Controlled Refractive Index Polymers: Polyphosphazenes with Chlorinated- and Fluorinated-, Aryloxy- and Alkoxy- Side-Groups

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A series of novel halogenated alkoxy and aryloxy polyphosphazenes have been synthesized via macromolecular substitution reactions carried out on poly(dichlorophosphazene). These polymers showed good film-forming properties and tunability of refractive index. Moreover, several examples combined low glass transition temperatures with high refractive index changes as a function of temperature − a prerequisite for optical switching applications. The refractive indices could be controlled over the range of 1.3889−1.5610 by alterations to the side-groups or side-group ratios. The birefringence ($n_{TE} - n_{TM}$) of these polyphosphazenes was shown to be highly dependent on the amount of aryloxy side-group attached to the polyphosphazene backbone. They showed evidence of thermal stability up to 400 °C. These properties, combined with the tailorability of the polyphosphazene system make chlorinated- and fluorinated-, alkoxy- and aryloxy-substituted polyphosphazenes possible candidates for optical waveguide and optical switching applications.

Introduction

Much research has been focused on the development of new organic and inorganic materials for optical and electrical applications.[1−4] Materials for use in optical applications should be optically transparent and have good film-forming properties, high thermal stability, tunable refractive indices, and low optical losses at the telecommunication wavelengths of 1.3 and 1.55 μm.[5] Polymers have emerged as a promising class of optical materials due to their impact-resistance, ease of fabrication, low density, and cost-effective technologies. However, most organic polymers suffer from limited thermal stability, and high optical propagation losses which originate from light absorption from higher harmonics of molecular vibrations in the near-infrared region of the spectrum.[6,7] This problem is associated with the aliphatic C−H, O−H, and N−H bonds found in these polymers.[6,7] Replacement of aliphatic C−H bonds with elements of higher mass, as in C−D, C−Cl, and C−F units, substantially lowers the energy of fundamental bond vibration and has greatly reduced absorption at the telecommunication wavelengths.[2c] This strategy has decreased the optical loss and has led to the development of low-loss polymeric devices based on deuterated fluoromethacrylates, fluorinated polyimides, deuterated polysiloxanes, and fluorinated poly(arylene ether).[8−11] However, this has proved to be a costly approach, and has introduced complexity into both the monomer and polymer synthesis.[5,6]

Polyphosphazenes are hybrid organic−inorganic polymers that contain a backbone of alternating nitrogen and phosphorus atoms and yield many different chemical and physical properties depending on the structure of the two side-groups attached to each phosphorus atom.[12] Most polyphosphazenes are synthesized via the macromolecular replacement of chlorine atoms in poly-(dichlorophosphazene) with the use of various nucleo-

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philes. This provides a facile synthetic route to high-molecular-weight polymers with varying structures by the introduction of different side-groups and variations in the ratios of two or more different side-groups along each chain. Polyphosphazenes have several advantages over more traditional polymers for use in optical applications. First, the N−P backbone is thermo-oxidatively stable and lacks C−H bonds.[12] Second, the backbone has broad ranges of transparency from the mid-ultraviolet to the near-infrared. Third, the synthesis of poly(organophosphazenes) from a macromolecular intermediate allows the facile development of multiple-substituent polyphosphazenes with tunable physical properties such as T_g, refractive index, and birefringence. Thus, the properties needed for a specific optical application can be tailored simply by altering the side-group type or side-group ratio without the need for development of new monomers or polymerization conditions.[13−15] Recently, polyphosphazenes and functionalized-cyclotriphosphazenes have been investigated as high refractive index and nonlinear optical materials.[13−15]

In this work, we report the synthesis, and optical and thermal characterization, of novel polyphosphazenes that bear fluorinated- or chlorinated-, alkoxy- or aryloxy-substituents. These optically transparent, amorphous polymers can be tuned structurally to generate variable refractive indices, tailorable birefringence, and good film-forming properties. In addition, high values of dn/dT (change in refractive index with temperature) were found. These properties are important for both optical waveguide and optical switching applications.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Nippon Fine Chemical Co.) was purified by recrystallization from heptane and was sublimed at 55 °C (0.05 mmHg). Poly(dichlorophosphazene) was prepared by the ring opening polymerization of hexachlorocyclotriphosphazene at 250 °C as described previously.[16] Pentafluorophenol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, 2,4,5-trichlorophenol, 2,4-dichlorophenol, 2,2,2-trifluoroethanol, α,α,α-trifluoro-*m*-cresol, sodium hydride (60% dispersion in mineral oil), and tetra-*n*-butylammonium bromide were obtained from Aldrich and used as received. Tetrahydrofuran (Omnisolv) was dried over sodium benzophenone ketyl and was distilled under an atmosphere of dry argon. All reactions were performed under an atmosphere of dry argon with standard Schlenk techniques.

General. NMR spectra were obtained at 298 K using a Bruker AMX-360 NMR spectrometer resonating at 360.23 MHz for ¹H, 145.81 MHz for ³¹P, and 90.56 MHz for ¹³C. All ¹H and ¹³C NMR samples were prepared with deuterated THF (Isotec, 99.5%), unless otherwise noted, and referenced to tetramethylsilane (TMS). ³¹P NMR shifts are relative to 85%

phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, two Phenogel 10-*μ* linear columns (Phenomenex), and calibrated versus polystyrene standards (Polysciences). The samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (Omnisolv). Thermal gravimetric analyses (TGA) were obtained using a Perkin-Elmer TGA-7 under an atmosphere of dry nitrogen using a heating rate of 10 °C/min. Thermal data were obtained through differential scanning calorimetry (DSC) using a Perkin-Elmer-7 thermal analysis system equipped with a PC computer. Calibration of the Perkin-Elmer-7 thermal analysis system was achieved through use of indium and cyclohexane standards. Polymer samples were heated from −70 °C to 200 °C under an atmosphere of dry nitrogen. Approximately 20-mg samples were hermetically sealed in aluminum pans and heated at 20 and 40 °C/min.

General Method for Preparation of Mixed-Substituent Poly[bis(aryloxy)Phosphazenes]. Synthesis of [N=P-(OC₆H₄CF₃)₁.₀(OC₆F₅)₁.₀]ₙ (1). All mixed-substituent poly[bis(aryloxy) phosphazenes] aromatic side-group-containing polymers (**1**−**2**) were prepared in a similar manner by modification of a literature procedure.[17] The procedure for the synthesis of [N=P(OC₆H₄CF₃)₁.₀(OC₆F₅)₁.₀]ₙ (**1**) is given as a typical example. A solution of α,α,α,-trifluoro-*m*-cresol (7.0 g, 43.2 mmol) in 100 mL of THF was added dropwise to a suspension of sodium hydride (1.728 g, 43.2 mmol) in 100 mL of THF at room temperature. In a separate reaction, a solution of pentafluorophenol (11.93 g, 64.8 mmol) in 100 mL of THF was added to a suspension of sodium hydride (2.59 g, 64.8 mmol) and tetra-*n*-butylammonium bromide (1.0 g, 3.0 mmol) in 200 mL of THF. The first sodium aryloxide solution, sodium 3-trifluoromethylphenoxide, was added to an autoclave containing a solution of poly(dichlorophosphazene) (5.0 g, 43.2 mmol) in 600 mL of THF and the mixture was stirred for 30 min. The second aryloxide solution (sodium pentafluorophenoxide) was then added to the autoclave, which then was pressurized to 1 atm with argon, sealed, and heated to 150 °C. After 20 h, the autoclave was cooled to room temperature, and the contents were precipitated into acidified water. The polymer was purified further by precipitations from THF into deionized H₂O (2×) and hexanes (2×). Before the last precipitation into hexanes, the polymer solution was vacuum-filtered. The resultant polymer was dried in vacuo to yield a white solid.

Compound 1. ¹H NMR (THF-*d₈*): δ 6.80−6.95 (br, 3H), 7.12 (d, 1H). ¹³C NMR (THF-*d₈*): δ 113.72, 115.46, 118.47, 120.04, 121.48, 124.48, 126.82, 127.78, 128.14, 128.50, 128.87, 147.35. ³¹P NMR (THF-*d₈*): δ −19.3.

[N=P(OC₆H₃Cl₂)₁.₀(OC₆F₅)₁.₀]ₙ (2a). ¹H NMR (THF-*d₈*): δ 6.75−7.25 (br, 3H). ¹³C NMR (THF-*d₈*): δ 118.77, 123.16, 125.00, 127.66, 133.80, 134.87, 136.57, 137.19, 139.85, 142.65. ³¹P NMR (THF-*d₈*): δ −21.9, −23.8.

[N=P(OC₆H₃Cl₂)₀.₆(OC₆F₅)₁.₄]ₙ (2b). ¹H NMR (THF-*d₈*): δ 6.75−7.25 (br, 3H). ¹³C NMR (THF-*d₈*): δ 118.77, 123.16, 125.00, 127.66, 133.80, 134.87, 136.57, 137.19, 139.85, 142.65. ³¹P NMR (THF-*d₈*): δ −21.9, −23.8.

General Method for Preparation of Poly[(alkoxy)-(aryloxy)phosphazenes] (Polymers 3a−5). Synthesis of [N=P(OC₆H₃Cl₂)₀.₆(OCH₂(CF₂)₃CF₂H)₁.₄]ₙ (3a). The poly-[(alkoxy)(aryloxy)phosphazenes] (**3a**−**5**) were prepared in a similar manner. The procedure for the synthesis of [N=P(OC₆H₃Cl₂)₀.₆(OCH₂(CF₂)₃CF₂H)₁.₄]ₙ (**3a**) is given as a typical example. A solution of 2,4−dichlorophenol (4.22 g, 25.9 mmol) in 100 mL of THF was added dropwise to a suspension of sodium hydride (1.04 g, 25.9 mmol) in 150 mL of THF at room temperature. In a separate reaction, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (21.05 g, 90.7 mmol) was added to a suspension of sodium hydride (3.63 g, 90.7 mmol) in 250 mL of THF. The sodium 2,4-dichlorophenoxide solution was then added to a

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2-L round-bottom flask containing a solution of poly(dichlorophosphazene) (5.0 g, 43.2 mmol) in 500 mL THF, and the mixture was stirred at room temperature for 4 h. The second nucleophile, sodium octafluoropentoxide, was added to this reaction mixture and the system was warmed to 50 °C. After 24 h, the reaction mixture was cooled to room temperature, and the contents were precipitated into acidified water. The polymer was purified further by precipitations from THF into deionized H_2O (2×) and hexanes (2×). Before the last precipitation into hexanes, the polymer solution was vacuum-filtered. The resultant polymer was dried in vacuo to yield a white, rubbery solid.

Compound 3a. ^{1}H NMR (THF-d_8): δ 4.30 (s, 2H), 6.50 (t, 1H), 6.80−7.50 (br, 3H). ^{13}C NMR (THF-d_8): δ 61.0 (t, 27 Hz), 103.89 (t, 32 Hz), 106.33 (t,31 Hz), 108.75 (quin, 34 Hz), 112.86 (m), 120.35, 124.73, 126.10, 128.64, 143.80. ^{31}P NMR (THF-d_8): δ -8.1, −12.4, −18.8.

[N=P(OC$_6$H$_3$Cl$_2$)$_{1.0}$(OCH$_2$(CF$_2$)$_3$CF$_2$H)$_{1.0}$]$_n$ (3b). ^{1}H NMR (THF-d_8): δ 4.30 (s, 2H), 6.50 (t, 1H), 6.80−7.50 (br, 3H). ^{13}C NMR (THF-d_8): δ 61.0 (t, 27 Hz), 103.89 (t, 32 Hz), 106.33 (t, 31 Hz), 108.75 (quin, 34 Hz), 112.86 (m), 120.35, 124.73, 126.10, 128.64, 143.80. ^{31}P NMR (THF-d_8): δ -8.7, −14.3, −19.8.

[N=P(OC$_6$H$_3$Cl$_2$)$_{1.4}$(OCH$_2$(CF$_2$)$_3$CF$_2$H)$_{0.6}$]$_n$ (3c). ^{1}H NMR (THF-d_8): δ 4.30 (s, 2H), 6.50 (t, 1H), 6.80−7.50 (br, 3H). ^{13}C NMR (THF-d_8): δ 61.0 (t, 27 Hz), 103.89 (t, 32 Hz), 106.33 (t, 31 Hz), 108.75 (quin, 34 Hz), 112.86 (m), 120.35, 124.73, 126.10, 128.64, 143.80. ^{31}P NMR (THF-d_8): δ −10.1, −16.1, −21.6.

[N=P(OC$_6$H$_2$Cl$_3$)$_{0.4}$(OCH$_2$(CF$_2$)$_3$CF$_2$H)$_{1.6}$]$_n$ (4a). ^{1}H NMR (THF-d_8): δ 4.50 (s, 2H), 6.60 (t, 1H), 7.70 (br, 2H). ^{13}C NMR (THF-d_8): δ 63.64 (t, 27 Hz), 106.40 (t, 32 Hz), 109.19 (t, 31 Hz), 111.63 (quin, 34 Hz), 115.32 (m), 118.28, 123.36, 125.64, 130.47, 132.26, 146.01. ^{31}P NMR (THF-d_8): δ −5.9, −11.2.

[N=P(OC$_6$H$_2$Cl$_3$)$_{1.0}$(OCH$_2$(CF$_2$)$_3$CF$_2$H)$_{1.0}$]$_n$ (4b). ^{1}H NMR (THF-d_8): δ 4.40 (s, 2H), 6.50 (t, 1H), 7.70 (br, 2H). ^{13}C NMR (THF-d_8): δ 63.64 (t, 27 Hz), 106.40 (t, 32 Hz), 109.19 (t, 31 Hz), 111.63 (quin, 34 Hz), 115.32 (m), 118.28, 123.36, 125.64, 130.47, 132.26, 146.01. ^{31}P NMR (THF-d_8): δ -6.7, −14.2, −20.5.

[NP(OC$_6$H$_2$Cl$_3$)$_{1.6}$(OCH$_2$(CF$_2$)$_3$CF$_2$H)$_{0.4}$]$_n$ (4c). ^{1}H NMR (THF-d_8): δ 4.40 (s, 2H), 6.50 (t, 1H), 7.50 (br, 2H). ^{13}C NMR (THF-d_8): δ 63.64 (t, 27 Hz), 106.40 (t, 32 Hz), 109.19 (t, 31 Hz), 111.63 (quin, 34 Hz), 115.32 (m), 118.28, 123.36, 125.64, 130.47, 132.26, 146.01. ^{31}P NMR (THF-d_8): δ -10.0, −15.1, −22.0.

[N=P(OC$_6$H$_2$Cl$_3$)$_{0.4}$(OCH$_2$CF$_3$)$_{1.6}$]$_n$ (5). ^{1}H NMR (THF-d_8): δ 4.50 (s, 2H), 7.50 (br, 2H). ^{13}C NMR (THF-d_8): δ 62.12, 117.26, 120.30, 121.54, 123.37, 124.12, 126.42, 128.50, 130.24, 144.30. ^{31}P NMR (THF-d_8): δ -6.6, −11.6, −18.0.
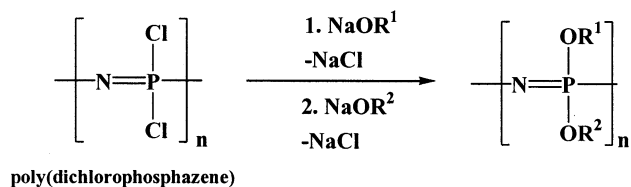
Preparation of Polyphosphazene Films. Solutions (5 wt %) of polyphosphazenes (1−5) in dry cyclohexanone were filtered through 0.2-μm membrane filters and were spin-coated onto silicon wafers to form 3−5-μm films of uniform thickness. The polyphosphazene films were soft baked in an oven to remove residual solvent and heat aged at 150 °C overnight.

Optical Characterization. Optical Characterization (refractive index (n_{TE}, n_{TM}), birefringence ($n_{TE} - n_{TM}$), film thickness, and thermooptic coefficient (dn/dT) of the polyphosphazene films was performed by Lightwave Microsystems Corp. through use of a FilmTek 4000, which is a computerized thin film characterization system that combines fiber-optic spectrophotometry with multiangle differential power spectral density analysis.

Results and Discussion

Polymer Synthesis. In an attempt to synthesize amorphous polyphosphazenes with variable refractive indices for potential use in optical waveguide or optical switching applications, we have used chlorinated- and fluorinated-, alkoxy and aryloxy side-groups with the minimum number of aliphatic C−H bonds to minimize optical absorption at the telecommunication wave-

Scheme 1

poly(dichlorophosphazene)

Polymer	R[1] (amount)	R[2] (amount)
1	CF$_3$-phenyl (1.0)	F$_5$-phenyl (1.0)
2a	F$_5$-phenyl (1.0)	Cl,Cl-phenyl (1.0)
2b	F$_5$-phenyl (0.6)	Cl,Cl-phenyl (1.4)
3a	Cl,Cl-phenyl (0.6)	-CH$_2$(CF$_2$)$_3$CF$_2$H (1.4)
3b	Cl,Cl-phenyl (1.0)	-CH$_2$(CF$_2$)$_3$CF$_2$H (1.0)
3c	Cl,Cl-phenyl (1.4)	-CH$_2$(CF$_2$)$_3$CF$_2$H (0.6)
4a	Cl,Cl,Cl-phenyl (0.4)	-CH$_2$(CF$_2$)$_3$CF$_2$H (1.6)
4b	Cl,Cl,Cl-phenyl (1.0)	-CH$_2$(CF$_2$)$_3$CF$_2$H (1.0)
4c	Cl,Cl,Cl-phenyl (1.4)	-CH$_2$(CF$_2$)$_3$CF$_2$H (0.6)
5	Cl,Cl,Cl-phenyl (0.4)	-CH$_2$CF$_3$ (1.6)

lengths (1.3 and 1.55 μm). Mixed-substituent, poly[bis-(aryloxy)phosphazenes] (1−2) and poly[(alkoxy)(aryloxy) phosphazenes] (3a−5) were synthesized via the sequential macromolecular replacement of the chlorine atoms in poly(dichlorophosphazene) with an appropriate sodium aryloxide, followed by the addition of a second sodium aryloxide or alkoxide in excess (1.5 equiv/remaining Cl) to yield fully substituted polymers (Scheme 1). In the case of the poly[bis(aryloxy)phosphazenes] (1−2), full substitution of poly(dichlorophosphazene) was difficult because of steric effects and the insolubility of the sodium aryloxides. Therefore, these reactions were carried out in a pressurized autoclave (5 bar) at 150 °C using a phase transfer catalyst (tetra-*n*-butylammonium bromide). The poly[(alkoxy)(aryloxy) phosphazenes] (3a−5) were prepared under milder conditions at ambient temperature or with gentle heating at atmospheric pressure. The reaction byproduct, sodium chloride, and the excess sodium alkoxides or aryloxides were removed from the polymers through repeated precipitations of a polymer solution into deionized water and hexanes. Subsequent drying under reduced pressure yielded polymers 1−5, which were characterized by multinuclear NMR (^{1}H, ^{31}P, and ^{13}C), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Char-

Table 1. Physical Properties of Polyphosphazenes 1−5

polymer	composition ratio[a] ($\mathbf{R^1 : R^2}$)	M_n ($\times 10^3$)[c]	M_w/M_n[c]	T_g[d]	T_d[e]
1	−	680	4.4	75	450
2a	45:54[b]	370	10.2	40	439
2b	64:36[b]	375	2.7	61	482
3a	29:71	570	7.4	−44	426
3b	41:59	590	1.5	−26	400
3c	74:26	618	2.4	7	430
4a	16:84	461	2.5	−57	435
4b	40:60	847	2.3	9	426
4c	66:34	807	3.0	38	432
5	20:80	748	2.1	−30	419

[a] Calculated from ^{1}H NMR spectra. [b] Calculated from ^{31}P NMR spectra. [c] GPC values versus polystyrene standards. [d] Measured by DSC. [e] 5% weight loss measured by TGA.
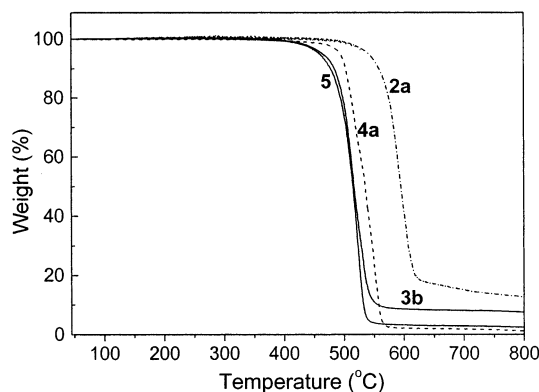
Figure 1. TGA thermograms of polyphosphazenes **2a**, **3b**, **4a**, and **5**.

acterization data are reported in Table 1. The synthesis method yielded high molecular weight, fully substituted, poly[bis(aryloxy)phosphazenes](**1−2**) and poly[(alkoxy)-(aryloxy) phosphazenes] (**3a−5**) in good yields (65−70% based on [NPCl$_2$]$_n$) The products were readily soluble in THF, DMF, and cyclohexanone. Polymer films of **1−5** were obtained through solution casting from cyclohexanone to produce thick, ductile and optically transparent samples. The side-group ratios of polymers **1−5** were estimated from both ^{31}P and ^{1}H NMR data and found to be in good agreement with the feed ratios of the sodium aryloxides and alkoxides (Table 1).

Thermal Properties. Polymeric materials for use in optical or electronic applications must display sufficient thermal stability to withstand prolonged periods of thermal variation during device fabrication and operation.[1,2,18] Polyphosphazenes **1−5** demonstrate superior stability against chain fragmentation and side-group volatilization as depicted in the TGA thermograms shown in Figure 1. The initial thermal decomposition temperatures (T_d) (Table 1) of polyphosphazenes **1−5** are in excess of 400 °C (>440 °C for poly[bis(aryloxy)-phosphazenes] (**1−2**)) which are comparable to those of poly(arylene ethers) and poly(pentafluorostyrene-*co*-glycidyl methacrylate).[9,19] However, it should be recognized that these values probably over-estimate the thermal stability because weight loss values in this temperature range often reflect the volatilization of species formed by decomposition at lower temperatures. The high flexibility of the backbone in polyphosphazenes

Table 2. Optical Properties of Polyphosphazenes 1−5

polymer	Cl/F[a]	n_{TE}	n_{TM}	Δn	dn/dT ($\times 10^{-4}$)[b] below T_g	dn/dT ($\times 10^{-4}$)[b] above T_g
1	−	1.4895	1.5172	0.0277	1.56	2.45
2a	0.4	1.5604	1.5936	0.0332	1.24	1.22
2b	0.93	1.5610	1.5857	0.0247	1.34	1.33
3a	0.093	1.4095	1.4184	0.0089	2.40	2.74
3b	0.174	1.4376	1.4484	0.0108	2.49	2.95
3c	0.712	1.5210	1.5459	0.0249	2.61	3.06
4a	0.071	1.3889	1.3936	0.0047	2.52	2.66
4b	0.25	1.4459	1.4577	0.0118	2.58	2.96
4c	0.730	1.5368	1.5561	0.0193	2.59	3.18
5	0.25	1.4388	1.4427	0.0039	2.80	3.00

[a] Molar Cl/F content determined from side group ratios. [b] All values for dn/dT obtained at 1.55 μm.

can give rise to low glass transition temperatures (T_g). This is exemplified by polymers **1−5** which have T_g's in the range from −57 to 75 °C (Table 2). The amorphous nature of these polymers was confirmed through optical microscopy and the absence of any crystalline melting transitions in the DSC traces. The glass transition temperatures of the poly[(alkoxy)(aryloxy) phosphazenes] (**3a−5**) decrease with increasing amounts of the fluorinated alkoxy side-group due to the flexibility of the aliphatic alkyl chain which increases the free volume of the polymer.[23] Although the glass transition temperatures of polyphosphazenes **3a−5** are near or below 0 °C, these polymers show good dimensional stability as thin films and can be cross-linked if needed for a specific application.[9,20]

Optical Properties. Generally, the refractive index of polymeric materials for optical applications is tailored to a specific range by molecular weight variations or through the blending of different polymers.[21] However, molecular weight control can be difficult and irreproducible, and polymer blends can undergo phase separation over time which alters the optical properties of these materials. The series of chlorinated- and fluorinated-, alkoxy- and aryloxy-substituted polyphosphazenes discussed here allows the refractive index to be modified by changing the polymer side-groups or side-group ratios at the molecular level. The refractive indices (n_{TE} and n_{TM}) of these polymers **1−5** ranged from 1.3889 to 1.5936 (Table 2), and were highly dependent on the chlorine and fluorine content of the side-groups (Figure 2). In other polymers, chlorine atoms or chlorinated side-groups generally increase the refractive index of small molecules and polymers; whereas the incorporation of fluorine atoms or fluorinated side-groups decreases the refractive indices of similar polymers.[4,8−11] Our results are in good agreement with this trend. As shown in Figure 2, the refractive indices of polymers **2b−5** are directly related to the molar Cl/F ratio. The polyphosphazenes with high Cl/F ratios such as **2b**, **3c**, and **4c**, displayed high refractive indices, with n_{TE} values in excess of 1.50. The opposite trend applies to those polyphosphazenes with low Cl/F ratios, such as **3a** and **4a**, which have n_{TE} values of 1.4095 and 1.3889, respectively. The relationship between the Cl/F ratio

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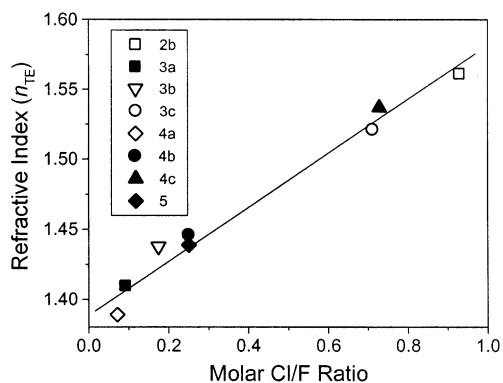
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Figure 2. Refractive index dependence on Cl/F ratio in selected polyphosphazenes.
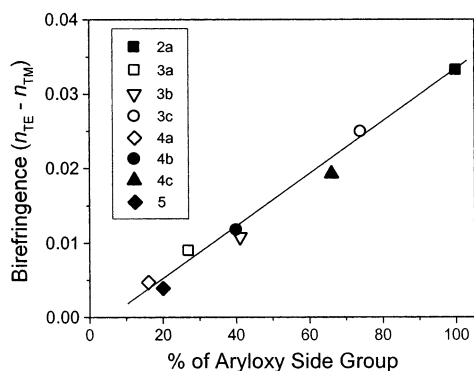

Figure 3. Birefringence changes as a function of aryloxy content in selected polyphosphazenes.

and the refractive index of the polymer also applies to polymers with different side-groups. For example, polyphosphazenes **4b** and **5** bear different fluorinated-alkoxy side-groups in dissimilar amounts, yet the Cl/F content of both polymers is similar, and this gives comparable refractive indices. Polyphosphazenes that contain chlorinated- and fluorinated-, alkoxy- and aryloxy-substituents provide a readily tailorable system in which the refractive index of a polymer can be adjusted through the Cl/F content. At the same time the specific halogenated side-groups can be chosen to impart targeted physical properties, such as glass transition temperatures, for a given optical application. This avoids the synthesis of new deuterated- or halogenated- monomers and polymers.

Birefringence ($\Delta n = n_{TE} - n_{TM}$) in polymer systems arises from the ordering of aromatic groups or orientation of polymer chains during processing and leads to optical scattering losses.[22,23] Highly ordered or semicrystalline polymers such as poly(tetrafluoroethylene) scatter light due to refractive index anisotropy between microdomains which results in substantial optical loss.[24] It is for this reason that amorphous, isotropic materials are normally required for optical applications.[1–3] Figure 3 illustrates the dependence of the birefringence of various poly[bis(aryloxy)phosphazenes] and poly[(alkoxy)(aryloxy) phosphazenes] on the amount of aryloxy side-groups present. The large birefringence of poly[(pentafluorophenoxy)(2,4-dichlorophenoxy)phosphazene] (**2a**) (Table 2) is typical of poly[bis(aryloxy)phosphazenes], many of which are semicrystalline. The microcrystal-

linity arises as a result of the co-orientation of the aromatic side-groups along the phosphazene backbone.[22,23] The incorporation of flexible co-substituents such as fluorinated-alkoxy side-groups reduces orientation and greatly decreases the birefringence to near 0.004 for polyphosphazenes **4a** and **5** as shown in Table 2. This value is significantly lower than that of fluorinated polyimides and is comparable to that of poly(arylene ethers).[8–11,20,25] To further reduce the birefringence, mixed substituent poly[bis(alkoxy)phosphazenes] with halogenated aliphatic side-groups have been synthesized and are currently under investigation. The incorporation of various compositions of chlorinated- and fluorinated-, alkoxy- and aryloxy-side groups linked to the polyphosphazene chain allows the control of birefringence and refractive index. Because many optical devices, such as waveguides, consist of a core and cladding assembly with small differences in refractive index between layers, the ability to tune refractive indices is extremely useful.

The dn/dT values of n_{TE} for polyphosphazenes **1–5** were examined, above and below the glass transition temperature, as shown in Table 2. Polymers **1–5** displayed thermooptic coefficients (dn/dT) that range from 1.24×10^{-4} to 2.80×10^{-4} below the T_g and 1.22×10^{-4} to 3.18×10^{-4} above the T_g. These values are comparable to those of halogenated and nonhalogenated cross-linked acrylate polymers.[2c] The large variation in refractive index with changes in temperature, especially above the T_g, makes polyphosphazenes **1–5** well suited for use in thermooptic switching applications.[2] An initial evaluation of polyphosphazene **2a** via photothermal deflection spectroscopy revealed a preliminary optical loss of 0.24 dB/cm at 1.55 μm which presumably arises from a combination of absorption and scattering losses from intrinsic and extrinsic sources.

Conclusions

We have synthesized in good yields a series of amorphous, high-molecular-weight polyphosphazenes with chlorinated- and fluorinated-, alkoxy- and aryloxy-side-groups. These display excellent thermal stability, good film-forming properties, and tunable optical properties. The polymers showed variable refractive indices, and controllable birefringence, depending on the Cl/F content and the amount of aryloxy side-groups attached to the phosphazene backbone. The high thermooptic coefficient values (dn/dT) are especially useful for devices in which thermal jump actuation is utilized for switching optical communications signals from one optical circuit to another. These properties, combined with the tailorability of the polyphosphazene system, make polyphosphazenes **1–5** promising candidates for both optical waveguide and optical switching applications.

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