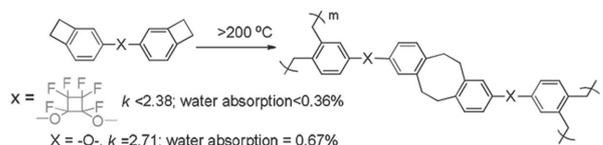


New Fluoropolymers Having Both Low Water Uptake and a Low Dielectric Constant

Fengkai He, Kaikai Jin, Jiajia Wang, Yijie Luo, Jing Sun, Qiang Fang*

Polymers with both low water uptake and a low dielectric constant have seen interest from both the electronic and microelectronic industries for several years. They play a crucial role in maintaining the good operating situation of devices, whereas most other materials are unsatisfactory. In this contribution, two new fluoropolymers are reported, which are derived from the thermo-crosslinking reaction of functional monomers containing perfluorocyclobutane and benzocyclobutene moieties. These polymers show water uptake ranging from 0.11 to 0.31% after immersion in boiling water (near 98 °C) for 96 h, and exhibit dielectric constants (k) of below 2.4 at a range of frequencies from 0.1 MHz to 30 MHz. In contrast, a comparative polymer without perfluorocyclobutane units has a k value of more than 2.70 and water uptake of 0.67%, respectively, suggesting that the low water absorption and dielectric constants of the fluoropolymers can be attributed to the existence of perfluorocyclobutane groups in the molecular backbone. These results also indicate that the properties of the fluoropolymers are superior to these of the most commercial polymeric low- k materials, implying that these fluoropolymers could be used as the varnish for enameled wire in the electrical industry and as encapsulation resins in the microelectronics industry.



1. Introduction

Much attention has been paid to polymers and oligomers that have both low water absorption and low dielectric constants in the past few decades because they are one of the most important basic materials used in the electrical and electronic industries.^[1–5] For example, fabrication of the insulating varnish for enameled wire in the electrical industry requires materials with low moisture absorption and a low dielectric constant (low k).^[1] These materials are also required for the production of printed circuit boards

(PCB) in the electronics industry.^[1] In many cases, a low dielectric constant endows the polymers with good insulating properties, and low water uptake helps the polymers retain their insulating properties. In recent years, with the rapid development of multilevel interconnection technology, the production of ultra-large scale integration (ULSI) circuits has generated an urgent requirement for low k materials to lower the resistance-capacitance (RC) delay generated with the minimization of electronic devices.^[1,2] Although many low k materials have been well investigated and developed,^[6–11] those having both low water absorption and low dielectric constants are rare. Hence, further development of materials with both low water absorption and low dielectric constants is still necessary.

Of the various low k organic materials, benzocyclobutene-based polymers have been well known for many years.^[12–19] These materials have high thermostability and low dielectric properties. In particular, their films exhibit very low roughness and high hydrophobic ability, which is very desirable for their application in

F. He, K. Jin, J. Wang, Y. Luo, Dr. J. Sun, Prof. Q. Fang
Key Laboratory of Organofluorine Chemistry and Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032, PR China
E-mail: qiangfang@sioc.ac.cn

the electrical and microelectronic industry. Therefore, they have been recognized as an important candidate for high performance materials. However, in many cases, the polymers show k values of higher than 2.7, which is unsatisfactory for their application in high-frequency printed circuit boards, as well as in ULSI.

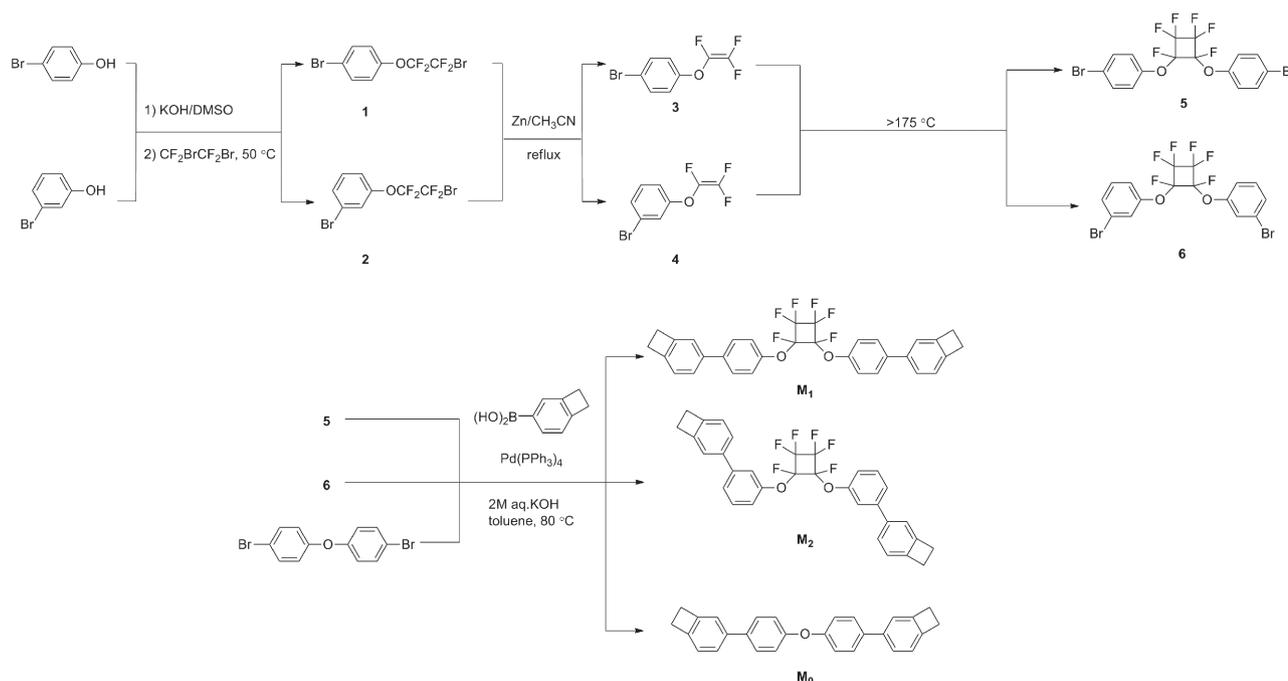
It has been noted that fluoropolymers usually show low dielectric constants and the introduction of fluoro groups into the main chains or side chains of polymers can efficiently enhance their dielectric properties.^[20–22] Amongst fluoropolymers, those containing perfluorocyclobutane (PFCB) units have recently received much attention, due to their excellent properties including low water uptake and very good dielectric properties.^[23–30] However, the thermostability of PFCB-containing polymers is usually not favorable due to their linear chain structure. Thus, attaching PFCB units to benzocyclobutene-based polymers may form new polymers that possess both low k values and high thermostability. In this paper, two new monomers containing a PFCB unit and two benzocyclobutene units were therefore designed and synthesized. Their chemical structure is depicted in Scheme 1. For comparison, a comparative monomer without the PFCB unit was also prepared. The results showed that the cured PFCB-containing monomers had k values of less than 2.40 at a range of frequencies from 0.1 to 30 MHz. It was very interesting that the cured PFCB-containing polymer possessed water absorption ranging from 0.11 to 0.31% after soaking in boiling water (near 98 °C) for 96 h. In contrast, the cured comparative monomer had a k value

of 2.71 and a water uptake of 0.67%, respectively. It has also been noted that many linear PFCB-containing polymers showed 5 wt% loss at a temperature of about 440 °C, whereas the polymers derived from monomers containing both PFCB and benzocyclobutene units exhibited this at a temperature of near 460 °C, suggesting that the combination of the PFCB units and benzocyclobutene units can increase the thermostability of PFCB-containing polymers. Obviously, these results imply that the introduction of the PFCB units into the benzocyclobutene-based polymers greatly decreased not only the k values of the polymers, but also the water absorption of the polymers. Such characteristics of the PFCB-containing polymers suggest that they would be very suitable as the encapsulation resins of integrated circuit (IC) dies used in the microelectronics industry, as well as for the matrix used for fabrication of high-frequency printed circuit boards.

2. Experimental Section

2.1. Materials and Instrumentation

The starting materials were purchased from Sigma Aldrich and TCI and were used as received unless otherwise mentioned here. All solvents were dried over CaH₂ and distilled under reduced pressure before use. Benzocyclobutene-4-boronic acid was purchased from Chemtarget Technologies Co., Ltd, China, and purified by chromatography using a mixture of ethyl acetate and *n*-hexane (1:40, v/v) as the eluent. ¹H NMR, ¹⁹F NMR, and ¹³C NMR spectra were obtained on a Bruker 400 spectrometer.



■ Scheme 1. Procedure for the synthesis of the new monomers (**M**₁ and **M**₂) and a comparative monomer (**M**₀).

Elemental analysis was carried out on an Elementar vario EL III system. FT-IR spectra were obtained on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetry (DSC) was completed on a TA Instrument DSC Q200 at a heating rate of 10 °C min⁻¹ under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a TG 209F1 apparatus with a heating rate of 10 °C min⁻¹ in N₂. High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific LTQ FT Ultra.

2.2. Synthesis

2.2.1. 1-Bromo-4-(2-bromo-1,1,2,2-tetrafluoroethoxy)benzene (**1**)

A mixture of 4-bromophenol (20 g, 115.6 × 10⁻³ mol), KOH (9.73 g, 173.4 × 10⁻³ mol), DMSO (100 mL), and toluene (150 mL) was heated to reflux, and the water formed during the reaction was removed. After keeping the mixture at this temperature for 12 h, the mixture was cooled to 0 °C, and 1,2-dibromotetrafluoroethane (45 g, 173.4 × 10⁻³ mol) was added dropwise over 1 h. The mixture was allowed to heat to 50 °C and was maintained at this temperature for an additional 11 h. After being cooled to room temperature, the reaction solution was poured into 100 mL of water, and extracted with ethyl acetate. The organic layer was washed with water three times, dried over anhydrous Na₂SO₄, and filtered. The filtrate was evaporated under reduced pressure to obtain a residue, which was purified by chromatography using *n*-hexane as the eluent. Pure compound **1** was prepared with a yield of 80% (32.5 g) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.52 (d, 2H), 7.12 (d, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -68.12 (m, 2F), -86.20 (m, 2F).

2.2.2. 1-Bromo-3-(2-bromo-1,1,2,2-tetrafluoroethoxy)benzene (**2**)

A similar route to that used for the synthesis of compound **1** gave compound **2** in a yield of 82% as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.42–7.46 (m, 2H), 7.27–7.30 (m, 1H), 7.19 (d, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -68.21 (m, 2F), -86.08 (m, 2F).

2.2.3. 1-Bromo-4-((1,2,2-trifluorovinyl)oxy)benzene (**3**)

Zinc powder (11.89 g, 181.86 × 10⁻³ mol) was added slowly to a solution of compound **1** (32 g, 90.93 × 10⁻³ mol) in acetonitrile (40 mL). The mixture was heated to reflux and kept at this temperature for 24 h. After cooling to room temperature, the mixture was separated by filtration. The filtrate was concentrated, and the obtained residue was purified by chromatography using *n*-hexane as the eluent. Compound **3** was prepared in a yield of 69.5% (16 g) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, 2H), 7.00 (d, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -119.12 (dd, 1F), -126.02 (dd, 1F), -134.44 (dd, 1F).

2.2.4. 1-Bromo-3-((1,2,2-trifluorovinyl)oxy)benzene (**4**)

Using an analogous method to that used for the synthesis of compound **3**, compound **4** was synthesized in a yield of 79% as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.32–7.34 (m, 1H), 7.22–7.27 (m, 2H), 7.04–7.06 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -119.09–118.68 (dd, 1F), -125.97–125.42 (dd, 1F), -134.65–134.20 (dd, 1F).

2.2.5. 4,4'-((Perfluorocyclobutane-1,2-diyl)bis(oxy))bis(bromobenzene) (**5**)

Compound **3** (15 g, 59.5 × 10⁻³ mol) was sealed in a flask, heated to 175 °C, and maintained at this temperature for 24 h. After cooling to room temperature, the reaction mixture was separated by chromatography using a mixture of ethyl acetate and *n*-hexane (1:20, v/v) as the eluent. Compound **5** was thus obtained in a yield of 81% (12.1 g) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.45 (dd, 4H), 7.02 (dd, 4H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -126.7–132.9 (m, 6F).

2.2.6. 3,3'-((Perfluorocyclobutane-1,2-diyl)bis(oxy))bis(bromobenzene) (**6**)

This compound was obtained in a yield of 86.7% as a colorless oil using a similar procedure to that used for the preparation of compound **5**.

¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.36 (m, 2H), 7.28–7.33 (m, 2H), 7.20–7.22 (m, 2H), 7.06–7.14 (dd, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -126.64–131.61 (m, 6F).

2.2.7. Monomer **M1**

A mixture of **5** (2.00 g, 3.95 × 10⁻³ mol), benzocyclobutene-4-boronic acid (1.46 g, 9.88 × 10⁻³ mol), Pd(PPh₃)₄ (228.36 mg, 197.62 × 10⁻⁶ mol), aq. K₂CO₃ (2 mL, 6 mL), and toluene (20 mL) was heated to 80 °C and maintained at that temperature for 12 h. After cooling to room temperature, the resulting solution was poured into water (20 mL), and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained residue was purified by chromatography using *n*-hexane as the eluent to give a white solid, which was further purified by recrystallization from methanol to afford **M1** in a yield of 91.7% (2 g).

¹H NMR (400 MHz, CDCl₃): δ = 7.48 (dd, 4H), 7.33 (t, 2H), 7.21 (dd, 4H), 7.16 (s, 2H), 7.11 (dd, 2H), 3.22 (s, 8H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -126.7–131.2 (m, 6F). ¹³C NMR (126 MHz, CDCl₃): δ = 151.60, 146.39, 145.20, 139.80, 139.07, 128.50, 126.04, 122.85, 121.44, 118.85, 29.47, 29.43. HRMS-ESI (*m/z*): Calcd. C₃₂H₂₂F₆O₂ [M]⁺ 552.1524; Found 552.1514. Anal. Calcd. C₃₂H₂₂F₆O₂ C, 69.56; H, 4.01; F, 20.63; Found C, 69.59; H, 4.08; F, 20.71.

Analogously, **M2** and **M0** were synthesized with yields of 91.59 and 92.8%, respectively. **M2** was a colorless viscous liquid.

¹H NMR (400 MHz, CDCl₃): δ = 7.28–7.37 (m, 8H), 7.23 (s, 2H), 7.10–7.13 (m, 4H), 3.22 (s, 8H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -126.63–131.25 (m, 6F). ¹³C NMR (126 MHz, CDCl₃): δ = 152.99, 146.42, 145.67, 144.44, 139.03, 129.95, 126.12, 124.22, 122.88, 121.51, 117.26, 116.45, 29.47, 29.44. HRMS-ESI (*m/z*): Calcd. C₃₂H₂₃F₆O₂ [M+H]⁺ 553.1597; Found 553.1586. Anal. Calcd. C₃₂H₂₂F₆O₂: C, 69.56; H, 4.01; F, 20.63; Found: C, 69.43; H, 4.12; F, 20.61.

M0 consisted of white crystals.

^1H NMR (400 MHz, DMSO- d_6): δ = 7.62 (d, 4H), 7.44 (d, 2H), 7.34 (s, 2H), 7.15 (d, 2H), 7.11 (d, 4H), 3.36 (s, 8H). ^{13}C NMR (126 MHz, CDCl_3): δ = 156.56, 146.36, 144.79, 139.76, 137.65, 128.63, 126.00, 122.86, 121.43, 119.16, 29.56, 29.47. HRMS-ESI (m/z): Calcd. $\text{C}_{28}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 375.1743; Found 375.1742. Anal. Calcd. $\text{C}_{28}\text{H}_{22}\text{O}$ C, 89.81; H, 5.92; Found: C, 90.03; H, 5.81.

2.3. Preparation of Samples for the Measurement of k Values and Moisture Absorption

A monomer (**M1** or **M2** or **M0**) was placed in a flat-bottomed glass tube with a diameter of 10.0 mm and a height of 85 mm and filled with argon. The tube was heated to 180 °C and kept at this temperature for 30 min so that a transparent melting liquid was obtained. After being kept at this temperature for an additional 4 h, the liquid became a solid. The temperature was then elevated, and maintained at 200 °C for 4 h, 220 °C for 5 h, 240 °C for 3 h, and 250 °C for 5 h, respectively. A completely cured sample was thus obtained.

2.4. Measurement of Moisture Absorption

A fully cured sample with a diameter of 10.0 mm and a thickness of 10.0 mm was dried in vacuo until a constant weight (0.0001 g) was achieved. The sample was then placed into 25 mL of boiling water in a glass flask equipped with a condenser. After maintaining the sample at this temperature for 96 h, the sample was removed from the water, and the residue of the water on the surface of the sample was removed using filter paper. The sample was weighed, and the moisture uptake was reported as the increase of the weight of the sample after immersion in the boiling water. The final data were obtained from the average of the results from 5 samples.

2.5. Measurement of Dielectric Constant

The dielectric constant (k) of the cured samples was measured in the frequency range from 0.1 to 30 MHz using the parallel-plate capacitor method^[23,25,31] at room temperature using a 4294A Precision Impedance Analyzer (Agilent). The cylindrical samples with average diameters of 10.0 mm were polished until their thicknesses were 2.50 ± 0.5 mm. After the samples were thoroughly dried under vacuum, aluminum was deposited via vacuum evaporation on both sides of the samples as electrodes.

3. Results and Discussion

3.1. Synthesis and Characterization

The synthetic route to the fluoro-containing monomers is depicted in Scheme 1. As can be seen from Scheme 1, fluoro-containing monomers **M1** and **M2** were prepared with overall yields of more than 40% through a four-step procedure. The obtained monomers were soluble in common organic solvents. In addition,

M2 was a sticky liquid, which could be easily spin-coated to form a film, suggesting that this monomer has good processability.

The chemical structures of the monomers were confirmed by ^1H NMR, ^{13}C NMR, ^{19}F NMR, and elemental analysis, and the detailed data are summarized in the Supporting Information. The peak at 3.22 ppm for the benzocyclobutene four-member ring was observed in the ^1H NMR spectra of **M1** and **M2**, and such a group was also found at 1460 cm^{-1} in the FT-IR spectra of the monomers. The perfluorocyclobutane group was detected at 960 cm^{-1} in the FT-IR spectra of the monomers. Thus, all data were in good accordance with the proposed structures.

3.2. Thermo-Crosslinking Reaction

Upon heating at a high temperature, the benzocyclobutene four-member ring has a tendency to form a highly reactive *o*-quinodimethane intermediate, which easily polymerizes to produce poly(*o*-xylylene).^[8] Such a ring-opening reaction was also observed in this case, and monitored by DSC. The results are shown in Figure 1. As depicted in Figure 1, all monomers showed an onset temperature of about 200 °C and a maximum exothermic temperature of near 260 °C. Because **M2** was a sticky liquid, it did not show an endothermic peak. It was also observed that **M2** showed very low viscosity when it was heated to temperatures of up to 40 °C. This characteristic of **M2** was attributed to its meta-linked structure, which made **M2** have a zig-zag shape and inhibited the formation of crystals. This behavior of **M2** suggests that it has good processability. In many cases, good processability of materials is highly desirable in industry. It can also be seen from Figure 1 that the fluoro-containing monomers (**M1** and **M2**) exhibited

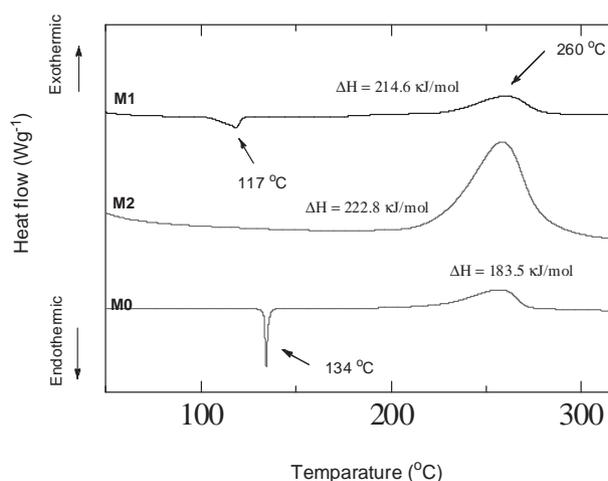
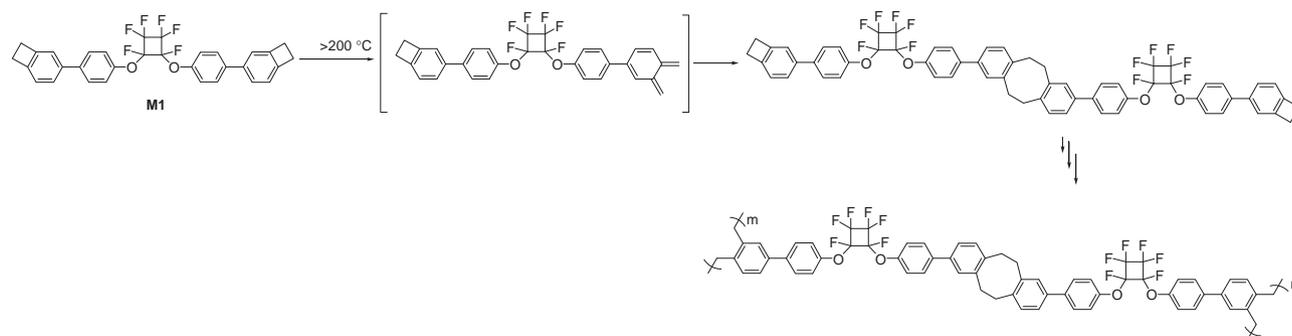


Figure 1. DSC traces of monomers at a heating rate of 10 °C min^{-1} .



■ Scheme 2. Thermo-crosslinking reaction of the monomer containing benzocyclobutene units.

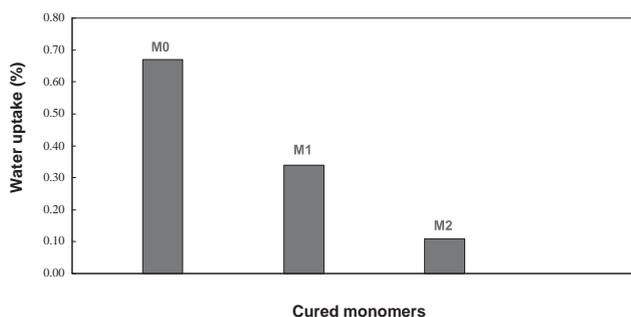
higher enthalpy (ΔH) than the fluoro-free monomer (**M0**), meaning that the perfluorocyclobutane group had a large effect on the thermo-crosslinking behavior of the monomers.

The thermo-crosslinking degree of the monomers was also monitored by FT-IR spectroscopy. When heated at 250 °C for 5 h, the monomers converted to insoluble and infusible resins. FT-IR spectra of the resins exhibited the characteristic peak^[8] of the benzocyclobutene unit at 1460 cm^{-1} disappearing, suggesting that the monomers had been fully thermo-crosslinked (see Figure S9 in the Supporting Information).

In order to help understand the ring-open reaction of the monomers, their thermo-crosslinking process is described in Scheme 2.^[8,20] Because their ring-opening reactions are similar, only the reaction of **M1** is given.

3.3. Water Uptake of the Cured Monomers

The water uptake of the thermo-crosslinked monomers was measured by immersing them into boiling water (near 98 °C), and keeping them at that temperature for 96 h. The results showed that cured **M0** had a water uptake of 0.67%, whereas cured **M1** and **M2** showed moisture absorptions of 0.31 and 0.11%, respectively, as depicted in Figure 2. The good hydrophobic properties of



■ Figure 2. Water uptake of the cured monomers.

cured **M1** and **M2** are attributed to the existence of perfluorocyclobutane groups on the backbone of the polymers. Of the cured monomers, cured **M2** showed the lowest water uptake. This is probably due to the meta-linked zig-zag shape of the molecular chain, which can greatly restrain the aggregation of the polymer chains. As a result, a large free volume was formed in the cured resin. In many cases, large free volume implies that there are nanoscale interspaces or pores in cured resins.^[31] Usually, fluoro-containing interspaces or pores show good hydrophobic behavior.^[32] Thus, **M2** showed very low water absorption.

3.4. Dielectric Behaviors of the Cured Monomers

The dielectric constants of the cured monomers were measured by the capacitance method, and the results are indicated in Figure 3. It can be seen that the average k values of the cured **M1** and **M2** remained below 2.38 at a range of frequencies varying from 0.1 MHz to 30 MHz. Usually, benzocyclobutene-based polymers show dielectric constants of more than 2.6^[8] The low k values of the cured **M1** and **M2** indicate that the introduction of the perfluorocyclobutane units into the polymer backbone can efficiently improve the dielectric properties of the polymers.

The dissipation factors ($\tan d$) of the cured monomers were also measured, which were less than 3.00×10^{-3} in the range of frequencies from 0.1 MHz to 30 MHz.

3.5. Thermostability of the Cured Monomers

Thermostability of the cured monomers was investigated by TGA, and the results are shown in Figure 4. Usually, linear PFCB-containing polymers have a 5 wt% loss temperature of about 440 °C.^[25] In this case, however, the cured monomers exhibited the temperature at near 460 °C (Figure 4). Such results suggest that the combination of the PFCB units and benzocyclobutene units can increase the thermostability of PFCB-containing polymers.

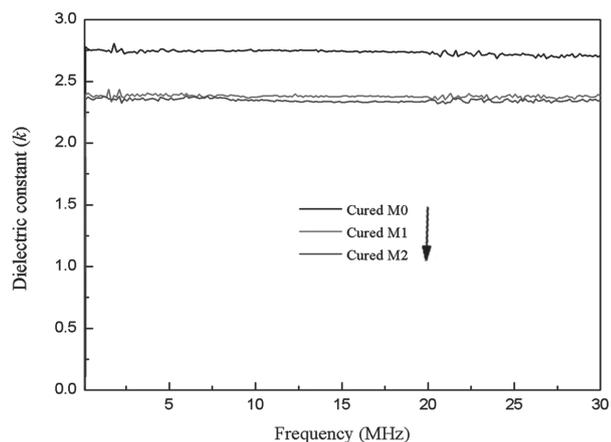


Figure 3. Dielectric constants (k) of the cured monomers.

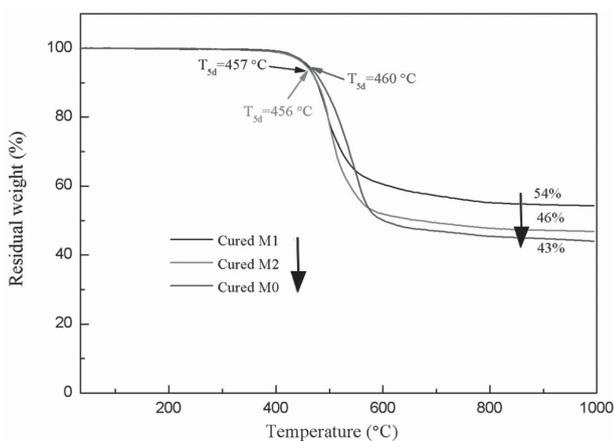


Figure 4. TGA curves of the cured monomers at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 . The percentages represent the char yields of the cured monomers at $1000\text{ }^{\circ}\text{C}$.

4. Conclusions

In summary, two new monomers containing both benzocyclobutene and perfluorocyclobutane units have been successfully synthesized. When heated at high temperature, the monomers converted to insoluble and infusible resins, which showed water uptake ranging from 0.11 to 0.31% after soaking in boiling water (near $98\text{ }^{\circ}\text{C}$) for 96 h, and exhibited dielectric constants (k) of below 2.4 at a range of frequencies from 0.1 to 30 MHz. Such low k values and the low water uptake of these polymers are superior to those of the most commercial polymeric low- k materials. In comparison with perfluorocyclobutane-containing resins, the polymer only containing benzocyclobutene units showed a k value of more than 2.70 and water uptake of 0.67%. These results suggest that these new fluoropolymers could be utilized as the varnish for enameled wire in the electrical industry and as encapsulation resins in the microelectronics industry.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: Financial support from the Ministry of Science and Technology of China (2011ZX02703, 2015CB931900) and the Natural Science Foundation of China (NSFC, No. 21374131 and 21574146) is gratefully acknowledged.

Received: September 16, 2015; Revised: October 5, 2015; Published online: November 6, 2015; DOI: 10.1002/macp.201500394

Keywords: benzocyclobutene; dielectric constant; fluoropolymers; thermostability; water absorption

- [1] W. Volksen, R. D. Miller, G. Dubois, *Chem. Rev.* **2010**, *110*, 56.
- [2] G. Maier, *Prog. Polym. Sci.* **2001**, *26*, 3.
- [3] X.-Y. Zhao, H.-J. Liu, *Polym. Int.* **2010**, *59*, 597.
- [4] K. Maex, M. R. Baklanov, D. Shamiryan, F. Iacopi, S. H. Brongersma, Z. S. Yanovitskaya, *J. Appl. Phys.* **2003**, *93*, 8793.
- [5] H. Treichel, G. Ruhl, P. Ansmann, R. Wurl, C. Muller, M. Dietlmeier, *Microelectron. Eng.* **1998**, *40*, 1.
- [6] J. Yang, S. Liu, F. Zhu, Y. Huang, B. Li, L. Zhang, *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 381.
- [7] T. M. Long, T. M. Swager, *J. Am. Chem. Soc.* **2003**, *125*, 14113.
- [8] J. Tong, S. Diao, K. Jin, C. Yuan, J. Wang, J. Sun, Q. Fang, *Polymer* **2014**, *55*, 3628.
- [9] K. Tsuchiya, Y. Shibasaki, M. Aoyagi, M. Ueda, *Macromolecules* **2006**, *39*, 3964.
- [10] Y. Huang, J. Economy, *Macromolecules* **2006**, *39*, 1850.
- [11] K. Tsuchiya, H. Ishii, Y. J. Shibasaki, S. J. Ando, M. Ueda, *Macromolecules* **2004**, *37*, 4794.
- [12] R. A. Kirchhoff, K. J. Bruza, *Prog. Polym. Sci.* **1993**, *18*, 85.
- [13] M. F. Farona, *Prog. Polym. Sci.* **1996**, *21*, 505.
- [14] R. J. Hohlfelder, D. A. Maidenberg, R. H. Dauskardt, Y. Wei, J. W. Hutchinson, *J. Mater. Res.* **2001**, *16*, 243.
- [15] X. Zuo, R. Yu, S. Shi, Z. Feng, Z. Li, S. Yang, L. Fan, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6246.
- [16] X. Zuo, X. Zhao, B. Liu, S. Yang, L. Fan, *J. Appl. Polym. Sci.* **2009**, *112*, 2781.
- [17] Y. Wang, J. Sun, K. Jin, J. Wang, C. Yuan, J. Tong, S. Diao, F. He, Q. Fang, *RSC Adv.* **2014**, *4*, 39884.
- [18] G. A. Deeter, D. J. Venkataraman, W. Kampf, J. S. Moore, *Macromolecules* **1994**, *27*, 2647.
- [19] M. J. Marks, J. K. Sekinger, *Macromolecules* **1994**, *27*, 4106.
- [20] S. Tian, J. Sun, K. Jin, J. Wang, F. He, S. Zheng, Q. Fang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 20437.
- [21] E. Murotani, J.-K. Lee, M. Chatzichristidi, A. A. Zakhidov, P. G. Taylor, E. L. Schwartz, G. G. Malliaras, C. K. Ober, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2362.
- [22] F. He, C. Yuan, K. Li, S. Diao, K. Jin, J. Wang, J. Tong, J. Ma, Q. Fang, *RSC Adv.* **2013**, *3*, 23128.
- [23] C. Yuan, K. Jin, K. Li, S. Diao, J. Tong, Q. Fang, *Adv. Mater.* **2013**, *25*, 4875.
- [24] J. Wang, K. Li, C. Yuan, K. Jin, S. Tian, J. Sun, Q. Fang, *Macromol. Chem. Phys.* **2015**, *216*, 742.
- [25] C. Yuan, J. Wang, K. Jin, S. Diao, J. Sun, J. Tong, Q. Fang, *Macromolecules* **2014**, *47*, 6311.
- [26] S. Y. Cho, H. R. Allcock, *Chem. Mater.* **2007**, *19*, 6338.

- [27] K.-S. Lee, M.-H. Jeong, Y.-J. Kim, S.-B. Lee, J.-S. Lee, *Chem. Mater.* **2012**, *24*, 1443.
- [28] A. R. Neilson, S. M. Budy, J. M. Ballato, W. Dennis Smith Jr., *Macromolecules* **2007**, *40*, 9378.
- [29] B. Y. Lim, J.-T. Hwang, J. Y. Kim, J. Ghim, D. J. Vak, Y.-Y. Noh, S.-H. Lee, K. A. Lee, J. Heeger, D.-Y. Kim, *Org. Lett.* **2006**, *8*, 4703.
- [30] C. A. Corley, A. J. Guenther, C. M. Sahagun, K. R. Lamison, J. T. Reams, M. K. Hassan, S. E. Morgan, S. T. Iacono, J. M. Mabry, *ACS Macro Lett.* **2014**, *3*, 105.
- [31] L. Kong, Y. Cheng, Y. Jin, Z. Ren, Y. Li, F. Xiao, *J. Mater. Chem. C* **2015**, *3*, 3364.
- [32] S.-J. Ding, P.-F. Wang, D. W. Zhang, J. T. Wang, W. W. Lee, *Mater. Lett.* **2001**, *49*, 154.