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Postpolymerization of a Fluorinated and Reactive Poly(aryl ether): An Efficient Way To Balance the Solubility and Solvent Resistance of the Polymer

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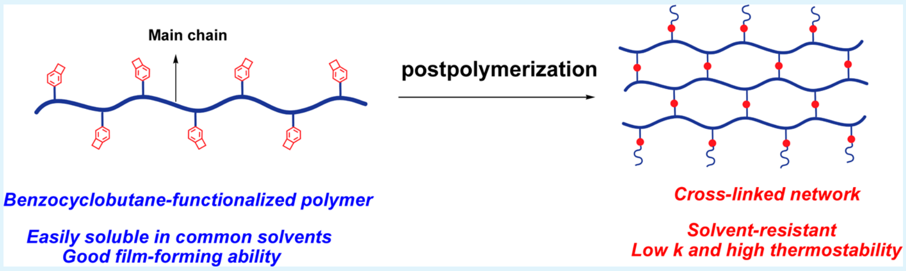
S *Supporting Information*



ABSTRACT: A new fluorinated poly(aryl ether) with reactive benzocyclobutene groups as the side chain was successfully synthesized. This polymer showed a number-average molecular weight (M_n) of 200 000 and had good solubility and film-forming ability. After being postpolymerized at high temperature (>200 °C), the polymer film converted to a cross-linked network structure, which was insoluble in the common organic solvents. Such results suggest that the postpolymerization is an efficient way to achive the balance between the solubility and the solvent resistance of the polymer. TGA data showed that the postpolymerized polymer had a 5 wt % loss temperature at 495 °C and a residual of 61% at 1000 °C under N_2. The cross-linked film also exhibited good dielectric properties with an average dielectric constant of about 2.62 in a range of frequencies from 1 to 30 MHz. With regard to the mechanical properties, the cross-linked film had hardness, Young's modulus, and bonding strength to a silicon wafer of 1.22, 8.8, and 0.89 GPa, respectively. These data imply that this new polymer may have potential applications in the electrical and microelectronics industry.

KEYWORDS: *synthesis, postpolymerization, fluorinated poly(aryl ether)s, benzocyclobutene dielectric constant, thermostability*

■ INTRODUCTION

As an important class of high-performance materials, poly(aryl ether)s (PAE), comprising aryl units and ether linkages, have been known for many years. These polymers exhibit excellent radiation resistance, high thermostability, low dielectric constants, and good mechanical properties.[1] Therefore, they have been widely used as materials for the production of automotive, computer, and telecommunication parts, as well as employed as the matrix resins for the fabrication of fiber-reinforced composites utilized in the electrical and electronics industry.[2−6]

Among various PAE, those containing fluoro groups have received much attention in the recent years.[7−11] The introduction of fluorine atoms into PAE can endow the polymers with low dielectric constant and moisture uptake due to the low polarizability of the C−F bond and the surface energy of fluorine. Accordingly, many fluorinated PAE have been investigated and developed, of which the PAE containing perfluorophenyl units, $-CF_3$ groups, and perfluorocyclobutane moieties are particularly gathering attention.[12−14] These fluorinated PAE exhibit high glass transition temperature (T_g) and excellent optical properties and are expected to be used in areas such as optical communications, ultralarge scale integration circuits, and flat-panel display.[15−19] However, most of the PAE are unsuitable for a solution process because they show low solubility in the common organic solvents. In order to enhance the solubility, a general strategy is to introduce the side chains to the backbone of PAE. Nevertheless, the improvement of solubility usually results in the poor solvent resistance of the polymers. Thus, how to realize a balance between the solubility and the solvent resistance of the polymers is a challenging task.

Recently, postpolymerization modification is of particular interest to researchers.[20−24] After postpolymerization, functional (or reactive) groups will endow polymers (or oligomers) with new chemical structures and properties. This inspires us to develop new PAE with good solubility and solvent resistance.

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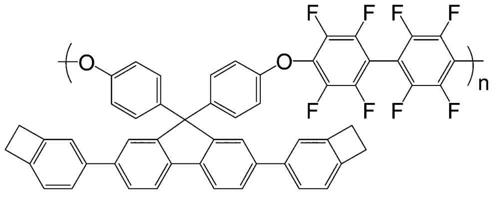
Our strategy is to introduce one or more reactive groups into the PAE as the side chains. First, the side chains could improve the solubility of the PAE. Further, the reactive groups in the PAE could polymerize or cross-link to form new polymers, which have higher molecular weight and certain cross-linking density. Thus, they could possess the ability to resist organic solvents.

It is noted that benzocyclobutene (BCB) is a highly reactive molecule. When heated at high temperature, the four-membered ring on benzocyclobutene opens to produce a highly reactive *o*-quinodimethane intermediate. This active intermediate either forms a product with an eight-membered ring via self-coupling or produces a copolymer through the Diels−Alder reaction.[25−27] On the basis of the characteristic of benzocyclobutene, we incorporate BCB units into a fluorinated PAE as the side chains to produce a reactive polymer, whose chemical structure is shown in Chart 1. This polymer (PDFB) is easily soluble in common organic solvents and is readily converted to cross-linked matrixes after heating (postpolymerization). The cross-linked PDFB exhibits high thermostability, low dielectric constant, and good solvent resistance, suggesting that the polymer could be used as the insulating varnish[28] for the preparation of enameled copper wire in the electrical industry, encapsulation resins[29] of integrated circuit (IC) dies in the microelectronics industry, resin[30] for the production of high-performance printed circuit board in the electronics industry, and the surface sizing agents[31] for the high-performance glass fiber or carbon fiber utilized in the aerospace industry. In this contribution, we report the detailed results.

Chart 1. Chemical Structure of a Reactive Polymer in This Work



PDFB

EXPERIMENTAL SECTION

Materials and Instrumentation. All starting chemicals were purchased from Aldrich and used as received unless otherwise stated. Benzocyclobutene-4-boronic acid was purchased from Chemtarget Technologies Co., Ltd. and purified by a SiO_2 gel column chromatograph using a mixed eluent of ethyl acetate and *n*-hexane (40:1, v/v). Characterization: ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm) 7.67 (d, 1H), 7.49 (s, 1H), 7.14 (d, 1H), 3.24 (s, 4H). *N*-Methyl-2-pyrrolidone (NMP) was dried over CaH_2 and distilled under reduced pressure before use.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. FT-IR spectra were run on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetry (DSC) was carried out with TA Instrument DSC Q200 at a heating rate of 10 °C/min under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a TG 209F1 apparatus with a heating rate of 10 °C/min in N_2 and air atmosphere, respectively. Elemental analysis was carried out on an Elementar vario EL III system. Molecular weights were measured at room temperature by GPC with a Waters Breeze2a 200 GPC system, equipped with a UV detector using tetrahydrofuran (THF) as the eluent and versus polystyrene standards. The dielectric constants (k) of the cross-linked polymer film were measured in a range of frequencies from 1 to 30 MHz at room temperature using a 4294A Precision impedance analyzer (Agilent). The surface toughness of the polymer film was measured by atom force microscopy (AFM) on a Shimadzu SPM-9500J3 system. The mechanical properties of the cross-linked polymer film were measured on a TI-700 UbiI nanomechanical test instrument and a CSM-UNHT/NST nanomechanical integrated test system. The thickness of polymer film was measured by field emission scanning electron microscopy (FE-SEM) on a FE-SEM S-4800. The contact angle of water on the surface of the cross-linked film was measured at room temperature using a sessile drop method on a dynamic contact angle measurement instrument (JC2000C), and deionized water was selected as the testing liquid.

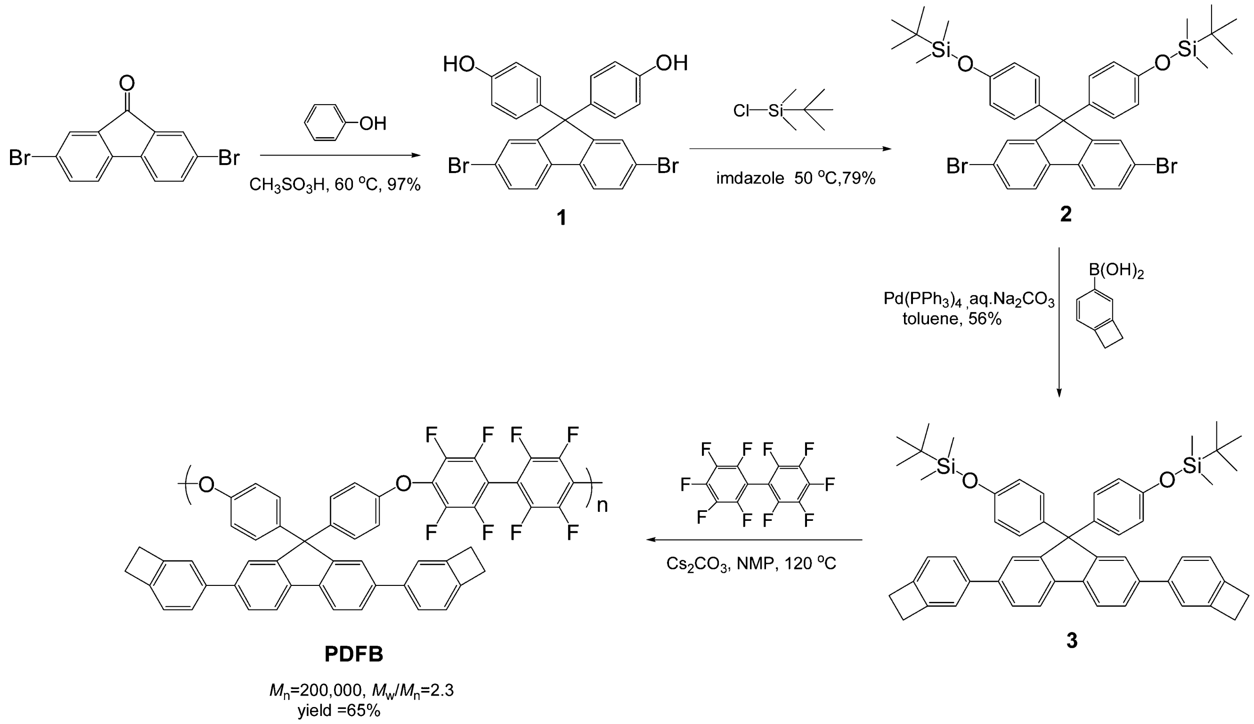
Synthesis. *Synthesis of 2,7-Dibromo-9,9-bis(4-hydroxyphenyl)-fluorene (**1**).* This compound was synthesized according to a reported procedure. A mixture of phenol (50.2 g, 533.42 mmol), 2,7-dibromo-9-fluorenone (18.10 g, 53.25 mmol), and methanesulfonic acid (70 mL) was stirred at 60 °C for 8 h and then cooled to room temperature. The reaction mixture was poured into water, and the precipitate was filtered and washed with water. The crude **1** was thus prepared. To purify **1**, a solution of crude **1** in ethyl acetate was added dropwise to *n*-hexane to obtain a precipitate. The precipitate was filtrated and dried under reduced pressure to give 26.31 g of pure **1** as a white powder (97.2% yield). ^1H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 9.40 (s, 2H), 7.89 (d, 2H), 7.58 (dd, 2H), 7.48 (d, 2H), 6.88 (d, 4H), 6.66 (d, 4H). Anal. Calcd for $C_{25}H_{16}Br_2O_2$: C, 59.08; H, 3.17; Br, 31.45. Found: C, 59.05; H, 3.17.

*Synthesis of TBS-Protected 2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene (**2**).* A solution of **1** (26.01 g, 51.18 mmol), *tert*-butylchlorodimethylsilane (TBS-Cl, 31.00 g, 205.68 mmol), and imidazole (17.35 g, 254.85 mol) in dichloromethane (200 mL) was stirred at 50 °C for overnight. The reaction mixture was treated under reduced pressure to remove the solvent and excess of *tert*-butylchlorodimethylsilane. The obtained residue was dissolved in dichloromethane (200 mL), and the solution was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent, **2** was obtained as white crystals in a yield of 79.3% with a purity of 99.41% (HPLC). ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.56 (d, 2H), 7.49−7.42 (m, 4H), 6.98 (d, 4H), 6.70 (d, 4H), 0.97 (s, 18H), 0.19 (s, 12H). Anal. Calcd for $C_{37}H_{44}Br_2O_2Si_2$: C, 60.32; H, 6.02. Found: C, 60.35; H, 5.81.

*Synthesis of Monomer (**3**).* Under an argon atmosphere, a mixture of benzocyclobutene-4-boronic acid (1.48 g, 10 mmol), **2** (2.50 g, 3.4 mmol), $Pd(PPh_3)_4$ (0.39 g, 0.34 mmol), Na_2CO_3 (1.40 g, 13.6 mmol), H_2O (7.5 mL), and toluene (30 mL) was stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was diluted with ethyl acetate (100 mL). The solution was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent, crude **3** was obtained. The purification of crude **3** was run on a SiO_2 gel column chromatography using a mixture of *n*-hexane and dichloromethane (10:1, v/v) as the eluent. Finally, pure monomer **3** was prepared by recrystallization from acetone as a white crystal in a yield of 56.4% with a purity of 98.96% (HPLC). ^1H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 7.81 (d, 2H), 7.62−7.53 (m, 4H), 7.42 (dd, 2H), 7.28 (s, 2H), 7.20−7.10 (m, 6H), 6.75−6.68 (m, 4H), 3.24 (s, 8H), 0.98 (s, 18H), 0.20 (s, 12H). Anal. Calcd for $C_{53}H_{58}O_2Si_2$: C, 81.28; H, 7.46. Found: C, 81.22; H, 7.44.

Polymerization. A mixture of decafluorobiphenyl (223.4 mg, 0.669 mmol), monomer **3** (523.3 mg, 0.668 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), and NMP (15 mL) was stirred at 120 °C for 12 h under an argon atmosphere. After being cooled to room temperature, the reaction mixture was diluted with $CHCl_3$ (50 mL). The solution was washed with water (3 × 100 mL) and dried over anhydrous Na_2SO_4. When the solvent was removed, a filmlike residue was obtained. The residue was redissolved in $CHCl_3$ (about 50 mL), and cyclohexane was added to the solution to form a white precipitate. The precipitate was dried at 80 °C in a vacuum for 12 h. The polymer was thus prepared in a yield of 65%. GPC analysis: M_n = 200 000, M_w/M_n = 2.3. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.79 (d, 2H), 7.59−7.48 (m, 4H), 7.37 (d, 2H), 7.26 (t, 6H), 7.09 (d, 2H), 6.90 (d, 4H), 3.19 (s, 8H). ^{19}F NMR (376 MHz, $CDCl_3$), δ (TMS, ppm): −137.72 to −138.24

Scheme 1. Procedure for the Synthesis of the Monomer and the Polymer



(m, 4F), −152.68 (d, 4F). Anal. Calcd for $(C_{53}H_{28}F_8O_2)_n$: C, 75.00; H, 3.33; F, 17.91. Found: C, 74.37; H, 3.39; F, 17.16.

Postpolymerization of the Polymer. A solution of PDFB in xylene (35 mg/mL) was spin-coated on the surface of an aluminum-backed silicon wafer (a heavily doped single crystal silicon with a resistivity of 3.5×10^{-3} Ω cm). The silicon wafer with PDFB film was placed into a quartz tube furnace and heated to 150 °C under reduced pressure to remove a trace of the solvent. After being maintained at the temperature for 1 h, the film was allowed to be heated to 330 °C under N_2 during a period of 5 h. When kept at 330 °C for 5 h, the film was completely converted to a cross-linked network, and it was insoluble in organic solvents. This cross-linked film was used for the measurement of the surface toughness and contact angle. For the measurement of the dielectric properties of the cross-linked film, aluminum was deposited on the surface of the film via vacuum evaporation as a top electrode (diameter = 3.0 mm). A parallel plate capacitor was thus fabricated. The dielectric properties of the film were determined and calculated according to the previously reported method.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. Generally, poly(aryl ether)s are prepared by a nucleophilic substitution reaction between a bisphenol and an aryl halide in the presence of inorganic bases such as K_2CO_3 or NaOH. When the nucleophilic substitution reaction was carried out in our case, however, the polymer (PDFB) was obtained in a low molecular weight of (M_n < 10 000). Further raising the reaction temperature to near 160 °C gave a higher M_n (~20 000), which could risk the cross-linking of benzocyclobutene in PDFB. Hence, a suitable route for synthesis of PDFB is required.

It is noted that the reaction of silylated bisphenols with activated aryl dihalides could give poly(aryl ether)s with high molecular weight.[32,33] This motivated us to use a new procedure for the synthesis of PDFB. For this purpose, a silylated bisphenol (**3**) was prepared (Scheme 1).

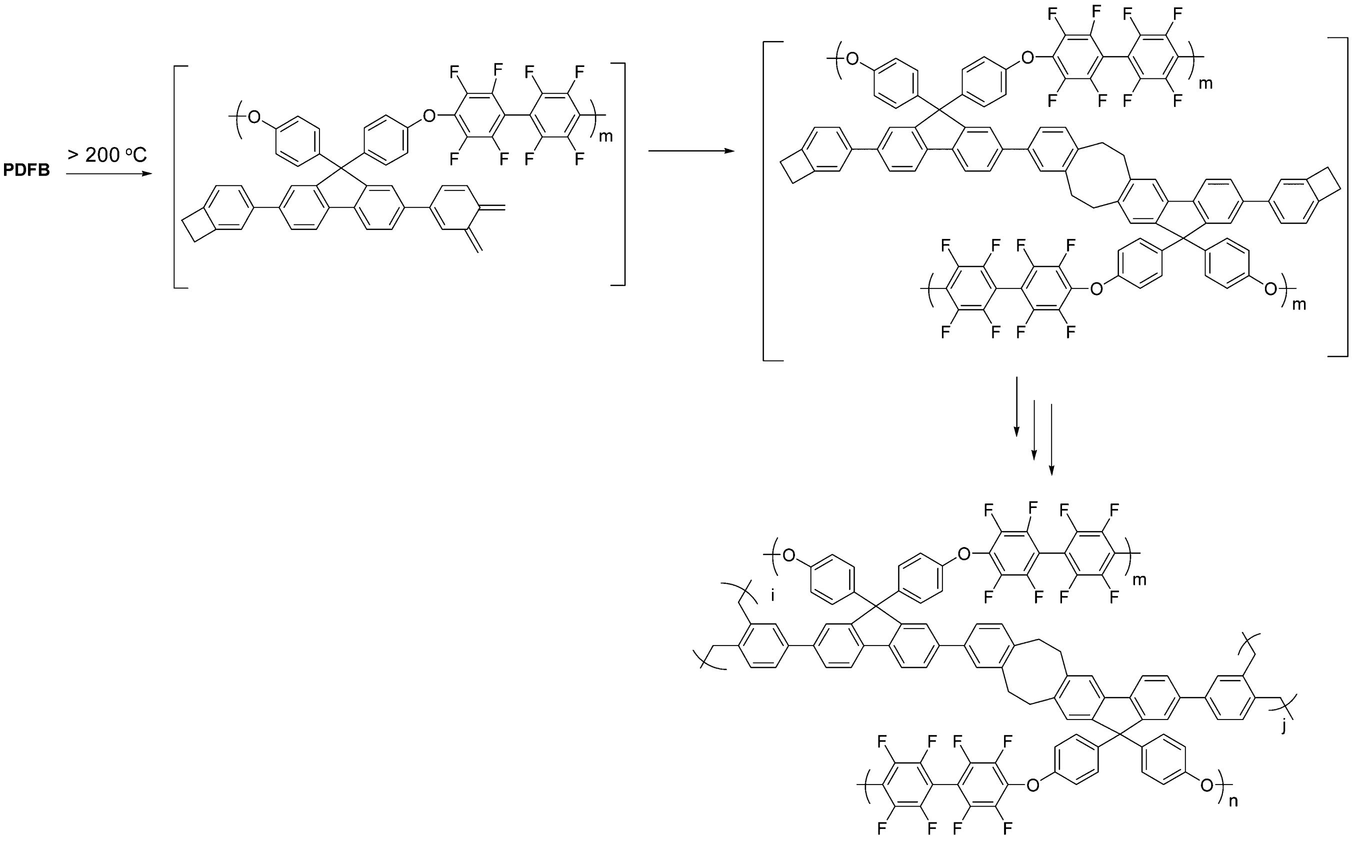
Usually, the reaction between silylated bisphenols and fluorinated aryl compounds was carried out in the presence of CsF.[32,33] Considering that CsF showed high moisture absorption, we undertook the polymerization by using Cs_2CO_3 as the catalyst.[34] The Cs_2CO_3-mediated reaction may undergo the following process: (1) Cs_2CO_3 transformed to CsOH in the presence of trace of water, (2) CsOH attacked silylated bisphenols to form the cesium salts of phenols, and (3) the cesium salts reacted with fluorinated arenes to give the ethers of arenes and CsF. Further, the formed CsF reacted with silylated bisphenols to achieve a catalyzing cycle.[32,33]

It was found in our case that the solubility of Cs_2CO_3 was crucial for the polymerization. For example, Cs_2CO_3 was insoluble in THF and toluene, resulting in the polymerization not occurring in these solvents. An examination indicated that Cs_2CO_3 was easily soluble in NMP. Accordingly, we ran the polymerization in NMP. It was also found that the temperature had a big effect on the molecular weight of the polymer. We then investigated the polymerization that was carried out at different temperatures (e.g., 80, 100, 120, and 160 °C). The best result was obtained when the reaction temperature was 120 °C. In that case, PDFB was prepared with a M_n of 200 000 and PDI (polydispersion index) of 2.3. According to the M_n, the number of the repeating unit of PDFB was estimated at about 235. The polymerization at 160 °C gave a gel, suggesting the high reactivity of monomer **3** at high temperature.

The obtained polymer is white in color and fiberlike. It is easily soluble in common organic solvents such as chloroform, toluene, and THF. Casting or spin-coating from a solution of the polymer in xylene gives a colorless transparent film with toughness, suggesting that the polymer processes good film-forming ability.

The chemical structure of PDFB is confirmed by IR, ^1H NMR, and ^{19}F NMR spectra and elemental analysis. The detailed data are shown in the Supporting Information and Experimental Section. The characteristic IR absorption peaks of

Scheme 2. Postpolymerization Reaction of PDFB at High Temperature



the benzocyclobutene group appear at 1460 cm^{-1}. The ^{1}H NMR spectrum shows the H peak of cyclobutene at 3.19 ppm. These data indicate that the benzocyclobutene unit was not ring-opened during the polymerization. ^{19}F NMR exhibited the F signals of biphenyl units at a region ranging from −137 to −152 ppm (see the Supporting Information).

Postpolymerization. On the basis of ring-opening of the benzocyclobutene group at high temperature, we investigated the postpolymerization (or thermal cross-linking) of PDFB. The reaction is depicted in Scheme 2 and is monitored by DSC (Figure 1). As can be seen from Figure 1, the thermal cross-linking starts at about 220 °C and the peak is at 294 °C. Such thermal cross-linking behavior of PDFB is similar to that of the polymers containing benzocyclobutene groups.[14]

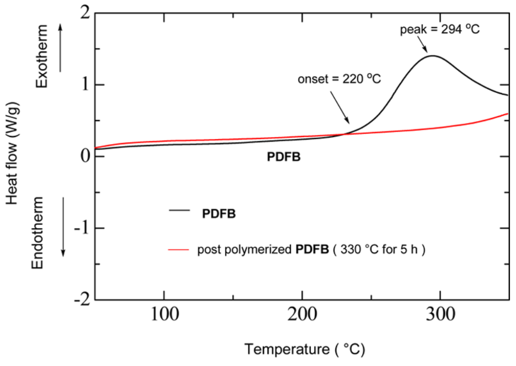


Figure 1. DSC traces of PDFB and postpolymerized PDFB under N$_2$ with a heating rate of 10 °C/min.

The postpolymerization degree of PDFB is also estimated by DSC traces. After the polymer film is maintained at 330 °C for 5 h, the DSC trace indicates that no exothermic peak is observed, suggesting that the postpolymerization has completed.

A comparison of the FT-IR spectra of PDFB with that of postpolymerized PDFB (called P-PDFB) indicates (see Supporting Information, Figure S4) that the characteristic absorption of cyclobutene at 1460 cm^{-1} disappears in P-PDFB after postpolymerization, meaning that PDFB has fully converted to P-PDFB.

Optical Properties and Solvent Resistance. Figure 2 shows the UV−vis−NIR spectrum of PDFB film. For comparison, the spectrum of P-PDFB film is also depicted in the figure. As can be seen from Figure 2, PDFB showed a transmittance of higher than 97% in a range of wavelengths from 400 to 1100 nm, similar to that of the fluorinated

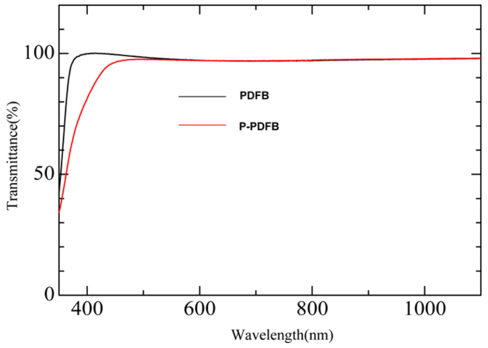


Figure 2. UV−vis−NIR spectra of PDFB and P-PDFB.

poly(aryl ether)s. However, P-PDFB film indicated lower transmittance, ranging from 400 to 500 nm, compared with PDFB. The reason was that there was a lot of cross-linked aryl units on the backbones of P-PDFB, which showed absorption at 400−500 nm.

The solvent resistance of P-PDFB was also measured. Sample disks of P-PDFB with a thickness of 1.0 mm and a diameter of 10.0 mm were immersed into common organic solvents, such as THF, chloroform, toluene, and NMP. After being kept at 30 °C for 10 h, the films were removed from the solvents and did not show any cracks. Moreover, the weight increase of the films was less than 5% (see Table 1), suggesting that the film showed slight swelling. These results indicate that P-PDFB has good solvent resistance.

Table 1. Weight Change of P-PDFB in the Common Solvents[a]

solvent	weight increase (%)
$CHCl_3$	1.8
toluene	1.6
THF	3.3
NMP	2.4

[a] The measurement procedure is as following: P-PDFB films are immersed in the solvents at 30 °C for 10 h, moved out from the solvents, washed with ethyl acetate, and finally dried under vacuum until a constant weight (within 0.0001 g) is achieved.

Film Uniformity, Hydrophobicity, and Dielectric Properties of P-PDFB. Some of thermally cross-linkable polymers or oligomers, such as epoxy and phenolic resins, showed shrinkage when they were treated at high temperature. As the results, the surface of their films exhibited great roughness. However, the postpolymerization of PDFB in our case gave a P-PDFB film with good surface uniformity. An atomic force microscopy (AFM) image (Figure 3a) indicates that the surface roughness of P-PDFB film is less than 0.3 nm over a 4 μm square area. Furthermore, the field emission scanning electron microscopy (FE-SEM) image (Figure 3b) manifests that the P-PDFB film spin-coated on a silicon wafer has a smooth surface. These data indicate that PDFB exhibits less shrinkage during postpolymerization under high temperature. From a view of application, less shrinkage is very desirable for the production of electronic devices with high quality.

The hydrophobicity of P-PDFB film was investigated by the water contact angle test. On the surface of a P-PDFB film, the water contact angle was measured as 101.9° (Figure 4), indicating the good hydrophobicity of the film. The high hydrophobicity is also required for the production of devices in the microelectronics and electrical industry, because it can protect the devices from moisture uptake.

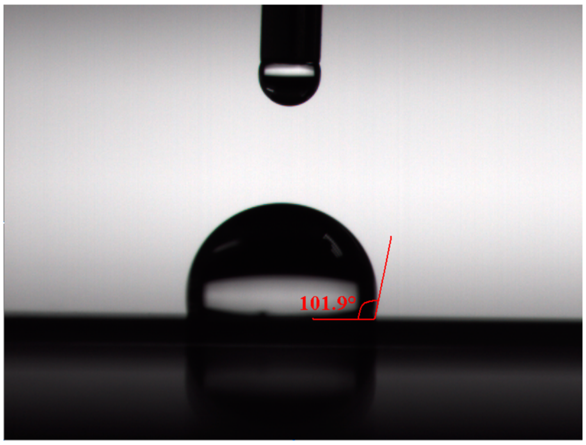


Figure 4. Contact angle of water on a P-PDFB film.

The dielectric constants of P-PDFB films were measured by the capacitance method. The thickness of the film was determined by field-emission scanning electron microscopy (FE-SEM) (see Figure 3b). The dielectric constant (*k*) and dielectric loss (tan *δ*) of the film are indicated in Figure 5. The average *k* value of P-PDFB film is below 2.6, with a dielectric loss below 2×10^{-2} in a range of frequencies varying from 1 to 30 MHz. Moreover, the film shows a dielectric constant of only 2.46 at 30 MHz, which is comparable to the values of the commercially available, organic, low-*k* materials, such as polyimides (3.1−3.4)[14] and polycyanate esters (2.61−3.12).[14]

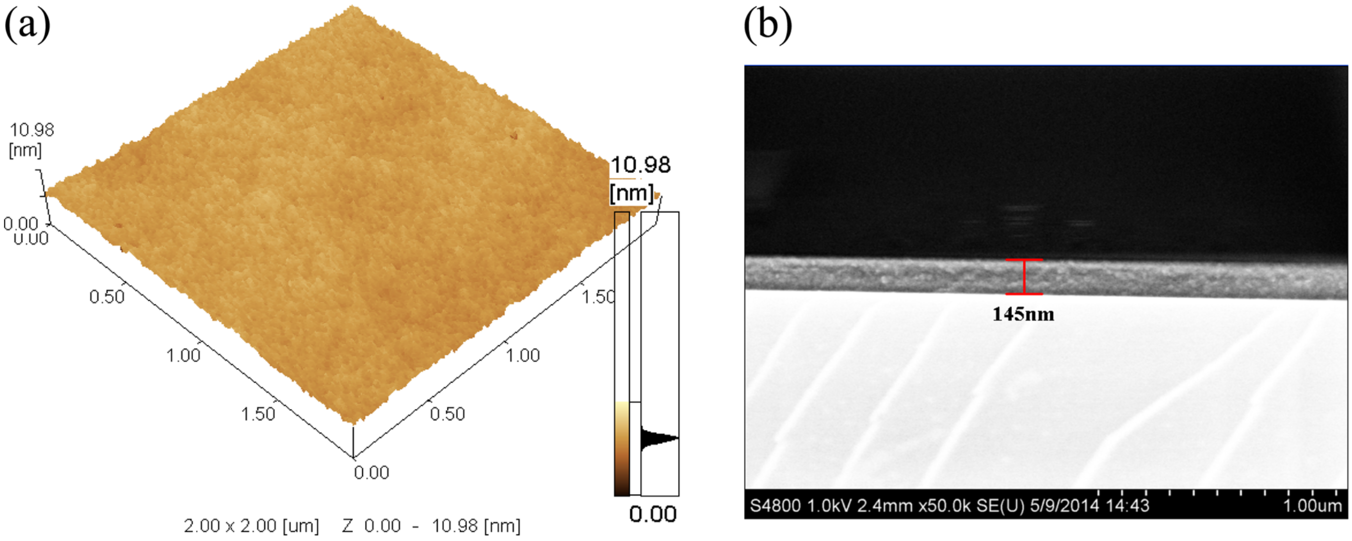


Figure 3. AFM (a) and PE-SEM (b) images of P-PDFB film on a silicon wafer.

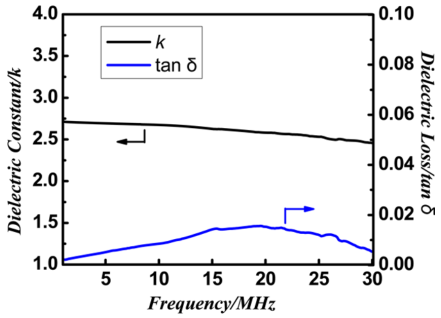


Figure 5. Dielectric constant and dielectric loss of a P-PDFB film at different frequencies at room temperature.

This low dielectric constant that the polymer exhibits is probably attributed to fluoro groups in the polymer.

Thermostability and Mechanical Properties of P-PDFB. The thermostability of P-PDFB was evaluated by thermal gravimetric analysis (TGA). Figure 6 shows the TGA curves of P-PDFB in N_2. P-PDFB exhibits a 5 wt % loss temperature at 495 °C and a residual weight of 61% at 1000 °C. This high heat resistance of P-PDFB implies that the polymer could meet the requirements for insulating enameled wire and print circuit boards, as well as potential application in the field of fire-resistant materials.

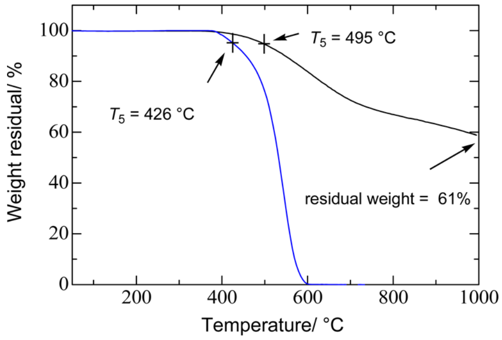


Figure 6. TGA curves of P-PDFB in N_2 (black) and air (blue) with a heating rate of 10 °C/min.

The mechanical properties of P-PDFB film were measured on a nanoindentation/scratch system. The results exhibited that the polymer film had an average hardness of 1.22 GPa and a Young's modulus of 8.80 GPa. The bonding strength between the film and a silicon wafer was measured as 0.89 GPa. Those data suggest that P-PDFB is satisfactory as the encapsulation resins for integrated circuit (IC) dies and structural adhesives for application in the microelectronics industry.

CONCLUSIONS

In summary, we have successfully synthesized a fluorinated poly(aryl ether) with thermosetting benzocyclobutene groups as the side chain (PDFB). This polymer has high molecular weight and is easily soluble in the common organic solvents. Upon treatment of PDFB film via a postpolymerization procedure at high temperature, the polymer film converts to a cross-linked network structure (P-PDFB), which shows good solvent resistance. Such results exhibit that the postpolymerization is an efficient way to realize the balance between the solubility and the solvent resistance of the polymer. Moreover, P-PDFB has low dielectric properties with an average dielectric constant below 2.46 in a range of frequencies varying from 1 to 30 MHz. Furthermore, P-PDFB film exhibits high thermostability with a 5 wt % loss temperature of 495 °C and a residual of 61% at 1000 °C under N_2. AFM images indicate that the P-PDFB film has excellent surface smoothness and good hydrophobicity. Nanoindentation and scratch tests show that the P-PDFB film possesses good mechanical properties, with hardness, Young's modulus, and bonding strength with a silicon wafer surface of 1.22 GPa, 8.8, and 0.89 GPa, respectively. These data indicate that PDFB is suitable for utilization in industry as the insulating varnish for the preparation of enameled copper wire, resin for the production of high-performance multilayer-printed board, encapsulation resins for IC dies, and the surface sizing agents for high-performance glass fiber or carbon fiber.

ASSOCIATED CONTENT

Supporting Information

NMR spectra and FT-IR spectra of the monomer and polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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