

## Soluble Low- $\kappa$ Poly (aryl ether ketone) Copolymers Containing Pendant Adamantyl Group and Long Aliphatic Side Chains

Jinyu Ba, Zhi Geng, Jianxin Mu

College of Chemistry, Engineering Research Center of High Performance Plastics, Ministry of Education, Jilin University, ChangChun 130012, People's Republic of China

Correspondence to: J. X. Mu (E-mail: jianxin\_mu@jlu.edu.cn)

**ABSTRACT:** The aromatic diphenol monomers, 4-(1-adamantyl)-1,3-benzene diol (AdRES) and 4-(6-(4-hydroxyphenyl)undecan-6-yl)phenol (BISPR5R5) were successfully synthesized and used to synthesize a new series of poly (aryl ether ketone) copolymers (AdRES-BISPR5R5-PEEKs) with different percentages of two diphenol monomers by nucleophilic aromatic substitution polycondensation. The structure of copolymers was confirmed using FTIR and  $^1\text{H}$  NMR spectroscopy and their thermal and mechanical properties and solubilities were determined. It was found that the flexibility and toughness properties of the copolymers could be controlled by varying the molar ratio of diphenol monomers containing the pendent rigid adamantyl group and the flexible long side chains. They also showed low dielectric constants ( $\kappa = 2.50\text{--}2.88$  at 1 MHz) and low water absorptions. It revealed that the symmetrical long aliphatic side chains were more conducive for reducing the polarity of the polymer chains, loosening the polymer packing, and subsequently reducing polymers' density and dielectric constants than the pendent rigid adamantyl group. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 193–200, 2013

**KEYWORDS:** copolymers; dielectric properties; mechanical properties; structure-property relations

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### INTRODUCTION

Next generations of microelectronic devices request further miniaturized systems. In this context, further reduction in the dielectric constant of these materials used as interlayer dielectrics is needed to avoid cross-talk between conducting wires as electronic devices continue to shrink and many efforts have been paid to develop new polymer materials compatible with  $\kappa \ll 3$  resolution. In particular, poly (aryl ether ketone)s (PAEKs) have achieved an excellent position among other thermoplastic polymers by the virtue of their superior properties, such as thermal stability, high heat-distortion temperature, chemical inertness, electrical performance, and flame retardancy.<sup>1–8</sup> The dielectric constants of most PAEKs are between 3.1 and 3.5 and a variety of approaches of physical and chemical modification have been attempted in order to obtain lower dielectric constants of PAEKs.<sup>9–19</sup> The introduction of bulky pendant groups along the polymer backbone has been one such approach, and there are several classes of polymer materials containing bulky pendant rigid groups reported in the literatures.<sup>20–25</sup> For example, Timothy M. Long reported that the introduction of the bulky triptycene fragment in the polymer could reduce any chain packing and increase free volume, and finally decrease the dielectric constant of the resulting poly-

mers.<sup>22</sup> Similarly, Dong Wan Seo suggested that poly (ether sulfone)s carrying pendent bulky imide side group with a low dielectric constant could be prepared.<sup>26</sup> Although their dielectric constants are lower, poor mechanical properties because of the bulky rigid side groups compromise their use.

We wonder whether, in another approach, a class of flexible bulky side groups could be incorporated into polymers to reduce the dielectric constant without detrimentally affecting the mechanical properties of polymers. Scott Gronewald found that poly (aryl ether ketones) bearing alkyl side chains had a lower dielectric constant.<sup>27,28</sup> Therefore, this work was an attempt to synthesize a variety of PAEKs containing the flexible symmetrical long aliphatic side chains, so the monomer, 4-(6-(4-hydroxyphenyl)undecan-6-yl)phenol (BISPR5R5) was selected. Its symmetrical structure with low polarity was propitious to reduce the polarity of the polymer chains and subsequently reduce the dielectric constant of the polymer. Simultaneously, the monomer 4-(1-adamantyl)-1,3-benzene diol (AdRES) was selected to copolymerize with 4,4'-difluorobenzophenone (DFB) and BISPR5R5 via the nucleophilic aromatic substitution polymerization. Considering that adamantane ( $\text{C}_{10}\text{H}_{16}$ ) is a nonpolar rigid polycyclic cage hydrocarbon and the large steric size of the adamantane ring could reduce any chain packing and

increase the rigidity of the polymer chains, which, in turn, will endow the copolymers with high glass transition temperatures to improve thermal stability of copolymer.<sup>29</sup>

Herein in this investigation, we attempted to synthesize PAEK copolymers containing bulky pendant rigid adamantyl group and the symmetrical long aliphatic side chains. The incorporation of bulky aliphatic substituent on the polymer backbone would lead to several property modification of the copolymers, which included decreasing crystallization, improving solubility, enhancing glass transition temperature, lowering dielectric constant, and moisture absorption of polymers.<sup>30–37</sup> This copolymerization approach provided a versatile way to design a variety of PAEKs with well-controlled polymer structures, a wide range of dielectric constants, and mechanical properties. It was discovered that the dielectric constants of these polymers decreased with the increase of the molar content of the flexible symmetrical long side chains, which offered the advantage of lowering the dielectric constants.

## EXPERIMENTAL

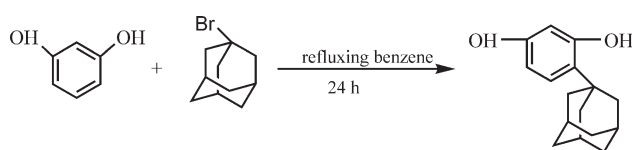
### Materials

1-Bromoadamantane was purchased from Chongqing Wanli-kang Company (Chongqing, China) and sublimed under pressure reduction at 90°C before used. Nanoscale polyoxometalates (POM) was purchased from Jilin Ruiyang Industrial Trade. 6-Undecanone was purchased from Zhonggang Group. Benzene, toluene, methanol, petroleum ether (90–120°C), and anhydrous potassium carbonate were purchased from Tianjin Chemical Reagent. Tetrahydrofuran (THF) and sulfuric acid were purchased from Beijing Chemical Reagent. Resorcinol and phenol were purchased from Sinopharm Chemical Reagent and were used as received. Tetramethylene sulfone (TMS) was purchased from Jinzhou Oil Refinery and purified by vacuum distillation. Mercaptoacetic acid was purchased from Aldrich Chemical Company. 4,4'-Difluorobenzophenone (DFB) was purchased from Changzhou Huashan Chemical Co. Ltd., China, and the conventional poly (ether ether ketone) (PEEK) (prepared from hydroquinone and 4,4'-difluorobenzophenone) was prepared in our laboratory according to the standard procedures.<sup>4,6</sup> Other common reagents were obtained from commercial sources and used as received.

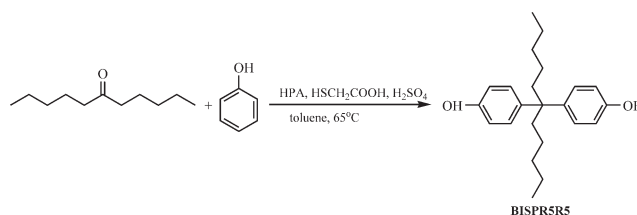
### Monomer Synthesis

**Preparation of 4-(1-adamantyl)-1,3-benzene diol (AdRES).** AdRES was synthesized by following the published procedures (Scheme 1).<sup>34</sup>

Yield: 75%.  $M_p$ : 244°C (DSC). IR (KBr,  $\text{cm}^{-1}$ ): 3479  $\text{cm}^{-1}$  and 3390  $\text{cm}^{-1}$  (—OH stretching), 2904  $\text{cm}^{-1}$  and 2855  $\text{cm}^{-1}$  (adamantine—CH<sub>2</sub> and C—H stretching). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 9.01 (s, 1 H), 8.92 (s, 1 H), 6.81–6.79



**Scheme 1.** Synthesis of monomer AdRES.



**Scheme 2.** Synthesis of monomer BISPR5R5.

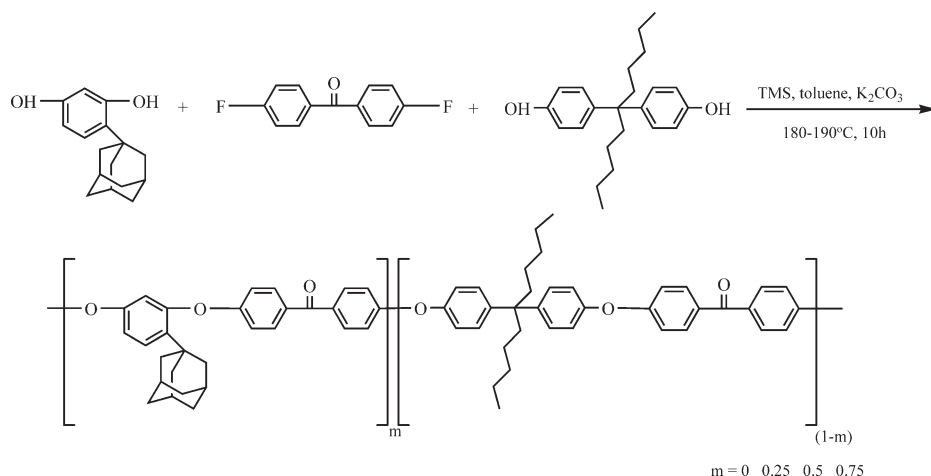
(d, 1 H,  $J = 8.4$  Hz), 6.23–6.22 (d, 1 H,  $J = 2.5$  Hz), 6.14–6.10 (dd, 1 H,  $J_1 = 8.4$  Hz,  $J_2 = 2.5$  Hz), 1.99–1.69 (15 H). Elem. Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>2</sub> (244.32): C, 78.65%; H, 8.25%. Found: C, 78.63%; H, 8.21%.

**Preparation of 4-(6-(4-hydroxyphenyl)undecan-6-yl)phenol (BISPR5R5).** BISPR5R5 was synthesized by following the published procedures (Scheme 2).<sup>38</sup>

The synthesis process of BISPR5R5 is an electrophilic substitution reaction, accompanied by the removal of water. 6-Undecanone, mercaptoacetic acid, and nanoscale POM were dissolved in toluene in a three-necked round bottom flask equipped with a nitrogen inlet and outlet under the liquid level, mechanical stirrer, and a Dean-Stark trap fitted with condenser. Phenol was added with stirring. A moment later, a trace amount of sulfuric acid was added in a dropwise manner within 1 h. The pale golden reaction mixture was stirred overnight at 65°C until there was no water brought out, and it would take about 24 h. Finally, the color of the solution turned from yellow to red. Additional toluene was added and the mixture was washed with water until it became neutral. Excess phenol was removed by distillation under reduced pressure and steam distillation. The resulting solid was recrystallized from toluene/petroleum ether (2/3 by volume ratio) to give a white crystalline product. Yield: 50%.  $M_p$ : 148°C (DSC). IR (KBr,  $\text{cm}^{-1}$ ): 3328  $\text{cm}^{-1}$  (—OH stretching), 2924  $\text{cm}^{-1}$  (CH<sub>2</sub> asymmetric stretching) and 2863  $\text{cm}^{-1}$  (CH<sub>2</sub> symmetric stretching). 726  $\text{cm}^{-1}$  ((CH<sub>2</sub>)<sub>n</sub> plane swing stretching, indicating that there were long side chains in the diphenol). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 9.12 (s, 2 H), 6.92–6.89 (d, 4 H,  $J = 8.4$  Hz), 6.64–6.61 (d, 4 H,  $J = 8.4$  Hz), 1.92–0.74 (22 H). Elem. Anal. Calcd for C<sub>23</sub>H<sub>32</sub>O<sub>2</sub> (340.24): C, 81.12%; H, 9.50%. Found: C, 81.10%; H, 9.48%.

### Polymer Synthesis

All the copolymers were synthesized via aromatic nucleophilic substituted reaction by a similar procedure as depicted in Scheme 3. The typical copolymerization of 50%AdRES-50%BISPR5R5-PEEK was carried out as follows: 4-(1-adamantyl)-1,3-benzene diol (AdRES) (1.8311 g, 0.0075 mol), 4-(6-(4-hydroxyphenyl)undecan-6-yl)phenol (BISPR5R5) (2.5518 g, 0.0075 mol), 4,4'-difluorobenzophenone (DFB) (3.2708 g, 0.015 mol), and an excess of potassium carbonate (2.4824 g, 0.018 mol) were dissolved in TMS (25 mL) with a 20% solid content and toluene (10 mL) in a reaction flask fitted with a nitrogen inlet and outlet, mechanical stirrer, and a Dean-Stark trap fitted with condenser. The mixture was heated to 130°C with stirring under nitrogen for 3 h to remove produced water by azeotropic distillation with toluene, and then the toluene was substantially removed from the reaction flask until the flask



**Scheme 3.** Synthesis of AdRES-BISPR5R5-PEEK copolymers.

temperature reached 180°C. The reaction mixture was maintained at 180–190°C for 10 h to afford a high molecular weight polymer and then was poured into distilled water. The crude precipitated polymer was pulverized, washed by hot distilled water and ethanol several times, and dried at 100°C for 24 h to yield off-white powder of 50%AdRES-50%BISPR5R5-PEEK.

### Characterization

The FTIR spectra (KBr) were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. <sup>1</sup>H NMR was recorded on a Bruker 510 NMR spectrometer (500 MHz) using DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as solvent with tetramethyl silane as a reference. The elemental analyses were carried out with a MOD-1106 elemental analyzer. Gel permeation chromatograms (GPCs) using polystyrene as a standard were obtained on a Waters 410 instrument with THF or N,N-dimethyl formamide (DMF) as an eluent at a flowrate of 1 mL/min. Mass spectra were obtained using a Japanese SHIMADZU company AXIMA-CFR mass spectrometer with THF as a solvent. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 821<sup>e</sup> instrument at a heating rate of 10°C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10°C/min and polymers were contained within open platinum pans on a Perkin-Elmer TGA-7. Mechanical properties of the thin films (about 0.1 mm, cast from THF solutions onto the glass plates, and followed by heating at 40–80°C in vacuo) were evaluated at room temperature on a Shimadzu AG-I Universal Tester without strain gauge type extensometer at a strain rate of 2 mm/min. The water uptakes of the polymer were measured by immersion of the polymer films (1 × 3 cm<sup>2</sup>, cast from THF solutions onto the glass plates, dried at 120°C for 24 h in vacuo before used) into deionized water at 25°C for 72 h, then the films were taken out and wiped with tissue paper for removal of any water on the surface. The water uptakes were calculated from the difference in the weights before and after this procedure. The density of the polymer films was measured by a top-loading electronic balance (ALFA MIRAGE SD-200) coupled with a density kit based on Archimedes' principle at 23°C. The dielectric properties of the polymer films (diameter

5.5 mm and thickness 0.05–0.2 mm, cast from THF solutions onto the glass plates and then coated with silver by a vacuum evaporation method) were obtained using an HP 4192 A impedance analyzer at room temperature and the frequency was 10<sup>3</sup>–10<sup>6</sup> Hz. The dielectric constant  $\kappa$  of the film was calculated using the formula of a parallel plate capacitor:

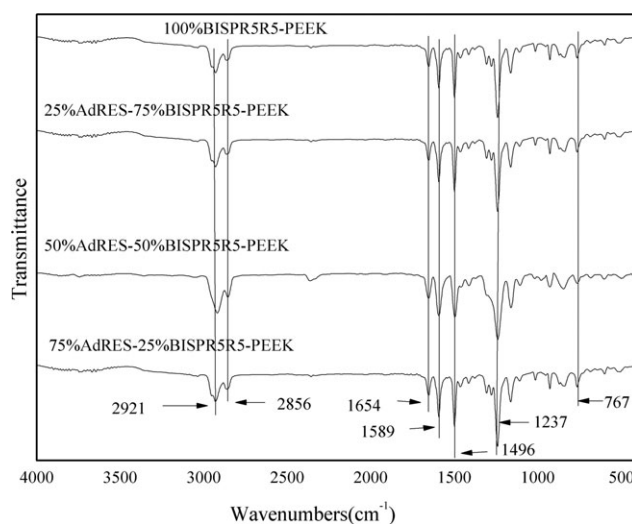
$$\kappa = \frac{Ct}{\epsilon_0 A}$$

where  $C$  is the capacitance of the metal-insulator-metal element,  $\epsilon_0$  is the vacuum dielectric permittivity,  $A$  is the area of the electrode, and  $t$  is the thickness of the capacitor.

## RESULTS AND DISCUSSION

### Monomer Synthesis

The aromatic diphenol monomers, 4-(1-adamantyl)-1,3-benzenediol (AdRES) was synthesized via the Friedel–Crafts reaction and 4-(6-(4-hydroxyphenyl)undecan-6-yl)phenol (BISPR5R5) was synthesized via the condensation of phenol and



**Figure 1.** FTIR spectra of AdRES-BISPR5R5-PEEK copolymers.

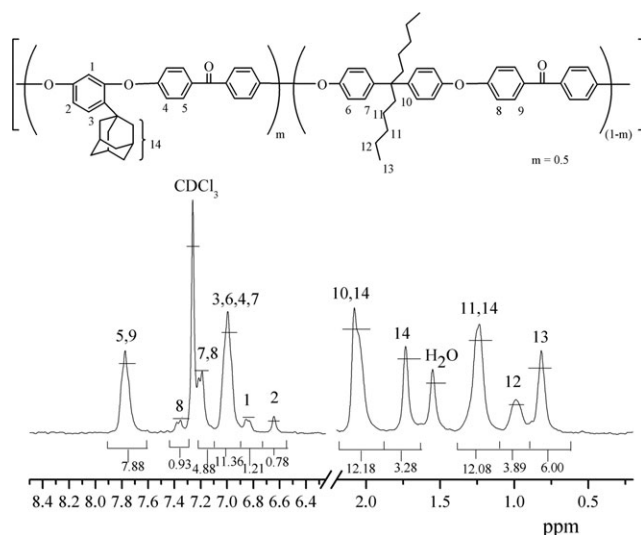


Figure 2.  $^1\text{H}$  NMR spectrum of 50%AdRES-50%BISPR5R5-PEEK.

6-undecanone in acidic condition. As reported, when we synthesized the monomer BISPR5R5, the experimental condition played a key role.<sup>38</sup> To obtain a high yield and high selectivity of the bisphenol monomer, we used the POM as the catalyst and the mercaptoacetic acid as the cocatalyst. Moreover, the concentration of phenol in the reaction system was much higher than that of 6-undecanone with the molar ratio of 10 : 1, which could ensure that the para-position of every phenol molecule was substituted by the carbocation generated by 6-undecanone. In the beginning, sulfuric acid was used to decrease the concentration of water in the system. Later, the nitrogen was led in to remove the generated water continuously. Finally, the balance of the reaction was destructed that was conducive to the positive reaction. The chemical structure of AdRES and BISPR5R5 was confirmed using FTIR and  $^1\text{H}$  NMR.

### Polymer Synthesis

A new series of poly (aryl ether ketone)s containing pendant adamantyl group and long aliphatic side chains were derived from AdRES and BISPR5R5 with DFB by a nucleophilic polycondensation reaction as shown in Scheme 3. They were random copolymers. The FTIR spectroscopy confirmed the formation of AdRES-BISPR5R5-PEEK copolymers (Figure 1). The characteris-

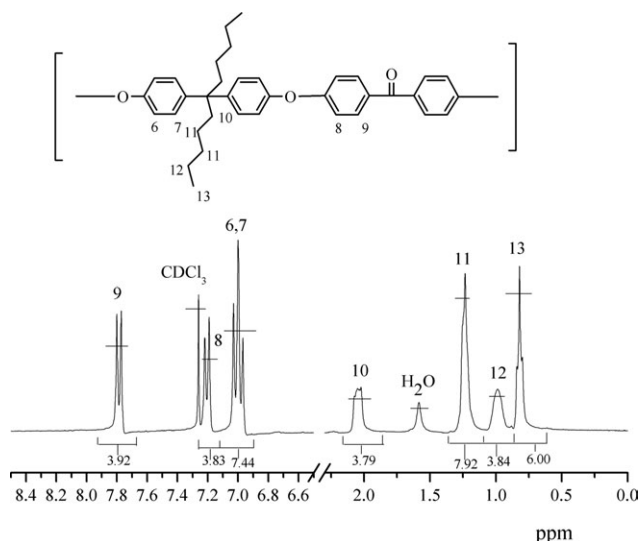


Figure 3.  $^1\text{H}$  NMR spectrum of 100%BISPR5R5-PEEK.

tic absorption bands of aromatic ring appeared near  $1589\text{ cm}^{-1}$  (C—H) and  $1496\text{ cm}^{-1}$  (C—C), the characteristic absorption bands of carbonyl group (C=O) appeared at  $1654\text{ cm}^{-1}$ , the characteristic absorption bands of aryl ether linkages (Ar—O—Ar) were observed near  $1237\text{ cm}^{-1}$ . And the characteristic absorption at  $2921$  and  $2856\text{ cm}^{-1}$  were assigned to the stretching vibration (C—H) of the adamantyl group. One band assigned to the plane swing stretching vibration of  $(\text{CH}_2)_n$  group was observed at  $767\text{ cm}^{-1}$ , indicating that there were long side chains in the polymers. Simultaneously, chemical structures of AdRES-BISPR5R5-PEEK copolymers were identified by  $^1\text{H}$  NMR, as shown in Figures 2–3. It gave the assignment of each proton and the spectrum agreed well with the proposed molecular structures of the polymers. It had been observed that the proton peaks of the phenyl ring (1, 2) and the adamantyl group (14) disappeared in the spectrum of 100%BISPR5R5-PEEK.

### Characterization of AdRES-BISPR5R5-PEEK Copolymers

**Solubility of the Copolymers.** The solubility behavior of the copolymers in some solvents was listed in Table I. It is well known that the conventional PEEK could not be dissolved in most known organic solvents. In sharp contrast, the AdRES-BISPR5R5-PEEKs exhibited good solubility in different solvent

Table I. Solubility of AdRES-BISPR5R5-PEEK Copolymers

Polymer	Solvent							
	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{CCl}_4$	THF	DMSO	NMP	DMAc	DMF
PEEK	--	--	--	--	--	--	--	--
100%BISPR5R5-PEEK	++	++	++	++	--	++	+-	+-
25%AdRES-75%BISPR5R5-PEEK	++	++	++	++	--	++	+-	+-
50%AdRES-50%BISPR5R5-PEEK	++	++	++	++	--	++	+-	+-
75%AdRES-25%BISPR5R5-PEEK	++	++	++	++	--	++	+-	+-

The solubility was determined at 5% solid content: ++, soluble at room temperature; +-, soluble on heating; --, insoluble.  $\text{CH}_2\text{Cl}_2$ , methylene dichloride;  $\text{CHCl}_3$ , chloroform;  $\text{CCl}_4$ , carbon tetrachloride; THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide. PEEK, prepared from hydroquinone and 4,4'-difluorobenzophenone.

**Table II.** Molecular Weight and Thermal Properties of AdRES-BISPR5R5-PEEK Copolymers

Polymer	$T_g^a$ (°C)	$DT_5^b$ (°C)	$DT_{10}^c$ (°C)	$M_w^d$ ( $10^4$ )	$M_n^d$ ( $10^4$ )	PDI <sup>e</sup>
100%BISPR5R5-PEEK	110	435	451	5.98	2.67	2.24
25%AdRES-75%BISPR5R5-PEEK	132	455	476	7.03	4.32	2.04
50%AdRES-50%BISPR5R5-PEEK	156	459	486	4.95	2.33	2.15
75%AdRES-25%BISPR5R5-PEEK	185	398	516	6.19	3.41	1.82

<sup>a</sup>From the second heating trace of DSC measurements conducted at a heating rate of 10°C/min.

<sup>b</sup>5% weight loss temperatures measured by TGA at a heating rate of 10°C/min in N<sub>2</sub>.

<sup>c</sup>10% weight loss temperatures measured by TGA at a heating rate of 10°C/min in N<sub>2</sub>.

<sup>d</sup>Relative to polystyrene standard, using THF as the eluent.

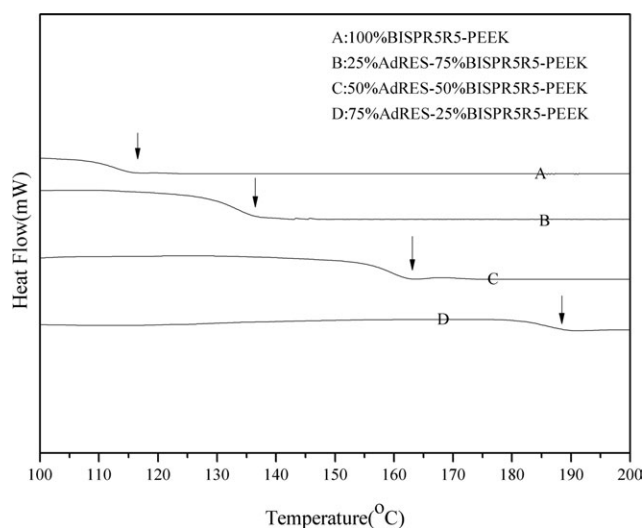
<sup>e</sup>Polydispersity index.

systems, which included aprotic polar solvents such as THF, DMF, and NMP as well as aprotic nonpolar solvents such as CCl<sub>4</sub>. That is, the solubility of PAEKs was remarkably improved and the good solubility of the copolymers could be due to the incorporation of the bulky pendant adamantyl group and flexible long side chains, which disturbed the close packing of the polymer chains and led to the increased free volume. Therefore, it would become easy for solvents to penetrate into the polymer system and solubilize the polymer. Meanwhile, the structure of the symmetrical long aliphatic side chains promoted the dissolution in nonpolar solvents. In short, the copolymers demonstrated a very good film-forming ability.

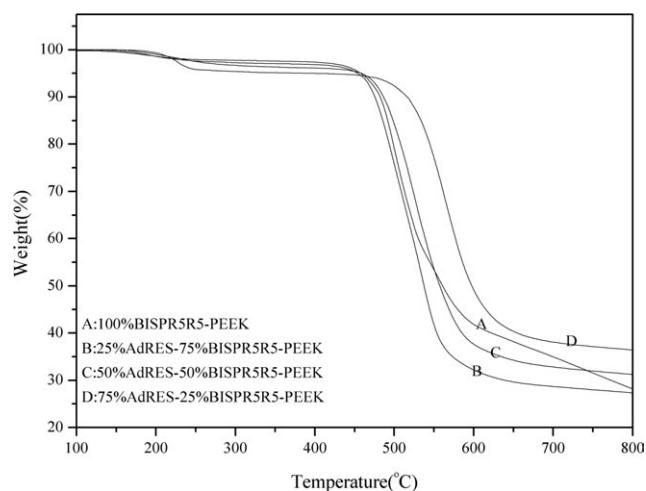
**Molecular Weight and Thermal Properties of the Copolymers.** The molecular weights of the copolymers were summarized in Table II. The GPC data revealed that all of the copolymers presented high molecular weight that  $M_n$  was in the range of 2.33–4.32, 10<sup>4</sup> g/mol and  $M_w$  of 4.95–7.03, 10<sup>4</sup> g/mol. The polydispersities of the copolymers were about 1.82–2.24. These results described that despite the monomers AdRES and BISPR5R5 containing bulky side groups, the copolymers with high molecular weight could be obtained if they copolymerized with each other.

Thermal properties of polymer films are vital to their application in microelectronics. Generally, the glass transition temperatures ( $T_g$ ) of polymers reflect their segmental mobility, especially when the involved samples experience an identical thermal history, so DSC experiments of the copolymers were performed under N<sub>2</sub> atmosphere and the results were depicted in Figure 4. The AdRES-BISPR5R5-PEEK copolymers showed an elevated glass transition of 110, 132, 156, and 185°C (Table II), respectively, as the adamantyl group's content increased and no melting endotherms were observed in the DSC traces, which confirmed the amorphous nature of the copolymers. The bulky rigid adamantyl group and the long side chains had great effect on the glass transition temperature of the copolymers and destroyed the crystallinity of the copolymers, too. The combination of side-chain rigidity and size of the adamantyl group, along with ortho interaction with the adjacent backbone unit, appeared to require much more energy to carry out the segmental mobility at higher  $T_g$ .

To examine the thermal durability of these films, we performed thermo gravimetric analysis (TGA) with results as shown in Figure 5 and temperatures of 5% weight loss and 10% weight loss for the copolymers as given in Table II. TGA curves of the copolymers exhibited significantly decline in the temperature range of 200–750°C and clearly described the experience of two-step weight loss procedure during the heating treatment.



**Figure 4.** DSC curves of AdRES-BISPR5R5-PEEK copolymers.



**Figure 5.** TGA curves of AdRES-BISPR5R5-PEEK copolymers in N<sub>2</sub>.



**Table III.** Mechanical Properties of AdRES-BISPR5R5-PEEK Copolymers

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
100%BISPR5R5-PEEK	51.4	2.79	91
25%AdRES-75%BISPR5R5-PEEK	44.6	2.30	30
50%AdRES-50%BISPR5R5-PEEK	41.3	2.90	21
75%AdRES-25%BISPR5R5-PEEK	38.2	2.65	5

Because of the instability of the large aliphatic substituent, the first degradation stage with temperature around 200°C was attributed to the pendant aliphatic hydrocarbon segment weight loss. The second degradation stage above 450°C resulted from the weight loss of the thermal decomposition of the aromatic components in the main chains. Because the thermal stability of the meta aromatic ring was better than that of the quaternary carbon bridge, the temperature of 10% weight loss experienced a raise with an increasing adamantyl group's content. All in all, the introduction of rigid pendant adamantyl group improved the thermal properties of the copolymers.

**Mechanical Properties of the Copolymers.** The mechanical properties of the polymer films casting from THF were summarized in Table III. The polymer films exhibited tensile strengths of 38.2–51.4 MPa, Young's modulus of 2.30–2.90 GPa, and elongations at break of 5–91%. Their tensile strength and Young's modulus were high enough and presented little change between each other, but elongation at break apparently increased with the increased molar loading ratio of BISPR5R5. According to application requirements for new intermetal dielectrics, tensile modulus of the materials should exceed 1 GPa and elongation at break more than 5%. From this point of view, it could be concluded that the prepared films with good mechanical properties, especially excellent flexibility, would meet the requirements of mechanical properties for applications.

**Density, Water Absorption, and Dielectric Properties of the Copolymers.** Table IV summarizes the water absorption, the density, and the electrical properties of the copolymers. Moisture absorption of the polymer films were measured by immersing these films in distilled water at 25°C for 72 h and calculated the weight changes. The moisture absorption of the films was low and was in the range of 0.34–0.78%, because of the hydrophobic nature of the adamantyl group and the long aliphatic side chains elements.

The dielectric properties of the copolymers were studied using samples with a parallel plate capacitor configuration. Figure 6 presented the dielectric constant ( $\kappa$ ) as a function of frequency ( $f$ ) for the AdRES-BISPR5R5-PEEKs, ranging from  $10^3$  Hz to  $10^6$  Hz at room temperature. The dielectric loss factors for these films were between  $5.7 \times 10^{-3}$  and  $8.5 \times 10^{-3}$  at 1 MHz and their dielectric constants ( $\kappa = 2.50$ – $2.88$  at 1 MHz) were lower than that of the conventional PEEK ( $\kappa = 3.27$  at 1 MHz) under the same measurement conditions.

To facilitate the observation and the comparison of the regular pattern, we have provided the three-dimensional graphic (Figure 7) to make the relationship among the density, water absorption, and dielectric constant more clear and understandable. As the long side chains' content increased, the higher the moisture absorption rate, the smaller was the packing density (Table IV) of the polymer system, corresponding to the larger free volume and a lower dielectric constant.

As mentioned previously, the low dielectric constant of the copolymers was mainly attributed to the fact that the introduction of the pendent adamantyl group and symmetrical long side chains, which have low molecular dipole, and the noncoplanar vibrational structure loosened the polymer packing and increased the free volume and subsequently reduced their density and dielectric constants. Moreover, as the long side chains' content increased, the  $\kappa$  value of the polymer films remarkably decreased and even reached 2.5 (1 MHz) for the 100% BISPR5R5-PEEK. It revealed that the flexible long side chains were more conducive for loosening the polymer packing and subsequently reducing their density and dielectric constants than the pendent rigid adamantyl group. In addition, the polarity of the polymer chains reduces gradually with the increasing in the number of the symmetrical long aliphatic side chains,

**Table IV.** The Density, Water Absorption and Dielectric Properties of AdRES-BISPR5R5-PEEK Copolymers

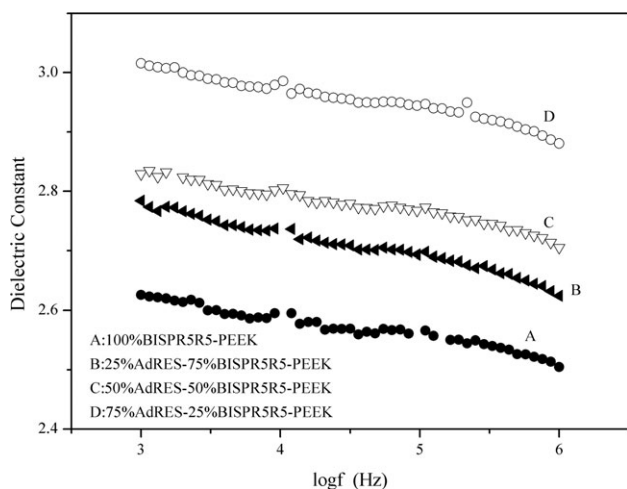
Polymer	Water absorption (%) <sup>a</sup>	Density $\rho$ (g/cm <sup>3</sup> ) <sup>b</sup>	Dielectric constant (At 1 MHz) <sup>c</sup>	Dielectric loss ( $\tan \delta \times 10^{-3}$ , 1 MHz)
PEEK <sup>d</sup>	-	-	3.27	-
100%BISPR5R5-PEEK	0.78	1.10	2.50	8.5
25%AdRES-75%BISPR5R5-PEEK	0.58	1.13	2.62	5.7
50%AdRES-50%BISPR5R5-PEEK	0.47	1.14	2.71	7.4
75%AdRES-25%BISPR5R5-PEEK	0.34	1.16	2.88	8.4

<sup>a</sup>Calculated from the difference in the weights before and after immersion of the polymer films in water.

<sup>b</sup>The density of the polymer membranes.

<sup>c</sup>The dry dielectric constants measured at room temperatures.

<sup>d</sup>PEEK, prepared from hydroquinone and 4,4'-difluorobenzophenone.



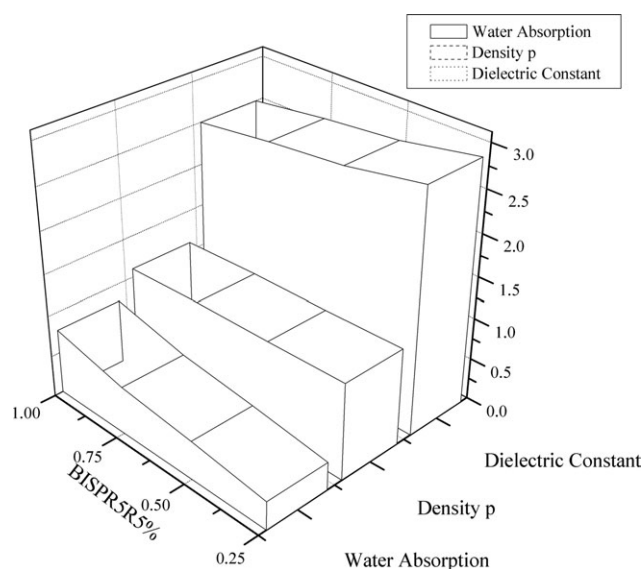
**Figure 6.** The dielectric constants of frequency ( $f$ ) measured from  $10^3$  Hz to  $10^6$  Hz at room temperature.

which is vital to obtain a lower dielectric constant. And, this proved the variation of water absorption. The large aliphatic substituent forced chains further apart in the copolymers and generated unoccupied volume capable of containing more water molecules.<sup>39</sup>

It was enriching to discover that these copolymers present potential utility for the microelectronics industry, in which a low dielectric constant is desired to prevent crosstalk between conducting paths.

## CONCLUSION

A series of novel poly (aryl ether ketone) copolymers containing pendant adamantyl group and long aliphatic side chains had been successfully synthesized. The resulting PAEK copolymers were amorphous and exhibited good solubility, good thermal



**Figure 7.** The illustration for the relationship among the density, water absorption, and dielectric constant.

stabilities, and low water absorptions. The dielectric constants of AdRES-BISPR5R5-PEEKs (at 1 MHz) had a decrease of 0.39–0.77 compared to that of the conventional PEEK and they also exhibited enough strength and outstanding flexibility. Moreover, we discovered that the symmetrical long side chains decreased the dielectric constant more effectively than the pendent adamantyl group did. On the basis of the above-mentioned results, these copolymers containing bulky pendent groups along the polymer backbone may be considered as good potential candidates for insulated materials in microelectronic devices, optical materials, and gas-separation membranes.

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