This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A new polymer with low dielectric constant based on trifluoromethyl substituted arene: preparation and properties

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

A new polymer with low dielectric constant is reported here. This polymer contains a trifluoromethyl substituted phenyl unit and a binaphthyl unit, and shows high thermostability with a glass transition temperature of 244 °C and a 5 wt% loss temperature at 518 °C in nitrogen. The polymer also exhibits good film-forming ability and the formed films exhibit high hydrophobicity with a contact angle to water of 103.6°. In a range of frequencies from 1 to 25 MHz, the polymer reveals an average of dielectric constants of about 2.56. In regard to the mechanical properties, the polymer film shows an average hardness of 0.37 GPa and a Young’s modulus of 15.07 GPa. Those results imply that the polymer could be used as the varnish for enameled wire, sizing agents for high performance carbon-fiber, and the matrix resin for production of laminated composites utilized in the print-circuit-boards (PCB) industry.

1. Introduction

Polymers with low dielectric constants (low $k$) have been paid much attention for many years because they are a kind of necessary materials for fabrication of insulating varnish of enameled wire in electrical industry as well as for production of printed-circuit-boards (PCB) in electronic industry. In recent years, the development of multilevel interconnection technology in the production of ultra-large scale integration (ULSI) circuits has raised an urgent requirement to the low $k$ materials due to the fact that they play a very important role for decreasing the cross-talk noise, power dissipation and interconnect signal delay (RC delay) generated with the minimization of electronic devices in microelectronic industry. Accordingly, various polymers have been well investigated and many low $k$ materials have been developed. Nevertheless, commercially available low $k$ polymers utilized at the high frequencies (> 10 MHz) are rare. It is known that the materials having a $k$ value of below 3.0 at the high frequencies can meet the requirement of 90 nm procedure in ultra-large scale integration (ULSI) circuits. Moreover, such low $k$ materials are also desirable for the production of high frequency printed circuit boards. Therefore, exploring and developing the polymers with a low $k$ value at high frequencies are still necessary.

So far, there are two manners to scale down the dielectric constants of polymers. One is to use the polymers containing least polarizable bonds such as C-F bond in molecular backbone and/or side chains, the other is to generate pores in polymer networks. However, favorable size and distribution of the pores should be carefully controlled.

Based on that polymeric materials have an advantage of easy structure design, consequently, their $k$ values and other properties such as thermostability and mechanical properties could be tunable via well defining molecular structures. It is noted that poly(aryl ether)s show high bonding strength to metals and low thermal expansion coefficient (CTE) and that fluoro-containing polymers exhibit lower $k$ values. Thus, the studies on the synthesis and properties of the new poly(aryl ether)s with fluoro groups are significant.

Previously, we have reported a thermally cross-linkable molecule composed of bis(trifluoromethyl)benzene and benzocyclobutene units, which shows both low dielectric constant at high frequencies and high thermostability. In order to further investigate the properties of the organic materials containing bis(trifluoromethyl)benzene units, we design and synthesize a new polymer composed of a binaphthyl unit and a bis(trifluoromethyl)benzene unit, whose chemical structure is shown in Scheme 1. The polymer exhibits good film-forming ability and the formed films possess high hydrophobicity with a contact angle to water of 103.6°. In a range of frequencies from 1 to 25 MHz, the polymer reveals an average of dielectric constants of about 2.56. Moreover, the polymer shows high...
thermostability and good mechanical properties. Those data suggest that the polymer could be used as the insulating varnish for enameled wire, sizing agents for high performance carbon-fiber, and the matrix resin for production of laminated composites utilized in the printed circuit boards (PCB) industry.

Scheme 1. Chemical structure of the new polymer in this work.

2. Experimental

Materials
All starting materials were purchased from Aldrich and Acros companies and used without further purification unless an additional statement elsewhere. 1,4-Bis(tri-fluoromethyl)-3,5-dibromobenzene (1, 7.438 g, 20 mmol), NaOH (2.8 g, 70 mmol), DMSO (60 mL), and toluene (100 mL) was heated to reflux (near 150 °C), and the water formed during the reaction was removed by a Dean-Stark trap. After being kept at the temperature (about 150-160 °C) for 8 h, the reaction mixture was cooled to room temperature, and poured into 200 mL of water, extracted with ethyl acetate. The organic layer was washed with saturated brine and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using n-hexane as an eluent on silica gel. The obtained product was further purified by recrystallization from n-hexane, Pure monomer 2 was obtained as a white solid in a yield of 67% with a purity of 99.6% (HPLC). ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.02-7.03 (dd, 2H), 7.25 (s, 2H), 7.45-7.49 (t, 2H), 7.54-7.57 (td, 4H), 7.73-7.75 (d, 2H), 7.92-7.94 (m, 2H), 8.15-8.17 (dd, 2H). ¹³F NMR (376 MHz, CDCl₃) δ (TMS, ppm): -62.57 (s, 6F). ¹⁹C NMR (100 MHz, CDCl₃) δ (TMS, ppm): 113.98, 117.94, 121.64, 122.36, 125.01, 125.48, 125.81, 126.65, 127.79, 127.19, 128.11, 135.23, 150.62, 151.86.

Synthesis of the polymer
Monomer 2 (0.498 g, 1 mmol) was dissolved in 1,1,2,2-tetrachloroethane (3.5 mL) at room temperature under argon. The obtained solution was cooled to -5 °C, and then added to a mixture of anhydrous iron(III) chloride (0.406 g, 2.5 mmol) in 1,1,2,2-tetrachloroethane (1.5 mL) under argon atmosphere. After being stirred at -5 °C for 24 h, the reaction mixture was poured into methanol (200 mL) containing a small amount of concentrated HCl. The obtained precipitate was purified by column chromatography on neutral Al₂O₃ with CHCl₃ as the eluent. As the solvent were evaporated, the polymer was re-dissolved in chloroform and reprecipitated with methanol. A yellowish power was thus obtained, which was dried at 80 °C for 12 h under vacuum to get polymer sample. Yield: 80%. Characterization: ¹H NMR (400 MHz, acetone-d₆) δ (TMS, ppm): 7.37-7.39 (d, 2H), 7.46-7.54 (m, 4H), 7.59-7.61 (d, 2H), 7.64-7.70 (m, 2H), 7.78 (s, 2H), 8.37-8.39 (d, 2H). ¹³C NMR (376 MHz, acetone-d₆) δ (TMS, ppm): -62.87 (s, 6F). ¹⁹F NMR (376 MHz, acetone-d₆) δ (TMS, ppm): -62.57 (s, 6F). ¹⁹C NMR (100 MHz, CDCl₃) δ (TMS, ppm): 113.01, 118.56, 121.11, 121.91, 123.83, 126.04, 126.59, 126.86, 127.52, 128.01, 134.60, 134.79, 150.61, 152.05. Elemental analysis, Cacld. for C₁₆H₁₀O₂F₂C: 67.47; H, 3.24; F, 22.87; Found: C, 67.65; H, 3.45; F, 22.86.

Preparation of the Film for the Measurement of k value, Surface Toughness and Contact Angle
A polymer solution in toluene (30 wt%) was spin-coated on an aluminum-backed silicon wafer (heavily doped single crystal silicon with a resistivity of 3.5×10⁵ Ω·cm) to form a film. The wafer was placed into a quartz tube furnace and kept at 180 °C for 3 h to completely remove the solvent. Thus the films for measurement of surface toughness and contact angles were obtained.

To prepare the film used for the measurement of k value, an additional procedure was used and described as following: surface of the obtained film was deposited aluminum as a top electrode (the diameter = 3 mm) via vacuum evaporation. The
thickness of the film was measured by field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

Synthesis and characterization

As shown in Scheme 2, monomer 2 was prepared by the etherization reaction between 1,4-bis(trifluoromethyl)-2,5-dibromobenzene (1) and 1-naphthol in the presence of a strong base. Because compound 1 contained -CF$_3$ groups with strong electron-withdrawing ability, the aromatic ring was greatly activated. Therefore, monomer 2 was easily prepared in a moderated yield. In contrast, in many cases, the etherization reaction between aryl halides and phenols was not easy and needed the transition metal complexes as the catalysts.$^{51,52}$ The chemical structure of monomer 2 was characterized by $^1$H NMR, $^{19}$F NMR, $^{13}$C NMR and elemental analysis, as shown in experimental section.

![Scheme 2](image)

Scheme 2. The procedure for the synthesis of monomer and polymer.

The target polymer was synthesized by employing an oxidative homopolymerization route (Scholl reaction). In most cases, the Scholl polycondensation was carried out in the presence of Fe(III) in nitrobenzene.$^{21,53}$ To avoid using highly toxic nitrobenzene, we chose 1,1,2,2-tetrachloroethylene as the solvent to study the polymerization.$^{54}$ Initially, when the reaction was run at room temperature, gelation occurred and an insoluble deep-yellow solid was obtained, suggesting that monomer 2 possessed very high reactivity. When lowering the temperature to 0 °C, the reaction gave the polymer with two fractions. One was insoluble gel, and the other was soluble in common organic solvents. The soluble part showed a $M_n$ of 11,800. Further examination of the polymerization at -5 °C exhibited that the $M_n$ increased to 17,000. However, when the polymerization was run at a temperature of below -10 °C, the polymer was obtained with lower $M_n$ (see Table 1). These results implied that the reactivity of monomer 2 increased with the rising of the temperature.

It was noted that the amount of oxidant (FeCl$_3$) also had an influence on the Scholl reaction.$^{21,53}$ Sequently, we changed the molar ratio between FeCl$_3$ and monomer 2 from 2:1 to 2.5:1, the reaction gave the polymer with higher $M_n$. The best result was obtained when the molar ratio of FeCl$_3$/monomer 2 was 2.5:1 and the polymerization was run at -5 °C. The obtained polymer with a $M_n$ of 62,000 was used to do the following performance tests.

The obtained polymer was soluble in common organic solvents such as THF, toluene and chloroform, and had good film-forming ability when cast from either chloroform or toluene solutions. The polymer film was transparent, flexible and pale-yellow in color.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)$^a$</th>
<th>FeCl$_3$ (equiv)$^b$</th>
<th>$M_n$$^c$</th>
<th>$M_w$$^d$</th>
<th>PDI$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>2.0</td>
<td>11,800</td>
<td>22,300</td>
<td>1.89</td>
</tr>
<tr>
<td>2</td>
<td>-5</td>
<td>2.0</td>
<td>17,000</td>
<td>33,500</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>-10</td>
<td>2.0</td>
<td>11,700</td>
<td>23,200</td>
<td>1.99</td>
</tr>
<tr>
<td>4</td>
<td>-15</td>
<td>2.0</td>
<td>9,700</td>
<td>17,000</td>
<td>1.77</td>
</tr>
</tbody>
</table>

$^a$Temperature of the polymerizations. $^b$Equivalents comparing to monomer 2. $^c$The number average molecular weight; $^d$The weight average molecular weight; $^e$Distribution of molecular weight.

The chemical structure of the polymer was confirmed by $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, and elemental analysis (EA). The results are listed in experimental section. Taking as an example, $^{13}$C NMR of the polymer is shown in Fig. 1. All data of $^{13}$NMR for the polymer is shown in Fig. 1. All data of $^{13}$NMR for the polymer are consistent with the proposed.

![Fig. 1](image)

Fig. 1. An expanded $^{13}$C NMR spectrum of the polymer (100 MHz, CDCl$_3$, 25 °C).

Thermostability of the polymer
Fig. 2 DSC trace of the polymer at a heating rate of 10 °C/min in N₂.

Fig. 2 shows the DSC trace of the polymer, which indicates that the polymer has a glass transition temperature ($T_g$) at 244 °C. This high $T_g$ is attributed to the existence of rigid rod-like binaphthyl units in the polymer backbone. TGA analysis (Fig. 3) shows that the polymer exhibits a 5 wt% loss temperature at 518 °C and shows a residual of 53.22% at 1000 °C under nitrogen. Even in air, the polymer also possesses high heat resistance with a 5 wt% loss temperature at 474 °C. From the view of application, the heat resistance of the polymer could meet the requirements of insulating enameled wire and print-circuit-boards (PCB). Fig. 3 TGA curves of the polymer at a heating rate of 10 °C/min in N₂ (red line) and air (blue line).

Dielectric and Mechanical Properties of the polymer

The dielectric constant of the polymer film was measured by the capacitance method. Fig. 4 reveals the relationship of dielectric constants ($k$) and dielectric loss (tan δ) with frequency ranging from 1 to 25 MHz at room temperature. As depicted in Fig. 4, the polymer film shows an average $k$ value of about 2.56. This dielectric constant is comparable to the values of the commercially organic low-$k$ materials such as polyimides (3.1-3.4) and polycyanate esters (2.61-3.12). Such good dielectric properties that the polymer exhibits are probably caused by -CF$_3$ groups with large free volume.

Fig. 4 Dielectric constants ($k$) and dissipation factors (tan δ) of the polymer film depending on the frequencies.

The mechanical properties of the polymer film were measured on a nano indenter system. The polymer film showed an average hardness of 0.37 GPa and a Young’s modulus of 15.07 GPa, respectively. It is noted that the low $k$ materials utilized in microelectronic industry must possess high hardness and Young’s modulus to meet the requirement of a back-end-of-the-line (BEOL) production procedure. Based on its mechanical properties, the polymer is satisfied the BEOL procedure.

Morphology, Film Uniformity and Hydrophobicity of the Polymer

Fig. 5 shows X-ray diffraction (XRD) patterns of the polymer in two forms (powder and casting film). As shown in Fig. 5, the polymer is essentially amorphous, suggesting that there is no close aggregation between polymer chains. Thus, the polymer exhibits low density, which is favorable for decreasing of the dielectric constant of the polymer.

Fig. 5 XRD patterns of the polymer in two forms (powder and casting film).

Fig. 6 illustrates the contact angle of water on the polymer film, which indicates the high hydrophobicity of the polymer. Such high hydrophobicity is very efficient for keeping constant
insulating properties when the materials are used under moisture condition.

![Fig. 6 Contact angle of water on the polymer film.](image)

An AFM image of the polymer film is shown in Fig. 7. As illustrated in Fig. 7, the polymer shows good film uniformity with the surface roughness less than 5 nm over a 4 µm square area.

![Fig. 7 An AFM image of the polymer film on a silicon wafer.](image)

4. Conclusions

A new polymer with a trifluoromethyl substituted arene was synthesized via oxidative coupling polymerization. The polymer has a glass transition temperature of 244 °C and shows a 5 wt% loss temperature at 518 °C in nitrogen. The polymer films exhibit high hydrophobicity with a contact angle to water of 103.6°. Moreover, the polymer reveals an average of dielectric constants of about 2.56 in a range of frequencies from 1 to 25 MHz. In regard to the mechanical properties, the polymer film shows an average hardness of 0.37 GPa and a Young’s modulus of 15.07 GPa, respectively. Those data suggest that the polymer could be used as the varnish for enameled wire, sizing agents for high performance carbon-fiber, and the matrix resin for production of laminated composites utilized in the print-circuit-boards (PCB) industry.

Acknowledgements

Financial supports from Ministry of Science and Technology of China (2011ZX02703) and the Natural Science Foundation of China (NSFC, No. 21374131) are gratefully acknowledged.

Notes and references

The table of contents

A polymer based on trifluoromethyl substituted arene was synthesized with high molecular weight ($M_n$) of 62,000 by the Scholl reaction. The polymer film showed low dielectric constants of about 2.56 in a range of frequencies from 1 to 25 MHz. Moreover, the polymer revealed high thermostability and good mechanical properties, suggesting that the polymer had potential applications in electronic industry.

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

A new polymer with low dielectric constant based on trifluoromethyl substituted arene: preparation and properties

ToC figure