Synthesis and Characterization of Phenylphosphine Oxide Containing Perfluorocyclobutyl Aromatic Ether Polymers for Potential Space Applications

Jianyong Jin,[†] Dennis W. Smith, Jr.,*[,†] Chris M. Topping,[†] S. Suresh,[†] Shengrong Chen,[†,‡] Stephen H. Foulger,[§] Norman Rice,[||] Jon Nebo,[||] and Bob H. Mojazza[||]

Department of Chemistry, School of Materials Science and Engineering, and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, South Carolina 29634-0973, and Triton Systems Inc., 200 Turnpike Road, Chelmsford, Massachusetts 01824

Received August 21, 2003; Revised Manuscript Received October 4, 2003

ABSTRACT: A novel class of phenylphosphine oxide (PPO) containing perfluorocyclobutyl (PFCB) polymers has been developed for potential use as multifunctional materials in space environments. The reaction of *p*-BrArOCF=CF$_2$ (for Ar = phenyl and biphenyl) with *tert*-butyllithium affords the lithium reagent smoothly below −20 °C. Subsequent substitution with phenylphosphonic dichloride provides the first bis(trifluorovinyl ether) monomers containing the PPO group. Polymerization proceeds thermally above 150 °C to give polymers that exhibit glass transition temperatures of 169 and 224 °C, respectively, and catastrophic weight loss by TGA in N$_2$ and air above 450 °C (10 °C/min). Copolymerization with bis(4,4′-trifluorovinyloxy)biphenyl affords film-forming transparent thermoplastic copolymers with high T_g (>140 °C) and good thermal stability (>450 °C). Initial evaluations with ground-based simulation of atomic oxygen (AO) rich space environments indicate that the PPO group imparts significant space durability to PFCB polymers.

Introduction

Polymers containing the phenylphosphine oxide (PPO) group have been studied extensively for a number of applications in recent years. McGrath et al. reported the synthesis and flame-retardant properties of aromatic polyphosphonates and arylene ether phenylphosphine oxide containing polymers.[1−5] McGrath[6,7] and Cabasso[8] further studied the metal complexation of phosphorus containing polymers. Polymers containing the PPO group are also known to exhibit excellent adhesion properties to metal substrates[9,10]and miscibility with many thermoplastic and thermosetting polymers. Due to the noncoplanar structure of triarylphosphine oxide and the intensely polar P=O bond, polymers containing the PPO group are usually amorphous[2] and provide low birefringence[10] and high refractive index.[1] The incorporation of the triarylphosphine oxide moiety has brought about an increase in solubility of polyamides and polyimides in common organic solvents.[11,12] In addition, nonlinear optical properties of polymers bearing pendent phosphine oxide group chromophores have also been studied due to the excellent electron-accepting ability of the PPO group.[13]

A notable feature of the PPO group is atomic oxygen (AO) resistance. Connell and co-workers at NASA Langley have developed a series of PPO containing poly(arylene ether)s[14,15] and arylene ether heterocyclic polymers designed for durability in space environments.[16,17] Although long-term AO exposure experiments remain in progress, short-term space flight studies and ground-based space environment simulations have shown that PPO containing polymers possess excellent AO resistance.[14] X-ray photoelectron spectroscopy (XPS) analysis indicated that, after AO exposure, a dense surface layer of phosphate was formed which inhibits further erosion and may also promote self-healing of damage caused by space debris.[18−22] Successful commercial examples of space polymers exist (Triton Systems, Inc.),[23] such as PPO containing polyarylene ether benzimidazole (TOR), PPO containing polyarylene ether (COR), and low-color PPO containing polyimide (TOR-RC).

Perfluorocyclobutyl (PFCB) aromatic ether polymers are a unique class of partially fluorinated polymers prepared by the free radical mediated thermal cyclodimerization of aryl trifluorovinyl ether monomers in bulk or solution above 150 °C.[24−27] PFCB polymers retain many classical properties of fluoropolymers including low dielectric constant, low surface energy, thermal and thermal oxidative stability, and chemical resistance, while offering many advantages, such as improved processability, optical clarity, tailorable refractive index, and thermal mechanical properties.

While current PFCB programs focus primarily on microphotonics,[27] the combined extreme environment and optical properties of these materials suggested that they might be suitable for optical space applications provided AO resistance could be achieved. Here we report the incorporation of the PPO group into the PFCB thermoplastic backbone via the synthesis of novel difunctional monomers **4** and **8** (Schemes 1 and 2). The synthesis of trifunctional monomer 1,1,1-tris(4-trifluorovinyloxy)phenylphosphine oxide (**9**) has been reported

---

* To whom correspondence should be addressed. E-mail: dwsmith@clemson.edu.

[†] Department of Chemistry and Center for Optical Materials Science and Engineering Technologies, Clemson University.

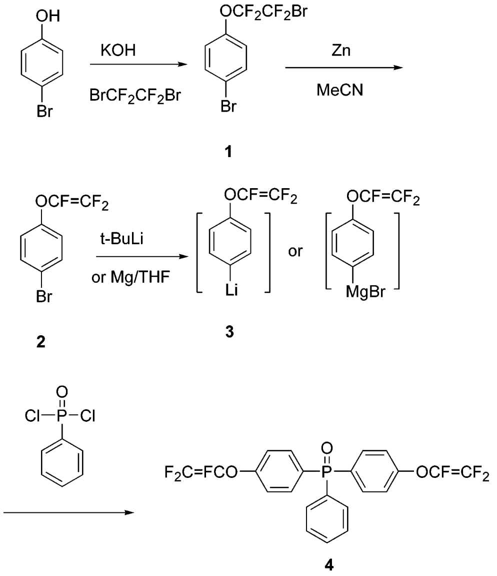
[‡] Present address: Tetramer Technologies, LLC, Clemson, SC 29631.

[§] School of Materials Science and Engineering and Center for Optical Materials Science and Engineering Technologies, Clemson University.

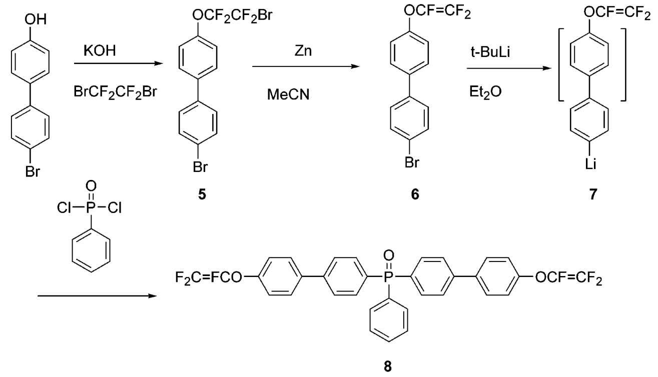
[||] Triton Systems Inc.

10.1021/ma035241g CCC: $25.00

Scheme 1. Preparation of Monomer 4



Scheme 2. Preparation of Monomer 8



previously.[24] In this paper we describe new thermoplastic PFCB polymers containing the PPO unit, their copolymers with traditional PFCB-forming monomers, and the initial evaluation of their space durability.

Experimental Section

General Procedures. ^{1}H NMR (500 MHz), proton-decoupled ^{13}C NMR (125 MHz), ^{19}F NMR (470.6 MHz), and ^{31}P NMR (121 MHz) spectra were obtained using JEOL Eclipse$^+$ 500 and Bruker AF-300 spectrometer systems, respectively. Chloroform-*d* was used as the solvent and chemical shifts reported were internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), $CFCl_3$ (0 ppm), and H_3PO_4 for ^{1}H, ^{13}C, ^{19}F, and ^{31}P nuclei, respectively. Yields refer to isolated yields of compounds estimated to be greater than 95% pure as determined by NMR. Infrared analyses were performed on thin films on ZnSe plates using a ThermoNicolet Magna-IR 550 FTIR spectrometer equipped with a Nic-Plan FTIR microscope. Thirty-two scans at a resolution of 4 cm^{-1} were collected for each sample (the background was ZnSe). Gas chromatography/mass spectrometry (GC/MS) data were obtained using a Varian Saturn GC/MS instrument. Elemental analysis data were obtained from Atlantic Microlab, Inc. (Norcross, GA). Gel permeation chromatography (GPC) data were collected in THF using a Waters 2690 Alliance system with refractive index detection at 35 °C, and equipped with two consecutive Polymer Labs PLGel 5 mm mixed-D and mixed-E columns. Retention times were calibrated against Polymer Labs Easical PS-2 polystyrene standards. ^{19}F NMR end group analysis was performed as described earlier.[25,26] DSC and TGA data were obtained from a Mettler-Toledo 820 DSC and 851 TGA/SDTA system at a heating rate of 10 °C/min in both nitrogen and air atmospheres. The glass transition temperatures (T_g) were obtained from a second heating after quick cooling. The reported T_g value was taken at the midpoint of the Cp curve. Refractive index data were obtained at 1550 nm on thin films (spin coated on silicon wafers from THF solution) using a Metricon model 2010 prism coupler system from Metricon Co.

Film Preparation and Space Durability. Films were cast from polymer solutions (ca. 20% w/w) in *N*,*N*-dimethylacetamide (DMAc) or THF. Solutions were doctored onto glass plates, dried for several hours under nitrogen at 90−250 °C, and removed by peeling under warm running water. AO, solar absorptivity (α), and thermal emissivity (ϵ) tests were carried out at the NASA Marshall Space Flight Center's AO Beam Facility as described elsewhere.[22]

Materials. Dibromotetrafluoroethane was generously donated by The Dow Chemical Co. and purified by washing with water and 10% sodium carbonate solution and drying over $CaCl_2$, followed by distillation. 4-Bromo(trifluorovinyloxy)benezene[25] and 4,4′-bis(trifluorovinyloxy)biphenyl[28] were prepared as described previously and are commercially available from Tetramer Technologies, LLC, and distributed by Oakwood Chemicals, Inc., Columbia, SC (see http://www.oakwoodchemical.com). Other chemicals and reagents were purchased from Aldrich or Fisher Scientific and used as received unless otherwise stated.

Preparation of Lithium Reagents 3 and 7. A 100 mL three-neck round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet, a rubber septum, and an addition funnel was charged with compound **2** or **6** (30 mmol) and dry ether (45 mL). The reaction was cooled to −78 °C, and *tert*-butyllithium (17.7 mL, 1.1 equiv) was added slowly from a dropping funnel. After complete addition, the reaction was maintained at −78 °C for 1 h before addition of the substrate.

Bis(4-trifluorovinyloxyphenyl)phenylphosphine Oxide (4). Phenylphosphonic dichloride (3.9 g, 20 mmol) was added dropwise via an addition funnel into an ether solution of aryllithium reagent **3** (40 mmol) at −78 °C. After complete addition, the reaction was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with dilute HCl and washed with water, and the organic phase was dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography on silica gel using hexane and ethyl acetate (1:1) as eluent. Monomer **4** was obtained as a pale yellow oil in 80% yield. The analysis of **4** was as follows. IR (neat): ν 1834 (w, $CF{=}CF_2$), 1595 (s, Ar), 1496 (s, Ar), 1317 (s), 1289 (s), 1273 (s), 1204 (s), 1173 (s, P=O), 1143, 1119, 1015 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.2−7.24 (4H, d), 7.47−7.52 (2H, td), 7.55−7.60 (1H, td), 7.65−7.70 (2H, m), 7.70−7.76 (4H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 115.9, 128.5, 128.7, 129.3, 131.5, 132.0, 132.4, 134.1, 134.4, 146.8, 157.7 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ −118.6 (1F, dd), −125.3 (1F, dd), −134.7 (1F, dd) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 28.3 ppm. GC/MS: (M^+ calcd as $C_{22}H_{13}O_3PF_6$ 470) *m/z* 469, 372, 281, 200, 152, 125, 77, 50. Anal. Calcd for $C_{22}H_{13}F_6O_3P$ (Found): C, 56.18 (56.40); H, 2.79 (2.78).

4-Bromo-4′-(trifluorovinyloxy)biphenyl (6). This compound was prepared similarly as previously reported[25] (Scheme 2). Compound **6** was obtained in 50% yield as a white solid by silica gel chromatography (hexane as eluent). The analysis of **6** was as follows. Mp: 53.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15−7.19 (d, 2H), 7.38−7.43 (d, 2H), 7.52−7.58 (dd, 4H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ −119.3 (1F, dd), −126.2 (1F, dd), −133.8 (1F, dd) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 115.6, 117.0, 121.8, 128.0, 129.3, 131.4, 132.7, 136.9, 139.0, 146.9, 154.9 ppm. GC/MS: (M^+ calcd as $C_{14}H_8F_3OBr$ 328) *m/z* 328, 152. Anal. Calcd for $C_{14}H_8F_3OBr$ (Found): C, 51.09 (51.62); H, 2.45 (2.46).

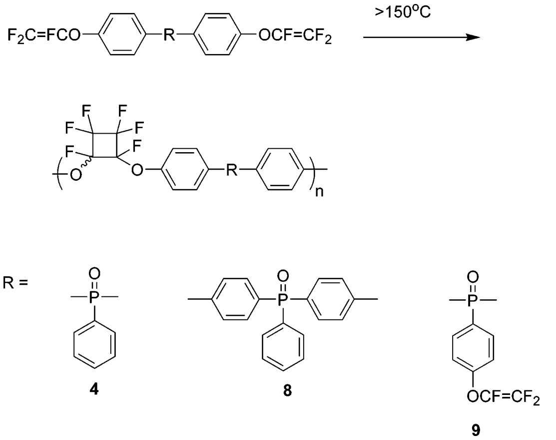
Bis(4-trifluorovinyloxybiphenyl)phenylphosphine Oxide (8). Phenylphosphonic dichloride (3.9 g, 20 mmol) was added dropwise via an additional funnel into an ether solution of lithium reagent **7** (40 mmol) at −78 °C. After complete addition, the mixture was slowly warmed to room temperature and stirred for 2 h. The reaction was quenched with dilute HCl and washed with water, and the organic phase was dried with anhydrous $MgSO_4$ and filtered. Removal of solvents under

Table 1. Selected Properties for PPO Containing PFCB Copolymers

	wt %		M_n		T_g/°C[c]	T_d/°C[d]	
polym	**4**, **8**	**10**	NMR (n)[a]	GPC (M_w/M_n)[b]	DSC	N_2	air
poly4	100	0	5050 (11)	4650 (1.49)	169	470	468
4-*co*-10	50	50	7970 (20)	5660 (2.06)	144	458	464
4-*co*-10	25	75	20200 (55)	16440 (3.97)	143		
poly8	100	0		2900 (2.98)[e]	224	457	422

[a] End group analysis by ^{19}F NMR. [b] GPC in chloroform vs polystyrene. [c] DSC at 10 °C/min in N_2. [d] 5 wt % loss. [e] Polymerized by DSC experiment.

Scheme 3. Polymerization of PPO Containing Difunctional PFCB Monomers 4 and 8, and Trifunctional Monomer 9



reduced pressure afforded a viscous yellow crude product. Compound **8** was obtained in 50% yield as a white solid by silica gel chromatography (1:1 hexane/ethyl acetate). The analysis of **8** was as follows. IR (neat): ν 1833 (w, CF=CF$_2$), 1602 (s, Ar), 1516 (s, Ar), 1489 (s, Ar), 1314 (s), 1276 (s), 1193 (s), 1172 (s, P=O), 1140, 1122, 1005 (w) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.17−7.22 (d, 4H), 7.47−7.53 (dt, 2H), 7.55−7.69 (m, 9H), 7.71~7.82 (m, 6H) ppm. ^{19}F NMR (470 MHz, CDCl$_3$): δ −119.2 (1F, dd), −126.1 (1F, dd), −133.9 (1F, dd) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 116.5, 127.1, 128.8, 129.0, 130.9, 131.8, 132.2, 132.8, 134.7, 136.8, 143.6, 144.9, 147.1, 149.2, 155.2 ppm. MS: (M$^+$ calcd as $C_{34}H_{21}F_6O_3P$ 622) m/z 622, 524, 427, 357, 152. Anal. Calcd for $C_{34}H_{21}F_6O_3P$ (Found): C, 65.60 (65.40); H, 3.40 (3.55).

Polymerization. In a 100 mL three-neck round-bottom flask equipped with a mechanical stirrer and a N$_2$ inlet, monomer **4** was homopolymerized and copolymerized with bis(trifluorovinyloxy) biphenyl (**10**) with different compositions at 160 °C for 4 h and 200 °C for 8 h. Polymerizations were performed in the bulk at early conversions after minimum quantities of mesitylene were added to maintain stirring. After polymerization, the polymers were dissolved in THF and precipitated in methanol. The polymerization for monomer **8** was studied only in a DSC experiment. The resulting PFCB polymers have good solubility in most common organic solvents, such as THF and dichloromethane. Selected properties are presented in Table 1. For example, the analysis of **poly4** was as follows. IR (neat): ν 1595 (s, Ar), 1498 (s, Ar), 1306 (s), 1206 (s), 1178 (s, P=O), 1120, 1095, 963 (s, cyclobutane-F$_6$) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.15−7.22 (2H, d), 7.26−7.32 (2H, d), 7.42−7.52 (2H, br), 7.53−7.59 (1H, m), 7.60−7.72 (6H, br) ppm. ^{19}F NMR (470 MHz, CDCl$_3$) shows the characteristic series of multiplets representing the perfluorocyclobutyl fluorine signals ranging from −126 to −133 ppm. Anal. Calcd for $(C_{22}H_{13}F_6O_3P)_n$ (Found): C, 56.2 (56.43), H, 2.8 (2.86). Complete characterization was carried out for **poly8** similarly as presented for **poly4** and is consistent with the structure proposed (Scheme 3). The refractive indexes for **poly4** and **poly8** were measured to be 1.5395 and 1.5877 at 1550 nm, respectively.

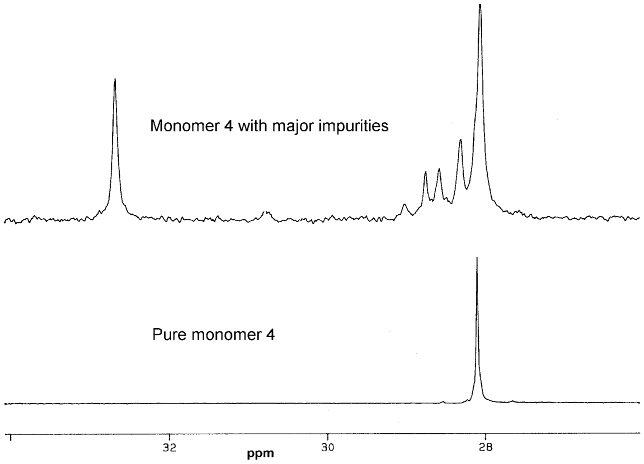
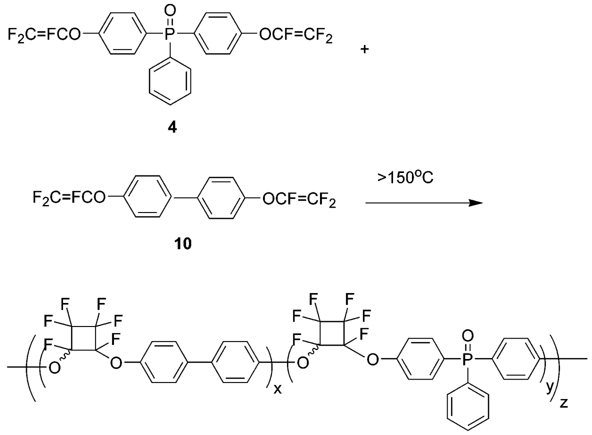


Figure 1. ^{31}P NMR spectra of crude (top) and pure (bottom) monomer **4** prepared from the Grignard reagent.

Scheme 4. Copolymerization of PPO Containing Monomers



Results and Discussion

The increasing importance of the gossamer spacecraft has urged the development of high-performance space polymers with optical clarity and space environment durability.[19,20] Our strategy has been to incorporate the PPO group into a versatile class of semifluorinated aryl ether polymers containing the PFCB linkage. Novel PPO containing monomers **4** and **8** were prepared by using our established intermediate strategy via aryllithium chemistry (Schemes 1 and 2).[29] High-yielding lithium reagents **3** and **7** were prepared by classic metal−halogen exchange reaction while leaving the trifluorovinyl ether group intact. For more cost-effective scale-up and processing, the Grignard reagent of compound **2** was also prepared and reacted with phenylphosphonic dicholoride to give monomer **4** in excellent yield (90%). The Grignard reagent, however, is less reactive than the lithium reagent, and the nucleophilic substitution reaction yielded more byproducts as shown by the ^{31}P NMR spectra in Figure 1.

Aryl trifluorovinyl ether monomers undergo thermal step growth polymerization via radical mediated cyclopolymerization, affording high molecular weight linear or network PFCB polymers and copolymers depending on the average functionality of the monomers.[26] Monomer **4** was homopolymerized and copolymerized with bis(trifluorovinyloxy)biphenyl (**10**) at three different compositions (Schemes 3 and 4). The GPC of homopolymer **poly4** in THF (relative to polystyrene) gave a

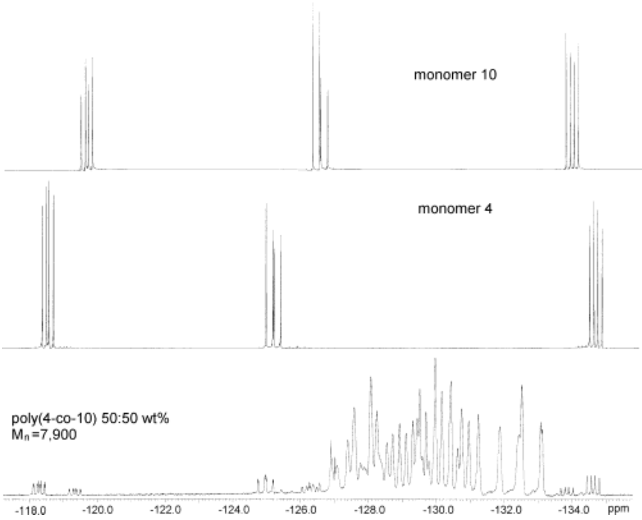


Figure 2. ^{19}F NMR spectra of monomers **4** and **10** and their copolymer in CDCl$_3$.

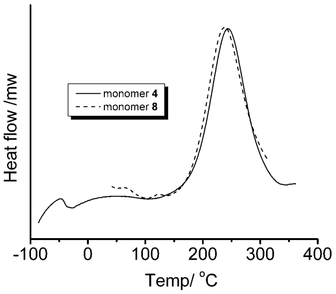


Figure 3. Polymerization of monomers **4** and **8** by DSC (10 °C/min).

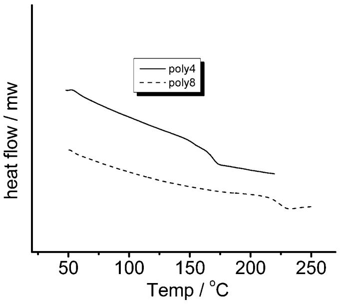


Figure 4. DSC (10 °C/min) analysis of **poly4** and **poly8**.

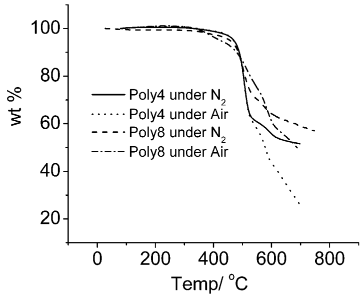


Figure 5. TGA of **poly4** and **poly8** in nitrogen and air at 10 °C/min.

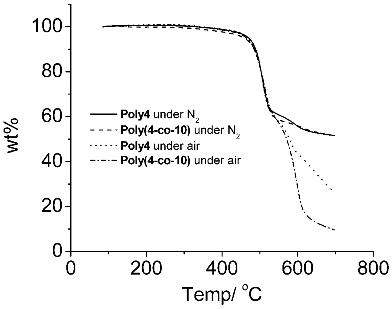


Figure 6. TGA of **poly4** and copolymers in nitrogen and air at 10 °C/min.

monomodal distribution with $M_w = 7000$ ($M_w/M_n = 1.5$). As summarized in Table 1, the molecular weight of the copolymers is much higher than that of the homopolymer presumably due to enhanced solubility during polymerization. In addition, the effect of molecular weight limiting trace impurities (e.g., monofunctional byproducts) known to be present in monomer **4** is diluted during copolymerization. Transparent, flexible, and tough films with slight yellow color were obtained from **poly(4-*co*-10)**. The molecular weight calculated using end group analysis[25,26] by ^{19}F NMR is close to the GPC results for the copolymers. Figure 2 exhibits the ^{19}F NMR spectra of monomer **4**, **10**, and **poly(4-*co*-10)** (50:50 wt %). The chemical shift differences for the vinyl fluorine signals in monomers **4** and **10** are clearly resolved, and the spectrum for **poly(4-*co*-10)** shows the decrease in vinyl fluorine signals and the concomitant increase of complicated multiplets ranging from −126 to −133 ppm, which represents the six possible perfluorocyclobutyl rings (e.g., both *cis* and *trans* isomers of **4**−**4**, **4**−**10**, and **10**−**10** linkages) each containing six nonequivalent fluorine atoms.

As shown in Figure 3, monomers **4** and **8** have very similar thermal polymerization behavior. The onset of thermal cyclodimerization of the aryl trifluorovinyl ether group in **4** and **8** is detected around 140 °C, and the exothermic peak reaches a maximum at 243 °C. These characteristics are similar to those of other bis- and tristrifluorovinyl ether aromatic monomers,[26] which suggests—along with ^{19}F NMR data indicating nearly equal monomer consumption rates—that the PPO group imparts negligible influence on the PFCB thermal cyclodimerization kinetics. In terms of enthalpy, the polymerization of monomers **4** and **8** is close to that of the previously reported thermosetting PPO monomer **9**[24] on the basis of the enthalpy per trifluorovinyl ether group ($-\Delta H = 18-20$ kcal/mol). Both **poly4** and **poly8** were found to be amorphous with no crystalline transitions observed by DSC (Figure 4) as expected for the stereorandom PFCB polymerization that typically affords an equal fraction of *cis* and *trans* 1,2-disubstituted cyclobutanes. The glass transition temperatures (T_g) of **poly4** and **poly8** were found to be 169 and 224 °C, respectively.

Figure 5 displays the TGA results for **poly4** and **poly8** in nitrogen and air. The thermal stability of **poly4** under air is nearly identical to that under nitrogen below 520 °C. This result indicates that the PPO group does not detract from the inherent thermal stability of PFCB polymers and may indeed increase the thermooxidative stability. The temperature at 5% weight loss was measured to be 470 °C for **poly4** and 457 °C for **poly8** under nitrogen. For space polymer applications in low Earth orbit (LEO), glass transition temperatures and thermal and thermal oxidative stability in this range have been sufficient. Under nitrogen and air atmospheres, the homopolymers and copolymers show similar catastrophic weight loss by TGA. Under air, however, the copolymers decomposed more completely as expected (Table 1 and Figure 6).

Table 2. Space Environment Simulation Data for Selected PFCB Polymers

material	AO fluence (atoms/cm^2)	mass loss (wt %)	solar absorptivity (α)		thermal emissivity (ϵ)	
			preexposure	postexposure	preexposure	postexposure
poly(4-*co*-10)	2.6×10^{20}	2.2 (0.85)[a]	0.163	0.193	0.680	0.650
poly10	3.88×10^{20}	33.2 (8.6)[a]	0.144	0.164	0.565	0.411

[a] AO fluence normalized mass loss percent.

A key property of PPO containing PFCB polymers is their expected resistance to atomic oxygen (AO) due to the PPO content, which has been established in many ground-simulated and space tests for the TOR materials.[20,23] AO is formed by the photodissociation of upper atmosphere O$_2$ by short-wavelength UV radiation and is a prevalent species in LEO between the altitude of 160 and 800 km.[15−17] AO is very reactive and quickly erodes organic polymers if they are unprotected.[19] AO durability was evaluated by mass loss caused by erosion after an AO exposure level of $(2-6) \times 10^{20}$ atoms/cm^2 (equivalent to an exposure of 4 month duration in LEO) and with accompanied UV irradiation comparable to several hundred ESHs (equivalent solar hours). Table 2 presents the data for **poly(4-*co*-10)** containing 12.5 wt % monomer **4**. This copolymer gave higher quality films for the AO tests and was similar in molecular weight and other properties to the copolymer containing 25 wt % shown in Table 1. The copolymer experienced only 2.2 wt % mass loss compared to 33.2 wt % for **poly10** (without PPO), which equates to an AO fluence normalized mass loss ratio of 1:10. These preliminary results indicate an order of magnitude increase in AO-erosion resistance for a PFCB copolymer containing only 12.5 wt % PPO monomer **4**. The solar absorptivity (α) relates to the quantity of incoming solar energy that is absorbed by the film, while the thermal emissivity (ϵ) describes the ability of the film to radiate energy from the surface.[22] After AO exposure, the α value will increase and the ϵ value will decrease due to the change of the optical transparency of the film. Incorporation of the PPO monomer did not show a significant change in the solar absorptivities and thermal emissivities. However, the thermal emissivities of **poly10** (without PPO) decreased dramatically.

Conclusions. The reaction of *p*-BrArOCF═CF$_2$ (for Ar = phenyl and biphenyl) with *tert*-butyllithium afforded the aryllithium reagent smoothly below −20 °C. Upon treatment with phenylphosphonic dichloride, two novel bis(trifluorovinyl ether) monomers containing the phenylphosphine oxide group were successfully prepared. Polymerization proceeded thermally above 150 °C and gave thermoplastic polymers that exhibited glass transition temperatures of 169 and 224 °C, respectively. Copolymerization with bis(4,4′-trifluorovinyloxy)biphenyl gave film-forming transparent thermoplastic copolymers with high T_g (>140 °C) and good thermal stability (>450 °C). Preliminary atomic oxygen resistance tests indicated an order of magnitude increase in PFCB AO resistance when 12.5 wt % PPO monomer was incorporated into PFCB copolymers.

Acknowledgment. We thank the Air Force Office of Scientific Research (STTR with Triton Systems, Inc.), National Textiles Center, the South Carolina NASA Space Grant Consortium, SC EPSCoR, and the National Science Foundation (DMR-CAREER Award to D.S.) for partial support, and 3M Corp. for 3M Pre-tenured Faculty Awards (D.S. and S.F.) for financial support. We also thank The Dow Chemical Co. for starting materials, Mettler Toledo for donation of the DSC820 and 851TGA/SDTA system, and NASA Marshal for space environment simulation data. We gratefully acknowledge Kim Ivey (Clemson University) for assistance with FTIR data, and S. Kumar, P. Go, and H. Liu for synthetic expertise. D.W.S. is a Cottrell Scholar of Research Corporation.

References and Notes

(1) Shobha, H. K.; Johnson, H.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2904.
(2) Ghassemi, H.; McGrath, J. E. *Polymer* **1997**, *38*, 3139.
(3) Meyer, G. W.; Pak, S. J.; Lee, Y. J.; McGrath, J. E. *Polymer* **1995**, *36*, 2303.
(4) Grubbs, H. J.; Smith, C. D.; McGrath, J. E. *Polym. Mater. Sci. Eng.* **1995**, *65*, 111.
(5) Smith, C. D.; Grubbs, H. J.; Websler, H. F.; Gungor, A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *3*, 211.
(6) Bonaplata, E.; Ding, H.; Hanson, B. E.; McGrath, J. E. *Polymer* **1995**, *36*, 3035.
(7) Bonaplata, E.; Priddy, D. B.; Smith, C. D.; McGrath, J. E. *Polym. Mater. Sci. Eng.* **1994**, *70*, 405.
(8) Liu, S.; Cabasso, I. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 889.
(9) Yoon, T. H.; Lee, Y. J.; Gungor, A.; Smith, C. D.; McGrath, J. E. In *Adhesion Society Proceedings*, Hilton Head, SC., Spring 1992; Vol. 15, p 200.
(10) Jeong, K. U.; Kim, J.-J.; Yoon, T.-H. *Polymer* **2001**, *42*, 6019.
(11) Fitch, J. W.; Reddy, V. S.; Youngman, P. W.; Wohlfahrt, G. A.; Cassidy, P. E. *Polymer* **2000**, *41*, 2301.
(12) Zhang, Y. H.; Tebby, J. C.; Wheeler, J. W. *Eur. Polym. J.* **1999**, *35*, 209.
(13) Chane-Ching, K.; Lequan, M.; Lequan, R. M.; Kajzar, F. *Chem. Phys. Lett.* **1995**, *242*, 598.
(14) Smith, J. G., Jr.; Thompson, C. M.; Watson, K. A.; Connell, J. W. *High Perform. Polym.* **2002**, *14*, 225.
(15) Smith, J. G., Jr.; Connell, J. W.; Hergenrother, P. M. *Polymer* **1994**, *35*, 2834.
(16) Connell, J. W.; Smith, J. G., Jr.; Hergenrother, P. M. *Polymer* **1995**, *36*, 5.
(17) Connell, J. W.; Smith, J. G., Jr.; Hedrick, J. L. *Polymer* **1995**, *36*, 13.
(18) Connell, J. W. *High Perform. Polym.* **2000**, *12*, 43.
(19) Connell, J. W. In *Fluoropolymer 2000*; Smith, D. W., Jr., Ed.; EPS: Hattiesburg, MS, 2001; p 74.
(20) Connell, J. W.; Watson, K. A. In *Gossamer Spacecraft: Membrane and Inflatable Structures Technology for Space Applications*; Jenkins, C. H. M., Ed.; AIAA: Reston, VA, 2001; p 243.
(21) Smith, J. G., Jr.; Connell, J. W.; Hergenrother, P. M. *NASA Tech. Briefs* **1994**, *18*, 32.
(22) Watson, K. A.; Palmieri, F. L.; Connell, J. W. *Macromolecules* **2002**, *35*, 4968.
(23) See http://www.tritonsys.com.
(24) Babb, D.; Boone, H.; Smith, D. W., Jr.; Rudolf, P. *J. Appl. Polym. Sci.* **1998**, *69*, 2005.
(25) Smith, D. W., Jr.; Babb, D. A. *Macromolecules* **1996**, *29*, 852.
(26) Smith, D. W., Jr.; Babb, D. A.; Shah, H. V.; Hoeglund, A.; Traiphol, R.; Perahia, D.; Bone, H. W.; Langhoff, C.; Radler, M. *J. Fluorine Chem.* **2001**, *104*, 109.
(27) Smith, D. W., Jr.; Chen, S.; Kumar, S. M.; Ballato, J.; Topping, C.; Shah, H. V.; Foulger, S. H. *Adv. Mater.* **2002**, *14*, 1585.
(28) Babb, D. A.; Ezzell, B. R.; Clement, K. S.; Richey, W. F.; Kennedy, A. P. *J. Polym Sci, Part A: Polym. Chem.* **1993**, *31*, 3465.
(29) Junmin, J.; Narayan, S.; Neilson, R.; Oxley, J.; Babb, D.; Rondan, N.; Smith, D. W, Jr. *Organometallics* **1998**, *17*, 783.

MA035241G