Novel Highly Fluorinated Perfluorocyclobutane-Based Phosphazene Polymers for Photonic Applications

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Novel cyclophosphazenes containing aryl trifluorovinyl ether functional units together with the corresponding perfluorocyclobutane (PFCB) phosphazene polymers have been synthesized and characterized. These polymers have desirable properties for low optical loss waveguide applications. The monomers used in this study were prepared from sodium 4-(trifluorovinyloxy)phenoxides and cyclophosphazenes with fluorinated alkoxy or aryloxy side groups. The resulting polymers, produced by $2\pi + 2\pi$ cyclopolymerization of the aromatic trifluorovinyl ether moieties, showed good chemical stabilities and high thermal stabilities (T_d up to 330 °C). Tough and transparent thin films of these polymers were readily prepared by solvent-free processes using spin-coating of the monomers. By adjusting the ratio of monomers, the refractive index of the polymers could be controlled from 1.4528 to 1.5187 at 1550 nm, with exceptionally low birefringence of $\Delta n = 0$ to 0.0003 ± 0.0002. A propagation optical loss lower than ~0.25 dB/cm at 1550 nm was determined from the polymer films, for the TE polarization by measuring the scattered light intensity along the slab waveguide length. Such good thermal and optical properties demonstrate that these novel PFCB-based phosphazene polymers are promising candidates for optical waveguide or optical device materials.

Introduction

Polymer optical waveguides have attracted considerable attention for their possible application as components in optical communication systems because of their ease of manufacture at low temperature and low cost of processing.[1,2] However, most hydrocarbon polymers have high optical losses in the near-infrared region, resulting mostly from (a) second harmonic (overtone) vibrational absorption of C–H bonds, (b) scattering loss from the ordered structure, pinholes, or voids, and (c) absorption loss from charge-transfer interactions. These shortcomings can be reduced by shifting the associated vibrational absorption signals toward longer wavelengths through replacing hydrogen atoms with heavier atoms such as deuterium or halogens, especially chlorine or fluorine.[3,4b,f] Therefore, perfluorinated polymers have attracted much recent attention because they show low optical loss.

For perfluorinated polymers to be of use in real photonic devices, they must satisfy a set of challenging requirements, such as good thermal stability, chemical and environmental resistance, satisfactory mechanical properties, precise refractive index controllability, low propagation loss, low birefringence, good processability, ease of manufacturing at low temperatures, ease of integrated device fabrication, and low cost. Various polymers have been tested as optical waveguide materials, including acrylic polymers, polyimides, perfluorocyclobutane polymers, polycarbonates, fluorinated poly(vinyl ethers), epoxy polymers, polysiloxanes, and hyperbranched polymers.[4]

Among these polymers, fluoropolymers containing the perfluorocyclobutane (PFCB) linkage, formed by step-growth cycloadditions of aryl trifluorovinyl ether monomers, possess many advantages over classical fluorinated polymers. These attributes include high thermal/oxidative stability, high chemical resistance, excellent processability, and optical properties.[5–7] PFCB aromatic ether polymers are generally synthesized by the thermal step-growth cycloadditions of trifluorovinyl ether monomers in bulk or solution without the need for an initiator or catalyst. Recent studies of PFCB polymers for optical waveguide applications focus primarily on the thermal cyclopolymerization of different fluorinated aryl trifluorovinyl ether monomers to obtain a variety of

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homopolymers and random copolymers containing the PFCB aromatic ether linkage.[8]

A series of highly fluorinated, siloxane-containing tetrafunctional aryl trifluorovinyl ether monomers and PFCB aromatic ether polymers have been studied and were shown to have good optical transparency (0.30 dB/cm at 1310 nm).[8a] However, the siloxane units in the aryl trifluorovinyl ether monomers are unstable to moisture and acid so that the synthetic process is tedious, and the resulting PFCB polymers are prone to hydrolysis. Furthermore, PFCB-based polyester(arylene ether)s[8b] and naphthalene-based poly(perfluorocyclobutyl ether)s[8c] have been synthesized and were shown to exhibit good optical and thermal properties for optical waveguide applications. However, their high birefringence and relatively low glass transition temperatures do not satisfy the requirements of optical waveguide materials. To produce PFCB polymers that satisfy these required properties, we have undertaken a study to examine other functionalities which may complement the existing PFCB polymer properties. One such moiety predicted to provide significant advantages for PFCB polymers is the versatile cyclophosphazene ring.

Significant efforts have been devoted to the synthesis of organofunctional phosphazene polymers due to their unique combination of properties, which include their optical transparency at the optical communication wavelengths, their thermal stability, controlled stiffness or flexibility, and their chemical stability. In particular, the incorporation of phosphazene units has been used to tailor specific properties of an existing base macromolecular function to give hybrid polymers. Another important advantage for the introduction of cyclophosphazene rings is the ease with which different combinations of side groups can be linked to the cyclic organophosphazene. As the side groups are changed, the specific properties such as refractive index, dielectric constant, and moisture absorption can be easily tuned.[9,10]

Here, we describe our initial efforts to construct novel phosphazene-containing aryl trifluorovinyl ether monomers and PFCB polymers therefrom. Two of their most important optical properties for photonic components, which are optical propagation loss at 1550 nm and birefringence ($\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$), were also investigated for optical waveguide applications. The functional PFCB polymers are the first examples of an inorganic phosphazene hybrid PFCB system.

Experimental Section

Materials. 1,2-Dibromotetrafluoroethane was purchased from SynQuest and was used without further purification. 4-Bromophenol, zinc granules, and trimethylborate were obtained from Aldrich Chemical Co. and were used as received. 2,2,2-Trifluoroethanol (Aldrich) was dried over calcium hydride and distilled before use. Other solvents such as THF and acetonitrile were purified by procedures described in the literature.[11] The reaction mixtures were maintained under an atmosphere of dry nitrogen.

Instruments. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WM-360 NMR spectrometer operated at 360, 90, and 145 MHz, respectively. ^{1}H NMR spectra were referenced to trimethylsilane signals while ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Thermogravimetric analyses (TGA) were carried out with a Perkin-Elmer TGA 7 using 3–10 mg of samples. The temperature was raised from 30 to 700 °C at a heating rate of 10 °C/min in a nitrogen atmosphere with a gas flow rate of 50 mL/min. Thermal heat flow was monitored with a TA DSC 1000 instrument at a scan rate of 5 °C/min in a nitrogen atmosphere. The near-IR spectra of the polymers were obtained using a Bruker IFS 66/S spectrometer coupled with a Hyperion 3000 FT-IR microscope. The refractive index of the polymer film was determined using a prism coupler (Metricon 2010 M) with a 1550 nm diode laser as a monitoring beam, with an experimental error of ±0.0002. The optical propagation losses were measured using the prism coupling technique using a scanning fiber method on a variable length of a slab waveguide. The cross-section images of slab waveguides were scanned with a scanning electron microscope (FEI Quanta 200).

4-(2-Bromotetrafluoroethoxy)bromobenzene (1). To a 100 mL vessel fitted with a Dean–Stark azeotropic distillation assembly were added 4-bromophenol (15.13 g, 87.47 mmol), KOH (4.91 g, 87.47 mmol), DMSO (50 mL), and xylene (1.2 mL). The mixture was heated to 100 °C (ca. 0.5 mmHg) for 48 h, during which time water was removed to give a dry salt solution. The solution was cooled to room temperature, and $BrCF_2CF_2Br$ (25.00 g, 96.22 mmol) was added slowly. The solution was stirred for 24 h at room temperature, after which the reaction mixture was diluted with water and extracted with methylene chloride, and the organic phase was washed three times with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give 24.25 g (71.6%) of the bromotetrafluoroethyl ether **1** as a clear liquid: bp 100–110 °C (20 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.07 (d, 2H), 7.47 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 110.40 (m, CF_2), 113.52 (m, CF_2), 115.79 (m, CF_2), 118.54 (m, CF_2), 120.30, 123.41, 132.91, 147.85.

4-(Trifluorovinyloxy)bromobenzene (2). To a 100 mL dry vessel under nitrogen was added bromo ether **1** (24.00 g, 68.20 mmol) slowly over 30 min to a stirred mixture of zinc granules (4.91 g, 75.02 mmol) in acetonitrile (60 mL) at 80 °C. The mixture was refluxed for 10 h, and the solvent was then evaporated; the crude product was extracted with hexane, dried over anhydrous $MgSO_4$, concentrated, and distilled (bp 65–75 °C, 20 mmHg), giving 13.29 g (77.0%) of **2** as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 6.95 (d, 2H), 7.43 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 117.4, 132.8, 132.97, 133.63, 146.98, 154.2.

4-(1,2,2-Trifluorovinyloxy)phenylboronic Acid (3). To a solution of 4-(trifluorovinyloxy)bromobenzene (**2**) (4.29 g, 16.94 mmol) in dry ether (30 mL) was added dropwise *t*-BuLi (11.96 mL, 20.33 mmol, 1.7 M in pentane) at −78 °C. Then the reaction mixture was stirred for 1 h at −78 °C to give the lithium reagent. Under a nitrogen atmosphere at −78 °C, a solution of trimethylborate (2.11 g, 20.33 mmol) in ether (20 mL) was added dropwise to the lithium reagent prepared above. After the addition of trimethylborate, the reaction mixture was allowed to warm to room temperature and was stirred for 4 h. The reaction mixture was quenched with dilute HCl and washed with water, and the organic phase was dried over anhydrous $MgSO_4$. The product was dried under reduced pressure

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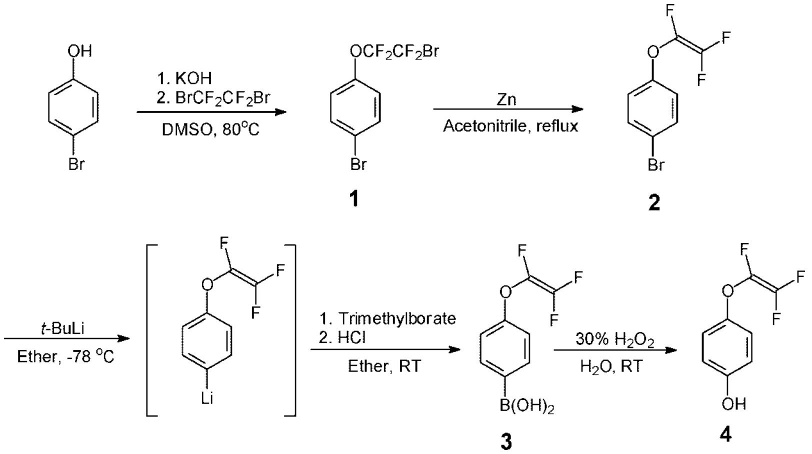
Scheme 1. Synthesis of Aryl Trifluorovinyl Ether Intermediate 4



to give 2.90 g (78.5%) of **3** as a brown waxy solid. This compound was used for the next reaction without further purification.

4-(Trifluorovinyloxy)phenol (4). 4-(1,2,2-Trifluorovinyloxy)-phenylboronic acid (**3**) (2.90 g, 13.31 mmol) was mixed with aqueous H_2O_2 (30%, 2.0 mL) and water (40 mL) under air for 24 h at room temperature. The crude product was extracted into ether and was washed with water, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography over silica gel and hexane/ethyl acetate (20:1) to afford 1.82 g (72.0%) of **4** as light yellow oil. ^{1}H NMR ($CDCl_3$): δ 5.0 (s, 1H), 6.70 (d, 2H), 6.88 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 116.1, 120.0, 120.7, 146.2, 143.1, 208.1.

Trifluoroethoxyphosphazene (5). To a solution of sodium hydride (60% dispersion in mineral oil; 2.28 g, 56.95 mmol) in anhydrous THF was added 2,2,2-trifluoroethanol (5.70 g, 56.95 mmol) under a nitrogen atmosphere over a period of 40 min, and the mixture was then stirred at room temperature for 12 h. Then, the reaction mixture was added dropwise to a solution of hexachlorocyclotriphosphazene (6.00 g, 17.26 mmol) in anhydrous THF, and the mixture was stirred at room temperature for 24 h. The crude product was extracted with ethyl acetate, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography over silica gel and hexane/ethyl acetate (30:1) to afford 1.55 g (16.7%) of **5** as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 4.32–4.35 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 22.17.

Trifluoroethoxytrifluorovinyloxyphenoxyphosphazene Monomer (6). To a solution of sodium hydride (60% dispersion in mineral oil; 0.066 g, 1.68 mmol) in anhydrous THF was added 4-(trifluorovinyloxy)phenol (**4**) (0.32 g, 1.68 mmol) under a nitrogen atmosphere over a period of 10 min, and the mixture was then stirred at room temperature for 12 h. The reaction mixture was added dropwise to a solution of **5** (0.27 g, 0.50 mmol) in anhydrous THF and stirred at room temperature for 24 h. The crude product was extracted with ethyl acetate, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography over silica gel and hexane/ethyl acetate (30:1) to afford 0.25 g (49.8%) of **6** as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 6.72–7.15 (m, 12H), 4.32–4.35 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 13.43.

Fluorophenoxyphosphazene (7). To a solution of sodium hydride (60% dispersion in mineral oil; 4.03 g, 100.67 mmol) in anhydrous THF was added 4-fluorophenol (11.29 g, 100.67 mmol) under a nitrogen atmosphere over a period of 40 min, followed by stirring at room temperature for 12 h. The reaction mixture was then added dropwise to a solution of hexachlorocyclotriphosphazene (10.00 g, 28.76 mmol) in anhydrous THF with stirring at room temperature for 24 h. The crude product was extracted with ethyl acetate, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography over silica gel and hexane/ethyl acetate (100:1) to afford 6.44 g (62.9%) of **7** as a yellowish waxy solid. ^{1}H NMR ($CDCl_3$): δ 6.85–7.29 (m, 12H). ^{31}P NMR ($CDCl_3$): δ 18.72.

Fluorophenoxytrifluorovinyloxyphenoxyphosphazene Monomer (8). To a solution of sodium hydride (60% dispersion in mineral oil; 0.12 g, 2.88 mmol) in anhydrous THF was added 4-(trifluorovinyloxy)phenol (**4**) (0.55 g, 2.88 mmol) under a nitrogen atmosphere over a period of 10 min, followed by stirring at room temperature for 12 h. Then, the reaction mixture was added dropwise to a solution of **7** (0.50 g, 0.87 mmol) in anhydrous THF and stirred at room temperature for 24 h. The crude product was extracted with ethyl acetate, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography over silica gel and hexane/ethyl acetate (30:1) to afford 0.60 g (66.5%) of **8** as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 6.78–6.85 (m, 24H). ^{31}P NMR ($CDCl_3$): δ 9.23.

Polymerization. Bulk polymerization of monomers **6** and **8** was carried out by heating the neat liquid on a glass plate at 130 °C under nitrogen for 1 h and then heating at 180 °C for 15 h. After cooling, polymers **9** (from monomer **6**) and **10** (from monomer **8**) were recovered as clear tack-free films in essentially quantitative yield.

Preparation of Polymer Films. To determine the refractive indices, solvent-free monomers **6** and **8** were used without any other components. For the refractive index tuning, trifluorovinyloxyphenoxyphosphazene monomer mixtures were prepared by combining monomers **6** and **8**. The silicon substrate was treated with an adhesion promoter, Exfix (ChemOptics, ZAP-1020), to enhance the adhesion between silicon and the polymer. The solutions were filtered with a syringe through a 0.45 μm poly(tetrafluoroethylene) (PTFE) membrane and were spin-coated onto silicon substrates with a spin speed of 2500–5000 rpm. Each spin-coated film was heated at 130 °C for 1 h and at 180 °C for 15 h under a nitrogen atmosphere to give a highly transparent film. For near-IR measurements, solvent-free monomers **6** and **8** were filtered with a syringe through a 0.45 μm PTFE membrane and were thermally polymerized in 0.1 cm quartz cells at 130 °C for 1 h and 180 °C for 15 h under a nitrogen atmosphere.

Slab Waveguide Fabrication and Propagation Loss Measurement. To fabricate slab optical waveguides, the bottom cladding layer was prepared as follows. After spinning the low-index cladding monomer Exguide (ChemOptics, ZPU13–405) onto the wafer at 1000 rpm for 30 s, this monomer was exposed to UV light (50 mW/cm^2) for 5 min under a nitrogen atmosphere. The sample was then baked at 160 °C for 30 min. The core layer was processed in the manner described above for the trifluorovinyloxyphenoxyphosphazene monomers.

The optical loss of the waveguides was determined by use of a prism coupler using a laser diode with a 1550 nm wavelength output. The light intensity scattered from the surface of the waveguide was measured by scanning with a fiber-optic probe and photodetector down the length of a propagating waveguide.

Results and Discussion

Design and Synthesis of Monomers. For potential applications in integrated optical waveguide devices, optical polymers should not only exhibit high thermal stability and good solvent resistance but also low optical loss and a low birefringence. To achieve a low optical loss, both light scattering and absorption should be avoided in the near-infrared region (NIR), especially at the transmission wavelengths commonly used in telecommunications (1330 and 1550 nm). By replacing hydrogen atoms with heavier atoms (halogens), the absorption loss can be lowered by shifting the vibrational overtone absorption to longer wavelengths, away from the regions of interest.

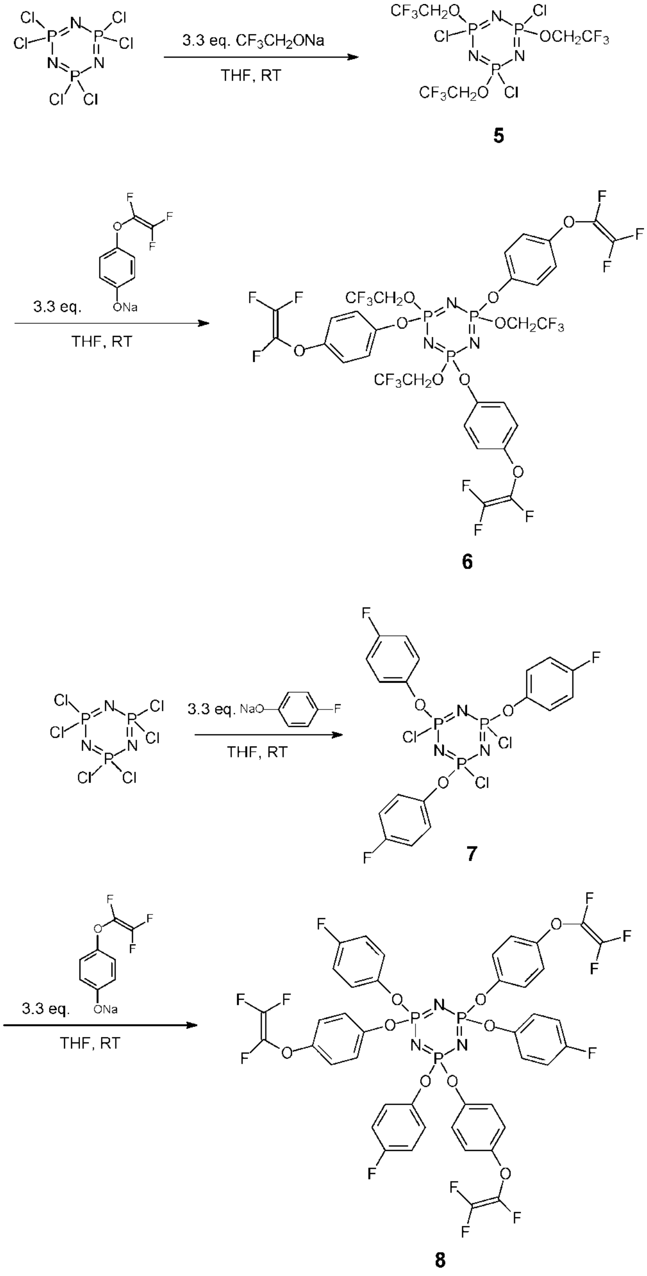
Cyclophosphazene rings that contain fluorinated side groups are good starting materials for the preparation of trifluorovinyloxyphenoxy monomers because of the useful properties of phosphazene rings such as their thermal stability, rigidity, and chemical stability.[12] Thermal stability will be increased if the polymer is composed of small rings linked together. Thus, the incorporation of rigid cyclic phosphazene rings into a polymer network should generate stiff matrix structures that could provide a high glass transition temperature.

Another important advantage for the introduction of cyclophosphazene rings is the ease with which different combinations of organic side groups can be linked to the cyclophosphazene. As the side groups are changed (more specifically as the ratio of aryloxy side groups on cyclophosphazene rings is changed), the refractive indices can be easily tuned. Another advantage is the optical transparency of the phosphazene unit which extends from the near-infrared to about 200 nm in the ultraviolet. This provides some stability against damage by intense light.[12]

For the synthesis of monomers **6** and **8**, a functionalized trifluorovinyl ether intermediate **2**, which could be converted to the boronic acid (**3**), was synthesized in two steps from a commercially available phenol via fluoroalkylation with $BrCF_2CF_2Br$ followed by zinc-mediated elimination. After treatment of aromatic bromide **2** with *t*-BuLi in the presence of trimethylborate, in situ lithiation and substitution gave boronic acid intermediate **3**. The phenol intermediate **4**, which could be easily linked to the cyclophosphazene ring, was prepared from the boronic acid **3** in the presence of hydrogen peroxide (Scheme 1).

Cyclophosphazenes with fluorinated organic side groups were prepared by replacement of the chlorine atoms in hexachlorocyclotriphosphazene using sodium trifluoroethoxide or sodium fluorophenoxide. Aryl trifluorovinyl ethers were then introduced to give trifluorovinyloxyphenoxy phosphazene monomers (Scheme 2).

Scheme 2. Synthesis of Trifluorovinyloxyphenoxyphosphazene Monomers 6 and 8



Bulk Polymerization and Thermal Properties of the Resulting Polymers. Differential scanning calorimetry (DSC) was used to monitor the $[2\pi + 2\pi]$ cyclodimerization of the monomers in the bulk state (Figure 1). All the monomers showed exothermic polymerization peaks between 120 and 300 °C based on their DSC profiles. The cyclopolymerization of tetrafluoroethylene has been reported to occur with a $\Delta H = -50$ to -60 kcal/mol due to this specific fluoroolefin reactivity.[13] Monomers **6** and **8** showed the typical cyclopolymerization of fluoroolefins behavior, with an exothermic $T_{\mathrm{onset}} = 120$–128 °C and a measured $\Delta H = \sim -60$ kcal/mol

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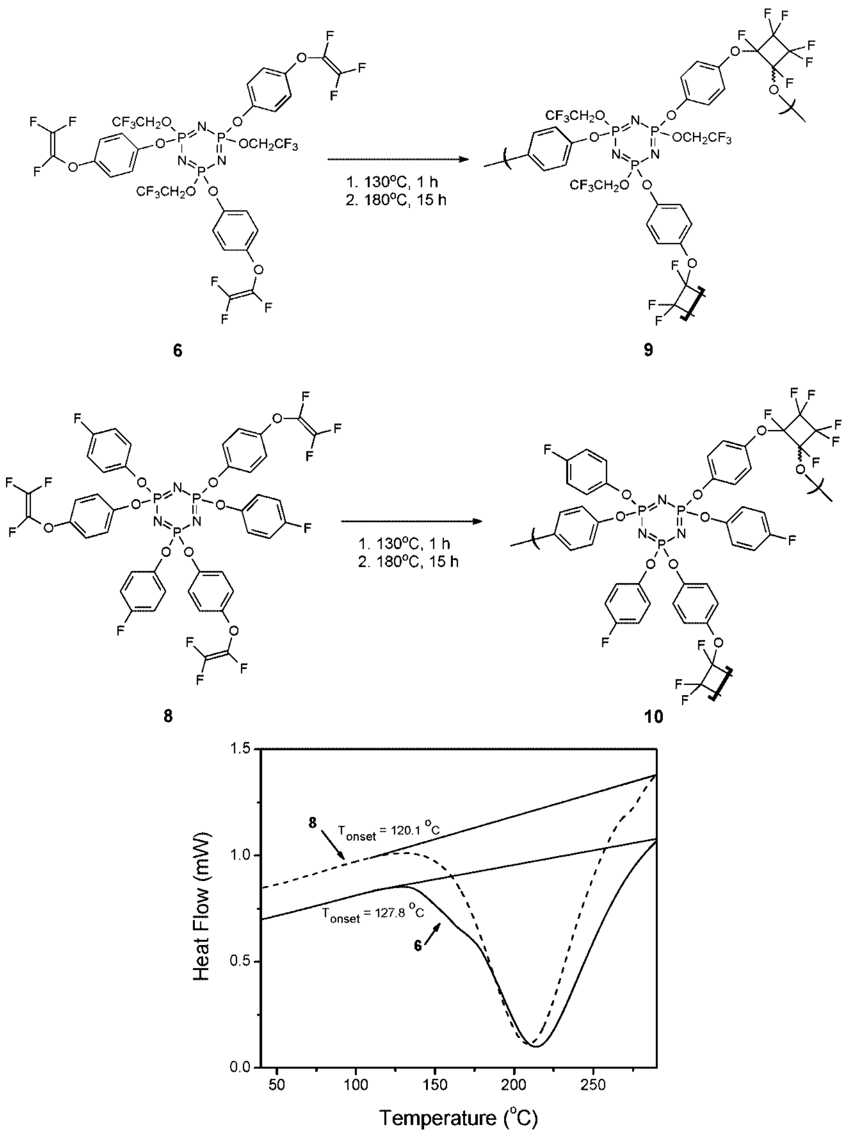

Figure 1. Polymerization of monomers **6** and **8** by DSC (5 °C/min).

(DSC, 5 °C/min). After polymerization, the resultant polymers were insoluble in common organic solvents such as acetone, methylene chloride, chloroform, THF, DMF, and DMSO. This result indicates the formation of highly cross-linked cyclomatrix polymers by the cyclodimerization.

Thermal stability is also an important issue for optical components. Figure 2 shows thermogravimetric analysis curves for perfluorocyclobutane phosphazene polymers. The polymers showed high thermal stabilities (10 wt % loss at 330 °C for polymer **9** and 358 °C for polymer **10**) due to the network structure. It is noteworthy that polymer **10** showed a slightly higher thermal stability than polymer **9** probably due to the rigid aromatic structures attached to the cyclophosphazene rings. The glass transition temperatures (T_g) of polymers **9** and **10** were not detectable, possibly due to their highly cross-linked structure. The thermal polymerization condition and thermal properties of polymer **9** and **10** are summarized in Table 1.

Refractive Indices and Birefringences of Polymer Films. The refractive indices n_{TE} and n_{TM} of the polymer films were determined by a prism coupling method using a monitoring light source of 1550 nm. For comparison, all the polymer films were processed using the same procedure of thermal polymerization as described in the Experimental Section. The measured refractive indices at 1550 nm were determined as 1.4528–1.5187 and 1.4525–1.5186 for the TE and TM mode, indicating the birefringence $\Delta n = n_{TE} - n_{TM}$, of 0–0.0003 (Table 2).

The refractive index of a polymer is intrinsically affected by factors such as free volume, polarizability, and wavelength.[14] Polymer **9** (from monomer **6**) shows a much lower refractive index than polymer **10** (from monomer **8**) because the lower steric hindrance and lower aromaticity of monomer **6** tend to increase the free volume and reduce the chain packing, while at the same time decreasing the electronic polarizability of the polymer. It is also significant that these PFCB phosphazene polymers show birefringence values lower than those of most fluorinated polymers designed for

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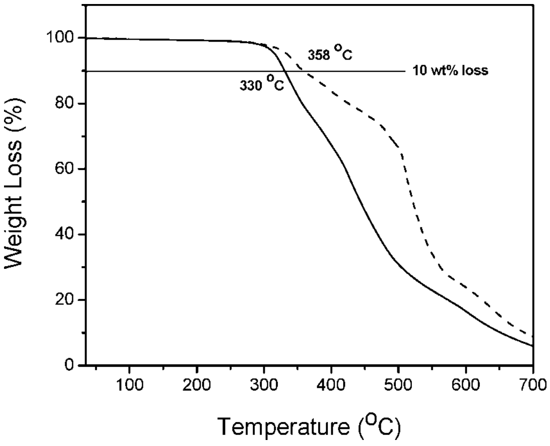

Figure 2. TGA of polymers **9** (solid line) and **10** (dashed line) in nitrogen.

Table 1. Thermal Properties of PFCB Phosphazene Polymers

polymer	curing *T* (°C)	T_g (°C)[a]	T_d (°C)[b]
9	180	not detectable	330
10	180	not detectable	358

[a] DSC thermogram obtained with a heating rate of 10 °C/min. [b] Temperature of 10% weight loss determined in a nitrogen atmosphere with a heating rate of 10 °C/min.

Table 2. Refractive Indices and Birefringences of PFCB Phosphazene Polymers

weight ratio (polymer **9**:polymer **10**)	wavelength (1550 nm)		
	n_{TE}	n_{TM}	Δn (±0.0002) ($n_{TE} - n_{TM}$)
10:0	1.4528	1.4525	0.0003
7:3	1.4679	1.4679	0
5:5	1.4858	1.4856	0.0002
3:7	1.4919	1.4916	0.0003
0:10	1.5187	1.5186	0.0001

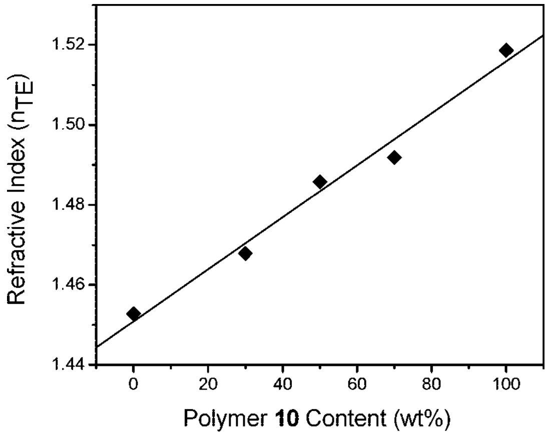

Figure 3. Dependence of refractive index of polymer **9** on polymer **10** content.

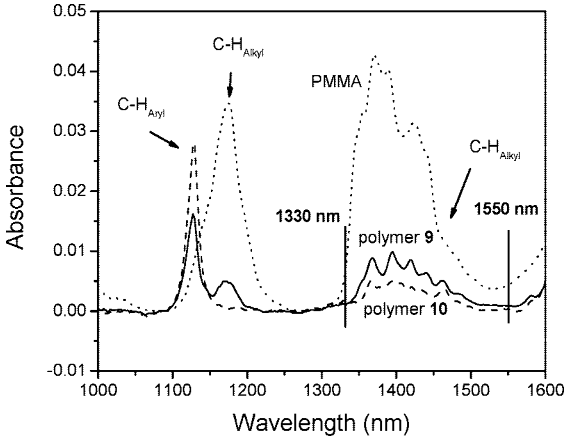

Figure 4. Near-IR absorption spectra of PFCB phosphazene polymers and reference PMMA sample.

use in optical waveguides.[15] Such low values of birefringence are possibly due to the isotropic polymer structure that results from the introduction of highly cross-linked network structures of **6** and **8** into the polymer chains.

Control of the refractive index is exceedingly significant for optical waveguide materials. A linear relationship was found between the refractive index of the polymers and the polymer **10** content (Figure 3). Thus, by varying the polymer **10** content from 0 to 100 wt %, the refractive index of the TE mode increased linearly from 1.4528 to 1.5178 for polymer **9**. This linear relationship represents an opportunity for fine-tuning of the refractive index by changing the feed ratio of the monomers.

Optical Absorption and Propagation Optical Loss of Films. Optical absorption is one of the dominant factors that causes the propagation loss in an optical waveguide. The PFCB phosphazene polymers show a low optical absorption because they contain either small amounts or no aliphatic C–H bonds, which reduces the absorption over the whole detected spectral range. As shown in Figure 4, the influence of fluorination on the C–H vibrational overtones was obvious in the second overtone band region (~1200 nm). The hydrogen content of polymers **9**, **10**, and poly(methyl methacrylate) (PMMA), given by the percent of aliphatic C–H bonds per the total number of bonds in the repeating unit,[16] was 6.9, 0, and 53.5%, respectively. It was clear that the intensity of the C–H$_{alkyl}$ overtone absorption by the fluorinated polymers was dramatically reduced as the hydrogen content was reduced. In addition, the absorption of the PFCB phosphazene polymers at 1330 and 1550 nm is much lower than that of PMMA. The absorption of these wavelengths is determined by stretching vibrations and combination tones with deformation vibrations of C–H bonds. The absorption of PFCB phosphazene polymers and PMMA was fitted to the equation loss $= -10/L \log T$, where L is the thickness of the sample and T is the transmission, to yield the loss in dB/cm and summarized in Table 3.

Propagation loss of the film was determined by measuring the transmitted and scattered power according to the waveguide length. This method uses a prism to couple the light into the waveguide and detectors, to measure the reflected and transmitted intensity.[17]

A slab waveguide structure as in Figure 5 was fabricated to determine the propagation optical loss of the polymer film. The top layer, prepared by thermal curing of the trifluoro-

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Table 3. Optical Loss of PFCB Phosphazene Polymers

polymer film[a]	optical loss (dB/cm) 1550 nm	optical loss (dB/cm) 1330 nm	hydrogen content[b] (%)
9	0.091	0.12	6.9
10	0.033	0.17	0
PMMA	0.43	0.58	53.3

[a] Standardized sample thickness of 1.0 mm. [b] % of the number of aliphatic C–H bonds per the total number of bonds in the repeating unit.

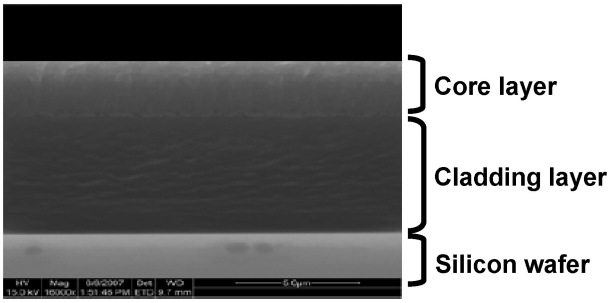

Figure 5. Cross-sectional image of slab waveguide from polymer **9** as a core layer and ZPU 13-405 as a cladding layer. The scale bar indicates 5.0 μm.

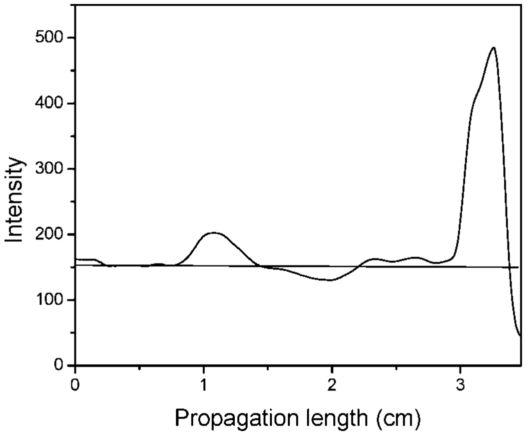

Figure 6. Light intensity scattered from the surface of the slab waveguide (polymer **10**) along waveguide length (peak at left due to particle and peak at end due to light emerging from end of guide). Good fit to underlying exponential obtained by fitting to regions between peaks.

vinyloxyphenoxyphosphazene monomers, must have a slightly higher index of refraction to yield the waveguide "core", and the system should be coupled to the layer stack. To minimize optical loss due to reflection from the cladding layer, ZPU13-405 (n_{TE} at 1550 nm = 1.4075 after photocuring), the refractive index of which is lower than the PFCB phosphazene core, was used for the preparation of the cladding layer.

The relationship between the scattered power of the PFCB phosphazene polymer film and waveguide length is shown in Figure 6. The propagation losses at 1550 nm, which were obtained from the exponential fit, were 0.25 and 0.14 dB/cm for polymers **9** and **10**, respectively. The optical loss determined in this study was lower than the reported value for a deuterated polysiloxane (0.43 dB/cm at 1550 nm),[18] a fluorinated hyperbranched polymer,[19] or poly(pentafluorostyrene-*co*-glycidyl methacrylate) (0.42 dB/cm at 1550 nm).[20] This result indicates that the thermally polymerizable **6** and **8** are good candidates as core or cladding materials for the optical waveguide devices.

Conclusion

Novel trifunctional trifluorovinyloxyphenoxyphosphazene monomers containing fluorinated side groups were designed and synthesized. The novel inorganic–organic hybrid perfluorocyclobutane-based phosphazene polymers, obtained after thermal cyclodimerization of the monomers, gave optical films with low optical loss, low birefringence, and high thermal stability up to 330 °C. The refractive indices at 1550 nm of these PFCB phosphazene polymers were determined as 1.4528–1.5187 and 1.4525–1.5186 for the TE and TM mode, which indicated excellent low birefringence of $\Delta n = 0$ to 0.0003 ± 0.0002. These polymers also showed a linear dependency of their refractive indices on the feed ratio of monomers, thereby allowing fine-tuning of the refractive indices of the polymers. Optical loss measurements of these polymers using near-IR absorption showed an optical loss as low as 0.033–0.091 dB/cm, and the propagation optical losses of slab waveguides measured by the prism coupler were 0.14–0.25 dB/cm at the wavelength of 1550 nm, which is suitable for the fabrication of integrated optical waveguide devices.

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