

Synthesis and Properties of Fluorinated Bis-benzocyclobutene-Terminated Arylene Ether Monomers

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ABSTRACT: Four novel bis-benzocyclobutene-terminated arylene ether monomers, 1,1'-bis[4-(4'-benzocyclobutenyloxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (BOPP3FE), 1,1'-bis[4-(4'-benzocyclobutenyloxy)phenyl]-1-(3',5'-dinitrofluoromethyl)phenyl-2,2,2-trifluoroethane (BOPP9FE), 2,2'-bis[4-(4'-benzocyclobutenyloxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BOP6FP), and 2,2'-bis[4-(4'-benzocyclobutenyloxy)phenyl]propane (BOPP) were prepared and characterized. All the four monomers showed similar curing behaviors under N₂ (Differential scanning calorimetry: extrapolated onset and peak temperatures at 225–229°C and 261–263°C) and demonstrated low and steady melt viscosities between 110 and

200°C, indicating their good processability. After cure, the resulting BCB resins exhibited high T_g (232–282°C) and excellent thermal stability ($T_{5\%} > 433^\circ\text{C}$). The resins also showed good mechanical properties with the flexural strengths of 68–88 MPa and the flexural modulus of 2.52–3.15 GPa. Moreover, the resins also exhibited low dielectric constants (2.58–2.88), low dissipation factors (2.7 to 8.4×10^{-4}) and low water absorptions in boiling water for 24 h (0.29–0.59%). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2781–2791, 2009

Key words: fluorinated; benzocyclobutene; viscosity; dielectric properties; water absorptions

INTRODUCTION

Benzocyclobutene (BCB)-based polymers have emerged as a new generation of high-performance materials for a spectrum of structural and electronic applications due to the versatile reaction chemistry of BCB as well as the combined advantages of processability and material properties.^{1–6} One important class of them is the BCB resins with highly cross-linked network structures from bis-BCB monomers containing diverse linking groups, which connects two BCB moieties. The chemical structures of these linking groups can strongly influence many of the properties of their final resins.

Tan and Arnold, and Zhang et al.^{7–9} developed a series of heat-resistant BCB resins derived from 4-amino-BCB and various dianhydrides. The rigid imide linking groups provide the final resins with good thermal stability. However, these resins are usually accompanied with the drawback of poor processability. Dow researchers prepared another BCB resin ori-

ginated from 4-bromo-BCB and a divinylsiloxane, which has been extensively used as interlayer dielectric for thin film electronics applications because of its low dielectric constant, low water absorption, and outstanding processability.^{10–13} However, the resin shows mean thermo-oxidative stability, which is mainly related to the siloxane linking group containing many aliphatic methyl groups.¹⁴ In addition, a number of BCB monomers and oligomers from bisphenol A PC, polyethersulfones, and polyetherketones terminated by 4-hydroxy-BCB have been prepared.^{5,15–18} Although these resins exhibit excellent solvent and ignition resistance, they still have the drawbacks of high dielectric constants and water absorptions because of the highly polar ester groups, sulfone groups and carbonyl groups in the linking groups.

Fortunately, a recent U.S. patent¹⁹ has disclosed a series of multifluorinated BCB resins derived from $\alpha,\alpha,\alpha,2,3,5,6$ -heptafluorotoluene, bisphenol F, and 4-hydroxy-BCB, which may be the next generation of low- k interlayer dielectric material for electronic applications. The incorporation of fluorinated groups into these resins results in low dielectric constant and low water absorption because of the small dipole and low polarizability of C–F bond as well as the nonpolar character of the fluorocarbon groups.^{20,21} Moreover, the arylene ether linking groups bring these resins outstanding thermal stability and low melt

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viscosities, which are very suitable for a wide variety of coating and molding process. However, no other fluorinated BCB resins containing arylene ether linking groups have been reported so far.

In this study, three novel fluorinated BCB resins of BOP6FP, BOPP3FE, and BOPP9FE containing various arylene ether linking groups, which derived from three fluorinated bisphenols and 4-bromo-BCB, have been prepared. For comparison, a nonfluorinated BCB resin of BOPP with similar chemical structures originated from bisphenol A and 4-bromo-BCB has also been prepared. To develop new BCB resins with excellent combined properties for electronic applications, the relationships between the molecular structures and their rheological properties, curing behaviors, thermal stability, dielectric properties, water resistance of the precursor monomers, and their cured resins have been systematically investigated.

EXPERIMENTAL

Materials

Bromobenzene and 3,5-bis(trifluoromethyl)bromobenzene (Acros) was purified by distillation before use. 2-Methylbenzyl chloride was purchased from Wuhan Youji industrial company limited (Wuhan, China) and purified by distillation before use. Magnesium turnings (Acros) were used as received. Anhydrous lithium trifluoroacetate was prepared in this laboratory by reaction of lithium hydroxide with trifluoroacetic acid at 5°C for 4 h, and then dried under vacuum at 130°C for 6 h. Tetrahydrofuran (THF) and diethyl ether were freshly distilled in nitrogen over sodium before use. Trifluoromethanesulfonic acid (98%, Aldrich), phenol, cuprous chloride, methanol, trifluoroacetic acid, and iodine (Beijing Beihua Fine Chemicals Co., Beijing, China) were used as received. 2,2'-Bis[(4-hydroxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (bisphenol F) and 2,2'-bis[(4-hydroxy)-phenyl]propane (bisphenol A) were purchased from Aldrich and recrystallized before use. 4-Bromo-BCB was synthesized from 2-methylbenzyl chloride by the method of flash vacuum pyrolysis and bromination according to the literature with some modifications.^{22–24}

Monomer synthesis

2,2,2-Trifluoroacetophenone (3FAP)

A mixture of anhydrous lithium trifluoroacetate (60.0 g, 0.50 mol), magnesium (11.7 g, 0.48 mol), freshly distilled THF (350 mL), and anhydrous diethyl ether (50 mL) were placed into a 1000 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, a N₂ inlet and a reflux condenser. After the anhydrous lithium trifluoroacetate was completely dissolved under stirring, bromoben-

zene (70.7 g, 0.45 mol), additional freshly distilled THF (50 mL), and anhydrous diethyl ether (50 mL) were added through the dropping funnel. Iodine (0.1 g) was added and the flask was slowly heated at 60°C to initialize the reaction. Then, the reaction mixture was stirred at refluxing for 4 h. After the obtained black solution was cooled to ambient temperature, a mixture of concentrated hydrochloric acid (36%, 80 mL) and distilled water (150 mL) was slowly added with agitation. The aqueous phase was separated and the organic phase was washed successively with saturated sodium chloride solution and distilled water until the aqueous phase was neutral. The organic phase was dried with anhydrous magnesium sulfate overnight and filtered, followed by rotary distilling. The resulting solution was purified by two distillations and the fraction of 132°C was collected. A colorless liquid was afforded (43.9 g, 56.1%). ¹H-NMR (CDCl₃, δ, ppm): 7.86 (q; 2H) and 7.38–7.46 (m; 3H). ¹³C-NMR (CDCl₃, δ, ppm): 120.8 (q, ¹J_{C–F} = 272.2 Hz), 122.3 (s), 129.5 (s), 130.5 (s), 135.5 (s), and 175.2 (q, ²J_{C–F} = 37.3 Hz). FTIR (KBr): 1737 cm⁻¹ (C=O; s), 1274 and 1142 cm⁻¹ (C–F; s).

3',5'-Ditrifluoromethyl-2,2,2-trifluoroacetophenone (9FAP)

Using 3,5-bis(trifluoromethyl)bromobenzene as starting material, a colorless liquid with a boiling point of 138°C was finally afforded according to the procedure described above. Yield: 51.2%. ¹H-NMR (CDCl₃, δ, ppm): 8.25 (s; 1H) and 8.52 (s; 2H). ¹³C-NMR (CDCl₃, δ, ppm): 114.5 (q, ¹J_{C–F} = 285.9 Hz), 121.4 (q, ¹J_{C–F} = 273.1 Hz), 127.3 (s), 128.2 (s), 130.2 (s), 131.5 (q, ²J_{C–F} = 36.8 Hz), and 176.1 (q, ²J_{C–F} = 37.6 Hz). FTIR (KBr): 1741 cm⁻¹ (C=O; s), 1380, 1279, and 1145 cm⁻¹ (C–F; s).

1,1'-Bis[(4-hydroxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (HPP3FE)

3FAP (17.4 g, 0.10 mol) and phenol (37.6 g, 0.40 mol) were added to a 250 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, a N₂ inlet, and a reflux condenser. The system was purged with nitrogen three times before heating to 45°C to form a homogenous solution. Then trifluoromethanesulfonic (15.1 g, 0.1 mol) was added dropwise and the solution was stirred at 60°C. After 1 h, a pale yellow solid slowly appeared and the reaction was continuously stirred at 60°C for 10 h. The product was washed with boiling water six times and recrystallized from a mixture of ethanol and water (using 1/1 v/v ethanol/water) to give a white solid (29.6 g, 86.2%), mp 233°C. ¹H-NMR (DMSO-*d*₆, δ, ppm): 9.60 (s; 2H); 7.33–7.40 (m; 3H); 7.05–7.07 (d; 2H); 6.81–6.84 (d; 4H) and 6.74–6.77 (d; 4H). ¹³C-

NMR (DMSO- d_6 , δ , ppm): 157.3 (s), 141.0 (s), 131.1 (s), 130.6 (s), 129.8 (s), 128.7 (q, $^1J_{C-F}$ = 285.9 Hz), 128.5 (s), 127.9 (s), 115.4(s), and 63.9 (q, $^2J_{C-F}$ = 23.1 Hz). Mass spectrometry (MS): (EI+, m/e , % relative intensity): 344 (M^+ , 15), 275 ($M-69^+$, 100). Elemental analysis: Calcd. for $C_{20}H_{15}F_3O_2$: C, 69.76%; H, 4.39%. Found: C, 69.71%; H, 4.37%. FTIR (KBr): 3261 cm^{-1} (O—H; s), 1377 and 1153 cm^{-1} (C—F; s), 1252 cm^{-1} (C—O; s).

1,1'-Bis[(4-hydroxy)phenyl]-1-(3',5'-dinitrofluoromethyl)phenyl-2,2,2-trifluoroethane (HPP9FE)

9FAP (31.0 g, 0.10 mol) and phenol (37.6 g, 0.40 mol) were added to a 250 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, a N_2 inlet, and a reflux condenser. The following procedures were performed according to the synthesis of HPP3FE described earlier. A white crystal was afforded with a melting point of 155°C (42.5 g, 88.5%). 1H -NMR (DMSO- d_6 , δ , ppm): 9.76 (s; 2H); 8.15 (s; 1H); 7.83 (s; 2H); 6.99–7.02 (d; 4H) and 6.79–6.82 (d; 4H). ^{13}C -NMR (DMSO- d_6 , δ , ppm): 157.8 (s), 144.1 (s), 130.9 (q, $^2J_{C-F}$ = 32.7 Hz), 130.8 (s), 129.8 (s), 128.7 (s), 127.9 (q, $^1J_{C-F}$ = 285.7 Hz), 122.7 (q, $^1J_{C-F}$ = 231.6 Hz), 122.1 (s), 115.9(s), and 63.8 (q, $^2J_{C-F}$ = 23.6 Hz). MS: (EI+, m/e , % relative intensity): 480 (M^+ , 14), 411 ($M-69^+$, 100). Elemental analysis: Calcd. for $C_{22}H_{13}F_9O_2$: C, 55.01%; H, 2.73%. Found: C, 55.07%; H, 2.71%. FTIR (KBr): 3298 cm^{-1} (O—H; s), 1372, 1279, and 1157 cm^{-1} (C—F; s), 1235 cm^{-1} (C—O; s).

1,1'-Bis[4-(4'-benzocyclobutenyloxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (BOPP3FE)

20 mL of Methanol and 200 mL of benzene were added to a 500 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, a N_2 inlet, and a condenser. The system was purged with nitrogen three times before adding sodium (4.6 g, 0.2 mol) to form a suspension of sodium methoxide in benzene. Then HPP3FE (37.8 g, 0.11 mol) was added. Benzene and methanol were distilled off to leave a white powder of the bisphenol salt. When the salt had cooled, the condenser was arranged for reflux. Then 200 mL of pyridine was added. The stirred mixture was brought to reflux and 4-bromo-BCB (42.2 g, 0.23 mol) was added rapidly through the dropping funnel. This was followed at once by the addition of cuprous chloride (3.0 g, 0.03 mol). The reaction mixture was brought back to reflux and held at reflux for 12 h under a blanket of nitrogen. The reaction mixture was then poured into 600 mL of water and hydrochloric acid was added until acidified. The product was extracted into three 200 mL portions of dichloromethane and the dichloro-

methane solution filtered. Dichloromethane was removed by distillation. Distillation at 0.1 mm removed 4-bromo-BCB from the residue. The crude product was purified by chromatographic column (using 1/20 v/v hexane/ethyl acetate) to give a white powder (30.9 g, 51.2%). 1H -NMR (DMSO- d_6 , δ , ppm): 7.33–7.37 (m; 3H); 7.03–7.05 (q; 4H); 6.94–6.96 (d; 4H); 6.86–6.88 (d; 4H); 6.83–6.85 (q, 2H); 6.78–6.79 (d, 2H); and 3.05 (s; 8H). ^{13}C -NMR (DMSO- d_6 , δ , ppm): 157.3 (s), 154.8 (s), 146.6 (s), 140.8 (s), 139.5 (s), 133.3 (s), 130.9 (s), 129.2 (s), 128.4 (s), 128.1 (q, $^1J_{C-F}$ = 284.3 Hz), 127.9 (s), 124.2 (s), 118.9 (s), 116.9 (s), 114.9 (s), 63.5 (q, $^2J_{C-F}$ = 23.6 Hz), 28.6 (s), and 28.5 (s). MS: (EI+, m/e , % relative intensity): 548 (M^+ , 20), 479 ($M-69^+$, 100). Elemental analysis: Calcd. for $C_{36}H_{27}F_3O_2$: C, 78.82%; H, 4.96%. Found: C, 78.73%; H, 5.00%. FTIR (KBr): 1466 cm^{-1} (C—H of the four-membered ring; s), 1372, 1279, and 1157 cm^{-1} (C—F; s), 1244 and 1069 cm^{-1} (C—O; s).

1,1'-Bis[4-(4'-benzocyclobutenyloxy)phenyl]-1-(3',5'-dinitrofluoromethyl)phenyl-2,2,2-trifluoroethane (BOPP9FE)

When HPP9FE was used as starting material, a white powder was also afforded according to the synthetic procedures of BOPP3FE described. Yield: 49.6%. 1H -NMR (DMSO- d_6 , δ , ppm): 8.31 (s, 1H); 7.57 (s, 2H); 7.11–7.13 (d; 2H); 7.04–7.06 (d; 4H); 6.98–7.00 (d; 4H); 6.90–6.93 (d; 2H); 6.88 (s, 2H); and 3.11 (s; 8H). ^{13}C -NMR (DMSO- d_6 , δ , ppm): 158.4 (s), 155.1 (s), 147.1 (s), 143.1 (s), 141.5 (s), 132.0 (s), 131.3 (s), 131.2 (q, $^2J_{C-F}$ = 32.7 Hz), 129.8 (s), 127.7 (q, $^1J_{C-F}$ = 286.3 Hz), 124.6 (s), 123.4 (q, $^1J_{C-F}$ = 272.9 Hz), 123.1 (s), 119.4 (s), 117.8 (s), 115.3 (s), 64.0 (q, $^2J_{C-F}$ = 24.2 Hz), 29.0 (s), and 28.9 (s). MS: (EI+, m/e , % relative intensity): 684 (M^+ , 48), 615 ($M-69^+$, 100). Elemental analysis: Calcd. for $C_{38}H_{25}F_9O_2$: C, 66.67%; H, 3.68%. Found: C, 66.77%; H, 3.66%. FTIR (KBr): 1467 cm^{-1} (C—H of the four-membered ring; s), 1367, 1280, and 1155 cm^{-1} (C—F; s), 1259 and 1066 cm^{-1} (C—O; s).

2,2'-Bis[4-(4'-benzocyclobutenyloxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BOP6FP)

Using bisphenol F as starting material, the crude product was also afforded according to the synthetic procedures of BOPP3FE described and recrystallized from ethanol to give a white crystal, mp 103°C. Yield: 46.8%. 1H -NMR (DMSO- d_6 , δ , ppm): 7.29–7.31 (d, 4H); 7.12–7.14 (d, 2H); 6.99–7.01 (d; 4H); 6.91–6.94 (q; 2H); 6.87–6.88 (d; 2H) and 3.12 (s; 8H). ^{13}C -NMR (DMSO- d_6 , δ , ppm): 159.6 (s), 155.2 (s), 147.6 (s), 142.2 (s), 132.2 (s), 126.8 (s), 125.1 (s), 124.9 (q, $^1J_{C-F}$ = 288.1 Hz), 120.1 (s), 117.7 (s), 116.1 (s), 64.2 (q, $^2J_{C-F}$ = 24.6 Hz), 29.5 (s), and 29.4 (s). MS: (EI+,

m/e, % relative intensity): 540 (M^+ , 100), 471 ($M-69^+$, 28). Elemental analysis: Calcd. for $C_{31}H_{22}F_6O_2$: C, 68.89%; H, 4.10%. Found: C, 68.69%; H, 4.16%. FTIR (KBr): 1466 cm^{-1} (C—H of the four-membered ring; s), 1279 and 1173 cm^{-1} (C—F; s), 1247 and 1073 cm^{-1} (C—O; s).

2,2'-Bis[4-(4'-benzocyclobutenyloxy)phenyl]-propane (BOPP)

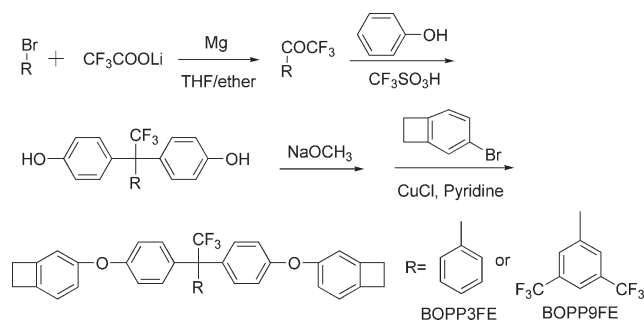
Using bisphenol A as starting material, a white powder was also afforded according to the synthetic procedures of BOPP3FE described. Yield: 53.8%. 1H -NMR (DMSO- d_6 , δ , ppm): 7.17–7.19 (d; 4H); 7.05–7.07 (d; 2H); 6.83–6.85 (d; 4H); 6.80–6.82 (d; 2H); 6.75–6.76 (d; 2H); 3.09 (s; 8H); and 1.61 (s; 6H). ^{13}C -NMR (DMSO- d_6 , δ , ppm): 156.2 (s), 155.9 (s), 146.9 (s), 145.1 (s), 140.6 (s), 128.3 (s), 124.5 (s), 118.8 (s), 117.7 (s), 114.7 (s), 42.0 (s), 31.1 (s), 29.1 (s), and 28.9 (s). MS: (EI+, *m/e*, % relative intensity): 432 (M^+ , 24), 417 ($M-15^+$, 100). Elemental analysis: Calcd. for $C_{31}H_{28}O_2$: C, 86.08%; H, 6.52%. Found: C, 85.59%; H, 6.58%. FTIR (KBr): 1464 cm^{-1} (C—H of the four-membered ring; s), 1260 and 1054 cm^{-1} (C—O; s).

General procedure for preparing BCB resins

The four monomers cured in an oven under nitrogen at 215°C/1 h, 245°C/1 h and postcured at 270°C/2 h, which were determined by differential scanning calorimetry (DSC) tracing of them. After cure, samples were allowed to cool slowly to room temperature to prevent cracking. The obtained resins were all transparent and light yellow in color.

Characterization

1H -NMR spectra was recorded with a Bruker MSL-400 spectrometer using $CDCl_3$ and DMSO- d_6 as solvents. FTIR spectra were obtained using a Perkin-Elmer 782 Fourier transfer infrared spectrophotometer. Mass spectra were recorded on an AEI MS-50 mass spectroscopy. DSC and thermal gravimetric analysis (TGA) were performed on a Perkin-Elmer 7 series thermal analysis system in nitrogen at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was carried out by a Perkin-Elmer 7 series thermal analysis system in nitrogen using at a heating rate of 5°C/min. Mechanical properties were performed on an Instron 3365 Tensile Apparatus with 60 × 15 × 3 mm³ specimens in accordance with GB 1449-87 at a drawing rate of 2 mm/min.²⁵ The solubility was determined as follows: 2.0 g of a BCB monomer or its cured resin was mixed with 8.0 g of a solvent at room temperature (20% solid content). The mixture was then mechanically stirred in nitrogen for 24 h. Water absorptions were determined by weighing the



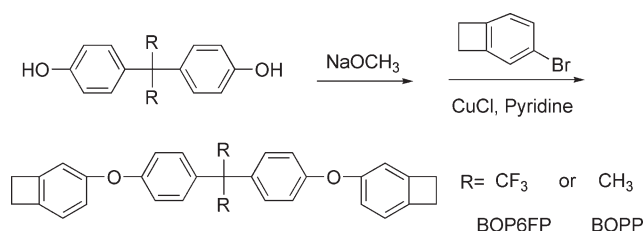
Scheme 1 Synthesis of BOPP3FE and BOPP9FE.

changes of fully cured samples (Φ 50 × 3 mm²) before and after immersion in boiling water for every 24 h. The electrical properties were measured on a Hewlett-Packard 4284A Precision LCR meter. The dielectric constant and dissipation factor were determined by the bridge method with an LKI-1 capacitance meter at a frequency of 1 MHz at 25°C. Rheological measurements were conducted on an AR2000 rheometer of TA Instruments. The measurements for the compacted monomer disks were performed using a parallel-plate fixture (diameter: 25 mm, gap: 1.0 mm) by flow mode with a shear rate of 10 s⁻¹ and a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Monomer synthesis

Two novel fluorinated BCB monomers of BOPP3FE and BOPP9FE were synthesized via a three-step reaction process (Scheme 1). First, fluorinated trifluoroacetophenone of 3FAP and 9FAP were prepared by the Grignard reaction between anhydrous lithium trifluoroacetate and bromobenzene in the presence of magnesium in THF/ether. Second, bisphenol intermediates were synthesized by the coupling reaction of fluorinated trifluoroacetophenone with phenol catalyzed by trifluoromethanesulfonic acid at 60°C. The possible reaction mechanism might be that the carbonyl group activated by the three α -substituted fluorine atoms in trifluoroacetophenone was protonated by the Lewis acid, resulting in carbonium ion which acted as an electrophile for aromatic substitution.²⁶ Then the desired BCB monomers were afforded by Ullmann etherification reaction between the fluorinated bisphenol intermediates and 4-bromo-BCB catalyzed by cuprous chloride in refluxing pyridine. Another two BCB monomers of BOP6FP and BOPP were obtained via a one-step reaction process by Ullmann etherification reaction between the commercial available bisphenol F and A with 4-bromo-BCB (Scheme 2). The four BCB monomers were afforded in moderate yields of 46.8–53.8%, which might be attributed to a copper



Scheme 2 Synthesis of BOP6FP and BOPP.

catalyzed thermal opening of the four membered ring since cuprous chloride has been known to lower the temperature of the polymerization exotherm peak for certain bis-BCB monomers.²

Figure 1 is the FTIR spectra of the four BCB monomers. Absorptions at about 1250 and 1060 cm^{-1} , were assigned as the symmetric and asymmetric stretching vibration of C—O. The characteristic absorptions of O—H in bisphenol intermediates located in the region of 3000–3500 cm^{-1} disappeared in the BCB monomers, indicating that the bisphenol compounds were completely terminated by 4-bromo-BCB. In addition, absorptions at about 1460 cm^{-1} were attributed to the in-plane ring stretching vibration of C—H in the strained four-membered ring.^{9,27}

Figures 2 and 3 show $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of BOPP3FE and BOPP9FE, respectively, in which all the protons and C atoms in these spectra can be assigned clearly. For example, in the $^1\text{H-NMR}$ spectrum of BOPP9FE [Fig. 3(a)], the methylene protons of the four-membered ring (H_1 and H_2) were observed at 3.11 ppm. The protons adjacent to the $-\text{CF}_3$ groups (H_8 and H_9) shifted to the downfield because of the strong electron-withdrawing effect of the two $-\text{CF}_3$ groups, which were observed at 7.57 and 8.31 ppm, respectively. In the $^{13}\text{C-NMR}$ spectrum [Fig. 3(b)], the

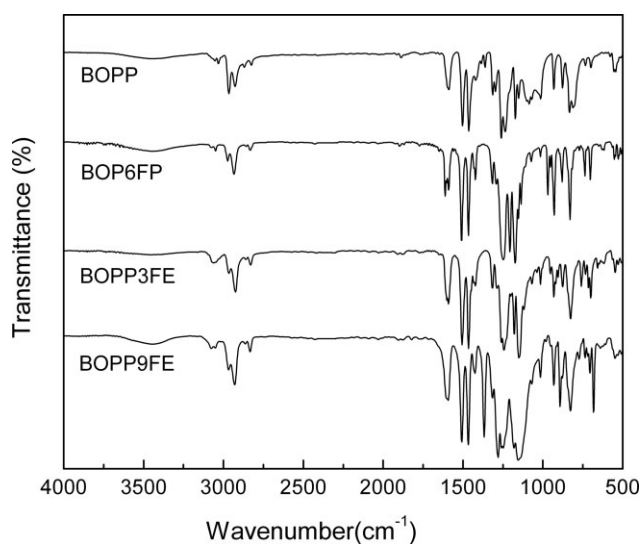


Figure 1 IR spectra of the four BCB monomers.

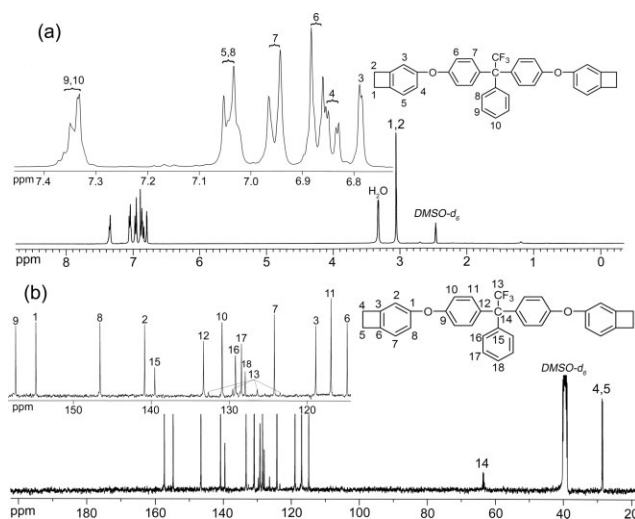


Figure 2 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of BOPP3FE.

aliphatic carbons (C_4 , C_5 , and C_{14}) were observed at 28.9, 29.0, and 64.0 ppm, respectively. Interestingly, quartet absorption peaks were also observed in the $^{13}\text{C-NMR}$ spectrum. C_{14} , C_{19} , C_{13} , and C_{17} exhibited clear quartet absorptions at 63.6–64.4, 119.2–127.5, 123.2–132.4, and 130.8–132.1 ppm, respectively, probably due to the $^1J_{\text{C-F}}$ and $^2J_{\text{C-F}}$ coupling of the carbons with the fluorine atoms in BOPP9FE. Obviously, the coupling effect decreased with the increase in distance between carbon atom and fluorine atom as determined by the coupling constants.

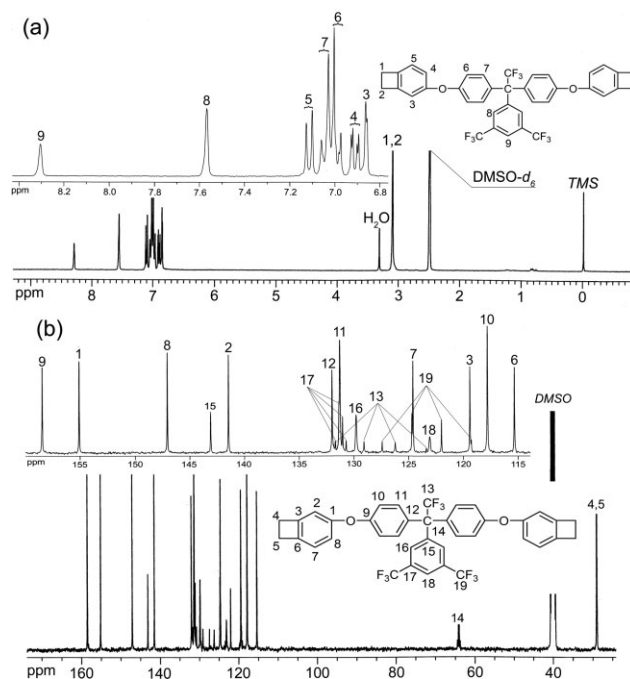


Figure 3 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of BOPP9FE.

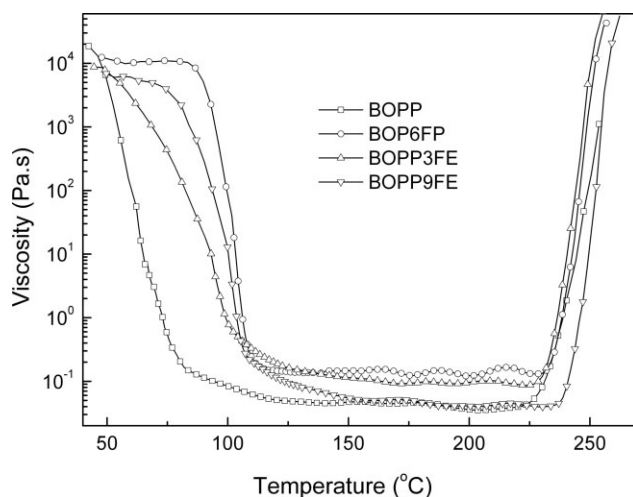


Figure 4 Dependencies of complex viscosity on temperatures for the monomers.

The elemental analysis results of these four monomers were in good agreement with the calculated ones. In the mass spectra of BOP6FP, BOPP3FE, and BOPP9FE, the characteristic peaks at 471, 479, and 615 (M-69, lost a $-\text{CF}_3$ group) were detected, respectively. While in the mass spectra of BOPP the characteristic peak at 417 (M-15, lost a $-\text{CH}_3$ group) was detected. The characterization by NMR, FTIR, EL, and elemental analysis confirmed that all the BCB monomers have the proposed chemical structures.

Rheological properties of the four BCB monomers

The dependencies of complex viscosity on temperatures for the four monomers were evaluated by rheological measurement under parallel plate flow mode with a heating rate of $5^\circ\text{C}/\text{min}$ from 40°C to about 260°C . The dynamic thermal melt complex viscosity curves are shown in Figure 4, and complex melt viscosity data are tabulated in Table I. The viscosities of BOPP, BOP6FP, BOPP3FE, and BOPP9FE decreased with the increase of temperature from 40°C , 90°C to 110°C , 55°C to 106°C , and 95°C to 110°C , respectively, which is attributed to the molecular movement. Then, the viscosities of them remained steady as the temper-

ature increased to no higher than 225°C . Finally, as the temperature enhanced continuously, the viscosities of them increased dramatically because the gelation occurred during this stage. It is also observed that BOP6FP and BOPP3FE exhibited bigger minimum melt viscosities than BOPP and BOPP9FE, which suggests that the molecular interactions of the former are stronger than that of the latter. It can be concluded that all the BCB monomers are very suitable for a wide variety of coating and molding process because of their low and steady melt viscosities between 110 and 200°C , which maybe result from the flexible arylene ether linking groups.

Curing behavior of the four BCB monomers

The cure mechanism of BCB is based on the propensity of the four-membered ring to undergo electrocyclic ring opening at elevated temperatures to provide reactive *o*-quinodimethane that will undergo dimerization and polymerization, or react with an attendant dienophile to form a Diels-Alder adduct. The typical cure temperature ranges from 170 to 300°C .⁶ DSC measurement was employed to investigate the thermal curing behavior of these four BCB monomers. Figure 5 shows the DSC curves and a summary of key aspects to the plots are summarized in Table II. Although BOPP and BOP6FP have the similar structure, BOP6FP showed a melting point at 103°C whereas BOPP exhibited no melting pointing before cure but a glass transition at -5°C . It can be interpreted by the much bigger volume of $-\text{CH}_3$ in BOPP than that of $-\text{CF}_3$ in BOP6FP, which destroyed the order and dense packing of the molecular chain and hindered BOPP crystallization. Likewise, BOPP3FE and BOPP9FE showed no melting points and only demonstrated the glass transitions (T_g) at 21 and 16°C before cure, respectively, which were attributed to the bulky phenyl substituents. The four BCB monomers exhibited similar curing behavior. All of them demonstrated broad exotherms starting at 225 – 229°C (extrapolated onset temperatures) and reaching the peak temperature at 261 – 263°C , which was ascribed to the ring opening of BCB group and the subsequent network-forming reactions. The curing behaviors of these

TABLE I
Complex Melt Viscosity Data of the Four BCB Monomers

Monomer	Complex melt viscosity (Pa s) at				
	50°C	70°C	90°C	150°C	200°C
BOPP	6.6×10^3	2.4	1.1×10^{-1}	5.1×10^{-2}	3.6×10^{-2}
BOP6FP	1.1×10^4	1.1×10^4	5.2×10^3	1.5×10^{-1}	1.2×10^{-1}
BOPP3FE	7.8×10^3	6.9×10^2	1.9×10^1	1.1×10^{-1}	9.7×10^{-2}
BOPP9FE	6.9×10^3	4.9×10^3	2.8×10^2	5.4×10^{-2}	4.1×10^{-2}

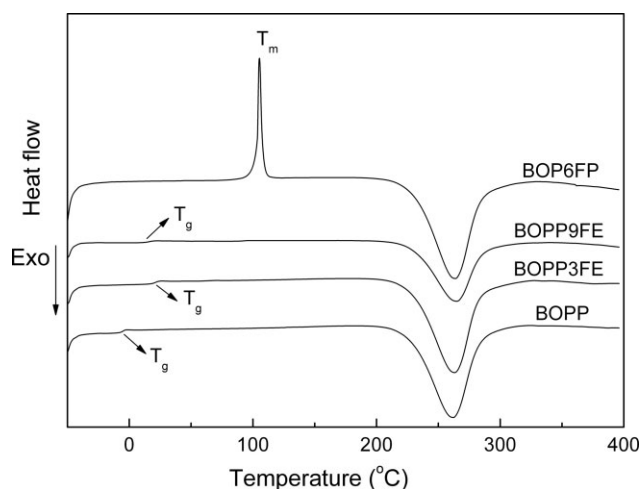


Figure 5 DSC curves of the four BCB monomers.

four monomers coincided well with that of the bis-BCB-terminated arylene ether monomers developed by Tan et al.⁵

Curing conditions are very important for BCB resins. The nonisothermal DSC method was used to investigate the curing conditions for these BCB monomers. It is found that the exothermic peak temperature (T_p) of the curing curves shifted to a higher temperature with an increasing heating rate (β). It is well known that the starting temperature (T_0) of the exothermic reaction corresponds to the crosslink temperature. T_p is relative to the curing temperature and the postcuring temperature is associated with the terminal temperature of the exothermic reaction (T_e). Then, β was extrapolated to zero so that we can approximately determine the curing temperature. Therefore, the crosslinking temperature, the curing temperature and the postcuring temperature of BOPP9FE were 215, 246, and 269°C, respectively, as shown in Figure 6. In the same way, the corresponding temperatures of other three monomers were obtained and summarized in Table III. It can be found that the crosslinking temperatures, the curing temper-

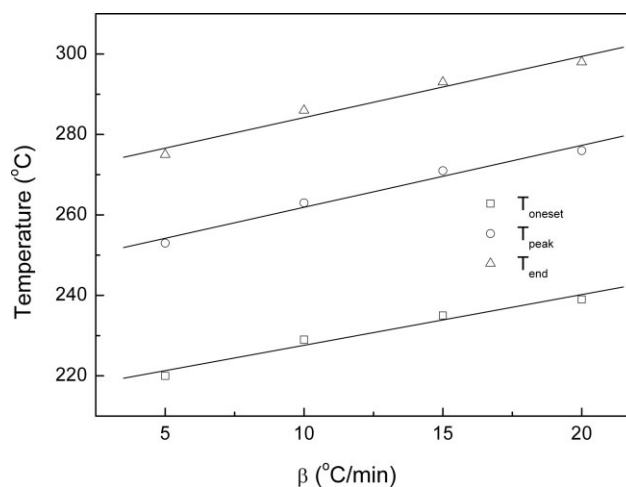


Figure 6 Temperatures of crosslinking, curing, and post-curing for BOPP9FE.

atures and the postcuring temperatures of these BCB monomers were 211–215, 244–248, and 266–269°C, respectively. Therefore, the procedures of 215°C for 1 h, 245°C for 1 h and 270°C for 2 h were chosen as the curing conditions for them.

Figure 7 shows the FTIR spectra of these BCB monomers and their corresponding resins. There appeared the characteristic peaks at about 1460 cm^{-1} in these four monomers, which were attributed to the in-plane ring stretching vibration of C–H in the strained four-membered ring. After cure, these peaks disappeared completely and new peaks appeared at about 1490 cm^{-1} , which were related to the incessant release of strained four-membered ring of BCB during the cure process, implying that these BCB resins have cured fully.²⁷ The solubility of these monomers and their cured resins was tested in various organic solvents. It was found that all the monomers were readily soluble in low-boiling-point solvents such as CHCl_3 , THF, and acetone and in strong polar solvents such as NMP, DMAc, and DMF at room temperature to form homogeneous solution. However, after cure, these BCB resin samples neither dissolved nor obviously swelled in the above solvents tested, indicating that they are highly crosslinked polymers with network structures. The characterization by DSC, FTIR, and solubility confirmed that the cure of these bis-BCB monomers proceeded through the

TABLE II
DSC Data for the Four BCB Monomers^a

Monomer	T_m (°C)	Cure exotherm ^b			Cure enthalpy (J/g)	T_g (°C)
		T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)		
BOPP	– ^c	226	261	284	521	–5
BOP6FP	103	225	261	283	411	–
BOPP3FE	–	228	262	283	416	21
BOPP9FE	–	229	263	286	330	16

^a Conducted under N_2 at 10°C/min.

^b T_{onset} , T_{peak} , and T_{end} were extrapolated from the DSC curves.

^c Not detected.

TABLE III
Temperatures of Crosslinking (T_0), Curing (T_p), and Postcuring (T_e) of the Monomers

Monomer	T_0 (°C)	T_p (°C)	T_e (°C)
BOPP	213	246	268
BOP6FP	211	244	266
BOPP3FE	215	248	266
BOPP9FE	215	246	269

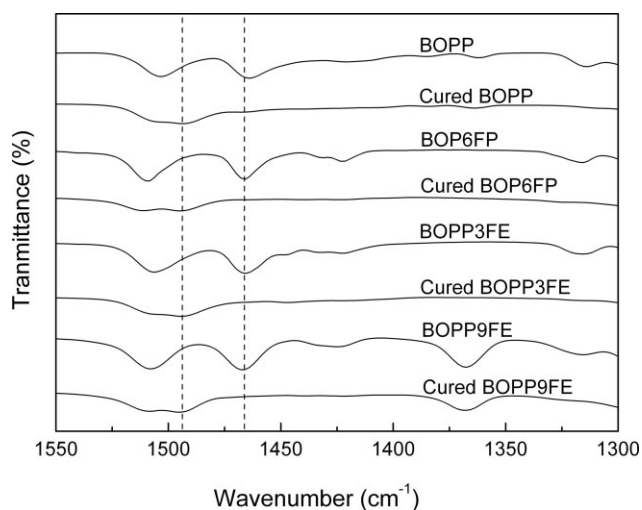


Figure 7 IR spectra of the four BCB monomers and their cured resins.

thermally initiated cyclobutene ring opening to yield reactive *o*-quinodimethane which then undergo dimerization and polymerization with one another randomly to form a highly crosslinked resin.^{6,7}

Thermal properties of the four cured resins

The thermal stability of cured BCB resins were evaluated by TGA measurement and the results are tabulated in Table IV. Figure 8 shows the TGA thermograms of these four cured BCB resins in nitrogen. All of them exhibited good thermal stability and no weight was lost before 400°C. The decomposition temperatures at 5% of weight loss (T_5) for cured BOPP, BOP6FP, BOPP3FE, and BOPP9FE were 482, 476, 470, and 461°C, respectively. However, the resins showed a rapid thermal decomposition when the temperature exceeded 450°C. Despite with the similar chemical structure, cured BOP6FP exhibited much higher thermal stability when compared with

TABLE IV
Thermal Properties of the Four BCB Resins

Sample	TGA (°C)				DMA (°C)	
	T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%)	G'_{onset}	$\tan \delta$
Cured BOPP	482	450	474	26.4	252	269
Cured BOP6FP	476	465	484	40.1	268	282
Cured BOPP3FE	470	440	466	33.2	271	281
Cured BOPP9FE	461	433	457	29.5	213	232

T_d : onset decomposition temperature; T_5 , T_{10} : decomposition temperatures at 5 and 10% of weight loss, respectively; R_w : residual weight retention at 700°C; G'_{onset} : onset temperatures of the storage modulus; $\tan \delta$: the peak temperature of the loss tangent.

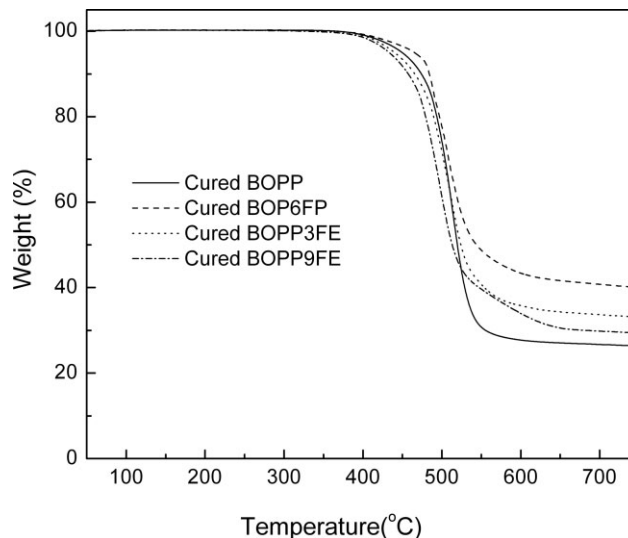


Figure 8 TGA curves of the four cured BCB resins.

cured BOPP. The former demonstrated a residual weight retention of 40.7% at 700°C, whereas the latter exhibited a residual weight retention of 26.7% at the same temperature. The improved thermal stability of cured BOP6FP is probably attributed to the presence of $-\text{CF}_3$ groups in the polymer backbone.

DMA curves of these cured BCB resins are shown in Figure 9 and the results are also summarized in Table IV. Their glass transition temperatures (the peak temperature of the loss tangent) are in the range of 232–282°C and the heights of loss tangent are in the range of 0.018–0.046. When the temperature increased from 50°C to T_g , these four cured resins only exhibited slight drops in the storage modulus, suggesting that all of them can retain good mechanical properties at elevated temperatures. Moreover, in comparison with the other three BCB resins, cured BOPP9FE exhibited a much lower T_g of 232°C, which maybe related to the

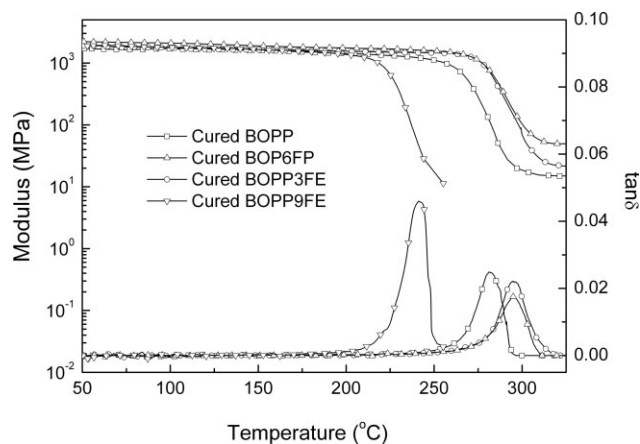


Figure 9 DMA curves of the four cured BCB resins.

TABLE V
Mechanical Properties of the Four Cured BCB Resins

Sample	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongations at breakage (%)
Cured BOPP	88	2.52	48	1.36	2.12
Cured BOP6FP	84	2.71	41	1.24	2.02
Cured BOPP3FE	81	2.94	45	1.35	2.25
Cured BOPP9FE	68	3.15	39	1.48	1.96

bulky phenyl groups and $-\text{CF}_3$ groups in the polymer backbone resulting in a bigger free volume.

Mechanical properties

These cured BCB resins demonstrated acceptable mechanical properties and the results are listed in Table V. The flexural strength and the flexural modulus of them resins are ranged at 68–88 MPa and 2.52–3.15 GPa. The tensile strength and tensile modulus as well as elongations at breakage are in the range of 39–48 MPa, 1.24–1.48 GPa, and 1.96–2.25%, respectively.

Moreover, as shown in Table VI, the retention ratios of the storage modulus (λ) for these cured BCB resins at 200°C to that at 50°C were in the range of 71.8–83.5%, and the λ of cured BOPP, BOP6FP, and BOPP3FE at 250°C to that at 50°C were in the range of 65.8–75.9%, indicating that these cured resins have excellent high-temperature mechanical properties. This is consistent with the character of bis-BCB resins with highly crosslinked network structures.²

Electrical and dielectric properties

As is well known, the electrical and dielectric properties of a BCB resin depends strongly on the group that links the two BCB moieties in the parent monomer. Highly polar linking groups tend to give BCB resins with relatively high (3.0–4.0) dielectric constants and large dissipation factors, whereas the nonpolar linking groups such as siloxane and hydrocarbons, on the other hand, yield polymers with dielectric constants of <3.0.² Table VII shows the

electrical and dielectric properties of these cured BCB resins. The volume resistivities (ρ_v) and surface resistivities (ρ_s) of them were in the range of 8.05×10^{15} to $8.46 \times 10^{16} \Omega \text{ cm}$ and 7.28×10^{16} to $8.65 \times 10^{17} \Omega$, respectively. The dielectric constants (ϵ_r) and the dielectric dissipation factors ($\tan \delta$) at 1 MHz were measured in the range of 2.58–2.88 and $2.7\text{--}8.4 \times 10^{-4}$, respectively. Fluorinated BCB resins exhibited better dielectric properties than cured BOPP. In addition, it can be seen that the dielectric constants and dissipation factors decreased as the fluorine-loading increased, which can be interpreted by the low polarizability of the C–F bond and the large free volume of the CF_3 groups. The dielectric properties of these fluorinated BCB resins are comparable with that of the bis-BCB resin containing siloxane linking group (2.57 at 1 MHz, from Ref. 2). The above results suggest that the CF_3 groups in the network structure of BCB resins played an important role in their electrical and dielectric performance.

Water absorption

Water absorption is a uniquely important property owing to waters' ubiquitous nature and its ability to strongly influence a polymer's mechanical and electrical properties. For example, the introduction of a small amount of water ($\epsilon_r = 78$) into a material will greatly increase its bulk dielectric constant and dissipation factor.²⁸ To a first approximation, water absorption of BCB resins follows in an intuitive way the hydrophilic or hydrophobic character of the linking group which connects the BCB moieties in the

TABLE VI
The Flexural Modulus at Different Temperatures Determined by DMA^a

Sample	Flexural modulus at (GPa)				λ (%)		
	50°C	150°C	200°C	250°C	150°C	200°C	250°C
Cured BOPP	1.72	1.60	1.43	1.11	93.0	83.5	65.8
Cured BOP6FP	2.22	1.89	1.75	1.57	85.1	79.9	71.4
Cured BOPP3FE	1.91	1.64	1.55	1.46	85.9	81.2	75.9
Cured BOPP9FE	1.91	1.65	1.38	–	86.4	71.8	–

^a λ , The ratio of the flexural modulus at the corresponding temperature to that at 50°C; –, Not detected because the temperature is over T_g .

TABLE VII
Electrical and Dielectric Properties of the Four Cured BCB Resins

Sample	F (%)	ρ_v (Ω cm)	ρ_s (Ω)	ϵ_r	$\tan \delta$
Cured BOPP	0	8.05×10^{15}	7.28×10^{16}	2.88	8.4×10^{-4}
Cured BOPP3FE	10.4	2.31×10^{16}	4.31×10^{17}	2.74	4.6×10^{-4}
Cured BOP6FP	21.1	4.87×10^{16}	7.34×10^{17}	2.69	4.1×10^{-4}
Cured BOPP9FE	25.0	8.46×10^{16}	8.65×10^{17}	2.58	2.7×10^{-4}

F, fluorine contents; ρ_v , volume resistivity; ρ_s , surface resistivity; ϵ_r , dielectric constant at 1 MHz at 25°C; $\tan \delta$: dissipation factor.

parent monomer. Figure 10 depicts the dependence of the water absorption of these cured resins on the time. It can be seen that the water absorptions of these BCB resins increased with the increase of time, and the water absorptions of the three fluorinated resins were much lower than that of cured BOPP, which is attributed to the strong hydrophobic character of the $-\text{CF}_3$ groups. When compared with cured BOP6FP, despite cured BOPP9FE has a higher fluorine-loading, it did not demonstrate a better water resistance. This maybe related to the bulky phenyl and $-\text{CF}_3$ in the polymer backbone of cured BOPP9FE resulting in a larger free volume, which allowed the H_2O molecules to diffuse into cured BOPP9FE more easily. In addition, these cured BCB resins showed the water absorptions of 0.38–0.79% in boiling water for 48 h (seen from Fig. 10), which are much lower than that of the bis-BCB resins containing ester linking groups or amide linking groups (0.9 and 1.4%, from Ref. 2), which may be due to the lower polarity of the arylene ether linking groups than that of the ester and amide linking groups. In particular, the water absorption of cured BOP6FP in boiling water for 24 h was as low as 0.29%, which is

comparable with that of the cured bis-BCB resin containing siloxane linking groups (0.25%, from Ref. 2).

CONCLUSIONS

Four novel bis-BCB-encapped arylene ether monomers were synthesized and characterized. All the four monomers showed similar curing behaviors under N_2 . They also demonstrated low and steady melt viscosities between 110 and 200°C because of the flexible arylene ether linking groups, which implies that they have outstanding processability. After cure, the resins derived from these precursor monomers exhibited good thermal stability, high retentions of the mechanical properties from 50 to 200–250°C, excellent dielectric properties and low water absorptions. Compared with cured BOPP, the three fluorinated BCB resins demonstrated relatively lower dielectric constants and water absorptions attributed to the incorporation of $-\text{CF}_3$ groups into the network structure of them. In conclusion, the excellent combined dielectric properties, thermal stability, water resistance, and processability of the fluorinated BCB resins would make them good candidates for protecting or insulating materials for microelectronic assembly and other high-tech fields.

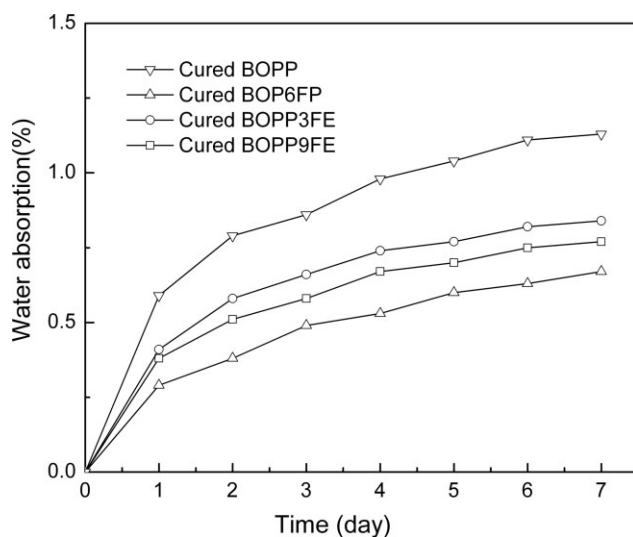


Figure 10 Water absorptions of the four cured BCB resins.

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