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Polymer 46 (2005) 6923–6932
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Synthesis and characterization of perfluorocyclobutyl (PFCB) polymers containing pendent phenylphosphine oxide

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Received 7 March 2005; received in revised form 26 May 2005; accepted 27 May 2005
Available online 23 June 2005

This paper is dedicated to Prof Darryl D. DesMarteau on the occasion of his 65th birthday

Abstract

Three phenylphosphine oxide (PPO) containing trifluorovinyl aryl ether monomers were synthesized and polymerized via thermal cyclodimerization affording perfluorocyclobutyl (PFCB) polymers containing PPO pendent groups. The new polymers exhibited moderate to high glass transition temperatures ($T_g = 145$–217 °C) and good thermal stability in nitrogen (5% weight loss, $T_d > 402$ °C). Copolymerization with traditional PFCB forming monomers such as 4,4′-(trifluorovinyloxy)biphenyl resulted in film forming transparent thermoplastic copolymers with improved solubility and further enhanced thermal stability. Semi-fluorinated PPO containing polymers of this type may find potential application as space environment durable materials.

Keywords: Phenyl phosphine oxide; Trifluorovinyl ether; Perfluorocyclobutyl (PFCB)

1. Introduction

Phenylphosphine oxide (PPO) containing polymers continue to attract considerable interest due to their notable attributes, such as flame-retardant properties [1], metal complexation [2–3] and atomic oxygen (AO) resistance [4–6]. In the past decade, Connell and co-workers at NASA Langley have developed a series of PPO containing poly(arylene ether)s (PAEs) and arylene ether heterocyclic polymers, such as polyetherimides (PEIs) and polybenzimidazoles (PBIs), designed for space durability in low Earth orbit (LEO) environments [5–10]. In a recent paper [9], two types of PPO containing PAEs with PPO group in the main chain and as pendent group have been reported. The structure/properties study indicated that the largest difference between the two configurations was that the polymer containing main chain PPO groups exhibited higher T_g, slightly higher thermal stability, but lower tensile strength than those with pendent PPO groups [9]. Furthermore, pendant PPO groups also contributed to enhanced solubility and reduced color of the polyimides over main chain PPO [8].

We previously reported the incorporation of the PPO group into the perfluorocyclobutyl (PFCB) aromatic ether polymer main chain via the synthesis of novel di-functional and tri-functional perfluorovinyl ether monomers [11,12] (Fig. 1). Compared to the hexafluoroisopropylidene (6F) linkage [13,14], the 1,2-disubstituted hexafluorocylcobutyl (PFCB) building block has the same fluorine content but much larger size, which can enhance optical transparency and low color. Initial evaluation of previous PPO containing PFCB copolymers has shown that PPO incorporation does impart AO resistance to PFCB polymers and low solar absorptivity [12]. Here, we report the synthesis and characterization of a new series of PFCB polymers and copolymers with pendent PPO groups containing the amide,

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doi:10.1016/j.polymer.2005.05.111

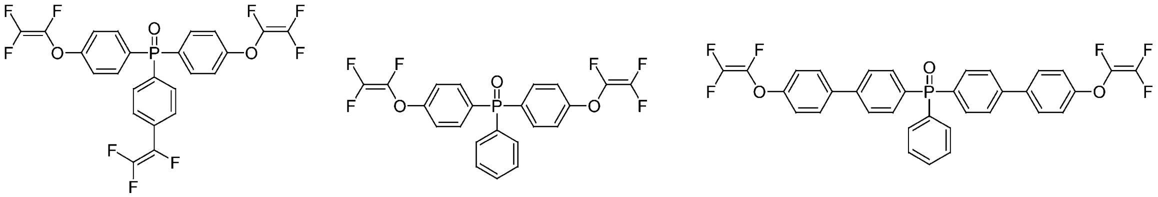

Fig. 1. Previously synthesized di- and tri-functional PPO containing trifluorovinyl ether monomers.

imine and ester linkage using PPO containing diamine and bisphenol starting materials established at NASA Langley [8,9].

2. Experimental part

2.1. Materials and instrumentation

4-Bromo(trifluorovinyloxy)benzene, 4-trifluorovinyloxybenzoic acid and 4,4′-(trifluorovinyloxy) biphenyl were prepared as described previously and are commercially available from Tetramer Technologies, L.L.C. and distributed by Oakwood Chemicals Inc., Columbia, SC (http://www.oakwoodchemical.com). [2,4-Bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (3-APPO) and 2,5-dihydroxyphenyldiphenylphosphine oxide (2,5-DHPPO) were generously provided by NASA Langley Research Center. All other chemicals and reagents were purchased from Aldrich or Fisher Scientific and used as received unless otherwise stated.

^{1}H NMR 500 MHz, proton decoupled ^{13}C NMR 125 MHz and ^{19}F NMR 470.6 MHz spectra were obtained using a JOEL Eclipse$^+$500 spectrometer system. Chloroform-*d* was used as the solvent and chemical shifts reported were internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm) and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C and ^{19}F nuclei, respectively. 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. 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. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analysis was performed using a Bruker Daltonics omniflex MALDI mass spectrometer equipped with a N_2 laser at 337 nm. The matrix for all measurements was 2,5-dihydroxybenzoic acid (DHB). The concentration ratio of matrix to sample was about 50:1 (wt%) and as cationization agent, lithium sulfate was added in about 10 wt%. The components were mixed in a mortar without solvent. Films were cast from polymer solutions (ca. 20 wt%) in THF. Solutions were doctored onto glass plates, dried for several hours, and removed by peeling under warm running water. Dynamic mechanical analysis (DMA) data of the films were obtained using a TA instruments dynamic mechanical analyzer DMA-2980 operating in the tensile mode. Films were placed in a vacuum oven at 50 °C for 1 day prior to testing. Sample size is 11 mm (length)×8 mm (width)×0.12 mm (thickness). Scans were made at a frequency of 1 Hz and a heating rate of 3 °C/min between 30 and 250 °C.

2.2. Synthesis of 4-[(trifluorovinyl)oxy]benzoyl chloride (**1**)

Compound **1** was prepared similarly as previously reported [15]. Freshly distilled thionyl chloride (20 mL) was added to 4-(trifluorovinyloxy)benzoic acid (2.18 g, 10 mmol) in a round bottomed flask fitted with a reflux condenser. A drying tube (filled with anhydrous calcium carbonate) was added and the stirred solution was heated to reflux for 3 h. Excess thionyl chloride was removed by distillation (90–100 °C, atmospheric pressure) to reveal the crude product as viscous brown oil. Purification by kugelrohr distillation (80–90 °C, 0.5 mmHg) gave **1** as

Table 1

Selected characterization data for the copolymers

Polymer	Feed ratio wt% (mol%)		Measured composition[a] (mol%)		M_n[b] (M_w/M_n)	T_g[c] (°C)	$T_{d\ 5\ wt\%}$[d] (°C)
	3	**6**	**3**	**6**			
Poly**3**	100	0	100	0	$CHCl_3$ insoluble	217	418
Poly(**3**-*co*-**6**)	50 (28)	50 (72)	23	77	4880 (1.7)	191	446
Poly(**3**-*co*-**6**)	25 (11)	75 (89)	9	91	26,180 (6.9)	168	465

[a] By ^{1}H NMR.

[b] GPC in chloroform vs. polystyrene.

[c] DSC at 10 °C/min in N_2.

[d] TGA at 10 °C/min in N_2.

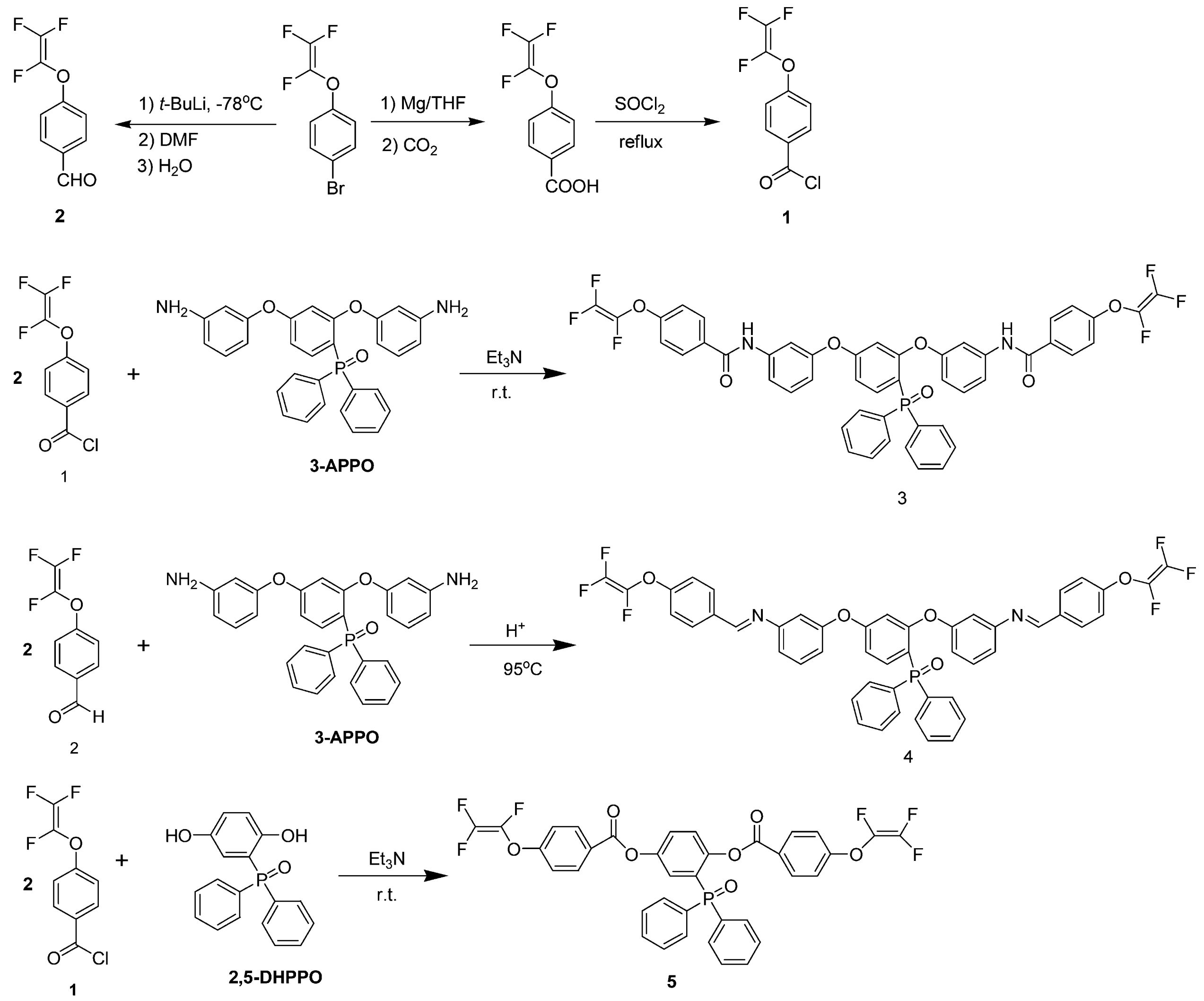

Fig. 2. Synthesis of difunctional trifluorovinyl ether monomers (**3**–**5**) with pendent PPO group.

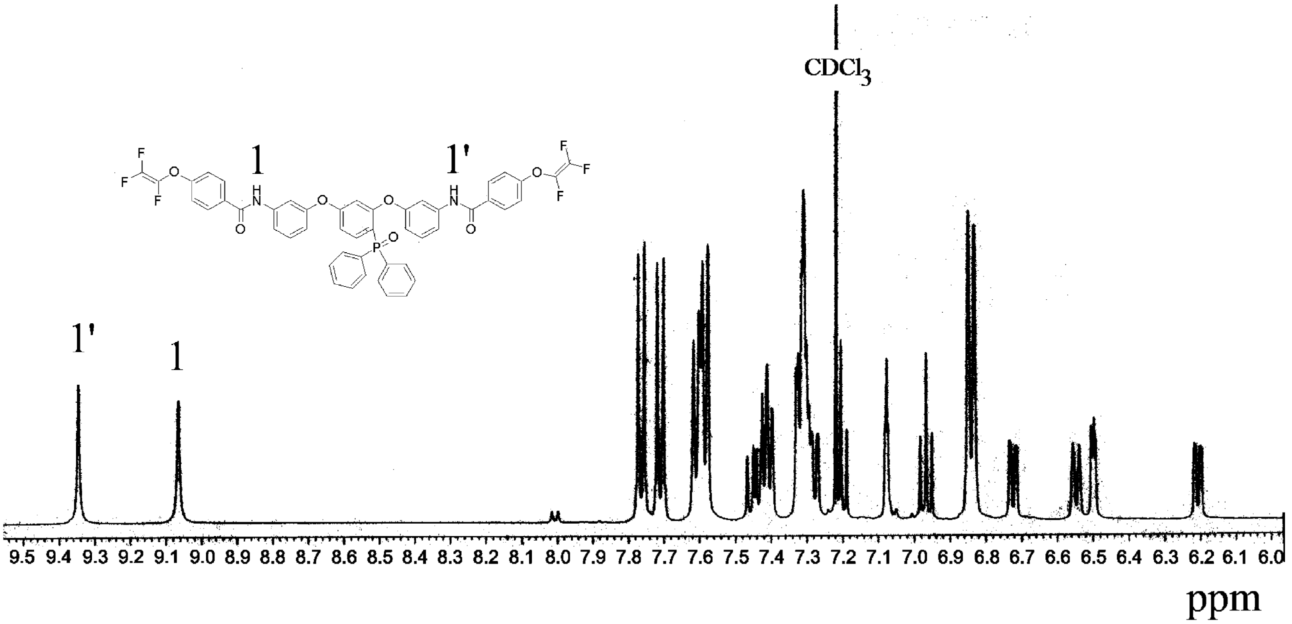

Fig. 3. ^{1}H NMR spectra for monomer **3** in $CDCl_3$.

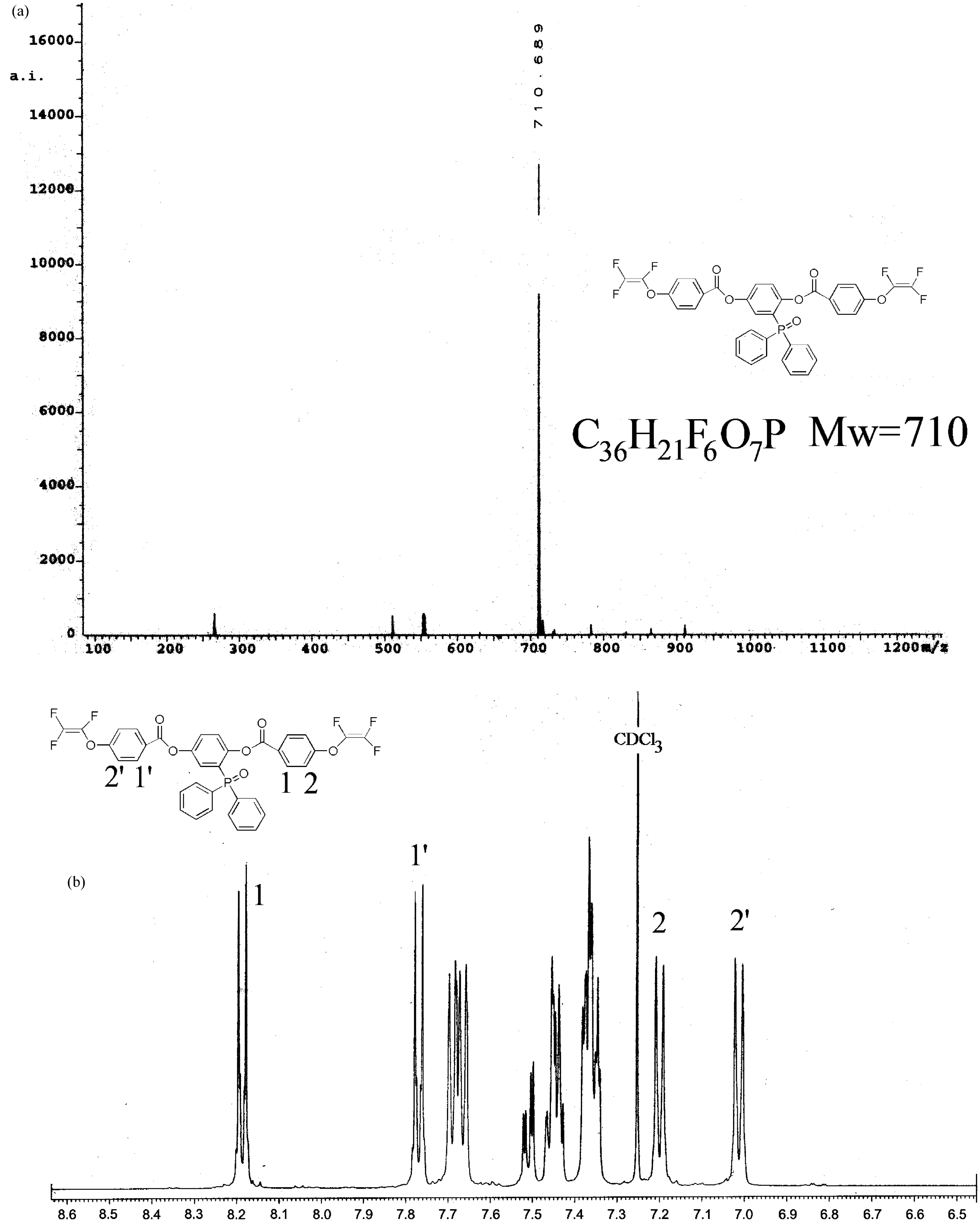

Fig. 4. (a) MALDI-TOF, (b) ^{1}H NMR and (c) ^{19}F NMR spectra for monomer **5**.

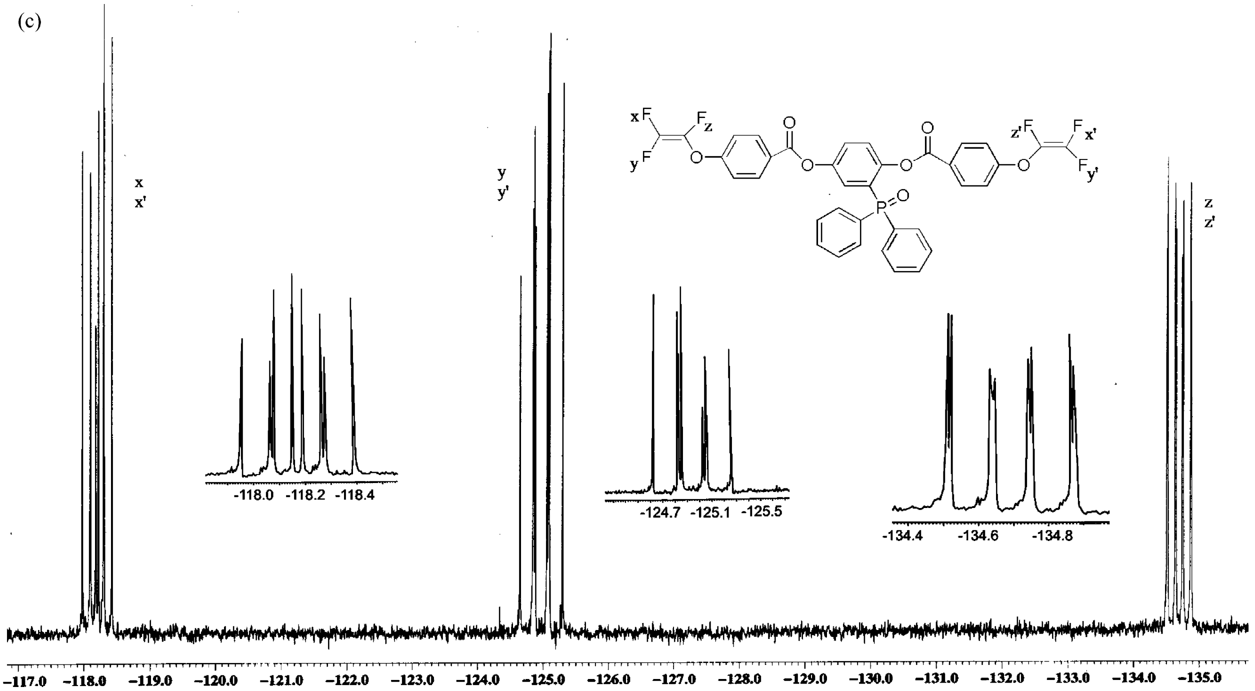

Fig. 4 (*continued*)

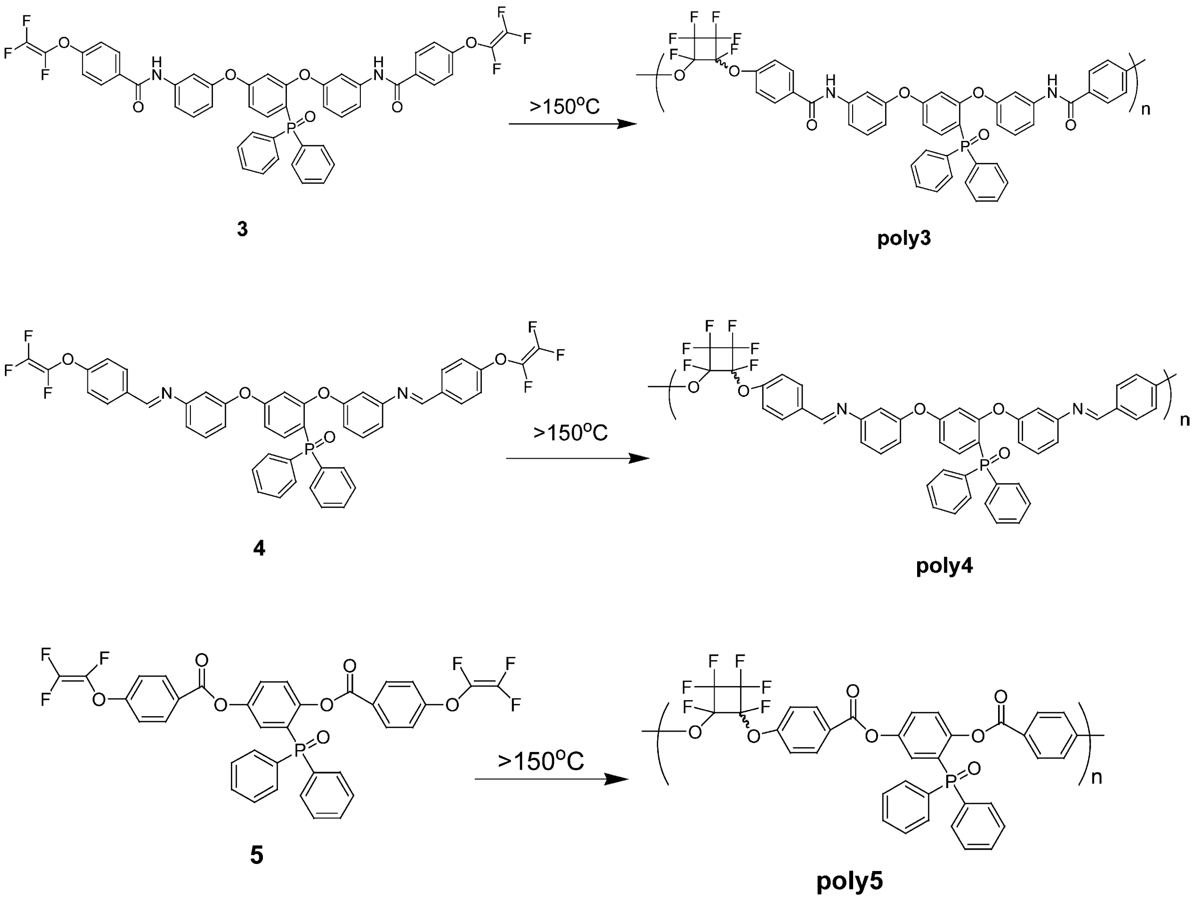

Fig. 5. Thermal cyclopolymerization of monomers **3**–**5**.

clear colorless oil with a strong irritating smell (1.8 g) in 76% yield.

2.3. Synthesis of 4-(trifluorovinyloxy)benzaldehyde (**2**)

To a 500 mL three neck flask equipped with a dropping funnel and N_2 purge was added 80 mL of freshly distilled diethyl ether and 20.0 g (79 mmol) of 4-bromo(trifluorovinyloxy)benzene at -78 °C. *t*-Butyl lithium (51 mL, 1.7 M solution in pentane, 1.1 equiv) was then added drop-wise and the solution was stirred for 2 h. The lithium reagent was quenched with DMF (58 mL, 10 equiv) by slow addition and the solution was slowly warm to room temperature and stirred for 2 h. Excess water as added and the crude product was extracted with ether and distilled via kugelrohr to give **2** as clear colorless oil (11.6 g) in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.87 (1H, s), 7.84 (2H, d), 7.16 (2H, d) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.5, 163.1, 147.7 (td), 133.3, 132.2 (dt), 131.8, 115.9 ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$) δ: -118.9, -125.6, 135.2 ppm. GC/MS (M^+ Calcd as $C_9H_5O_2F_3=202$) *m/z*: 202, 173, 155, 105, 77, 51.

2.4. Synthesis of monomer (**3**)

To a 250 mL three neck flask equipped with N_2 purge was added [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (3-APPO) (4.88 g, 10 mmol) and anhydrous 1,4-dioxane (70 mL) under an inert atmosphere. The mixture was warmed to 50 °C with stirring to give a pale brown solution. On cooling to room temperature, triethylamine (3.0 mL, 22 mmol) was added followed by freshly distilled acid chloride **1** (5.16 g, 22 mmol) drop wise over 2 min. A white precipitate was observed immediately and the reaction mixture was stirred at room temperature for 3 h. Water was then added and the crude product was extracted with methylene chloride. The organic portion was washed thoroughly with HCl (aq, 0.5 M) followed by $NaHCO_3$ (aq, sat.) and finally water. The product (**3**) was obtained as a white solid upon precipitation from hexane in 84% yield and 95+% purity (NMR). ^{1}H NMR (500 MHz, $CDCl_3$): 6.22–6.26 (1H, dd), 6.52–6.56 (1H, dd), 6.56–6.60 (1H, d), 6.74–6.78 (1H, d), 6.84–6.90 (4H, d), 6.98–7.02 (1H, t), 7.12–7.14 (1H, s), 7.22–7.26 (1H, t), 7.30–7.38 (6H, m), 7.42–7.50 (2H, m), 7.60–7.68 (6H, m), 7.72–7.76 (2H, d), 7.76–7.82 (2H, d), 9.15 (1H, s), 9.44 (1H, s) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): -118.6 ppm (1F, dd), -118.7 ppm (1F, dd), -125.5 ppm (1F, dd), -125.6 ppm (1F, dd), -134.4 ppm (1F, dd), -134.5 ppm (1F, dd). MALDI-TOF (M^+ Calcd as $C_{48}H_{31}F_6O_7N_2P=893$) *m/z*: 893. Anal. Calcd for $C_{48}H_{31}F_6O_7N_2P$ (Found): C, 64.57 (64.38); H, 3.48 (3.45); N, 3.14 (3.02).

2.5. Synthesis of monomer (**4**)

To a 150 mL single neck round bottom flask, 3-APPO diamine (4.92 g, 10 mmol) and 4-(trifluorovinyloxy)benzylaldehyde (**2**) (4.646 g, 2.3 equiv) were dissolved in dry dioxane (60 mL). One drop of acetic acid was added as catalyst and the mixture was heated to 95 °C and stirred for 12 h. Dioxane was then removed under reduced pressure, and the product was dissolved in methylene chloride and precipitated from hexanes. Upon filtration and drying, monomer **4** was obtained as a yellow solid in 58% yield and 90% purity by NMR. ^{1}H NMR (500 MHz, $CDCl_3$): 6.41–6.50 (3H, m), 6.73–6.77 (1H, d), 6.81–6.89 (3H, m), 6.93–6.97 (1H, d), 7.12–7.19 (5H, m), 7.29–7.34 (1H, t), 7.35–7.42 (5H, m), 7.42–7.49 (2H, m), 7.73–7.81 (4H, m), 7.83–7.88 (3H, m), 7.89–7.95 (1H, dd), 8.21 (1H, s), 8.32 (1H, s) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): -118.6 ppm (1F, dd), -118.7 ppm (1F, dd), -125.5 ppm (1F, dd), -125.6 ppm (1F, dd), -134.3 ppm (1F, dd), -134.3 ppm (1F, dd) ppm. MALDI-TOF (M^+ Calcd as $C_{48}H_{31}F_6O_5N_2P=861$) *m/z*: 861.

2.6. Synthesis of monomer (**5**)

Similar to the synthesis of monomer **3**, freshly prepared acid chloride **1** (4.36 g, 20 mmol) was mixed with a THF suspension of 2,5-dihydroxyphenyldiphenylphosphine oxide (2,5-DHPPO) (2.48 g, 8 mmol) and Et_3N (2.78 mL, 20 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 12 h. As the reaction proceeded, 2,5-DHPPO suspension was slowly dissolved and consumed giving a soluble product in THF. The reaction was quenched with dilute HCl and the product was extracted with methylene chloride, washed with water, and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography on silica gel using hexane:ethyl acetate (3:2) as eluent ($R_f=0.3$). Monomer **5** was isolated as a white powder in 85% yield and 95+% purity (NMR). ^{1}H NMR (500 MHz, $CDCl_3$): 6.99–7.03 (2H, d), 7.18–7.22 (2H, d), 7.33–7.40 (5H, m), 7.42–7.48 (3H, m), 7.49–7.53 (1H, dd), 7.64–7.72 (4H, dd), 7.75–7.80 (2H, d), 8.17–8.21 (2H, d) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): -118.1 ppm (1F, dd), -118.2 ppm (1F, dd), -124.9 ppm (1F, dd), -125.0 ppm (1F, dd), -134.7 ppm (1F, dd), -134.7 ppm (1F, dd). MALDI-TOF (M^+ Calcd as $C_{36}H_{21}F_6O_7P=710$) *m/z*: 710.

2.7. Polymer synthesis

The thermal polymerization for monomers **3**–**5** was studied initially by DSC experiments. Monomer **3** was selected to copolymerize with 4,4′-(trifluorovinyloxy) biphenyl (**6**) with two different compositions at 160 °C for 4 h and 180 °C for 48 h. Copolymerization was performed in the bulk at early conversions, where after a minimum amount of mesitylene was added to maintain stirring. After polymerization, the soluble polymers were dissolved in THF and precipitated in methanol to give white fibrous polymers in essentially quantitative yield. Selected properties of the copolymers are presented in Table 1. The ^{19}F NMR spectrum (DMSO-d_6) of poly**3** shows the typical series of multiplets representing the perfluorocyclobutyl (PFCB) fluorine atoms ranging from −126 to −131 ppm. The ^{19}F NMR spectra for the copolymers poly(**3**-*co*-**6**) also gave the diagnostic PFCB pattern.

3. Results and discussion

3.1. Monomer synthesis

Previously reported [11,12] incorporation of the PPO group into trifluorovinyl ether monomers utilized a versatile trifluorovinyl ether containing organometallic reagent [16] and its nucleophilic substitution reaction with phosphorus trichloride and phenylphosphonic dichloride. The initial evaluation of those main chain PPO PFCB polymers has shown encouraging results in terms of AO resistance, solar absorptivity, and thermal emittance measured at NASA Marshall Laboratories [12].

Recent interest [8–10] in pendent PPO polymers for enhanced solubility, low color and better mechanical properties led us to develop a new series of pendent PPO PFCB aryl ether polymers. The starting materials, [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (3-APPO) and 2,5-dihydroxyphenyldiphenylphosphine oxide (2,5-DHPPO) have been used to prepare novel space environment durable polyetherimides (PEIs) and poly(arylene ether)s (PAEs), respectively, by Connell and co-workers [8,9]. Also a novel dianhydride derived from 2,5-DHPPO and a corresponding series of polyimides were prepared [10].

Using these starting materials and our versatile trifluorovinyl aromatic ether intermediates, three new pendent PPO PFCB forming monomers containing the amide (**3**), imine (**4**) and ester (**5**) linkages were prepared as shown in Fig. 2. Commercially available 4-bromo(trifluorovinyloxy) benzene was easily converted to the acid chloride (**1**) and benzaldehyde (**2**) using well established Grignard and aryl lithium chemistry, respectively [15–17]. Condensation with the diamine or bisphenol gave the target monomers in fair to good un-optimized isolated yields.

Fig. 3 shows the ^{1}H NMR spectrum of diamide monomer **3**. Although the compound consists of only aromatic and amide protons, all the signals are surprisingly clearly resolved. Due to the unsymmetrical structure, the two amide proton signals are clearly different and located at 9.34 and 9.06 ppm, respectively. Fig. 4(a)–(c) shows the characterization of monomer **5** by ^{1}H NMR, ^{19}F NMR and MALDI-TOF MS. Interestingly, the fluorine signals for the two trifluorovinyl ether groups are slightly different due to the subtle asymmetry in the molecule (Fig. 4(c)).

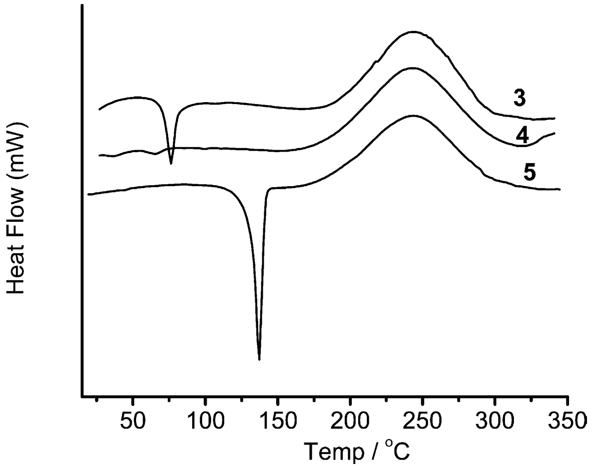

Fig. 6. DSC polymerization of monomers **3**–**5** at 10 °C/min.

3.2. Thermal cyclopolymerization

Upon heating above 150 °C, trifluorovinyl aromatic ether monomers undergo classical step growth [2π+2π] cyclopolymerization giving perfluorocyclobutyl (PFCB) aryl ether polymers [17–20] (Fig. 5). As shown from the DSC graph (Fig. 6), monomers **3** and **5** exhibit melting transitions around 76 and 137 °C, respectively. After melting, exothermic polymerization is detected between 150 and 320 °C corresponding to thermal cyclodimerization, where the exothermic peak reaches a maximum at 250 °C. Polymerization profiles for these PPO monomers (**3**–**5**) are similar to that observed for most other PFCB polymerizations. Subsequent heating in the DSC gave clear and reproducible T_g values of 145 and 217 °C for poly**5** and poly**3**, respectively. A glass transition for imine containing poly**4** was not observed by DSC.

After polymerization, poly**5** was soluble in most organic solvents, such as chloroform and THF, while poly**3** was

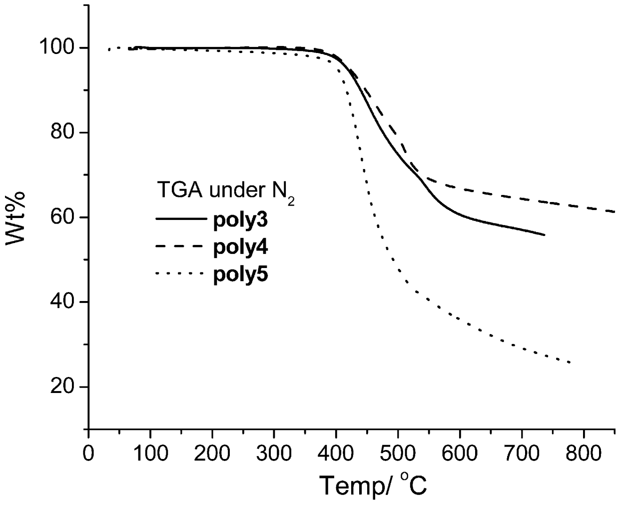

Fig. 7. TGA for poly**3**–**5** in nitrogen at 10 °C/min.

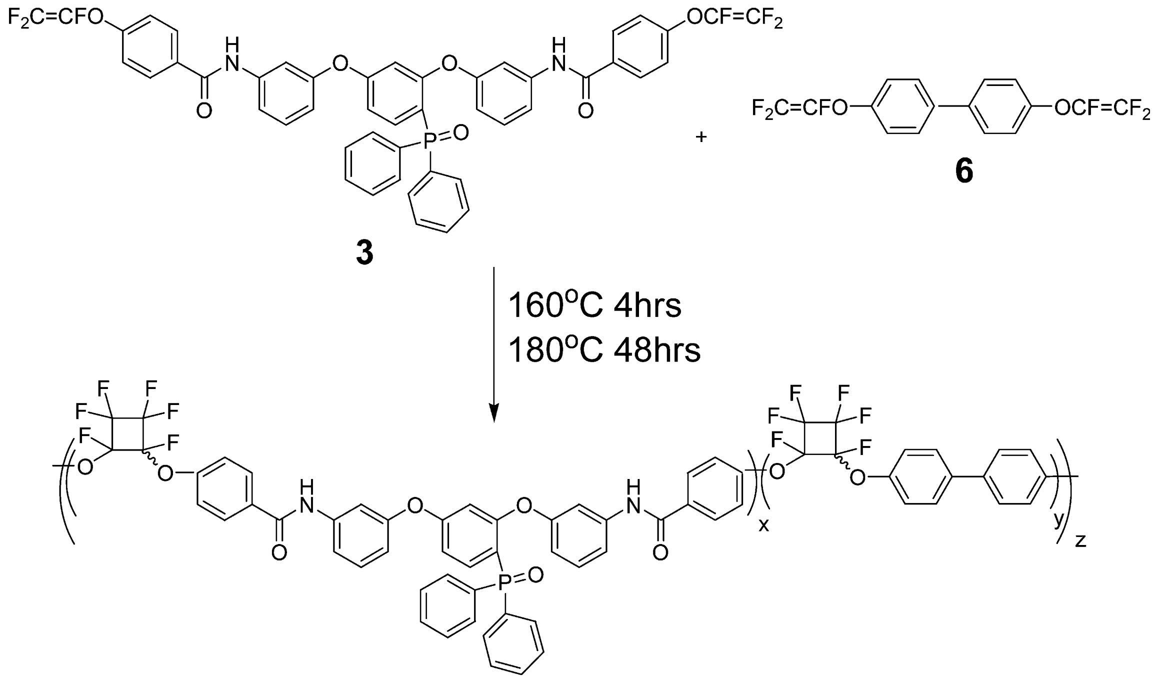

Fig. 8. Copolymerization of PPO containing monomer **3** with 4,4′-(trifluorovinyloxy)biphenyl **6**.

soluble only in polar solvents such as DMF. The imine containing polymer, poly**4**, exhibited poor solubility in common solvents. The GPC analysis in chloroform for poly**5** gave $M_w = 24{,}000$ and $M_w/M_n = 3.4$. The insolubility, lack of T_g and intense dark violet color of **poly4** after polymerization suggests that cross linking through the imine may have occurred. The ^{19}F NMR spectra for the soluble polymers exhibit the typical series of multiplets representing the perfluorocyclobutyl (PFCB) fluorine signals ranging from −126 to −131 ppm.

Fig. 7 depicts the TGA results for poly**3**–**5** under nitrogen. The thermal decomposition temperatures for amide (poly**3**) and imine (poly**4**) linked PFCB polymers are slightly higher than that for the ester linked polymer

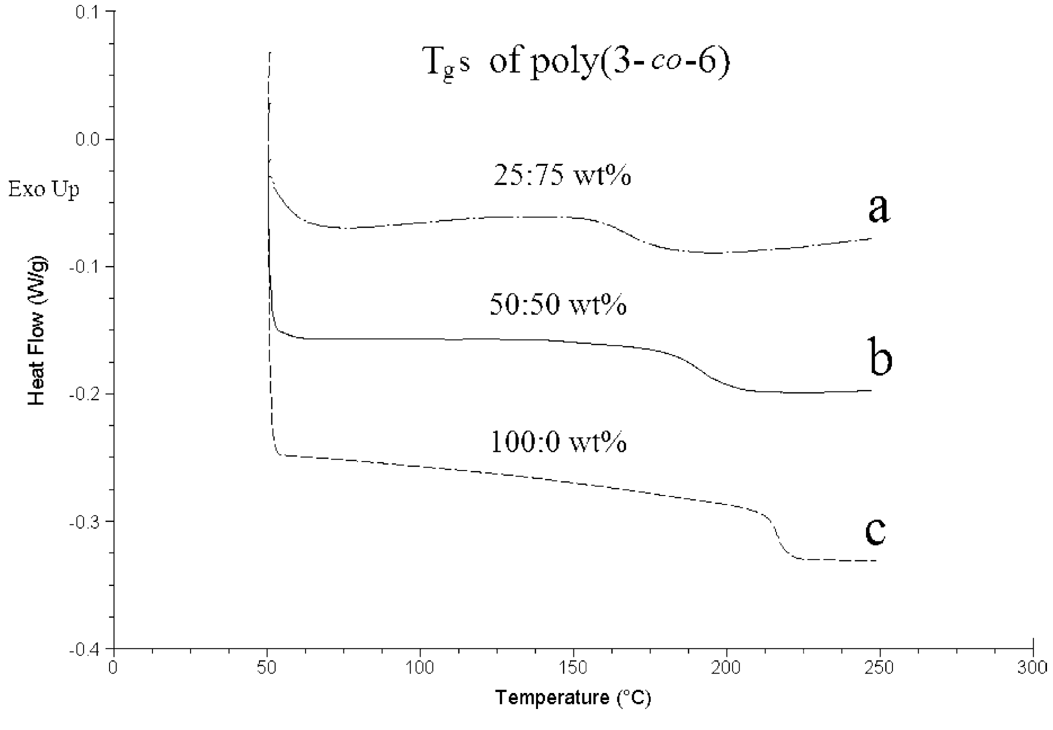

Fig. 9. DSC analysis for poly(**3**-*co*-**6**) at 10 °C/min.

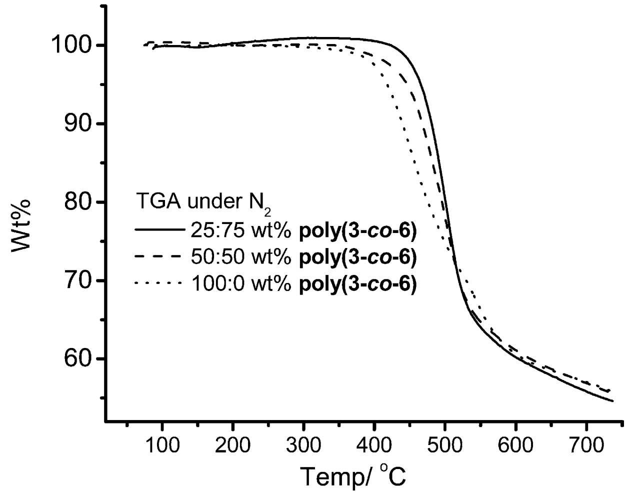

Fig. 10. TGA for poly(**3**-*co*-**6**) at 10 °C/min.

(poly**5**). The temperature at 5% weight loss under nitrogen was measured to be 418, 421 and 402 °C, respectively. Compared to our previously reported main chain PPO PFCB polymers ($T_{d\ 5\ wt\%} > 457$ °C) [12], these pendent PPO polymers are less thermally stable by TGA under these conditions as observed similarly for poly(arylene ether)s mentioned earlier [9]. Although the rate of PPO decomposition should remain relatively constant, a volatile product is more likely when the PPO group is pendant than when imbedded in the main chain.

3.3. Copolymerization with 4,4′-(trifluorovinyloxy)biphenyl

In order to improve the solubility and film forming properties of these PPO pendent PFCB polymers, the reliable strategy of copolymerization with commercial high molecular weight forming and highly soluble trifluorovinyl ether monomers was employed. Fig. 8 depicts the random copolymerization of monomer **3** with 4,4′-(trifluorovinyloxy)biphenyl (**6**). The ^{19}F NMR spectra for the copolymers poly(**3**-*co*-**6**) shows the expected series of multiplets representing the many perfluorocyclobutyl (PFCB) fluorine signals ranging from -126 to -131 ppm. Although it was not possible to determine composition from the ^{19}F NMR data, the ^{1}H NMR spectra provided enough resolution for known aromatic proton signals from both monomer **3** and monomer **6** to estimate the composition which agreed well with the feed ratio (Table 1).

As summarized in Table 1, the molecular weight of the copolymers and thermal stabilities increase with the increasing content of comonomer **6**. Furthermore, copolymer solubility becomes much better as expected. For example, poly(**3**-*co*-**6**) (25:75) is soluble (>50 wt%) in many common organic solvent, such as methylene chloride, chloroform and THF. The low GPC molecular weight measured for poly(**3**-*co*-**6**) (50:50 wt%) is due to partial solubility in chloroform. Transparent and flexible films with slight yellow color were obtained from poly(**3**-*co*-**6**) (25:75). This copolymer exhibited a large polydispersity (6.9) presumably due to thermal gradients and hot spots from poor mixing commonly observed for high temperature bulk polymerization over long periods of time.

Well defined single glass transition temperatures for the copolymers were detected by DSC (Fig. 9) and a reasonable fit with the Fox equation indicated a nearly ideal random copolymerization. Fig. 10 displays the TGA results for the

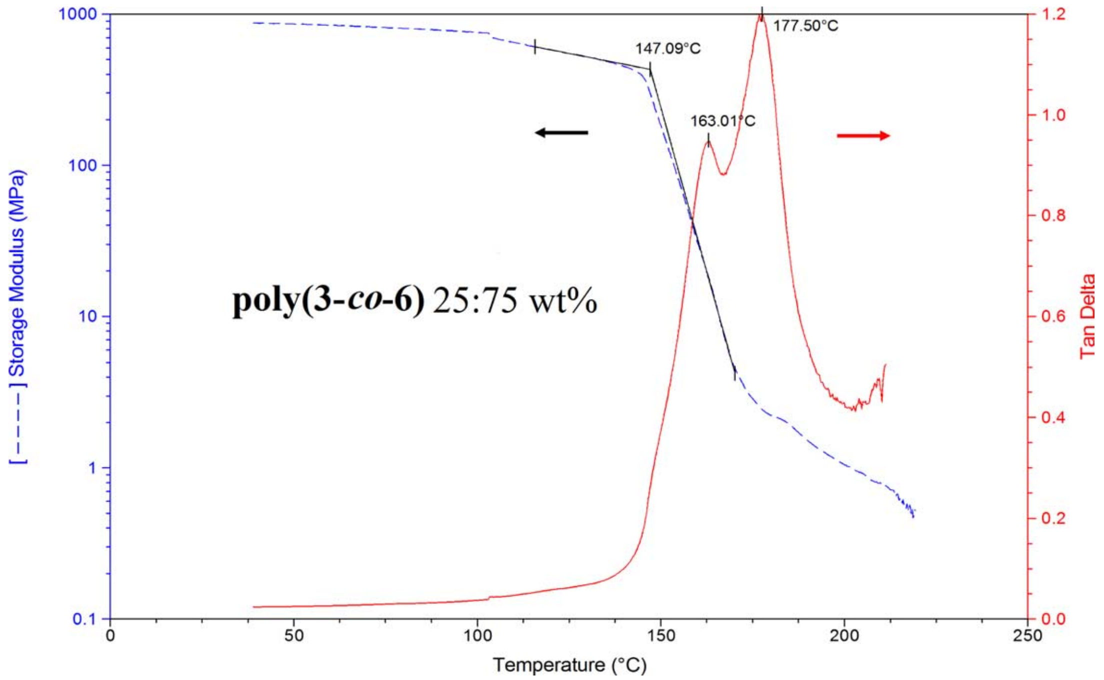

Fig. 11. DMA for poly(**3**-*co*-**6**) (25:75 wt%) (3 °C/min, 1 Hz, tensile mode).

copolymers, where clearly, copolymerization further enhanced thermal stability, presumably due to higher molecular weight and a decrease in pendant PPO groups.

Dynamic mechanical analysis (DMA) was also used to characterize the copolymers due to its greater sensitivity over DSC. Fig. 11 shows the DMA data for poly(**3**-*co*-**6**) (25:75). The onset of decline in the storage modulus occurred at about 147 °C, which corresponds to the glass transition of the copolymer. For the loss curve, two main tan δ peaks can be clearly resolved at 163 and 177.5 °C, respectively. From the Fox equation, a T_g value of 171 °C was predicted compared to the fairly broad glass transition measured at 168 °C by DSC (Fig. 9 curve (a)). Therefore, the DMA data might suggest that poly(**3**-*co*-**6**) is not entirely random and subtle blocks of poly**6** known to possess a T_g ca. 160 °C are detected [20].

4. Conclusions

In summary, three new difunctional trifluorovinyl ether monomers with pendent PPO groups were prepared by simple condensation reactions. The monomers underwent thermal cyclopolymerization to give PFCB polymers with varied solubility and good thermal stability. Pendent PPO PFCB polymers and copolymers exhibit slightly decreased thermal stability in nitrogen than do main chain PPO polymers as expected. Copolymerization with traditional PFCB forming monomers such as 4,4′-(trifluorovinyloxy) biphenyl gave film forming transparent thermoplastic copolymers with improved solubility and further enhanced thermal stability.

Acknowledgements

We thank the Air Force Office of Scientific Research (STTR with Triton Systems, Inc.), the South Carolina NASA Space Grant Consortium, SC EPSCoR, the National Science Foundation (DMR-CAREER Award to DS) for partial support. We also thank Dr John Connell at NASA Langley Research Center for starting materials and Dr Sybille Glaser for MALDI expertise. D. W. Smith Jr, is a Cottrell Scholar of Research Corporation.

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