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SHORT COMMUNICATION

High optical transparency and low dielectric constant of novel organosoluble poly(ether ketone amide)s derived from an unsymmetrical diamine containing trifluoromethyl and methyl pendant groups

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Abstract A series of novel fluorinated poly(ether ketone amide)s (PEKAs) were prepared from an unsymmetrical aromatic diamine, (4′-(4″-amino-2″-trifluoromethylphenoxy)-3′,5′-dimethylphenyl)(4-aminophenyl)-methanone (**1**), with various aromatic dicarboxylic acids using the phosphorylation polycondensation technique. The PEKAs had inherent viscosities ranging from 0.43 to 0.65 dl/g. All the fluorinated PEKAs could be soluble in many polar organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N′*-dimethylacetamide (DMAc), *N,N′*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF). Flexible and tough polymer films could be prepared by casting from DMAc solvent. The PEKA films exhibited high optical transparency with a cutoff wavelength of 354–365 nm and good mechanical properties with tensile strengths of 78–98 MPa and elongations at break of 11.5–18.5%. They showed glass-transition temperatures in the range of 288−323 °C and the onset decomposition temperatures in the range of 450−461 °C in nitrogen atmosphere. Meanwhile, the PEKA films possessed low dielectric constants of 1.98–2.71 at 1 MHz and low moisture absorption (<2%). Due to their properties, the fluorinated PEKAs could be considered as photoelectric and microelectronic materials.

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Introduction

Wholly aromatic polyamides (aramids) have been well known for their high temperature stability, excellent mechanical strength and good chemical resistance, which qualify them as high-performance polymeric materials [1–5]. Fibers obtained from anisotropic solutions of these high-performance materials have been used in applications where high thermal stability and mechanical strength are required. Aromatic polyamides like other aromatic and heterocyclic polymers are quite intractable materials because they are infusible and insoluble in organic solvents. Purely aromatic polyisophthalamides, for instance, are soluble only in a few aprotic polar solvents containing dissolved inorganic salts which are mainly caused by the highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding. Moreover, the high moisture absorptions of aromatic polyamides, compared with other polymer materials, have resulted in obvious negative effect on their mechanical properties as well as electrical insulating and dielectric performance. Consequently, many efforts have been made to improve their solubility and dielectric properties without much impairing their thermal stability and mechanical properties. The successful approaches employed with those purposes include: introducing flexible ether linkage and bulky pendant groups into the polymer chain to minimize crystallization; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallization; and forming a non-coplanar structure, thereby, making crystallization impossible [6–11].

Recently, considerable attention has been devoted to the fluorinated aromatic polymers, including fluorinated polyimides, polyamides, poly(aryl ether)s, and so on [12–17]. It was found that the incorporation of flexible fluorinated groups into macromolecular backbones resulted in great benefits for improving polymer solubility as well as optical and dielectric performance, which attributed to the small dipole and the low polarizability of the C–F band as well as the increase in free volume [18–20].

As part of the efforts to gain the high-performance polymers with good solubility for advanced microelectronics applications, this paper mainly reported the syntheses of a series of novel poly(ether ketone amide)s bearing trifluoromethyl and methyl pendant groups. The solubility, optical, dielectric, thermal, and physical properties of these PEKAs were also investigated and discussed.

Experimental

Materials

The diamine, (4′-(4″-amino-2″-trifluoromethylphenoxy)-3′,5′-dimethylphenyl)-(4-aminophenyl)-methanone (mp, 137–139 °C) was synthesized according to the method reported in the preceding studies [21]. The commercially available aromatic dicarboxylic acids such as terephthalic acid (**2a** or TPA; Aldrich), isophthalic acid (**2b** or IPA; Alfa), 4,4′-diphenyldicarboxylic acid (**2c** or DBA; Alfa), and 2,2′-bis(4-carboxyphenyl)hexafluoropropane (**2d** or 6FBA; Chriskev) were used as received. Calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 4 h prior to use. NMP (Aladdin), pyridine (Py; Aladdin), triphenyl phosphite (TPP; Aladdin) and other solvents were purified according to the standard methods.

Measurements

NMR spectra were measured on a Bruker AV 400 MHz instrument with dimethyl sulfoxide-d_6 (DMSO-d_6) as a solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. Elemental analysis was carried out on a Carlo-Erba 1106 system. Differential scanning calorimetry (DSC) analysis was performed on a PE Diamond DSC instrument at a heating rate of 20 °C/min in nitrogen atmosphere. Glass-transition temperatures were read at the middle of the transition in the heat capacity from the second heating scan after quick cooling from 380 °C at a cooling rate of 20 °C/min. Thermogravimetric analysis (TGA) of the polymer samples was measured on a Netzsch TG 209F1 instrument at a heating rate of 20 °C/min in nitrogen atmosphere. Ultraviolet–Visible (UV–Vis) spectra of the polymer films were recorded on a PerkinElmer Lambda 35 UV–Vis spectrophotometer at room temperature. The dielectric constant was determined on an Agilent 4291B instrument at a frequency of 1 MHz to 1.1 GHz at 25 °C. Prior to test, the polymer film samples were dried at 150 °C for 10 h. The tensile properties were performed on an Instron 3365 Tensile Apparatus with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 40−70 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The equilibrium water absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

Polymer synthesis

General procedure of the polymerization

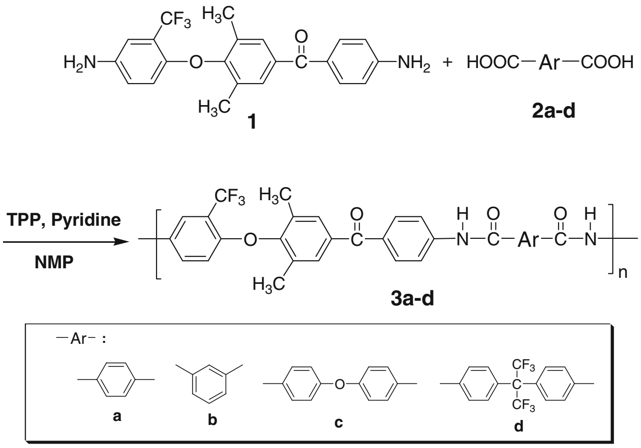
A generally synthetic procedure for the poly(ether ketone amide)s is described as follows. A flask was charged with a mixture of 1.5 mmol diamine, 1.5 mmol aromatic dicarboxylic acids, 2.5 mL TPP, 1.0 mL pyridine, 5 mL NMP and 0.3 g calcium chloride. The reaction mixture was maintained at 110 °C under nitrogen atmosphere for 4 h. As the polycondensation proceeded, the reaction mixture became viscous gradually. The resultant solution of the polymer was poured slowly into 300 ml of stirred methanol giving rise to a tough, fiber-like polymer precipitate. The product was collected by filtration, thoroughly washed by methanol and hot water, and dried.

FT-IR, ^{1}H-NMR, and elemental analysis data of PEKA **3a**

FT-IR (film): 3,312 (−NHCO−), 1,659 (C═O), 1,242 (C−O−C), 1,177, 1142 (−CF_3) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 10.79 (d, *J*= 6.5, 1H), 10.63 (d, *J* = 6.5, 1H), 8.33 (s, 1H), 8.14 (m, 4H), 8.03 (d, *J* = 8.4, 2H), 7.96 (d, *J* = 8.8, 1H), 7.88 (d, *J* =8.0, 2H), 7.62 (s, 2H), 6.65 (d, *J* = 8.8, 1H), 2.17 (s, 6H). Elemental Analysis: Calcd. For $(C_{30}H_{22}F_3N_2O_4)_n$ $(531.5)_n$: C, 67.79; H, 4.17; N, 5.27. Found: C, 66.91; H, 4.22; N, 5.32.

FT-IR, ^{1}H-NMR and elemental analysis data of PEKA **3b**

FT-IR (film): 3,313 (−NHCO−), 1,659 (C═O), 1,232 (C−O−C), 1,177, 1,130 (−CF_3) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 10.82 (d, *J* = 6.5, 1H), 10.66 (d, *J* = 6.5, 1H), 8.57 (d, *J* = 5.2, 1H), 8.32 (s, 1H), 8.20 (m, 2H), 8.05 (d, *J* = 8.4, 2H), 7.96 (d, *J* = 8.8, 1H), 7.87 (d, *J* = 8.4, 2H), 7.74 (t, *J* = 7.8, 1H), 7.61 (s, 2H), 6.65 (d, *J* = 8.8, 1H), 2.16



Scheme 1 Synthesis of fluorinated PEKAs **3a-d**

(s, 6H). Elemental Analysis: Calcd. For $(C_{30}H_{22}F_3N_2O_4)_n$ $(531.5)_n$: C, 67.79; H, 4.17; N, 5.27. Found: C, 66.84; H, 4.19; N, 5.21.

FT-IR, ^{1}H-NMR and elemental analysis data of PEKA **3c**

FT-IR (film): 3,318 (−NHCO−), 1,656 (C=O), 1,239 (C−O−C), 1,173, 1,129 ($-CF_3$) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 10.61 (s, 1H), 10.45 (s, 1H), 8.31 (s, 1H), 8.08 (m, 4H), 8.02 (d, J = 8.4, 2H), 7.92 (d, J = 8.8, 1H), 7.86 (d, J = 8.4, 2H), 7.60 (s, 2H), 7.23 (m, 4H), 6.63 (d, J = 8.8, 1H), 2.16 (s, 6H). Elemental Analysis: Calcd. For $(C_{36}H_{25}F_3N_2O_5)_n$ $(622.59)_n$: C, 69.45; H, 4.05; N, 4.50. Found: C, 68.47; H, 4.09; N, 4.38.

FT-IR, ^{1}H-NMR, and elemental analysis data of PEKA **3d**

FT-IR (film): 3,307 (−NHCO−), 1,658 (C=O), 1,240 (C−O−C), 1,177, 1,136 ($-CF_3$) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 10.81 (s, 1H), 10.64 (s, 1H), 8.32 (s, 1H), 8.07 (m, 4H), 8.01 (d, J = 8.4, 2H), 7.89 (d, J = 9.2, 1H), 7.85 (d, J = 8.0, 2H), 7.60 (s, 2H), 7.57 (m, 4H), 6.62 (d, J = 9.2, 1H), 2.15 (s, 6H). Elemental Analysis: Calcd. For $(C_{39}H_{25}F_9N_2O_4)_n$ $(756.61)_n$: C, 61.91; H, 3.33; N, 3.70. Found: C, 60.20; H, 3.41; N, 3.90.

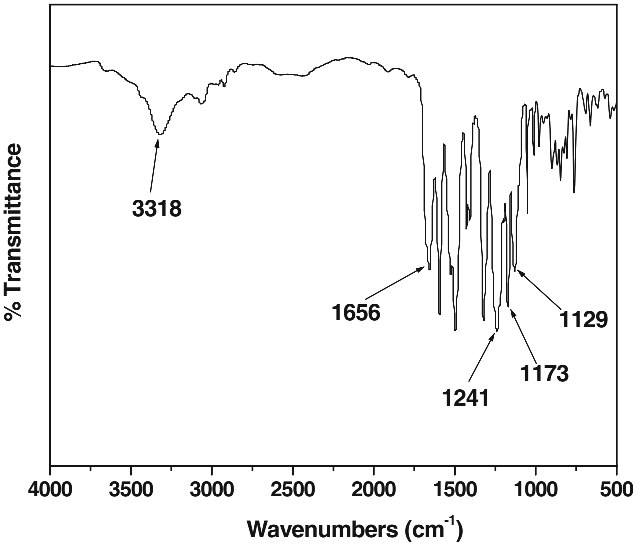


Fig. 1 FT-IR spectrum of PEKA **3c**

Results and discussion

Polymer synthesis

According to the phosphorylation polycondensation first described by Yamazaki et al. [22, 23], a series of new fluorinated poly(ether ketone amide)s **3a–d** were synthesized from the unsymmetrical aromatic diamine **1** with various aromatic dicarboxylic acids **2a–d** (Scheme 1). All the polymerizations in NMP proceeded and afforded homogeneous solutions, indicating that the polymers possessed good solubility in the polymerization medium. The polymers were obtained in almost quantitative yields and the inherent viscosities between 0.43 and 0.65 dL g^{-1} in DMAc solution are summarized in Table 1. All of the PEKAs could be fabricated into transparent and flexible films, indicating medium- to high-molecular-weight polymer formation.

FT-IR, ^{1}H-NMR, and elemental analysis confirmed the chemical structures of these PEKAs, and corresponding data are given at the "Polymer synthesis" section. The FT-IR spectra of the PEKAs showed the characteristic absorptions around 3,310 and 1,658 cm^{-1}, which are characteristic of N–

Table 1 Inherent viscosity and solubility behavior of these PEKAs

Polymers	η_{inh} (dL g $^{-1}$)	Solvents						
		NMP	DMAc	DMF	DMSO	$CHCl_3$	THF	Acetone
3a	0.56	+++	+++	+++	++	+−	++	−
3b	0.51	+++	+++	+++	+++	+−	++	−
3c	0.65	+++	+++	+++	+++	+	+++	S
3d	0.43	+++	+++	+++	+++	+	+++	S

Measured at a concentration of 0.5 g dL^{-1} in DMAc at 30°C. +++ 50 mg sample dissolved in 1 mL solvent (5%), ++ soluble at 3%, + soluble at 1%, +− partly soluble, *S* swelling, − insoluble

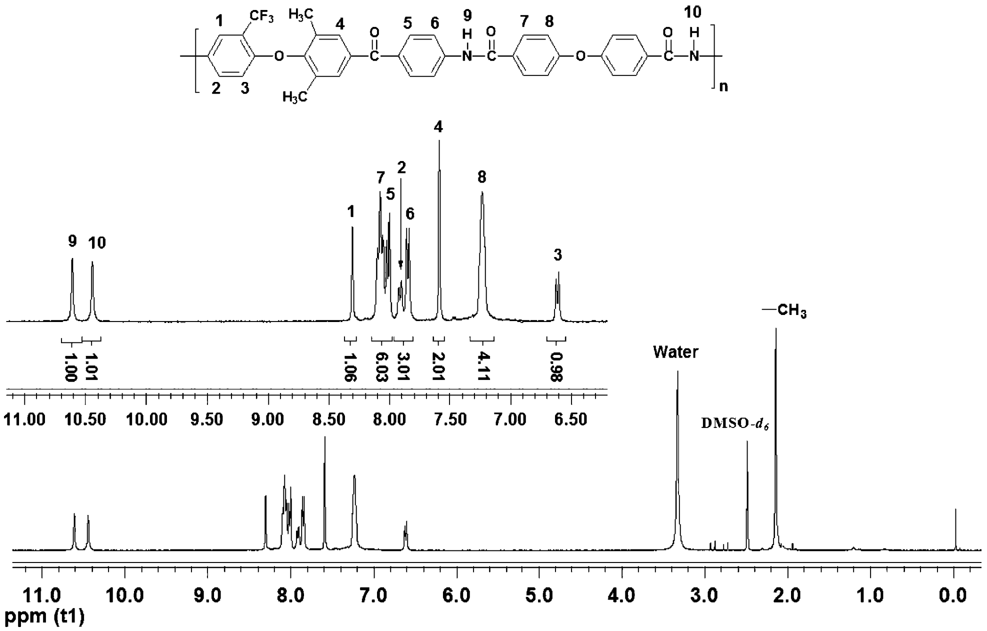


Fig. 2 ^{1}H-NMR spectrum of PEKA **3c** in DMSO-d_6

H stretching and carbonyl stretching (C═O), respectively. The strong absorption bands were observed in the region of 1,100–1,300 cm^{-1} due to the C–O–C and C–F multiple stretching. As a typical example, the FT-IR and ^{1}H-NMR spectra of PEKA **3c** was illustrated in Figs. 1 and 2, respectively. The assignments of each proton are given in the Fig. 2. The formation of amide groups was verified by the resonance signals of amide protons at δ 10.61 and 10.45 in the ^{1}H-NMR spectrum. These results clearly confirm that the prepared PEKAs are consistent with the proposed structures. Elemental analyses are also generally in good agreement with the proposed structures, missing only the values found for the C-percentages that are always lower than the theoretical ones. That certainly can be attributed to the very aromatic nature of these polyamides, which commonly leave a small coal residue in the standard conditions of microanalysis.

Polymer solubility

The solubility of these fluorinated PEKAs was tested in various organic solvents, and the results were listed in Table 1. All the polymers were readily soluble in polar solvents, such as NMP, DMAc, DMF, DMSO, and THF at room temperature or at heating. The maximum dissolvability of the polymers in NMP, DMAc, and DMF even exceeded more than 5.0 % (mg mL^{-1}). Apparently, the good solubility of the PEKIs could be attributed to the bulky trifluoromethyl and methyl pendant groups introduced at the *ortho*-position of ether linkage, which appears to hinder the rotation of C−O−C bond and force the two phenyl rings into adopting a non-coplanar conformation. This, in turn, disrupts the crystal packing and provides enhanced solubility.

Mechanical and optical properties

All PEKAs could be readily processed to flexible, creasable, and essentially colorless films by casting from

Table 2 Mechanical and optical properties of the PEKA films

Polymers	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)	λ_{cutoff} (nm)	T_{450} (%)
3a	98	12.3	1.9	365	81
3b	82	13.5	1.8	357	80
3c	93	18.5	1.6	354	85
3d	78	11.5	1.7	358	87

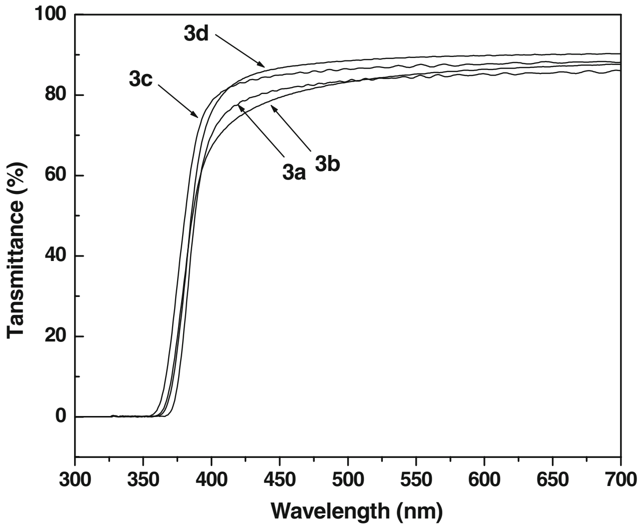


Fig. 3 UV−Vis spectra of PEKA films

Table 3 Thermal properties of these PEKAs

Polymers	T_g[a] (°C)	T_d[b] (°C)	T_{10}[b] (°C)	Char yield (%)[c]
3a	323	450	445	53
3b	313	454	431	53
3c	288	461	443	41
3d	308	456	447	27

[a] From the second trace of DSC measurements conducted at a heating rate of 20°C/min

[b] Onset decomposition and 10% weight loss temperatures in TGA at 20°C/min heating rate

[c] Residual weight retention at 800°C

solutions in DMAc. The tensile properties of the PEKA films are summarized in Table 2. Their tensile strengths, elongations at break, and initial moduli of polymer films were in the range of 78–98 MPa, 11.5–18.5%, and 1.6–1.9 GPa, respectively. The optical properties of the fluorinated PEKA films are also given in Table 2, and the UV–Vis spectra of these films, about 30 µm thick, are shown in Fig. 3. It could be seen from Table 2 that these fluorinated PEKA films exhibited good transparency, the UV cutoff wavelength ($\lambda_{\mathrm{cutoff}}$) was in the range of 354–365 nm, and the transparency at 450 nm (T_{450}) was higher than 81%. As expected, the introduction of bulky pendant groups and non-coplanar conformation effectively disrupt the dense packing of molecular chains and lead to low color and high optical transparent polymer films.

Thermal properties

The thermal properties of the PEKAs are summarized in Table 3. DSC was used to determine the glass-transition temperature (T_g) values of the PEKAs with a heating rate of 20°C/min under nitrogen. The T_g values of these PEKAs ranged from 288 to 323°C (Fig. 4). High glass-transition temperature of these PEKAs mainly attributed to the introduction of trifluoromethyl and dimethyl groups into the *ortho*-position of the ether linkages, which hinder the rotation around C-O-C bond of the two phenyl rings, and increase the chain rigidity. As expected, the PEKA **3c** derived from dicarboxylic acid DBA showed the lowest T_g value due to the increasing flexibility of polymer chain determined by the ether linkage between the phenyl units, whereas the PEKA **3a** obtained from dicarboxylic acid TPA had the highest T_g value due to the rigid phenyl unit. The thermal stabilities of these fluorinated PEKAs were studied by TGA under nitrogen, and TGA thermograms for PEKAs **3a-d** are also shown in Fig. 4. The onset decomposition temperatures (T_d) and 10% weight loss temperatures (T_{10}) in nitrogen were determined from the original TGA thermograms and are given in Table 3. The T_d and T_{10} of the fluorinated PEKAs in nitrogen stayed in the range of 450–461°C and 431–447°C, respectively. They left more than 27% char yield at 800°C in nitrogen. The TGA data indicated that these PEKAs had fairly high thermal stability even with the introduction of bulky trifluoromethyl and methyl pendant groups.

Table 4 Dielectric constant and water absorption of the PEKA films

Polymers	Film thickness (um)	Dielectric constant (dry) 1 MHz	10 MHz	100 MHz	1 GHz	Water absorption (%)
3a	45	2.14	2.02	1.99	1.98	1.80
3b	60	2.71	2.56	2.52	2.51	1.35
3c	65	2.43	2.28	2.23	2.21	1.42
3d	48	1.98	1.82	1.78	1.76	1.15

Dielectric constant and water absorption

The dielectric constants and water absorption of all PEKAs were measured, and the results were summarized in Table 4.

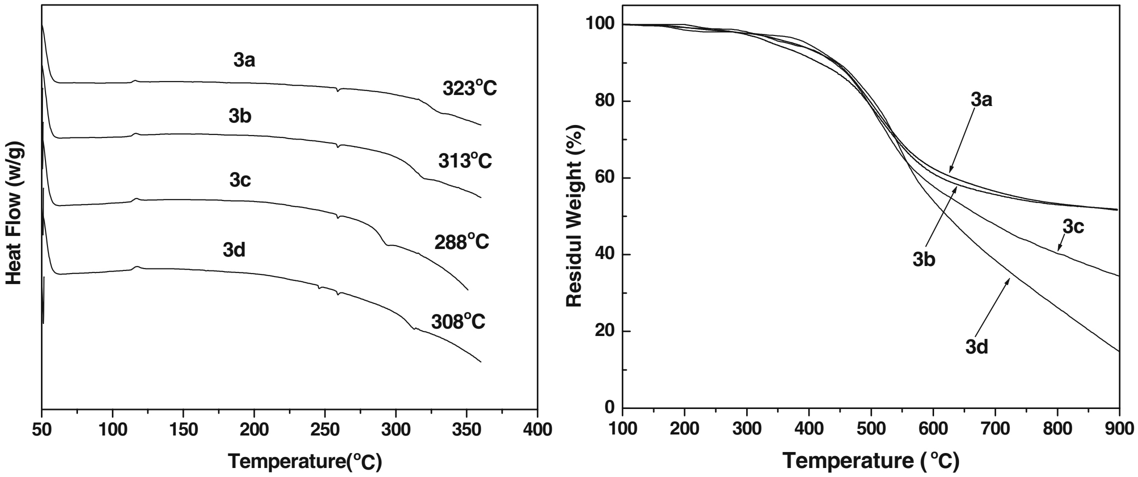


Fig. 4 DSC and TGA curves of PEKAs **3a–d** at a heating rate of 20°C/min in N_2

The PEKAs **3a-d** showed the dielectric constants at 1 MHz and 1 GHz in the range of 1.98−2.71 and 1.76−2.51. The decreased dielectric constants could mainly be attributed to the trifluoromethyl groups in the polymer chains. The low polarizability of trifluoromethyl groups, combined with the bulky free volumes of laterally dimethyl groups, endowed the PEKAs with low dielectric constants. PEKA **3d** exhibited the lowest dielectric constant among this series of polymers because of the highest fluorine content in the repeat unit. It presents utility for the microelectronics industry, in which a low dielectric constant is desired to prevent crosstalk between conducting paths. As expected, the PEKAs also exhibited lower water absorptions (1.15−1.80%) due to the hydrophobic nature of the trifluoromethyl groups. The low water absorptions also ensure that these PEKAs have stable dielectric performance.

Conclusions

A series of novel poly(ether ketone amide)s containing trifluoromethyl pendant groups and non-coplanar conformation, were prepared from an unsymmetric aromatic diamine **1** and various aromatic dicarboxylic acids by the phosphorylation polycondensation. The introduction of bulky pendant groups and non-coplanar conformation is an effective way to improve their solubility, optical and dielectric properties without substantial diminution of their physical properties. All of the synthesized PEKAs exhibited good thermal stability, low dielectric constants, and water absorption. Meanwhile, they showed high optical transparency and good mechanical properties. Thus, these PEKAs demonstrated an eminent combination property and could be considered as potential high-temperature-resistant materials for optical or microelectronic applications.

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