Facile One-Pot Synthesis and Thermal Cyclopolymerization of Aryl Bistrifluorovinyl Ether Monomers Bearing Reactive Pendant Groups

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ABSTRACT: A diverse pool of aryl bistrifluorovinyl ether (BTFVE) compounds with reactive pendant groups were prepared in a facile, high yielding three step "one-pot" synthesis from commercial 4-bromo(trifluorovinyloxy)benzene. Monomers were confirmed from ATR–FTIR, ^{1}H, ^{13}C, and ^{19}F NMR, and HRMS analysis. Aryl BTFVE compounds were thermally polymerized to afford perfluorocyclobutyl (PFCB) aryl ether polymers with high number–average molecular weight (M_n) for homopolymers (17,050–27,090) and copolymers with 4,4′-bis(trifluorovinyloxy)-biphenyl monomers (27,860–56,500). The PFCB aryl ether homo- and copolymers collectively possess high thermal stability (>299 °C in N_2) and are readily solution processable producing optically transparent films. The thermal polymerization was achieved and reactive moieties remained intact, aside from those functionalized with acrylates. In the case with acrylate functionalized polymers, orthogonal polymerization was achieved by first photopolymerizing the acrylates followed by thermal curing of the aryl trifluorovinyl ether endgroups. Preliminary results in this study produced the successful preparation of photodefinable PFCB aryl ether material. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1887–1893, 2010

KEYWORDS: aryl trifluorovinyl ethers; fluoropolymers; lithography; PFCB aryl ether polymers; polyethers

INTRODUCTION The introduction of fluorine in polymers continues to be important in the development of advanced materials exhibiting high thermal and thermo-oxidative stability, chemical resistance, and superior electrical insulating ability.[1] Perfluorocyclobutyl (PFCB) aryl ether polymers are a unique and versatile class of partially fluorinated linear and network polymers used for photonics,[2–6] electro-optics,[5,7,8] proton exchange membranes,[9,10] hybrid composites,[11–14] atomic oxygen (AO) resistance,[15,16] and liquid crystalline materials.[17,18] Consolidated reviews on PFCB aryl ether polymers have been recently reported.[19,20] Most notably, PFCB aryl ether polymers retain many desired properties of fluoropolymers, including low optical attenuation and high thermal performance, while offering many advantages, such as highly tailorable refractive index for the core and cladding, and excellent solution and melt processibility.[2] PFCB aryl ether polymers are traditionally prepared from the thermal [2+2] cyclopolymerization of the aryl trifluorovinyl ether (TFVE) monomers without the need for a catalyst or initiator, resulting in conversions in nearly quantitative yield.[21] The kinetics of the step-growth cycloaddition polymerization has been reported using Raman spectroscopy[22] and, more recently, evidence for the biradical intermediate has been identified by electron paramagnetic resonance (EPR) spectroscopy.[23]

Traditionally, aryl TFVE containing monomers are prepared in two steps starting from phenolic precursor via alkylation with 1,2-dibromotetrafluoroethane ($BrCF_2CF_2Br$), followed by zinc-mediated dehalogenation. This was established by Babb et al.[21] at The Dow Chemical Company who first reported the synthesis of 3-trifluorovinyloxy-α,α,α-trifluorotoluene, 1,3-bis(trifluorovinyloxy)benzene, 4,4′-bis(trifluorovinyloxy)biphenyl and 1,1,1-(trifluorovinyloxyphenyl)ethane from phenolic feedstocks.

There are limited commercial phenolic precursors available in order to produce a functionally diverse pool of aryl TFVE ether monomers. Therefore, a methodology was established by Neilson and Smith et al.[19,24] that utilized 4-bromo(trifluorovinyloxy)benzene, now commercially available, for the preparation of diverse aryl TFVE monomers tailored for

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specific material applications. By employing halogen–metal exchange, the Grignard (or lithiated) of 4-(trifluorovinyloxy)-benzene can be reacted with a collection of electrophiles installing carboxylic acid, acyl chloride, aldehyde, alcohol, and amine groups in very good yields with retention of the fluoroolefin.[25] Furthermore, it has been shown 4-bromo(trifluorovinyloxy)benzene is also tolerant to Suzuki cross-coupling conditions affording terphenyl,[17] 4,6-disubstituted pyrimidines,[26] and hexa-*peri*-hexabenzocoronene monomers.[3] Therefore, this methodology has become general utility for the modular preparation of a vast pool of monomers tailored for specific applications.

Kuo and Liu[27] reported the one-pot preparation of tertiary alkyl carboxylates and sulfonates from ketones. The aryl lithium reagent was initially added to the carbonyl compound; without quenching the lithium alkoxide to give the tertiary alcohol, the desired tertiary carboxylate ester was prepared by adding the acyl chloride *in situ*. This one-pot procedure is remarkable from an industrial point of view: it is simple and efficient, affording an overall yield considerably higher than those obtained from a traditional two-step process. We initially attempted to repeat this procedure by trapping methyl acetate with a solution of 4-lithium(trifluorovinyloxy)benzene, yielding the tertiary alcohol. However, this tertiary alcohol was not stable and rapidly dehydrated. Realizing the potential utility of an analogous alcohol monomer, we began a study to synthesize the trifluoromethyl (—CF_3) analog, which was predicted to be stable against dehydration. The Grignard reagent, rather than a lithium reagent, derived from the commercial 4-bromo(trifluorovinyloxy)benzene was successfully prepared and quenched with methyl trifluoroacetate. On the basis of these results, we have developed a new three-step "one-pot" synthetic procedure for the synthesis of new aryl bistrifluorovinyl ether (BTFVE) derivatives with reactive pendant moieties. This one-pot process is operationally simple, high yielding, and tolerant to functionally diverse electrophiles affording a new series of aryl BTFVE derivatives. Their synthesis, characterization, and thermal cyclopolymerization to PFCB aryl ether polymers are discussed.

EXPERIMENTAL

Materials and Methods

Chemicals and solvents used were purchased from Sigma Aldrich or Alfa Aesar and used without purification unless otherwise stated. 4-Bromo(trifluorovinyloxy)benzene and 4,4′-bis(4-trifluorovinyloxy)biphenyl (**BP**) were donated by Tetramer Technologies, L.L.C. (Pendleton, SC) and are available commercially through Oakwood Chemicals, Inc. (Columbia, SC). The following acyl chlorides were used to prepare monomers **M1**–**M5**: acryloyl chloride (**M1**), methacryloyl chloride (**M2**), cyclopropanecarbonyl chloride (**M3**), cyclobutanecarbonyl chloride (**M4**), and 6-bromohexanoyl chloride (**M5**). HPLC grade THF was dried and deoxygenated using a Pure-Solv solvent purification system from Innovative Technologies. All glassware was flame dried and allowed to cool in a desiccator prior to use. All reagent manipulations were performed in nitrogen.

Instrumentation

Column chromatography was performed using Sorbent Silicagel (230–450 mesh, Sorbent Technologies). Thin layer chromatography (TLC) was carried out on polyester support plates coated with silica gel 60F254 (Aldrich). Visualization was achieved using a UV lamp. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a JEOL Eclipse+ 300 and chemical shifts were recorded in ppm (δ) with reference to internal tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C, and ^{19}F NMR, respectively. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of neat samples was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a diamond ATR attachment. High resolution mass spectrometry (HRMS) data were obtained at the University of Illinois Mass Spectrometry Laboratory (Urbana-Champaign, IL) on a Micromass Q-TOF Ultima Mass spectrometer using electrospray ionization (ESI) in positive mode as the source. Differential scanning calorimetry (DSC) analysis was performed on a TA Q1000 instrument in nitrogen at a heating rate of 10 °C/min up to 200 °C. The glass transition temperature (T_g) was obtained from a second heating cycle using TA Universal Analysis 2000 software suite. Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo 851 instrument in nitrogen at a heating rate of 10 °C/min up to 800 °C. Gel permeation chromatography (GPC) data were collected in $CHCl_3$ from a Waters 2690 Alliance System with photodiode array detection. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. Molecular weights were obtained using polystyrene as a standard (Polymer Labs Easical PS-2).

General Procedure for Synthesis of Monomers (M1–M5)

To a flame dried 100-mL three-neck round bottom flask fitted with a condenser and a nitrogen inlet side-neck, were added magnesium (1.2 g, 48 mmol) and freshly distilled THF (50 mL). A small crystal of I_2 and a few drops of 4-bromo(trifluorovinyloxy)benzene were added and the reaction was carefully spot heated (heat gun) to initiate the Grignard reaction. After initiation, the remaining 4-bromo(trifluorovinyloxy)benzene (10.12 g, 40 mmol) was added drop wise over 15 min to maintain reflux, followed by reflux for additional 2 h, and then cooled to 0 °C. Methyltrifluoroacetate (1.34 mL, 13.3 mmol) was added drop wise at 0 °C over 10 min and then slowly warmed to 50 °C for another 1 h. The reaction mixture was then cooled to 0 °C and appropriate acyl chloride (40 mmol) was added drop wise over a period of 30 min. The reaction mixture was warmed slowly to room temperature and stirred for 24 h. The organic products were extracted into CH_2Cl_2 (50 mL), washed with DI H_2O (2 × 50 mL), dried over anhydrous $MgSO_4$, and vacuum filtered. After rotary evaporation, the crude oil was purified by column chromatography on silica gel using 100% hexanes, then 80% hexanes–20% CH_2Cl_2 (v/v) for elution (R_f typically 0.3). NOTE: For the acrylate containing monomers (M1 and M2), solvent evaporation was conducted below 40 °C and the

glass reaction vessels were covered with Al foil to avoid thermal and UV initiated polymerization.

1,1-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-2,2,2-trifluoroethyl Acrylate (M1)

M1 was obtained as a pale yellow oil in 65% yield. ATR–FTIR (neat) υ 3024, 1830, 1753, 1630, 1606, 1508, 1314, 1165, 827; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.48 (d, J = 8.9 Hz, 4H), 7.14–7.11 (d, J = 8.9 Hz, 4H), 6.52–6.46 (d, 1H, —C*H*=CH_2), 6.28–6.19 (d, 1H, *trans*-CH=C*H*$_2$), 5.98–5.95 (d, 1H, *cis*-CH=C*H*$_2$); ^{19}F NMR (283 MHz, $CDCl_3$) δ −71.2 (s, —C*F*$_3$, 3F), −119.0 (dd, *cis*-CF=C*F*$_2$, 2F, F_a), −125.5 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.2 (dd, —C*F*=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 111.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.5, 155.4, 146.9 (td, —CF=C*F*$_2$, ^1J = 274.0, ^2J = 66.5 Hz), 133.1 (dt, —*C*F=CF_2, ^1J = 257.3 Hz, ^2J = 47.2 Hz), 133.0, 131.7, 130.5, 128.1, 125.9, 122.1, 115.5, 85.3 (q, J = 28.9 Hz, —*C*F$_3$); HRMS (ESI–TOF) (*m/z*) $[M + Na]^+$ calcd. for $C_{21}H_{11}O_4F_9$, 521.0411; found, 521.042.

1,1-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-2,2,2-trifluoroethyl Methacrylate (M2)

M2 was obtained as a pale yellow oil in 60% yield. ATR–FTIR (neat) υ 3024, 1832, 1753, 1636, 1610, 1508, 1315, 1165, 827; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.47 (d, J = 8.9 Hz, 4H), 7.14–7.11 (d, J = 8.9 Hz, 4H), 6.28 (s, *cis*-CH=C*H*$_2$, 1H), 5.73 (s, *trans*-CH=C*H*$_2$, 1H), 1.98 (s, —C(C*H*$_3$)=CH_2, 3H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −71.2 (s, —C*F*$_3$, 3F), −119.0 (dd, *cis*-CF=C*F*$_2$, 2F, F_a), −125.6 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, —*C*F=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 163.7, 155.4, 146.7, (td, —CF=C*F*$_2$, ^1J = 274.0, ^2J = 66.5 Hz), 136.2, 133.7 (dt, —*C*F=CF_2, ^1J = 257.3 Hz, ^2J = 47.2 Hz), 131.8, 130.5, 127.5, 126.0, 122.1, 115.5, 85.3 (q, J = 28.9 Hz, —*C*F$_3$); GC–EIMS (70 eV) *m/z* (% relative intensity) 512 (15, M^+), 427 (30), 232 (30), 183 (35), 183 (35), 104 (10), 69 (100).

1,1-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-2,2,2-trifluoroethyl Cyclopropanecarboxylate (M3)

M3 was obtained as a pale yellow oil in 50% yield. ATR–FTIR (neat): υ 3043, 2930, 1830, 1753, 1606, 1510, 1313, 1165, 827; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.44 (d, J = 8.9 Hz, 4H), 7.14–7.11 (d, J = 8.9 Hz, 4H), 1.82–1.77 (m, 1H, —C*H*—), 1.04–0.93 (m, 4H, —C*H*$_2$—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −71.20 (s, —CF_3, 3F), −119.0 (dd, *cis*-CF=C*F*$_2$, 2F, F_a), −125.6 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, —C*F*=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.1, 155.3, 147.3 (unresolved splitting of —CF=C*F*$_2$), 132.1, 130.4, 126.0, 122.0, 115.4, 84.5 (unresolved splitting of —C*F*$_3$), 13.8, 9.0; HRMS (ESI–TOF) (*m/z*) $[M + Na]^+$ calcd. for $C_{22}H_{13}O_4F_9$, 535.0568; found, 535.0594.

1,1-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-2,2,2-trifluoroethyl Cyclobutanecarboxylate (M4)

M4 was obtained as a pale yellow oil in 51% yield. ATR–FTIR (neat) υ 3043, 2958, 1832, 1762, 1608, 1508, 1314, 1165, 830; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.43 (d, J = 8.6 Hz, 4H), 7.13–7.10 (d, J = 8.6 Hz, 4H), 3.35–3.30 (m, 1H, —C*H*—), 2.32–2.25 (m, 4H, —C*H*$_2$—), 2.10–2.00 (m, 2H, —C*H*$_2$—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.9 (s, —C*F*$_3$, 3F), −119.0 (dd, *cis*-CF=C*F*$_2$, 2F, F_a), −125.6 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, —C*F*=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 155.3, 147.0 (td, —CF=C*F*$_2$, ^1J = 274.0, ^2J = 66.5 Hz), 133.5 (dt, —*C*F=CF_2, ^1J = 257.3 Hz, ^2J = 47.2 Hz), 132.4, 130.3, 126.0, 122.1, 115.5, 84.3 (q, J = 28.9 Hz, —*C*F$_3$), 38.7, 25.0, 18.4; HRMS (ESI–TOF) (*m/z*) $[M + Na]^+$ calcd. for $C_{23}H_{15}O_4F_9$, 549.0724; found, 549.0750.

[1,1-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-2,2,2-trifluoroethyl]-6-bromohexanoate (M5)

M5 was obtained as a pale yellow oil in 45% yield. ATR–FTIR (neat) υ 3043, 2958, 2930, 1830, 1768, 1610, 1508, 1314, 1165, 828; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.48 (d, J = 8.9 Hz, 4H), 7.14–7.11 (d, J = 8.9 Hz, 4H), 3.39 (t, J = 6.5 Hz, 2H, —C*H*$_2$Br), 2.51 (t, J = 7.2 Hz, 2H, —COC*H*$_2$—), 1.88–1.83 (m, 2H, —C*H*$_2$—), 1.60–1.55 (m, 2H, —C*H*$_2$—), 1.40–1.38 (m, 2H, —C*H*$_2$—); ^{19}F NMR (282.8 MHz, $CDCl_3$) δ −70.9 (s, —C*F*$_3$, 3F), −119.0 (dd, *cis*-CF=C*F*$_2$, 2F, F_a), −125.5 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, —C*F*=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.7, 155.3, 147.6 (td, —CF=C*F*$_2$, ^1J = 274.0, ^2J = 66.5 Hz), 133.5 (dt, —*C*F=CF_2, ^1J = 257.3 Hz, ^2J = 47.2 Hz), 132.2, 130.4, 125.9, 122.1, 115.5, 84.6 (q, J = 28.9 Hz, —*C*F$_3$), 34.9, 33.3, 32.4, 27.5, 23.9; HRMS (ESI–TOF) (*m/z*) $[M + Na]^+$ calcd. for $C_{24}H_{18}O_4F_9Br$, 643.0142; found, 643.0157.

General Polymerization and Copolymerization Procedure

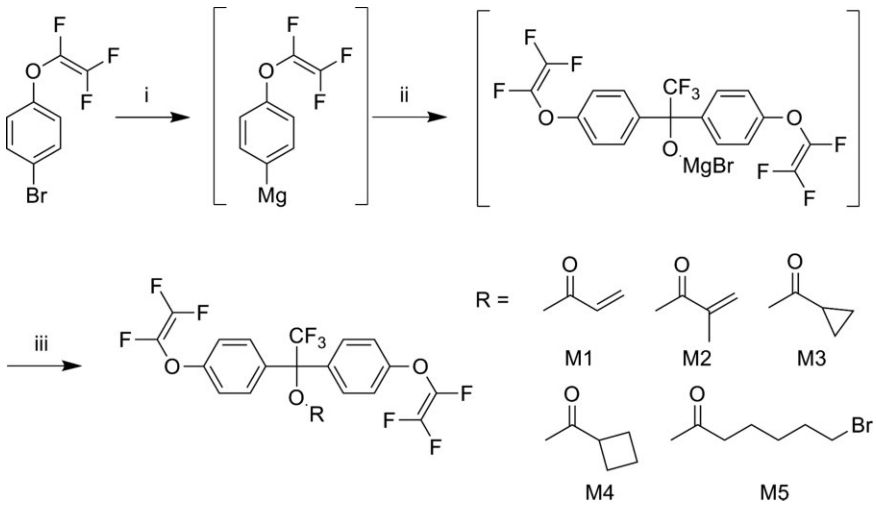
Specified amounts of monomers were charged in a glass ampoule previously flame-dried under vacuum. The ampoule was vacuum sealed and then placed in a sand bath preheated to 165 °C or 175 °C for 48 h. After cooling to room temperature, the ampoule was then cracked and the crude solid was dissolved into a minimum amount of THF and then precipitated into a large excess of methanol, vacuum filtered, washed liberally with MeOH, and dried in a vacuum oven at 60 °C for 24 h.

PFCB Aryl Ether Polymer (P3)

ATR–FTIR (neat) υ 3020, 1755, 1610, 1508, 1217, 955; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.38 (m, 4H), 7.06–7.04 (d, J = 8.3 Hz, 2H), 7.19–7.17 (d, J = 8.3 Hz, 2H), 1.78–1.73 (m, 1H, —C*H*—), 0.96–0.90 (m, 4H, —CH_2CH_2—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −71.2 (s, —C*F*$_3$, 3F), −119.0 (dd, residual *cis*-CF=C*F*$_2$, 2F, F_a), −125.5 (dd, *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, residual —C*F*=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.3–(−132.7) (m, cyclobutyl-F_6).

PFCB Aryl Ether Polymer (P4)

ATR–FTIR (neat) υ 3020, 1750, 1608, 1508, 1217, 957; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.38 (m, 4H), 7.06–7.04 (d, J = 6.9 Hz, 2H), 7.19–7.16 (d, J = 8.6 Hz, 2H), 3.29–3.26 (m, 1H, —C*H*—), 2.26–2.21 (m, 4H, —C*H*$_2$—), 1.98–1.85 (m, 2H, —C*H*$_2$—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.80 (s, —C*F*$_3$, 3F), −118.9 (dd, residual *cis*-CF=C*F*$_2$, 2F, F_a), −125.6 (dd, residual *trans*-CF=C*F*$_2$, 2F, F_b), −134.1 (dd, residual —C*F*=CF_2,



SCHEME 1 One-pot synthesis of aryl bis-trifluorovinyl ether (BTFVE) monomers. Reagents and chemicals: (i) Mg/THF; (ii) CF_3COOCH_3, 0–50 °C, 1 h; (iii) RCOCl, 0 °C, r.t., 24 h.

2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.3–(−132.7) (m, cyclobutyl-F_6).

PFCB Aryl Ether Polymer (P5)

ATR–FTIR (neat) υ 3043, 2958, 1763, 1608, 1508, 1217, 955; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.37 (m, 4H), 7.20–7.17 (d, J = 7.9 Hz, 2H), 7.08–7.05 (d, J = 8.3 Hz, 2H), 3.35 (t, J = 6.5 Hz, 2H, —CH_2Br), 2.46 (t, J = 7.2 Hz, 2H, —COCH_2—), 1.84–1.80 (m, 2H, —CH_2—), 1.64–1.60 (m, 2H, —CH_2—), 1.46–1.43 (m, 2H, —CH_2—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.84 (s, —CF_3, 3F), −119.0 (dd, residual *cis*-CF=CF_2, 2F, F_a), −125.4 (dd, residual *trans*-CF=CF_2, 2F, F_b), −134.1 (dd, residual —CF=CF$_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.2–(−132.7) (m, cyclobutyl-F_6).

PFCB Aryl Ether Copolymer P(3-co-BP)

ATR-FTIR (neat): υ 3043, 2958, 1762, 1608, 1508, 1217, 957; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.38 (m), 7.06–7.04 (m), 7.19–7.17 (m), 1.78–1.73 (m, 1H, —CH—), 0.96–0.90 (m, 4H, —CH_2CH_2—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.7 (s, —CF_3, 3F), −119.2 (dd, residual *cis*-CF=CF_2, 2F, F_a), −125.7 (dd, residual *trans*-CF=CF_2, 2F, F_b), −134.2 (dd, residual —CF=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.1–(−132.5) (m, cyclobutyl-F_6).

PFCB Aryl Ether Copolymer P(4-co-BP)

ATR–FTIR (neat): υ 3043, 2958, 1766, 1608, 1508, 955; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.38 (m), 7.06–7.04 (m), 7.19–7.16 (m), 3.29–3.26 (m, 1H, —CH—), 2.26–2.21 (m, 4H, —CH_2—), 1.98–1.85 (m, 2H, —CH_2—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.9 (s, —CF_3, 3F), −119.0 (dd, residual *cis*-CF=CF_2, 2F, F_a), −125.5 (dd, residual *trans*-CF=CF_2, 2F, F_b), −134.1 (dd, residual —CF=CF$_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.3–(−133.7) (m, cyclobutyl-F_6).

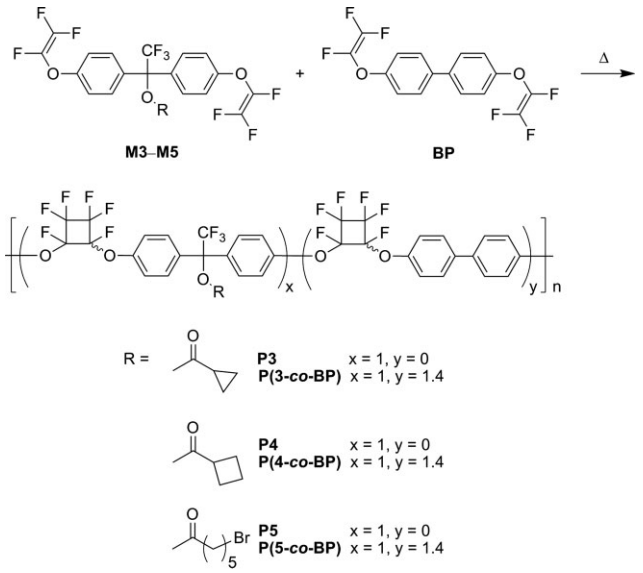
PFCB Aryl Ether Copolymer P(5-co-BP)

ATR–FTIR (neat): υ 3043, 2958, 1750, 1608, 1508, 1217, 956; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.45 (m), 7.14–7.11 (m), 3.42–3.37 (m, 2H, —CH_2Br), 2.53–2.49 (m, 2H, —COCH_2—), 1.88–1.83 (m, 2H, —CH_2—), 1.60–1.55 (m, 2H, —CH_2—), 1.40–1.38 (m, 2H, —CH_2—); ^{19}F NMR (283 MHz, $CDCl_3$) δ −70.9 (s, —CF_3, 3F), −119.0 (dd, residual *cis*-CF=CF_2, 2F, F_a), −125.5 (dd, residual *trans*-CF=CF_2, 2F, F_b), −134.1 (dd, residual —CF=CF$_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), −127.3–(−132.7) (m, cyclobutyl-F_6).

RESULTS AND DISCUSSION

Aryl BTFVE compounds **M1**–**M5** were synthesized from a three-step "one-pot" procedure as shown in Scheme 1. The sequence protocol followed (i) preparation of Grignard reagent using 4-bromo(trifluorovinyloxy)benzene, (ii) quenching with methyltrifluoroacetate, and (iii) addition of acyl chloride to the Grignard adduct. This yielded pendent BTFVE compounds **M1**–**M5** in nearly quantitative yield based on conversion using ^{19}F NMR analysis (*vide infra*). Pendant groups installed on the monomers include reactive acrylates (**M1** and **M2**), strained cycloalkanes (**M3** and **M4**), and 1-bromoalkane (**M5**). Overall isolated yield of pure products using column chromatography were moderate to good (45–65%). Elucidation of all compounds was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR, ATR–FTIR, and HRMS.

Characteristic ^{1}H, ^{13}C, and ^{19}F NMR peak shifts and splitting patterns of compounds **M1**–**M5** agreed with the reported structures; this data is available in the Supporting Information. From proton NMR spectra, the aromatic regions demonstrate ABA′B′ system peaks characteristic of the 1,4-benzene rings (J = 8.9 Hz). The other proton peaks agree with pendent groups attached to the carbon linkage via the carboxyl ester. For ^{13}C NMR, peak shifts at ca. 170.0 ppm support the successful introduction of the carbonyl group (C=O) of the ester bond. The singlet at −71.0 ppm in the ^{19}F NMR spectra attributed to the —CF_3 group attached to the carbon linkage between the two benzene rings. The yield of the pendent products was determined using this characteristic peak by ^{19}F NMR, as its chemical shift was different from the tertiary alcohol compound and methyltrifluoroacetate with diagnostic peaks at −74.4 and −74.0 ppm, respectively (*vide supra*). The aryl trifluorovinyl functional groups produce a



SCHEME 2 Thermal [2+2] cyclopolymerization of BTFVE monomers **M3–M5** producing PFCB aryl ether homopolymers **P3–P5** and copolymers (**P(3-*co*-BP)**-**P(5-*co*-BP)**).

characteristic AMX pattern at −119, −125, and −132 ppm (J_{AM} = 59.2 Hz, J_{MX} = 95.4 Hz, J_{AX} = 108.5 Hz). Furthermore, the molecular formula of all monomers was confirmed from HRMS.

Attempts to install more sterically hindered substrates such as 2,3,4,5,6-perfluorobenzene-carbonyl-, carbazole-9-carbonyl-, fluorene-9-carbonyl-, or benzyl group via the three-step "one pot" methodology was unsuccessful. Addition of the corresponding acyl chlorides and upon aqueous work-up only afforded the tertiary alcohol compound in quantitative yield. These results were confirmed by ^{19}F NMR that only showed the exclusive formation of the single peak at

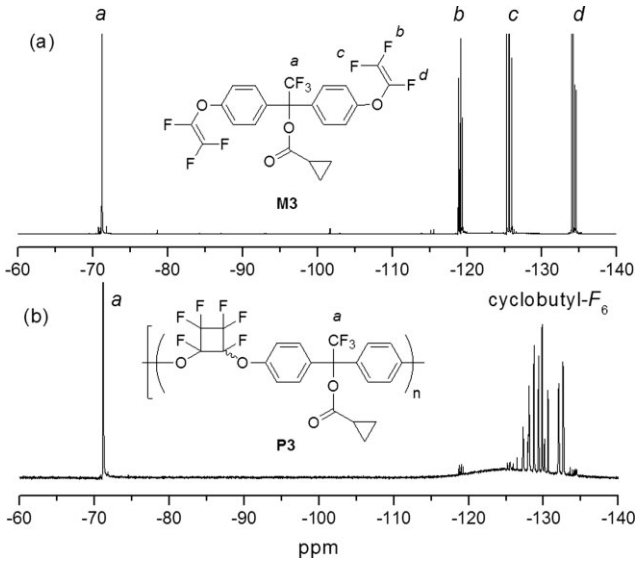


FIGURE 1 ^{19}F NMR overlay of (a) BTFVE monomer **M3** conversion to (b) PFCB aryl ether homopolymer **P3** in $CDCl_3$.

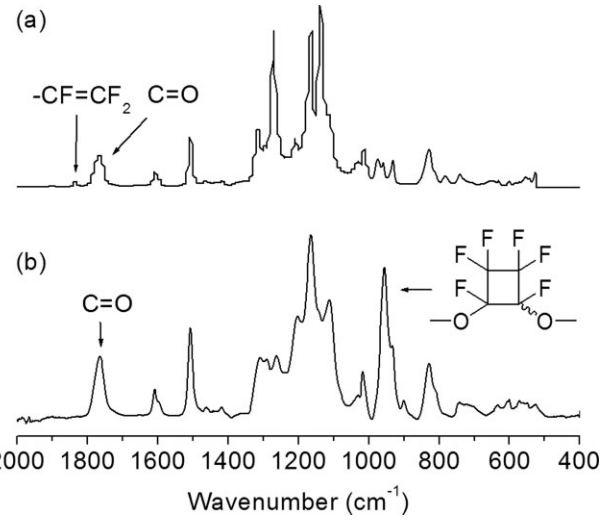


FIGURE 2 ATR–FTIR (neat) overlay of (a) BTFVE monomer **M3** conversion to (b) PFCB aryl ether homopolymer **P3**.

approximately −74.0 ppm for all substrates that corresponded to the —CF_3 moiety of the tertiary alcohol compound. The formation of this trace peak (<3–5%) appeared at about −71.0 ppm. Furthermore, isolation of this minor product by column chromatography proved difficult and its

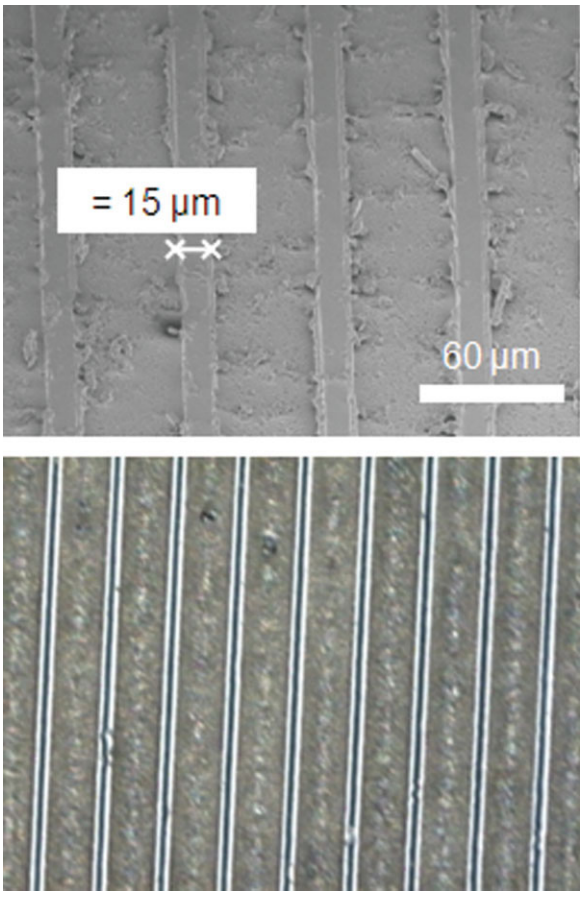


FIGURE 3 SEM (top) and optical microscope (bottom) images of grating structure fabrication by direct photolithography of **M1**.

TABLE 1 Selected Properties of PFCB Aryl Ether Homopolymers and Copolymers

Polymer	Molar Feed Ratio 3–5:BP	Calculated Composition[a]	M_n (PDI)[b]	T_g (°C)[c]	T_d (°C)[d]
P3[e]	1:0	1:0	17,050 (1.85)	108	397
P4[e]	1:0	1:0	27,090 (1.95)	108	363
P5[e]	1:0	1:0	12,700 (2.85)	58	299
P(3-*co*-BP)[f]	1:1.4	1:1.3	56,100 (2.75)	86	387
P(4-*co*-BP)[f]	1:1.4	1:1.38	56,500 (2.36)	90	372
P(5-*co*-BP)[f]	1:1.4	1:1.6	27,860 (2.82)	64	302

[a] Based on ^{1}H NMR integration.
[b] GPC in $CHCl_3$ using polystyrene as standard.
[c] DSC (10 °C/min) in nitrogen determined by second heating cycle.
[d] TGA onset (10 °C/min) of chain extended polymers in nitrogen.
[e] 165 °C for 48 h.
[f] 175 °C for 48 h.

identity remains unclear. Therefore, we attribute the inability to introduce these electrophiles is possibly due to their highly hindered structure in addition to the less reactive Grignard adduct.[28]

Aryl BTFVE monomers (**M3**–**M5**) were then thermally homopolymerized in bulk at 165 °C for 48 h to afford high molecular weight PFCB aryl ether polymers (**P3**–**P5**) (Scheme 2). Homopolymerization in excess of 180 °C at extended reactions times greater than 24 h produced insoluble gels. On the other hand, the aryl BTFVE monomers were also copolymerized at 175 °C with 4,4′-bis(4-trifluorovinyloxy)biphenyl (**BP**) to afford the respective PFCB aryl ether copolymers **P(3-*co*-BP)**–**P(5-*co*-BP)**. The linear cyclopolymerization was monitored by ^{19}F NMR and ATR–FTIR spectroscopy. ^{19}F NMR showed the quantitative conversion of the aryl trifluorovinyl ether AMX pattern to the PFCB aryl ether ring multiplets (Figure 1). The multiplet for the PFCB aryl ether ring afforded predominately head-to-head formation of stereorandom isomers.[21,29] Also, the polymerization was followed by ATR–FTIR as shown in Figure 2. The overlay clearly shows the disappearance of the fluoroolefin stretch at about 1830 cm^{-1} and formation of the characteristic PFCB aryl ether breathing mode vibration at 960 cm^{-1}. Both ^{1}H and ^{19}F NMR and ATR–FTIR indicated the conversion to PFCB aryl ether polymers or copolymers with functional groups intact.

The direct polymerization of acrylate-containing monomers (**M1** and **M2**) or even copolymerization with 4,4′-bis(trifluorovinyloxy)biphenyl (**BP**) was unsuccessful. Even polymerizations at lower temperatures (150 °C) produced insoluble material indicating the possibility of a network structure. DSC analysis showed monomers **M1** and **M2** displayed two discrete exothermic peaks at 110 °C and 150 °C which may be attributed to the thermal activation of the acrylate group (—CH=CH_2) and fluoroolefin (—CF=CF_2), respectively (see Supporting Information, Figure S9). It is well known that aryl TFVEs, in general, do not appreciably undergo high molecular weight polymerization through free radical initiation.[30,31]

Another strategy was considered by first initiating side-chain acrylate polymerization of monomers **M1** (or **M2**) followed by post-PFCB aryl ether polymerization. An analogous strategy has been reported by others for the preparation of PFCB aryl ether polymers in concomitant atom transfer radical polymerization (ATRP).[32,33] In the present study, liquid monomer **M1** was used to initially prepare photodefinable materials. Preliminary studies showed **M2** undergoes bulk photopolymerization to produce insoluble polymers that where shown to swell in $CHCl_3$ and toluene. Photodefinable core layers were then prepared using a liquid, bulk mixture of monomer **M1** and 3 wt % 2,2-diethoxyacetophenone (DEAP) as the photoinitiator. A spin cast film on a Si wafer was exposed to an UV light (λ = 365 nm, 5.8 mJ/s) through the photomask for 200 s. The pattern was finally developed by washing off the unreacted monomer with hexanes. The resulting pattern was postcured at 90 °C for 2 h and at 200 °C for 2 h. The final pattern structures are shown in Figure 3. The grating has a width of 15 μm and spacing of 40 μm. This preliminary study showed the successful preparation of photodefinable PFCB aryl ether material utilizing acrylate functionality. Future work to optimize the system is ongoing.

Table 1 shows selected physical properties of PFCB aryl ether homopolymers (**P3**–**P5**) and copolymers (**P(3-*co*-BP)**–**P(5-*co*-BP)**). The linear, step-growth polymers and copolymers were produced in moderate to high number-average molecular weight (M_n) each with a narrow polydispersity index (PDI). The resulting polymers are solution processable in common organic solvents (e.g., $CHCl_3$, THF, and acetone) to produce optically transparent, free-standing films. The nature of the stereorandom PFCB aryl ether polymer afforded entirely amorphous polymers with glass transition temperatures (T_g) ranging 58–108 °C. Copolymerization with **BP** showed significantly lower T_g's compared with the homopolymers. The introduction of pendant functional groups did not appear to jeopardize the thermal stability of the polymers as the thermal decomposition at onset (T_d) in nitrogen is comparable to typical PFCB aryl ether polymer systems.

CONCLUSIONS

We prepared five functionally diverse aryl BTFVE monomers with reactive pendant moieties by way of a simple, facile three step "one-pot" procedure in moderate to good isolated yields. These monomers underwent bulk homo- and copolymerization to afford high molecular weight, thermally robust PFCB aryl ether polymers. The ability to solution process these polymers into transparent, free-standing films makes them attractive for a multitude of patterning and optical applications. In particularly, pendant acrylate aryl BTFVE

monomers can be used in photolithography templating followed by thermal curing producing PFCB aryl ether crosslinked networks. Furthermore, pendant cycloalkanes and the 1-bromoalkane PFCB aryl ether polymers are anticipated to undergo postfunctionalization by nucleophilic substitution. This strategy is the focus of our continued work.

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