Highly Fluorinated Trifluorovinyl Aryl Ether Monomers and Perfluorocyclobutane Aromatic Ether Polymers for Optical Waveguide Applications

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ABSTRACT: A series of novel trifunctional and tetrafunctional trifluorovinyl aryl ether monomers and perfluorocyclobutane (PCFB) aromatic ether polymers have been synthesized and characterized. These PFCB polymers exhibit desirable properties for low loss optical waveguide applications. Monomers used in this study were prepared from the key intermediate, 4-bromophenyl trifluorovinyl ether. Through thermal dimerization of the aromatic trifluorovinyl ether moieties, these monomers can be either melt or solution polymerized to form PFCB-containing prepolymers with good processability for the fabrication of optical waveguides. After a post-thermal cross-linking process, the resulting thermosets possess low optical loss (0.30 dB/cm at 1310 nm with 1% of DR-1 doping), high thermal stability ($T_{\rm g}$: 85–350 °C), good solvent resistance, and low surface roughness.

Introduction

High-speed information optics, once so prohibitively expensive that only long-haul communications was feasible, is being applied to ever-shorter distances, penetrating from metro-area to access and intracomputer interconnect networks. However, the pace of developing higher bandwidth and more cost-effective solutions to sustain the rapid growth of bandwidth presents huge challenges and opportunities for materials and optical scientists and engineers. Among the candidate material systems, high expectations have been placed on polymers as the materials choice for highly integrated optical components and planar lightwave circuits. State-of-the-art optical polymers are particularly attractive in integrated optical waveguide devices because they offer rapid processability, costeffectiveness, high yields, high performance such as lower optical loss and smaller birefringence compared to those of silica, power-efficient thermal actuation due to larger thermooptic coefficient than in silica, and compactness owing to a large refractive index contrast.^{1,2} Although the work of integrated polymer components is going on globally in the areas of switches, modulators, lasers, amplifiers, and sensors, the ideal optical polymers are limited to a few kinds of polymers such as polyacrylates, polyimides, polycarbonates, and cyclobutenes.

Perfluorocyclobutane (PFCB) aryl ether polymers were first prepared in Dow Chemical through the radical-mediated thermal cyclopolymerization of trifluorovinyl ethers. These PFCB polymers do represent a unique class of optical polymers with a combination of excellent processability and high performance such as low dielectric constant, low moisture absorption, good thermal and thermal oxidative stability, low birefringence, and optical transparency.³⁻⁷ In this paper, we report the synthesis and characterization of a series of novel trifunctional and tetrafunctional trifluorovinyl aryl ether monomers (Figure 1) and the resulting PFCB aromatic ether polymers. The trifunctional monomer consists of triazine as the center core to form a rigid structure with three trifluorovinyl ether groups. The tetrafunctional monomers are highly fluorinated with two siloxane linkages that contain four trifluorovinyl ether groups. Highly fluorinated monomers are desirable for minimizing the absorption optical loss at the telecommunication operating wavelengths (1.3 and 1.55 μ m) because the heavier fluorine atoms shift the overtone absorption signal to a longer wavelength. The siloxane-containing structural units are introduced into PFCB polymers because of their chemical, thermal, and oxidative resistance and flexibility at low temperatures.

Experimental Section

All chemicals were purchased from Aldrich, SynQuest, or Lancaster Synthesis Inc. and used as received unless otherwise specified. Tetrahydrofuran (THF) and ether were distilled under nitrogen from sodium with benzophenone as the indicator. Pyridine was distilled over calcium hydride. The intermediate 4-bromophenyl trifluorovinyl ether was synthesized by modifying the method that was reported previously in the literature.⁸

¹H NMR spectra (200 MHz) were taken on a Bruker-200 FT NMR spectrometer, and ¹⁹F 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 differental 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 Waters Styragel 7.8 \times 300 mm column and a Waters 410 differential refractometer with THF as the solvent. All imaging was conducted in the tapping mode on a digital multimode Nanoscope III scanning force microscope, with 512 \times 512 data acquisitions at a scan speed of 1.4 Hz in air at room temper-



Figure 1. Highly fluorinated trifluorovinyl aromatic ether monomers.

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ature. Oxide-sharpened silicon nitride tips with integrated cantilevers of the nominal spring constant of 0.38 N/m were used. 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 \sim 1.5 mW.

Tris[(4-trifluorovinyloxy)phenyl]triazine (2). To a wellstirred solution of 4-bromophenyl trifluorovinyl ether (5.31 g, 21.0 mmol) in dry ether (30 mL) at -78 °C was added tertbutyllithium (12.4 mL, 21.0 mmol, 1.7 M in pentane) dropwise under a nitrogen atmosphere. The mixture was stirred at -78°C for 1.0 h followed by the addition of cyanuric chloride (1.29 g, 7.0 mmol). The reaction mixture was warmed slowly to room temperature and stirred for 1 h and then quenched with water. The mixture was extracted with hexane for three times. The organic layers were collected, washed with water, and dried over Na₂SO₄. The solvent was then removed by rotary evaporation under reduced pressure, and the crude product was purified through a packed neutral aluminum oxide column eluting with hexane and hexane/methylene chloride (20/1) to afford a white solid (1.46 g, 35%). ¹H NMR (200 MHz, CDCl₃, TMS): δ 7.19 (6H, d, J = 9.20 Hz), 8.67 (6H, d, J = 9.20 Hz). ¹⁹F NMR (300 MHz, CDCl₃, C₆F₆): δ 38.08 (3F, dd, cis-CF=

CF₂, F_c), 46.72 (3F, dd, *trans*-CF=CF₂, F_b), 53.53 (3F, dd, CF= CF₂, F_a), ($J_{ab} = 109.9$ Hz, $J_{ac} = 55.0$ Hz, $J_{bc} = 113.8$ Hz). Anal. Calcd for C₂₇H₁₂F₉N₃O₃: C, 54.28; H, 2.02; N, 7.03. Found: C, 54.10; H, 1.95, N, 6.97. ESI-MS (*m*/*z*): calcd, 597.1; found, 597.0.

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1,10-[Bis(tridecafluoro-1,1,2,2-tetrahydroctyl)[bis(4trifluorovinyloxy)phenylsiloxyl]]perfluoro-1H,1H,10H,-10H-decane (3). To a 100 mL three-neck round-bottom flask were added 7.59 g (30 mmol) of 4-bromophenyl trifluorovinyl ether and 45 mL of dry ether. The mixture was placed under N_2 and cooled to -78 °C, and *t*-BuLi (17.6 mL, 30 mmol, 1.7 M in pentane) was added dropwise via a syringe and allowed to stir for 1 h. Tridecafluoro-1,1,2,2-tetrahydroctyltrichlorosilane (4.41 mL, 15 mmol) was added dropwise via a syringe to the mixture and allowed to stir for 24 h. The mixture was filtered followed by solvent removal. HOCH₂(CF₂)₈CH₂OH (1.73 g, 3.75 mmol) was added to the mixture, along with pyridine (1.22 mL, 15 mmol) and THF (20 mL). The mixture was allowed to stir for 30 min at room temperature, after which the solvent was removed and the crude product was separated quickly twice over neutral aluminum oxide eluting with hexane to afford a clear liquid (6.20 g, 87%). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.57 (4H, t, J = 10.0 Hz), 2.15 (4H, m), 4.10 (4H, t, J = 13.3 Hz), 7.14 (8H, d, J = 7.82 Hz), 7.47 (8H, d, J = 8.79 Hz). ¹⁹F NMR (300 MHz, CDCl₃, C₆F₆): δ

-85.20 (22F, m), 38.28 (4F, dd, *cis*-CF=CF₂, F_c), 46.49 (4F, dd, *trans*-CF=CF₂, F_b), 49.45 (16F, m), 53.40 (4F, dd, CF=CF₂, F_a), 56.76 (4F, m), ($J_{ab} = 97.6$ Hz, $J_{ac} = 61.0$ Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for C₅₈H₂₈F₅₄O₆Si₂: C, 36.61; H, 1.48. Found: C, 36.47; H, 1.40. ESI-MS (*m*/*z*): calcd, 1902.1; found, 1902.1.

1,10-Bis[methyl[bis(4-trifluorovinyloxy)phenylsiloxyl]]perfluoro-1H,1H,10H,10H-decane (4). To a 100 mL three-neck round-bottom flask were added 7.59 g (30 mmol) of 4-bromophenyl trifluorovinyl ether and 45 mL of dry ether. The mixture was placed under N_2 and cooled to -78 °C, and t-BuLi (17.6 mL, 30 mmol, 1.7 M in pentane) was added dropwise via a syringe and allowed to stir for 1 h. Trichloromethylsilane (4.41 mL, 15 mmol) was added dropwise via a syringe to the mixture and allowed to stir for 24 h. The mixture was filtered followed by solvent removal. HOCH₂(CF₂)₈CH₂-OH (1.73 g, 3.75 mmol) was added to the mixture, along with pyridine (1.22 mL, 15 mmol) and THF (20 mL). The mixture was allowed to stir for 30 min at room temperature, after which the solvent was removed and the crude product was separated quickly twice over neutral aluminum oxide eluting with hexane to afford a clear liquid (3.36 g, 72%). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.55 (6H, s), 4.01 (4H, t, J = 13.3Hz), 6.97 (8H, d, J = 8.78 Hz), 7.54 (8H, d, J = 8.78 Hz). ¹⁹F NMR (300 MHz, CDCl₃, C₆F₆): δ 38.0 (4F, dd, cis-CF=CF₂, F_c), 46.14 (4F, dd, trans-CF=CF₂, F_b), 49.73 (16F, m), 53.40 (4F, dd, CF=CF₂, F_a), $(J_{ab} = 97.6 \text{ Hz}, J_{ac} = 48.8 \text{ Hz}, J_{bc} = 115.9$ Hz). Anal. Calcd for C44H26F28O6Si2: C, 42.66; H, 2.12. Found: C, 42.55; H, 2.04. ESI-MS (m/z): calcd, 1238.1; found, 1238.2

1,4-[Bis(tridecafluoro-1,1,2,2-tetrahydroctyl)[bis-(4-trifluorovinyloxy)phenylsiloxyl]]tetrafluorohydroquinone (5). To a 100 mL three-neck round-bottom flask were added 7.59 g (30 mmol) of 4-bromophenyl trifluorovinyl ether and 45 mL of dry ether. The mixture was placed under $N_{\rm 2}$ and cooled to -78 °C, and t-BuLi (17.6 mL, 30 mmol, 1.7 M in pentane) was added dropwise via a syringe and allowed to stir for 1 h. Tridecafluoro-1,1,2,2-tetrahydroctyltrichlorosilane (4.41 mL, 15 mmol) was added dropwise via a syringe to the mixture and allowed to stir for 24 h. The mixture was filtered followed by solvent removal. Tetrafluorohydroquinone (0.68 g, 3.75 mmol) was added to the mixture, along with pyridine (1.22 mL, 15 mmol) and THF (20 mL). The mixture was allowed to stir for 30 min at room temperature, after which the solvent was removed and the crude product was separated quickly twice over neutral aluminum oxide eluting with hexane to afford a clear liquid (5.42 g, 89%). ¹H NMR (200 MHz, CDCl₃, TMS): δ 1.56 (4H, t, J = 10.0 Hz), 2.10 (4H, m), 7.15 (8H, d, J = 8.79 Hz), 7.48 (8H, d, J = 8.79 Hz). ¹⁹F NMR (300 MHz, CDCl₃, C₆F₆): δ -85.11 (22F, m), 38.06 (4F, dd, cis-CF=CF₂, F_c), 46.34 (4F, dd, *trans*-CF=CF₂, F_b), 49.82 (4F, s), 53.32 (4F, dd, CF=CF₂, F_a), 56.47 (4F, m), (*J*_{ab} = 91.5 Hz, *J*_{ac} = 61.0 Hz, $J_{bc} = 109.9$ Hz). Anal. Calcd for $C_{54}H_{24}F_{42}O_6Si_2$: C, 39.96; H, 1.49. Found: C, 39.85; H, 1.40. ESI-MS (m/z): calcd, 1622.0; found. 1622.1.

1,9-[Bis(tridecafluoro-1,1,2,2-tetrahydroctyl)[bis(4-trifluorovinyloxy)phenylsiloxyl]]hexafluorobisphenol (6). To a 100 mL three-neck round-bottom flask were added 7.59 g (30 mmol) of 4-bromophenyl trifluorovinyl ether and 45 mL of dry ether. The mixture was placed under N2 and cooled to –78 °C, and *t*-BuLi (17.6 mL, 30 mmol, 1.7 M in pentane) was added dropwise via a syringe and allowed to stir for 1 h. Tridecafluoro-1,1,2,2-tetrahydroctyl trichlorosilane (4.41 mL, 15 mmol) was added dropwise via syringe to the mixture and allowed to stir for 24 h. The mixture was filtered followed by solvent removal. Hexafluorobisphenol (1.26 g, 3.75 mmol) was added to the mixture, along with pyridine (1.22 mL, 15 mmol) and THF (20 mL). The mixture was allowed to stir for 30 min at room temperature, after which the solvent was removed and the crude product was separated quickly over neutral aluminum oxide eluting with hexane to afford a clear liquid (5.24 g, 79%). ¹H NMR (Ž00 MHz, CDCl₃, TMS): δ 1.40 (4H, t, J = 10.0 Hz), 2.10 (4H, m), 6.98 (4H, d, J = 8.79 Hz), 7.06 (4H, d, J = 8.78 Hz), 7.14 (8H, d, J = 8.78 Hz), 7.47 (8H, d, J = 8.78 Hz). ¹⁹F NMR (300 MHz, CDCl₃, C₆F₆): δ -85.20 (22F, m), 38.08 (4F, dd, *cis*-CF=CF₂, F_c), 46.36 (4F, dd, *trans*-CF=CF₂, F_b), 49.80 (6F, s), 53.34 (4F, dd, CF=CF₂, F_a), 56.72 (4F, m), $(J_{ab} = 91.6 \text{ Hz}, J_{ac} = 61.0 \text{ Hz}, J_{bc} = 109.9 \text{ Hz})$. Anal. Calcd for C₆₃H₃₂F₄₄O₆Si₂: C, 42.58; H, 1.82. Found: C, 42.50; H, 1.76. ESI-MS (*m*/*z*): calcd, 1776.1; found, 1776.2.

Solution Polymerization of 3. Monomer **3** (0.300 g, 0.16 mmol, 30 wt %) dissolved in mesitylene (0.700 g, 5.82 mmol) was heated at 150 °C in a 15 mL two-neck round-bottom flask under nitrogen for 30 h. The molecular weight was monitored using GPC.

Solution Copolymerization of 2 and 3. Monomers (0.300 g, 30 wt %) were weighed out by molar ratio 3:2 of monomer **2** and **3**, dissolved in mesitylene (0.700 g, 5.82 mmol), and heated at 150 °C in a 15 mL two-neck round-bottom flask under nitrogen for 19 h. The molecular weight was monitored using GPC.

Substrate Preparation. The glass substrates were cleaned 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 the Piranha cleaning procedure. The substrates were soaked in a solution of sulfuric acid (H₂SO₄):hydrogen peroxide (H₂O₂) (2:1) for 15 min, 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 for disposal. 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 μ m Teflon filter) solution of the prepolymer onto the substrate 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. The fourth sample was heated to 200, 225, 250, and 300 °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.

Results and Discussion

Synthesis and Polymerization of Highly Fluorinated Monomers. Suitable optical materials for waveguide applications must exhibit low optical loss, implying both improved processing to avoid light scattering and low absorption in the near-infrared (NIR), especially at 1310 and 1550 nm, the transmission wavelengths used in telecommunications. Low absorption can be achieved by replacing hydrogen atoms with heavier atoms (halogens), shifting the high-absorption signal toward longer wavelengths. Compared to the commercially used monomer **1** (Tetramer and Oakwood), a series of novel and highly fluorinated aromatic trifluorovinyl ether monomers such as the trifunctional one, **2**, and the tetrafunctional ones, **3–6**, have been recently developed (Figure 1).

Monomers 2-6 were synthesized using the 4-bromophenyl trifluorovinyl ether as the key intermediate (Figure 2). The synthesis of monomer 2 is through a onepot, two-step reaction process. The whole process involved the formation of the organolithium derivative of the 4-bromophenyl trifluorovinyl ether using *t*-BuLi,⁹ followed by the in-situ addition of cyanuric chloride to form 2 via the nucleophilic substitution. The use of cyanuric chloride allowed for the synthesis of a more compact and rigid monomer compared to monomer 1. The triazine group further decreases the optical loss at 1310 and 1550 nm by decreasing the C–H content in the resulting polymer.



Figure 2. Synthesis of trifunctional monomer 2 and tetrafunctional monomers 3–6.

The general synthetic procedures for monomers 3-6are also shown in Figure 2. Similar to the synthesis of monomer **2**, the first step involved is the preparation of a reactive carbanion through the lithiation of 4-bromophenyl trifluorovinyl ether at -78 °C with *t*-BuLi in ether. Tridecafluoro-1,1,2,2-tetrahydroctyltrichlorosilane or trichloromethylsilane was then added in situ to form a disubstituted silyl chloride. The last step was to condense the disubstituted silyl chloride with either a fluorinated alkyl diol or a fluorinated aromatic diphenol to form the monomers containing four trifluorovinyl aromatic ether groups. The organolithium derivative of the 4-bromophenyl trifluorovinyl ether intermediate appears to be stable at a low temperature. This derivative then reacts readily with an electrophile to create a variety of trifluorovinyl ether compounds. The fluorinated alkyl chains incorporated allow for an increase in the flexibility of the monomer, and the high fluorine content helps to reduce moisture absorption, dielectric constant, and optical loss.

Polymerization of the monomers was performed both in melt and in solution. Because of an increased doublebond strain and a lower π -bond energy of fluoroolefins, the cyclodimerization of aromatic trifluorovinyl ether functionality is favored to form fluorinated C–C single bonds.¹⁰ Differential scanning calorimetry (DSC) was used to determine and monitor the $[2\pi + 2\pi]$ cyclodimerization of the monomers in bulk. After the polymerization of aromatic trifluorovinyl ether monomers, an equal mixture of *cis*- and *trans*-1,2-disubstituted PFCBs is obtained in the polymer. This is due to the mechanism of stepwise head-to-head cycloaddition to form the more stable diradical intermediate followed by rapid ring closure.^{3b,c} Solution polymerizations in mesitylene at 150 °C for monomer **3** and a mixture of **2** and **3** in a 3:2 molar ratio were performed to prepare film samples (Figure 3). After several hours, the monomers began cross-linking, causing the molecular weight to increase (Table 1). The concentration of monomer or comonomers used was 30 wt % in mesitylene. The progress of monomer to polymer conversion was monitored by GPC. The desired degree of polymerization was to obtain a material with molecular weight near 10 000.

Properties of PFCB Thermoset Polymers. DSC and thermogravimetric analysis (TGA) were used to measure the thermal properties of the materials. As expected, the more flexible polymers exhibited a lower glass transition temperature (T_g) and decomposition temperature (T_d) due to the long fluorinated alkyl side chain and the bridges (Table 2). The methyl end group for monomer 4 compared to the long fluoroalkyl side chains in monomers **3** increases both the T_g and T_d of the resulting polymer because it offers less flexibility. The different bridges also affect the thermal properties of the monomers. A flexible bridge gives the PFCB polymer a lower T_g and T_d as seen in monomer **3** while the incorporation of the aromatic rings in monomers 5 and 6 causes the monomer to be more rigid, resulting in both higher T_g and T_d of PFCB polymers.



Figure 3. Copolymerization of monomers 2 and 3.

Table 1. Molecular Weight of PFCB Polymer and Copolymer during Solution Polymerization in Mesitylene at 150 °C Monitored by GPC

monomer	polymerization time at 150 °C in mesitylene (h)	M _w	Mn	M _w /M _n
3	30	4959	2567	1.93
2 and 3	16	7922	3263	2.43
(3:2 molar ratio)	19	9402	3717	2.53

Table 2. Thermal Properties of Thermoset PFCBPolymers Achieved by Bulk Polymerization for 0.5 h at250 °C under Nitrogen

polymer from monomer ^a	T_{g} (°C) ^b	<i>Т</i> _d (°С) ^с	polymer from monomer ^a	T_{g} (°C) ^b	<i>Т</i> _d (°С) ^с
2	>350	422	5	116	402
3	93	310	6	115	381
4	137	412			

^{*a*} Bulk polymerization at 250 °C for 0.5 h under nitrogen. ^{*b*} By DSC at 10 °C/min under nitrogen. ^{*c*} By TGA at 10 °C/min under nitrogen.

Thin films were prepared by spin-coating the solution onto a glass substrate after filtering the crude prepolymerized product. The samples were heated for 24 h in a vacuum oven to remove the solvent and then cured to 200, 225, 250, and 300 °C. For the polymer derived from monomer 3, the molecular weight obtained was \sim 5000 with a final polymer concentration of \sim 50 wt % in mesitylene. The resulting solution was spun onto glass substrates at a spread rate of 500 rpm for 3 s and a spin rate of 650 rpm for 15 s. After curing the samples, the thickness of the film was measured to be $\sim 1 \ \mu m$. For the copolymer derived from 2 and 3 (3:2 molar ratio), the molecular weight obtained was $\sim 10\,000$ with a final polymer concentration of \sim 40 wt % in mesitylene. The solution was spun onto glass substrates at a spread rate of 500 rpm for 3 s and a spin rate of 600 rpm for

Table 3. Thermal Properties of Thermoset PFCB Polymerand Copolymer Films Cured at Different Temperaturesfor 0.5 h under Nitrogen.

prepolymer film from monomer ^a	curing temp (°C)	T_{g} (°C) ^b	$T_{\mathrm{d}}(^{\mathrm{o}}\mathrm{C})^{c}$
3	200 225	88 90	276
	250	93	316
2 and 3 (3:2 molar ratio)	200	85	329 306
	225 250	108 139	309 339
	300	170	348

 a Prepared from the polymerization of monomer in mesitylene at 150 °C under nitrogen and spin-coating the prepolymer solution. b By DSC at 10 °C/min under nitrogen. c By TGA at 10 °C/min under nitrogen.

15 s. After curing the samples, the thickness of the film was measured to be $\sim 4 \ \mu m$. Data for the thermal analysis of the films prepared are given in Table 3. The final temperature of curing also affects the $T_{\rm g}$ and $T_{\rm d}$. The T_{g} 's become much higher with curing at higher temperatures because of the telechelic nature of PFCB polymers. For the films from the monomer 3, the higher curing temperature gives T_g data similar to that of the bulk polymerization at the same temperature such as 250 °C. At the lower curing temperatures, the degree of cross-linking of the polymer is relatively small so that the two measurements give lower T_{g} 's than that for the bulk material. It has been shown that cross-linking can enhance the mechanical properties of polymers at high temperatures and increase the $T_{\rm g}$.¹³ However, film coloration was observed at curing temperatures above 250 °C. The films changed from being colorless to having a hint of yellow color possibly due to oxidation or decomposition of the film at higher temperatures.

Solubility of the films cured at different temperatures was also tested (Table 4). The solvents used were cyclopentanone, tetrahydrofuran (THF), and dimethyl-



Figure 4. Tapping mode AFM topographs of surfaces of the copolymer from monomers **2** and **3** (3:2) cured at (A) 225 °C for 0.5 h, RMS = 0.53 nm, and at (B) 250 °C for 0.5 h, RMS = 0.52 nm.

formamide (DMF), which are commonly used in device fabrication. The films cured at 200 °C were found to be slightly soluble in these solvents while the films cured at 225 °C and above exhibited good solvent resistance.

The film samples prepared visually appeared to be uniform and crack-free. Atomic force microscopy (AFM) was employed to study the morphology and surface properties of the materials (Figures 4). The morphology of the spin-coated copolymer film at final curing temperatures of 225 and 250 °C were studied in tapping mode.^{12,13} The RMS surface roughnesses were both small and similar, 0.53 nm at 225 °C and 0.52 nm at 250 °C. The surfaces of the spin-coated films exhibit uniform fractal morphology, which is characteristic for glassy polymers.¹⁴ AFM images obtained show that the films are fairly uniform, and no phase separation is observed.



Figure 5. Optical loss spectra of the copolymer from monomers **2** and **3** (3:2 molar ratio) at the final curing temperature of (A) 200 °C and (B) 225 °C for 0.5 h measured by PDS with \sim 1 wt % DR-1 dopant.

Optical loss measurements were obtained using the photothermal deflection spectroscopy (PDS)¹⁵ for the copolymer derived from the monomers of 2 and 3 (3:2) at the final curing temperatures of 200 and 225 °C. To measure the optical loss, these films were doped with ~ 1 wt % DR-1 for the PDS calibration because the prepared films of polymer itself were colorless and transparent. Thus, the intrinsic optical loss of the polymers should be lower than that obtained from the spectrum. From the spectra (Figure 5), the optical losses for the copolymer cured at 200 °C were measured to be 0.30 dB/cm at 1310 nm and 0.45 B/cm at 1550 nm. The copolymer cured at 225 °C also gave similar results with losses of 0.35 dB/cm at 1310 nm and 0.47 dB/cm at 1550 nm. The refractive index of the copolymer can be tuned through different ratios of the rigid aromatic monomer 2 and the highly fluorinated monomer 3. Although the siloxane linkages in the polymers containing monomers 3-6 are susceptible to hydrolysis, however, the high fluorination in these monomers significantly decreases the moisture sensitivity of the resulting polymers.

 Table 4. Solubility of Thermoset PFCB Polymers and Copolymers Cured at Different Temperatures for 0.5 h under Nitrogen

polymer film from monomer	final curing temp (°C)	color of film	cyclopentanone	THF	DMF
3	200	colorless	soluble	soluble	soluble
	225	colorless	insoluble	insoluble	insoluble
	250	slightly yellow	insoluble	insoluble	insoluble
	300	yellow	insoluble	insoluble	insoluble
2 and 3 (3:2)	200	colorless	insoluble	soluble	soluble
	225	colorless	insoluble	insoluble	insoluble
	250	slightly yellow	insoluble	insoluble	insoluble
	300	yellow	insoluble	insoluble	insoluble

Conclusion

A series of highly fluorinated trifluorovinyl ether containing monomers and PFCB polymers with siloxane linkages were synthesized and characterized. Through the copolymerization between a monomer with highly fluorinated and flexible alkyl chains and a more rigid comonomer, its thermal properties can be fine-tuned by varying the composition as well as the final curing temperature of the films. The copolymer exhibited good adhesion on substrates, and thick, homogeneous, "crackfree" films with good solvent resistance were attainable. Optical loss measurements of these films (with 1% dopant for calibration) using PDS show very low optical loss (0.30 dB/cm at 1310 nm and 0.45 dB/cm at 1550 nm) which demonstrates their suitability for the fabrication of low optical loss waveguides.

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