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Research article

Preparation and properties of transparent poly(aryl ether ketone) films with low dielectric constant

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Abstract. The objective of this study is to prepare a new poly(aryl ether ketone) (PAEK) with low dielectric constant, high transparency and heat resistance by introducing fluorine atoms and phenolphthalein (PHPH) groups into the polymer backbone. The chemical structure of PAEK random copolymers was characterized by Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR) and X-ray diffraction (XRD),, and the molecular weight of PAEK was determined by gel permeation chromatography (GPC). It is found that these random copolymers are soluble in common organic solvents, especially low boiling point solvents, such as $CHCl_3$, tetrahydrofuran (THF) and dimethylacetamide (DMAc). Transparent, uniform and flexible films were prepared by casting from DMAc solvent. The PAEK copolymers exhibit high glass transition temperature (163–220 °C by differential scanning calorimetry (DSC) and 168–227 °C by dynamic mechanical analysis (DMA)) and thermal stability with 5% weight loss temperatures of 461–525 °C. The PAEK films show good mechanical properties with tensile strengths of 50–62 MPa. The dielectric constant (k) is only 2.31–3.08, and the loss tangent is only 0.003–0.009 at 1 MHz. All films exhibit excellent optical transparency, their UV cutoff wavelength is shorter than 386 nm, and the transmittance at 450 nm is higher than 80%.

Keywords: *Smart polymers, poly(aryl ether ketone), soluble, low dielectric constant, transparency*

1. Introduction

Integrated circuits are becoming smaller and more integrated with the rapid development of information and microelectronics technology. However, the miniaturization of circuits brings about an increase in capacitance and resistance, which may cause crosstalk and delay and consequently seriously affect signal transmission. This problem can be effectively improved by reducing the dielectric constant and dielectric loss of the electronic materials [1, 2]. Low dielectric materials should have a low dielectric constant ($k < 3.0$, at 1 MHz) and high glass transition temperature ($T_g > 170\,°C$) [3–6]. Traditional transparent materials such as glass have been gradually replaced by multifunctional polymer materials that are lighter, more flexible and impact resistant, easier to shape, and cheaper. More and more optoelectronic and microelectronic components are made of transparent materials, especially in applications such as display screens, mobile phones, and 5G (5th generation mobile networks) mobile device casings [7, 8]. To meet the growing demand of the semiconductor industry and integrated circuit systems, expand the application of poly(aryl ether ketone) (PAEK) in various fields; there is an urgent need to develop transparent PAEK film materials with excellent dielectric properties [9–11]. PAEK is a high-temperature resistant thermoplastic with excellent dielectric properties

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in addition to excellent mechanical properties, heat resistance and chemical corrosion resistance [12, 13]. Polyether ether ketone (PEEK) is one of the most common commercial PAEK materials with a dielectric constant of 3.3 (at 1 MHz) [14–16], which does not meet the requirement of microelectronic applications. Physical or chemical modification is required to improve the optical transparency and reduce the dielectric constant in order to prepare PAEK films with good dielectric properties [17–20].

Traditional PEEK is a semi-crystalline polymer that is only soluble in concentrated sulfuric acid. For this, many approaches have been proposed to improve the solubility of PEEK polymers [21, 22], and novel transparent polymer film materials can be prepared by solvent casting, scraping and spin coating. The resulting transparent films can be easily stretched and cut into different shapes, and thus have wide applications in electronic devices, medical health, weapon, architecture, automobiles, aerospace and food packaging.

The dielectric constant of material is closely related to the polymer structure. According to the Debye equation [23], reducing the number of polarized molecules or the density of polar groups per unit volume is an effective method to prepare low dielectric constant polymers. Since the dielectric constant of air is 1.0, introducing nano-porous materials into the material can reduce the dielectric constant of the composite. However, the presence of nanopores will reduce the mechanical properties of polymer materials and enhance their hygroscopicity through opening pores, leading to deterioration of electrical properties during processing and application. Therefore, it remains challenging to develop low dielectric constant polymer materials [24, 25]. Previous studies have suggested that introducing large-volume side groups [26–28], asymmetric structures [3, 29] or twisted non-coplanar structures [30] can reduce the stacking density of materials and increase the free volume of polymers. The introduction of large-volume side groups contributes to improving the solubility and dielectric properties of the polymer by destructing PAEK molecular structure and hindering the effective stacking of macromolecular chains to increase the space-free volume and reduce the crystallinity of PAEK. The destruction of the PAEK crystalline structure also results in excellent optical transparency, and the rigid structure of large-volume side groups can improve the heat resistance, thermal stability and tensile strength of polymers [31, 32]. Phenolphthalein (PHPH) monomer contains a cyclic lactone and three bulky non-coplanar distorted benzene rings, which could increase the free volume of the polymer, and reduce the number of polarized groups per unit volume. Ba *et al.* [33] prepared a series of new PAEK copolymers by varying the molar ratio of bisphenol monomers containing pendent rigid adamantyl groups and flexible long side-chains, and these polymers showed low dielectric constants (2.50–2.88 at 1 MHz) and excellent solubility. Due to the strong attraction of electrons outside the nucleus of fluorine atoms and the large interaction between electrons and atomic nucleus, the electron cloud has high density and low polarizability when polarized by the external electric field. Introduction fluorine-containing groups with larger volumes into polymer molecules can reduce the stacking density of the polymer and increase the free volume of the polymer, thereby reducing the dielectric constant of the polymer and improving the transparency. It can also improve the thermal properties of the polymers due to the small atomic size of fluorine element and the high binding energy of C–F bond [34–36]. Liu *et al.* [37] reported the synthesis of novel fluorine-containing PAEK with (3-fluoromethyl) phenyl or (3,5-difluoromethyl) phenyl moieties with low dielectric constants (2.69–2.78 at 1 MHz).

In this study, hexafluorobisphenol A (6F-BPA) and phenolphthalein (PHPH) moieties were introduced into the PAEK backbone through molecular structure design, and a series of novel PAEK transparent films with low dielectric constant, high transparency and heat resistance were obtained by adjusting the ratio of PHPH and 6F-BPA. These novel PAEK films could be used in electronic communications, computers, LED and other fields

2. Experimental

2.1. Materials

Hexafluorobisphenol A (6F-BPA) was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Xylene, phenolphthalein (PHPH), 4,4′-difluorobenzophenone (DFBP), *N*-methyl-2-pyrrolidinone (NMP) and sulfolane (TMS) were obtained from Shanghai Aladdin Chemical Reagent (China). The potassium carbonate (K_2CO_3) was obtained from Jiangsu Youlide Co., Ltd. *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), chloroform ($CHCl_3$) and tetrahydrofuran (THF) were supplied by Tiantai Fine Chemical Co., Ltd. (China). Commercial PEEK film (PEEK-KF001, 50 µm thick) was purchased from Dongguan Kaifeng Industry Co., Ltd. (China). All chemicals were used as received without further purification.

2.2. Synthesis of PAEK random copolymers

A novel PAEK-containing phenolphthalein and trifluoromethyl was synthesized by solution polycondensation [37–39], as shown in Figure 1. The new PAEK copolymers with a PHPH/6F-BPA molar ratio of 100:0, 75:25, 50:50, 25:75 and 0:100 were named as PAEK-1, PAEK-2, PAEK-3, PAEK-4 and PAEK-5, respectively. For instance, the polymerization process of PAEK-2 with a PHPH/6F-BPA molar ratio of 75:25 was as follows. TMS (40 ml), PHPH (2.38 g, 0.0075 mol), 6F-BPA (0.84 g, 0.0025 mol), DFBP (2.18 g, 0.010 mol), K_2CO_3 (1.38 g, 0.010 mol) and xylene (20 ml) were mechanically stirred, heated to 135 °C with a heating jacket, and then reacted at constant temperature for 2 h. After that, the reaction temperature was gradually raised to 170 °C to remove water from the reaction by azeotropic distillation. After xylene was removed by distillation, the temperature of the system was held at 220 °C for about 6 h. When the solution viscosity no longer changed significantly, the solution was poured into 500 ml of deionized water. The polymer powder was washed several times with hot distilled water and methanol, and then dried at 120 °C for 24 h.

DMAc solvent (10 ml) and purified PAEK particles (1.0 g) were added to a three-necked flask successively and heated slowly to 100 °C under mechanical agitation. After continuous stirring for 2 h, the uniform PAEK solution was slowly poured onto a preheated clean glass plate in the oven. The solution was put in an atmospheric oven at 80 °C for 12 h. After that, it was transferred to a vacuum oven at 100 °C for 24 h. PAEK films were obtained after natural cooling to room temperature, and all films were 50±0.5 µm thick.

2.3. Characterizations

2.3.1. Chemical structure analysis

The Fourier transform infrared (FT-IR) spectra of PAEK copolymers were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Electron, USA) in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} over 32 scans at room temperature. KBr pellets were used, and five spectra were averaged. The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker (Billerica, MA, USA) 510 NMR spectrometer (400 MHz) at room temperature (25 °C) using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal standard. The X-ray diffraction (XRD) patterns were recorded using an Ultima IV X-ray diffractometer

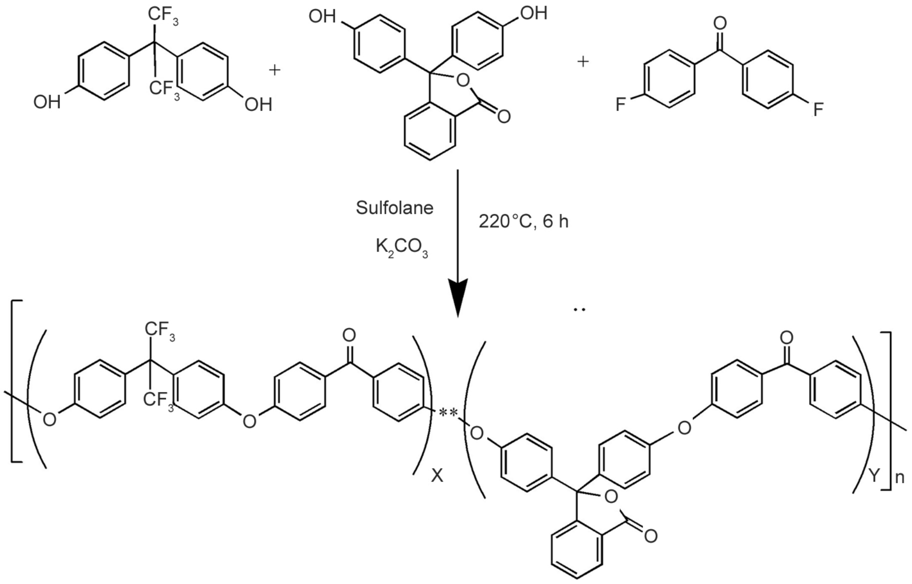

Figure 1. The synthetic route of PAEK random copolymers, where X and Y are the mole fractions of 6F-BPA monomer and PHPH in the feed, respectively.

(Rigaku, Japan) at scattering angles (2θ) of 5–60° with a step of 4°·min^{-1}.

2.3.2. GPC analysis

Gel permeation chromatography (GPC) was performed using PL-GPC 50 (Agilent Technologies Co., Palo Alto, California, USA) instrument with DMF as the eluent and polystyrene as the standard.

2.3.3. Solubility analysis

The organic solubility was measured in various organic solvents (10 mg of PAEK powder/1.0 ml of organic solvent) at room temperature (25 °C).

2.3.4. Thermal analysis

The PAEK copolymers' glass transition temperatures (T_g) were measured using a DSC8500 differential scanning calorimeter (DSC) with a scanning rate of 10 °C·min^{-1} under an N_2 atmosphere from 30 to 300 °C. All PAEK random copolymers were scanned twice for heating and cooling to eliminate the thermal history from 50 to 360 °C at a heating rate of 10 °C·min^{-1} under an N_2 atmosphere. The glass transition temperature (T_g) was recorded at the second heating scan. Thermogravimetric analysis (TGA) was performed on an SDT-Q600 analyzer (TA, USA) under N_2 atmosphere. Samples were heated from 30 to 800 °C at a heating rate of 10 °C·min^{-1}.

2.3.5. Mechanical test

The tensile properties of PAEK films were measured using an MTS E42.503 universal tensile testing machine, where the width of the dumbbell-shaped spline at the narrow part was 4 mm, the gauge length was 20 mm, the clamp spacing was 50 mm, and the stretching rate was 10 mm·min^{-1}. The loss factor curves, storage modulus, and loss modulus at different temperatures were measured with a TA Instruments DMA-Q800 in tensile mode at 1 Hz and 10 µm amplitude with a heating rate of 3 °C·min^{-1} and temperature scan from 50 to 350 °C.

2.3.6. Dielectric properties

The dielectric properties of PAEK films were measured using a Concept 40 (Novocontrol GmbH, Germany) broadband dielectric impedance spectrometer at room temperature with frequencies ranging from 10^3–10^6 Hz.

2.3.7. Optical properties

The transmittance of PAEK films was recorded on a Yoke 722 (Shanghai Yoke Co. Ltd., Shanghai, China) ultraviolet spectrophotometer in a wavelength range of 200–800 nm.

3. Results and discussion

3.1. Structure and molecular weight of PAEK copolymers

Figure 2 shows the FTIR spectra of PAEK copolymers with different PHPH/6F-BPA molar ratios. The characteristic absorption bands of carbonyl (–C=O) groups appear near 1730 cm^{-1}. A sharp characteristic peak appears at 1769 cm^{-1}, which is assigned to the stretching vibration of the lactone ring (O–C=O) of phenolphthalein, and its intensity decreases gradually with the decrease of PHPH content. The strong absorption peaks near 1598, 1502, and 1458 cm^{-1} are assigned to the skeleton vibration of the benzene ring on the main chain, while those near 1240 and 1206 cm^{-1} are assigned to the stretching vibration of

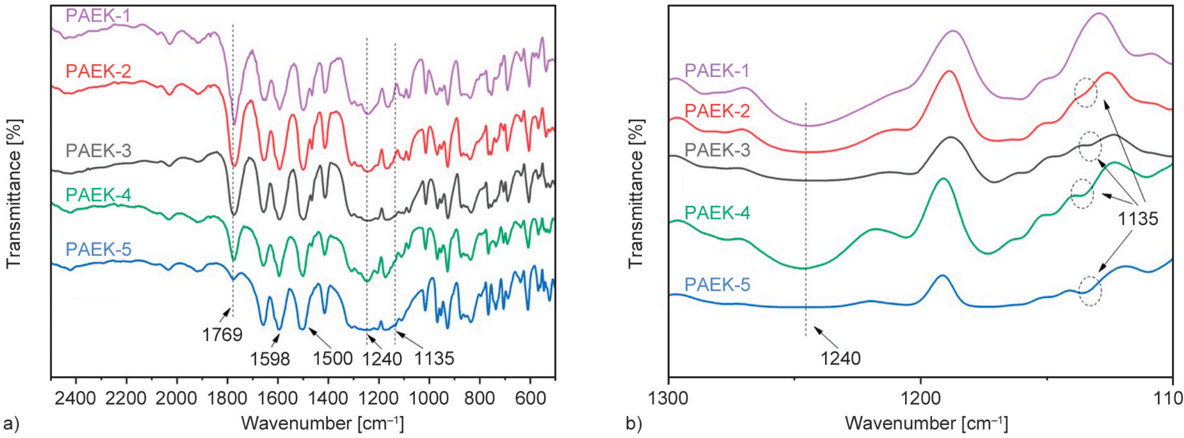

Figure 2. FTIR spectra of PAEK copolymers with different PHPH/6F-BPA molar ratios, a)in the wavenumber of 4000–400 cm^{-1}, b) in the wavenumber of 1300–1100 cm^{-1}.

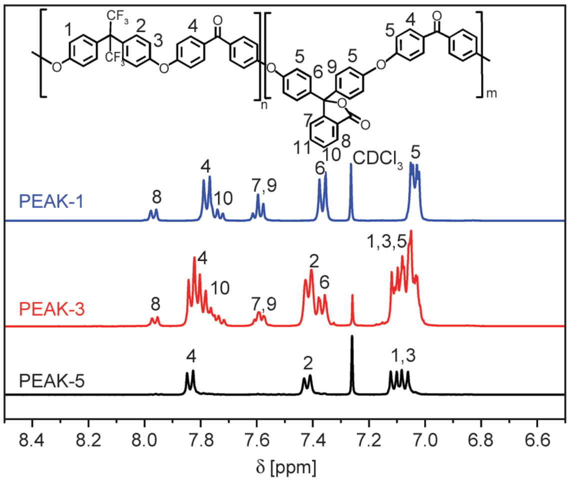

Figure 3. ^{1}H-NMR spectra of PAEK with different PHPH/6F-BPA molar ratios.

the aryl ether bond (Ar–O–Ar) on the main chain. The absorption band at 1135 cm^{-1} is the contraction vibration peak of the C–F band, and its intensity is increased with the increase of 6F-BPA content [40]. The structure of PAEK films was confirmed by ^{1}H-NMR, as shown in Figure 3. A resonance peak is observed at 7.80 ppm in all PAEK films, which is assigned to the protons of the benzene ring in benzophenone. The two resonance peaks at 7.41 ppm and 7.09 ppm correspond to the protons on the phenyl group of 6F-BPA. PAEK-3 has five resonance peaks at around 7.98, 7.71, 7.61, 7.38, and 7.04 ppm, which are assigned to the protons on the phenyl group from PHPH. Compared to PAEK-1 and PAEK-5, the peak at 7.80 ppm is slightly shifted in PAEK-3, which indicates that PAEK-3 is a random copolymer.

The XRD patterns of the polymers are shown in Figure 4. Although PEEK is a semi-crystalline polymer [14, 16], no crystalline peaks are observed, indicating that these PAEK films are novel amorphous polymers. The presence of large-volume side groups in PHPH destroys the symmetry of the polymer and increases the free volume. The introduction of the –CF_3 bond also reduces the tight packing of macromolecular chains and, thus, makes the copolymer become amorphous.

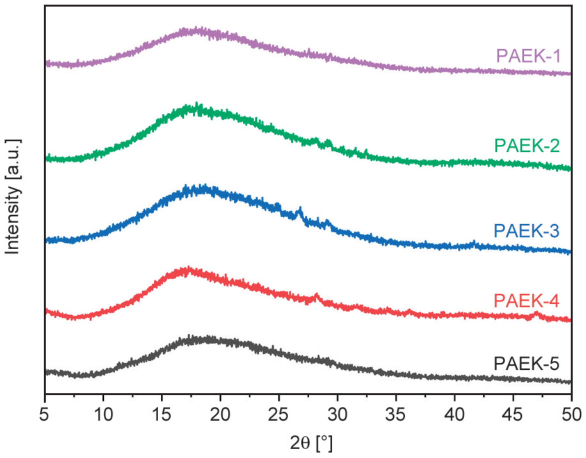

Figure 4. XRD spectra of PAEK with different PHPH/6F-BPA molar ratios.

Table 1. Molecular weights and distributions of PAEK copolymers.

Samples	PHPH/6F-BPA	M_n [10^4 g·mol^{-1}]	M_w [10^4 g·mol^{-1}]	PDI
PAEK-1	100:0	4.59	6.93	1.51
PAEK-2	75:25	4.15	6.77	1.63
PAEK-3	50:50	4.21	6.45	1.53
PAEK-4	25:75	4.02	6.01	1.49
PAEK-5	0:100	4.33	6.41	1.55

In conclusion, the FTIR, ^{1}H-NMR, and XRD results indicate that –CF_3 and PHPH groups are successfully introduced.

The molecular weights of samples were measured by GPC, as shown in Table 1. The numerical average molecular weights (M_n) are higher than $4 \cdot 10^4$ g·mol^{-1}, and the polydispersity index (PDI) values are below 1.7. As the molecular weights of polymers are approximately the same, the comparison of effective physical properties can be made based on molecular structure.

3.2. Solubility

The solubility of PAEKs in $CHCl_3$, THF, NMP, DMAc, and DMF is listed in Table 2. All PAEK films can be dissolved in common solvents, and their high solubility is attributed to the introduction of phenolphthalein and trifluoromethyl groups that can

Table 2. Solubility of PAEK copolymers.

Samples	NMP	DMAc	$CHCl_3$	THF	DMF
PAEK-1	+	+	+	+	+
PAEK-2	+	+	+	+	+
PAEK-3	+	+	+	+	+
PAEK-4	+	+	+	+	+
PAEK-5	+	+	+	+	+
PEEK	–	–	–	–	–

NMP: *N*-methylpyrrolidone;
DMAc: *N*,*N*-dimethylacetamide;
$CHCl_3$: chloroform;
THF: tetrahydrofuran;
DMF: *N*,*N*-dimethylformamide;
+: soluble at room temperature;
–: insoluble.

disturb the tight packing of polymer chains, increase the free volume and decrease the intermolecular force and crystallinity [41].

3.3. Thermal properties

The thermal properties of PAEK polymers were examined by DSC (Figure 5) and TGA (Figure 6), and the results are shown in Table 3. The T_g values of new PAEKs are higher than that of PEEK (143 °C) [14]. As shown in Figure 5, all the DSC curves of PAEKs have a single typical glass transition but no melting peaks, indicating that these copolymers are amorphous. Increasing the proportion of 6F-BPA monomer can decrease the proportion of PHPH monomer and, consequently the T_g value. At a PHPH/6F-BPA molar ratio of 25:75, the T_g value of PAEK-3 is 177 °C. This is because PHPH structural unit contains a cyclic lactone carbonyl group (O–C=O) and three bulky non-coplanar distorted benzene rings, which can increase the rotational steric hindrance in the molecular chain and therefore improve the T_g value [3]. In addition, the -CF_3 group has a large volume, and the aliphatic structure (–C–) is not easy to rotate and the fluorine atom would lead to internal plasticization [41]. Therefore, with the increase of 6F-BPA content, the T_g value of PAEK decreases with increasing 6F-BPA content, but it is still higher than 160 °C.

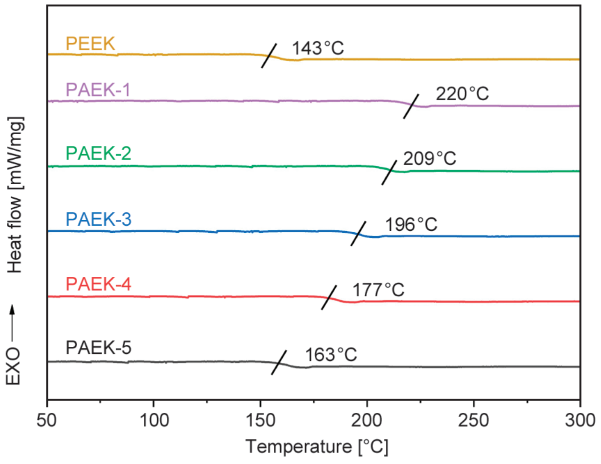

Figure 5. DSC curves of PAEK copolymers.

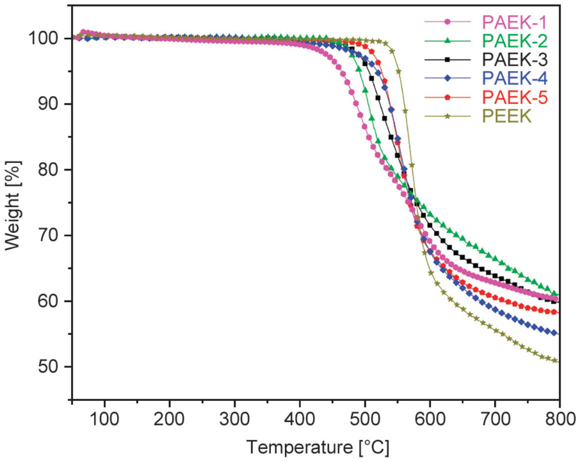

Figure 6. TGA curves of PAEK polymers.

It is seen from Figure 6 that PAEK copolymers have high thermal stability, where $T_{d5\%}$ (temperature at 5% weight loss) is higher than 460 °C and $T_{d10\%}$ (temperature at 10% weight loss) is 470–580 °C. The char yield at 800 °C is 50–63%. The lactone ring shows poor heat resistance, and PAEK-1 starts to decompose at 423 °C. Increasing the 6F-BPA content decreases the lactone ring content of PHPH and consequently increases the decomposition temperature of PAEK [42–44]. In conclusion, the thermal stability of PAEK copolymers increases with the increase of 6F-BPA content, and the polymers have sufficiently high T_g and excellent thermal stability.

3.4. Mechanical properties

Dynamic mechanical and tensile tests were performed to determine the influence of bisphenol content on the mechanical properties of PAEKs. As shown in Table 3, the introduction of large-volume

Table 3. Thermal and mechanical properties of the polymers.

Samples	T_g^a [°C]	T_g^b [°C]	$T_{d5\%}$ [°C]	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation at break [%]
PAEK-1	220	227	461	62±2	1.7±0.1	8.5±0.1
PAEK-2	209	217	486	59±3	1.6±0.2	7.3±0.2
PAEK-3	196	200	504	55±1	1.5±0.1	7.1±0.1
PAEK-4	177	180	516	53±2	1.4±0.1	6.2±0.3
PAEK-5	163	168	525	50±1	1.3±0.3	7.1±0.3
PEEK	148	143	551	96±4	1.9±0.2	150.0±0.2

T_g^a: glass transition temperature measured by DSC at a heating rate of 10 °C·min^{-1} under a nitrogen atmosphere;
T_g^b: glass transition temperature measured by DMA at a heating rate of 3 °C·min^{-1} under a nitrogen atmosphere;
$T_{d5\%}$: temperature at 5% weight loss.

groups into the main chain of PEEK leads to a decrease in the mechanical properties of the films. Traditional PEEK is a linear, fully aromatic crystalline polymer, and it has high tensile strength and elongation at break due to its rigid benzene ring, flexible ether bonds, and carbonyl groups can enhance the intermolecular force in its molecular chain, as well as its regular molecular segment structure. The introduction of large volume PHPH and lower polarity $–CF_3$ groups could disrupt the regular arrangement of PEEK and make the polymer have an amorphous structure. Then the distance between molecular chains is increased and the intermolecular interactions and molecular entanglement are reduced. As a result, the tensile strength is 50–62 MPa, and the tensile modulus is 1.3–1.7 GPa. With the increase of 6F-BPA segments, the rigidity of the molecular chain and the interaction force between molecular chains are reduced. As a result, the mechanical properties of the polymer films are also reduced.

3.5. Dynamic thermomechanical properties

The thermal mechanical properties of polymers were detected by dynamic thermomechanical analysis (DMA) (Figure 7), and the results are shown in Table 3. The storage modulus E' reflects the elastic component of viscoelasticity, and the stiffness of a material. The areas of the storage modulus curve where the values change rapidly correspond to the peaks in the tan δ curve, which represent the glass transition temperatureThe polymers’ glass transition temperature (T_g) increases as the proportion of PHPH group increases. The DMA results are in good agreement with the DSC results. The introduction of large volume groups reduces the regularity of the main chain and thus leads to a decrease in the initial storage modulus of PAEK films compared to PEEK. With the increase of 6F-BPA content and free volume, the rigidity of molecular chains and intermolecular interactions are reduced, and molecular chain segments are more likely to slide to sliding under external forces. Therefore, the temperature range for the rapid change in film energy storage modulus shifts towards low temperature with the increase of 6F-BPA content.

The plots of tan δ as a function of temperature are presented in Figure 7b. The damping of the material is also the internal friction, representing the ratio of the energy lost by the material during the weekly cycle to the maximum elastic energy storage. The areas in the storage modulus curve where the values change rapidly correspond to the peaks in the tan δ curve and each peak of tan δ corresponds to a specific relaxation process. Each curve exhibits a single and sharp loss peak. These results show that PAEK films have single and outstanding T_g. It is concluded that PAEK films have excellent thermal mechanical properties.

3.6. Dielectric properties

Figures 8a and 8b show the dielectric constant and dielectric loss curves of PAEK films with different 6F-BPA contents at frequencies of 10^3–10^6 Hz, respectively. PAEK films and commercial PEEK films are all 50±0.5 μm thick. Figure 8a shows that their dielectric constants are lower than commercial PEEK (3.3 at 1 MHz) and decrease as the test frequency increases. The PAEK with different structures show different dielectric constants, which can be explained by the Debye equation [23] (Equation (1)):

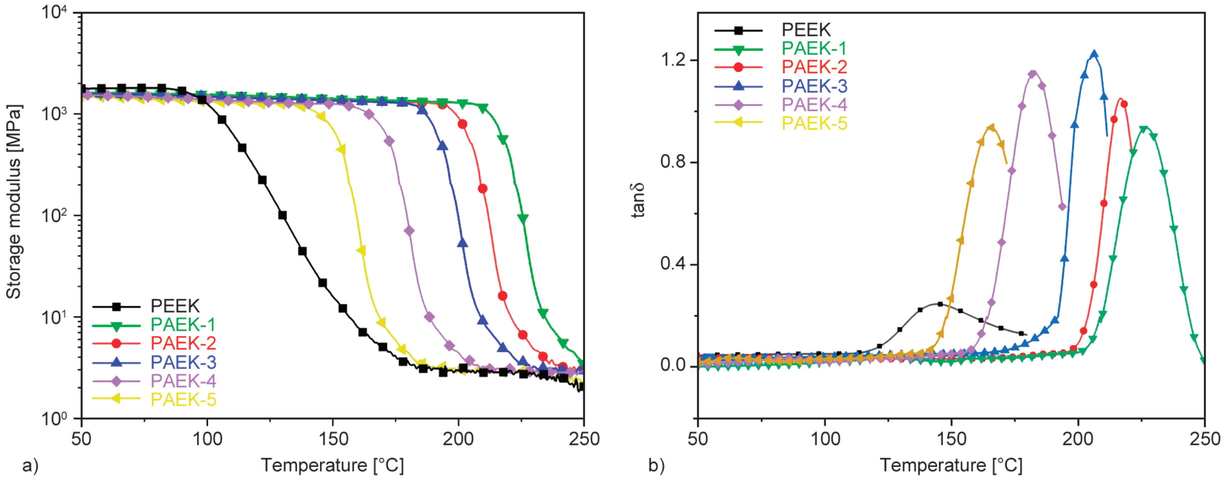

Figure 7. DMA curves of PAEK films: a) storage modulus and b) tan δ.

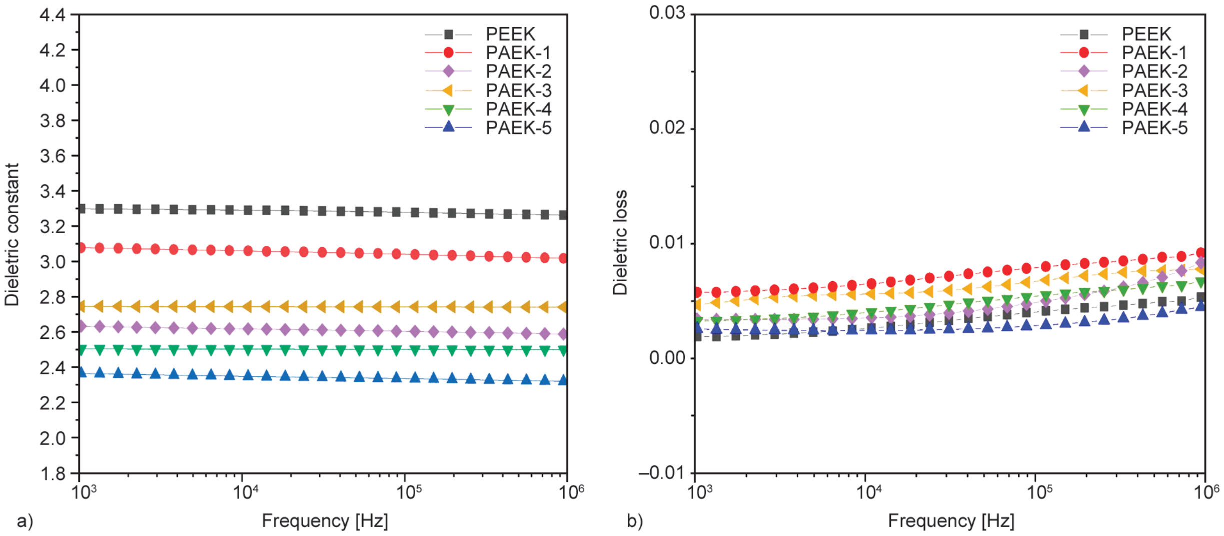

Figure 8. Frequency dependence of a) dielectric constant and b) dielectric loss of PAEK films at room temperature.

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

where ε_r is the dielectric constant, N is the number density of dipoles, α_e is the electric polarization, α_d is the distortion polarization, μ is the orientation polarization related to the dipole moment, k_b is the Boltzmann constant, and T is the temperature.

The introduction of large-volume structures with poor regularity can reduce the regularity and the stacking density of the polymer chain and consequently reduce the molar volume of the polymer and N. The large volume $-CF_3$ group has a C–F bond with low polarizability and large bond energy, making it difficult for the polymer to polarize and thus leading to reduction of α_e [41]. Therefore, the dielectric constant of PAEK films at 1 MHz decreases from 3.08 to 2.31 with the increase of the 6F-BPA content in the bisphenol system. Figure 8b reveals that PAEK films exhibit relatively low dielectric loss. The dielectric loss increases with the increase of frequency because the molecular movement can not follow up the variety of frequencies of the applied electric field [45]. At present, the dielectric constant of standard polyimide (PI) films used in the field of electronics and electrical appliances is about 3.2–3.6 (1 MHz), indicating that PAEK itself has a relatively low dielectric constant compared to PI. Compared to traditional PEEK, these novel PAEK films have lower dielectric constant and dielectric loss and better comprehensive performance.

The properties of previously reported PAEKs are summarized in Table 4. Low dielectric constant materials are needed in electronics and electrical appliances,

Table 4. Properties of PAEK polymers and copolymers.

Samples	T_g^a [°C]	$T_{d5\%}$ [°C]	Tensile strength [MPa]	Tensile modulus [GPa]	Dielectric constant at 1 MHz	Reference
PEEK-PFN-2	124	580.3	–	–	3.20	[46]
PAEKs	148–160	>527	95.2–104.0	2.68–3.06	2.75–2.95	[27]
APAEKs	–	530	65–70	1.6–2.0	2.6–2.7	[47]
DDSQ-PEEK	136	396	–	–	1.95	[48]
PNAEK	229^b	450	72.47	1.32	2.78	[49]
FPNAEK	225^b	443	76.58	1.39	2.49	[49]
AdRES-PEEK	181–250	460–492	41.3–48.3	2.07–3.82	2.69–2.95	[26]
AdNp-PEEK	205–278	480–508	55–89.5	1.95–2.15	2.67–2.92	[26]
NPEEK	167–194	472–545	62.8–104.1	1.5–3.18	2.57–2.99	[50]
iPrPEKC	186	455	95	2.73	2.81	[51]
iPrBPFL-x	209–232	439–478	82–95	1.84–1.86	2.67–2.79	[51]
PHPH/6F-BPA-PAEK	177–220	486–516	53–59	1.4–1.6	2.45–2.70	This work

T_g^a: glass transition temperature measured by DSC except for PNAEK and FPNAEK;
T_g^b: glass transition temperature measured by DMA;
–: not measured.

which helps to improve signal transmission speed and reduce signal delay and signal loss. Excellent heat resistance is also required to withstand the heat generated by the environment and devices. The new PAEK films prepared in this work have high heat resistance (T_g > 170 °C) and thermal stability ($T_{d5\%}$ > 480 °C), as well as low dielectric constant (2.45–2.70, 1 MHz). Polymer thin film materials with good heat resistance and low dielectric constant can replace traditional inorganic ceramic materials for interlayer dielectric (ILD) and intermetallic dielectric (IMD) in advanced chips.

3.7. Optical properties

Figure 9 shows the images of commercial PEEK film and PAEK films. It is seen that PAEK films have better transparency than commercial PEEK film. PAEK-1 and PAEK-2 films are slightly yellow, and they become colorless as more fluorine is introduced. Figure 10 shows the UV-vis spectra of PAEK films of 50±0.5 μm in the 200–800 nm wavelength range. The cutoff wavelength of PAEK films is 320–386 nm, and the higher the proportion of 6F-BPA in the bisphenol system, the smaller the cutoff wavelength of the polymer film and the higher the optical transmittance. The visible light transmittance of PAEK films at 450 nm can reach 80% or above, which is much higher than that of commercial PEEK. The introduction of $-CF_3$ group improves the transparency of PAEK films. This is mainly because the introduction of strong electronegative fluorine atoms causes damage to the conjugation and planar structure of PAEK molecular chain and hinders the conjugation of molecules, and therefore, the maximum absorption peak wavelength of visible light of the polymer shifts to the short wave direction and the transparency of the polymer is improved. Thus, it can be used as potential optoelectronic materials in display screens, mobile phones, and 5G mobile device casings [52–54].

Figure 9. Images of commercial PEEK film and PAEK films.

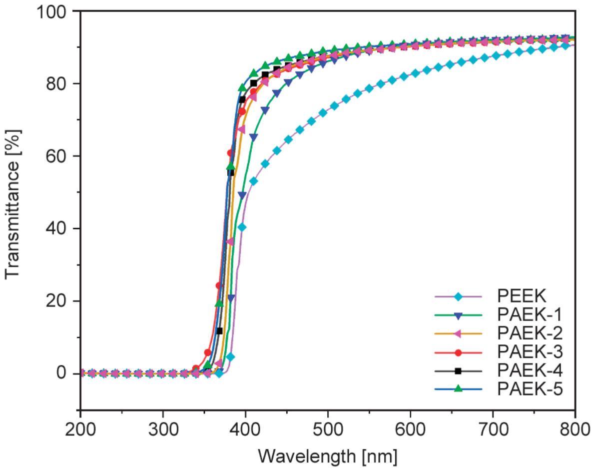

Figure 10. UV-vis spectra of PAEK films.

4. Conclusions

In this study, new PAEK copolymers containing $-CF_3$ and phenolphthalein groups have been successfully synthesized based on molecular design. These PAEK copolymers are amorphous and exhibit excellent film-forming ability. Compared to commercial PEEK, they exhibit good solubility in common organic solvents. With the increase of 6F-BPA content in the bisphenol system, the mechanical strength of the polymer film is decreased, and the thermal stability of the polymers, transparency and dielectric properties of the films are increased. When the mole fraction of 6F-BPA is 50%, T_g is 196 °C and $T_{d5\%}$ is 504 °C under a nitrogen atmosphere. The tensile strength of PAEK-3 film is 55 MPa, and the dielectric constant at 1 MHz is 2.60. The dielectric loss is 0.006. The visible light transmittance at 450 nm is 80%. The properties of copolymers differ depending on the proportion of copolymerization units. This study provides insights into the preparation of PAEK films with low dielectric constant, high optical transparency, good mechanical properties, and high thermal stability and expands the application of PAEK materials to microelectronics, optical waveguides, and display devices.

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