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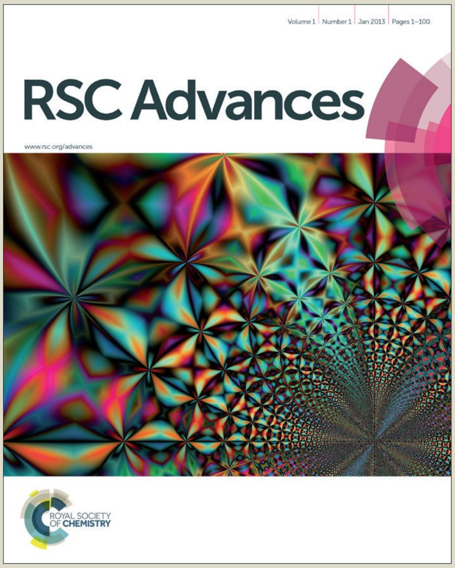

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High Performance Intrinsic Low-*k* Polymer Performed via Taking Synergistic Effect of Its Three Units: Adamantyl-perfluorocyclobutylidene-benzocyclobutene

Lingqiang Kong, Tianke Qi, Zhidong Ren, Yunxia Jin, Yan Li, Yuanrong Cheng, Fei Xiao*

Perfluorocyclobutylidene (PFCB) polymers have gained much interest as the next generation fluoropolymers due to their low dielectric constant, low surface energy, thermal and thermal oxidative stability, and chemical resistance. Herein we got an low-k crosslinked polymer by incorporating the bulk rigid adamantyl, perfluorocyclobutylidene and benzocyclobutene groups into a single monomer. The *k* value is 2.38 and the dielectric loss is less than 0.0004 at 1 MHz due to the effect of the C-F bond and the bulk rigid adamantyl group. The polymer film also showed excellent uniformity and planarity with the surface roughness less than 0.60 nm at 1×1 μm^2 area and good hydrophobicity with the water contact angle of 113.5°. Due to the high crosslinked network structure and the introduction of the rigid adamantly group, the polymer exhibited high young's modulus, high hardness and good thermal stability (Td > 400 °C in nitrogen).

Introduction

Continual efforts to reduce the feature size of microelectronic integrated circuits have brought about new obstacles such as signal crosstalk, resistive-capacitive delay and power dissipation.[1] These problems are mainly derived from unwanted capacitances due to the close proximity of the circuitry and electronic components.[2] To combat these problems, innovative efforts are constantly being carried out to design and synthesize new, low dielectric constant materials.[1,3] In view of the *k* value of air, it is widely accepted that the introduction of pores in materials, typically with pore sizes well below the smallest device features, 10 nm or less, is a promising method to produce low-k materials. Yang et al[4] have got the low-k poly(methylsilsesquioxane) (MSQ) film with *k* value of 1.5, which the pores radius was about 2.7 nm. Mehdipour-Ataei et al[5] prepared nanoporous polyimide films from graft co-polyimides. The average pore size was in the range of 35-70 nm and the *k* value was lowered to 2.30 at 1 MHz. Wang and co-workers[6] obtained nanoporous fluorinated polyimide films from PCL-PI-PCL triblock copolymer using retro-Diels-Alder reaction. The size of the pores was in the range 20-50 nm and the *k* value of the polymer was lowered to 2.10. Recently, the nanofiber with electrospinning provides another way to design and prepare the low-k materials. Wang et al[7,8] have prepared five kinds of polymers by the electrospinning method. They showed low *k* values (1.44-2.04) compared with the bulk polymer (3.0-6.3) at 1MHz. Liu et al[9] have fabricated polylactide-polyglycolide nanofibrous membranes by using an electrospinning setup. The *k* value of the nanofibrous membrane could be as low as 1.22. However, the low-k values of both nanoporous polymer and electrospinning nanofiber were not dependent on the bulk property of the materials, and mainly due to the formation of the holes. They always suffer from the moisture absorption and poor mechanical properties.[1,10-12]

To solve this problem, bulk polymers with low dielectric constants, good mechanical properties and good weather-ability have drawn much attention.[1] Benzocyclobutene (BCB) polymers[13-15] have been widely used as the low dielectric material in the microelectronic industry for their unique properties such as high thermal stability, low dielectric constant and dielectric loss, good flatness and mechanical properties.[16-18] In particular, 1,1,3,3-tetramethyl-1,3-bis[2'-(4'-benzocyclobutenyl)vinyl]disiloxane (DVS-BCB) with a *k* value of 2.6 has been commercialized by Dow Chemical Company as CYCLOTENE, which is one of the widely used dielectric materials for its excellent electrical, thermal, and planarization

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* *Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, P.R. China*
E-mail: feixiao@fudan.edu.cn

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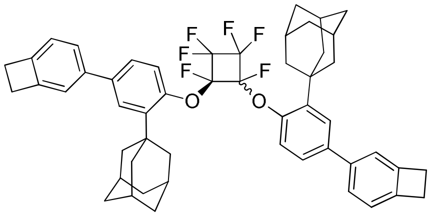
properties.[17,19-21] To meet the requirement of high performance wafer level packaging products, the development of dielectric polymer with lower dielectric constant is highly demanded.

It has been reported that incorporation of adamantyl group into a polymer can improve the its properties, such as increasing the glass transition temperature,[22-25] enhancing the hydrophobicity, and decreasing the dielectric constant.[26-30] In our previous work,[31] we introduced the adamantane into the core of benzocyclobutene siloxane and obtained the hydrophobic and heat resistant polymers with lower dielectric constants. The incorporation of fluorine-containing groups into polymers is another effective way to decrease the *k*-values, due to the small dipole and the low polarizability of the C-F bond as well as the increase of free volume. Perfluorocyclobutylidene (PFCB) polymers have gained much interest as the next generation fluoropolymers due to their many classical properties including low dielectric constant, low surface energy, thermal and thermal oxidative stability, and chemical resistance.[32-38] Fang[39] introduced the perfluorocyclobutylidene group into the naphthalene to obtain new amorphous low *k* fluoropolymer. It showed a low *k* value of 2.33 with a dielectric loss less than 0.0012 at 30 MHz, as well as the higher modulus and bonding strength. After that, Fang[40] introduced the perfluorocyclobutylidene into the organosiloxanes by post-polymerization to afford low *k* material with a dielectric constant of 2.33 and dielectric loss below 0.0021 at 30 MHz.

In this work, to investigate the synergistic effect of adamantly, perfluorocyclobutylidene and benzocyclobutene groups on the dielectric property, we combined the three kinds of units into a single molecule (Scheme 1) and obtained a low k polymer. It showed low dielectric constants (2.38) and low dielectric loss (< 0.001) in a wide range of frequency. Moreover, the high crosslinked polymer exhibited high thermal stability, good hydrophobicity, perfect uniformity and planarity.



BiAdFBCB

Scheme 1 Chemical Structure of the monomer BiAdFBCB

Experimental

Materials

1-Adamantanol (98%), 4-bromophenol (98%), 1,2-dibromoperfluoroethane (99%), bis(pinacolato)diboron (99%), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl_2, 99%), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 98%) and bis(triphenylphosphine)palladium(II) dichloride (Pd(pph_3)Cl_2, 98%) were purchased from J&K Scientific. 4-Bromobenzocyclobutene (4-BrBCB, 97%) was purchased from Chem-target Technologies Co. Ltd. Cesium carbonate (99%), zinc powder (99%) and potassium carbonate (99%) were purchased from Aldrich. Extra dry dimethyl sulphoxide (DMSO, 99.9+%), acetonitrile (99.9+%) and tetrahydrofuran (THF, 99%) were purchased from ACROS.

Characterization

^{1}H, ^{13}C and ^{19}F NMR were measured using Bruker DMX-500 Spectrometer. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet Magna-IR 550 II FT-IR spectrophotometer operating at a resolution of 4 cm^{-1} and using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60H simultaneous DTA-TG apparatus at a heating rate of 10 °C min^{-1} under nitrogen purge rate of 35 mL min^{-1}. Differential scanning calorimetry (DSC) was measured on a TA Q200 calorimeter. Nanoindentation analysis was carried out on a UNHT/NST instrument. Atomic force microscopy (AFM) was measured using SPM-9500J3. The water contact angle was performed on a Dataphysics OCA 15 instrument. Dielectric property was measured by the parallel-plate capacitor method with an agilent 4294A precision impedance analyzer at 25 °C. The solution of BiAdFBCB oligomer in mesitylene was spin-coated on a silicon wafer with a resistivity of 3.5×10^{-3} Ω·cm. Then, the film was degassed in vacuum and cured at 230 °C/1.5 h, 250 °C/1.5 h and 290 °C/0.5 h under nitrogen. Finally, aluminum was vapor-deposited on the surface of the film as electrodes for dielectric constant test. The thickness of BiAdFBCB polymer film is 0.265 μm and the electrode area was 0.0314 mm^2.

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Preparation of monomers

2-(4’-Benzocyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (I). 4-BrBCB (2.0 g, 11 mmol), bis(pinacolato)diboron (3.3 g, 12 mmol), Pd(dppf)Cl$_2$ (70 mg, 0.1 mmol), dppf (50 mg, 0.1 mmol), potassium acetate (3.2 g, 33 mmol) and 1,4-dioxane (40 mL) were added to a round bottom flask under nitrogen. The mixture was heated to reflux with stirring overnight. After the reaction was completed, it was poured into 100 mL water and extracted with petroleum ether (30 mL×3). The combined organic phase was washed with water (100 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was purified by flash chromatography (silica gel) to afford 2-(4’-benzocyclobutenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.1 g, 84%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.68 (d, 1H), 7.49 (s, 1H), 7.07 (d, 1H), 3.18 (s, 4H), 1.33 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 148.9, 144.6, 132.6, 127.6, 120.9, 82.7, 29.1, 28.8, 24.0.

4-Bromo-2-(1’-adamantyl)phenol (II). 4-Bromophenol (5.0 g, 29 mmol) and 1-adamantanol (4.4 g, 29 mmol) were dissolved in dichloromethane (DCM, 50 mL) in a round bottom flask, then a mixture of concentrated sulfuric acid (1.6 mL) and acetic acid (8 mL) was added dropwise to the reaction solution. The mixture was stirred at room temperature for 24 h, poured into 200 mL water. The organic phase was neutralized to pH 7 with triethylamine, washed with water (50 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was purified by flash chromatography (silica gel) to afford 4-bromo-2-(1’-adamantyl)-phenol (8.8 g, 100%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.29 (d, 1H), 7.16-7.14 (d d, 1H), 6.53 (d, 1H), 4.75 (s, 1H), 2.08 (s, 9H), 1.77 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 153.5, 138.7, 130.2, 129.3, 118.3, 113.3, 40.3, 36.9, 29.7, 28.9.

4-Bromo-2-(1’-adamantyl)-1-(2’-bromo-1’,1’,2’,2’-tetrafluoroethoxy)benzene (III). 2-(1-Adamantyl)-4-bromophenol (8.0 g, 26 mmol), cesium carbonate (17 g, 52 mmol) and DMSO (50 mL) were added to a 2-neck round bottom flask under nitrogen protection. The mixture was stirred at room temperature for about 30 min, then 1,2-dibromoperfluoroethane (19 g, 73 mmol) was added to the mixture slowly. The reaction mixture was stirred at 50 °C for about 12 h under nitrogen, poured into 150 mL water. It was extracted with petroleum ether (50 mL×3), the combined organic phase was washed with water (100 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was purified by flash chromatography (silica gel) to afford 4-bromo-2-(1’-adamantyl)-1-(2’-bromo-1’,1’,2’,2’-tetrafluoroethoxy)benzene (12 g, 91%) as a colerless oil. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.46 (d, 1H), 7.33 (d d, 1H), 7.23 (m, 1H), 2.08 (s, 3H), 2.03 (d, 6H), 1.76 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 148.1, 142.8, 131.4, 129.8, 120.3, 119.0, 118.3-116.1(m, -CF$_2$Br), 113.9-110.9(m, -OCF$_2$) 40.4, 37.3, 36.6, 28.8. ^{19}F NMR (470 MHz, CDCl$_3$, δ): -67.0 (t, 2F), -84.7 (m, 2F).

4-Bromo-2-(1’-adamantyl)-1-(trifluorovinyloxy)benzene (IV). 4-Bromo-2-(1’-adamantyl)-1-(2’-bromo-1’,1’,2’,2’- tetrafluoroethoxy)benzene (7.0 g, 14 mmol), activated zinc powder (3.7 g, 58 mmol) and acetonitrile (50 mL) were added to a round bottom flask under nitrogen. The reaction mixture was refluxed with stirring for about 24 h. Then it was cooled down to room temperature and filtered. The filtrate was concentrated and purified by flash chromatography (silica gel) to afford 4-bromo-2-(1’-adamantyl)-1-(trifluorovinyloxy)benzene (4.2 g 75%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 7.42 (d, 1H), 7.32-7.30 (d d, 1H), 6.89-6.87 (d d, 1H), 2.09-2.05 (m, 9H), 1.77 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 153.0, 141.1, 131.4, 129.9, 117.8, 115.7, 150.0-144.9 (d d d, =CF$_2$), 135.1-132.1 (m, -OCF), 40.6, 37.3, 36.7, 28.8. ^{19}F NMR (470 MHz, CDCl$_3$, δ): -118.7 (q, 1F), -126.4 (q, 1F), -134.2 (q, 1F).

1,2-Bis(2’-(1’’-adamantyl)-4’-bromophenoxy)hexafluorocyclobutane (V). 4-Bromo-2-(1’-adamantyl)-1-(trifluorovinyloxy)benzene (4.0 g, 10 mmol) was added to a round bottomed flask under nitrogen. It was heat to 200 °C for about 10 h and then cooled down to room temperature. The product was purified by flash chromatography (silica gel) to afford 1,2-bis(2’-(1’’-adamantyl)-4’-bromophenoxy)hexafluorocyclobutane (3.5 g, 88%) as a colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$, δ):7.45(d, 2H), 7.28-7.26(d d, 2H), 7.09-7.07(d d, 2H), 2.09(m, 18H), 1.78(s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$, δ):150.2, 140.7, 130.5, 128.9, 117.3, 116.3, 114.2(m), 112.1(m), 107.9(m), 105.7(m), 39.4, 36.5, 35.8, 28.0. ^{19}F NMR (470 MHz, CDCl$_3$, δ): -128.4~-128.9 (m, 6F).

1,2-Bis(2’-(1’’-adamantyl)-4’-(4’’-benzocyclobutyl)-phenoxy)hexafluorocyclobutane (BiAdFBCB). 1,2-Bis(4’-bromo-2’-(1’’-adamantyl)phenoxy)hexafluorocyclobutane (2.3 g, 3.0 mmol), Pd(PPh$_3$)Cl$_2$ (0.10 g, 0.15 mmol), 4-pinacolatoboronbenzocyclobutene (2.1 g, 8.9 mmol), potassium carbonate (1.2 g, 8.9 mmol), THF (50 mL) and water (10 mL) were added into a 100 mL round bottom flask under nitrogen protection. The mixture was heated to reflux with stirring overnight. Then it was cooled to room temperature and 30 mL water was added. The mixture was extracted with ethyl acetate (30 mL×3). The combined organic phase was washed with saturated salt water (50 mL), dried over NaSO$_4$, filtered and

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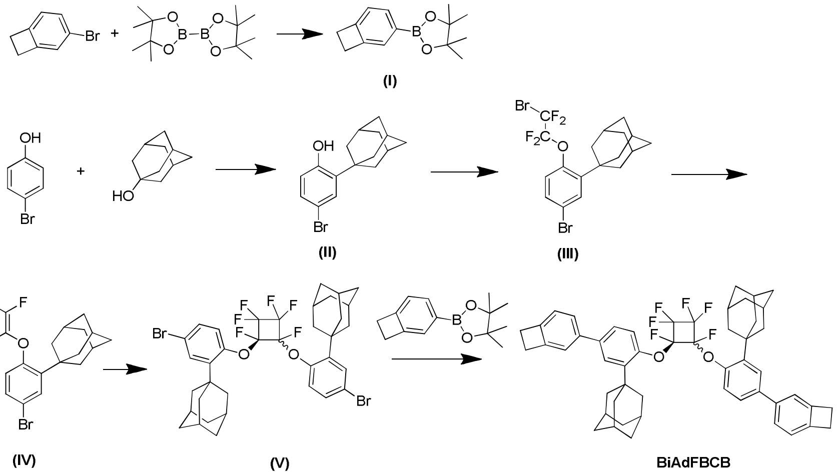
concentrated. The residue was purified by flash chromatograph to afford the 1,2-bis(2’-(1’’-adamantyl)-4’-(4’’-benzocyclobutyl)-phenoxy)hexafluorocyclobutane (1.8 g, 74%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.51(d, 2H), 7.37-7.35(d d, 2H), 7.30-7.29(m, 4H), 7.23(s, 2H), 7.01(d, 2H), 3.20(s, 8H), 2.20(s, 12H), 2.13(s, 6H), 1.81(t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ):150.4, 145.4, 144.1, 138.9, 138.4, 138.0, 126.2, 125.2, 124.7, 121.9, 120.7, 114.9, 112.3 (m), 110.0 (m), 108.0 (m), 105.8 (m), 39.8, 36.4, 36.0, 28.6, 28.5, 28.2. ^{19}F NMR (470 MHz, $CDCl_3$, δ): -128.5~-129.0 (m, 6F). MALDI-TOF-MS: m/z = 820.4 (M^+, 100%), 821.4 (61%). Mass Calculated for $C_{52}H_{50}F_6O_2$: 820.94.

Preparation of polymer film

The BiAdFBCB monomer (1.0 g) was dissolved in mesitylene (3.0 g) and heated at 180°C for 18~20 h to afford the oligomers.[41,42] Then the oligomer was spin-coated on a silicon wafer and heated at 230 °C/1.5 h, 250 °C/1.5 h and 290 °C/0.5 h in vacuum. After cooling down to room temperature, the polymer films were used for testing.

Results and discussion

The synthetic route of the monomer BiAdFBCB is shown in Scheme 2. The Suzuki reagent containing BCB group, 2-(4’-benzocycolbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (I), was obtained from 4-BrBCB and bis(pinacolato)diboron by Suzuki reaction in high yield. 1-Admantanol and 4-bromophenol were reacted in DCM solution with catalytic amounts of concentrated sulfuric acid to give 4-bromo-2-(1’-adamantyl)phenol (II). Then it was reacted with $BrCF_2CF_2Br$ and followed by Zn-mediated elimination to afford 4-bromo-2-(1’-adamantyl)-1-(trifluorovinyloxy)benzene (IV). The perfluorocyclobutane intermediate, 1,2-bis(2’-(1’’-adamantyl)-4’-bromophenoxy)hexafluorocyclobutane (V), was prepared via the bulk thermal [2π + 2π] cycloaddition of IV at 200 °C. Finally, the target molecule, BiAdFBCB, was obtained by Suzuki reaction of (V) and (I). The structure changes of the intermediates were followed by NMR, as shown in the experimental section. And the structure of BiAdFBCB was confirmed by ^{1}H, ^{13}C and ^{19}F NMR, FTIR, and MALDI-TOF-MS (Supporting information Fig. S1).



Scheme 2 Synthetic route of BiAdFBCB

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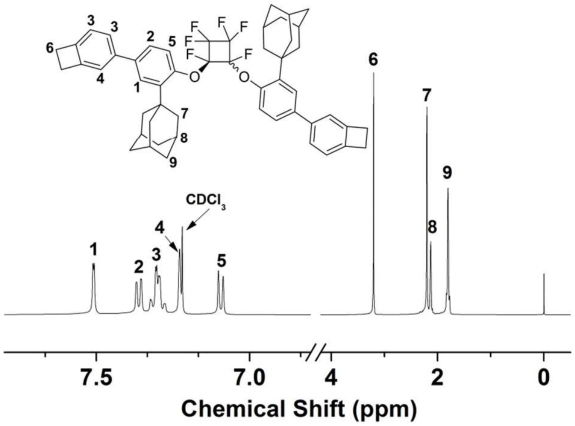

Fig. 1 ^{1}H NMR spectrum of BiAdFBCB

The ^{1}H NMR spectrum and the proton assignment of BiAdFBCB is shown in Fig. 1. The peaks between 7.51 and 7.01 ppm belong to the protons of benzene rings. The singlet at 3.20 ppm is the characteristic peak of the protons on the four-membered ring of BCB. The single peaks at 2.20 and 1.81 are attributed to the methylene of adamantyl groups. The peak at 2.13 is assigned to the protons attached to the three tertiary carbons. Fig. 2 shows the ^{13}C NMR spectrum of BiAdFBCB. The peaks between 150.4 and 114.9 are attributed to the carbons of the benzenes. The peaks at 28.6 and 28.5 ppm are assigned to the methylene carbons of the BCB ring. Due to the split of the fluorine, the carbons of perfluorocyclobutylidene show weak and multiplet peaks between 105-113 ppm. The peaks at 39.8, 36.4, 36.0 and 28.2 ppm are assigned to the carbons of adamantane. Both ^{1}H NMR and ^{13}C NMR are in good agreement with the chemical structure of BiAdFBCB.

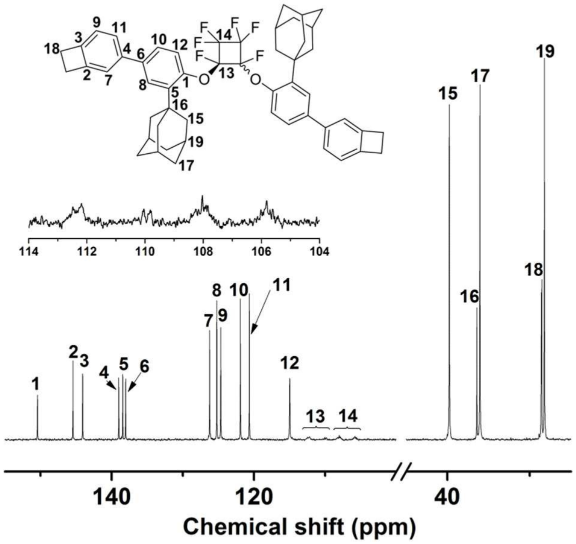

Fig. 2 ^{13}C NMR spectrum of BiAdFBCB

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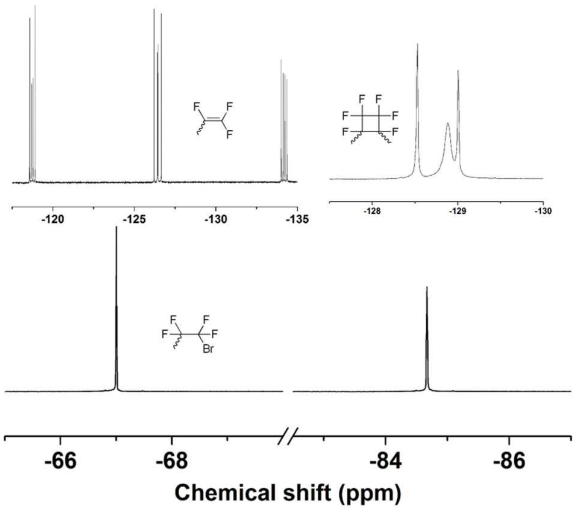

Fig. 3 ^{19}F NMR spectra of precursors and BiAdFBCB

Fig. 3 shows the ^{19}F NMR spectra of the precursors and BiAdFBCB. The chemical shifts of the fluorine in –CF_2-CF_2Br appear at -67.0 and -84.7 ppm. The peaks at -118.7, -126.4 and -134.2 ppm are attributed to the fluorine of -CF=CF_2. When -CF=CF_2 was dimerized to perfluorocyclobutylidene, the multiplet peaks appeared at -128.5~-129.0 ppm.

Fig. 4 compares the FTIR of BiAdFBCB and its precursors. The CF_2=CFO stretching vibration peak at 1834.2 cm^{-1} disappeared after dimerization,[36,43] and a new strong peak of perfluorocyclobutylidene appeared at 962.4 cm^{-1}. This suggested that the trifluorovinyl had turned into perfluorocyclobutylidene completely.

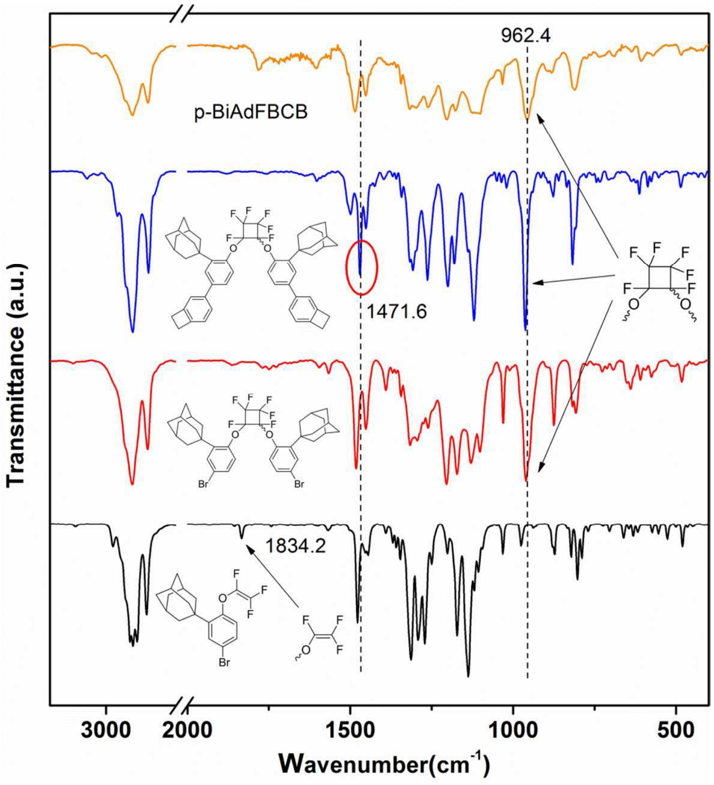

Fig. 4 FT-IR spectra of precursors, BiAdFBCB and p-BiAdFBCB

The polymerization of BiAdFBCB is due to the strained four-membered ring opening reaction of BCB and the following radical polymerization or Diels-Alder reaction, as illustrated in Scheme 3. The FT-IR of

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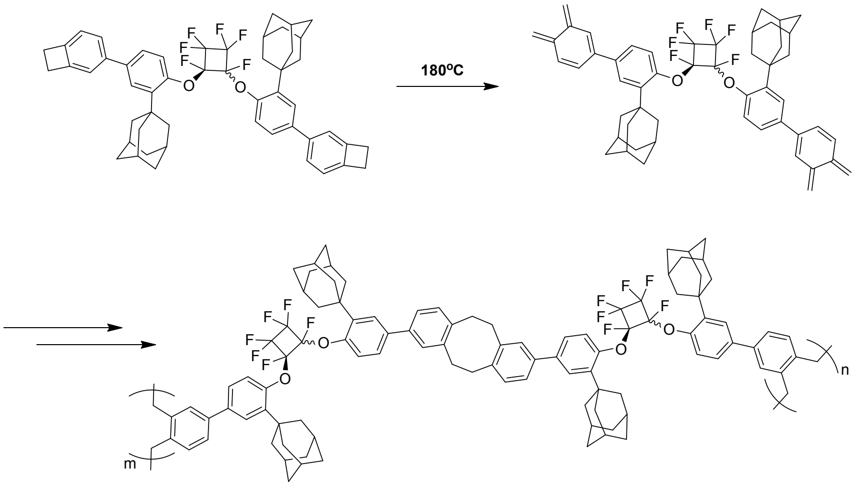
the cured polymer p-BiAdFBCB is also shown in Fig. 4. The characteristic peak of the four-membered ring of BCB at 1471 cm^{-1} disappeared after the monomer was cured.[44,45] And the strong peak of perfluorocyclobutylidene still exists at 962.4 cm^{-1}. The polymer was highly crosslinked due to the two BCB rings in the monomer. Fig. 5 shows the schematic crosslinked mesh structure of the BiAdFBCB polymer.



Scheme 3 The polymerization mechanism of p-BiAdFBCB

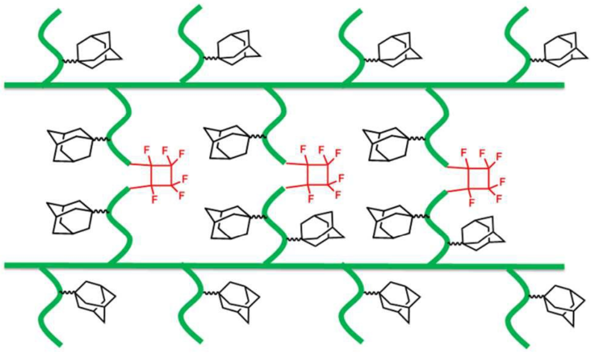


Fig. 5 Schematic crosslinked mesh structure of p-BiAdFBCB

In order to study the polymerization of BiAdFBCB, the curing reaction was monitored by DSC with a heating rate of 10 °C min^{-1} under nitrogen. As shown in Fig. 6, the endothermic peak indicates the melting point of BiAdFBCB at about 96.3 °C. The curing profile of BiAdFBCB shows an onset temperature at about 200 °C and peak temperature at 260.7 °C. The exothermic enthalpy of polymerization of BiAdFBCB is about 151.2 kJ mol^{-1}.

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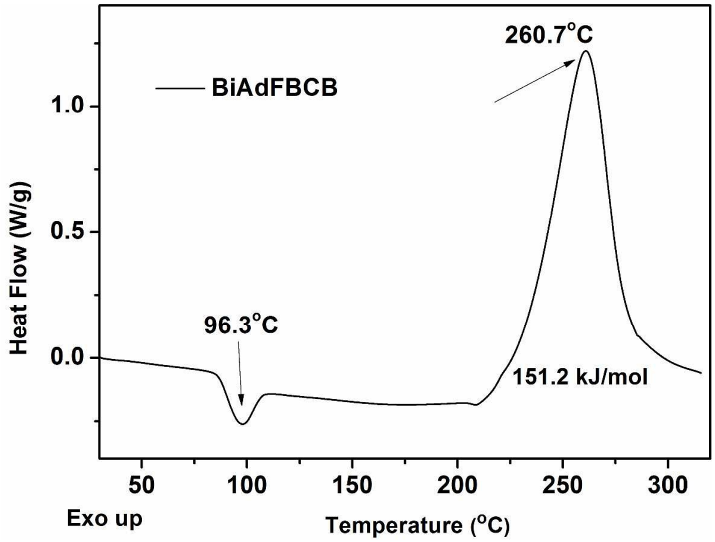

Fig. 6 DSC traces of monomer BiAdFBCB at different heating rates

The frequency dependency of dielectric constant (*k*) and dielectric loss (tan δ) of the cured BiAdFBCB (p-BiAdFBCB) film at room temperature are shown in Fig. 7. The *k* value of p-BiAdFBCB film is 2.38 and the average dielectric loss is below 0.0005 in a range of frequencies varying from 100 KHz to 5 MHz. Moreover, the dielectric constant is independent on the frequency in the testing range of frequency. The *k* value is much lower than those of reported low-*k* materials[12], such as BCB, polyarylenes, polybenzoxazoles.

The introduction of perfluorocyclobutylidene into the polymer can lower the molecular polarizability and the surface energy. Besides, the non-polar bulky rigid adamantyl group can increase the free volume and reduce the packing density of the polymer. Fig. 5 intuitively shows the structure of the polymer and it is easily to understand the effect of the introduction of adamantyl and perfluorocyclobutylidene. These factors further decrease the *k* value of BCB, resulting in low *k* of p-BiAdFBCB.

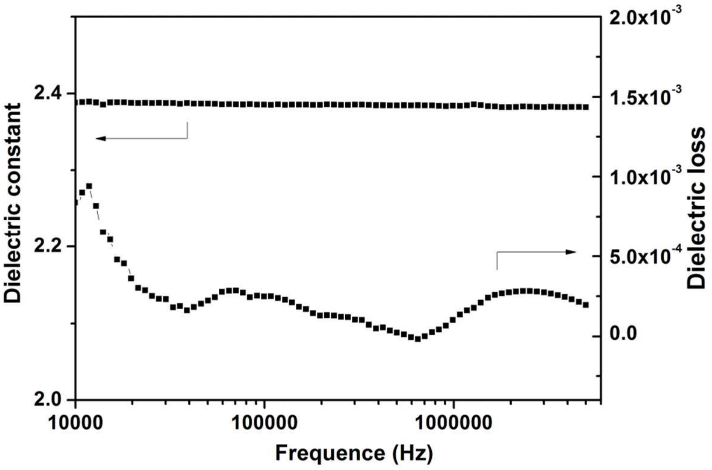

Fig. 7 Frequency dependency of dielectric constant and dielectric loss of p-BiAdFBCB

The morphology is an important factor for the application of low *k* materials in electronic packaging. The surface morphology of the polymer film on a silicon wafer was investigated using atomic force microscopy (AFM). Both planar graph and stereogram are shown in Fig. 8. The average surface roughness (Ra) of p-BiAdFBCB was 0.60 nm in a 1.0×1.0 μm^2 area, exhibiting perfect uniformity and planarity. The p-BiAdFBCB film also shows good hydrophobicity with a water contact angle of 113.5°, as shown in Fig. 9. This suggests the low moisture absorption of the polymer, which may effectively prevent the influence of moisture on the dielectric properties.

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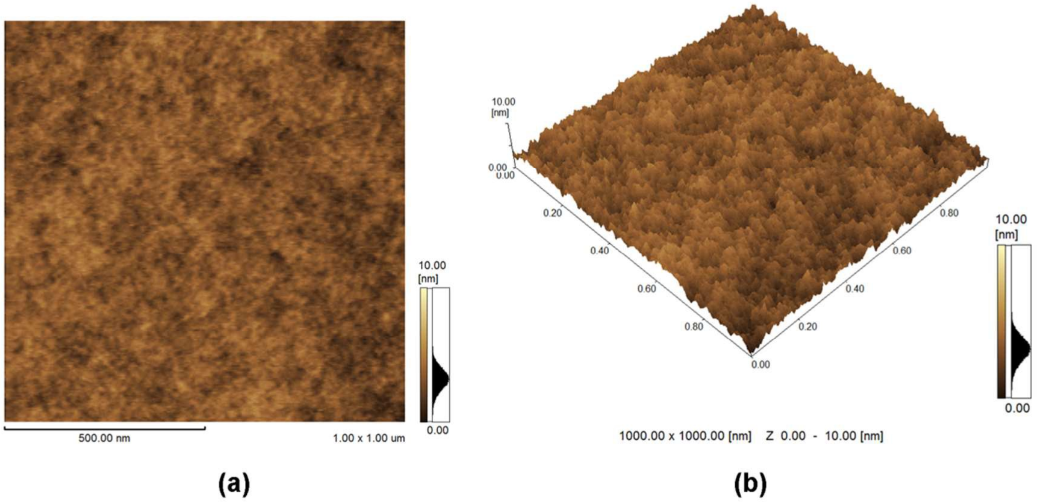

Fig. 8 AFM images of p-BiAdFBCB film on silicon wafer: (a) planar graph; (b) stereogram (45°)

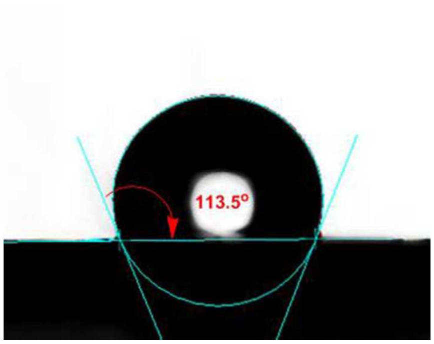

Fig. 9 Contact angle of water on the p-BiAdFBCB films

The thermostability of p-BiAdFBCB was evaluated by DSC and thermal gravimetric analysis (TGA). DSC trace does not show any glass transition in a range of temperatures from 30 to 370 °C (inset of Fig. 10), suggesting a good thermal stability of the polymer that the Tg is probably higher than 370 °C. The high thermostability was also revealed by TGA results (Fig. 10), in which p-BiAdFBCB showed the 5 wt% loss temperature of 447 °C and the 10 wt% loss temperature of 461 °C. Furthermore, p-BiAdFBCB showed a high residual weight of about 65% at 850 °C in nitrogen.

The mechanical property of p-BiAdFBCB film was determined by a nanoindentation system. As shown in Fig. 11, the film had an average hardness of 0.769 ± 0.004 GPa and a Young's modulus of 10.9 ± 0.1 GPa. Both the average hardness and Young's modulus are higher than that of the high crosslinked organosilicon polymer containing perfluorocyclobutylidene group (hardness 0.392 GPa, Young's modulus 10.06GPa) prepared by Fang.[40]

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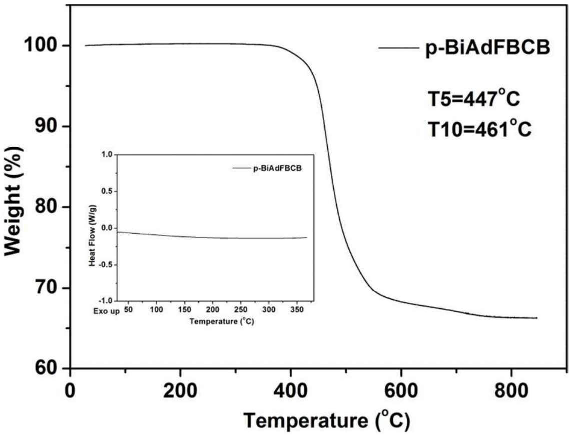

Fig. 10 TGA and DSC curves of p-BiAdFBCB

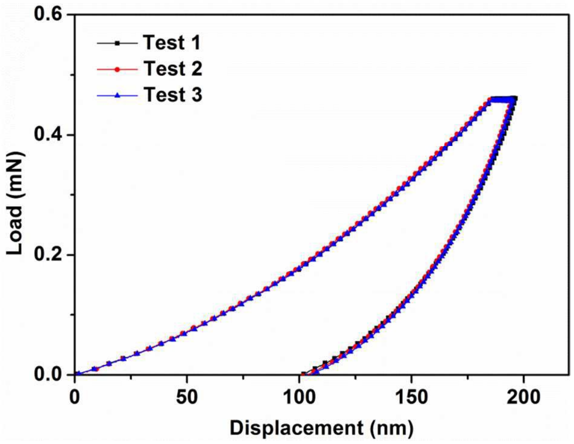

Fig. 11 The nanoindentation curves of p-BiAdFBCB film

Conclusions

In summary, we have designed and synthesized a new bulk low *k* polymer by combination of three low polar units of adamantyl, perfluorocyclobutylidene and benzocyclobutene. It shows a dielectric constant of 2.38 with the dielectric loss less than 0.0004 at 1 MHz. The *k* value and the dielectric loss were lower than most of the previously reported low *k* polymers such as BCB, polyarylenes, polybenzoxazoles, polycyanate esters and epoxy resins. Such low *k* and low dielectric loss properties were due to the synergistic effect of adamantly, perfluorocyclobutylidene and benzocyclobutene in the polymer. The polymer film also showed excellent uniformity with the surface roughness of 0.60 nm at 1×1 μm^2 area and good hydrophobicity with the water contact angle of 113.5°. Due to the introduction of rigid adamantyl group and the high crosslinked structure, the polymer exhibited high thermal stability, high hardness and the high young's modulus. The good dielectric, thermal and mechanical performance of the benzocyclobutene polymer containing adamantyl and perfluorocyclobutylidene groups showed potential application in microelectronic packaging.

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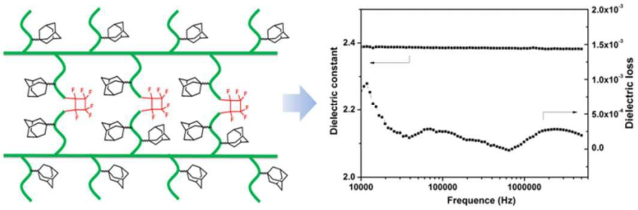

Intrinsic high crosslinked low-*k* benzocyclobutene polymer functionalized with adamantyl and perfluorocyclobutylidene.