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Structures and properties of polyimide fibers containing fluorine groupsJingjing Chang,^a Weiwei Liu,^a Mengying Zhang,^a Li Cao,^a Qiyang Ge,^a Hongqing Niu,^{*b}Gang Sui^b and Dezhen Wu^{*a}

^a State Key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Corresponding author. Tel. /fax: +86 10 6442 1693.

E-mail address: wdz@mail.buct.edu.cn (Dezhen Wu).

^b Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

Corresponding author. Tel. /fax: +86 10 6442 4654.

E-mail address: niuhq@mail.buct.edu.cn (Hongqing Niu).

ABSTRACT

A series of copolyimide (co-PI) fibers containing fluorine groups were successfully obtained based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), *p*-phenylenediamine (*p*-PDA), 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 4,4'-oxydianiline (ODA) via a typical two-step wet-spinning method. The increased 6FDA moieties in the system resulted in unexpected great changes on the structures and properties of the resultant PI fibers. Regarding mechanical performances of the PI fibers, the tensile strength and initial modulus of the fibers decreased from 2.56 to 0.13 GPa and 91.55 to 2.99 GPa,

respectively. Two-dimensional wide angle X-ray diffraction (2D WAXD) confirmed the existence of highly oriented structures along the fiber axial direction, while this feature gradually disappeared after the introduction of bulky trifluoromethyl pendant groups. SEM results suggested the presence of defects such as macrovoids structures with the increased 6FDA moieties. Besides, the dielectric permittivity was found to decrease from 3.46 to 2.78 in the frequency of 10M Hz as a result of the incorporation of 6FDA. Moreover, the co-PI fibers possessed excellent thermal-oxidative stabilities with the 5 % weight loss temperature ranging from 495 to 552 °C under nitrogen atmosphere.

KEYWORDS: polyimide fibers; fluorine; mechanical properties; molecular packing; dielectric properties

1 Introduction

Aromatic polyimide (PI) and copolyimide (co-PI) fibers are in the class of thermally stable polymeric fibers that generally based on stiff polymer backbone.^{1,2} Over the past decades, a number of advances have been made in the field of PI fibers since they were initially proposed.³ In this regard, recently, PI fibers have received adequate attentions owing to the excellent mechanical properties, outstanding thermal-oxidative stabilities, superior chemical and irradiation resistance as well as good electric and dielectric performances and consequently, offering tremendous opportunities to be utilized in diverse applications such as aerospace, engineering, atomic energy and microelectronic industries.⁴⁻¹¹

Currently, a typical two-step technique is primarily adopted in the preparation of PI fibers.¹² It involves the copolymerization of dianhydrides and diamines in dipolar aprotic solvent such as dimethylacetamide (DMAc), dimethylformamide (DMF), and N-methyl-2-ketopyrrolidone (NMP) to yield the corresponding poly (amic acid) (PAA) solution, which is then extruded into a coagulation bath to get as-spun PAA fibers and subsequently being converted into the final PI fibers through thermal or chemical imidization process.¹³⁻¹⁵ Herein, much efforts have been paid to combine various dianhydrides and diamines to obtain new brand of PI fibers, since subtle variations in the chemical structures of the reaction components have critically affected the comprehensive performances of the resulting PI fibers.¹⁶⁻¹⁹ For instance, Niu et al. introduced 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone containing both -NH- and =N- groups into the 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)/ *p*-phenylenediamine (*p*-PDA) backbone to increase the rigidity of polymer chains and

intermolecular associations, while the resultant PI fibers exhibited the tensile strength and initial modulus up to 2.8 and 115.2 GPa, respectively.²⁰ Chang et al. proposed a new approach in fabricating PI fibers by incorporating 4,4'-oxydianiline (ODA) into the polymer backbone and as a result, the fibers possessed the optimum tensile strength of 2.53 GPa and initial modulus of 53.10 GPa.¹⁴ Although the preparation of high-strength-high-modulus PI fibers has deserved much attentions, the development of functional PI fibers is still in need of exploration. For example, Yin et al. incorporated 5-amino-2-(4-aminobenzene)benzoxazole (BOA) into the BPDA/ 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) polymer backbone to improve the hydrophobic properties of the resultant PI fibers when employed in the hot and humid environment.¹⁹ Specifically, due to the excellent insulation performances, the reduced dielectric permittivity of PI fibers is of significance when occupied in microelectronic industries. It is thus no doubt that the introduction of fluorine groups will be one of the most efficient approaches to reduce the dielectric permittivity of the PI fibers due to the low molar polarization ratio of F atom.²¹⁻²³ However, this feature will inevitably affect the mechanical and thermal performances of the PI fibers, which impedes the advancement with respect to large scale applications. Dong et al. have prepared a series of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB)/BIA fibers based on a one-step wet-spinning technique. It was found that the increased TFMB moieties resulted in the decreased mechanical as well as thermal properties, while the solubility of the PI fibers in aprotic polar solvents was enhanced, ascribing to the incorporation of bulky pendant trifluoromethyl groups which inhibit close packing and reduce the chain regularity.^{17, 24} Unfortunately, the dielectric properties of PI fibers containing fluorine groups have been rarely involved.

Therefore, it is worthy investigating the structure-property relationship of the resulting PI fibers after the introduction of fluorine groups, which will serve as a general rule in designing and preparing functional PI fibers.

In the present work, a series of co-PI fibers were prepared via a two-step wet-spinning method, derived from the copolymerization of BPDA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), *p*-PDA, BIA and ODA in DMAc solvent. Herein, we focus on the effect of 6FDA on the dielectric performances of the resultant co-PI fibers, and also systematically investigate the mechanical and thermal properties, structural evolution and morphologies of the resulting co-PI fibers with the increased 6FDA moieties.

2 Experimental

2.1 Materials

The monomers BPDA and 6FDA were purchased from Shi Jiazhuang Hai Li Chemical Company, and purified by sublimation prior to use. The monomers *p*-PDA, BIA and ODA were obtained from Changzhou Rongtuo Chemical Company and purified by recrystallization. The solvent DMAc (analytical pure) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and utilized after distillation. The deionized water used in the experiment was prepared by the Laboratory Water Purification System.

2.2 Preparation of the co-PI fibers

The co-PI fibers were prepared by a typical two-step wet-spinning method based on the following procedures. The precursor PAA spinning solutions were firstly synthesized by mixing equimolar amounts of dianhydrides and diamines in DMAc solvent under a dried atmosphere. In such case, the molar ratio of the diamines *p*-PDA/BIA/ODA was 7/2/1, while the molar ratio of the dianhydrides BPDA/6FDA varied from 10/0 to 0/10. After filtrated and degassed prior to use, the viscous solution was extruded into a coagulation bath through a spinneret (120 holes, 70 μm in diameter) to get as-spun PAA fibers. The PAA fibers were then washed by deionized water to remove the residual solvent DMAc and dried in the oven with the temperature of 80 $^{\circ}\text{C}$. Subsequently, the dried fibers were delivered into ovens at the temperature ranging from 280 to 500 $^{\circ}\text{C}$ with concomitant drawing on the spinning rollers to obtain the resultant PI fibers. The chemical structure of the co-PI fibers prepared in the present work is illustrated in Fig. 1.

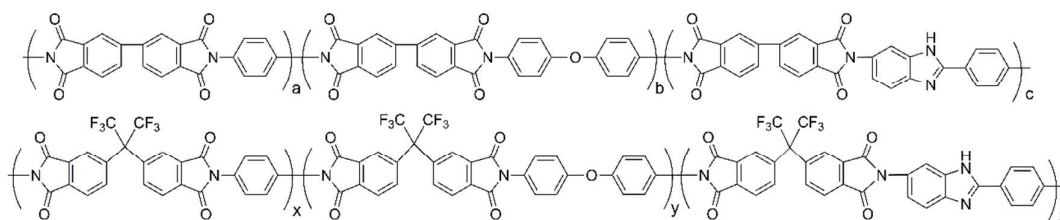


Fig. 1 The chemical structure of the co-PI fibers

2.3 Characterization

Fourier transform infrared (FT-IR) measurement was carried out on Nexus 670 made by Nicolet Company with scanning wavenumber ranging from 4000 to 400 cm^{-1} .

The intrinsic viscosities of the co-PAA solutions were measured using a Germany SCHOTT 52510 Ubbelohde viscometer at 35 $^{\circ}\text{C}$.

The mechanical properties of PI fibers were conducted on an Instron 3344 instrument with a gauge length and extension speed of 250 mm and 125 mm min⁻¹, respectively. For each group of fibers, at least 15 filaments were tested and the average value was used as the representative.

Two-dimensional wide angle X-ray diffraction (2D WAXD) was performed on a Bruker D8 Discover diffractometer equipped with GADDS as a 2D detector. X-ray diffraction measurements were taken from transmission mode at room temperature using Ni-filtered Cu K α ($\lambda = 0.154$ nm) radiation operated at 40 kV and 40 mA. The order degree X of macromolecule can be confirmed by the equation:

$$X = \frac{U_0}{I_0} \times \frac{I_X}{U_X} \times 100\% \quad (1)$$

where U_0 and U_X denote to the backgrounds of the reference sample and experimental sample, and I_0 and I_X are integral intensities of diffraction lines of the reference sample and experimental sample, respectively.²⁵⁻²⁷ Also, the degree of molecular orientation can be calculated by integrating the corresponding intensity of azimuthal scans along the isolated and preferred crystalline plane.²⁸⁻³⁰ The degree of molecular orientation of the fibers is calculated based on the Hermans equation:

$$f = (3 \langle \cos^2 \phi \rangle - 1) / 2 \quad (2)$$

where f is the degree of molecular orientation along the fiber axis direction and ϕ represents the angle between the fiber axis and c-axis crystal unit cell. The numerical values of the mean-square cosines in the equation above are determined by corrected intensity distribution $I(\phi)$ diffracted from the crystalline plane by Gaussian fitting following the equation:

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (3)$$

The surface and cross-sectional fractured morphologies of the co-PI fibers were recorded on a ZEISS scanning electron microscope (SEM) operating at 20 kV. The co-PI fibers were embedded in epoxy resin and fractured in liquid nitrogen for cross-sectional morphologies measurements. Also, the samples were coated with Pt before observation.

The measurements of permittivity and dielectric loss factor were performed using an Agilent 4294A precision impedance analyzer equipped with a 16451B dielectric test fixture in the frequency range of 1K Hz-10M Hz. In the present work, the short PI fibers (1 wt%) cut with 0.5 mm in length and epoxy resin (E51) were mixed and stirred at room temperature. The mixture was hot pressed at 80 °C into disked-shape sample of 25 mm in diameter and 2 mm in thickness.

Thermo gravimetric analysis (TGA) was performed with a TGA Q50 instrument at a heating rate of 10 °C min⁻¹ from 50 to 750 °C under nitrogen atmosphere.

3 Results and Discussion

3.1 FT-IR analysis

The co-PI fibers were obtained with the initial copolymerization of dianhydrides and diamines via a two-step wet-spinning method. Different chemical composition of the PI fibers directly leads to various features of the resultant PI fibers. In the present work, the

chemical structures of the co-PI fibers with different molar ratios of BPDA/6FDA were confirmed by FT-IR as revealed in Fig. 2. All the fibers exhibit four characteristic absorption bands at 1785, 1714, 1354 and 720 cm^{-1} , ascribing to the C=O asymmetrical stretching of imide groups, C=O symmetrical stretching of imide groups, C-N stretching and C=O bending of imide ring, respectively.³¹ Meanwhile, there is no evidence of the characteristic absorption bands of PAA fibers (1660 cm^{-1} for amide-I band and 1550 cm^{-1} for amide-II band), indicating high imidization degree of the resulting PI fibers.¹³ Moreover, the co-PI fibers exhibit the absorption bands at 3357 cm^{-1} for N-H groups and 1252 cm^{-1} for C-F groups, suggesting that both the two groups have been successfully incorporated into the polymer backbone. Also, it is notable that the intensity of the N-H groups decreases simultaneously with the increased 6FDA contents, deriving from the low reactivity of the bulky trifluoromethyl groups.

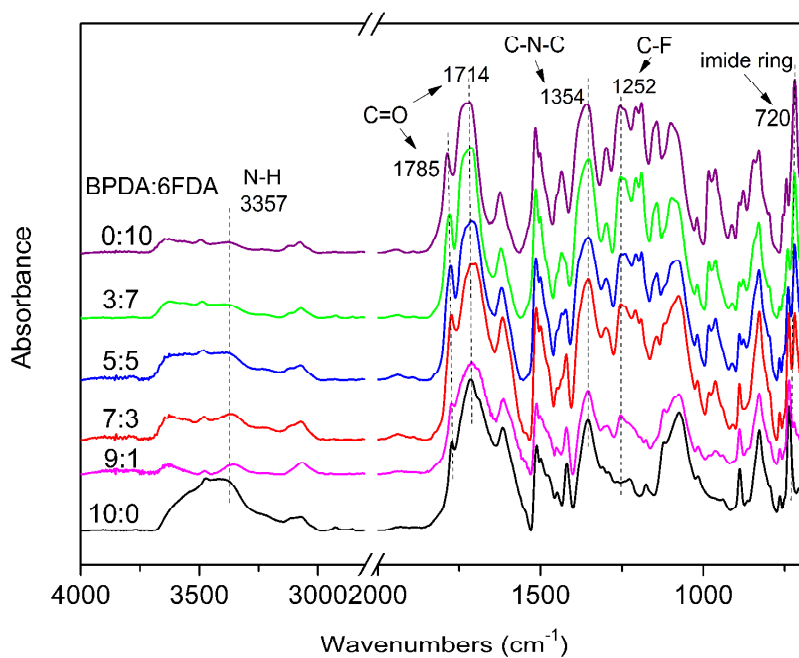


Fig. 2 FT-IR curves of the co-PI fibers with different molar ratios of BPDA/6FDA.

3.2 Mechanical properties

With regard to the polymeric fibers, the mechanical properties of the fibers are considered as one of the most significant targets when employed in engineering applications. Currently, the intrinsic viscosities of the synthesized co-PAA solutions and mechanical properties of the co-PI fibers in terms of the tensile strength, initial modulus and elongation were evaluated. All the results are summarized in Table 1, while the stress-strain curves of the co-PI fibers are shown in Fig. 3. Apparently, the introduction of 6FDA generates a sharp reduction in the mechanical properties of the resultant PI fibers. It is observed that the PI-1 fibers exhibit the tensile strength of 2.56 GPa and initial modulus of 91.55 GPa, while the value decreases to 0.13 and 2.99 GPa at a BPDA/6FDA molar ratio of 0/10, respectively. The reduced mechanical properties of the PI fibers are critically dependent on the incorporation of 6FDA moieties. The strong electronegativity of F atom leads to the decreased electrophilicity of the carbonyl groups of the dianhydride and reactivity of nucleophilic amino groups, which strongly limits the molecular weight of the resulting PAA solutions as reflected in the intrinsic viscosities in Table 1. Meanwhile, the bulky trifluoromethyl pendant groups inhibit close packing and reduces the chain regularity, leading to the decreased stacking density and intermolecular associations in the polymer chains.²⁴ Above all, since the unfavorable factors are dominated in the system, the corresponding mechanical performances of the resultant PI fibers are inevitably impaired.

Table 1 The intrinsic viscosities of the synthesized co-PAA solutions with different molar ratios of BPDA/6FDA and the mechanical properties of the corresponding co-PI fibers

PI Fibers	Molar ratio of BPDA/6FDA	Intrinsic viscosity (dL/g)	Tensile Strength (GPa)	Initial Modulus (GPa)	Elongation (%)
PI-1	10/0	2.08	2.56 ± 0.15	91.55 ± 0.95	3.25 ± 0.21
PI-2	9/1	1.94	1.63 ± 0.04	61.96 ± 0.89	3.47 ± 0.10
PI-3	7/3	1.43	0.85 ± 0.01	19.90 ± 0.14	9.83 ± 0.18
PI-4	5/5	1.42	0.40 ± 0.01	9.44 ± 0.09	15.28 ± 0.80
PI-5	3/7	1.25	0.20 ± 0.01	4.27 ± 0.09	26.18 ± 3.22
PI-6	0/10	1.10	0.13 ± 0.01	2.99 ± 0.13	31.54 ± 3.30

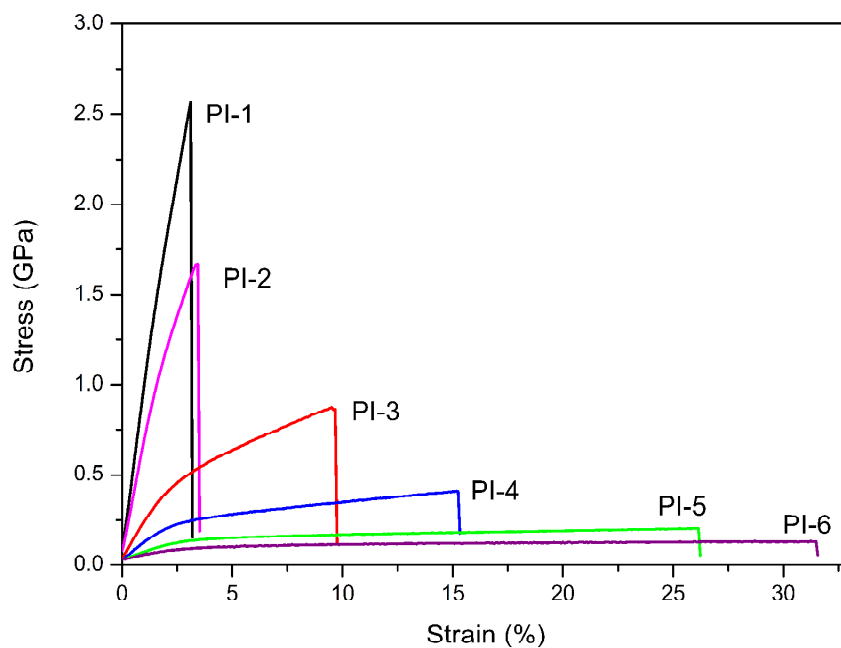


Fig. 3 The stress-strain curves of the co-PI fibers with different molar ratios of BPDA/6FDA.

3.3 Molecular packing

For aromatic PI fibers, the molecular chains are drawn to orient along the fiber axial direction. During the thermal treatment process, the polymer chains have a better opportunity to rearrange themselves into defect-free positions to form regular molecular alignment due to the removal of micromolecules.³² In this regard, two basic structure parameters, order degree and molecular orientation of the macromolecules are of critically significance in determining the comprehensive performances of the resultant PI fibers. Fig. 4 shows the 2D WAXD patterns of the co-PI fibers with different molar ratio of BPDA/6FDA. For PI-1 fibers, the fibers exhibit clear diffraction streaks along the meridian direction, revealing highly oriented molecular arrangement in the fiber axial direction. On the equator, the obscure equatorial streaks originated from lateral packing of the polymer chains correspond to the poor lateral packing order in the fibers. Moreover, dramatic changes occur in the WAXD patterns after the introduction of 6FDA contents, since the regular molecular alignments are gradually destroyed by the incorporation of bulky trifluoromethyl pendant groups. For instance, the clear diffraction streaks on the meridian direction gradually disappear when the molar ratio of BPDA/6FDA is 7/3, meanwhile, the diffraction streaks on the equator direction become much weaker with the increased 6FDA moieties. Consequently, the diffraction streaks in both directions converge together for PI-4, PI-5 and PI-6 fibers, suggesting the destruction of anisotropic features in the polymer chains, which is resulted from the random distribution of the segments that connect with the bulky trifluoromethyl pendant groups in the polymer chains. Furthermore, there is no evidence of diffraction streaks in the quadrants, indicating that the obtained co-PI fibers do not exhibit well-defined 3D crystalline structures.

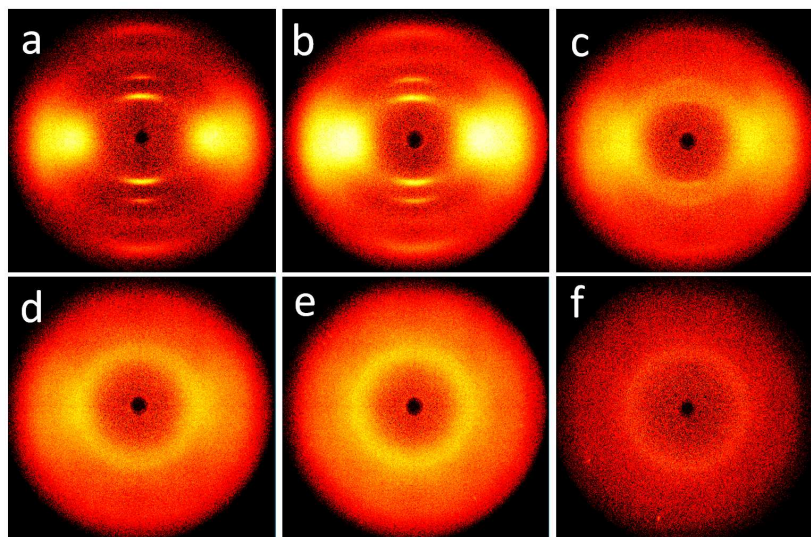


Fig. 4 2D WAXD patterns of the co-PI fibers with different molar ratios of BPDA/6FDA.

(a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4; (e) PI-5; (f) PI-6

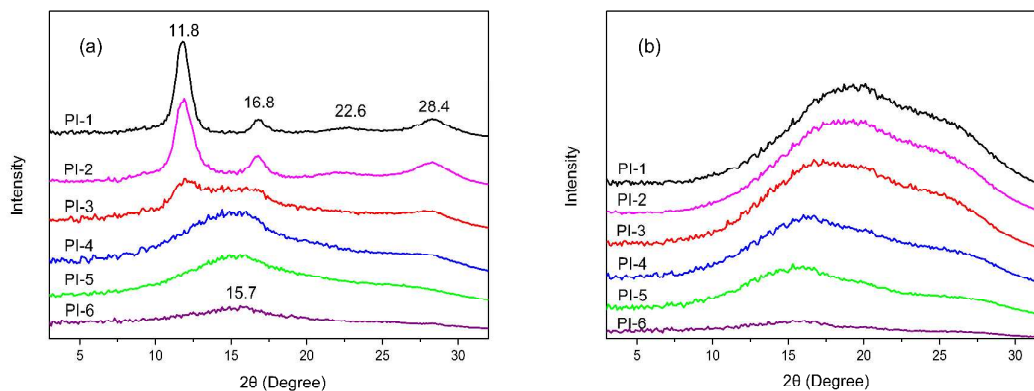


Fig. 5 The WAXD profiles of the co-PI fibers with different molar ratios of BPDA/6FDA.

(a) meridian direction; (b) equator direction

In order to investigate the structural evolution of the PI fibers after the introduction of 6FDA, the corresponding WAXD profiles of the PI fibers along the

meridian and equator direction are collected as depicted in Fig. 5(a) and 5(b), respectively. Along the meridian direction, for PI-1 fibers, four diffraction peaks at 11.8° ($d = 0.749$ nm), 16.8° ($d = 0.527$ nm), 22.6° ($d = 0.393$ nm) and 28.4° ($d = 0.314$ nm) are identified. Based on the accumulative progress in the present work, it was found that the lowest energy conformation for BPDA/*p*-PDA units was obtained as a repeat length of 1.587 nm.²⁰ The value is close to the twice of the observed data at $2\theta = 11.8^\circ$ ($0.749 \times 2 = 1.498$ nm) and the diffraction peak is set to be the (002) plane. Therefore, the peak at $2\theta = 16.8, 22.6$ and 28.4° can be assigned to be (003), (004) and (005) plane, respectively. Also, with the increased 6FDA moieties, the intensity of the diffraction peak at 11.8° decreases rapidly with further introduction of 6FDA, meanwhile, the diffraction angle gradually shifts from 11.8 to 15.7° , resulting in the decreased chain repeat length along the fiber axial direction. It is possibly ascribed to the fact that the flexibility of the polymer chains is improved after replacing BPDA with 6FDA, since the dianhydride 6FDA possesses more rotatable bonds than BPDA. In addition, the diffraction peaks at $16.8, 22.6$ and 28.4° gradually broaden and totally disappear for PI-6 fibers, demonstrating the gradually loss of ordered molecular arrangement along the fiber axial direction.

On the equator, a series of broad peaks in the range of 15 - 25° can be observed for all the fibers, representing a typical amorphous behavior of polymer chains in the transverse direction of the fibers. As compared with that of PI-1 fibers, the intensity of the diffraction peak gradually decreases with the incorporation of 6FDA, revealing the reduction of lateral packing order of the polymer chains. Specially, since the fibers do not exhibit 3D crystalline structures, the order degree X of the molecules can be measured according to eqn (1) as shown in Table 2. The introduction of 6FDA into the

polymer backbone inhibits close packing of the polymer chains and inevitably results in the reduced order degree of the molecule chains.

Moreover, the degree of molecular orientation of (002) plane of the co-PI fibers was also calculated based on eqn (2) and (3). From the results in Table 2, it can be observed that the degree of molecular orientation decreases along with the increased 6FDA contents, which is in consistence with the mechanical properties of PI fibers. Above all, it can be concluded that both the order degree and molecular orientation are of importance in controlling the mechanical performances of the resulting PI fibers in the present work.

Table 2 The order degree of the polymer chains along the equator direction and degree of molecular orientation of (002) plane of the co-PI fibers

PI Fibers	Order Degree	Degree of Orientation
PI-1	12.87 U_0/I_0	0.89
PI-2	11.38 U_0/I_0	0.87
PI-3	8.35 U_0/I_0	0.79
PI-4	4.90 U_0/I_0	0.73
PI-5	4.83 U_0/I_0	0.67
PI-6	2.82 U_0/I_0	0.57

3.4 SEM analysis

It is well known that the mechanical properties of the resulting PI fibers are critically governed by various diamine ratios, and thus influencing the morphologies of the fibers. Herein, the surface and fractured cross-section morphologies of the co-PI fibers were

recorded by SEM observation to investigate the structure-property relationship of the prepared PI fibers. The SEM photographs of the PI fibers with a BPDA/6FDA molar ratio of 10/0, 9/1, 7/3, 5/5, 3/7 and 0/10 are depicted in Fig. 6. The PI-1 fibers exhibit a homogeneous surface and dense as well as uniform fractured morphologies. After the introduction of 6FDA into the polymer backbone, drastic changes occur in the morphologies of the obtained PI fibers. With the increased 6FDA contents, some gullies on the surface and microvoids structures on the cross-section could be observed, especially for PI-6 fibers. During wet spinning, a dual-diffusion process will take place in the coagulation bath, in which the solvent diffuses into the coagulation bath and coagulant diffuses into the fibers. The diffusion rate differs from the surface to the core of the fibers. The surface freezes first to form a tough skin, which restricts the diffusion process into the core of the fibers and accordingly, leading to the loose core.³³ In such case, since the pure water is adopted to be the coagulant, the concentration gradient is extensively increased that the inner and outer force can't reach equilibrium, resulting in the irregular and asymmetric cross-section morphologies with the increase of 6FDA contents. Meanwhile, it was reported that low intrinsic viscosity of the PAA solution yielded fibers with macrovoids, which has well confirmed the presence of detectable macrovoids in the fibers with the increased 6FDA moieties in the present work.^{34, 35} Consequently, it is suggested that the 6FDA moieties have critically influenced the morphologies of the resulting PI fibers, and thus leading to the significantly reduced mechanical performances of the co-PI fibers.

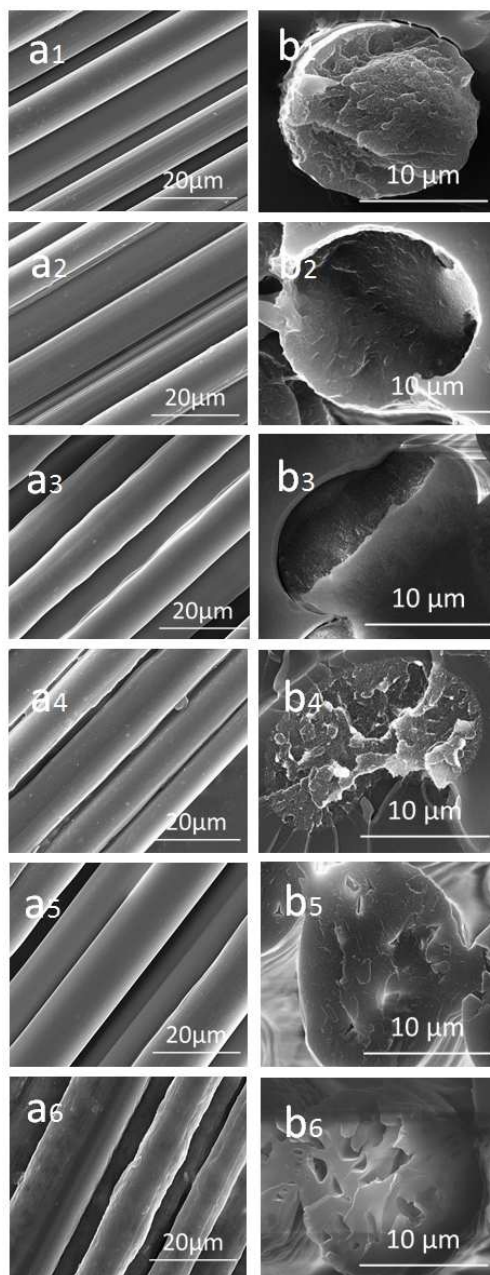


Fig. 6 SEM photographs of the surface (a₁-a₆) and fractured cross-section (b₁-b₆) morphologies of the co-PI fibers

(1) PI-1; (2) PI-2; (3) PI-3; (4) PI-4; (5) PI-5; (6) PI-6

3.5 Dielectric properties

Owing to the low molar polarization ratio of F atom and large free volume induced by the bulky trifluoromethyl groups, the introduction of 6FDA is expected to reduce the dielectric permittivity of the resultant PI-epoxy composites. Fig. 7 illustrates the dependence of dielectric permittivity and loss tangent of the PI-epoxy composites with different molar ratios of BPDA/6FDA on frequency. The dielectric permittivity demonstrates the capability to store microwave energy, and the dielectric loss reflects the ability to dissipate the stored energy into heat. It is interestingly noted that the dielectric permittivity decreases as a function of frequency with different molar ratios of BPDA/6FDA, indicating a frequency-dependent behavior. Moreover, the dielectric permittivity decreases from 3.46 to 2.78 in the frequency of 10M Hz with the increased 6FDA contents, which is mainly originated from the increased free volume of the polymer chains. Also, the increased macrovoids structures in the fibers as revealed by SEM will contribute to the decreased dielectric permittivity. On the other hand, the composites exhibit a typical frequency-dependent feature of dielectric loss in the low frequency range, ascribing to the fact that the dielectric response can match the interfacial polarization at low frequency. In addition, the dielectric loss of the composites varies in a low level, giving evidence of little effect on the dissipation of thermal energy resulting from the stored electromagnetic energy after the incorporation of 6FDA into the polymer backbone. In conclusion, the addition of 6FDA leads to the reduced dielectric permittivity of the resulting PI-epoxy composites, which is in well accordance with our expectations.

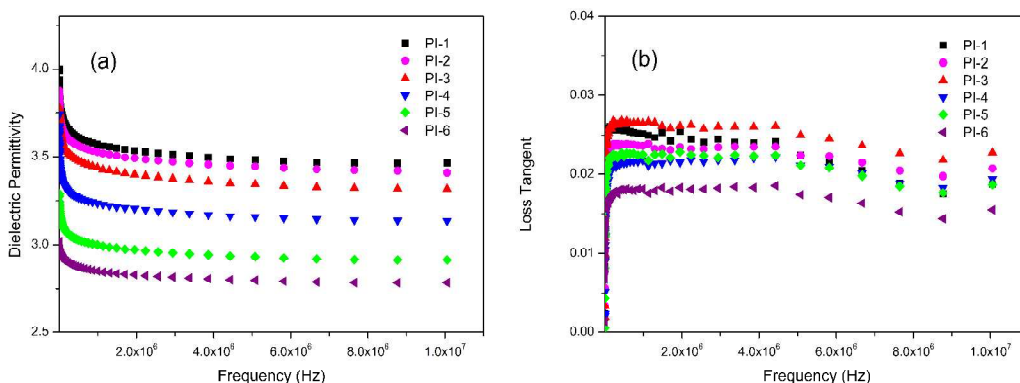


Fig. 7 Dependence of (a) dielectric permittivity and (b) loss tangent of the PI-epoxy composites with different molar ratios of BPDA/6FDA on frequency

3.6 Thermal properties

The thermal-oxidative stabilities of the co-PI fibers with different molar ratios of BPDA/6FDA were evaluated by TGA measurements as illustrated in Fig. 8. A typical one-step thermal degradation behavior under a nitrogen atmosphere is presented for all the co-PI fibers. The 5 % weight loss temperatures can be observed in the range of 495–552 °C under nitrogen atmosphere, and the char yields for all the samples at 750 °C are above 55 %, implying that the co-PI fibers exhibit excellent thermal-oxidative stabilities. Moreover, it can be identified that the PI fibers decompose at lower temperature with the increased 6FDA contents, which is attributed to the decreased stacking density and increased free volume of the polymer chains induced by the introduction of $-\text{CF}_3$ pendant groups.

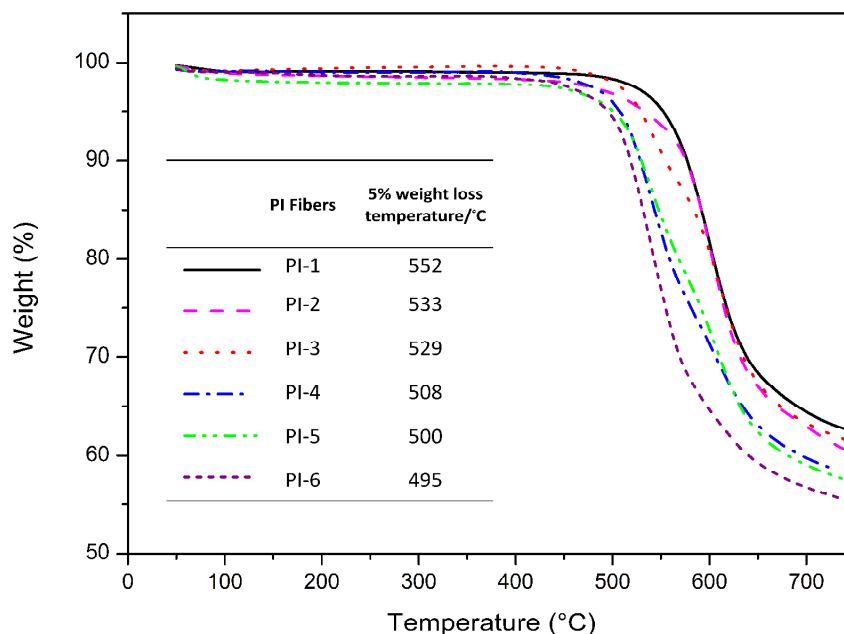


Fig. 8 TGA curves of the co-PI fibers with different molar ratios of BPDA/6FDA under nitrogen atmosphere

4 Conclusion

Novel co-PI fibers containing fluorine groups have been successfully prepared via a two-step wet-spinning method, derived from the combination of BPDA, 6FDA, *p*-PDA, BIA and ODA. Due to the strong electronegativity of F atom and bulky trifluoromethyl groups induced by 6FDA moieties, the mechanical and thermal as well as dielectric properties were seriously affected. Herein, the mechanical properties of the co-PI fibers were rapidly decreased with the introduction of 6FDA. The tensile strength and initial modulus of the PI fibers at a BPDA/6FDA molar ratio of 10/0 was 2.56 and 91.55 GPa, while the value decreased to 0.13 and 2.99 GPa when the molar ratio of BPDA/6FDA was 0/10, respectively. Two-dimensional wide angle X-ray diffraction (2D WAXD) showed that the molecular chains were oriented along the fiber axial direction, while

further introduction of 6FDA resulted in the loss of ordered molecular alignment in the fibers due to the restricted close packing induced by trifluoromethyl groups. Meanwhile, the molecular orientation was found to rapid decrease with the increased 6FDA contents, which was also responsible for the impaired mechanical performances of the PI fibers. SEM observation showed that the incorporation of 6FDA led to the presence of gullies on the surface and macrovoids structures on the cross-section, which still had critical correlation with the decreased mechanical properties of the PI fibers. Moreover, the dielectric permittivity was found to decrease from 3.46 to 2.78 in the frequency of 10M Hz with the increased 6FDA contents, associating to the increased free volume of the polymer chains and macrovoids structures in the fibers. Additionally, the fibers exhibited excellent thermal-oxidative stabilities with the 5 % weight loss temperature ranging from 495 to 552 °C under nitrogen atmosphere after the introduction of 6FDA moieties. In conclusion, the present work has investigated the structure-property relationships of the co-PI fibers containing fluorine groups based on molecular design.

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Figure Captions

Figure 1 The chemical structure of the co-PI fibers.

Figure 2 FT-IR curves of the co-PI fibers with different molar ratios of BPDA/6FDA.

Figure 3 The stress-strain curves of the co-PI fibers with different molar ratios of BPDA/6FDA.

Figure 4 2D WAXD patterns of the co-PI fibers with different molar ratios of BPDA/6FDA. (a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4; (e) PI-5; (f) PI-6

Figure 5 The WAXD profiles of the co-PI fibers with different molar ratios of BPDA/6FDA. (a) meridian direction; (b) equator direction

Figure 6 SEM photographs of the surface (a₁-a₆) and fractured cross-section (b₁-b₆) morphologies of the co-PI fibers. (1) PI-1; (2) PI-2; (3) PI-3; (4) PI-4; (5) PI-5; (6) PI-6

Figure 7 Dependence of (a) dielectric permittivity and (b) loss tangent of the PI-epoxy composites with different molar ratios of BPDA/6FDA on frequency

Figure 8 TGA curves of the co-PI fibers with different molar ratios of BPDA/6FDA under nitrogen atmosphere

Table Captions

Table 1 The intrinsic viscosities of the synthesized co-PAA solutions with different molar ratios of BPDA/6FDA and the mechanical properties of the corresponding co-PI fibers

Table 2 The order degree of the polymer chains along the equator direction and degree of molecular orientation of (002) plane of the co-PI fibers

Structures and properties of polyimide fibers containing fluorine groups

Jingjing Chang,^a Weiwei Liu,^a Mengying Zhang,^a Li Cao,^a Qiyan Ge,^a Hongqing

Niu,^{*b} Gang Sui^b and Dezhen Wu^{*a}

Graphical and Textual Abstract

The fluorine groups were successfully incorporated into the polymer backbone, and the structure-property relationship of the resulting polyimide fibers were systematically investigated.

