Synthesis of Novel Copoly(ether ether ketones): Property Evaluation and Microstructure Analysis by NMR

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ABSTRACT: A series of copolymers were prepared by the reaction of various bisphenols with a 50:50 molar ratio of two bisfluoro compounds, 4,4′-bis(1-fluoro-2-trifluoromethyl benzyl) benzene and 4,4′-difluorobenzophenone. The synthesized polymers were well characterized for their thermal, mechanical, and electrical performances. The copolymers showed a better set of properties than their analogous homopolymers derived from 4,4′-bis(1-fluoro-2-trifluoromethyl benzyl) benzene and bisphenols. The microstructures of the copolymers were analyzed by ^{1}H-, ^{13}C-, ^{19}F-, distortionless enhancement by polarization transfer 90, two-dimensional ^{1}H–^{1}H homonuclear correlation spectroscopy, and ^{13}C–^{1}H correlation spectroscopy NMR techniques. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1292–1305, 2005

Key words: NMR; mechanical properties; dielectric properties

INTRODUCTION

Aromatic poly(ether ketones) (PEKs) can be prepared via electrophilic or nucleophilic polycondensation.[1,2] PEKs are well known as high-performance engineering thermoplastics because of their high thermal stability, good solvent resistance, and excellent mechanical properties.[3–5] Since the commercialization of poly(ether ether ketone) (PEEK)[6] by ICI in 1977, a number of new PEKs have been synthesized in an effort to improve their overall properties.[7–9]

PEEK is a condensation product of 1,4-dihydroxy benzene and 4,4′-difluorobenzophenone. PEEK is used widely in aerospace fields as a matrix resin for advanced composites[7] and in the electronics industry.[10] However, PEEK cannot be processed by casting from a solvent because of its low solubility, and it requires a high molding temperature because of its high melting temperature (T_m), around 340°C. In addition, it has a fairly low glass-transition temperature (T_g 143°C), and its dimensional stability is relatively low because it is semicrystalline.[7]

Many studies have been carried out to improve the low solubility, high T_m (i.e., low processability), and low T_g of PEEK.[3–5,7–9] Replacement of the 1,4-phenylene group in PEEK with a 4, 4′-biphenylene[11] group raised the T_g. However, the polymer was highly crystalline and has not gained commercial value because of its extremely high T_m (395°C). Hergenorther synthesized PEKs containing 2,6-substitution on the naphthalene unit. These polymers possessed higher T_g's but lower solubilities in organic solvents.[12] Wang and coworkers prepared PEKs containing the unsymmetrical benzonaphthone[13] and 1,8-dibenzoylnaphthalene[14] units, which showed high T_g's and improved solubility. Endo et al. reported PEKs containing 2,6-dimethyl-1,5-naphthalene.[15,16] These polymers had higher T_g's but decreased thermal stability. Yoshida and Hay reported soluble PEKs[17] containing 1,5-dibenzoylnaphthalene units. Ritter and Thorwirth[18] synthesized 1,5-naphthylene based PEKs endowed with long alkoxy side chains. The introduction of long alkoxy side chains enhanced the solubility of PEKs remarkably. However, these polymers were thermally less stable because of oxidizable alkoxy groups. Maier and coworkers[19,20] reported several indane-based PEKs with good solubility. The reported polymers were amorphous in nature and showed high T_g's but poor thermooxidative stability.

The introduction of fluorine into a polymer can result in a significant change in the polymer's properties. The insertion of fluorine or fluorine-

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containing moieties into the macromolecular chain increases solubility, thermal stability, flame resistance, T_g, and optical transparency and decreases crystallinity, the dielectric constant, water absorption, and color.[21,22] Several semifluorinated PEKs have been prepared by several researchers[23–27] that showed improved properties in comparison to their nonfluorinated analogues.

Copolymerization is particularly attractive because the tailoring of the properties of the resulting polymers is possible even on a molecular level. In this article, we report a detailed synthesis and characterization of novel processable copoly(ether ketones) with one semifluorinated comonomer, 1,4-bis(4-fluoro-3-trifluorometthy benzyl) benzene.

EXPERIMENTAL

General considerations

The elements carbon and hydrogen were analyzed by the Prejel, method and nitrogen was analyzed by the Jeldhal method. All NMR experiments were done with a 400-MHz Bruker AVANCE DPX NMR instrument with $CDCl_3$ as the internal reference at 7.25 and 77.0 ppm for ^1H and ^{13}C, respectively. For ^{19}F-NMR, $CFCl_3$ at 0.00 ppm was used as an external reference. The complete structural assignment of the homopolymers and copolymers was done with the help of ^1H-, ^{13}C-, ^{19}F-, distortionless enhancement by polarization transfer (DEPT) 90, two-dimensional (2D) ^1H–^1H homonuclear correlation spectroscopy (Homo COSY), and carbon–proton correlation spectroscopy (^{13}C–^1H XH CORR) NMR techniques. Gel permeation chromatograms were obtained with a Waters instrument. Tetrahydrofuran (THF) was used as eluent, and Styragel HR-4 columns were employed. The molecular weight and polydispersity index (PDI) are reported versus monodisperse polystyrene standards. Differential scanning calorimetry (DSC) measurements were made on a TA Instruments DSC-2920 instrument at a heating/cooling rate of 20°C/min under nitrogen. T_g was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments thermogravimetric analyzer (model TGA-2950). A heating rate of 10°C/min was used for the determination of the decomposition temperature (T_d) at 5% weight loss under synthetic air. The mechanical properties of the thin polymer films were obtained at room temperature on a Minimat 2000 miniature materials tester (Rheometric Scientific) at a strain rate of 5%/min. Dynamic mechanical analysis (DMA) was performed on a Netzsch DMA-242 C instrument in the tension mode on thin film (80–100 μm) samples at a heating rate of 5°C/min (1 and 10 Hz). The dielectric constant of the polymer films was measured by the parallel plate capacitor method with a YHP 4278 capacitance meter at 1 KHz and 30°C.

Starting materials

All reagents were purchased from Acros (Lancaster, England) or Fluorochem Chemical Co. and were used as received unless otherwise noted. *N*-Methylpyrrolidone (NMP; Fluka) and dimethylformamide (DMF; E Merck, India) were purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure. The compound 1,4-bis(4-fluoro-3-trifluoromethy benzyl) benzene was prepared according to a method reported earlier.[28]

Syntheses of the polymers

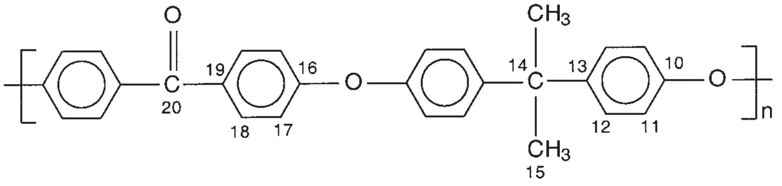
PEEKs

Polymerization reactions were carried out in a 50-mL, round-bottom flask equipped with a stirring bar, condenser, and nitrogen inlet. In a typical procedure, the flask was charged with an equimolar amount of 4,4′-bisfluorobenzophenone and respective bishydroxy compounds in the presence of K_2CO_3 as the base and NMP as a solvent. The solvent was taken as 10–15 wt % of the solid content depending on the exact structures.

Copoly(ether ether ketones)

We synthesized the copolymers by taking 0.5 mol % of each of the bisfluoro monomers in comparison to bishydroxy monomers. Syntheses were carried out in a 50-mL, round-bottom flask equipped with a stirring bar, condenser, and nitrogen inlet. NMP (25 wt %) was used as the solvent, and toluene was taken to remove water azeotropically. Initially, the reaction was carried out for 3 h at 140°C, and then, the temperature was increased to 210°C to facilitate the reaction. The reactions were allowed to run until the solution became highly viscous. After the solution was cooled room temperature, 20 mL of THF was added to dilute the mixture; the polymer was recovered by precipitation from about 800 mL of methanol containing a few milliliters of HCl. Fibrous solid was isolated. These products were washed several times with boiling water to remove any inorganic impurities, dried *in vacuo*, dissolved in THF, reprecipitated in excess methanol, and dried *in vacuo* at 70°C for 24 h.

1a



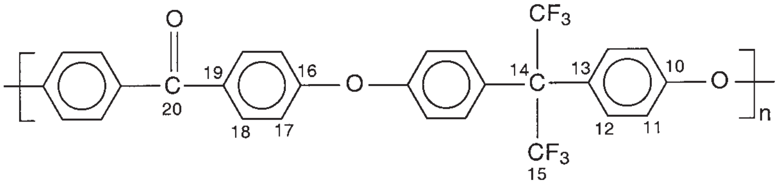
ANAL. Calcd for $C_{28}H_{22}O_3$ (406.4788 g/mol): C, 82.73%; H, 5.45%. Found: C, 82.89%; H, 5.90%.

IR (KBr, cm^{-1}): 3296, 3038 (C—H stretching for an aromatic ring); 2968 (—CH_3 stretching); 2594, 2446, 2081, 2035, 1903, 1651, 1613 (C═O and C═C ring stretching skeleton band); 1504, 1417, 1385, 1304, 1171 (series of bands due to C—F absorption); 1081, 1014 (aromatic C—O—C); 952, 928, 874, 768, 687 (aromatic C—H bending out of plane).

^{1}H-NMR ($CDCL_3$, δ, ppm): 7.71 (d, *J* = 8 Hz, 4H, H18), 7.19 (d, *J* = 8 Hz, 4H, H12), 6.95 (d, *J* = 8 Hz, 4H, H17), 6.92 (d, *J* = 8 Hz, 4H, H11), 1.79 (s, 6H, H15).

^{13}C-NMR ($CDCL_3$, δ, ppm): 194.58 (C20); 161.74 (C16); 153.75 (C10); 147.04 (C19); 136.1 (C13); 132.47 (C18); 128.63 (C12); 119.84 (C17); 117.43 (C11); 42.66 (C14); 31.31, 30.98 (C15).

1b



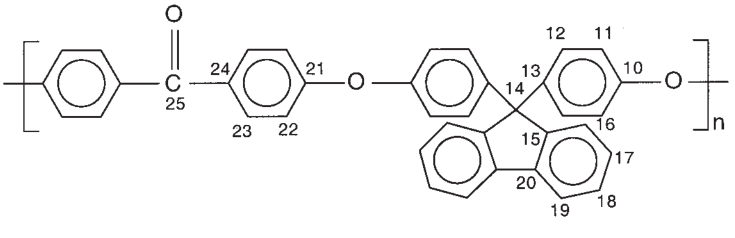
ANAL. Calcd for $C_{28}H_{16}F_6O_3$ (514.421 g/mol): C, 65.37%; H, 3.13%. Found: C, 64.93%; H, 3.49%.

IR (KBr, cm^{-1}): 3269, 3016, 2928 (C—H stretching for an aromatic ring); 2574, 2416, 2071, 2015, 1889, 1647, 1603 (C═O and C═C ring stretching skeleton band); 1494, 1415, 1365, 1171, 1109 (series of bands due to C—F absorption); 1081, 1004 (aromatic C—O—C); 948, 884, 798 (aromatic C—H bending out of plane).

^{1}H-NMR ($CDCL_3$, δ, ppm): 7.77 (d, *J* = 8 Hz, 4H, H18), 7.35 (d, *J* = 8 Hz, 4H, H12), 7.04 (d, *J* = 8 Hz, 4H, H17), 7.00 (d, *J* = 8 Hz, 4H, H11).

^{13}C-NMR ($CDCL_3$, δ, ppm): 194.32 (C20), 160.38 (C16), 156.91 (C10), 133.31 (C19), 132.63 (C18), 132.27 (C12), 129.08 (C13), 124.44 (q, *J* = 272 Hz, C15), 119.16 (C17), 118.59 (C11), 64.19 (m, *J* = 25.4 Hz, C14).

1c



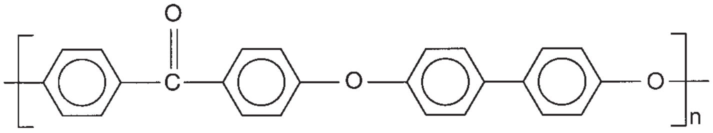
ANAL. Calcd for $C_{38}H_{24}O_3$ (528.604 g/mol): C, 86.34%; H, 4.57%. Found: C, 85.98%; H, 4.91%.

IR (KBr, cm^{-1}): 3062, 2926 (C—H stretching for an aromatic ring); 2593, 2448, 2444, 2078, 2029, 1913, 1658, 1593 (C═O and C═C ring stretching skeleton band); 1503, 1447, 1415, 1384, 1253, 1167, 1108 (series of bands due to C—F absorption); 1015 (aromatic C—O—C); 951, 928, 872, 782, 766 (aromatic C—H bending out of plane).

^{1}H-NMR ($CDCL_3$, δ, ppm): 7.70 (d, *J* = 8 Hz, 2H, H19), 7.66 (d, *J* = 8 Hz, 4H, H23), 7.34 (d, *J* = 8 Hz, 2H, H16), 7.30 (t, *J* = 8 Hz, 2H, H18), 7.22 (t, *J* = 8 Hz, 2H, H17), 7.14 (d, *J* = 8 Hz, 4H, H12), 6.91 (d, *J* = 8 Hz, 4H, H22), 6.85 (d, *J* = 8 Hz, 4H, H11).

^{13}C-NMR (CDCL$_3$, δ, ppm): 194.25 (C25), 161.37 (C21), 154.80 (C10), 151.29 (C15), 142.15 (C20), 140.34 (C13), 132.62 (C24), 132.45 (C23), 129.97 (C12), 128.16 (C17), 128.03 (C18), 126.34 (C16), 120.65 (C19), 119.90 (C11), 117.64 (C22), 64.79 (C14).

1d

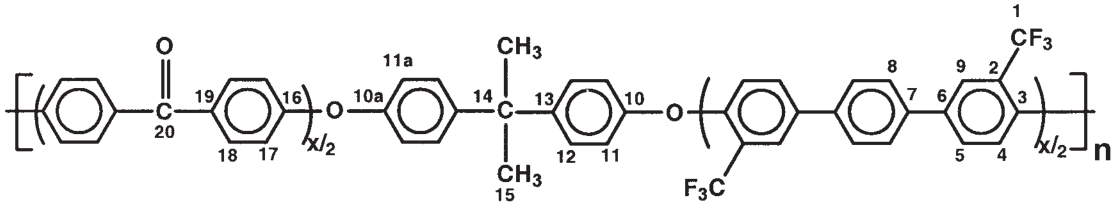


ANAL. Calcd for $C_{25}H_{16}O_3$ (373.396): C, 80.29%; H, 4.31%. Found: C, 80.71%; H, 4.17%.

IR (KBr, cm^{-1}): 3026, 2947 (C—H stretching for an aromatic ring); 2586, 2447, 2045, 1867, 1668, 1587 (C═O and C═C ring stretching skeleton band); 1515, 1452, 1378, 1246, 1187, 1110 (series of bands due to C—F absorption); 1007 (aromatic C—O—C); 956, 924, 879, 787 (aromatic C—H bending out of plane).

This polymer was not soluble in NMR solvents.

2a



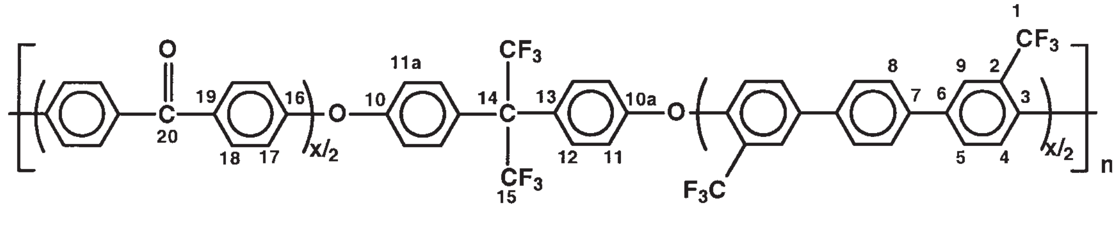
ANAL. Calcd for $C_{48}H_{32}F_6O_3$ (770.768 g/mol): C, 74.79%; H, 4.18%. Found: C, 74.98%; H, 4.09%.

IR (KBr, cm^{-1}): 3038, 2971, 2873 (C—H stretching for an aromatic ring); 2585, 2448, 2410, 2082, 2039, 1904, 1777, 1667, 1651, 1614, 1591 (C═O and C═C ring stretching skeleton band); 1482, 1234, 1127, 1051, 1013 (series of bands due to C—F absorption); 1004 (aromatic C—O—C); 927, 817, 689 (aromatic C—H bending out of plane).

^{1}H-NMR (CDCL$_3$, δ, ppm): 7.84 (S, 2H, H9), 7.72 (d, J = 8 Hz, 4H, H18), 7.61 (d, J = 8 Hz, 2H, H5), 7.57 (S, 4H, H8), 7.2 (d, J = 8 Hz, 8H, H12), 6.97–6.92 (broad signal, 14H, H4, H17, H11, H11a), 1.59 (t, 6H, H15).

^{13}C-NMR (CDCL$_3$, δ, ppm): 194.68 (C20), 161.77 (C16), 155.51 (C3), 154.41 (C10a), 153.75 (C10), 146.97 (C19), 138.91 (C7), 135.30 (C6), 132.52 (C18), 132.37 (C12), 131.77 (C5), 128.63 (C13), 127.76 (C8), 125.59 (d, J = 4.6 Hz, C9), 123.68 (q, J = 271.3 Hz, C1), 121.77 (q, J = 31 Hz, C2), 119.86 (C17), 119.61 (C4), 119.43 (C11a), 117.44 (C11), 42.65 (C14), 31.31 (C15).

2b



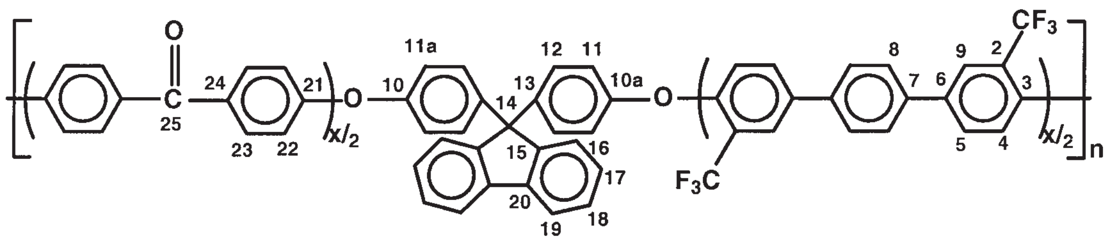
ANAL. Calcd for $C_{48}H_{26}F_{12}O_3$ (878.711 g/mol): C, 65.61%; H, 2.98%. Found: C, 65.76%; H, 3.02%.

IR (KBr, cm^{-1}): 3018, 2951, 2876 (C—H stretching for an aromatic ring); 2535, 2431, 2082, 2039, 1924, 1787, 1653, 1625, 1597 (C═O and C═C ring stretching skeleton band); 1478, 1263, 1147, 1057 (series of bands due to C—F absorption); 1003 (aromatic C—O—C); 931, 827, 729 (aromatic C—H bending out of plane).

^{1}H-NMR (CDCL$_3$, δ, ppm): 7.87 (S, 2H, H9), 7.77 (d, J = 8 Hz, 4H, H18), 7.18 (d, J = 8 Hz, 2H, H5), 7.60 (S, 4H, H8), 7.35 (d, J = 8 Hz, 8H, H12), 7.06 (d, J = 8 Hz, 2H, H4), 7.04 (d, J = 8 Hz, 4H, H17), 7.00 (d, J = Hz, 8H, H11).

^{13}C-NMR (CDCL$_3$, δ, ppm): 194.40 (C20), 160.41 (C16), 157.60 (C10a), 156.96 (C10), 154.03 (C3), 138.94 (C7), 136.57 (C6), 133.38 (C19), 132.63 (C18), 132.28 (C12), 132.02 (C5), 129.13 (C13), 126.24 (q, C9, J = 3.6 Hz), 122.8 (q, J = 31.9 Hz, C2), 127.91 (C8), 123.49 (q, J = 271.3 Hz, C1), 123.03 (q, J = 268 Hz, C15), 121.07 (C4), 119.18 (C17), 188.91 (C11), 118.63 (C11a), 64.18 (septet, J = 25.5 Hz, C14).

2c



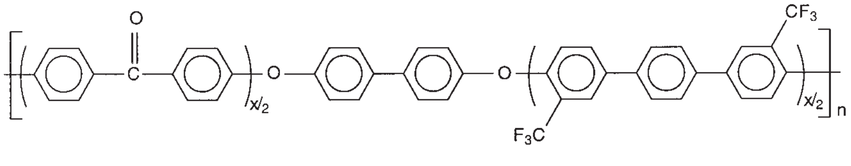
ANAL. Calcd for $C_{57}H_{34}F_6O_3$ (892.891 g/mol): C, 78.02%; H, 3.83%. Found: C, 78.11%; H, 3.74%.

IR (KBr, cm^{-1}): 3037, 2954 (C—H stretching for an aromatic ring); 2446, 2028, 1912, 1656, 1593, 1527 (C═O and C═C ring stretching skeleton band); 1498, 1447, 1437, 1416, 1332, 1306, 1251, 1162, 1053, 1028 (series of bands due to C—F absorption); 1015 (aromatic C—O—C); 928, 823, 747, 605 (aromatic C—H bending out of plane).

^{1}H-NMR (CDCL$_3$, δ, ppm): 7.79 (S, 2H, H9), 7.70 (d, *J* = 8 Hz, 4H, H19), 7.66 (d, *J* = 8 Hz, 4H, H23), 7.55 (d, *J* = 8 Hz, 2H, H5), 7.52 (S, 4H, H8), 7.34 (d, *J* = 8 Hz, 4H, H16), 7.29 (t, *J* = 8 Hz, 4H, H18), 7.22 (t, *J* = 7 Hz, 4H, H17), 7.14 (d, *J* = 8 Hz, 8H, H12), 6.92 (d, *J* = 8 Hz, 2H, H4), 6.90 (d, *J* = 8 Hz, 4H, H22), 6.86 (d, *J* = 8 Hz, 4H, H11), 6.85 (d, *J* = 8 Hz, 4H, H11a).

^{13}C-NMR (CDCL$_3$, δ, ppm): 194.45 (C25), 161.0 (C21), 155.44 (C10a), 155.14 (C3), 154.81 (C10), 151.31 (C15), 142.0 (C20), 140.35 (C13), 138.87 (C7), 135.50 (C6), 132.63 (C24), 132.45 (C23), 131.72 (C5), 129.97 (C12), 128.16 (C17), 128.03 (C18), 127.73 (C8), 126.36 (C16), 125.96 (d, *J* = 4.7 Hz, C9), 123.60 (q, *J* = 271.3 Hz, C1), 121.96 (q, *J* = 31 Hz, C2), 120.64 (C19), 119.89 (C11 and C4), 119.46 (C11a), 117.64 (C22), 64.786 (C14).

2d



ANAL. Calcd for $C_{45}H_{26}F_6O_3$ (728.687 g/mol): C, 74.17%; H, 3.59%. Found: C, 74.28%; H, 3.64%.

IR (KBr, cm^{-1}): 3038, 2927 (C—H stretching for an aromatic ring); 2412, 2032, 1905, 1644, 1594, 1528 (C═O and C═C ring stretching skeleton band); 1486, 1437, 1416, 1334, 1257, 1163, 1053, 1027 (series of bands due to C—F absorption); 1005 (aromatic C—O—C); 933, 823, 766 (aromatic C—H bending out of plane).

RESULTS AND DISCUSSION

Synthesis of the homopolymers and copolymers

The homopolymers were synthesized via a nucleophilic aromatic substitution polymerization with NMP as the solvent and K_2CO_3 as the base.[28,29] During polymerization, polymers with fluorine and biphenyl-

TABLE I
Physical Properties of the Polymers

Polymer	η_{inh} (0.5 wt % solution in DMF)	M_n	PDI	Film quality
1a	0.74	—	—	Flexible
1b	0.66	—	—	Flexible
1c	0.36	—	—	Brittle
1d	0.31	—	—	Brittle
2a	0.79	66,800	2.4	Flexible and tough
2b	0.78	44,500	2.3	Flexible and tough
2c	0.89	57,500	1.7	Flexible and tough
2d	0.38	24,300	2.3	Brittle

M_n = number-average molecular weight; η_{inh} = inherent viscosity.

TABLE II
Solubility of the Polymers in Various Common Organic Solvents

Polymer	NMP	DMF	DMSO	THF	Toluene	Acetone	$CHCl_3$
1a	+	+	−	+rr	+rr	−	+
1b	+	+	−	+rr	+rr	−	+
1c	+	+	−	+rr	+rr	−	+
1d	+	−	−	+rr	+rr	−	−
2a	+	+	−	+	+	−	+
2b	+	+	−	+	+	−	+
2c	+	+	−	+	+	−	+
2d	+	+r	−	+r	+	−	+r

+ = soluble at room temperature; − = insoluble at room temperature; +r = partially soluble at room temperature; +rr = soluble at reflux. DMSO = dimethyl sulfoxide.

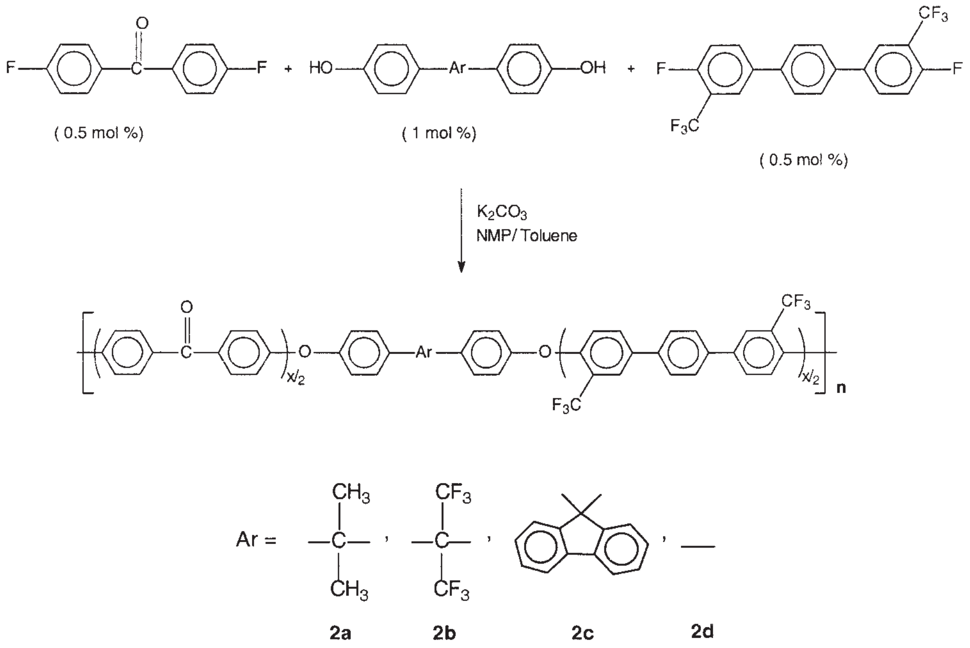


Figure 1 Reaction scheme and structures of the copolymers.

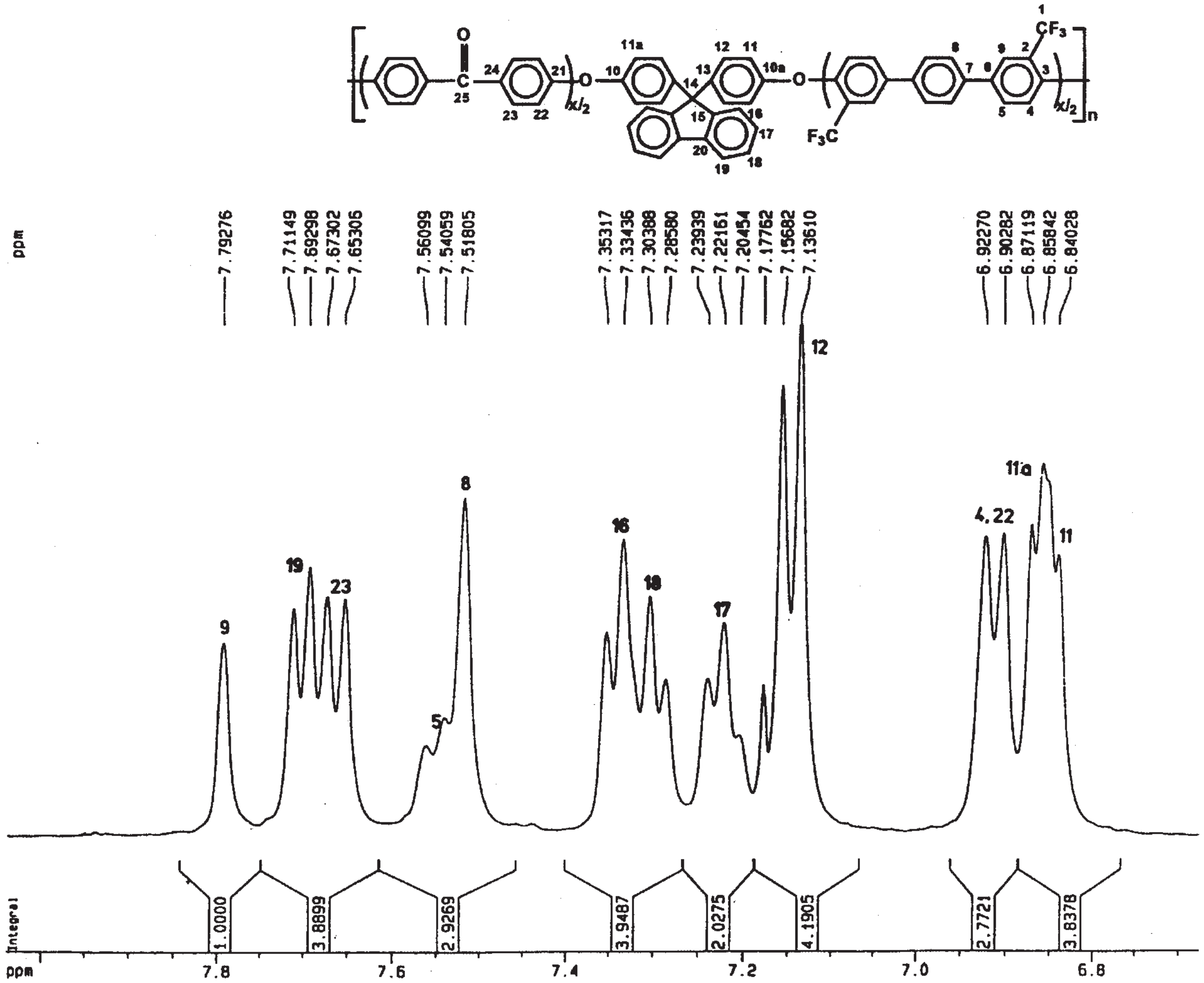


Figure 2 ^{1}H-NMR spectrum of copolymer **2c**.

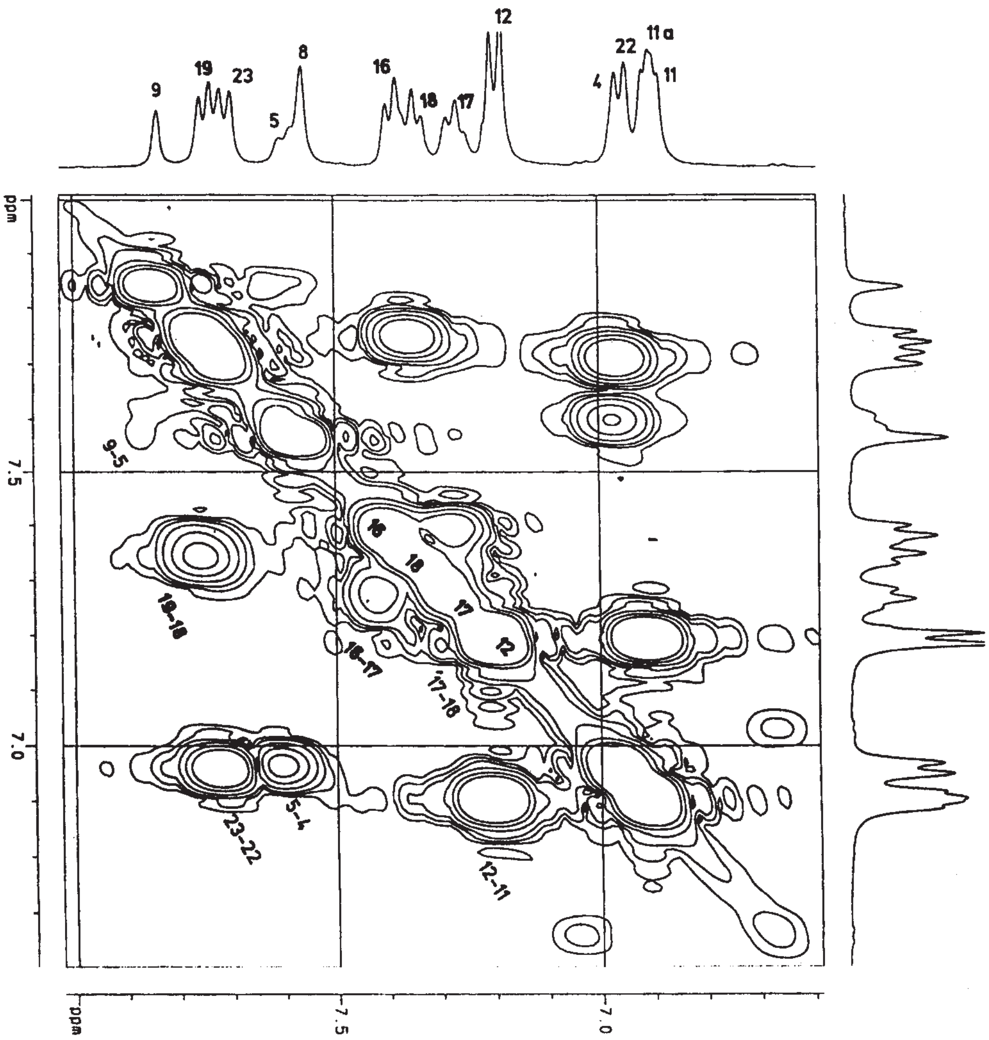


Figure 3 2D ^1H–^1H Homo COSY spectrum of copolymer **2c**.

containing moieties were precipitated. To avoid precipitation, excess solvent was used; that is, the solid content was 10 wt %. The increase in solvent led to low-molecular-weight polymers. A high molecular weight was obtained by optimization of the solid content through increases in the reaction time and temperature. Polymers synthesized from bisphenol A and bisphenol 6F did not show such precipitation, even when the solid content was 25 wt %.

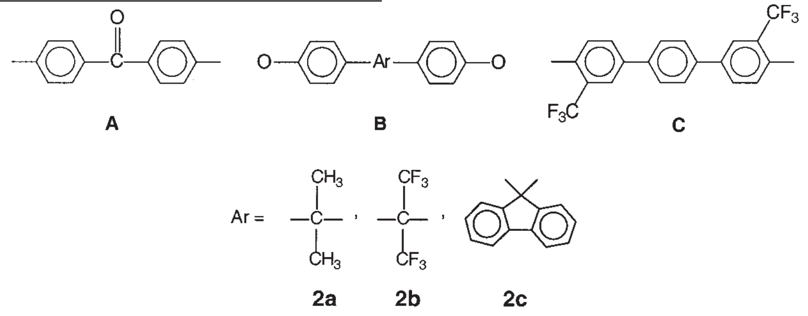
The copolymers were synthesized by the reaction of 0.5 mol % bisfluorobenzophenone and 0.5 mol % bis-1,4-(4-fluoro-3-trifluoromethyl benzyl) benzene and 1 mol % bishydroxy monomers. The polymerization of the copolymers was carried out at 25 wt % of the solid content. The polymers were synthesized via an aromatic nucleophilic substitution polymerization with K_2CO_3 as the base; NMP as a solvent and toluene were used for the azeotropic removal of water. During the initial stages of the reaction, bisphenoxide formation took place, and the water formed was removed azeotropically by toluene. The copolymers did not show any precipitation during the polymerization. The synthesis scheme and copolymer structures are shown in Figure 1. The inherent viscosity values of the polymers and other physical properties are given in Table I.

Polymer solubilities

The solubilities of the resulting PEEKs and copoly(ether ether ketones) were investigated in different organic solvents. We attempted to obtain 10% (w/v) solutions in different solvents of all of the polymers presented in Table II. Copolymers **2a–2c** exhibited very good solubility behavior in common organic solvents in comparison to the analogous homopolymers **1a–1c**. The better solubility behavior of the copolymers was due the presence of pendent trifluoromethyl groups,[28,29] which increased the fractional free volume of the polymers.

Spectroscopy

The spectroscopic data from Fourier transform infrared (FTIR) and ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy supported the structure of the PEEKs. These characterizations and elemental analysis did not indicate any degradation of the trifluoromethyl group. The analytical detail of all of the homopolymers and copolymers are given in the Experimental section. The FTIR spectra of these polymers showed aryl ether linkages (1140–1050 cm^{-1}) that were generated in the polymer-forming reaction[28] and also the stretching frequencies (1240–1150 cm^{-1}) corresponding to the trifluoromethyl group.[29] FTIR and ^{1}H-NMR did not show any signals corresponding to the terminal —OH or —F groups, which indicated high conversion. The exact analytical data for all of these polymers are listed in the Experimental section. It was not possible to record the NMR spectra of **1d** and **2d**, as they were not soluble in most of the deuterated organic solvents used for NMR:



Monomer sequences were assigned by NMR spectroscopy, which indicated a random copolymer. First, ^{1}H-NMR spectra of all of the polymers were recoded. The representative ^{1}H spectrum of copolymer **3c** is shown in Figure 2. Peaks were assigned on the basis of the electronic environment of the attached groups and spin–spin couplings. The integration ratio of different proton peaks assigned the reactivity ratio of the monomers. A representative ^{1}H-NMR spectrum with detailed assignments of the peaks of copolymer **2c** is shown in Figure 2. The spectrum showed distinct splitting patterns for all of the chemically different protons. A very good matching of integrated peak area vis-à-vis different protons was observed. The proton resonances in the range 6.5–8.0 ppm apparently arose from the proposed structures, where A, B, and C were represented by 4,4′ difluorobenzophenone unit, the bishydroxy monomer, and 1,4-bis(4-benzotrifluoride) benzene. The integration ratio of the protons of the B:A:C units showed a 2:1:1 ratio, respectively, in the polymer chain, which showed that the B units were attached with two different monomer units in a random manner.

The random nature of the copolymers could be understood well by the observation of the different proton and carbon signals for the proton and carbon marked by 10 and 11 in the copolymers. Proton number 11 of the B unit was shown at two different clearly distinct chemical shifts, 6.85 and 6.86 (H11a and H11), for **2c**. In copolymers **2a** and **2b**, the H11 peaks formed a broad signal. The carbons marked 10 and 11 in the copolymers showed differentiation in the chemical shifts 117.44 and 119.43 (C11) and 154.41 and 153.75 (C10) in **2a**; 118.91 and 118.63 (C11) and 157.60 and 156.96 (C10) in **2b**; and 155.44 and 154.81 (C10) and 119.89 and 119.46 (C 11) in **2c**.

To further elucidate the microstructure of the copolymers, ^{1}H–^{1}H 2D Homo COSY spectra of the copolymers were recorded, which showed the ^{1}H–^{1}H connectivity. Figure 3 shows the representative ^{1}H–^{1}H 2D Homo COSY spectrum of copolymer **2c**. The contours showed three-bond connectivity for the 5–4, 23–22, 12–11, 17–18, 16–17, and 19–17 protons and four-bond connectivity for the 9–5 protons. Again, the copolymers showed the same ratio 2:1:1 for B:A:C.

The ^{13}C-NMR spectrum of copolymer **2c** is shown in Figure 4. The detailed assignment of different carbons was difficult because of the complex nature of the spectrum. Complex ^{13}C-NMR was simplified with DEPT 90, which established quaternary and CH peak differentiation. The representative DEPT 90 spectrum of copolymer **2c** is shown in Figure 5. Carbon–proton single-bond connectivities were observed by 2D XH CORR NMR with DEPT 45 pulse for ^{13}C, which provides unambiguous assignment of the microstructure of the copolymer. A representative 2D XH CORR NMR spectrum of copolymer **2c** is shown in Figure 6.

In homopolymers **1a** and **1b**, proton 18 was downfield from proton 17 due to an electron-withdrawing effect of the carbonyl group. In **1c**, proton 19 was

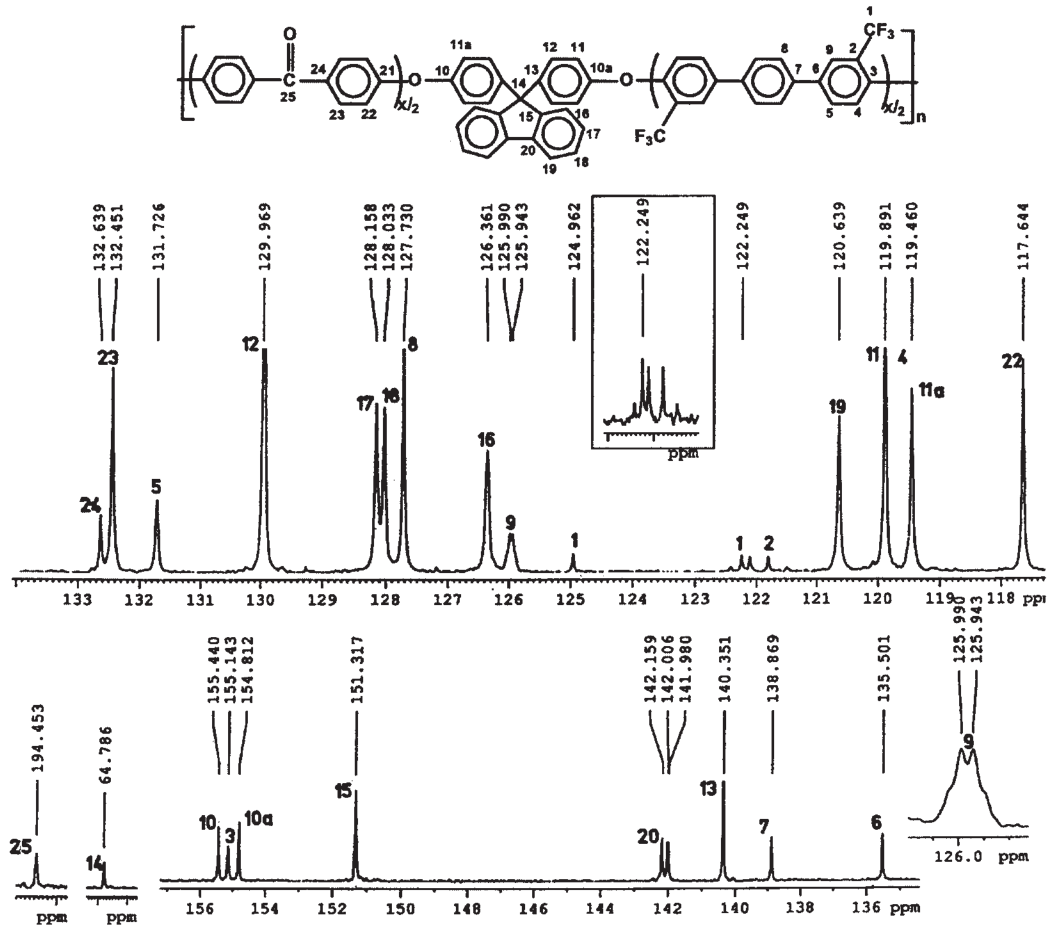


Figure 4 ^{13}C-NMR spectrum of copolymer **2c**.

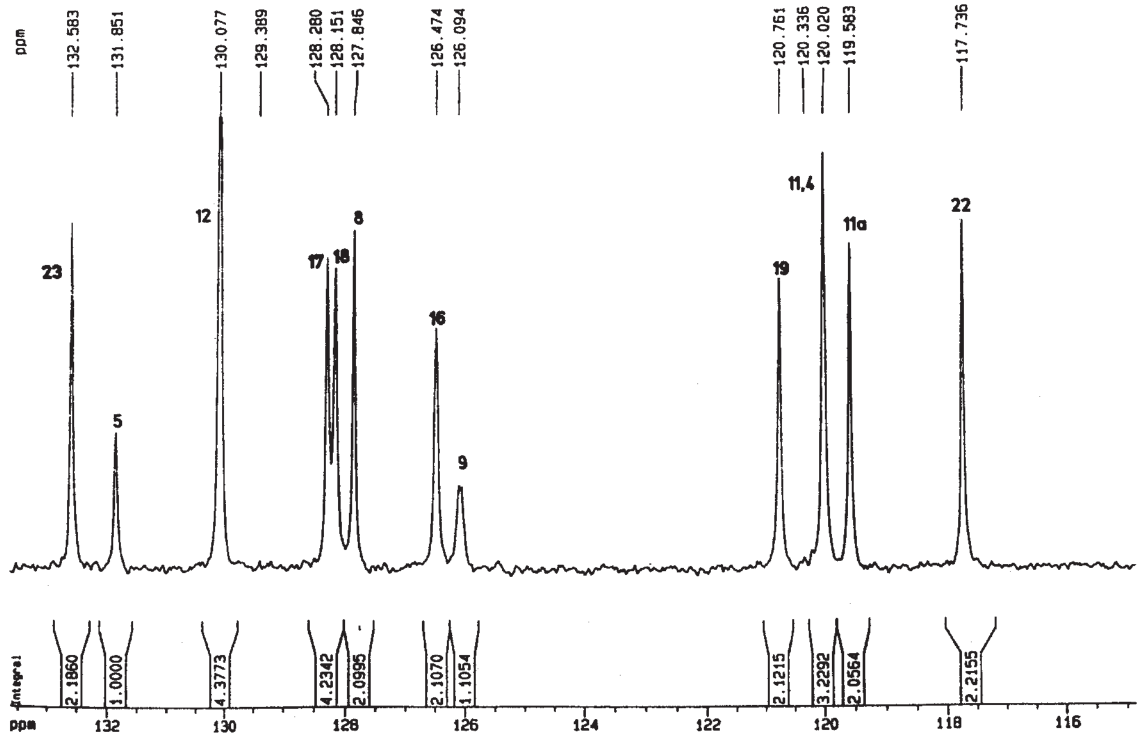


Figure 5 DEPT 90 spectrum of copolymer **2c**.

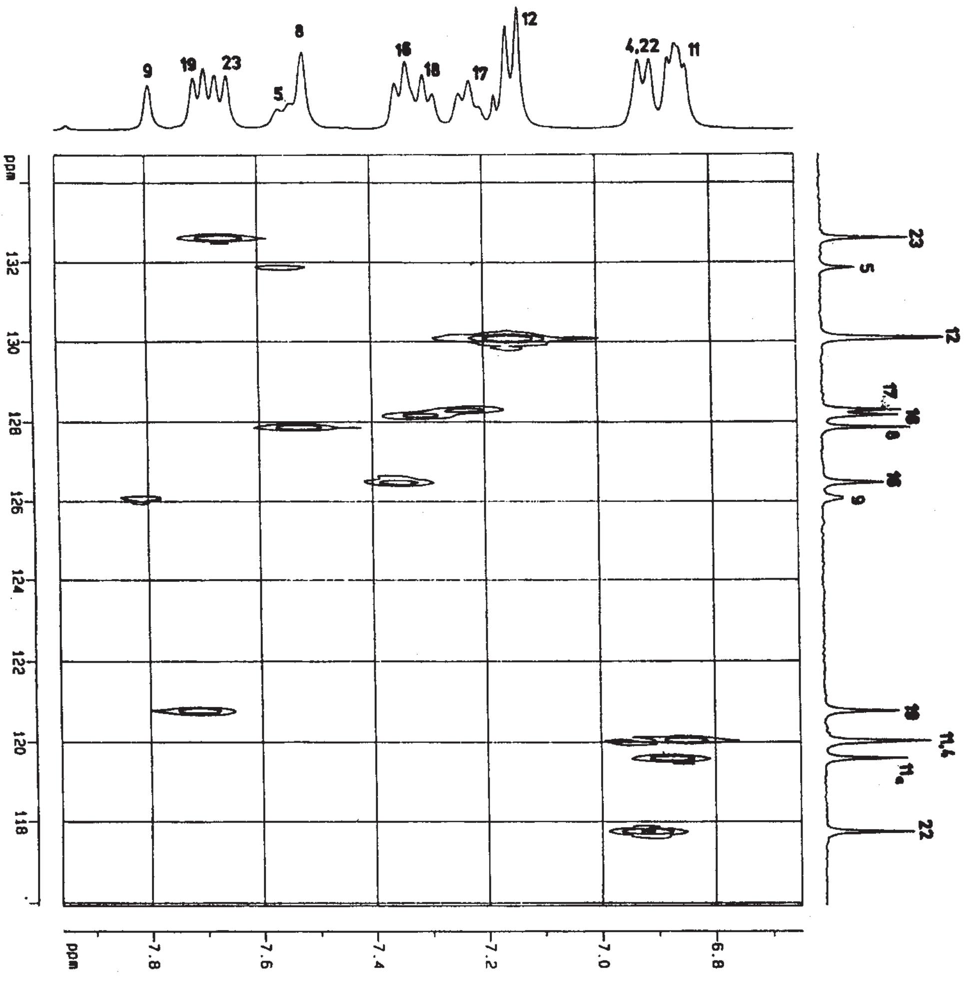


Figure 6 ^{13}C–^{1}H XH CORR spectrum of copolymer **2c**.

downfield from proton 23 because the desheilding effect of the ring electrons was more than that of the carbonyl group. The same pattern was observed in copolymers **2a**, **2b**, and **2c**. In all of copolymers, the H9 proton, which was ortho to CF_3, was always downfield or at a higher parts per million value than all of the protons of units A, B, and C. Carbons 1, 2, and 9 showed quartets due to coupling with the three fluorines of CF_3 in the range 272, 31, and 4.7 Hz for 1, 2, and 3 bonds couplings, respectively.

DSC measurements

PEEK and its copolymers showed T_g's up to 260°C in DSC. The results are summarized in Table III. Representative DSC plots are shown in Figure 7. The T_g values of the synthesized homopolymers were evaluated and compared with the earlier reported PEEKs;[30–34] the values were comparable. The copolymers were designed by the incorporation of 1,4-bis(4-fluoro-3-trifluoromethylbenzyl) benzene into the corresponding parent PEEKs. The incorporation of the comonomer increased the T_g of the copolymers compared to the corresponding homopolymer. T_g was calculated with eq. (1). This equation is

TABLE III
Thermal Properties of PEEKs and Copoly(ether ether ketones)

Polymer	T_g (°C)			T_d (°C) at 5% weight loss in air
	DSC		DMA	
1a	155[a]	151	151	445
1b	175[a]	163	178	494
1c	252[a]	251	254	512
1d	170[a]	181	—	450
2a	162[b]	173	176	461
2b	173[b]	187	193	493
2c	243[b]	261	257	518
2d	194[b]	188	—	458

[a] Reported value, refs. 17–19.
[b] Value calculated by $1/T_g = W_1/T_{g1} + W_2/T_{g2}$.

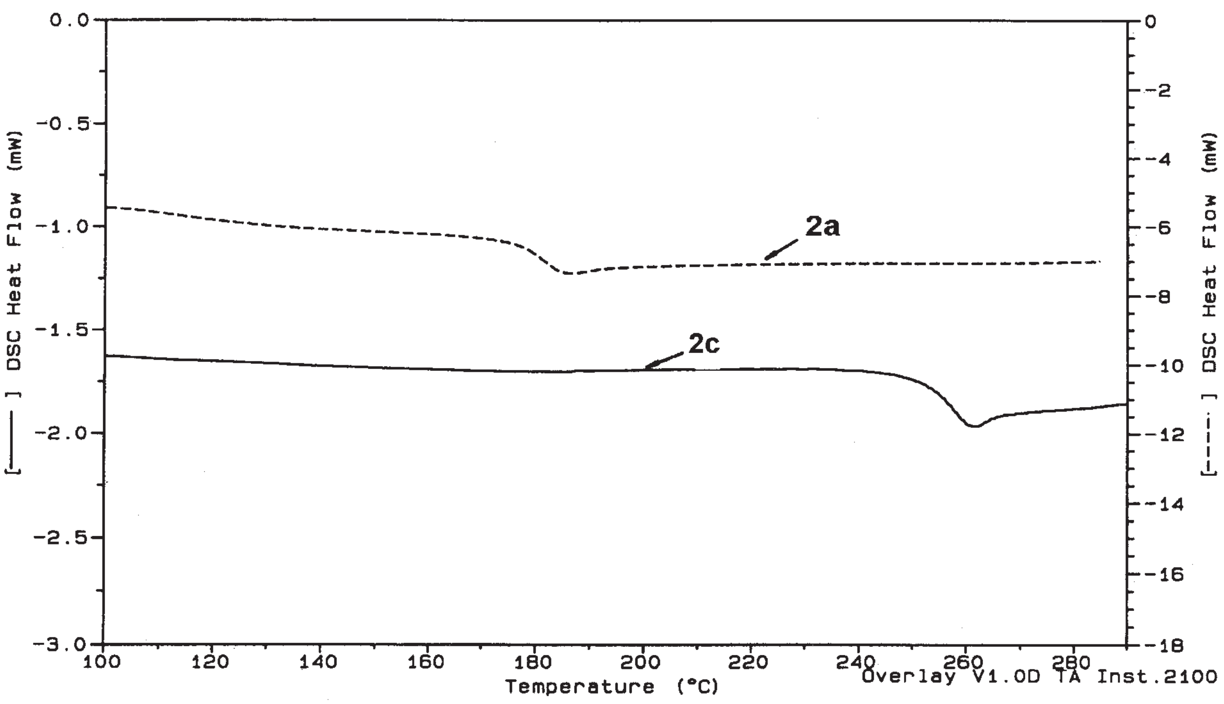


Figure 7 DSC plots of copolymer **2a** and **2c**.

generally used for blends, but the results from this calculation matched well with the observed T_g's:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \tag{1}$$

where W_1 and W_2 are the molar percentages of the comonomers and T_{g1} and T_{g2} are the glass-transition temperatures of the homopolymers.

Copolymer **2c** exhibited the highest T_g, which was due the presence of the rigid and bulkier fluorine moiety, which restricted the flexibility of the polymer chain.[29] Copolymer **2b** exhibited a higher T_g than **2a** because of the presence of a hexafluoroisopropylidine group. The higher T_g of copolymer **2d** in comparison to **2a** was attributed to the rigidity rendered by the biphenyl unit.

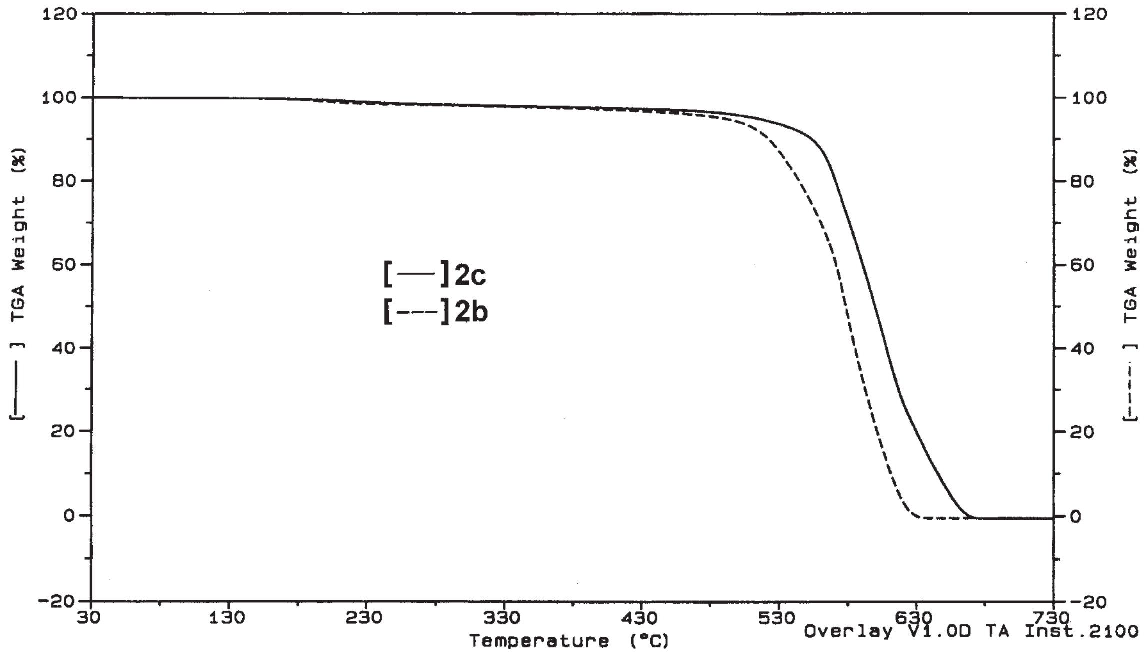
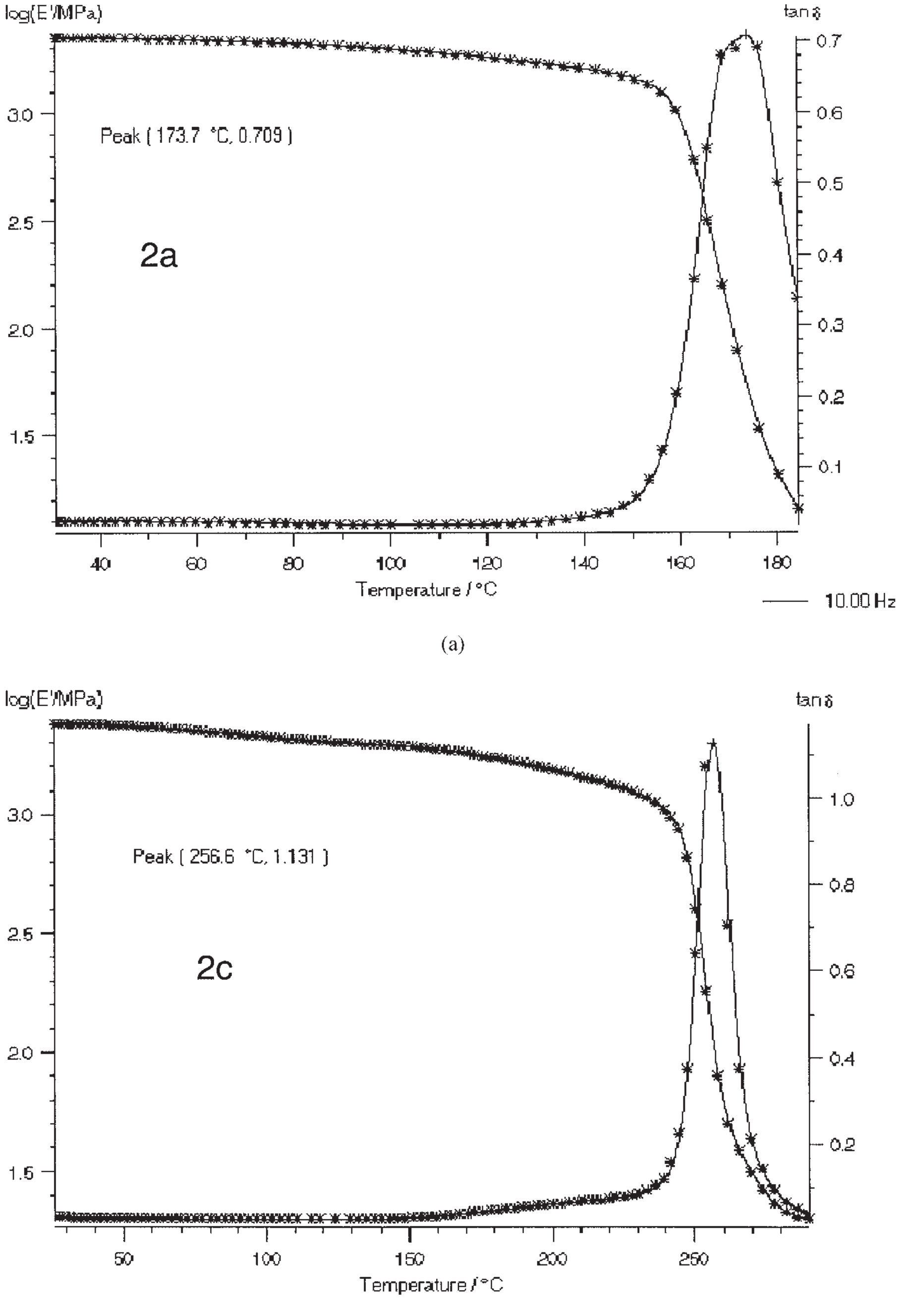


Figure 8 TGA plots of copolymer **2b** and **2c**.



(a)

(b)

Figure 9 DMA plots of copolymer **2a** and **2c**.

Thermal stability

The copolymers exhibited very good thermal stability, as summarized in Table III. Depending on the exact structures, these polymers showed thermal stability up to 518°C for 5% weight loss in synthetic air as determined by TGA. A representative TGA plot is shown in Figure 8. Copolymer **2c** exhibited the highest thermal stability because of the bulky rigid fluorine moiety. Polymer **2b** showed a higher thermal stability than **3a**; the lower thermal stability of **2a** was due to the presence of an oxidizable isopropylidine group. The unexpected lower thermal stabilities of homopolymer **1d** and copolymer **2d** were possibly due to the precipitation of the polymers from the reaction medium during polymerization, which in turn, resulted in a low-molecular-weight product.

DMA

The dynamic mechanical behaviors of the copolymers films (**2a** and **2c**) are shown in Figure 9. T_g's taken

TABLE IV
Mechanical Properties of the Polymers

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
1a	42	2.11	13
1b	53	2.23	17
1c	49	2.45	12
1d	—	—	—
2a	57	2.33	70
2b	62	2.17	65
2c	93	2.52	32
2d	—	—	—

TABLE V
Dielectric and Other Properties of the Polymers

Polymer	Fluorine content (%)	Water absorption (%)	RI (n)	$\varepsilon = n^2$ (optical)	$\varepsilon_{\mathrm{Calcd}}$[36]	$\varepsilon_{\mathrm{Exp}}$ (1 kHz)
1a	—	0.65	1.716	2.94	2.89	3.24
1b	22.15	0.47	1.668	2.78	2.68	2.89
1c	—	0.76	1.763	3.10	3.00	3.32
1d	—	0.71	1.772	3.13	3.05	—
2a	14.78	0.49	1.643	2.69	2.67	2.85
2b	25.94	0.22	1.613	2.60	2.57	2.65
2c	12.94	0.54	1.671	2.79	2.76	2.75
2d	15.64	0.33	1.675	2.80	2.74	2.78

$\varepsilon_{\mathrm{Calcd}}$ = calculated dielectric constant; $\varepsilon_{\mathrm{Exp}}$ = experimental dielectric constant; RI = refractive index.

from the tan δ peaks at 10 Hz are given in Table III. These values were in good agreement with the calorimetric T_g values. The polymers retained their mechanical properties up to their T_g's, as was observed from the storage modulus plots of the polymers. The initial modulus of the polymers was calculated from the storage modulus plots and is presented in Table IV.

Mechanical properties

The tensile properties of the copolymer were determined by the measurement of load or force as a function of crosshead displacement. Table IV illustrates the effect of the comonomer 1,4-bis(4-fluoro-3-trifluoromethyl benzyl) benzene on the parent homopolymers. All of the properties were evaluated from thin films cast from a DMF solution. Figure 10 shows the representative stress–strain plot of copolymer **2a**. The copolymers exhibited the expected ductile mechanical behavior characteristics of many materials containing aryl ether linkages[29,35] with elongations at break up to 70%, moduli up to 2.52 GPa, and tensile strengths up to 93 MPa. These values were comparable to those of high-performance thermoplastic materials such as PEEK and Ultem PEI.

Dielectric properties and refractive index

The dielectric constants of the copolymers films were determined from the refractive index values (with a sodium D light, λ = 589.3 nm) and from the capacitance values at 1 kHz with a capacitance meter at 30°C under wet conditions (45% relative humidity). The refractive index and dielectric constants are presented in Table V. The dielectric constant values of the copolymers were not very close to the values obtained by other methods (i.e., group contribution method with the Lorentz–Lorentz equation) but followed the same trend.[36]

The values calculated from refractive index values ($\varepsilon = n^2$) did not agree well with the theoretical values or the 1-kHz values. This was attributed to the fact that at optical frequencies, only the electronic polarization con-

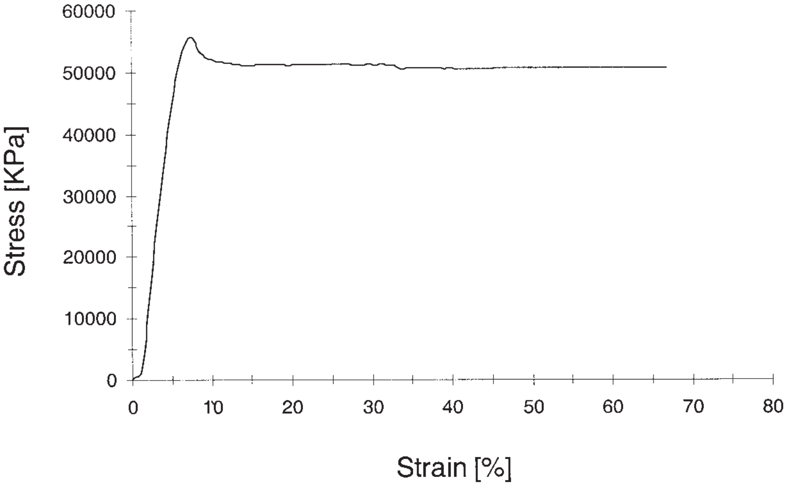


Figure 10 Stress–strain plots of copolymer **2a** and **2c**.

tributed to the dielectric constant. The dielectric constant also depended on the fluorine content; as the percentage fluorine increased, a decrease in the dielectric constant was observed, as summarized in Table V. Also, the fluorine content in the polymer structure largely affected the water absorption value.

CONCLUSIONS

Four new copolymers were prepared and were well characterized by NMR techniques. The NMR analyses confirmed the formation of a random copolymer structure. The copolymers exhibited a high thermal stability in air (518°C for 5% weight loss), high T_g's up to 261°C, a low dielectric constant (2.65 at 1 MHz), and better solubility in organic solvents than their analogous homopolymer structures derived from 1,4-bis(4-fluoro-3-trifluoromethyl benzyl) benzene and bisphenols.

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