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Synthesis and characterization of 4-[(per/polyfluoro)phenyloxy]-4′-vinylbiphenyls and their polymers

I.I. Selvaraj, R.L. Kirchmeier, J.M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, ID 84844-2343, USA

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Abstract

4-Trimethylsilyloxy-4′-vinylbiphenyl was treated with perfluorobenzene, substituted polyfluorobenzenes, and perfluoronaphthalene to give 4-[(per/polyfluoro)phenyloxy]-4′-vinylbiphenyls in the presence of catalytic amounts of CsF. The new monomers that resulted were characterized by mass spectra, ^{1}H and ^{19}F NMR, and IR spectroscopy. The new polymers obtained by polymerizing the monomers using AIBN-initiated free radical polymerization were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), ^{1}H and ^{19}F NMR and IR spectroscopies. The polymers were obtained as white powders and were soluble in all common organic solvents. They are thermally very stable and have high glass transition temperatures, T_g, i.e. >100°C. Copolymerization of one of the monomers, 4-pentafluorophenyloxy-4′-vinylbiphenyl, **3**, with different molar ratios of methylacrylate gave copolymers that have low glass transition temperatures compared with the homopolymer of the monomer, **3**, along with very high thermal decomposition temperatures, e.g. incorporation of even a small amount (2.1%) of **3** into the methylacrylate copolymer gave rise to a 50% char yield at 410°C and a glass transition temperature of 28°C.

Keywords: Per/polyfluorobenzenes; Fluoroarylethers; Pendant polymers

1. Introduction

Fluorinated polymers are well known for their potential applications because of their improved properties including enhanced chemical inertness, thermal stability, low surface energy, etc. These properties recommend fluoropolymers as elastomers [1], as nonstick surface coating materials [2,3] and as other high performance materials [4]. Although *p*-hydroxystyrene is an unstable monomer, *p*-hydroxy-*p*′-vinylbiphenyl (HVB) is a very stable monomer. Polymers derived from HVB and their derivatives exhibit very high thermal stability and good insulating properties [5–7]. Phosphazene derivatives of HVB and their polymers are shown to be useful materials in the biomedical field and as solid electrolytes in high density solid state batteries. These properties are governed by the groups substituted on phosphorus [8]. In the present work we have designed HVB derivatives where the fluoroaryloxy group is attached directly to the hydroxyl group in order to determine the effect of these groups on the end polymer. We have synthesized and characterized monomers and their polymers of (per/poly)-fluorophenoxyvinylbiphenyls, and also examined the copolymerization of one of the monomers (**3**) with methylacrylate.

2. Experimental

2.1. Materials

Aluminum chloride, acetyl chloride, sodium borohydride, zinc chloride, trichloroacetic acid, hexamethyldisilazane, hexafluorobenzene, pentafluorobenzonitrile, and octafluorotoluene were used as received. Cesium fluoride was kept in an oven at 160°C prior to use. Methylacrylate was washed with NaOH solution, dried and distilled prior to use. AIBN was recrystallized from methanol prior to use. Tetrahydrofuran (THF), dichloroethane (DCE) and other organic solvents were dried according to the literature procedures before use [9].

2.2. Measurements

^{1}H and ^{19}F NMR spectra were obtained on a Bruker AC200 or Bruker AC300 instrument by using $CDCl_3$ as solvent. Chemical shift values were reported with respect to TMS and CCl_3F for proton and fluorine, respectively. Melting points were obtained using a Meltemp melting

* Corresponding author. Tel.: + 1-208-885-6651; fax: + 1-208-885-6198.

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point apparatus. The melting points reported were uncorrected. Mass spectral data (EI) of monomers were collected by using a Finnigan GCQ or a Varian VG7070 HS mass spectrometer. Accurate mass data were obtained by using a Jeol JMS-AX505HA mass spectrometer. Infrared spectra were recorded on a Perkin–Elmer 1710 FT IR spectrometer either as neat films between KBr plates or as KBr disks. Thermal (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) data were collected using a Perkin–Elmer 7 series thermal analyzer under an argon atmosphere with a heating rate of 20°C/min. Isothermal TGA data were collected using the following conditions: the samples were heated to 200°C, hold time 1 h, further heated to 400°C, hold time 1 h. The heating rate was 10°C/min and the experiments were carried out under an argon atmosphere. The gel permeation chromatography (GPC) data were collected by using polystyrenes having a narrow dispersity as standards on a Waters 410 instrument. Ultrastyragel columns (30 cm × 7.8 mm) were used. UV grade THF was used as solvent at 40°C at a flow rate of 1.0 ml/min. The detector was a Waters 410 Refractive Index.

*2.2.1. Synthesis of 4-trimethylsilyloxy-4′-vinylbiphenyl (**2**)*

To a stirred solution of hydroxyvinylbiphenyl (**1**) (0.50 g) in 20 ml dry toluene, 0.82 g hexamethyldisilazane was added and refluxed for 12 h. After removing most of the solvent and hexamethyldisilazane, **2** was obtained as a yellow semisolid (Scheme 1). MS (EI) *m/z* (species, intensity): 268 (M^+, 100), IR (neat, cm^{-1}): 1602 (m); 1518 (s); 1494 (s); 1472 (m); 1397 (w); 1321 (w); 1233 (m); 1209 (m); 1173 (m); 1026 (m); 999 (s); 923 (m); 823 (m), ^1H NMR (δ): 0.45 ($Si(CH_3)_3$, s, 9H); 5.23, 5.28 (CH_2, d, 1H); 5.73, 5.81 (CH_2, m, 1H); 6.66–6.80 (dd, CH, 1H); 6.98–7.56 (biphenyl, m, 8H).

*2.2.2. Synthesis of 4-pentafluorophenyloxy-4′-vinylbiphenyl (**3**)*

To a stirred solution of **2** (0.68 g, 2.55 mM) and a catalytic amount of dry CsF in dry THF (20 ml), hexafluorobenzene (0.95 g, 5.10 mM) was added and refluxed for 12 h under nitrogen. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexanes and methylene chloride. Product **3** obtained as white solid flakes (yield, 0.50 g, 54%) melts completely at 144°C. MS (EI) *m/z* (species, intensity): 362 (M^+, 100); 336 ($M^+-C_2H_2$, 33). Accurate Mass (found, calculated): 362.0743, 362.0730 IR (KBr, cm^{-1}): 1602 (m); 1518 (s); 1494 (s); 1472 (m); 1397 (w); 1321 (w); 1233 (m); 1209 (m); 1173 (m); 1026 (m); 999 (s); 923 (m); 823 (m), ^1H NMR (δ): 5.23, 5.28 (CH_2, d, 1H); 5.73, 5.81 (CH_2, m, 1H); 6.66–6.80 (dd, CH, 1H); 6.98–7.56 (biphenyl, m, 8H), ^{19}F NMR (δ): −153.96 (2-F, m, 2F); −159.88 (4-F, t, 1F); −162.07 (3-F, t, 2F).

*2.2.3. Synthesis of 4-(p-cyanotetrafluorophenyloxy)-4′-vinylbiphenyl (**4**) and 4-(o-cyanotetrafluorophenyloxy)-4′-vinylbiphenyl (**4a**)*

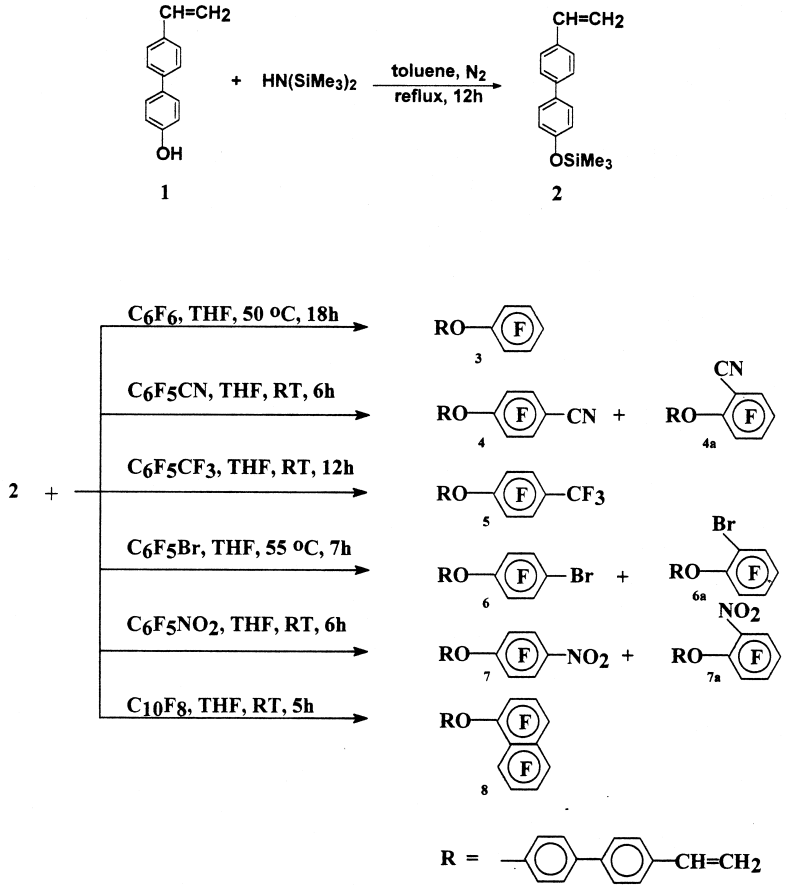
To a stirred solution of **2** (0.68 g, 2.55 mmol) and a catalytic amount of dry CsF in dry THF (20 ml), pentafluorobenzonitrile (1.00 g, 5.10 mmol) was added and stirred for 6 h under nitrogen. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexane : methylene chloride. The product was a mixture of **4** and **4a** (4 : 1 ratio) obtained as white flakes (yield, 0.40 g, 43%) that melt completely at 128°C. MS (EI) *m/z* (species, intensity): 369 (M^+, 66); 195 ($M^+-C_6F_4CN$, 100); 178 ($M^+-C_6F_4CN-OH$, 57), IR (cm^{-1}, KBr): 2246 (m); 1654 (m); 1627 (m); 1494 (s); 1443 (m); 1398 (m); 1320 (w); 1265 (s); 1233 (s); 1208 (s); 1191 (m); 1173 (s); 1122 (s); 997 (s); 957 (s); 926 (s); 822 (s), ^1H NMR (δ): 5.23, 5.28 (d, CH_2, 1H); 5.73, 5.81 (d, CH_2, 1H); 6.66–6.80 (dd, CH, 1H); 6.98–7.56 (m, biphenyl,8H), ^{19}F NMR (δ): for **4**: −132.51 (2-F, m, 2F); −150.55 (3F, m, 2F). For **4a**: −131.4 (6-F, td, 1F); −143.61 (5-F, t, 1F); −149.1 (3-F, dd, 1F); −157.69 (4-F, t, 1F).

*2.2.4. Synthesis of 4-[p-(trifluoromethyl)tetrafluorophenyloxy]-4′-vinylbiphenyl (**5**)*

To a stirred solution of **2** (0.68 g, 2.55 mM) and a catalytic amount of dry CsF in dry THF (20 ml), octafluorotoluene (1.20 g, 5.1 mM) was added and stirred for 6 h under nitrogen. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexanes : methylene chloride. The product **5** obtained as white flakes (yield, 0.70 g, 67%) melts at 125°C. MS (EI) *m/z* (species, intensity): 412 (M^+, 82); 195 ($M^+-C_6F_4CF_3$, 100), Accurate Mass (found, calculated): 412.0690, 412.0698, IR (cm^{-1}, KBr): 3038 (w); 1658 (s); 1629 (m); 1600 (s); 1502 (vs); 1430 (s); 1398 (m); 1342 (vs); 1314 (m); 1265 (w); 1237 (vs); 1183 (vs); 1153 (vs); 1082 (w); 997 (vs); 921 (s); 884 (s); 828 (s); 752 (w); 717 (s); 605 (w); 478 (m), ^1H NMR (δ): 5.23, 5.28 (d, CH_2, 1H); 5.73, 5.81 (d, CH_2, 1H); 6.66–6.80 (dd, CH, 1H); 6.98–7.56 (m, biphenyl, 8H), ^{19}F NMR (δ): −56.00 (CF_3, t, 3F); −140.36 (2-F, m, 2F); −151.90 (3F, m, 2F).

*2.2.5. Synthesis of 4-(p-bromotetrafluorophenyloxy)-4′-vinylbiphenyl (**6**) and 4-(o-bromotetrafluorophenyloxy)-4′-vinylbiphenyl (**6a**)*

To a stirred solution of **2** (0.68 g, 2.55 mM) and a catalytic amount of dry CsF in dry THF (20 ml), bromopentafluorobenzene (1.20 g, 5.1 mM) was added and stirred for 7 h at 55°C under nitrogen. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexane : methylene chloride. The product **6** obtained as white flakes (yield, 0.36 g, 33%) melts at 146–48°C. MS (EI) *m/z* (species, intensity): 422 (M^+, 31); 195 ($M^+-C_6F_4Br$, 100), 178 ($M^+-C_6F_4Br-OH$, 72), Accurate Mass (found, calculated): 421.9906, 421.9929 and 423.9898, 423.9911, IR (cm^{-1}, KBr): 3038 (w); 1627

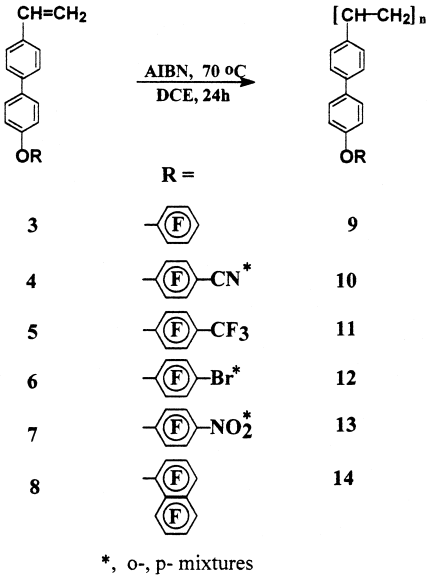


Scheme 1.

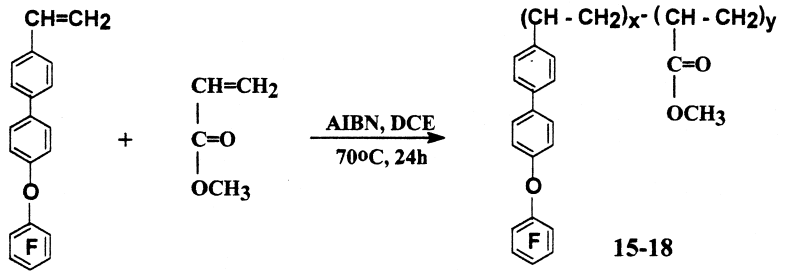
(m); 1601 (m); 1526 (w); 1495 (vs); 1487 (vs); 1397 (m); 1282 (w); 1223 (s); 1209 (s); 1192 (s); 1171 (m); 1132 (s); 1081 (s); 994 (s); 982 (s); 922 (s); 884 (s); 829 (s), ^{1}H NMR (δ): 5.23, 5.28 (d, CH_2, 1H); 5.73, 5.81 (d, CH_2, 1H); 6.66–6.80 (dd, CH, 1H); 6.98–7.56 (m, biphenyl, 8H), ^{19}F NMR (δ): for **6**, −133.29 (2-F, m, 2F); −152.77 (3F, m 2F), for **6a**, −131.12 (m, 1F); −150.85 (m, 1F); −154.98 (m, 1F); −158.29 (m, 1F).

2.2.6. Synthesis of 4-(p-nitrotetrafluorophenyloxy)-4′-vinylbiphenyl (7) and 4-(o-nitrotetrafluorophenyloxy)-4′-vinylbiphenyl (7a)

To a stirred solution of **2** (0.68 g, 2.55 mM) and a catalytic amount of dry CsF in dry THF (20 ml), pentafluoronitrobenzene (1.00 g, 5.10 mM) was added and stirred for 6 h under nitrogen. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexanes : methylene chloride. The product was a mixture of **7** and **7a** (4 : 1 ratio) obtained as white flakes (yield, 0.40 g, 43%) that melt completely at 114°C. MS (EI) *m/z* (species, intensity): 389 (M^+, 27); 195 (M^+–$C_6F_4NO_2$, 100); 178 (M^+–$C_6F_4NO_2$–OH, 78); 152 (M^+–$C_6F_4NO_2$–OH–O), IR (cm^{-1}, KBr): 1633 (m); 1601 (m); 1559 (vs); 1495 (m); 1415 (m); 1398 (m); 1360 (s); 1232 (m); 1208 (s); 1191 (m); 1174 (m); 1152 (m); 1109 (m); 1010 (s); 939 (m); 917 (m); 824 (s); 770 (m); 610 (w), ^{1}H NMR (δ): 5.23, 5.28 (d, CH_2, 1H); 5.73, 5.81 (d, CH_2, 1H);



Scheme 2.



Scheme 3.

6.66–6.80 (dd, CH, 1H); 6.98–7.56 (m, biphenyl,8H), ^{19}F NMR (δ): −145.97 (m); −146.48 (m); −148.33 (m); −150.58 (m); −156.88 (m).

2.2.7. Synthesis of 4-perfluoronaphthyloxy-4′-vinylbiphenyl (8)

To a stirred solution of 2 (0.68 g, 2.55 mM) and a catalytic amount of dry CsF in dry THF (20 ml), octafluoronaphthalene (1.38 g, 5 × 10 mM) was added and stirred for 12 h in nitrogen atmosphere. The oil obtained after removing THF was subjected to silica gel column chromatography by using a 5 : 1 mixture of hexane : methylene chloride. The product **8** obtained as white flakes (yield, 0.40 g, 39%) melts completely at 164°C. MS (EI) *m/z* (species, intensity): 448 (M^+, 100); 178 (M^+–$C_{10}F_7$–OH, 12), IR (cm^{-1}, KBr): 1653 (vs); 1602 (m); 1526 (m); 1495 (s); 1487 (s); 1463 (vs); 1408 (vs); 1240 (m); 1231 (m); 1217 (s); 1119 (s); 994 (m); 948 (vs); 913 (m); 830 (s), ^{1}H NMR (δ): 5.23, 5.28 (d, CH**2**, 1H); 5.73, 5.81 (d, CH_2, 1H); 6.66–6.80 (dd, CH, 1H); 7.02–7.56 (m, biphenyl, 8H), ^{19}F NMR (δ): −135.58 (dd); −144.98 (td); −146.29 (m); −146.82 (b,m); −154.15 (t); −154.67 (b,m).

2.3. Polymerization of monomers 3–8

In thick-walled vacuum sealed glass tubes the desired amount of the respective monomers and 2% AIBN were taken in 10 ml of DCE (Scheme 2). After the tube was heated at 70°C for 24 h, it was cooled to room temperature, opened and poured into large amounts of hexanes to precipitate the polymer. The polymers were dissolved in methylene chloride and reprecipitated by pouring into hexanes. Polymers **9**–**12**, and **14** were obtained as white powders from **3**–**6**, and **8**, respectively and **13** as a yellow powder from **7** after drying at an ambient temperature.

2.3.1. Spectral data for polymer 9

Yield, 40%, IR (KBr, cm^{-1}): 1602 (m); 1518 (s); 1494 (s); 1472 (m); 1397 (w); 1321 (w); 1233 (m); 1209 (m); 1173 (m); 1026 (m); 999 (s); 923 (m); 823 (m), ^{1}H NMR (δ): 0.80–2.0 (broad, m, CH–CH_2, 3H); 6.38–7.56 (broad, biphenyl, m, 8H), ^{19}F NMR (δ): −154.47 (b, 2-F, 2F); −159.98 (b, 4-F, 1F); −162.22 (b, 3-F, 2F).

2.3.2. Spectral data for polymer 10

Yield, 59%, IR (cm^{-1}, KBr): 3027 (m); 2925 (m); 2246 (m); 1650 (s); 1641 (s); 1561 (m); 1492 (vs); 1440 (s); 1400 (m); 1321 (m); 1265 (m); 1207 (vs); 1173 (s); 1123 (s); 1000 (vs); 959 (s); 819 (s); 567 (w); 524 (w), ^{1}H NMR (δ): 0.80–2.0 (broad, m, CH–CH2, 3H); 6.38–7.56 (broad, biphenyl, m, 8H), ^{19}F NMR (δ): −132.06 (2-F, m, 2F); −150.05 (3F, m, 2F) and −131.31 (6-F, 1F); −142.24 (5-F, 1F); −148.95 (3-F, 1F); −157.89 (4-F, 1F).

2.3.3. Spectral data for polymer 11

Yield, 40%, IR (cm^{-1}, KBr): 3037 (w); 1656 (s); 1600 (s); 1505 (vs); 1494 (s); 1430 (s); 1398 (m); 1348 (vs); 1310 (m); 1237 (vs); 1196 (vs); 1170 (vs); 1049 (w); 999 (vs); 921 (s); 884 (s); 828 (s); 819 (s); 744 (w); 717 (s); 603 (w); 568 (m); 499 (m), ^{1}H NMR (δ): 0.80–2.0 (b, m, CH–CH2, 3H); 6.98–7.56 (b, m, biphenyl, 8H), ^{19}F NMR (δ): −56.25 (CF_3, 3F); −140.48 (2-F, 2F); −152.52 (3F, 2F).

2.3.4. Spectral data for polymer 12

Yield, 50%, IR (cm^{-1}, KBr): 3026 (w); 2924 (s); 1604 (s); 1483 (vs); 1400 (m); 1282 (s); 1210 (vs); 1196 (vs); 1171 (vs); 1081 (vs); 1005 (vs); 982 (vs); 847 (vs); 821 (vs), ^{1}H NMR (δ): 0.80–2.0 (b, m, CH–CH_2, 3H); 6.98–7.56 (b, m, biphenyl, 8H), ^{19}F NMR (δ): −130.67 (b); −132.88 (b); −150.77 (b); −152.64 (b); −154.66 (b); −157.89 (b).

Table 1
Experimental details of the copolymerization of monomer **3** with methylacrylate

Copolymer	Monomer **3**, g (mmol)	Methylacrylate, g (mmol)	Yield (g, wt. %)
15	0.200 (0.55)	0.143 (1.66)	0.075, 22
16	0.200 (0.55)	0.095 (1.10)	0.070, 24
17	0.100 (0.27)	0.240 (2.79)	0.100, 30
18	0.050 (0.14)	0.300 (3.49)	0.120, 34

Table 2
Copolymer compositions and thermal and molecular weight data of copolymers **15**–**18**

Copolymer	Monomer **3**, mol%		$M_N \times 10^4$	$M_W \times 10^4$	M_W/M_N[b]	TGA (°C)[c]	50% char yield at (°C)	T_g (°C)
	In feed	In copolymer[a]						
15	25.0	52.0	5.3	7.2	1.36	417	490	93
16	33.3	68.4	5.7	8.4	1.46	380	478	97
17	9.0	5.8	5.7	11.7	2.06	385	415	—[d]
18	4.0	2.1	5.1	12.6	2.47	356	410	28

[a] From proton NMR.
[b] From GPC.
[c] Onset temperature.
[d] T_g was not detected in DSC.

*2.3.5. Spectral data for polymer **13***

Yield, 50%, IR (cm^{-1}, KBr): 3025 (w); 1632 (m); 1600 (m); 1557 (vs); 1500 (m); 1415 (m); 1400 (m); 1360 (s); 1230 (m); 1208 (s); 1191 (m); 1152 (m); 1109 (m); 1011 (s); 939 (m); 919 (m); 824 (s), ^{1}H NMR (δ): 0.80–2.0 (b, m, CH–CH_2, 3H); 6.98–7.56 (b, m, biphenyl, 8H), ^{19}F NMR (δ): −146.02 (b); −146.48 (b); −148.21 (b); −150.54 (b); −156.58 (b).

*2.3.6. Spectral data for polymer **14***

Yield, 40%, IR (cm^{-1}, KBr): 3037 (w); 1656 (s); 1600 (s); 1505 (vs); 1494 (s); 1430 (s); 1398 (m); 1348 (vs); 1310 (m); 1237 (vs); 1196 (vs); 1170 (vs); 1049 (w); 999 (vs); 921 (s); 884 (s); 828 (s); 819 (s); 744 (w); 717 (s); 603 (w); 568 (m); 499 (m), ^{1}H NMR (δ): 0.83–2.00 (b, m, CH–CH_2, 3H); 6.55–7.60 (b, m, biphenyl, 8H), ^{19}F NMR (δ): −56.25 (CF_3, 3F); −136.04 (b); −145.09 (b); −145.98 (b); −147.20 (b); −154.06 (b); −154.66 (b).

*2.4. Copolymerization of monomer **3** with methylacrylate*

2.4.1. General procedure

In a thick-walled vacuum sealed glass tube known amounts of the monomer **3** and methylacrylate and 2% AIBN were taken in 10 ml of DCE (Scheme 3). The tubes were heated at 70°C for 24 h. The tubes were cooled to room temperature, opened and poured into large amounts of hexane to precipitate the copolymers. Reprecipitation was performed twice by dissolving the copolymers in methylene chloride and pouring into hexanes. Table 1 gives the amount of the monomer **3** and methylacrylate used. The copolymers **15**–**18** were obtained as white powders after drying at an ambient temperature. The composition of monomers in the feed and in copolymers are tabulated in Table 2.

*2.5. Spectral data for copolymers **15**–**18***

*2.5.1. Copolymer **15***

^{1}H NMR (δ): 7.80–6.50 (m, b, biphenyl); 3.00–3.80 (m, b, –OCH_3); 1.00–2.50 (m, b, –CH–CH_2), ^{19}F NMR (δ): −154.20 (b, 2-F, 2F); −159.97 (b, 4-F, 1F); −162.11 (b, 3-F, 2F), IR (cm^{-1}): 3443 (m); 2951 (s); 1736 (vs); 1655 (m); 1605 (s); 1518.5 (vs); 1494 (vs); 1472 (s); 1450 (s);, 1400 (m); 1376 (m); 1319 (s); 1212 (vs); 1173 (vs); 1109 (m); 1021 (s); 1000 (vs); 821 (s); 570 (m); 524 (m).

*2.5.2. Copolymer **16***

^{1}H NMR (δ): 7.80–6.50 (m, b, biphenyl); 3.00–3.80 (m, b, –OCH_3); 1.00–2.50 (m, b, –CH–CH_2), ^{19}F NMR (δ): −154.23 (b, 2-F, 2F); −159.98 (b, 4-F, 1F); −162.17 (b, 3-F, 2F), IR (cm^{-1}): 3437 (m); 1735 (vs); 1605 (s); 1518 (vs); 1494 (vs); 1472 (s); 1450 (s);, 1400 (m); 1376 (m); 1319 (s); 1212 (vs); 1173 (vs); 1109 (m); 1020 (s); 1000 (vs); 821 (s); 568 (m); 524 (m).

*2.5.3. Copolymer **17***

^{1}H NMR (δ): 7.60–6.70 (m, b, biphenyl); 3.20–3.70 (m, b, –OCH_3); 1.10–2.50 (m, b, –CH–CH_2), ^{19}F NMR (δ): −154.17 (b, 2-F, 2F); −159.98 (b, 4-F, 1F); −162.13 (b, 3-F, 2F), IR (cm^{-1}): 3059 (m); 3000 (m); 2956 (s); 1736 (vs); 1605 (s); 1520 (vs); 1496 (vs); 1439 (s); 1381 (s); 1198 (vs); 1163 (vs); 1114 (s); 1059 (s); 1022 (s); 999 (vs); 827 (s); 571 (w); 527 (w).

*2.5.4. Copolymer **18***

^{1}H NMR (δ): 7.60–6.70 (m, b, biphenyl); 3.20–3.70 (m, b, –OCH_3); 1.10–2.50 (m, b, –CH–CH_2), ^{19}F NMR (δ): −154.11 (b, 2-F, 2F); −159.94 (b, 4-F, 1F); −162.12 (b, 3-F, 2F), IR (cm^{-1}): 3059 (m); 3000 (m); 2956 (s); 1736 (vs); 1605 (s); 1520 (vs); 1496 (vs); 1439 (s); 1381 (s); 1198 (vs); 1163 (vs); 1114 (s); 1059 (s); 1022 (s); 999 (vs); 827 (s); 571 (w); 527 (w).

3. Results and discussion

3.1. Synthesis of monomers

4-Hydroxy-4′-vinylbiphenyl (HVB, **1**) was synthesized by previously described procedure [10], and the syntheses of the monomers **3**–**8** are detailed in Scheme 1. Recently we reported an easier way to make fluorinated aryl ethers starting from pentafluorophenyl trimethylsilyl ethers and fluorobenzenes under very mild conditions by using CsF as a

Table 3
The molecular weight data and thermal data of homopolymers **9**–**14**

Polymer	$\overline{M}_N$ ($\times 10^4$)	$\overline{M}_W$ ($\times 10^4$)	$\overline{M}_W/\overline{M}_N$[a]	TGA (°C)[c]	50% char yield (°C)	T_g (°C)
9	29.7	38.9	1.31[b]	439	484	117
	4.7	5.8	1.27			
10	6.9	19.9	2.87	514	514	137
11	12.5	21.2	1.70	417	481	109
12	5.7	9.7	1.69	451	486	86
13	1.8	2.1	1.14	260	747	—[d]
14	5.8	10.0	2.17	432	494	—[d]

[a] From GPC.
[b] Bimodal distribution.
[c] Onset temperature.
[d] T_g was not detected in DSC.

catalyst [11]. This method was utilized in the synthesis of the title compounds by treating trimethysilyloxyvinylbiphenyl with two equivalents of hexafluorobenzene or other substituted fluorobenzenes. The reaction conditions required were a function of the substituents on the benzene ring, e.g. while there was no reaction with hexafluorobenzene and bromopentafluorobenzene at room temperature, the reaction proceeded at 55°C. However, the cyano-, trifluoromethyl- and nitro-substituted fluorobenzenes and perfluoronaphthalene reacted at room temperature. Earlier we had reported that trimethylsilyloxy-pentafluorobenzene did not react with hexafluorobenzene even at reflux for several days [11], and with other substituted fluorobenzenes, many days at reflux were required.

All of the monomers were obtained either as white flakes or fibrous solids after purification by silica gel column chromatography by using a hexane–methylene chloride solvent mixture in the ratio 5 : 1. Attempts to grow crystals for single crystal X-ray diffraction study failed. In the case of the cyano, nitro, and bromo derivatives both the *ortho*- and *para*-substituted products were formed. Although fluorine NMR spectra showed distinct peaks for the *para*- and *ortho*-substituted products for cyano and bromo derivatives, in the case of the nitro and naphthalene derivatives it was not

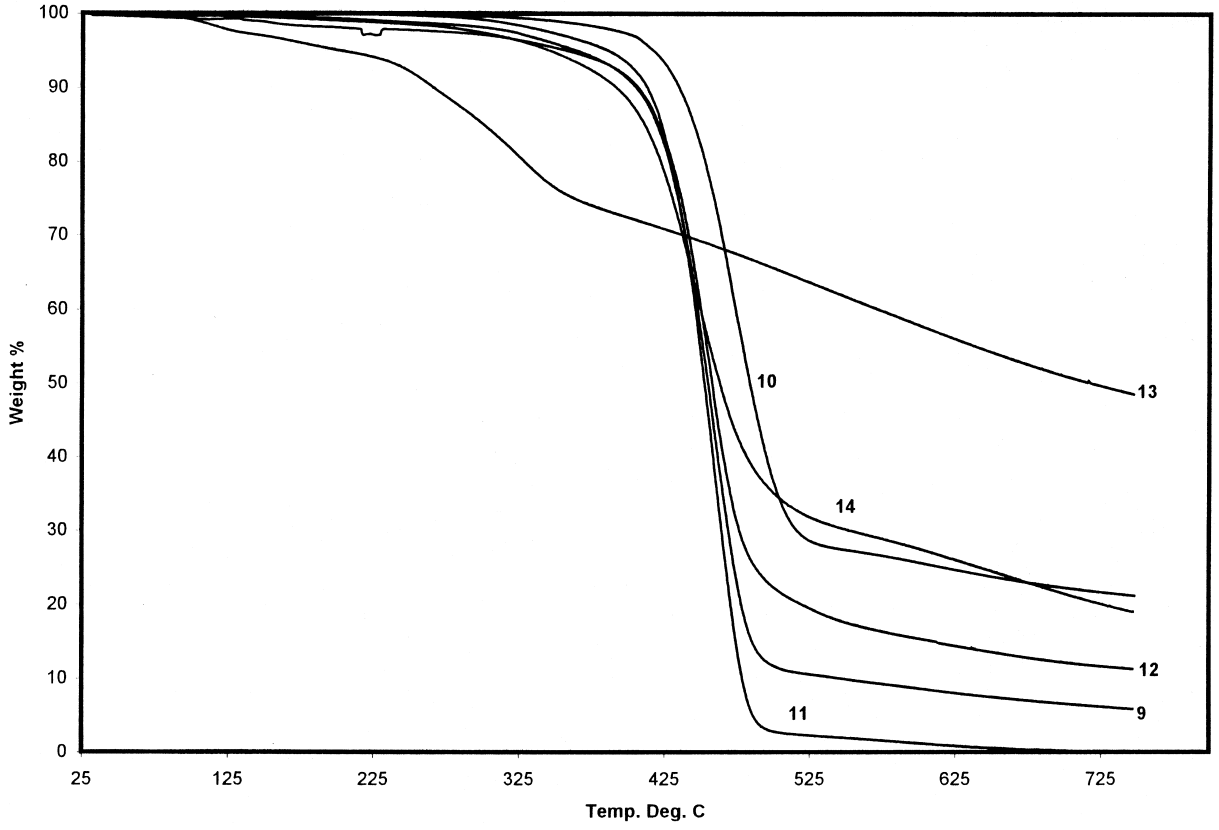


Fig. 1. Thermal analysis curves for the homopolymers **1**–**14**.

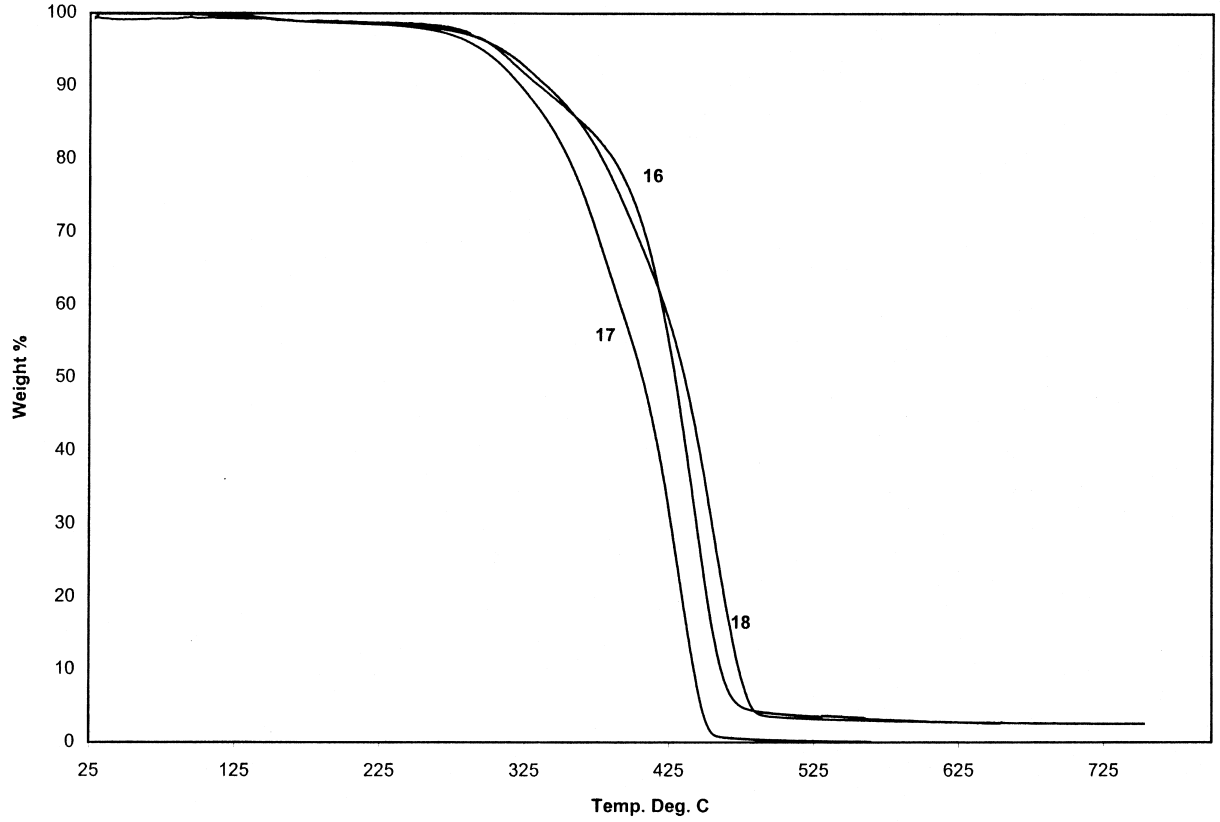


Fig. 2. Thermal analysis curves for the copolymers **16**–**18**.

possible to determine the ratio of *ortho* and *para* products. Each product (*ortho* and *para*) showed two identical peaks in the GC–MS spectrum with the same parent ion, although the fragmentation patterns differed. As we could not achieve separation by column chromatography, the mixture of *ortho* and *para* isomers was used for polymerization.

3.2. Polymer synthesis and characterization

The polymerization of monomers is described in Scheme 2. Except for the nitropolymer, **13**, all are obtained as white powders and are soluble in almost all common organic solvents, such as methylene chloride, chloroform, THF, etc., and insoluble in hydrocarbons, such as hexanes. Attempts to make thin films by solution casting revealed that these polymers were brittle. The maximum yield by free radical polymerization was not more than 40% and for **13** the yield was less than 10%. Even increasing the polymerization time (36 h) did not increase the yield. This might be attributed to the presence of the nitro group in the monomer. The polymers were characterized by proton and fluorine NMR and IR spectral methods. The absence of the vinyl functionality was confirmed by proton NMR and IR spectral data including the appearance of alkyl protons in the proton NMR spectra. Also, polymers **10** and **12**–**14** are mixtures derived from *para*- and *ortho*- isomers and copolymers of the two isomers which are not separable and cannot be differentiated by proton or fluorine NMR. Thus in Scheme 2 only the *para*-isomers are shown as reactants.

Molecular weight data and thermal data of the homopolymers **9**–**14** are summarized in Table 3 (see Fig. 1 for the thermal analysis curve for the homopolymers **9**–**14**). The molecular weights of the polymers obtained by GPC are functions of the substituent on the fluorophenoxy group. For example, with no substitution, **9** showed the highest molecular weight and the others in the order **11** > **14** > **10** > **12** > **13** corresponding to the groups CF_3, C_8F_7, CN, Br, and NO_2. Based on the low yield obtained for **13**, it is not surprising that the degree of polymerization was found to be very low. Thermogravimetric analyses showed that the polymers were thermally very stable. Two different heating rates (20°C and 10°C) were employed to demonstrate that the rate of heating did not alter the thermal behavior of decomposition. There was little decomposition observed up to at least 400°C for all the polymers. Although polymers **9** and **11** are almost completely decomposed above 600°C, polymers **10** and **12**–**14** have a char yield of 21%, 11%, 48% and 19% at 800°C, respectively. Among all the polymers reported here the best thermal behavior is observed for the nitro-derivative, **13**. In the case of **10** and **13** the higher char yield can be attributed to the presence of the cyano- and nitro-groups in the fluorinated phenyl ring where formation of carbon nitrides are well known thermally stable materials. The isothermal TGA result obtained for homopolymer

10 revealed that there was only 0.8% decomposition observed even after heating the sample at 200°C for 1 h. At 400°C the char yield was 95.5% and heating at 400°C for 1 h yielded 68.1% char. This clearly indicates that these polymers are more thermally stable than any simple organic polymers, such as polystyrene, polyalkylacrylates etc. Based on the DSC data all of the polymers have glass transition temperatures above 100°C and the absence of any melting endotherms revealed that these polymers were amorphous in nature. As expected with this rather high T_g, the materials were brittle and not surprisingly, attempts to carry out coating experiments were unsuccessful. In an effort to reduce the T_g, copolymers of **3** with methylacrylate were synthesized.

3.3. Copolymer synthesis and characterization

In Scheme 3 the copolymerization conditions are summarized. All of the copolymers are obtained as white powders and they are readily soluble in all common organic solvents except for hydrocarbons, such as hexanes. In Table 2, the composition of **3** in the feed and in the copolymer, the molecular weights and the thermal data of the copolymers are given. The amounts of monomer **3** incorporated in the copolymers **15** and **16** were analogous to previously reported copolymers of HVB and its derivatives, i.e. just as with HVB, the monomers reported here prefer to homopolymerize rather than to copolymerize with the methylacrylate monomer. The same trend was reported earlier even when electron withdrawing cyclophosphazenes were the pendant groups rather than fluoroaryl or naphthalene. However, in the case of copolymers **17** and **18**, the incorporation of **3** in the copolymer is less than the feed composition. This might be because of the small amount of monomer **3** available or to the excess of methylacrylate. The copolymers were characterized by proton and fluorine NMR, and IR spectral methods. The vinyl functionality was absent in the proton NMR and IR spectra. Also, the acrylate carbonyl stretching frequency was observed in the IR spectra. The thermogravimetric data showed that the thermal stability was very similar to that of the homopolymer of **3** (see Fig. 2 for the thermal analysis curves for the copolymers **16**–**18**). Even with the least amount (2.1%) of **3**, incorporated into the copolymer e.g. copolymer **18**, the material was thermally very stable. The isothermal TGA data obtained for copolymer **17**, where the incorporation of **3** was only 5.8%, show that even after maintaining at 200°C for 1 h the char yield was 98.5%. Further heating to 400°C gave a 71.5% char yield. This indicates that even 5.8% incorporation of monomer **3** into the methylacrylate copolymer imparts a greater thermal stability to the polymethylacrylate. However when the copolymer is heated at 400°C for 1 h, it produced 16.4% char. The results obtained by using differential scanning calorimetry showed that the T_g was lower than that of the homopolymer **9** and this is attributed to the presence of methylacrylate in the copolymers. The lowest T_g (28°C) was obtained for copolymer **18**. Also all the copolymers were amorphous materials based on the absence of any melting endotherms in the DSC results. Based on the GPC data the number average molecular weights, $\overline{M}_N$ of all the copolymers are in the range 5.1×10^4–5.7×10^4. The polydispersity was 1.36 and 1.46 where the incorporation of **3** was more than 50% and 2.06 and 2.47 where the composition of methylacrylate is in excess.

4. Conclusion

Six styrene derivative monomers and their polymers containing (per/poly)fluoroaryloxy groups as pendant groups were synthesized and characterized. An easier and convenient synthetic method was used by treating the trimethylsilylether with perfluorobenzenes in the presence of catalytic amounts of CsF. The polymers were soluble in most common organic solvents and showed very good thermal properties. Copolymers of these monomers with methylacrylate appear to be thermally stable materials having low T_g. Studies involving surface properties and surface morphology of these polymers are underway in our laboratory.

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