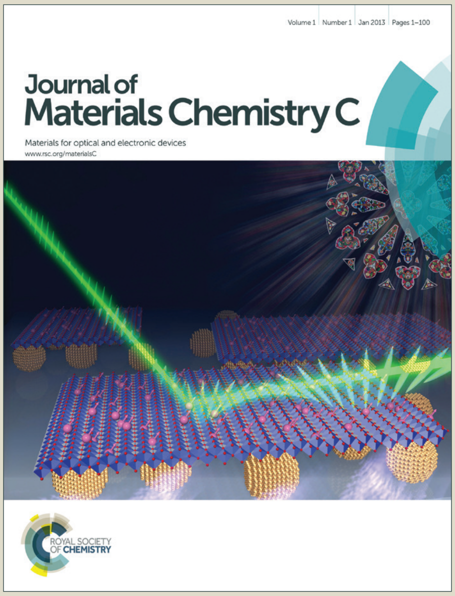
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Adamantyl-based benzocyclobutene low-*k* polymers with good physical properties and excellent planarity

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

Low dielectric polymers play an important role in replacing traditional inorganic dielectric materials in advanced electronic manufacturing due to their excellent physical and chemical properties. Herein we report the preparation and characterization of two novel low-*k* dielectric polymers by introducing adamantane into benzocyclobutene. Because the adamantyl group has low polarizability and can increase the free volume of the polymer, both polymers showed low dielectric constants (2.50) and low dielectric loss (< 0.001) at the frequency within 10 KHz - 5 MHz. They also showed excellent film uniformity and planarity with the surface roughness less than 0.6 nm and the good hydrophobicity with the contact angle larger than 107°. Due to the high cross-linked network structure, both of the adamantyl-based BCB polymers exhibited high glass transition temperature (> 350 °C), high storage modulus and good thermal stability (T_d > 400 °C in nitrogen). Especially, Ada-TVS-BCB polymer showed low coefficient of thermal expansion (41 μm/m°C). All of these good properties are in accord with the requirement of the interconnect fabrication of Cu metallization using the damascene process. Both of the polymers are suitable for the utilization in the electronic packing industry.

Introduction

The dielectric properties of the insulating layers in high density interconnect is an important factor, for the lower dielectric constant (low k) contributes synergistically to both higher circuit density and speed. The application of new low dielectric constants polymers will enable the development of future generations of lower cost and higher performance integrated circuits (ICs). In last decades, various low k materials[1-9] including silicates, polyimides, benzoxazine, SiLK, or benzocyclobutene have been developed, whereas commercially available low *k* materials with low cost are rare. To achieve low *k* materials, various methods have been reported,[1-3,10] such as introducing fluorinated groups into a polymer[4,5,11,12], introducing bulky non-polar groups[13] into a polymer or creating the porous structure in a polymer[14]. However, most of them reveal some defects, for example, the porous materials show ultra-low *k* value but they always exhibit easy moisture adsorption and poor mechanical properties. The fluorinated materials usually have low *k* values, but they always show poor adhesion to metal and poor dimensional stability. Therefore, introducing the bulky non-polar groups into the polymer becomes the feasible approach in designing and preparation of low *k* materials.

It is well know that adamantane as a compound represents the smallest unit of the diamond lattice, and consists of three fused cyclohexane rings in the “chair” configuration. It has long been considered a strain free molecule because the structure features are thought to be “ideal”. Due to its symmetrical bulky rigid and non-polar aliphatic structure, adamantane has high thermal stability and shows large free volume effect in a polymer. It has been always incorporated into the backbone or as a pendant group of many types of polymers to lower the dielectric constants[15] or increase the thermal stability.[16-18] The molar polarizability of the polymer can be “diluted” by increasing the content of adamantyl group in polymer. Furthermore, the massive rigid structure of adamantyl groups would change the symmetry of the polymer chains, thus reduce the packing density and increase the average molar volume of the polymer in the space.[19-22] Chern[21,23], Watanabe[24] and Mathews[25] had introduced adamantane into polyimides in the

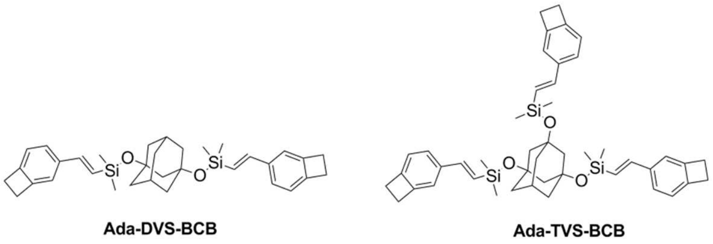
---

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

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

backbone or as a pendant, resulting in various kinds of polyimides with low dielectric constants and high thermal stability. Wang et al[19,26] has prepared a series of novel adamantane-based co-poly(aryl ether ketone)s and found that the dielectric constant decreased with the increase of the adamantyl content.

To lower the k value and improve the thermal stability and mechanical properties, adamantane group was introduced into the BCB siloxane and two novel low k polymers were obtained by curing the monomers (Scheme 1) at programmed temperature. Both polymers show low dielectric constants (2.5) and low dielectric loss (< 0.001) in a wide range of frequency. Moreover, they exhibit high cross-linked structure and high thermal stability with Td > 400 °C in nitrogen. They also show a good dimensional stability, especially the polymer p-Ada-TVS-BCB has low coefficient of thermal expansion of 41 μm/m°C.



Scheme 1 Chemical structure of Ada-DVS-BCB and Ada-TVS-BCB

Experimental

Materials

1,3-Adamantanediol (98%), 1,3,5-adamantanetriol (95%) and tri(o-tolyl)phosphine (P(o-tol)$_3$, 98%) were purchased from J&K Scientific. 4-Bromobenzocyclobutene (4-Br-BCB, 97%) was purchased from Chem-target Technologies Co. Ltd. Palladium (II) acetate (Pd(OAc)$_2$, 98%) was purchased from Strem Chemicals Inc. Extra dry tetrahydrofuran (THF, 99.9+%), acetonitrile (99.9+%), N, N-dimethylformamide (DMF, 99.9+%) and triethylamine (TEA, 99%) were purchased from ACROS.

Characterization

^{1}H NMR and ^{13}C NMR measurements were made using Bruker DMX-500 Spectrometer. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet Magna-IR 550 II FT-IR spectrophotometer, at a resolution of 4 cm^{-1}, with 32 scans 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. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 instrument by the three-point bending mode at a heating rate of 3 °C min^{-1} with the test frequency at 1 Hz. X-ray diffraction (XRD) was carried out using a Bruker D8 advance (Cu K$_\alpha$). Atomic force microscopy was carried out using SPM-9500J3. Contact angle of water testing 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. Ada-DVS-BCB and Ada-TVS-BCB were degassed in vacuum and cured at 180 °C/1 h, 210 °C/1 h, 230 °C/1.5 h, 250 °C/1.5 h and 290 °C/0.5 h in glass molds under nitrogen, and then the bulk polymers were polished as square blocks. Aluminum was vapor-deposited on both sides of the samples as electrodes for dielectric constant test. The thickness of p-Ada-DVS-BCB and p-Ada-TVS-BCB were 1.24 mm and 1.29 mm, respectively, and the electrode area was 12.50 mm×12.50 mm.

Synthesis of monomers

1,3-Bis(dimethylvinylsiloxy)adamantane (Ada-DVS).

1,3-Adamantanediol (4.0 g, 23.8 mmol), THF (70 mL), DMF (20 mL) and TEA (7.2 g, 71.4 mmol) were added to a 250 mL 3-neck round bottle flask under nitrogen protection. Chlorodimethylvinylsilane (7.2 g, 59.5 mmol) was added dropwise into the mixture cooled in an ice bath in 20 min. Then the reaction mixture was warmed to room temperature and stirred overnight. After the reaction was completed, 100 mL saturated salt solution was added and the mixture was extracted with petroleum ether (50 mL*3). The combined organic phase was washed with deionized water (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in 20 mL petroleum ether and purified by flash chromatography (silica gel) to afford Ada-DVS (7.8 g, 97%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.23-6.14 (m, 2H), 5.95-5.91 (d d, 2H), 5.76-5.70 (d d, 2H), 2.19 (s, 2H), 1.81 (s, 2H), 1.62 (s, 8H), 1.41 (s, 2H), 0.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 139.3, 130.5, 72.7, 53.1, 43.7, 33.8, 30.4, 0.0.

1,3-Bis((2'-(4'-benzocyclobutenyl)vinyl)dimethylsiloxy)adamantane (Ada-DVS-BCB).

Ada-DVS (6.4 g, 19.0 mmol), 4-Br-BCB (8.7 g, 47.5 mmol), $Pd(OAc)_2$ (0.43 g, 1.9 mmol), $P(o\text{-}tol)_3$ (1.2 g, 3.8 mmol) and TEA (13.9 g, 95 mmol) were added into a 250mL 3-neck round bottle flask under nitrogen protection. Then acetonitrile (100 mL) was added to the mixture by syringe. The mixture was heated to reflux with stirring for 48 h under nitrogen. After the reaction was completed, 100 mL water was added and the mixture was extracted with ethyl acetate (80 mL*3). The combined organic phase was washed with saturated salt solution (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (silica gel, UV 254 nm) to afford Ada-DVS-BCB (6.8 g, 67%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25 (d, 2H), 7.19 (s, 2H), 7.01 (d, 2H), 6.92-6.89 (d, 2H), 6.39-6.35 (d, 2H), 3.16 (s, 8H), 2.19 (s, 2H), 1.89 (s, 2H), 1.69 (t, 8H), 1.41 (s, 2H), 0.27 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 146.3, 146.1, 145.2, 137.4, 127.7, 126.3, 122.6, 120.2, 73.9, 54.5, 44.9, 34.9, 31.5, 29.6, 29.4, 1.6.

1,3,5-Tris(dimethylvinylsiloxy)adamantane (Ada-TVS).

1,3,5-Adamantanetriol (3 g, 16.3 mmol), THF (90 mL), DMF (20 mL) and TEA (9.1 mL, 65.2 mmol) were added into a 250 mL 3-neck round battle flask under nitrogen protection. Chlorodimethylvinylsilane (7.87 g, 65.2 mmol) was added dropwise to the mixture cooled in an ice bath in 20 min. Then the reaction mixture was warmed to room temperature and stirred overnight. After the reaction was completed, 100 mL saturated salt solution was added and the mixture was extracted with petroleum ether (50 mL*3). The combined organic phase was washed with deionized water (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in 20 mL petroleum ether and purified by flash chromatography (silica gel) to afford Ada-TVS (6.2 g, 98%) as a colorless oil which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.23-6.14 (m, 3H), 5.98-5.93 (d d, 3H), 5.77-5.71 (d d, 3H), 2.20 (s, 1H), 1.72 (q, 6H), 1.54 (d, 6H), 0.20 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 139.2, 130.9, 73.2, 52.2, 42.6, 28.8, 0.0.

1,3,5-Tris((2'-(4'-benzocyclobutenyl)vinyl)dimethylsiloxy)adamantane (Ada-TVS-BCB).

Ada-TVS (5.0 g, 12.9 mmol), 4-Br-BCB (8.2 g, 45.0 mmol), $Pd(OAc)_2$ (0.29 g, 1.3 mmol), P(o-tol)$_3$ (0.78 g, 2.57 mmol), TEA (12.5 mL, 90.1 mmol), acetonitrile (100 mL) and water (1 mL) were added into a 250 mL 3-neck round bottle flask under nitrogen protection. The reaction mixture was heated to reflux and stirred for 10 h under nitrogen. After the reaction was completed, 100 mL water was added. The mixture was extracted with ethyl acetate (80 mL*3). The combined organic phase was washed with saturated salt solution (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (silica gel, UV 254 nm) to afford Ada-TVS-BCB (7.1 g, 79%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34 (d, 3H), 7.28 (s, 3H), 7.10 (d, 3H), 7.01-6.98 (d, 3H), 6.47-6.43 (d, 3H), 3.26 (s, 12H), 2.28 (s, 1H), 1.98-1.88 (q, 6H), 1.66 (s, 6H), 0.35 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 146.4, 146.2, 145.5, 137.4, 127.4, 126.5, 122.7, 120.3, 74.3, 53.5, 43.7, 29.9, 29.7, 29.5, 1.6.

Preparation of BCB Polymers

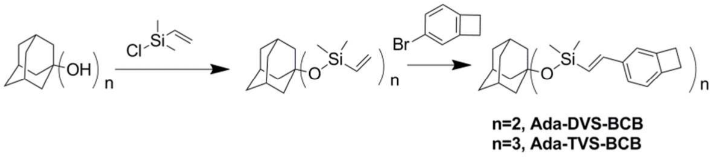
Monoliths of Ada-DVS-BCB and Ada-TVS-BCB were prepared by placing the monomer directly into the glass mold. After degassing in a vacuum oven at 130 °C for 0.5 h, the molds were heated stepwise at 180 °C/1 h, 210 °C/1 h, 230 °C/1.5 h, 250 °C/1.5 h and 290 °C/0.5 h. After cooled down to room temperature, the thermosetting resins were polished as rectangular bars with a size of 20.00 mm×6.20 mm×0.87 mm (p-Ada-DVS-BCB) and 20.00 mm×5.79 mm×0.97 mm (p-Ada-TVS-BCB) for DMA test.

The monomer (1.0 g) was dissolved in mesitylene (3.0 g) and refluxed for 30~48 hours to afford the oligomers.[27,28] Then the oligomer was spin-coated on the silicon wafer and heated at 250 °C for about 4 hours in vacuum. After cooling down to room temperature, the polymer films were used for AFM and water contact angle tests.

Results and discussion

Preparation and Characterization of the BCB Monomers

The monomers were prepared by two steps as shown in Scheme 2. The adamantanol reacted with vinyldimethylchlorosilane to form the vinyl-containing intermediate which was used in the following Heck reaction without further purification to afford Ada-DVS-BCB or Ada-TVS-BCB. We found that the heck reaction time can be reduced considerably by addition of a catalytic amount of water. All the monomers structure was confirmed by NMR (support information). The synthetic route is simple and convenient. Both monomers are colorless oil, which are convenient for the further process.



Scheme 2 Synthetic route of Ada-DVS-BCB and Ada-TVS-BCB

Fig. 1 shows the ^{1}H NMR spectra of Ada-DVS-BCB and Ada-TVS-BCB. Due to the similar structure, both spectra are nearly same except for the integration. The peaks at 7.25, 7.19 and 7.01 ppm are attributable to the protons of the benzene ring. The double peaks at 6.92 and 6.39 ppm belong to the protons on the olefinic group. The splitting *J* value is 19 Hz, suggesting a trans-olefin structure. The characteristic singlet at 3.17 ppm is attributable to the protons on four-membered ring of BCB. The peak at 0.27 ppm is assigned to the methyl protons attached to Si. The protons of adamantyl group appear at 2.19, 1.89, 1.69 and 1.41 ppm for Ada-DVS-BCB and at 2.28, 1.98 and 1.66 ppm for Ada-TVS-BCB.

Fig. 2 shows the ^{13}C NMR spectra of the two monomers. The peaks at 146.3, 146.1, 145.2, 137.4, 127.7 and 126.3 ppm were attributed to the carbon of the benzene. The olefinic carbon resonances appear at 122.6 and 120.2 ppm. The peaks at 29.6 and 29.4 ppm are assigned to the methylene carbons of the BCB ring. The singlet at 1.6 ppm is attributed to the methyl carbon attached to Si. The carbons of adamantyl group appear at 73.9, 54.5, 44.9, 34.9 and 31.5 ppm for Ada-DVS-BCB and at 74.3, 53.5, 43.7 and 29.9 ppm for Ada-TVS-BCB. Both ^{1}H NMR and ^{13}C NMR are in good agreement with the chemical structure of Ada-DVS-BCB and Ada-TVS-BCB.

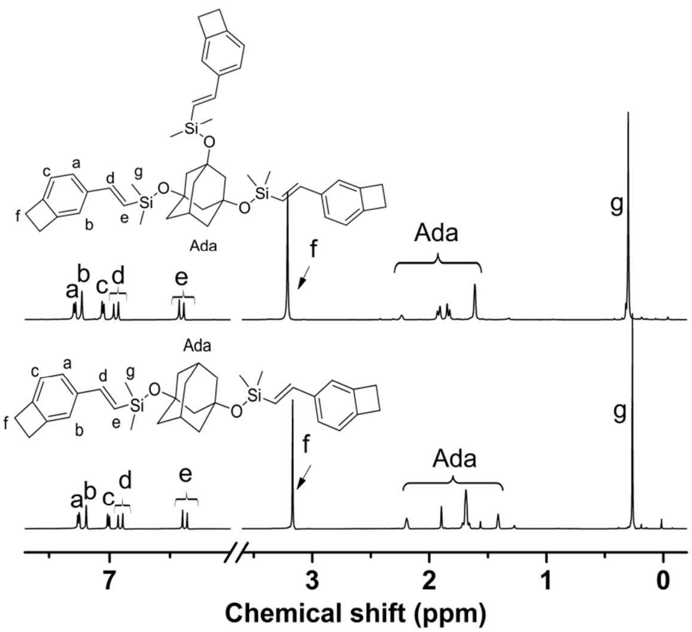


Fig. 1 ^{1}H NMR spectra of Ada-DVS-BCB and Ada-TVS-BCB

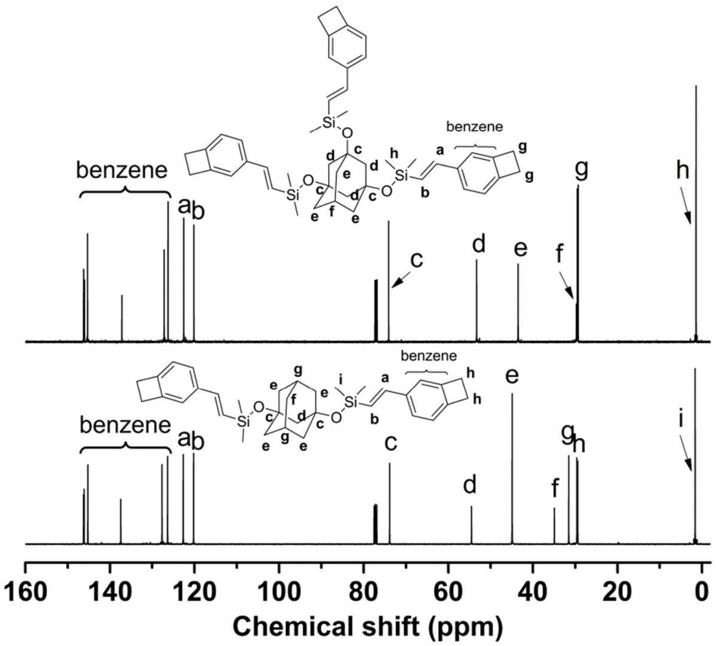


Fig. 2 ^{13}C NMR spectra of Ada-DVS-BCB and Ada-TVS-BCB

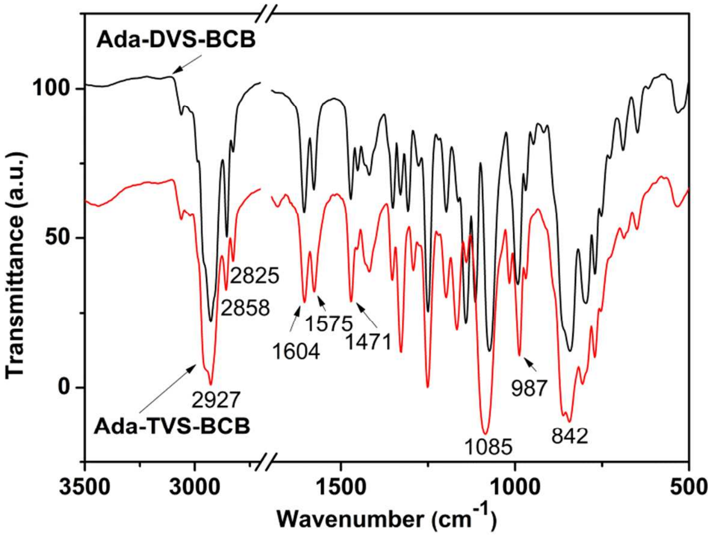


Fig. 3 FT-IR spectra of Ada-DVS-BCB and Ada-TVS-BCB

Fig. 3 shows the FT-IR spectra of Ada-DVS-BCB and Ada-TVS-BCB. Both spectra show the C-H stretching vibration of methyl and methylene at 2927, 2858 and 2825 cm^{-1}. The bands at 1604 cm^{-1} and 1575 cm^{-1} are due to the stretching vibration of C=C in the benzocyclobutene. The characteristic absorption for the deformation vibration of C-H in the strained four-membered ring of benzocyclobutene appears at 1471 cm^{-1}. The strong peak at 1085 cm^{-1} is attributable to the stretching vibration of Si-O-C. The absorption at 987 cm^{-1} is assigned to the out-of-plane bending vibration of olefinic C-H, it is another evidence for the trans-configuration of the olefinic group. The peak at 842 cm^{-1} is assigned to the bending vibration of Si-CH_3.[29]

Curing Behavior of the BCB Monomers

Both adamantyl-based BCB monomers are cured in a similar mechanism due to the same benzocyclobutene functional group in their structure. When the temperature was above 180 °C, the four-membered ring of benzocyclobutene opened and formed an o-quinodimethane active intermediate which can couple with each other or react with other olefin by Diels-Alder reaction.[30-32] The polymerization of Ada-DVS-BCB and Ada-TVS-BCB was followed by DSC and FT-IR. The resulting thermograms of DSC scan are shown in Figure 4. Due to the same benzocyclobutene groups in the structure, which can undergo a ring-opening and the following Diels-Alder addition or polymerization at elevated temperatures, both monomers showed similar curing profiles with an onset at 200 °C and a maximum at 258-259 °C. The exothermic enthalpy of polymerization of Ada-DVS-BCB and Ada-TVS-BCB are 200.9 and 355.4 kJ mol^{-1}, respectively. The ratio of the exothermic enthalpy is approximate to 2:3, which is in good accordance with the number of benzocyclobutene groups in the monomers.

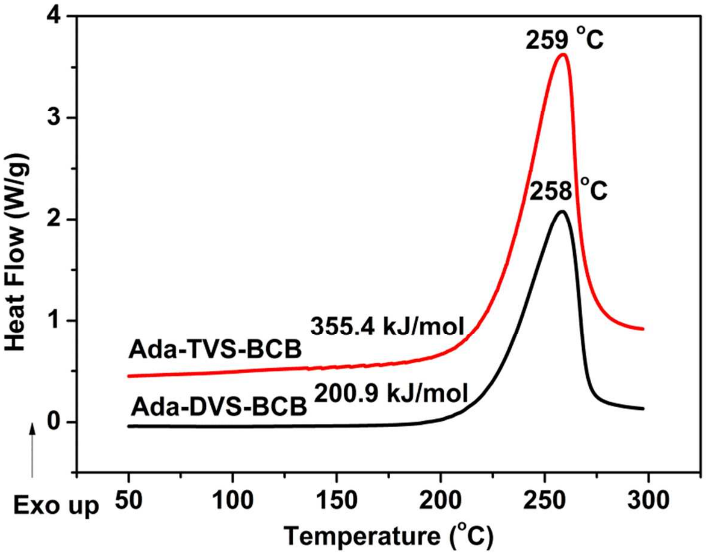


Fig. 4 DSC thermograms of Ada-DVS-BCB and Ada-TVS-BCB

Fig. 5 shows the FT-IR spectra of Ada-DVS-BCB and Ada-TVS-BCB and their polymers, p-Ada-DVS-BCB and p-Ada-TVS-BCB respectively. The peaks at 2825 cm^{-1} in both monomers, assigned to the stretching vibration of C-H in the four-membered ring of benzocyclobutene, disappeared after the monomers were cured.[33] The characteristic peak of BCB monomers at 1471 cm^{-1} was transferred to 1500 cm^{-1} after the polymerization.[34,35]

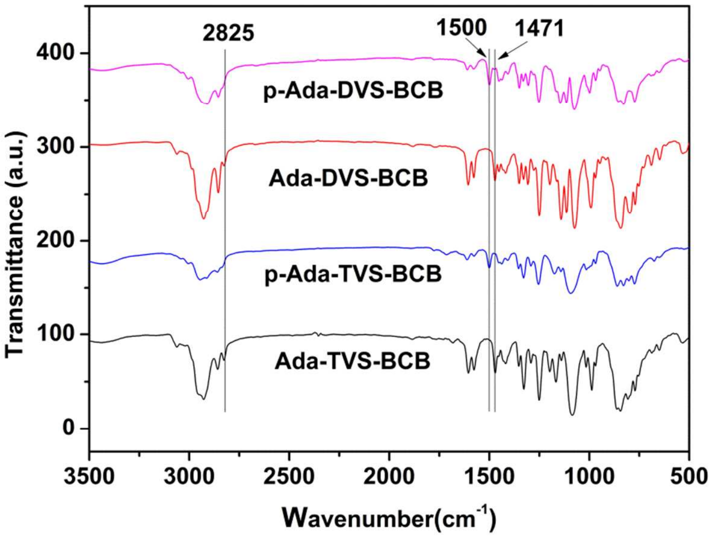


Fig. 5 FT-IR of Ada-DVS-BCB, Ada-TVS-BCB and their polymers

Dielectric Properties

Dielectric constant (*k*) is an important parameter for materials applied in electronic packaging industry. The lower the *k*, the faster the basic wave propagation velocity, the lower the line capacitance per unit length and the higher the characteristic impedance that can be obtained for a fixed conductor cross section. Dielectric loss is another important electrical parameter. The dielectric constants and dielectric loss of both polymers were shown in Fig. 6. The dielectric constants of p-Ada-DVS-BCB and p-Ada-TVS-BCB are 2.50 and 2.52 at 1 MHz, and the dielectric loss of p-Ada-DVS-BCB and p-Ada-TVS-BCB are 0.00035 and 0.00078 at 1MHz, respectively. The dielectric constants of both resins nearly do not change with the frequency within 10 KHz-5 MHz. Both of the resins show lower dielectric properties than those of most widely used low k materials, such as polyimides, polycyanate esters, SiLK, DVS-BCB[30,36,37] and CYC-BCB[28].

The low dielectric property of the p-Ada-DVS-BCB and p-Ada-TVS-BCB polymers can be explained by Clausius-Mossotti equation (Eqn 1)[1,2]

$$\frac{k-1}{k+2}=\frac{4\pi}{3}N\left(\alpha_e+\alpha_d+\frac{\mu^2}{3k_bT}\right) \qquad (1)$$

where k, k_b, N, α_e, α_d and μ is dielectric constant, Boltzmann constant, density of dipoles, electronic polarization, distortion polarization and the dipole moment, respectively. For both of p-Ada-DVS-BCB and p-Ada-TVS-BCB, introducing the C-C bonds can lower the electron density and make the molecule difficult to be polarized, resulting in the reduction of α_e and α_d. Moreover, the large rigid structure of adamantane can prevent the molecular stacking and increase the free volume of the polymer, thus decrease the N and μ. The reduction of all the factors (N, α_e, α_d and μ) in Eqn (1) demonstrates that the adamantyl-based polymers have low *k* property.

The X-ray diffraction (XRD) patterns as shown in Fig. 7 suggest that both of the adamantyl polymers are essentially amorphous. The XRD peak (2θ) = 14.2° and 14.6° corresponds to the *d* value[4,5,38,39] of 0.624 nm and 0.607 nm for p-Ada-DVS-BCB and p-Ada-TVS-BCB, respectively. The large *d* spacing indicates the large free volume, resulting in the low dielectric constants of the polymers. On the other hand, there are three BCBs coupled with one adamantyl group in p-Ada-TVS-BCB. More BCBs condense the interspace although it can increase the cross-linking density. Thus, both of the *d* value and the cross-linking density suggest that the dielectric constant of p-Ada-DVS-BCB is a little lower than that of p-Ada-TVS-BCB.

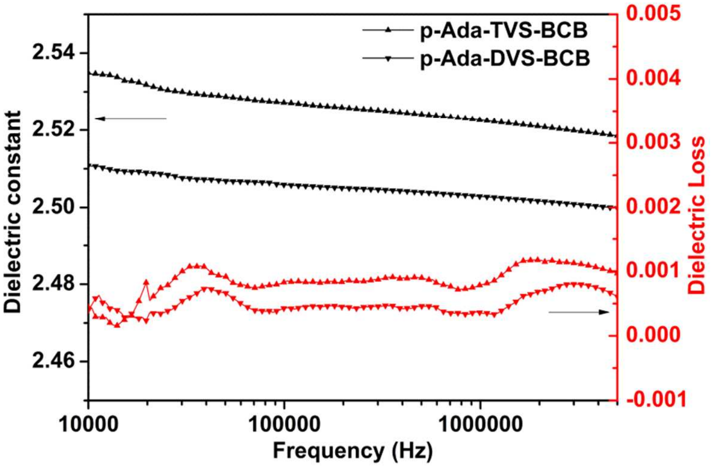


Fig. 6 Frequency dependency of dielectric constant and dielectric loss at room temperature of the polymers

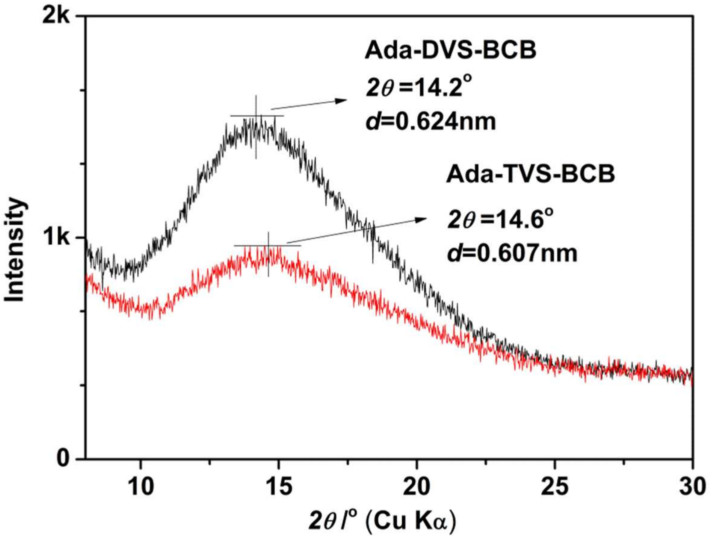
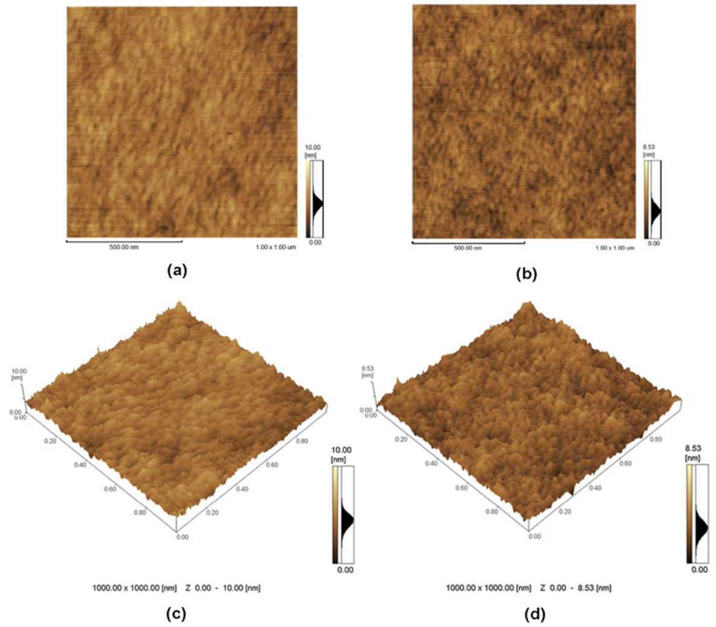


Fig. 7 X-ray diffraction (XRD) patterns of polymers (powder)

Morphology of the polymers

The surface morphology is crucial to the production of the low *k* materials. We investigated surface morphology of the polymer films on a silicon wafer using atomic force microscopy (AFM). Both planar graph and stereogram were shown in Fig. 8. The average surface roughness Ra of p-Ada-DVS-BCB and p-Ada-TVS-BCB were 0.57 nm and 0.52 nm in a 1.0×1.0 μm^2 area, respectively. Both films showed perfect uniformity and planarity.

We also studied the hydrophobicity by testing the contact angle of water on the surface of the films as shown in Fig. 9. The contact angle of p-Ada-DVS-BCB and p-Ada-TVS-BCB were 107.6° and 108.9°, respectively. Both films exhibit good hydrophobicity that could effectively prevent the moisture adsorption and the deterioration of the dielectric properties.



(a) (b)

(c) (d)

Fig 8 AFM images of polymer films on silicon wafer: p-Ada-DVS-BCB (a, c) and p-Ada-TVS-BCB (b, d); (a, b) planar graph, (c, d) stereogram (45°)

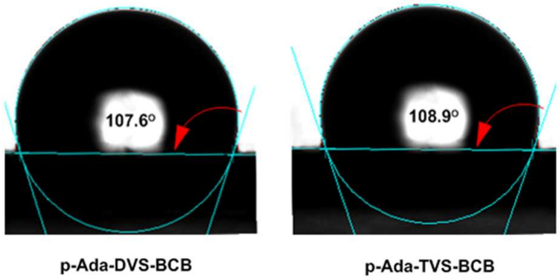


Fig. 9 Contact angle of water on the polymer films

Mechanical Properties

The DMA curves of the two BCB resins are shown in Fig. 10, both resins exhibit high storage modulus. The storage modulus at 30 °C of p-Ada-TVS-BCB (4.28 GPa) is higher than p-Ada-DVS-BCB (2.89 GPa). The high storage modulus of the resins is caused by the high cross-linking density and the introduction of rigid adamantane group. The glass transition temperature (T_g) of p-Ada-DVS-BCB is 353 °C taken as the peak temperature in tan δ curve. The storage modulus of the p-Ada-TVS-BCB only slightly decreases with the increase in temperature in a wide range from 30 to 300 °C. There is no peak in tan δ curve of p-Ada-TVS-BCB, that indicates its T_g is higher than 350 °C. The high T_g is attributed to the high cross-linking structure of the resins.

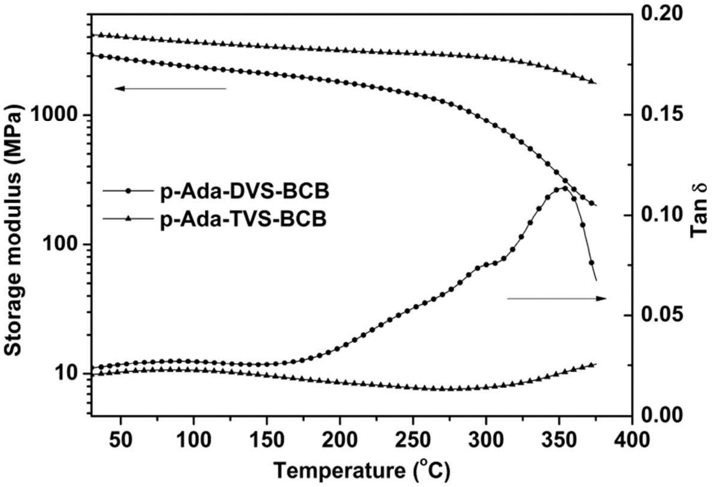


Fig. 10 DMA curves of the BCB polymers

The thermal expansion behaviors of the BCB polymers were examined by TMA and the results are shown in Fig. 11. The sample thickness of p-Ada-TVS-BCB and p-Ada-DVS-BCB is 0.9230 mm and 1.3642 mm, respectively. Both polymers show linear dimension change-temperature dependence over the measured temperature range. It is noted that both polymers do not show obvious point of inflexion in the dimension change-temperature curves, which is usually corresponding to the glass transition. As discussed above, p-Ada-DVS-BCB shows a glass transition temperature at about 353 °C in DMA measurement. The reason for this uncommon behavior is not clear, probably due to the low CTE difference between glassy state and rubbery state. Because of the higher cross-linking density, p-Ada-TVS-BCB has a lower CTE (41 μm/m°C) than p-Ada-DVS-BCB (76 μm/m°C) at glassy state. The CTE of p-Ada-TVS-BCB is also smaller than that of the resin DVS-BCB (65 μm/m°C) reported by Burdeaux (Dow Chemical).[37] This result points out that high cross-linking in the structure can enhance the dimensional stability. The low CTE and less temperature dependent characteristic enable the material a good matching with electronic components for application in temperature variable environment.

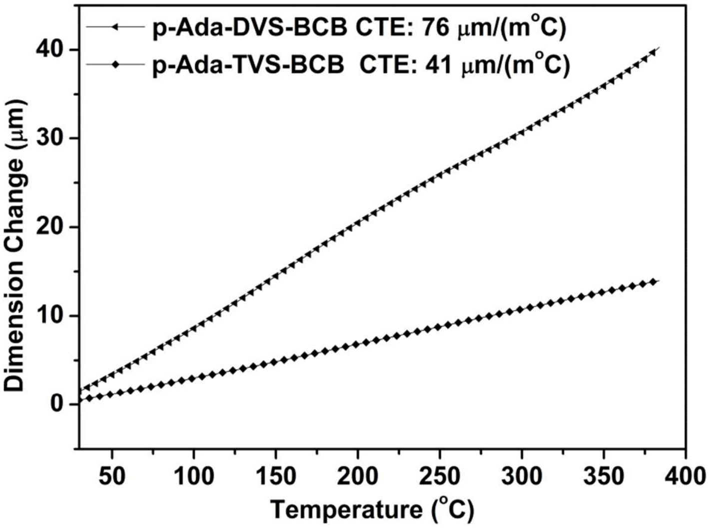


Fig. 11 Dimension change-temperature curve of the BCB resins (thickness: p-Ada-TVS-BCB, 0.9230 mm; p-Ada-DVS-BCB, 1.3642 mm)

Thermal Stability

The thermal stability of both BCB resins was evaluated by TGA, as shown in Fig. 12. The $T_{5\%}$ and $T_{10\%}$ value are chosen as the measure of thermal stability, which represent the temperature at five percent and ten percent mass loss. The $T_{5\%}$ of p-Ada-DVS-BCB and p-Ada-TVS-BCB is 430 °C and 433 °C in nitrogen, respectively. The $T_{10\%}$ of p-Ada-DVS-BCB and p-Ada-DVS-BCB is 440 °C and 443 °C in nitrogen, respectively. Both polymers have good thermal stability which is caused by the high cross-linking and the introduction of adamantyl group.

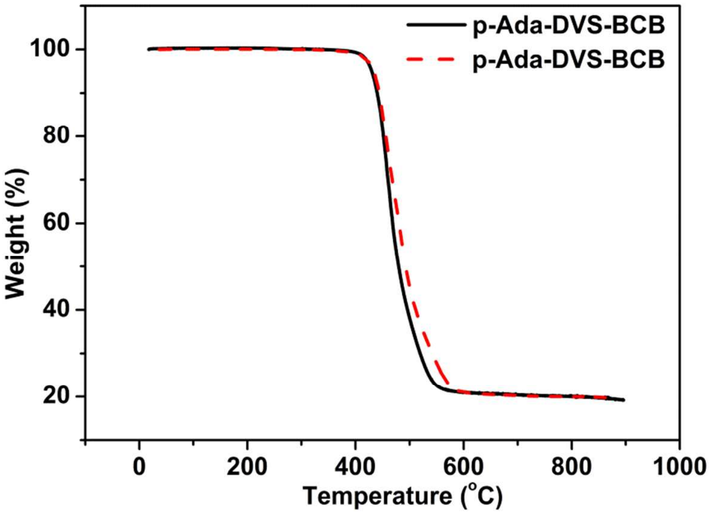


Fig. 12 TGA curves of the BCB polymers

Conclusions

By introducing a non-polar bulky adamantyl group into the backbone of BCB siloxane, we obtained and characterized two novel low-*k* dielectric polymers. The results showed that the introduction of adamantane had a great contribution to lower the dielectric constant and dielectric loss of the polymers. Both adamantyl-based BCB resins exhibited low dielectric constants (2.50-2.53) and low dielectric loss (0.0004-0.0008) at the frequency within 10 KHz - 5 MHz, respectively. They also showed excellent film uniformity with the surface roughness less than 0.6 nm and the good hydrophobicity with the contact angle larger than 107°. Due to the high cross-linked network structure, both of the BCB polymers exhibited high glass transition temperature and high modulus. Especially, p-Ada-TVS-BCB resin showed low CTE of 41 μm/m°C. The good dielectric, thermal and mechanical performance of admantane-containing benzocyclobutene resins showed potential application in microelectronic fabrication.

Acknowledgements

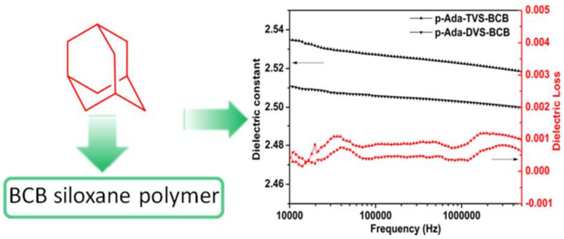
This research was supported by National Science and Technology Major Project of China (No. 2013ZX02505).

REFERENCES AND NOTES

1. W. Volksen, R. D. Miller and G. Dubois, *Chem. Rev.*, 2009, **110**, 56.

2. K. Maex, M. R. Baklanov, D. Shamiryan, F. Iacopi, S. H. Brongersma and Z. S. Yanovitskaya, *J. Appl. Phys.*, 2003, **93**, 8793.
3. G. Maier, *Prog. Polym. Sci.*, 2001, **26**, 3.
4. C. Yuan, J. Wang, K. Jin, S. Diao, J. Sun, J. Tong and Q. Fang, *Macromolecules*, 2014, **47**, 6311.
5. C. Yuan, K. Jin, K. Li, S. Diao, J. Tong and Q. Fang, *Adv. Mater.*, 2013, **25**, 4875.
6. J. Wang, K. Jin, F. He, J. Sun and Q. Fang, *RSC Adv.*, 2014, **4**, 40782.
7. B. Sharma, R. Verma, C. Baur, J. Bykova, J. M. Mabry and D. W. Smith, *J. Mater. Chem. C*, 2013, **1**, 7222.
8. Z. Geng, J. Ba, S. Zhang, J. Luan, X. Jiang, P. Huo and G. Wang, *J. Mater. Chem.*, 2012, **22**, 23534.
9. B. Yang, H. Xu, Z. Yang and X. Liu, *J. Mater. Chem.*, 2009, **19**, 9038.
10. J. Tong, S. Diao, K. Jin, C. Yuan, J. Wang, J. Sun and Q. Fang, *Polymer*, 2014, **55**, 3628.
11. Y. Wang, J. Sun, K. Jin, J. Wang, C. Yuan, J. Tong, S. Diao, F. He and Q. Fang, *RSC Adv.*, 2014, **4**, 39884.
12. S. Tian, J. Sun, K. Jin, J. Wang, F. He, S. Zheng and Q. Fang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20437.
13. T. M. Long and T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 14113.
14. X. Y. Zhao and H. J. Liu, *Polym. Int.*, 2010, **59**, 597.
15. Y. Su, W. Chen and F. Chang, *J. Appl. Polym. Sci.*, 2004, **94**, 932.
16. J. F. Espeso, Á. E. Lozano, J. G. de la Campa, Í. García-Yoldi and J. de Abajo, *J. Polym. Sci. A Polym. Chem.*, 2010, **48**, 1743.
17. Y. Watanabe, Y. Shibasaki, S. Ando and M. Ueda, *J. Polym. Sci. A Polym. Chem.*, 2004, **42**, 144.
18. K. Morita, T. Hashimoto, M. Urushisaki and T. Sakaguchi, *J. Polym. Sci. A Polym. Chem.*, 2013, **51**, 2445.
19. Z. Geng, Y. Lu, S. Zhang, X. Jiang, P. Huo, J. Luan and G. Wang, *Polym. Int.*, 2014, **63**, 333.
20. G. Hougham, G. Tesoro and A. Viehbeck, *Macromolecules*, 1996, **29**, 3453.
21. Y. Chern and H. Shiue, *Macromolecules*, 1997, **30**, 4646.
22. K. Matsumoto, Y. Shibasaki, S. Ando and M. Ueda, *Polymer*, 2006, **47**, 3043.
23. Y. Chern and H. Shiue, *Macromol. Chem. Phys.*, 1998, **199**, 963.
24. Y. Watanabe, Y. Shibasaki, S. Ando and M. Ueda, *Polym. J.*, 2005, **37**, 270.
25. A. S. Mathews, I. Kim and C. Ha, *J. Appl. Polym. Sci.*, 2006, **102**, 3316.
26. G. Wang, Z. Geng, X. Zhu, S. Zhang and X. Liu, *High. Perform. Polym.*, 2010, **7**, 779.
27. X. Zuo, R. Yu, S. Shi, Z. Feng, Z. Li, S. Yang and L. Fan, *J. Polym. Sci. A Polym. Chem.*, 2009, **47**, 6246.
28. J. Yang, Y. Cheng and F. Xiao, *Eur. Polym. J.*, 2012, **48**, 751.
29. E. Markovic, K. Nguyen, S. Clarke, K. Constantopoulos, J. Matisons and G. P. Simon, *J. Polym. Sci. A Polym. Chem.*, 2013, **51**, 5038.
30. R. A. Kirchhoff and K. J. Bruza, *Prog. Polym. Sci.*, 1993, **18**, 85.
31. Y. So, P. Foster, J. Im, P. Garrou, J. Hetzner, E. Stark and K. Baranek, *J. Polym. Sci. A Polym. Chem.*, 2006, **44**, 1591.
32. R. A. Kirchhoff, C. J. Carriere, K. J. Bruza, N. G. Rondan and R. L. Sammler, *J. Macromol. Sci. A Chem.*, 1991, **28**, 1079.

33. R. J. Spangler, B. G. Beckmann and J. H. Kim*, J. Org. Chem.*, 1977, **42**, 2989.
34. S. F. Hahn, S. J. Martin and M. L. McKelvy*, Macromolecules*, 1992, **25**, 1539.
35. R. V. Tanikella, S. A. Bidstrup Allen and P. A. Kohl*, J. Appl. Polym. Sci.*, 2002, **83**, 3055.
36. M. E. Mills, P. Townsend, D. Castillo, S. Martin and A. Achen*, Microelectron Eng*, 1997, **33**, 327.
37. D. Burdeaux, P. Townsend, J. Carr and P. Garrou*, J. Electron. Mater.*, 1990, **19**, 1357.
38. T. Yamamoto, Q. Fang and T. Morikita*, Macromolecules*, 2003, **36**, 4262.
39. Q. Fang and T. Yamamoto*, Polymer*, 2003, **44**, 2947.



Adamantane was introduced into the benzocyclobutene (BCB) siloxane to obtain two novel low-*k* polymers with excellent properties.