1 transitions in the thermal analysis. The presence of crystalline domains can cause light scattering, which affects the utility of polymers as optical materials. However, if the crystalline domain sizes are smaller than the wavelengths of light employed, scattering of light from the crystalline domains should not occur. Crystalline materials have a higher density than noncrystalline materials. Because refractive index is dependent on the degree of crystallinity, partially crystalline polymers would have a higher refractive index value than the corresponding completely amorphous materials. Comparisons of the calculated refractive index values of completely amorphous systems with the measured refractive index values should yield some insight into this question.

The glass transition values increased with the introduction of a halogen atom on the side group.[41] The iodo unit had a larger effect than the bromo unit. This is understandable considering that, although both iodine and bromine have roughly the same atomic volume, an iodine atom is 1.5 times heavier than a bromine atom. Consequently, it requires more energy for the main chain to achieve torsional mobility with a side group that contains iodine than it does for a comparable side group that contains bromine. This results in a higher glass transition temperature for the iodine-containing polymers. In addition, changing the position of the halogen atom to decrease the molecular symmetry of the side group structure decreases the polar interactions between side groups. This has the effect of both lowering glass transition temperature and increasing the solubility of the resultant polymer. Polymer **27** has a T_g of 69.5 °C compared to **26** with a T_g of 111.4 °C.

Table 5. Solid-State NMR Using CP MAS[a]

polymer	^{31}P NMR (ppm)	^{13}C NMR (ppm)
19	−9.3 (broad singlet)	153.77 (s), 135.17 (s), 133.87 (s), 124.17 (m), 118.83 (m)
20	−9.2 (broad singlet)	159.58 (s), 140.02 (s), 136.38 (s), 133.14 (s), 125.30 (s), 96.67 (m)

[a] ^{31}P NMR referenced against triphenylphosphine (δ = −6.0 ppm); ^{13}C NMR referenced against glycine (δ = 175.19, 44.23 ppm).

Solid-State NMR. Solid-state NMR studies were conducted on the two insoluble polymers **19** and **20** in order to obtain some level of characterization for these species. The results are given in Table 5. The spectra were obtained with the samples at ambient temperature (25 °C), which is below the glass transition temperatures of both polymers. As found for other phosphazene systems in the solid state, the ^{31}P resonance signal is broader than for solution spectra. Significant broadening in the ^{31}P MAS NMR spectra of elastomeric phosphazene polymers at temperatures below their glass transition temperatures is due to dipolar coupling of ^{31}P to ^{14}N.[42−44] The main-chain motions of these polymers cannot be isotropic or rapid at temperatures below the glass transition; otherwise this dipolar coupling would be completely averaged. This could also account for the broadening observed in the ^{13}C MAS NMR solid-state spectra. The side groups attached to the main chain share its molecular motions, making the line width of the side group carbons strongly temperature dependent.[42]

Many phosphazenes are semicrystalline below their glass transition temperature. In the solid state these polymers exist in a rigid, semicrystalline form. At temperatures above the glass transition temperatures, these polymers undergo a transition to a less crystalline, highly mobile, mesomorphic state. This mesomorphic phase shows a sharp resonance in the ^{31}P NMR spectrum, shifted upfield from its resonance signal in the semicrystalline state.[42] A similar phenomenon which could cause decreased crystallinity and increased mobility in a polymer should occur when a polymer is placed in solution. This could explain the difference in chemical shift value for the solution ^{31}P NMR spectrum of the polymer **18** (peak at −17.6 ppm), which is shifted upfield relative to the ^{31}P MAS NMR spectra of the polymers **19** (peak at −9.3 ppm) and **20** (peak at −9.2 ppm).

The resolution of the ^{13}C NMR solid-state spectra was not sufficiently high to separate the signals of the individual carbon atoms: they coalesce into several broad peaks. For **19** the signal of the carbon atom linked to bromine is not sufficiently separated from the remaining aromatic carbons, and this peak is buried within the aromatic resonance centered about 118.83 ppm. However, for **20**, the ^{13}C signal of the carbon linked to iodine was shifted sufficiently far from the other aromatic carbons that it could be detected distinctly as a broad peak at 96.67 ppm. This suggests that for **20** (and probably also for **19**) the side group structure was not altered by the synthetic conditions used to attach it to the polymer backbone.

Conclusions

We have shown that a range of high refractive index polymers, with varying physical properties, can be synthesized using the polyphosphazene skeleton as the supporting backbone structure. Control over the structure of each polymer was accomplished by the synthesis methodology, and an attempt was made to understand the effects of this control in order to design a system that can maximize useful properties and yet offer ease of processing. For example, as described earlier, the positioning of a halogen atom within the side group structure has a large effect on solubility but a minimal effect on the refractive index value of the polymer (**26** and **27**, Table 3). In addition, we found essentially no detrimental effect on the UV–visible absorption maximum of a polymer by variations in the location of the halogen atom (Table 2). Variations in the number of π-electrons in the side group and/or selection of the type of halogen used had a significant effect on the refractive index of the polymer. Finally, an additional increase in the refractive index value for these polymers was attributed to the extended P–N backbone. In this study, it has been demonstrated that the use of comblike polyphosphazene polymers, coupled with an appropriate choice of side group structures, offers a broad potential for the design of polymers with tunable optical properties, and these may be of interest in a number of engineering applications.

Experimental Section

General Procedures. Organic solvents were used as received, distilled from sodium using benzophenone as an indicator of solvent dryness, or distilled from calcium hydride. All water used in the synthetic procedures described was both distilled and deionized. The general procedure for the preparation of the starting poly(dichlorophosphazene) reagent is as described below. Small-molecule and polymer samples were submitted to Galbraith Analytical Laboratories for elemental analysis.

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, or D_2O (MSD Isotopes) as either the solvent or an internal reference. Solid-state NMR spectra were recorded using a Bruker AM 300 spectrometer fitted with a variable-tune MAS solid-state probe. UV–vis absorption spectra were recorded using a Shimadzu 310 PC UV–vis/near-IR spectrophotometer. Extinction coefficients were obtained from the slopes of plots from concentration versus absorption. Gel permeation chromatography (GPC) analysis was performed using a Hewlet-Packard 1090 liquid chromatograph with tetrahydrofuran as the solvent. Becke line analysis[45a,b] with an optical microscope employing immersion oils (accuracy ±0.002 at 25 °C) from Cargille Scientific was conducted to measure the refractive indices.

Poly(dichlorophosphazene) Preparation. Hexachlorocyclotriphosphazene (Ethyl Corp.) was recrystallized from heptane, followed by vacuum sublimation (0.02 mmHg, 40 °C). This material (200 g) was placed into a clean, dry glass tube and was seated under vacuum. The glass tube containing the cyclic trimer was placed in an oven fitted with a motorized rocking shelf (3 rocks/min) and was allowed to equilibrate at 250 °C as polymerization progressed. The tube was removed from the oven after 18 h and was allowed to cool to room temperature. The tube containing the polymer was freeze/thaw cycled with liquid nitrogen three times before opening. The glass tube was broken open under an argon atmosphere, and the polymer was removed and loaded into a sublimator. Unpolymerized cyclic trimer was removed from the polymer by vacuum sublimation (0.02 mmHg, 40 °C). The remaining poly(dichlorophosphazene) was stored in an inert atmosphere. Yield: 38.39 g (18%). ^{31}P NMR ($CDCl_3$ internal reference): δ (ppm) −18.21 (s).

Chemicals. Phenol, 4-bromophenol, and 4-iodophenol were obtained from Aldrich and were purified by vacuum sublimation before use. 2-Naphthol and 6-bromo-2-naphthol were obtained from Aldrich and were recrystallized from 20:80 diethyl ether:hexane with the use of activated carbon. The collected crystals were then dried and further purified by vacuum sublimation before use. 4-Phenylphenol and 4-bromo-4′-phenylphenol were obtained from Aldrich. The 4-phenylphenol was further purified by vacuum sublimation before use. 4-Bromoh4′-phenylphenol was used as received.

tert-Butyldimethylsilyl chloride (TBDMS chloride) was used as received from Aldrich and was employed as a protecting group for aromatic alcohols. The appropriately protected alcohols are named here according to the TBDMS acronym. All manipulations involving this compound were carried out in a glovebag under inert atmosphere conditions. A 1.0 M solution of *n*-butyl ammonium bromide in THF was used as obtained from Aldrich. This was employed as a deprotecting agent for the TBDMS group. 3,4-Dihydro-2*H*-pyran (DHP) with pyridinium *p*-toluenesulfonate (PPTS) as a catalyst was used as a protecting group for alcohols. These reagents were also used as received from Aldrich. The appropriately protected alcohols are named according to the acronym THP.

2-Bromoethanol, 2-iodoethanol, and iodine were used as received from Aldrich and were not purified further. NaH (Aldrich) was washed with dry hexane to remove the mineral oil before use. This was stored under inert atmosphere conditions. The *n*-butyllithium (1.6 M from Aldrich) was used as received.

Side Group Unit Syntheses. Synthesis of 6-Bromo-2-naphthol-(TBDMS) (1). One equivalent of 6-bromo-2-naphthol (16.60 g, 0.075 mol) was allowed to react with 1 equiv of TBDMS chloride (11.24 g, 0.075 mol) in 200 mL of dry THF and 15.6 mL of triethylamine (1.5 equiv). The reaction mixture was stirred at room temperature for 4h. The resultant product was then filtered to remove the solids. The liquid was rotoevaporated to dryness and was redissolved in diethyl ether (200 mL). Three extraction with water were carried out, and the ethereal layer was collected and dried over $MgSO_4$. The ether was removed by evaporation, and the resultant oil was chromatographed on a silica gel column. The product was eluted with hexanes and collected. The dry solid was recrystallized from hexane. White crystals, mp 62–65 °C; yield 93.7% (23.59 g). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.90 (s, 1H), 7.62 (d, 1H), 7.54 (d, 1H), 7.46 (d, 1H), 7.14 (m, 1H), 7.08 (d, 1H), 1.00 (s, 9H), 0.24 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 153.83, 133.07, 130.27, 129.59, 129.41, 128.44, 128.31, 123.08, 117.27, 114.89, 25.69, 18.25, −3.03. MS calcd for $C_{16}H_{21}BrOSi$ 337.1, found 337.1. Anal. Calcd: C, 56.97; H, 6.23; Br, 23.74. Found: C, 56.61; H, 6.28; Br, 24.36.

Synthesis of 6-Iodo-2-naphthol-(TBDMS) (2). One equivalent of **1** (18.0 g, 0.053 mol) was dissolved in 50 mL of dry THF in a 150-mL addition funnel. This was added slowly to 1.2 equiv of dry magnesium powder (1.56 g, 0.065 mol) in a three-necked, 250-mL, round-bottom flask previously purged with argon. Formation of the Grignard reagent was initiated with one drop of MeI. Compound **1** was added very slowly and sparingly at first without stirring. Formation of a green color indicated Grignard formation. The rate of addition of the starting compound was then increased, and the mixture was heated and stirred. After the addition was complete, the reaction mixture was refluxed gently overnight. The reaction mixture was cooled to room temperature and cannula-transferred into a 250-mL addition funnel previously purged with argon. This solution was added to 500 mL of dry diethyl ether containing excess iodine (27.12 g, 0.106 mol) at 0 °C with vigorous stirring over 2 h. After the addition was complete, the reaction mixture was allowed to warm to room temperature overnight. This mixture was then extracted with three generous portions of aqueous $NaHSO_3$ to destroy the excess iodine. The ethereal layer was collected and dried with $MgSO_4$. The ether was removed by rotoevaporation, and the oily product was chromatographed on silica gel with hexanes as eluant. The eluted product was collected and the hexanes were removed by evaporation. The product was a slightly yellow, oily solid, mp 38–41 °C; yield 28.6% (5.83 g). ^{1}H NMR($CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.60 (m, 2H), 7.39 (d, 1H), 7.07 (s, 1H), 7.04 (d, 1H), 1.01 (s, 9H), 0.24 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 153.99, 136.27, 134.52, 133.37, 130.89, 128.31, 128.28, 122.87, 114.86, 88.40, 25.68, 18.25, −2.95. MS calcd for $C_{16}H_{21}IOSi$ 384.1, found 384.1. Anal. Calcd: C, 50.0; H, 5.47; I, 33.07. Found: C< 49.96; H, 5.68; I, 32.93.

Synthesis of 6-Iodo-2-naphthol (3). One equivalent of **2** (5.83 g, 0.0151 mol) was dissolved in 500 mL of dry THF. This was allowed to react with 30.4 mL (2.0 equiv) of 1.0 M *n*-Bu_4NF in THF, added dropwise. The mixture was stirred at room temperature for 2 h. After this time the reaction mixture was rotoevaporated to dryness, and the oily product was redissolved in diethyl ether. This was extracted with three portions of water. The ethereal layer was dried over $MgSO_4$ and was evaporated to leave behind a yellow solid. This solid was recrystallized from heptane/ethyl acetate. The collected crystals were further purified by vacuum sublimation at 105 °C/0.01 mmHg. Slight yellow crystals, mp 136–138 °C; yield 87.2% (3.37 g). ^1H NMR ($CDCl_3$): δ (ppm) 8.12 (s, 1H), 7.62 (m, 2H), 7.40 (d, 1H), 7.09 (m, 2H), 5.1 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 154.13, 135.45, 134.92, 132.15, 130.48, 128.38, 128.03, 127.33, 118.54, 109.54, 88.18. 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-Bromo-4′-phenylphenol-(TBDMS) (4). One equivalent of 4-bromo-4′-phenylphenol (20.0 g, 0.080 mol), 1 equiv ot TBDMS chloride (12.11 g, 0.080 mol), and 16.8 mL of triethylamine (1.5 equiv) in 250 mL of dry THF were allowed to react in a similar manner as described for **1**. The reaction mixture was warmed gently for 4 h to achieve complete protection. Workup followed as described previously for **1**. White crystals, mp 86–87 °C; yield 67.6% (19.70 g). ^1H NMR ($CDCl_3$): δ (ppm) 7.50 (d, 2H), 7.40 (m, 4H), 6.87 (d, 2H), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.58, 139.80, 133.01, 131.72, 128.30, 127.90, 120.75, 120.44, 25.68, 18.23, −2.94. MS calcd for $C_{18}H_{23}BrOSi$ 363.1, found 363.1. Anal. Calcd: C, 59.50; H, 6.34; Br, 22.04. Found: C, 58.41; H, 6.30; Br, 21.57.

Synthesis of 4-Iodo-4′-phenylphenol-(TBDMS) (5). One equivalent of **4** (19.0 g, 0.057 mol) was dissolved in 50 mL of dry THF in a 150-mL addition funnel. This was added slowly to 1.3 equiv of dry magnesium powder (1.71 g, 0.070 mol) in a three-necked, 250-mL, round-bottom flask previously charged with argon. Formation of the Grignard reagent was initiated with one drop of methyl iodide. Compound **4** was added very slowly and sparingly at first without stirring. Following formation of a grayish color, which indicated Grignard formation, the rate of addition of the reagent was increased and the mixture was heated and stirred. After the addition was complete, the reaction mixture was refluxed overnight. The mixture was cooled to room temperature and cannula-transferred into a 250-mL, addition funnel previously purged with argon. This solution was added to 500 mL of dry diethyl ether containing excess iodine (34.56 g, 0.136 mol) at 0 °C with vigorous stirring over 2 h. After the addition was complete, the mixture was allowed to warm to room temperature overnight. This mixture was worked up and purified as described previously for **2**. White crystals, mp 87–89 °C; yield 36.7% (8.50 g). ^1H NMR ($CDCl_3$): δ (ppm) 7.70 (d, 2H), 7.40 (d, 2H), 7.26 (m, 2H), 6.89 (d, 2H), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.64, 140.40, 137.70, 133.03, 128.59, 127.86, 120.46, 92.12, 25.68, 18.23, −2.94. MS calcd for $C_{18}H_{23}IOSi$ 410.1, found 410.1. Anal. Calcd: C, 52.68; H, 5.61; I, 30.98. Found: C, 52.66; H, 5.46; I, 30.33.

Synthesis of 4-Iodo-4′-phenylphenol (6). One equivalent of **5** (8.50 g, 0.021 mol) was dissolved in 100 mL of dry THF. This was treated with 41.0 mL (2.0 equiv) of 1.0 M *n*-Bu_4NF in THF added dropwise. The mixture was stirred at room temperature for 2 h. After this time, the reaction mixture was rotoevaporated to dryness and the oily residue was redissolved in diethyl ether. This was extracted with three portions of water. The ethereal layer was dried over $MgSO_4$, and the ether was evaporated to leave behind a yellow solid. This solid was recrystallized from heptane/ethyl acetate. The collected crystals were further purified by vacuum sublimation at 125 °C/0.020 mmHg. White crystals, mp 192–194 °C; yield 95.0% (5.82 g). ^1H NMR (acetone-d_6): δ (ppm) 8.59 (s, 1H), 7.75 (d, 2H), 7.49 (d, 2H), 7.39 (d, 2H). ^{13}C NMR (acetone-d_6): δ (ppm) 158.32, 141.43, 138.59, 131.73, 129.21, 128.67, 116.58, 92.01. MS calcd for $C_{12}H_9IO$ 296.0, found 296.0. Anal. Calcd: C, 48.65; H, 3.04; I, 42.91. Found: C, 48.46; H, 3.03; I, 41.61.

Synthesis of 2-Naphthoxyethanol (7). A Williamson ether synthesis of this compound was carried out. One equivalent of 2-naphthol (7.65 g, 0.053 mol) was dissolved in 100 mL of 95% ethanol in a 250-mL, three-necked, round-bottom flask fitted with a reflux condenser and argon purge. An excess of KOH (6.73 g, 0.12 mol) was also dissolved in this mixture. To this was added dropwise 2.2 equiv of 2-bromoethanol (13.75 g, 0.110 mol) dissolved in 50 mL of 95% ethanol. After the addition was complete, the reaction mixture was heated to reflux (78 °C, 48 h). After this time, the mixture was worked up in the following manner. The ethanol solvent was removed by rotoevaporation and the residue was dissolved in diethyl ether. This was extracted with three generous portions of basic water. Following two more extractions with neutral water, the ethereal layer was collected and dried over $MgSO_4$. The ether was evaporated and the resultant tan solid was recrystallized from an ethyl acetate/hexane mixture. White crystals, mp 74–76 °C; yield 53.0% (5.31 g). ^1H NMR ($CDCl_3$): δ (ppm) 7.75 (m, 3H), 7.45 (t, 1H), 7.38 (t, 1H), 7.20 (m, 2H), 4.16 (t, 2H), 4.00 (t, 2H), 2.55 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.45, 134.37, 129.43, 129.01, 127.56, 126.69, 126.35, 123.70, 118.61, 106.76, 69.11, 61.29. MS calcd for $C_{12}H_{12}O_2$ 188.0, found 188.0. Anal. Calcd: C, 76.60; H, 6.38. Found: C, 76.74; H, 6.34.

Synthesis of 6-Bromo-2-naphthoxyethanol (8). This material was prepared in a similar manner to the method described for **7**, where 6-bromo-2-naphthol was used in place of 2-naphthol. The isolation of the product was as described for **7**. The resultant solid was recrystallized from an ethyl acetate/hexane mixture. Glossy, white crystals, mp 110–113 °C; yield 19.6% (2.61 g). ^1H NMR ($CDCl_3$): δ (ppm) 7.90 (s, 1H), 7.62 (d, 1H), 7.57 (d, 1H), 7.48 (d, 1H), 7.16 (d, 1H), 7.09 (s, 1H), 4.18 (t, 2H), 4.01 (t, 2H), 1.96 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.82, 132.91, 130.14, 129.69, 129.65, 128.61, 128.38, 119.73, 117.26, 106.79, 69.24, 61.40. MS calcd for $C_{12}H_{11}BrO_2$ 267.0, found 267.0. Anal. Calcd: C, 53.93; H, 4.12; Br, 29.96. Found: C, 54.00; H, 4.12; Br, 29.71.

Synthesis of 6-Iodo-2-naphthoxyethanol (9). This material was prepared in a similar manner to that described for **7**, where **3** was used in place of 2-naphthol. In addition, 2-iodoethanol was used instead of 2-bromoethanol. The isolation of the product was as described for **7**. The resultant solid was recrystallized from a methanol/hexane mixture. Glossy, white crystals, mp 140–142 °C; yield 71.6% (4.16 g). ^1H NMR (acetone-d_6): δ (ppm) 8.23 (s, 1H), 7.74 (d, 1H), 7.68 (d, 1H), 7.59 (d, 1H), 7.30 (s, 1H), 7.18 (d, 1H), 4.18 (t, 2H), 4.04 (t, 1H), 3.92 (m, 2H). ^{13}C NMR (acetone-d_6): δ (ppm) 158.54, 137.02, 135.41, 134.51, 131.59, 129.56, 129.23, 120.72, 107.48, 88.27, 70.69, 61.21. MS calcd for $C_{12}H_{11}IO_2$ 314.0, found 314.0. Anal. Calcd: C, 45.86; H, 3.50; I, 40.45. Found: C, 45.79; H, 3.54; I, 39.29.

Synthesis of (4-Phenylphenoxy)ethanol (10). This compound was synthesized as described for **7**. One equivalent of 4-phenylphenol (9.86 g, 0.058 mol) was dissolved in 150 mL of 95% ethanol in a 250-mL, three-necked, round-bottom flask fitted with a reflux condenser and argon purge. An excess of KOH (6.73 g, 0.12 mol) was dissolved in this mixture. To this mixture was added dropwise a solution of 2.2 equiv of 2-bromoethanol (16.25 g, 0.13 mol) dissolved in 50 mL of 95% ethanol. After the addition was complete, the reaction mixture was heated to reflux (78 °C, 48 h). After this time, monitoring of the reaction progress by TLC showed that a large portion of starting material was present. An additional equivalent of 2-bromoethanol and KOH were added. The reaction mixture was refluxed for another 48 h. After this time, the mixture was worked up and purified as described for **7**. Recrystallization from an ethyl acetate/pentane mixture at −50 °C gave white crystals, mp 118–120 °C; yield 45.6% (5.66 g). ^1H NMR (acetone-d_6): δ (ppm) 7.57 (m, 4H), 7.41 (t, 2H), 7.28 (t, 1H), 7.02 (d, 2H), 4.10 (t, 2H), 3.88 (t, 2H), 2.89 (s, 1H). ^{13}C NMR (acetone-d_6): δ (ppm) 159.72, 141.50, 134.18, 129.59, 128.69, 127.42, 127.20, 115.73, 70.60, 61.28. MS calcd for $C_{14}H_{14}O_2$ 214.0, found 214.0. Anal. Calcd: C, 78.50; H, 6.54. Found: C, 78.22; H, 6.68.

Synthesis of (4′-(4-Bromophenyl)phenoxy)ethanol (11). This compound was prepared in a similar manner to that described for **10**, where 4-bromo-4′-phenylphenol was used in place of 4-phenylphenol. The material was isolated in a similar manner to that described for **10**. The compound was recrystallized from an ethyl acetate/pentane mixture at −50 °C to give white crystals, mp 156−158 °C; yield 58.8% (6.89 g). ^{1}H NMR (acetone-d_6): δ (ppm) 7.57 (m, 6H), 7.03 (m, 2H), 4.10 (t, 2H), 3.87 (t, 2H), 2.83 (s, 1H). ^{13}C NMR (acetone-d_6): δ (ppm) 160.07, 140.70, 132.76, 132.06, 129.05, 128.66, 121.04, 115.86, 70.99, 61.90. MS calcd for $C_{14}H_{13}BrO_2$ 293.0, found 293.0. Anal. Calcd: C, 57.34; H, 4.44; Br, 27.30. Found: C, 57.04; H, 4.48; Br, 26.45.

Synthesis of (4′-(4-Iodophenyl)phenoxy)ethanol (12). This compound was prepared in a similar manner to that described for **10**, where **6** was used in place of 4-phenylphenol. In addition, 2-iodoethanol was used instead of 2-bromoethanol. The material was isolated in a similar manner to that described for **10**. The compound was recrystallized from hot methanol/hexane mixture to give white crystals, mp 186−188 °C; yield 96.8% (6.47 g). ^{1}H NMR (THF-d_8): δ (ppm) 7.73 (d, 2H), 7.53 (d, 2H), 7.36 (d, 2H), 6.99 (d, 2H), 4.01 (m, 3H), 3.80 (m, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 160.99, 141.34, 138.63, 133.04, 129.20, 128.40, 115.71, 92.98, 70.93, 61.51. MS calcd for $C_{14}H_{13}IO_2$ 340.0, found 340.0. Anal. Calcd: C, 49.41; H, 3.82; I, 37.35. Found: C, 49.06; H, 3.93; I, 35.14.

Synthesis of (4′-(4-Bromophenyl)phenoxy)ethanol-(THP) (13). THP-procted (4′-(4-bromophenyl)phenoxy)ethanol was prepared as described in the literature.[38] The compound was recrystallized from pentane/ethyl acetate. White crystals, mp 76−79 °C; yield 74.9% (18.48 g). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.51 (d, 2H), 7.45 (d, 2H), 7.39 (d, 2H), 6.98 (d, 2H), 4.71 (t, 1H), 4.17 (m, 2H), 3.87 (m, 3H), 3.53 (m, 1H), 1.65 (m, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 158.75, 139.71, 132.57, 131.74, 128.25, 127.88, 120.75, 115.10, 99.00, 67.54, 65.79, 62.19, 30.50, 25.40, 19.35. MS calcd for $C_{19}H_{21}BrO_3$ 377.0, found 377.0. Anal. Calcd: C, 60.48; H, 5.57; Br, 21.22. Found: C, 60.63; H, 5.54; Br, 21.78.

Synthesis of (2-Iodo-4-phenylphenoxy)ethanol (14). In a 2000-mL, three-necked, round-bottom flask purged with argon was dissolved 15.0 g (0.0.40 mol) of **13** in 400 mL of dry diethyl ether. This solution was cooled in a dry ice/acetone bath to which was added dropwise 1.2 equiv of a 1.6 M *n*-butyllithium solution (30.0 mL, 0.048 mol) over 1.5 h. After the addition was complete, the solution was allowed to warm to room temperature (24 h). The white precipitate was filtered off under argon, collected, and washed with 400 mL of dry diethyl ether, followed by a washing with 400 mL of dry hexane. This white salt was then dried under vacuum (2 h) and was stored under inert atmosphere conditions. The yield of the lithium salt was 8.40 g (0.028 mol, 70.0%). This salt was placed in a 250-mL powder addition funnel connected to a 1000-mL, three-necked, round-bottom flask charged with argon. This was then added at 0 °C (ice bath) to a stirred solution of dry diethyl ether (350 mL) containing 14.4 g (0.055 mol) of iodine. The addition was carried out slowly over 3 h. The mixture was stirred and allowed to warm to room temperature (12 h). The brown suspension in ether was extracted with several copious portions of aqueous $NaHSO_3$ to remove the excess iodine. The orange ethereal layer was collected and dried over $MgSO_4$. The ethereal layer was rotoevaporated to dryness and the residue was chromatographed on a silica gel column using a 5:1 pentane:THF eluent ratio. Three chromatographic separations were necessary in order to isolate the desired product. An attempt to crystallize the resultant crude, oily solid was not successful. The product was a colorless oil; yield 10.5% (1.22 g, 0.004 mol). A solution of this oil (5.0 g, 0.016 mol) in 100 mL of ethanol with PPTS (0.30 g, 0.0012 mol) was stirred at 55 °C for 6 h. After this, the reaction mixture was cooled, the ethanol was removed by rotoevaporation, and the solids were redissolved in diethyl ether. This solution was extracted with 3 × 200 mL portions of saturated brine solution. The ethereal layer was collected and dried over $MgSO_4$, after which the ether solvent was evaporated. The solid was recrystallized from pentane/ethyl acetate, stirred with activated carbon, and filtered through fuller's earth. The liquor was cooled and the resultant crystals were collected and dried. White crystals, mp 68−71 °C; yield 77.4% (3.06 g, 0.009 mol). ^{1}H NMR (acetone-d_6): δ (ppm) 8.05 (s, 1H), 7.60 (m, 3H), 7.43 (m, 2H), 7.34 (m, 1H), 7.08 (d, 1H), 4.19 (t, 2H), 3.94 (m, 2H), 2.86 (s, 1H). ^{13}C NMR (acetone-d_6): δ (ppm) 158.19, 139.94, 138.31, 136.43, 129.69, 128.95, 127.96, 127.32, 113.77, 87.48, 72.07, 61.26. MS calcd for $C_{14}H_{14}IO_2$ 340.0, found 340.0. Anal. Calcd: C, 49.41; H, 3.82; I, 37.35. Found: C, 49.30; H, 3.82; I, 37.19.

Polymer Preparation. Synthesis of $[N_3P_3(C_6H_5O)_6]_n$ (15). This compound was synthesized according to a method reported previously.[32] Spectral data match according to the literature. The polymer is a white, fibrous material. ^{31}P NMR ($CDCl_3$): δ (ppm) −18.6 (singlet). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.80 (m, 5H). ^{13}C NMR ($CDCl_3$): δ (ppm) 149.12, 129.42, 116.01, 112.10. Anal. Calcd: C, 62.30; H, 4.33; P, 13.42; N, 6.06. Found: C, 61.90; H, 4.60; P, 13.49; N, 6.85.

Synthesis of $[N_3P_3(4\text{-}BrC_6H_4O)_6]_n$ (16). This compound was synthesized according to a method reported previously.[46] Spectral data match according to the literature. The polymer is an off-white powder. ^{31}P NMR ($CDCl_3$): δ (ppm) −19.7 (singlet). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.30−6.40 (m, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm) 149.80, 132.20, 122.10, 118.00. Anal. Calcd: C, 37.00; H, 2.07; N, 3.61. Found: C, 38.59; H, 1.91; N, 3.79.

Synthesis of $[N_3P_3(4\text{-}IC_6H_4O)_6]_n$ (17). This compound was synthesized according to a method described previously for **16**, substituting 4-iodophenol for 4-bromophenol as the starting alcohol. However, in order to purify this material, the polymer was dissolved in refluxing dioxane after the first precipitation into water. A second precipitation into water from a concentrated mixture of polymer in a minimum amount of dioxane was carried out. Following this, all other purification steps were carried out as reported previously.[46] The product is a white solid that is insoluble in THF. ^{31}P NMR (NMP, D_2O internal standard): δ (ppm) −18.08 (singlet). ^{13}C NMR (NMP, D_2O internal standard): δ (ppm) 150.79, 138.61, 12.02, 89.06. Anal. Calcd: C, 31.93; H, 1.77; I, 56.32; P, 6.87; N, 3.10. Found: C, 29.11; H, 1.71; I, 52.41; P, 6.03; N, 2.86.

Synthesis of $[N_3P_3(2\text{-}C_{10}H_7O)_6]_n$ (18). Poly(dichlorophosphazene) (1.00 g: 0.61 g of Cl, 0.017 mol) was dissolved in 200 mL of dry dioxane in a 1000-mL, three-necked, round-bottom flask (flask A). This was fitted with a reflux condenser and argon purge. The mixture was warmed slightly and stirred in order to dissolve all the poly(dichlorophosphazene). An excess of 2-naphthoxy sodium salt (5.00 g, 0.061 mol) was formed in a separate, 500-mL, three-necked, round-bottom flask (flask B) as described. [One equivalent of 2-naphthol was dissolved in 150 mL of dry dioxane in a 250-mL addition funnel charged with argon. This was added dropwise to 1.2 equiv of sodium metal being stirred in 100 mL of dry dioxane in a three-necked, found-bottom flask fitted with a reflux condenser and argon purge. This mixture was stirred with warming (60 °C, 24 h).] Flask B was cooled to room temperature and the contents were cannula-transferred into a 500-mL addition funnel charged with argon. This mixture was added dropwise to flask A. After the addition was complete, the mixture was heated to reflux (100 °C, 72 h). ^{31}P NMR spectroscopy was conducted to monitor the reaction progress. When no further change in the ^{31}P NMR spectrum was apparent, the mixture was cooled to room temperature. Most of the solvent (80%) was removed by rotoevaporation, leaving behind a dark, viscous syrup. This was precipitated into 1000 mL of water. The precipitate was collected and redissolved in a minimum amount of THF. Several more precipitations were carried out into water, methanol, diethyl ether, and hexane. A white powdery product slightly soluble in THF was obtained and was dried under vacuum. ^{31}P NMR (THF-d_8): δ (ppm) −17.62 (singlet). ^{1}H NMR (THF-d_8): δ (ppm) 7.16 (s, 2H), 7.08 (d, 1H), 6.84 (s, 2H), 6.68 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 149.27, 133.79, 130.55, 128.78, 127.46, 127.19, 125.45, 124.25, 121.29, 117.23. Anal. Calcd: C, 72.51; H, 4.23; P, 9.37; N, 4.23. Found: C, 70.84; H, 4.04; P, 10.52; N, 4.19.

Synthesis of $[N_3P_3(6\text{-}Br\text{-}2\text{-}C_{10}H_7O)_6]_n$ (19). This polymer was synthesized in a manner similar to that described previously for **18**, where 6-bromo-2-naphthol was used in place of

2-naphthol as the starting alcohol. Isolation of this material was as described above for **18**. Because the white product was insoluble, it was placed in a Soxhlet extractor apparatus using methanol as the extraction solvent. Soxhlet extraction was carried out for 5 days. The resultant white powdery polymeric residue was dried under vacuum. It was not sufficiently soluble to allow solution NMR analysis. Anal. Calcd: C, 49.08; H, 2.45; Br, 32.72; P, 6.34; N, 2.86. Found: C, 47.79; H, 2.30; Br, 31.25; P, 6.36; N, 2.87.

Synthesis of $[N_3P_3(6\text{-}I\text{-}2\text{-}C_{10}H_7O)_6]_n$ (20). This polymer was synthesized in a similar manner to that described previously for **19**, where **3** was used in place of 6-bromo-2-naphthol. Workup of this material was as described above for **19**. The resultant white powdery polymer was not sufficiently soluble to allow solution NMR analysis. Anal. Calcd: C, 41.17; H, 2.06; I, 43.57; P, 5.32; N, 2.40. Found: C, 40.23; H, 2.16; I, 40.32; P, 5.13; N, 2.38.

Synthesis of $[N_3P_3(OCH_2CH_2O(2\text{-}C_{10}H_7O))_6]_n$ (21). Poly(dichlorophosphazene) (1 g: 0.61 g of Cl, 0.017 mol) was dissolved in 200 mL of dry THF in a 500-mL, three-necked, round-bottom flask (flask A). In a 1000-mL, three-necked, round-bottom flask (flask B) fitted with a reflux condenser and argon purge were placed 3.0 equiv of sodium hydride (1.22 g, 0.051 mol) and 100 mL of dry THF. This was mixed into a slurry. To this was added dropwise 3 equiv of **7** (9.59 g, 0.051 mol) dissolved in 100 mL of dry THF. This mixture was boiled at reflux (67 °C, 24 h). Flask A was cannula-transferred to an argon-charged, 500 mL addition funnel. This solution was added dropwise to flask B. When the addition was complete, the mixture in flask B was heated to reflux for 72 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. When no further change was evident, the mixture was cooled to room temperature. The polymer was isolated and purified as described for **18**. The white, powdery polymer was dissolved in 150 mL of THF and was transferred into a moistened, dialysis tube (permeable to molecular weight 6000–8000 g/mol and below). The polymer was dialyzed against 1000 mL of of THF (the reservois solvent was changed every 48 h). After 1 week, the polymer solution was removed from the dialysis bag and the solvent was removed under vacuum. The polymer was collected and dried under vacuum. The polymer was an off-white, clear gel, very soluble in THF. ^{31}P NMR (THF-d_8): δ (ppm) −6.43 (singlet). ^1H NMR (THF-d_8): δ (ppm) 7.37 (s, 1H), 7.17 (s, 2H), 7.05 (s, 2H), 6.82 (s, 1H), 6.67 (s, 1H), 4.50 (s, 2H), 3.97 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 156.63, 134.61, 129.36, 129.05, 127.47, 126.94, 126.01, 123.30, 118.65, 106.70, 64.91, 26.70. Anal. Calcd: C, 68.74; H, 5.25; P, 7.40; N, 3.34. Found: C, 68.40; H, 5.08; P, 7.67; N, 3.36.

Synthesis of $[N_3P_3(OCH_2CH_2O(6\text{-}Br\text{-}2\text{-}C_{10}H_6O))_6]_n$ (22). This compound was synthesized in the manner described for polymer **21**, using starting compound **8** in place of compound **7**. Isolation and purification of the polymer followed the method reported for **21**. A light green, transparent gel was collected which was very soluble in THF. ^{31}P NMR (THF-d_8): δ (ppm) −6.56 (singlet). ^1H NMR (THF-d_8): δ (ppm) 7.56 (s, 1H), 7.14 (d, 2H), 6.80 (m, 3H), 6.46 (s, 1H), 4.46 (s, 2H), 3.91 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 156.37, 132.51, 129.72, 129.27, 129.02, 128.27, 128.07, 118.98, 116.92, 106.13, 64.61, 27.21. Anal. Calcd: C, 49.91; H, 3.47; Br, 27.33; P, 5.37; N, 2.43. Found: C, 49.20; H, 3.56; Br, 25.26; P, 5.25; N, 2.33.

Synthesis of $[N_3P_3(OCH_2CH_2O(6\text{-}I\text{-}2\text{-}C_{10}H_6O))_6]_n$ (23). This compound also was synthesized according to the manner described for polymer **21**, using starting compound **9**. Isolation and purification of the polymer followed the method reported for **21**. A light yellow powder was collected which was very soluble in THF. ^{31}P NMR (THF-d_8): δ (ppm) −6.54 (singlet). ^1H NMR (THF-d_8): δ (ppm) 7.77 (s, 1H), 7.32 (d, 1H), 7.01 (d, 1H), 6.66 (s, 2H), 6.37 (s, 1H), 4.43 (s, 2H), 3.86 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 156.42, 135.92, 134.63, 132.77, 130.28, 128.13, 128.02, 118.73, 106.07, 88.20, 68.68, 28.40. Anal. Calcd: C, 42.92; H, 2.98; I, 37.85; P, 4.62; N, 2.09. Found: C, 42.79; H, 2.98; I, 37.28; P, 4.64; N, 2.07.

Synthesis of $[N_3P_3(OCH_2CH_2O(4\text{-}(C_6H_5)C_6H_4))_6]_n$ (24). Poly(dichlorophosphazene) (0.68 g, 0.012 mol of Cl) was dissolved in 100 mL of dry THF. This solution was added dropwise to the sodium salt of **10**, which was made in the following manner. Five grams (0.023 mol) of **10** was dissolved in 150 mL of dry THF. This solution was added dropwise to a stirred solution of 100 mL of dry THF mixed with sodium (0.54 g, 0.023 mol) in a 200 mL, three-necked, round-bottom flask. This was stirred at reflux overnight (67 °C, 24 h). The resultant polymer mixture was refluxed for several days. ^{31}P NMR spectroscopy was used to monitor the course of the reaction and determine when the reaction was complete. After 72 h, no further change in the ^{31}P NMR spectrum occurred, and the polymer solution was treated in the standard way as described for polymers **21**–**23**. A soluble, white polymer was collected. ^{31}P NMR (THF-d_8): δ (ppm) −6.23 (singlet). ^1H NMR (THF-d_8): δ (ppm) 7.07 (d, 7H), 6.64 (s, 2H), 4.51 (s, 2H), 4.04 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 158.39, 140.26, 133.23, 128.70, 128.56, 127.77, 126.26, 114.86, 69.07, 27.01. Anal. Calcd: C, 71.34; H, 5.52; P, 6.58; N, 2.97. Found: C, 68.40; H, 5.44; P, 7.04; N, 3.18.

Synthesis of $[N_3P_3(OCH_2CH_2O(4\text{-}Br\text{-}4'\text{-}(C_6H_4)C_6H_4))_6]_n$ (25). This compound was synthesized according to the manner already described for polymer **24**, where starting material **11** was substituted for compound **10**. Additional THF was used in this reaction in order to maintain the solubility throughout the reaction (twice the proportions used for **24**). The polymer was isolated and purified in a similar manner to that described for polymers **19**–**20**. A white precipitate, insoluble in THF, was collected and dried under vacuum. ^{31}P NMR (NMP, D_2O internal standard): δ (ppm) −6.68 (singlet). ^{13}C NMR (NMP, D_2O internal standard): δ (ppm) 158.80, 139.02, 132.11, 131.10, 128.30, 127.50, 120.40, 115.00, 64.82. Anal. Calcd: C, 53.42; H, 3.82; Br, 25.44; P, 4.93; N, 2.23. Found: C, 51.14; H, 3.55; Br, 23.96; P, 4.61; N, 2.04.

Synthesis of $[N_3P_3(OCH_2CH_2O(4\text{-}I\text{-}4'\text{-}(C_6H_4)C_6H_4))_6]_n$ (26). This compound was synthesized according to the manner already described for polymer **25**, where starting material **12** was substituted for the compound **11**. The polymer was isolated and purified in a similar manner to that described for polymer **25**. A white precipitate, insoluble in THF, was collected and dried under vacuum. ^{31}P NMR (NMP, D_2O internal standard): δ (ppm) −6.85 (singlet). ^{13}C NMR (NMP, D_2O internal standard): δ (ppm) 159.38, 139.47, 137.64, 131.88, 129.29, 127.59, 115.65, 92.88, 68.15. Anal. Calcd: C, 46.47; H, 3.32; I, 35.13; P, 4.29; N, 1.94. Found: C, 43.60; H, 2.99; I, 30.82; P, 5.54; N, 2.52.

Synthesis of $[N_3P_3(OCH_2CH_2O(2\text{-}I\text{-}4\text{-}(C_6H_5)C_6H_3))_6]_n$ (27). This compound was synthesized according to the manner already described for polymer **24** using compound **14** in place of compound **10**. The resultant mixture was refluxed. ^{31}P NMR spectroscopy was used to monitor the reaction and determine when the substitution was complete. After 72 h, no further change in the ^{31}P NMR spectrum occurred, and the polymer solution was purified in the standard way as described for polymers **21**–**24**. A soluble, white polymer was isolated. ^{31}P NMR (THF-d_8): δ (ppm) −6.72 (singlet). ^1H NMR (THF-d_8): δ (ppm) 7.82 (s, 2H), 7.10 (m, 5H), 6.40 (s, 1H), 4.65 (s, 2H), 4.12 (s, 2H). ^{13}C NMR (THF-d_8): δ (ppm) 156.75, 138.74, 137.33, 135.27, 129.49, 128.63, 127.84, 126.37, 112.40, 87.33, 63.10, 29.80. Anal. Calcd: C, 46.47; H, 3.32; I, 35.13; P, 4.29; N, 1.94. Found: C, 43.43; H, 3.08; I, 30.72; P, 6.10; N, 2.83.

Acknowledgment. This work was supported by a Graduate Fellowship to M.A.O. from the NASA Graduate Student Researcher's Program (Training Grant 42 U.S.C. 2451 ET SEQ). We thank Dr. Mary Anne Meador of NASA–Lewis Research Center, Cleveland, OH, for her technical assistance with the solid-state NMR spectroscopy. We also thank Mr. Dan Scheimann of NASA–Lewis Research Center for his assistance with the GPC experiments.

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(47) The naphthyl unit with two fused aromatic phenyl rings is planar and the p-orbital electrons from all the sp^2 carbon atoms are free to interact with one another. For the biphenyl unit, the single carbon–carbon bond that links two phenyl rings allows limited free rotation and allows the two phenyl rings to twist out-of-plane. Consequently, delocalization of the p-orbitals (from the sp^2 carbon atoms) of one phenyl ring with the other does not occur. In other words, the phenyl rings behave independently. The extent of conjugation influences optical absorption. However, it is the *number* of polarizable electrons present in a molecule that is the main factor that affects refractive index. Therefore naphthyl and biphenyl systems should have different optical absorption spectra but similar refractive indices.

MA950174E