Perfluorocyclobutane-Based Polyester(arylene ether)s for Applications in Integrated Optics

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ABSTRACT: Novel ester-containing aryl trifluorovinyl ether monomers and the resulting perfluorocyclobutane aromatic ether polymers have been synthesized and characterized to exhibit desirable properties for low optical loss waveguide applications. The monomers were prepared via a very mild esterification between the intermediate 4-trifluorovinyloxybenzoic acid and diphenol/triphenol using N,N-dicyclohexylcarbodiimide as the activating agent for carboxylic acid and 4-(dimethylamino)pyridinium 4-toluenesulfonate as the catalyst. Chloro and bromo atoms are incorporated into trifunctional trifluorovinyl aryl ether monomers to achieve good tunability in refractive index without introducing additional optical loss. Polymerization of the monomers proceeded in melt or solution to form perfluorocyclobutane-containing prepolymers with good processability. The combination of desirable optical polymer properties, such as thermal stability (T_g: 38−350 °C), solvent resistance, tunable refractive index (n: 1.447−1.546 at 1310 nm), and low optical loss (as low as 0.26 dB/cm at 1310 nm) can be achieved through the copolymerization of highly fluorinated and flexible difunctional monomers with chloro/bromo-containing rigid trifunctional monomers.

Introduction

The trend of efficiently moving data in the metropolitan and to the home will necessitate new broadbandwidth technologies such as optical networking. The use of dense wavelength division multiplexing (DWDM) in optical networks is challenging components manufacturers to design a variety of new devices that can be integrated into DWDM systems. The development of polymer-based optical waveguide devices has provided increasingly attractive alternatives or complements to inorganic components because of the desirable properties including the combination of flexibility and toughness, easier processability, and integration over inorganic counterparts.[1,2] In applications that lower cost and higher performance must be fused, such as optical waveguide switches and modulators, polymer can even outperform rival technologies. Particularly, polymers are suitable for short-distance optical interconnections and for the fabrication of many optical components such as splitters, combiners, multiplexers, switches, attenuators, and filters.[3] Although optical polymer systems have been developed for some time,[4] main materials used for optical waveguide are still limited to a few kinds of polymers such as polyacrylates and polyimides.[5] To use polymers in optical waveguide devices, one of the key requirements is that they must exhibit low optical loss. Fluoropolymers are ideal to fulfill this requirement because they possess low transmission loss at the telecommunication operating wavelengths (1310 and 1550 nm) because the heavier fluorine atoms shift the vibrational overtone absorption signals to longer wavelengths.

Compared to perfluoropolymers with very low optical loss but poor processability,[6] perfluorocyclobutane (PFCB) aryl ether polymers are a unique class of optical polymers.[7] PFCB polymers possess a combination of desirable properties like excellent processability, low dielectric constant, low moisture absorption, good thermal and thermal oxidative stability, low birefringence, and good optical transparency. PFCB polymers were first prepared by Dow Chemical through the radical-mediated thermal cyclopolymerization of trifluorovinyl aryl ethers.[8] In the past decade, a variety of trifluorovinyl aryl ether monomers and their resulting PFCB polymers have been developed to further extend the vast array of interesting properties.[9] Recently, a series of highly fluorinated, siloxane-containing tetrafunctional trifluorovinyl aryl ether monomers and PFCB aromatic ether polymers have been synthesized to exhibit good optical transparency (0.30 dB/cm at 1310 nm).[10] However, the siloxane linkages in these trifluorovinyl aryl ether monomers are sensitive to moisture and acid so that the purification of monomers is tedious, and the resulting PFCB polymers are susceptible to hydrolysis. In this paper, novel ester-containing difunctional and trifunctional trifluorovinyl aryl ether monomers are designed to simplify the synthesis and purification and to provide PFCB aromatic ether polymers with much better hydrolytic resistance compared to those with siloxane linkages. Chloro and bromo atoms are also introduced into trifunctional trifluorovinyl aryl ether monomers to provide PFCB aromatic ether polymers with good refractive index controllability without introducing additional optical loss. A variety of PFCB aromatic ether polymers with the combination of good thermal and chemical stability, controllable refractive index, low birefringence, and optical loss are demonstrated in this work.

Experimental Section

All chemicals were purchased from Aldrich, SynQuest, or Lancaster Synthesis Inc. and used as received unless otherwise specified. Diethyl ether was distilled under nitrogen from

sodium with benzophenone as the indicator. Methylene chloride was distilled over P_2O_5. The intermediate 4-bromophenyl trifluorovinyl ether was synthesized by using a modified procedure to a published method.[11] Intermediates, 2,4,6-trichloro-1,3,5-trihydroxybenzene, and 2,4,6-tribromo-1,3,5-trihydroxybenzene were synthesized from procedures used by Kajigaeshi et al.[12] 4-(Dimethylamino)pyridinium 4-toluene-sulfonate (DPTS),[13a] nonafluoropentyl-1-phenyl-1,1-bisphenol,[13b] and tris[(4-trifluorovinyloxy)phenyl]triazine monomer **8**[10] were prepared according to the reported procedures.

^{1}H NMR spectra (200 MHz) were taken on a Bruker-200 FT NMR spectrometer, and ^{19}F NMR spectra were recorded on a Bruker AF 300 spectrometer. Elemental analysis was taken at QTI (Whitehouse, NJ). ESI-MS spectra were obtained on a Bruker Daltonics Esquire ion trap mass spectrometer. Thermal analyses were performed on a TA Instruments 2010 differential scanning calorimeter (DSC) at a scan rate of 10 °C/min and a Hi-Res TGA 2950 thermogravimetric analyzer (TGA) at a scan rate of 10 °C/min, under a nitrogen atmosphere. Gel permeation chromatography (GPC) was run through a Waters 515 HPLC pump in conjunction with a Waters Styragel 7.8 × 300 mm column and a Waters 410 differential refractometer with THF as the solvent and calibrated using polystyrene samples of a known molecular weight. All surface imaging was conducted in the tapping mode on a digital multimode Nanoscope III scanning force microscope, with 500 × 500 data acquisitions at a scan speed of 1.4 Hz in air at room temperature. Oxide-sharpened silicon nitride tips with integrated cantilevers of the nominal spring constant of 0.38 N/m were used. The refractive indices and birefringence of the polymer films were measured using a Metricon model 2010 prism coupler. The photothermal deflection spectroscopy (PDS) experimental test bed of this study used a 1 kW Hg(Xe) dc short arc lamp as the broadband illumination source at 12.6 Hz chopping frequency, with a $^1/_8$ m dual-grating monochromator. The probe beam was a 10 mW CW He−Ne laser, attenuated to ~1.5 mW.

4-Trifluorovinyloxybenzoic Acid. To a 300 mL three-neck round-bottom flask, 4-bromophenyl trifluorovinyl ether (12.10 g, 48.0 mmol) and dry diethyl ether (60 mL) were added and placed under a nitrogen atmosphere. The solution was then cooled to −78 °C. *tert*-Butyllithium (29 mL, 1.7 M in pentane) was added dropwise to the solution and allowed to stir for 1 h. A stream of dry CO_2 was introduced into the solution and stirred at −78 °C for 45 min. The solution was warmed to room temperature for 30 min and acidified with an HCl solution (230 mL, 1.5 M). The white precipitate was collected, washed with H_2O and hexane, and dried in a vacuum oven to afford a white solid (6.57 g, 63%). ^{1}H NMR (200 MHz, CDCl₃): δ 7.17 (2H, d, $J = 8.79$ Hz), 8.14 (2H, d, $J = 8.78$ Hz). ^{19}F NMR (300 MHz, CDCl₃, C₆F₆): δ 38.00 (1F, dd, *cis*-CF=CFF, F_c), 47.66 (1F, dd, *trans*-CF=CFF_b, F_b), 54.10 (1F, dd, CF_a = CF₂, F_a), ($J_{ab} = 91.5$ Hz, $J_{ac} = 61.0$ Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for C₉H₅F₃O₃: C, 49.56; H, 2.31. Found: C, 49.39; H, 2.20. ESI-MS (*m*/*z*): calcd 218.0; found 218.1.

1*H*,1*H*,10*H*,10*H*-Perfluoro-1,10-decyl Bis(4-trifluorovinyloxybenzoate) (1). To a 100 mL three-neck round-bottom flask, 1*H*,1*H*,10*H*,10*H*-perfluoro-1,10-decanediol (1.39 g, 3.0 mmol), 4-trifluorovinyloxybenzoic acid (1.37 g, 6.3 mmol), DPTS (0.40 g, 1.35 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, *N*,*N*'-dicyclohexylcarbodiimide (DCC) (1.36 g, 6.6 mmol) was added to the solution and stirred for 1 h. Excess DCC (0.12 g, 0.6 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a white solid. The crude product was purified over silica gel with hexane−methylene chloride (1:1) as the eluent to afford a white solid (2.25 g, 87%). ^{1}H NMR (200 MHz, CDCl₃, TMS): δ 4.76 (4 H, t, $J = 13.3$ Hz), 7.15 (4 H, d, $J = 8.79$ Hz), 8.10 (4 H, d, $J = 8.79$ Hz). ^{19}F NMR (300 MHz, CDCl₃, C₆F₆): δ 38.06 (2 F, dd, *cis*-CF=CF₂, F_c), 47.42 (2 F, dd, *trans*-CF=CF₂, F_b), 49.00−53.00 (16 F, m), 53.60 (2 F, dd, CF=CF₂, F_a), ($J_{ab} = 91.3$ Hz, $J_{ac} = 68.5$ Hz, J_{bc}

= 109.9 Hz). Anal. Calcd for C₂₈H₁₂F₂₂O₆: C, 39.00; H, 1.40. Found: C, 38.77; H, 1.25. ESI-MS (*m*/*z*): calcd 862.0; found 862.1.

Tetrafluoro-1,4-phenyl Bis(trifluorovinyloxybenzoate) (2). To a 100 mL three-neck round-bottom flask, tetrafluorohydroquinone (0.55 g, 3.0 mmol), 4-trifluorovinyloxybenzoic acid (1.37 g, 6.3 mmol), DPTS (0.40 g, 1.35 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (1.36 g, 6.6 mol) was added to the solution and stirred for 1 h. Excess DCC (0.12 g, 0.6 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a yellowish-white solid. The crude product was purified over silica gel with hexane−methylene chloride (4:1) as the eluent to afford a yellowish-white solid (0.49 g, 28%). ^{1}H NMR (200 MHz, CDCl₃, TMS): δ 7.27 (4 H, d, $J = 8.79$ Hz), 8.23 (4 H, d, $J = 8.79$ Hz). ^{19}F NMR (300 MHz, CDCl₃, C₆F₆): δ 19.86 (4 F, s), 37.56 (2 F, dd, *cis*-CF=CF₂, F_c), 47.22 (2 F, dd, *trans*-CF=CF₂, F_b), 54.83 (2 F, dd, CF=CF₂, F_a), ($J_{ab} = 91.7$ Hz, $J_{ac} = 61.0$ Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for C₂₄H₈F₁₀O₆: C, 49.50; H, 1.38. Found: C, 49.39; H, 1.28. ESI-MS (*m*/*z*): calcd 582.0; found 582.2.

Hexafluoropropyl-2,2-diphenyl Bis(4-trifluorovinyloxybenzoate) (3). To a 100 mL three-neck round-bottom flask, hexafluoropropylbisphenol (1.01 g, 3.0 mmol), 4-trifluorovinyloxybenzoic acid (1.37 g, 6.3 mmol), DPTS (0.40 g, 1.35 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (1.36 g, 6.6 mmol) was added to the solution and stirred for 1 h. Excess DCC (0.12 g, 0.6 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a white solid. The crude product was purified over silica gel with hexane−methylene chloride (1:1) as the eluent to afford a white solid (1.83 g, 83%). ^{1}H NMR (200 MHz, CDCl₃, TMS): δ 7.22 (4 H, d, $J = 8.79$ Hz), 7.26 (4 H, d, $J = 8.79$ Hz), 7.49 (4 H, d, $J = 8.79$ Hz), 8.23 (4 H, d, $J = 8.79$ Hz). ^{19}F NMR (300 MHz, CDCl₃, C₆F₆): δ −68.08 (6 F, s), 37.93 (2 F, dd, *cis*-CF=CF₂, F_c), 47.40 (2 F, dd, *trans*-CF=CF₂, F_b), 54.21 (3 F, dd, CF=CF₂, F_a), ($J_{ab} = 91.6$ Hz, $J_{ac} = 61.0$ Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for C₃₃H₁₆F₁₂O₆: C, 53.82; H, 2.19. Found: C, 53.70; H, 2.11. ESI-MS (*m*/*z*): calcd 736.1; found 736.0.

Nonafluoropentyl-1,1,1-triphenyl Bis(4-trifluorovinyloxybenzoate) (4). To a 100 mL three-neck round-bottom flask, nonafluoropentyl-1-phenyl-1,1-bisphenol (1.48 g, 3.0 mmol), 4-trifluorovinyloxybenzoic acid (1.37 g, 6.3 mmol), DPTS (0.40 g, 1.35 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (1.36 g, 6.6 mmol) was added to the solution and stirred for 1 h. Excess DCC (0.12 g, 0.6 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a white solid. The crude product was purified over silica gel with hexane−methylene chloride (1:1) as the eluent to afford a clear yellowish-brown solid (2.18 g, 81%). ^{1}H NMR (200 MHz, CDCl₃, TMS): δ 7.19 (4 H, d, $J = 8.96$ Hz), 7.20 (4 H, d, $J = 8.78$ Hz), 7.32 (9 H, m), 8.20 (4 H, d, $J = 8.78$ Hz). ^{19}F NMR (300 MHz, CDCl₃, C₆F₆): δ −117.00 to −84.00 (9 F, m), 37.98 (2 F, dd, *cis*-CF=CF₂, F_c), 47.68 (2 F, dd, *trans*-CF=CF₂, F_b), 54.36 (2 F, dd, CF=CF₂, F_a), ($J_{ab} = 97.7$ Hz, $J_{ac} = 61.0$ Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for C₄₁H₂₁F₁₅O₆: C, 55.05; H, 2.37. Found: C, 54.92; H, 2.30. ESI-MS (*m*/*z*): calcd 894.1; found 894.0.

2,4,6-Trichloro-1,3,5-phenyl Tris(trifluorovinyloxybenzoate) (5). To a 100 mL three-neck round-bottom flask, 2,4,6-trichloro-1,3,5-trihydroxybenzene (0.83 g, 3.6 mmol), 4-trifluorovinyloxybenzoic acid (2.51 g, 11.5 mmol), DPTS (0.71 g, 2.4 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (2.67 g, 13.0 mmol)

was added to the solution and stirred for 1 h. Excess DCC (0.45 g, 2.2 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a residue. The residue was purified over silica gel with hexane−methylene chloride (2:1) as the eluent to afford a yellowish-white solid (1.89 g, 63%). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 7.26 (6 H, d, J = 8.79 Hz), 8.30 (6 H, d, J = 8.79 Hz). ^{19}F NMR (300 MHz, CDCl$_3$, C$_6$F$_6$): δ 37.54 (3 F, dd, *cis*-CF=CF$_2$, F$_c$), 47.50 (3 F, dd, *trans*-CF=CF$_2$, F$_b$), 54.27 (3 F, dd, CF=CF$_2$, F$_a$) (J_{ab} = 91.5 Hz, J_{ac} = 61.0 Hz, J_{bc} = 109.9 Hz). Anal. Calcd for C$_{33}$H$_{12}$Cl$_3$F$_9$O$_9$: C, 47.77; H, 1.46. Found: C, 47.60; H, 1.38. ESI-MS (*m/z*): calcd 827.9; found 827.7.

2,4,6-Tribromo-1,3,5-phenyl Tris(trifluorovinyloxybenzoate) (6). To a 100 mL three-neck round-bottom flask, 2,4,6-tribromo-1,3,5-trihydroxybenzene (1.16 g, 3.2 mmol), 4-trifluorovinyloxybenzoic acid (2.23 g, 10.2 mmol), DPTS (0.63 g, 2.1 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (2.67 g, 13.0 mmol) was added to the solution and stirred for 1 h. Excess DCC (0.40 g, 1.9 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a residue. The residue was purified over silica gel with hexane−methylene chloride (2:1) as the eluent to give a white crystalline solid (2.23 g, 72%). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 7.26 (6 H, d, J = 8.79 Hz), 8.30 (6 H, d, J = 8.79 Hz). ^{19}F NMR (300 MHz, CDCl$_3$, C$_6$F$_6$): δ 37.61 (3 F, dd, *cis*-CF=CF$_2$, F$_c$), 47.65 (3 F, dd, *trans*-CF=CF$_2$, F$_b$), 54.33 (3 F, dd, CF=CF$_2$, F$_a$) (J_{ab} = 91.5 Hz, J_{ac} = 61.0 Hz, J_{bc} = 109.9 Hz). Anal. Calcd for C$_{33}$H$_{12}$Br$_3$F$_9$O$_9$: C, 41.15; H, 1.26. Found: C, 41.32; H, 1.19. ESI-MS (*m/z*): calcd 959.8; found 959.6.

1,3,5-Phenyl Tris(trifluorovinyloxybenzoate) (7). To a 100 mL three-neck round-bottom flask, phloroglucinol (0.53 g, 4.2 mmol), 4-trifluorovinyloxybenzoic acid (2.75 g, 12.6 mmol), DPTS (0.83 g, 2.8 mmol), and dry methylene chloride (20 mL) were added and placed under a nitrogen atmosphere. After partial dissolution of the starting materials, DCC (2.86 g, 13.9 mmol) was added to the solution and stirred for 1 h. Excess DCC (0.45 g, 2.2 mmol) was added to the solution and allowed to stir for 24 h. The solution was then filtered and rinsed with methylene chloride. The filtrate was collected and dried over sodium sulfate. The solvent was removed to produce a residue. The residue was purified over silica gel with hexane−methylene chloride (1:1) as the eluent to give a yellowish-white crystalline solid (2.32 g, 76%). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 7.16 (3 H, s), 7.30 (6 H, dd, J = 8.79 Hz), 8.21 (6 H, dd, J = 8.79 Hz). ^{19}F NMR (300 MHz, CDCl$_3$, C$_6$F$_6$): δ 37.56 (3 F, dd, *cis*-CF=CF$_2$, F$_c$), 47.32 (3 F, dd, *trans*-CF=CF$_2$, F$_b$), 54.35 (3 F, dd, CF=CF$_2$, F$_a$) (J_{ab} = 91.5 Hz, J_{ac} = 61.0 Hz, J_{bc} = 109.9 Hz). Anal. Calcd for C$_{33}$H$_{15}$F$_9$O$_9$: C, 54.56; H, 2.08. Found: C, 54.38; H, 1.99. ESI-MS (*m/z*): calcd 726.1; found 726.0.

Solution Polymerization. Monomers (0.30 g, 30 wt %) were weighed out, dissolved in mesitylene (0.70 g), and then heated at 150 °C for several hours in 15 mL two-neck round-bottom flasks under nitrogen. Molecular weight was monitored using GPC.

Substrate Preparation. "Vycor" glass substrates were prepared by ultrasonicating in acetone for 5 min, methanol for 5 min, and chloroform for 5 min. Fused silica substrates for optical loss measurements were prepared through Piranha cleaning. The substrates were soaked in a solution of sulfuric acid (H$_2$SO$_4$):hydrogen peroxide (H$_2$O$_2$) (2:1) for 15 min, and rinsed with distilled water, followed by soaking in a solution of distilled water:hydrofluoric acid (HF) (10:1) for 10 s, and then rinsed with distilled water. The HF solution was neutralized with a sodium carbonate solution. The substrates were then dried in a vacuum oven for 24 h at 85 °C.

Film Preparation. Films were prepared by spin-coating the filtered (through a 0.2 μm Teflon filter) solution (30 wt %) of the prepolymer in mesitylene onto the "Vycor" substrate at

Table 1. Thermal Properties of PFCB Polymers and Copolymers Achieved by Bulk Polymerization for 0.5 h at 250 °C under Nitrogen

polymer from monomer	molar ratio	T_g (°C)[a]	T_d (°C)[b]
1		38	443
2		100	419
3		166	362
4		169	361
5		209	417
6		190	376
7		250	419
8		>350	422
1 and **5**	5:1	50	430
	1:1	96	414
	1:2	121	418
1 and **6**	5:1	61	405
	1:1	95	397
	1:2	147	396
1 and **7**	5:1	48	443
	1:1	142	441
	1:2	157	440
1 and **8**	5:1	55	442
	4:1	59	442
	3:1	60	440
	2:1	80	436
	1:1	133	418
	1:2	172	431

[a] By DSC at 10 °C/min under nitrogen. [b] By TGA at 10 °C/min under nitrogen.

a spin rate of 450 rpm for 30 s and soft-baked at 65 °C for 10 min. The residual solvent was evaporated in a vacuum oven overnight at 85 °C. The final curing was performed at 200 °C and held for 30 min for the first sample. The second sample was heated at 200 and 225 °C, each with a 30 min interval. The third sample was heated to 200, 225, and 250 °C, each with a 30 min interval. Each sample was allowed to cool and then reheated so that one sample could be removed from the micromanipulator to give transparent films. The films for the optical loss measurements were prepared on fused silica substrates at a spin rate of 450 rpm for 40 s and cured at 200 and 225 °C.

Results and Discussion

Design and Synthesis of Monomers. For potential use in integrated optical waveguide devices, optical polymers should exhibit not only high thermal stability and good solvent resistance but also low optical loss and controllable refractive index. To achieve low optical loss, light scattering and absorption should be avoided in the near-infrared region (NIR), especially at the transmission wavelengths commonly used in telecommunications (1310 and 1550 nm). By replacing hydrogen atoms with heavier atoms (halogens), the absorption loss can be lowered by shifting vibrational overtone absorption to longer wavelengths, away from the regions of interest. A series of novel bifunctional and trifunctional trifluorovinyl aryl ether monomers have been designed and synthesized in this work (Figure 1). Highly fluorinated moieties are introduced into the difunctional monomers **1**−**4**. The trifunctional monomers **5**−**7** consist of three trifluorovinyl ether groups and an aromatic core center, which form a more rigid and compact structure. Ester linkages were incorporated into the monomer structures for the ease of synthesis and purification. Chloro and bromo atoms are also introduced into trifunctional trifluorovinyl aryl ether monomers **5** and **6** to achieve good refractive index controllability without introducing additional optical loss.

For the synthesis of monomers **1**−**7**, a carboxylic acid derivative, 4-trifluorovinyloxybenzoic acid was synthesized based on the preparation of a reactive carbanion
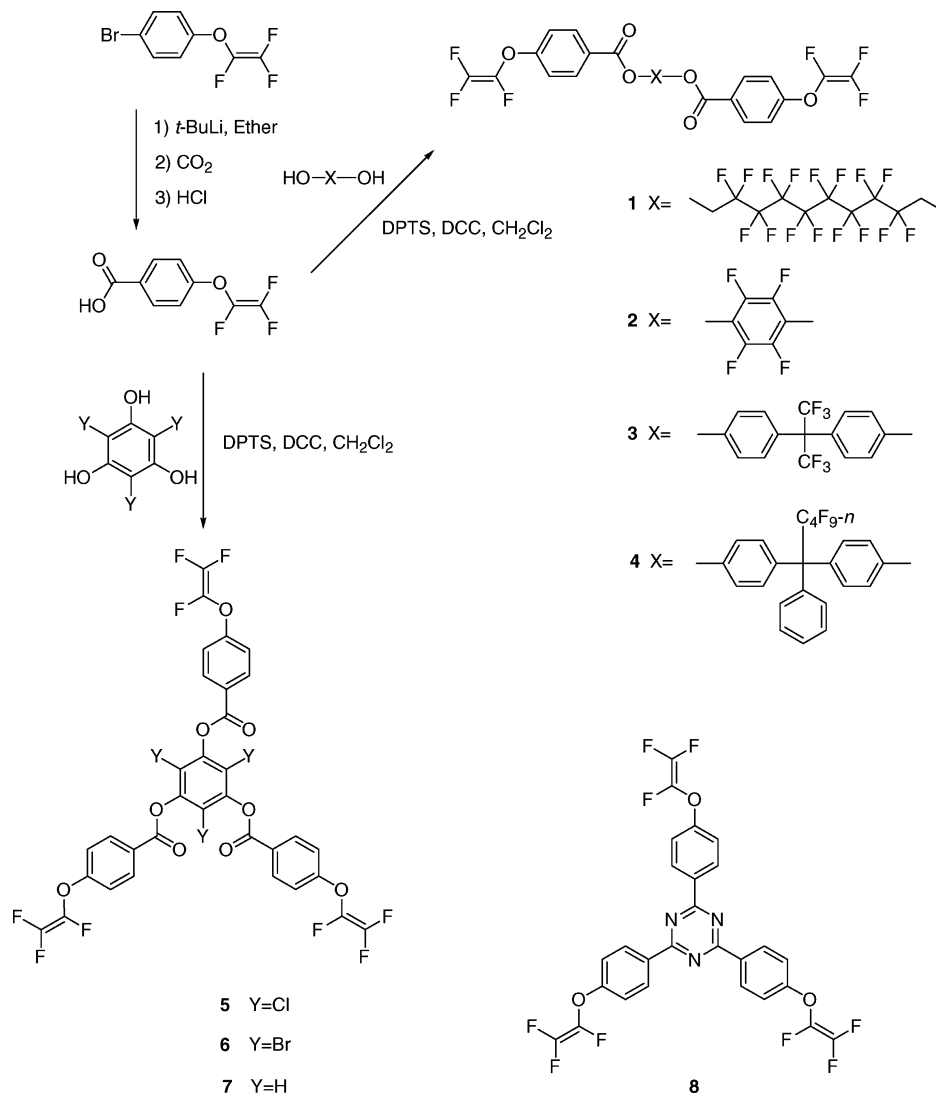
Figure 1. Synthesis of difunctional and trifunctional monomers **1**−**7**.

through the lithiation of 4-bromophenyl trifluorovinyl ether at −78 °C with *t*-BuLi in ether[14] followed by its nucleophilic reaction with carbon dioxide and the final acidification. With this intermediate, a series of bifunctional and trifunctional monomers were obtained through a mild esterification reaction at room temperature,[13] using dicyclohexylcarbodiimide (DCC) as the activating agent of carboxylic acid and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as the catalyst.

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 bulk. All the monomers exhibited exothermic polymerization peaks between 150 and 300 °C in their DSC profiles. After the bulk polymerization of monomers for 0.5 h at 250 °C under nitrogen, thermal properties of the achieved PFCB polymers were measured using DSC and TGA. Data for the thermal analysis of the polymers are given in Table 1.

For the bifunctional monomers **1**−**4**, each exhibits a different degree of flexibility by the variable bridge, which affects its glass transition temperature (T_g) and decomposition temperature (T_d). Monomer **1**, which contains a more flexible fluoroalkyl chain as bridge, is expected to have a lower T_g and T_d for the resulting polymer. Aromatic rings incorporated into the mono-

mers **2**−**4** are more rigid, so higher T_gs are expected for the resulting polymers. However, it is interesting to note that the measured T_d of the polymer derived from monomer **1** is much higher than the T_ds of the polymers from monomers **2**−**4** with aromatic bridges. This is probably due to the better stability of ester linkage generated from the alcohol groups compared to that from the phenol groups. For the trifunctional monomers **5**−**8**, the T_gs and T_ds are mainly affected by the different substituents on the core aromatic rings. The smaller substituents allow for more efficient packing, whereas the bulkier groups (chlorine and bromine) cause more steric hindrance. Therefore, the smaller groups such as hydrogen in the monomer **7** and the triazine group in the monomer **8** allow for a more compact structure, giving higher T_gs for the resulting polymers, whereas the chloro-containing monomer **5** and the bromo-containing monomer **6** exhibit lower T_gs for the obtained polymers. A broad range of T_gs can be reached in the polymers by the copolymerization of flexible monomer **1** and rigid monomers **5**−**8** (Tables 1 and 4).

Solution Polymerization and Properties of the Resulting Films. Solution polymerization and copolymerization of the monomers were performed in mesitylene at 150 °C under nitrogen to prepare polymer solutions (Figure 2). The concentration of the monomers

Table 2. Molecular Weight of PFCB Polymers and Copolymers during Solution Polymerization in Mesitylene at 150 °C Monitored by GPC

polymer from monomer	molar ratio	wt %	time (h)	M_w	M_n	M_w/M_n
1		30	26	2240	1820	1.23
			29	2390	1910	1.25
3		30	24	3260	2110	1.54
4		30	20	3330	2400	1.39
5		30	18	5020	2890	1.74
6		30	18	3270	2130	1.54
7		30	22	3570	2310	1.54
			30	7250	3390	2.14
8		20	18	6600	2280	2.89
1 and **5**	1:1	30	20	15240	5630	2.71
1 and **6**	1:1	30	20	5030	2910	1.73
1 and **7**	1:1	30	30	6010	3100	1.94
1 and **8**	5:1	30	28	3260	1980	1.65
			30	3500	2060	1.70
			46	5490	3220	1.70
	1:1	30	24	4650	2170	2.14
	1:2	30	23	14550	3710	3.92

or comonomers used was 30 wt %. The monomers were polymerized for several hours, causing the molecular weight to increase. Gel permeation chromatography (GPC) was used to monitor the monomer to polymer conversion and to determine the molecular weight of the polymer (Table 2). After heating the monomer solution for a suitable period of time, the polymer solution was filtered and allowed to settle.

Thin films were prepared by spin-coating the filtered solution onto glass substrates at a spin rate of 450 rpm for 30 s. The samples were heated for 24 h at 85 °C in a vacuum oven for solvent removal and then cured at 200, 225, and 250 °C. The thickness of the obtained films ranged from 1 to 4 μm. The films samples appeared visually to be uniform and crack-free. Film preparation for the homopolymer of bifunctional monomer **1** was difficult because of its high fluoro content, causing poor adhesion to the substrates. However, this difficulty was overcome by copolymerizing the bifunctional monomer with the trifunctional monomers.

Solubility of the films cured at different temperatures was also tested. The solvents used were cyclopentanone, tetrahydrofuran (THF), and dimethylformamide (DMF), which are commonly used in device fabrication. The polymers from bifunctional monomers exhibited poor solvent resistance due to their linear structures after curing at all three temperatures. The films cured at 200 °C for the homopolymers of trifunctional monomers or their copolymers with the difunctional monomer **1** were found to be slightly soluble in these solvents while all these films cured at 225 °C and above exhibited good solvent resistance due to the increased molecular weight as well as cross-linking with trifunctional monomers.

Tapping mode atomic force microscopy (AFM) was used to study the surface morphology and properties of the polymer films cured at 225 °C.[15] The rms surface roughness measured for the samples from monomers **1** and **5** ranged from 0.33 to 0.43 nm (Table 4). The surfaces of the spin-coated films exhibit uniform fractal morphology, which is characteristic for glassy polymers.[16] The obtained AFM images also show no phase separation happened in the films (Figure 3).

Table 3. Refractive Indices and Birefringences of Polymer Films Cured at Different Temperatures for 0.5 h Measured Using Prism Coupling (Metricon)

| polymer from monomer	molar ratio	curing T (°C)	wavelength (1310 nm)			wavelength (1550 nm)		
			n_{TE}	n_{TM}	Δn_{TE-TM}	n_{TE}	n_{TM}	Δn_{TE-TM}
1		200–250	$\leq$1.447	$\leq$1.447		$\leq$1.447	$\leq$1.447	
3		200	1.513	1.512	0.001	1.511	1.510	0.001
		225	1.511	1.508	0.003	1.509	1.507	0.002
		250	1.509	1.506	0.003	1.507	1.503	0.004
4		200	1.512	1.511	0.001	1.510	1.509	0.001
		225	1.510	1.508	0.002	1.508	1.506	0.002
		250	1.510	1.507	0.003	1.507	1.504	0.003
5		200	1.539	1.534	0.005	1.536	1.531	0.005
		225	1.537	1.531	0.006	1.534	1.528	0.006
		250	1.535	1.529	0.006	1.533	1.526	0.007
6		200	1.543	1.540	0.003	1.540	1.538	0.002
		225	1.542	1.536	0.006	1.539	1.534	0.005
		250	1.541	1.535	0.006	1.539	1.532	0.007
7		200	1.529	1.527	0.002	1.528	1.524	0.004
		225	1.528	1.520	0.008	1.526	1.520	0.006
		250	1.526	1.517	0.009	1.525	1.516	0.009
8		200	1.546	1.539	0.007	1.543	1.537	0.006
		225	1.542	1.534	0.008	1.539	1.532	0.007
		250	1.541	1.534	0.007	1.538	1.530	0.008
1 and **5**	1:1	200	1.489	1.488	0.001	1.487	1.487	0.000
		225	1.489	1.486	0.003	1.487	1.483	0.004
		250	1.488	1.486	0.002	1.485	1.482	0.003
1 and **6**	1:1	200	1.503	1.503	0.000	1.501	1.499	0.002
		225	1.502	1.500	0.002	1.500	1.496	0.004
		250	1.502	1.498	0.004	1.498	1.496	0.002
1 and **7**	1:1	200	1.489	1.488	0.001	1.486	1.484	0.002
		225	1.487	1.484	0.003	1.484	1.482	0.002
		250	1.485	1.480	0.005	1.482	1.476	0.006
1 and **8**	5:1	200–250	$\leq$1.447			$\leq$1.444		
	1:1	200	1.501	1.501	0.000	1.498	1.497	0.001
		225	1.500	1.498	0.002	1.498	1.494	0.004
		250	1.499	1.493	0.006	1.498	1.492	0.006
	1:2	200	1.510	1.506	0.004	1.509	1.504	0.005
		225	1.507	1.502	0.005	1.503	1.499	0.004
		250	1.504	1.497	0.007	1.502	1.494	0.008
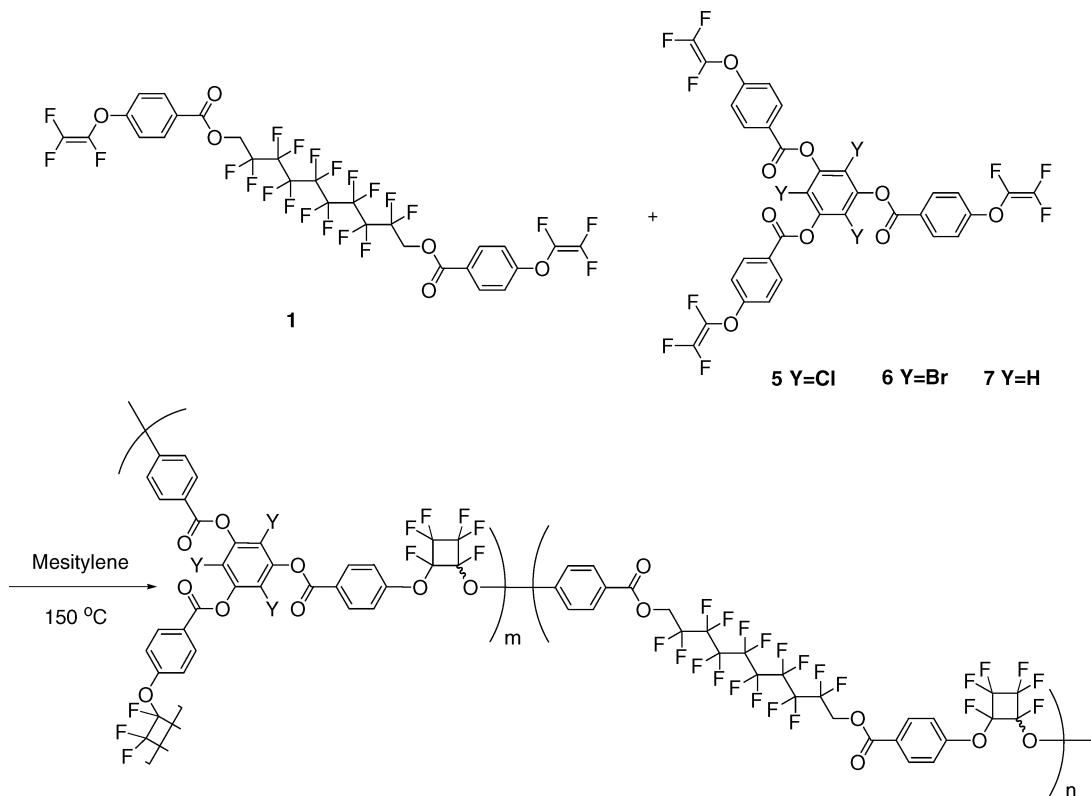
Figure 2. Copolymerization of monomers **1** and **5**−**7**.

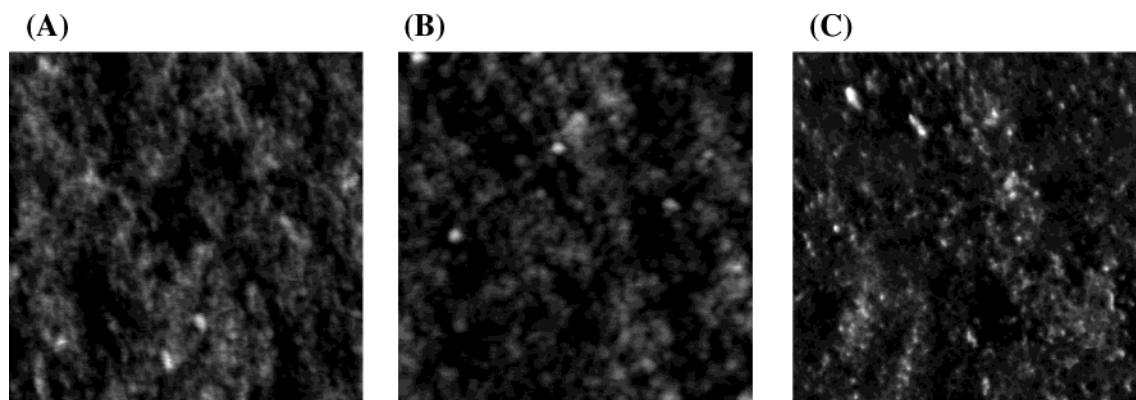**Figure 3.** Tapping mode AFM surface topographs of the homopolymer films from monomers **1** (A, 0.5 × 0.5 μm, rms = 0.33 nm) and **5** (C, 0.5 × 0.5 μm, rms = 0.43 nm) and their copolymer (1:1) film (B, 0.5 × 0.5 μm, rms = 0.36 nm) cured at 225 °C for 0.5 h.

Table 4. Thermal Stability, Surface Roughness, and Optical Properties of the Homopolymer Films from Monomers 1 and 5 and Their Copolymer (1:1) Film Cured at 225 °C for 0.5 h

polymer from monomer	T_g (°C)[a]	surface roughness (nm)	wavelength (1310 nm)			optical loss (dB/cm)
			n_{TE}	n_{TM}	Δn_{TE-TM}	
1	38	0.33	≤1.447	≤1.447		0.26
1 and **5** (1:1)	96	0.36	1.489	1.486	0.003	0.35
5	209	0.43	1.537	1.531	0.006	0.42

The refractive indices and birefringence of the polymer films were measured using a Metricon model 2010 prism coupler. Controllable refractive indices (n: 1.447−1.546 at 1310 nm) have been achieved by varying monomer structures and copolymerization (Table 3). The refractive index of a polymer is intrinsically influenced by factors such as free volume, polarizability, and wavelength.[1c,17] The polymer from monomer **1** displays much lower refractive index compared to the polymers from monomers **3**−**8** because high fluorination and less aromaticity of the monomer **1** tend to increase free volume and hydrophobicity while to decrease the po-

larizability of the polymer. The refractive index value of the polymer from monomer **1** is approximately equal to or lower than that of the substrate because only one mode was found before the light from the film propagation mode entered the substrate. Because of the introduction of heavier and bulkier atoms (Cl and Br) into monomers **5** and **6** to increase the polarizability, the corresponding polymers have higher refractive indices compared to that of the polymer from monomer **7**. Because of the more rigid heterocyclic core without ester linkages favors the close packing, the polymer from monomer **8** also possess higher refractive index than
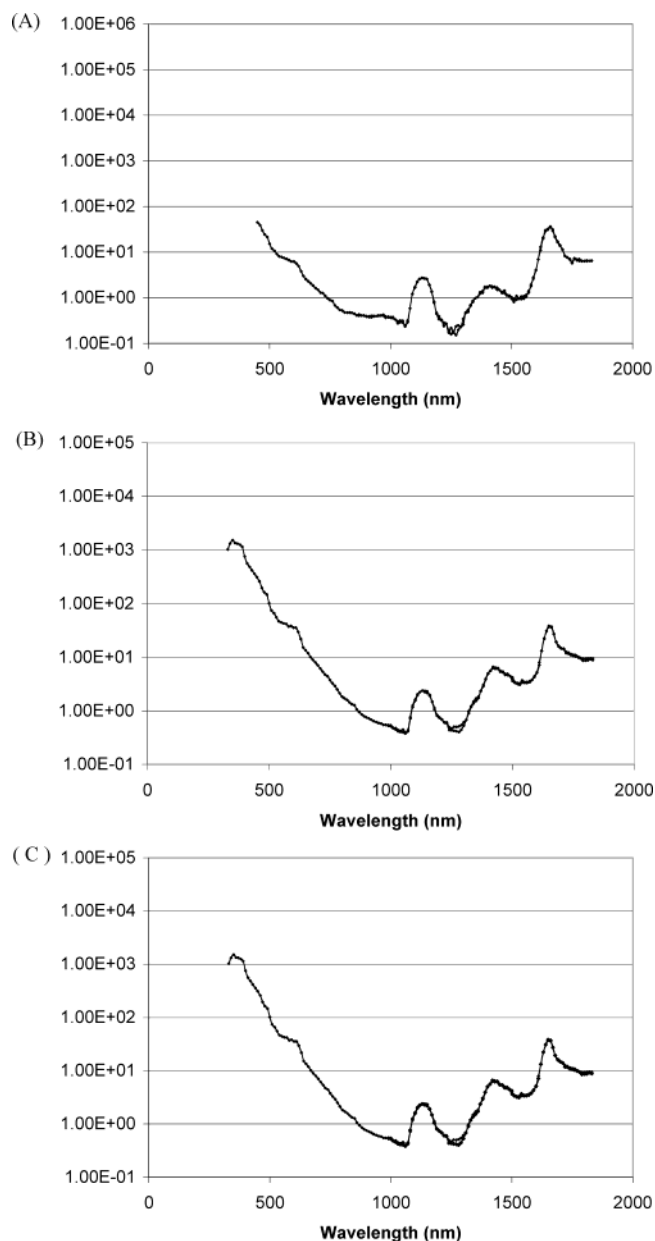
Figure 4. Optical loss spectra of the homopolymer films from monomers **1** (A) and **5** (C) and their copolymer (1:1) film (B) cured at 225 °C for 0.5 h measured by PDS.

that from monomer **7**. From the measured refractive indices, it can be seen that the refractive index of a polymer decreases as the curing temperature increases (Table 3). This is because the content of more polarizable and planar trifluorovinyl ether moieties decreases while the content of the less polarizable and more sterically hindered perfluorocyclobutyl linkages increases with further curing at higher temperatures. The detailed dependence of refractive index on formation of the PFCB linkages is under investigation and will be reported in another paper to further clarify the effects of free volume, polarizability, and wavelength. Through copolymerization of monomer **1** with monomers **5**−**8**, the refractive indices are tunable within a broad range. The measured birefringence ($n_{TE} - n_{TM}$) is between 0.001 and 0.01 for all of the film samples.

Optical loss measurements were obtained using photothermal deflection spectroscopy (PDS)[18] for the homopolymer and copolymer films cured at 225 °C (Figure 4 and Table 4). Because of high transparency of the

polymer films, the PDS saturation signal was not measurable. This problem was partially solved by evaluating the first overtone of the C−H stretch at 1660 nm using a reference polymer. Ultem 1000 was chosen as the reference polymer because the shape and position of the peak at 1660 nm were close to those of the samples. From the PDS spectra, the optical loss was as low as 0.26 dB/cm at 1310 nm. It is also shown from Table 4 that a good combination of polymer properties such as thermal stability, surface roughness, refractive index, and optical loss can be achieved through copolymerizing highly fluorinated and flexible monomer **1** with chlorine-containing and rigid monomer **5**. The systematic characterization of the resulting polymers and copolymers by PDS can also provide the relationship between optical loss and C:H ratio.

Conclusion

A series of trifluorovinyl-containing aryl ether monomers and PFCB polymers with ester linkages were synthesized and characterized. Chloro and bromo atoms were introduced into trifunctional trifluorovinyl aryl ether monomers to obtain PFCB aromatic ether polymers with good refractive index controllability without causing additional optical loss. A combination of desirable optical polymer properties such as thermal stability, solvent resistance, surface smoothness, refractive index tunability, and low optical loss can be achieved by varying monomer structures and copolymerization ratios. Optical loss measurements of these polymer films using PDS show optical loss as low as 0.26 dB/cm at 1310 nm can be achieved which is suitable for the fabrication of integrated optical waveguide devices.

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