

Design and synthesis of novel poly (aryl ether ketones) containing trifluoromethyl and trifluoromethoxy groups

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ABSTRACT

The high-frequency and high-speed communication in the 5 G era puts forward requirements for the dielectric properties of polymers. Introducing fluorine into poly(aryl ether ketone) can improve its dielectric properties. In this work, by introducing the fluorine group strategy, we successfully designed and synthesized three novel trifluoromethyl ($-\text{CF}_3$) or trifluoromethoxy ($-\text{OCF}_3$)-containing bisphenol monomers and their F-substitution PEK-based polymers (PEK-Ins). All these PEK-Ins exhibited good thermal, mechanical and dielectric properties. The $T_d 5\%$ of the three polymers is all higher than 520°C . The free volume fraction of novel polymers increased from 3.75% to 5.72%. Among the three polymers, exhibited the lowest dielectric constant of the films is 2.839, and the dielectric loss is 0.0048, ascribing to the increasing free volume. The Young's modulus of the polymer film is as high as 2.9 GPa and the tensile strength is as high as 84 MPa. PEK-Ins reduced the dielectric constant by introducing a low fluorine content. This study provides a new way to design PEK to synthesize low dielectric constant polymers.

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1. Introduction

With the development of communication technology, the high-frequency and high-speed transmission of signals has always been a research hotspot [1]. The speed and loss of signal transmission have a lot to do with the dielectric constant of the materials [2]. Generally, the dielectric constant is required to be less than 3, and the dielectric loss is less than 0.005 [3]. In addition, communication materials also need to be processed under high-temperature conditions. Therefore, electronic communication requires materials with heat resistance, low dielectric constant and loss [3–5]. Many researchers believe that the density and polarizability of dipoles are important factors affecting the dielectric constant of polymers [6–9]. Some special engineering plastics, such as epoxy resin [10–15], polybenzoxazole [16–19] and polyimide [20–24] have low intrinsic dielectric constant and excellent thermal properties, which can meet communication materials' requirements.

One of the methods commonly used by researchers is to increase the free volume of the material and decrease the polarization rate of the polymer, such as the

introduction of bulky rigid side groups, such as adamantyl, phenyl and $-\text{CF}_3$ groups into the polymer [25,26]. Ascribed to the strong electronegativity and large molar volume of the fluorine atom, it can greatly influence the molecular structure and polarizability [27–31], so the introduction of fluorine-containing groups, such as $-\text{CF}_3$ can simultaneously reduce the dielectric constant and loss of the polymer [23,26,32–46]. Many researchers have done many studies on the introduction of $-\text{CF}_3$ in polymer materials. Chih-Cheng Kuo [26] synthesized a variety of fluorine-containing polyimides. The dielectric constant is as low as 2.4 and the dielectric loss is as low as 0.004. Jialing Xia [38] used hexafluoro bisphenol A, bisphenol S and copolymerize with 4,4-dichlorodiphenylsulfone, and the obtained poly(aryl ether sulfone) had a dielectric constant as low as 2.5 and a dielectric loss as low as 0.008 at 1 kHz. Sun Handong [42] introduced perfluorononyl pendant groups in different molar ratios onto poly(aryl ether ketones), and successfully obtained poly(aryl ether ketones) with a low dielectric constant, which is 2.73 at 10 kHz. Zhi Geng [43] synthesized adamantane-based copoly (aryl ether ketone)s and the polymers have low dielectric constants ranging from 2.33 to 2.65 at 1 MHz. It can be seen from the literature that there are fewer previous

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studies on high-frequency dielectric constants. Amorphous PEK has excellent properties such as high heat resistance and mechanical properties, and it also has a low dielectric [47–49]. Researchers in our group introduced isopropyl groups into phenolphthalein-based poly(aryl ether ketones) (PEK-C), which increased the free volume of the material and reduced the dielectric constant and loss [48]. It can be seen that the introduction of a larger molar volume of side groups into PEK-C can reduce the dielectric constant and loss of the polymer.

This paper focuses on changing the side group structure of PEK-C to reduce the dielectric constant and loss at 10 GHz. Three new PPPBP-based monomers with different structures were obtained by introducing $-\text{CF}_3$ or $-\text{OCF}_3$ groups with different substitution sites on the side groups of phenolphthalein. The PEK-Ins were obtained by $\text{S}_{\text{N}}2$ nucleophilic polycondensation of new monomers and 4,4'-difluorobenzophenone. The PEK-Ins have the lowest dielectric constant of 2.839 and a dielectric loss of less than 0.007 at 10 GHz. All the polymers have good thermal, mechanical and solubility properties. To introduce $-\text{CF}_3$ or $-\text{OCF}_3$, the free volume of polymers can successfully increase, resulting in the dielectric constant and dielectric loss reduction. Our work provides a solution for the subsequent low dielectric polymer design.

2. Experimental

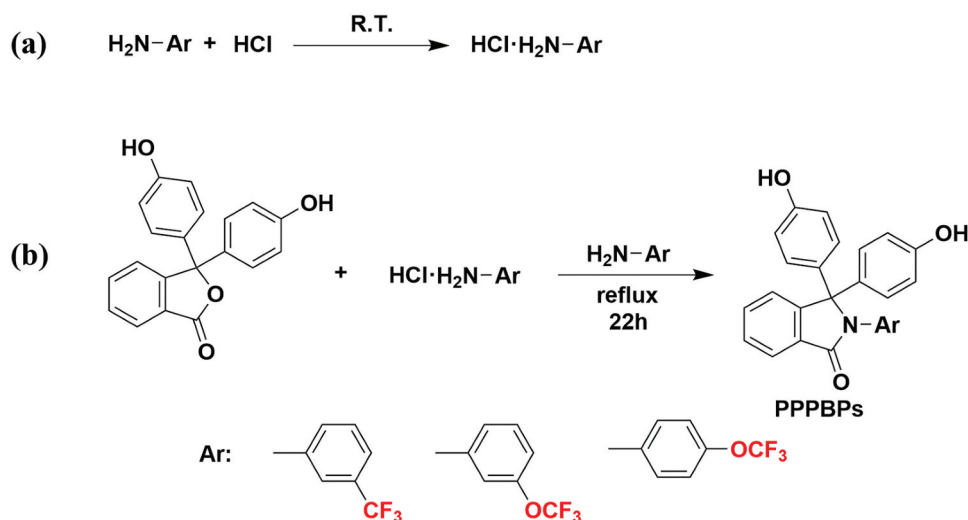
2.1. Materials

Phenolphthalein was purchased from Shanghai Macklin Biochemical Technology Co., Ltd., China. 3-trifluoromethylaniline, 3-trifluoromethoxyaniline and 4-trifluoromethoxyaniline were purchased from Shanghai Acme Biochemical Technology Co., Ltd., China. 1,4-dioxane

solution of hydrogen chloride and Potassium carbonate was purchased from Beijing Innochem Technology Co., Ltd., China. Hydrochloric acid and toluene were purchased from the Tianjin Damao Chemical Reagent Factory, China. NaOH was purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. 4,4'-difluorobenzophenone was synthesized in the laboratory. Sulfolane (SF) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. N, N-Dimethylacetamide (DMAc), and N, N-Dimethylformamide (DMF) were purchased from Guangdong Guanghua Technology Co., Ltd., China. All of the purchased materials were used without further purification.

2.2. Monomers synthesis

The synthesis route of three monomers is shown in Scheme 1. Explanation of the synthesis route using PPPBP-mCF as an example. (a): 3-(trifluoromethyl) aniline and hydrogen chloride solution in 1,4-dioxane were mixed at a molar ratio of 1:3. After the mixture was stirred for 2 h at room temperature, the 1,4-dioxane was removed by carrying out vacuum distillation, and dry 3-(trifluoromethyl) aniline hydrochloride was obtained. (b): Phenolphthalein (100 g 0.314 mol), 3-trifluoromethyl aniline hydrochloride (68.4 g, 0.346 mol) and 3-trifluoromethyl aniline (156.5 mL, 1.25 mol) were added into a three-neck flask, turn on nitrogen purging. The mixture was stirred and refluxed for 22 h. After that, the mixture was poured into hydrochloric acid (5 M, 400 mL), and the precipitate was filtered and washed with deionized water. Then the precipitate was dissolved in NaOH solution (5.9 wt%, 700 mL), and activated carbon (12 g) was



Scheme 1. Synthetic route of PPPBPs.

added into the mixture. After the mixture was stirred for 2 h at room temperature, activated carbon was filtered to obtain a purple filtrate. Hydrochloric acid (36 wt%, 150 mL) was added into the filtrate and a white precipitate appears. After filtering and drying the white precipitate, it was recrystallized in a mixed solvent of methanol/water (V/V) = 5:1, and white crystals were obtained. The yield was 96 g, 64% yield and 98% purity.

2.3. Polymers synthesis

The PEK-Ins were prepared by nucleophilic polycondensation. The specific synthesis route was shown in Scheme 2, which was briefly described using the PEK-Ins-mCF as an example. PPPBP-mCF (4.614 g, 10 mmol), Bis (4-fluorophenyl)-methanone (2.182 g, 10 mmol), Potassium carbonate (1.587 g, 11.5 mmol), Sulfolane (16.5 mL) and toluene (25 mL) were added into a three-necked flask under nitrogen atmosphere. The toluene was refluxed for 2 h at 135°C, and the toluene was removed for 0.5 h at 145°C, polymerized for 3 h at 200 °C. After the reaction was completed, DMAc (20 mL) was added into the mixture to dilute for 1 h. The solution was poured into a mixture of ethanol and water to obtain a white precipitate. Then, the precipitate was pulverized, boiled and washed 6–8 times and dried under vacuum at 170°C overnight. The polymer yield was 6.14 g, 96% yield.

2.4. Instruments and methods

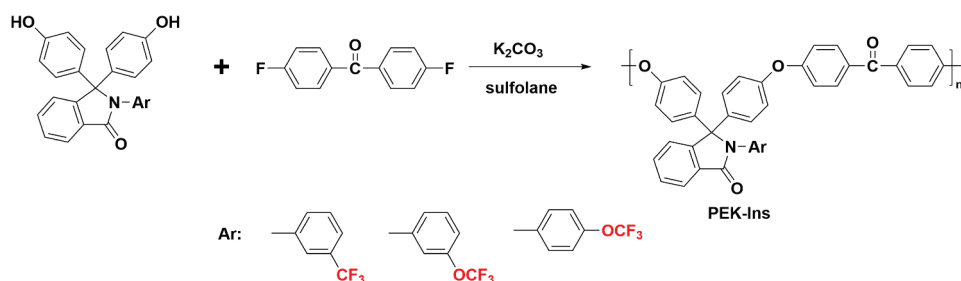
NMR spectra were characterized using a Bruker 400 M nuclear magnetic resonance spectrometer. The molecular weight and purity of novel monomers were characterized by Agilent Q-TOF 6540 High-Performance Liquid Chromatography with Acetonitrile and Water as Mobile Phase. The intrinsic viscosity of these polymers was characterized using an ISV100–2 Ubbelohde viscometer at 25°C. The molecular weights of the polymers were characterized using a Water 1515–2414 gel High-

performance liquid chromatography at 35°C with THF as the mobile phase at a speed of 1 mL/min. The aggregate state of the polymer was characterized using an X'pert Pro-1 x-ray diffractometer with an irradiation angle of 5–35°. The thermal stability of polymers was characterized by the TA Discovery TGA55 Thermogravimetric Analyzer (TGA) in an N₂ atmosphere at a range of 50–800 °C, a heating rate of 10 °C/min. The glass transition temperature (*T_g*) of the polymer was determined by secondary heating curve using a TA DSC25 Differential Scanning Calorimeter (DSC) at a temperature change rate of 10 °C/min. The mechanical properties of polymer films were characterized in tensile mode using an INSTRON 3366 universal material testing machine with a film size of 30 × 10 × 0.06 mm. The dielectric constant and dielectric loss of all films at 10 GHz were characterized using an Agilent E8362C 20 GHz PNA microwave network analyzer. The free volume of polymers was characterized using Ortec fast-fast coincidence positron annihilation lifetime spectroscopy. The water contact angle of all films was measured using a DSA100 contact angle meter. The water absorption of the polymers was tested by soaking the films in deionized water for 24 h at 23 °C. The preparation method of the polymer film: the polymer is dissolved in DMAc to prepare a homogeneous polymer solution with a concentration of 10–20%. The solution was coated uniformly on a clean and dry glass plate with a controlled film thickness and then allowed it to stand on a hot table at 120°C for 12 h, and polymer films with a thickness of 60 μm were obtained.

3. Results and discussion

3.1. Monomer preparation

We scaled up the synthesis of three new monomers in the laboratory, and the yield and purity of the obtained new monomers were as expected. The yield of PPPBP-mCF was 64%, and the purity was 98%. The yield of PPPBP-mOCF was 53%, and the purity was 98%. The yield of PPPBP-pOCF was 80%,



Scheme 2. Synthesis route of PEK-Ins.

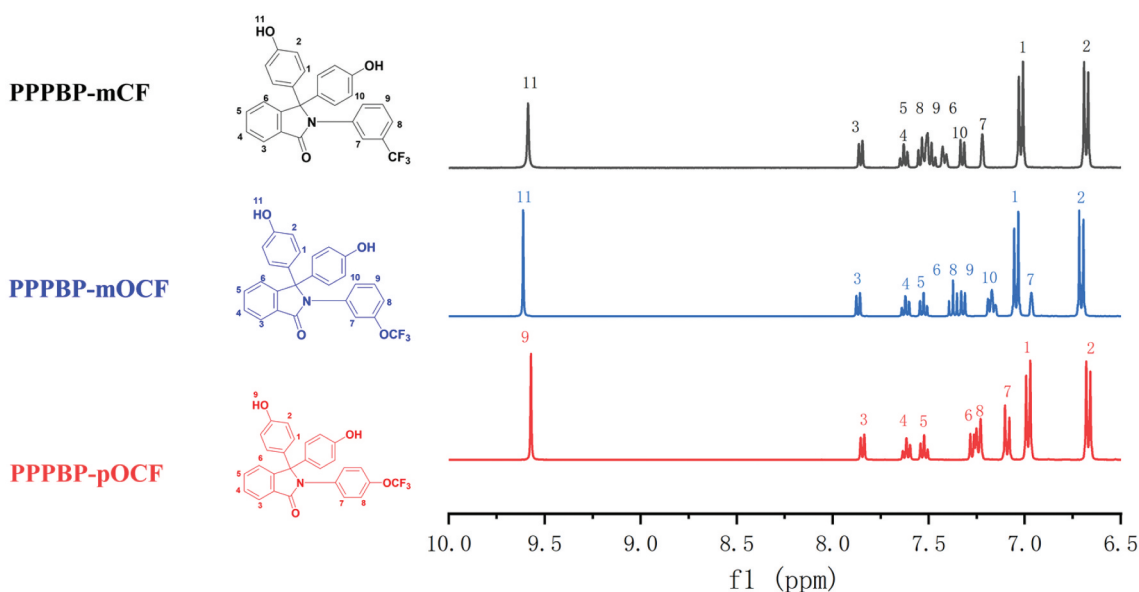


Figure 1. The ^1H -NMR spectra of PPPBPs.

and the purity was 99%. Among them, PPPBP-mCF with a mass of 96 g, PPPBP-mOCF with a mass of 80 g and PPPBP-pOCF with a mass of 120 g were obtained in their respective reactions.

The structure of three novel monomers was verified by ^1H NMR, ^{13}C NMR, ^{19}F NMR and mass spectrometry. The ^1H NMR spectra are shown in Figure 1. Taking PPPBP-mCF as an example, the introduction of $-\text{CF}_3$ shifted the phenolphthalein signal peak with the original chemical shift of 7.89 ppm to the lower field and added a series of signal peaks of 7.2–7.6 ppm, which was closely related to *m*- $-\text{CF}_3$. mass spectra, ^{13}C NMR spectra, ^{19}F NMR spectra and complete ^1H NMR spectra, which are shown in Figures S1 to S10 in the Supporting Information.

3.2. The molecular structures and compositions of PEK-Ins

The results of the molecular weight and viscosity of the polymers are shown in Table 1. The intrinsic viscosity of the three polymers is between 0.60 and 0.75 dL/g, the corresponding number average molecular weight is between 95–133kDa, and the reaction yield is 90.0%–

96.6%. All PEK-Ins have a low fluorine content of 8.7–8.9 wt%.

As shown in Figure 2, the synthesized polymer was characterized by ^1H NMR. The complete ^1H NMR spectra was given in Figures S11 to S13. By comparing the ^1H NMR of the monomer and the corresponding polymer, it can be found that the signal peak at the chemical shift of 9.61 ppm disappears after the polymerization reaction, and the electronic effect of the aromatic ether bond shifted the protons on the aromatic rings at positions 1 and 2 to the lower field. The chemical shifts were 6.99 ppm and 7.24 ppm, respectively, which indicated PEK-Ins were successfully obtained. The ^1H NMR of the polymer was integrated with H-3 as the standard, and the area ratio was consistent with the designed polymer structure.

The FT-IR of PEK-Ins is shown in Figure 3. The complete FT-IR spectra was given in Figures S14 to S16. The absorption peak of 1711 cm^{-1} is the stretching vibration absorption peak of the $\text{C}=\text{O}$ bond in the main chain. The absorption peak near 1238 cm^{-1} is the stretching vibration absorption peak of aromatic ether bonds. The absorption peak of 1325 cm^{-1} is the stretching vibration absorption peak of the $\text{C}-\text{F}$ bond.

Table 1. Molecular weight and η_{int} of PEK-Ins.

Polymers	η_{int} (dL/g)	Yield (%)	M_n (kDa)	M_w (kDa)	PDI	Fluorine content (wt%)
PEK-InsCF	0.75	90.0	133	200	1.50	8.9
PEK-InsOCF	0.60	93.0	108	236	2.18	8.7
PEK-InsOCF	0.73	96.6	95	196	2.06	8.7

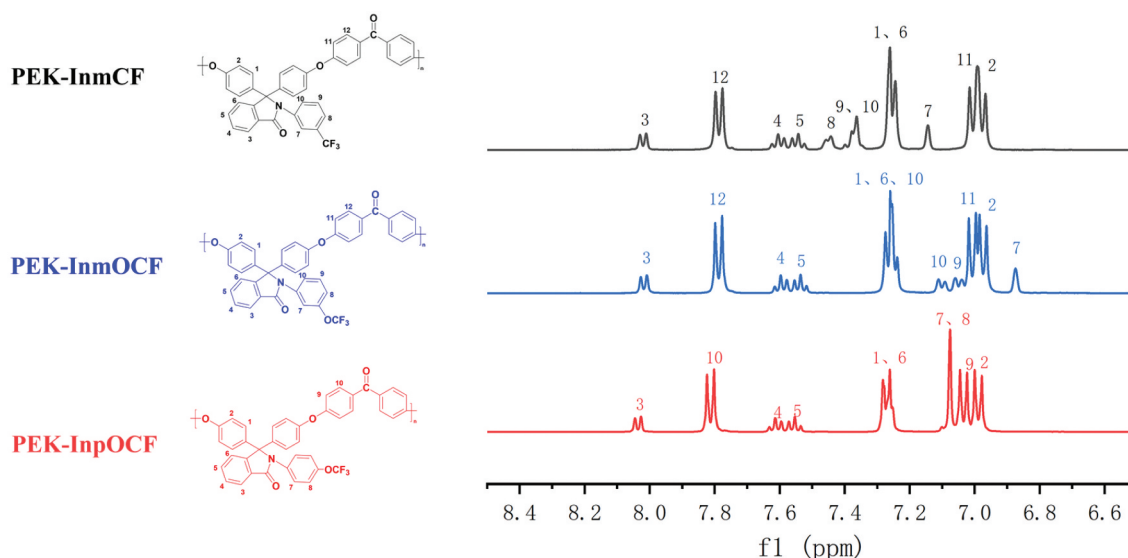


Figure 2. The ^1H -NMR spectra of PEK-Ins.

^{13}C NMR spectra and ^{19}F NMR spectra are shown in Figures S17 to S22 in the Supporting Information. The spectra of FT-IR and ^1H NMR, ^{13}C NMR and ^{19}F NMR were combined to prove that the PEK-Ins containing $-\text{CF}_3$ was successfully synthesized.

3.3. Thermal properties of PEK-Ins

The thermal properties of the polymers are shown in Table 2 and Figure 4. The introduction of fluorine-containing groups increases the thermal decomposition stability of the material. The 5% thermal weight loss temperature of PEK-Ins is above 520 °C. The introduction of the $-\text{CF}_3$ and $-\text{OCF}_3$ groups makes the glass transition temperature (T_g) of polymers different. PEK-InpOCF has the highest T_g . From this, it can be speculated that the introduction of asymmetric $-\text{CF}_3$ or $-\text{OCF}_3$ destroyed the π - π stacking between molecular chains, resulting in the decrease of T_g . In addition, the substituent of PEK-InmOCF is located in the meta position, which might be more conducive to reduce the intermolecular interaction, so the T_g of PEK-InmOCF is lower.

3.4. Solubility properties of PEK-Ins

The solubility of the three polymers in common organic solvents is shown in Table 3. The polymers show good solubility in solvents, such as chloroform, dichloromethane, DMF, DMAc, and NMP. Compared with PEK-C, which is insoluble in cyclohexanone, PEK-Ins showed good solubility in cyclohexanone. PAEK has a high glass transition temperature, which makes its melt processing needs to be carried out under high-temperature

conditions. Solution processing can be performed under more gentle conditions and is more energy efficient. Therefore, PEK-Ins have advantages in processing.

3.5. Aggregation structure of PEK-Ins

The Wide-Angle X-Ray Diffraction (WXR) test was carried out using the polymer powder. The results are shown in Figure 5. The WXR diffraction peaks of the polymers containing $-\text{OCF}_3$ substituents are smoother. It can be seen that the three polymers with different structures are all amorphous polymers.

Test results of free volume was shown in Figure 6. It can be seen from the test results that compared with PEK-In, the substituent Ar is benzene without the $-\text{CF}_3$ or $-\text{OCF}_3$ group. The introduction of a $-\text{CF}_3$ side group into the material can effectively increase the free volume of the polymer. The free volume fractions of the PEK-Ins are all greater than 5%. Among them, the PEK-InpOCF has the largest free volume, and the free volume fraction can reach 5.72%. The increase in free volume can effectively reduce the number of dipoles per unit volume of the material, to achieve the purpose of reducing the polymer's dielectric constant.

3.6. Mechanical, hydrophobic and dielectric properties of PEK-Ins

The test of polymer mechanical properties is shown in Table 4. The films' Young's modulus was more than 2GPa, and the tensile strength was more than 70MPa,

Table 2. Thermal properties of polymers.

Polymer	T_d 5% (°C)	T_d 10% (°C)	T_g (°C)
PEK-InmCF	521	541	213
PEK-InmOCF	538	554	197
PEK-InpOCF	527	542	228

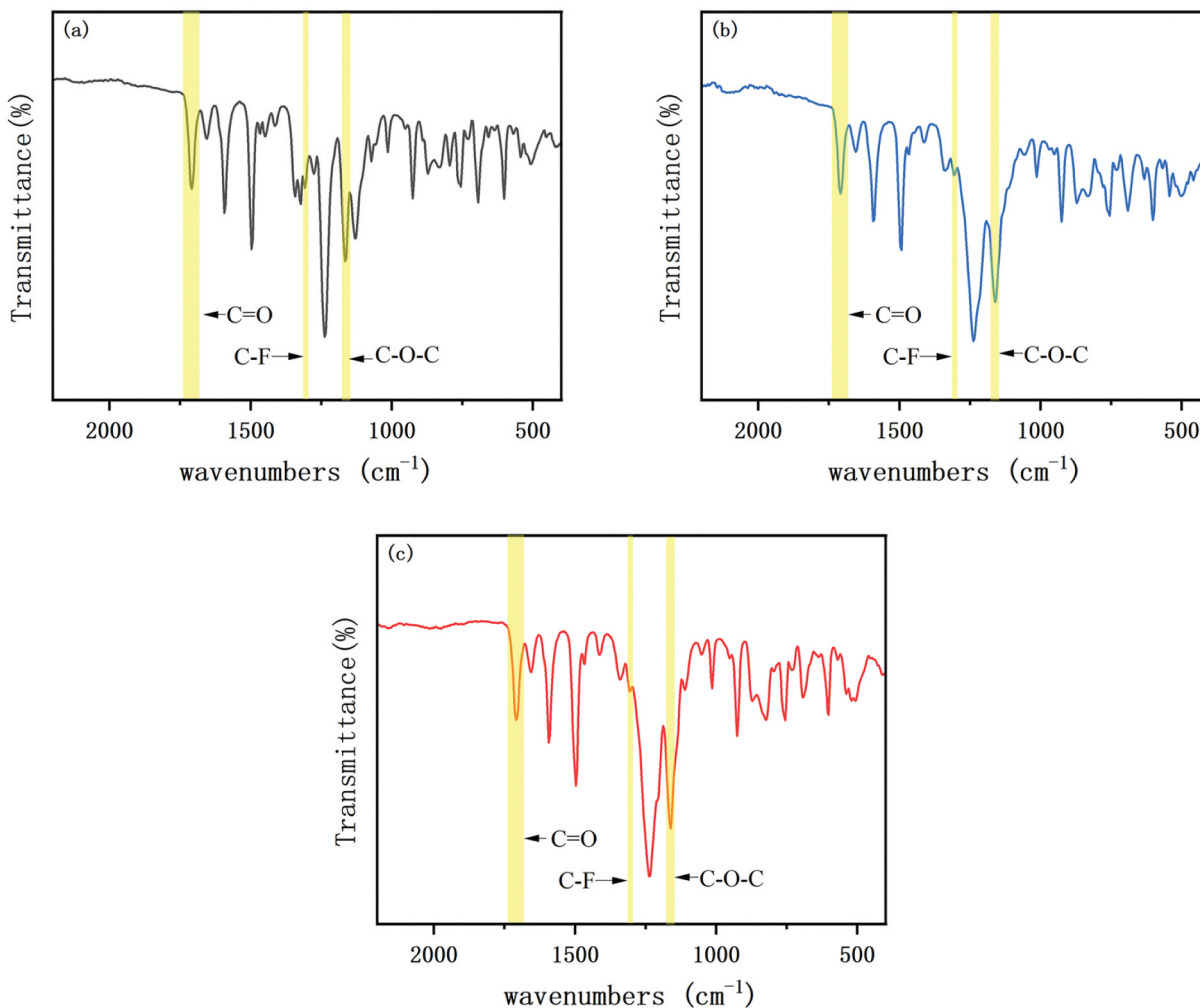
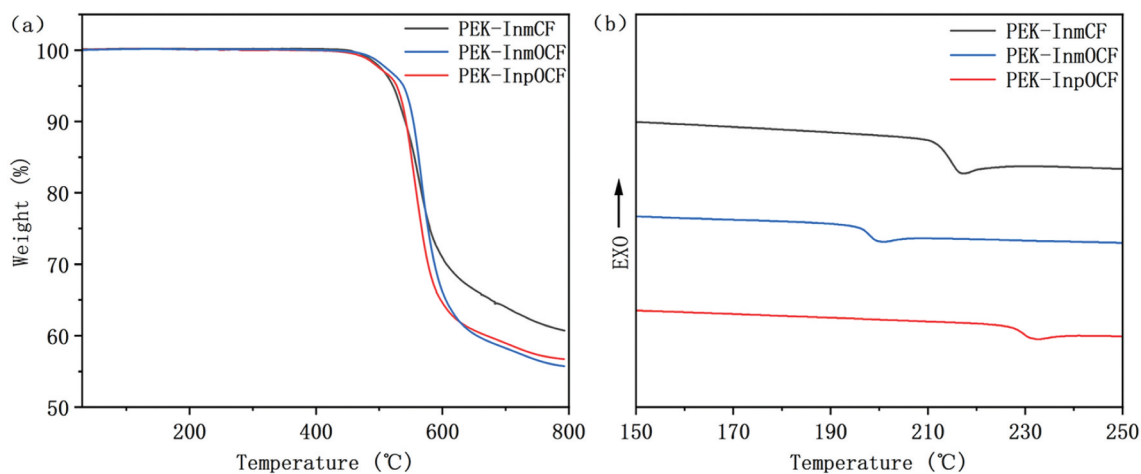
**Figure 3.** The FT-IR spectra of PEK-Ins: (a) PEK-InmCF; (b) PEK-InmOCF; (c) PEK-InpOCF.**Figure 4.** (A) TGA and (b) DSC curves of PEK-Ins.

Table 3. Solubility properties of polymers^{a,b}.

Polymer	CHCl ₃	DCM	BA	DMF	DMAc	NMP	DMSO	CYC
PEK-InmCF	+	+	±	+	+	+	+	+
PEK-InmOCF	+	+	-	+	+	+	+	+
PEK-InpOCF	+	+	-	+	+	+	+	+

+ represents the polymer complete dissolution in the solvent. ± represents polymer swelling or partial dissolution in the solvent. - represents polymer insoluble in the solvent. † 10 mg of the polymer was added into 1 mL of solvent at 25 °C. ‡ CHCl₃ is Trichloromethane, DCM is Dichloromethane, BA is Butyl acetate, DMF is N, N-Dimethylformamide, DMAc is N, N-Dimethylacetamide, NMP is N-Methyl-2-pyrrolidone, DMSO is Dimethyl sulfoxide, CYC is Cyclohexanone.

± represents polymer swelling or partial dissolution in the solvent

- represents polymer insoluble in the solvent

^a10 mg of the polymer was added into 1 mL of solvent at 25 °C

^bCHCl₃ is Trichloromethane, DCM is Dichloromethane, BA is Butyl acetate, NMP is N-Methyl-2-pyrrolidone, DMSO is Dimethyl sulfoxide, CYC is Cyclohexanone.

which proved that the films have good mechanical properties. PEK-InmCF has the best mechanical properties. The Young's modulus of the film is 2.9 GPa, and the tensile strength is 84.0 MPa. This is due to the smallest free volume and high molecular chain stacking density of PEK-InmCF.

The hydrophobicity and dielectric properties of the films were tested, and the result was shown in Table 5. The water contact angle of PEK-Ins films is 84.7°–92.4° and water absorption of the films is less than 1%. In particular, the water absorption of PEK-InmCF and PEK-InmOCF is 0.51%. All PEK-Ins showed some hydrophobicity. The films' dielectric constant is 2.839–3.039, and dielectric loss is lower than 1%. Since the free volume of PEK-InmOCF and PEK-InpOCF is significantly larger than that of PEK-InmCF, the dielectric constants of the –OCF₃ substituted films are lower. However, the dielectric loss of –OCF₃ is higher due to the oxygen atoms in –OCF₃. Among them, the PEK-InmOCF film has the

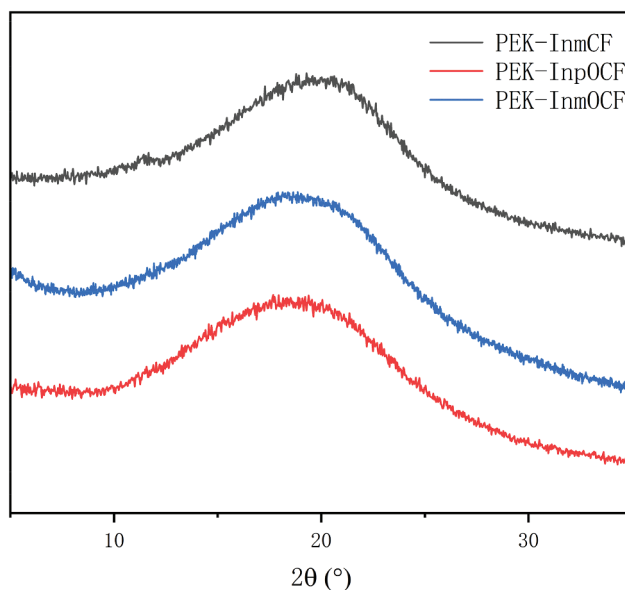
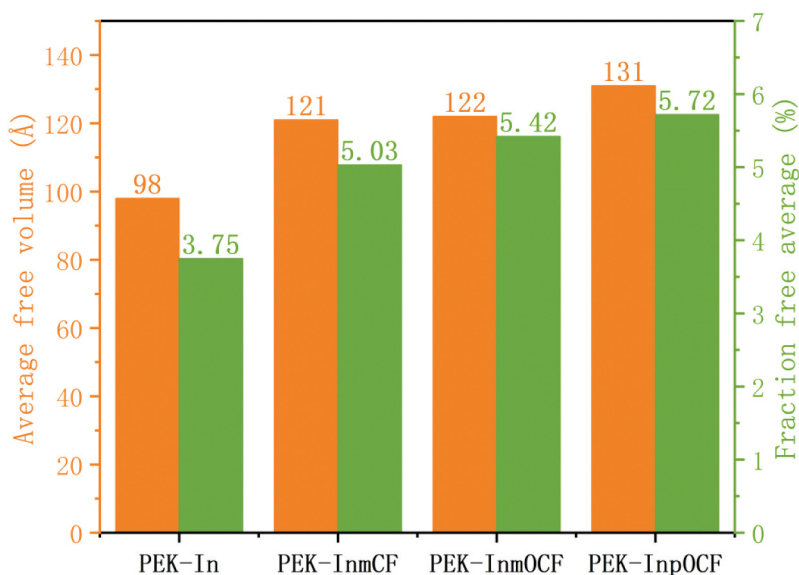
**Figure 5.** WXR D curves of PEK-Ins.**Figure 6.** Free volume comparison of PEK-Ins.

Table 4. Performance Testing of PEK-Ins.

Polymer	Young's modulus (GPa)	Tensile strength; (MPa)	Elongation at break (%)
PEK-InmCF	2.9	84.0	4.60
PEK-InpOCF	2.1	73.8	5.18
PEK-InmOCF	2.6	70.7	4.73

Table 5. Performance Testing of PEK-Ins.

Polymer	water contact angle (°)	water absorption (%)	Dielectric constant (@10GHz)	Dielectric loss (@10GHz)
PEK-InmCF	89.6	0.51	3.039	0.0048
PEK-InmOCF	92.4	0.51	2.839	0.0070
PEK-InpOCF	84.7	0.85	2.869	0.0063

lowest dielectric constant of 2.839, and PEK-InmCF film has the lowest dielectric loss of 4.8‰.

4. Conclusion

In this work, we synthesized three new $-CF_3$ or $-OCF_3$ -containing bisphenol monomers. Then PEK-Ins were then synthesized on this basis. The introduction of the $-CF_3$ or $-OCF_3$ group successfully increased the free volume, the free volume fraction of the polymers increased from 3.75% to 5.72%. The dielectric constant and dielectric loss of the materials is reduced, the lowest dielectric constant is 2.839, and the lowest dielectric loss is 0.0048. The solubility of the materials has increased, which is beneficial for solution processing to prepare thin films. PEK-Ins films also have excellent mechanical properties (Young's modulus >2 GPa, tensile strength >70 MPa), thermal properties ($T_{d5\%}>520$ °C) and hydrophobic properties (water absorption $<1\%$). This design strategy of introducing large volume and low polarizability side groups in the molecular chain can help increase the free volume and reduce the dielectric constant and dielectric loss of the polymer. In general, this F-substitution strategy provides an effective guideline to design low-dielectric polymers with good solubility and thermal stability.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

References

- [1] Hecht J. The bandwidth bottleneck that is throttling the Internet. *Nat.* **2016**;536(7615):139–142.
- [2] Egorov VN, Masalov VL, Nefyodov YA, et al. Dielectric constant, loss tangent, and surface resistance of PCB materials at K-band frequencies. *IEEE Trans Microwave Theory Tech.* **2005**;53(2):627–635.
- [3] Maier G. Low dielectric constant polymers for microelectronics. *Prog Polym Sci.* **2001**;26(1):3–65.
- [4] Volksen W, Miller RD, Dubois G. Low dielectric constant materials. *Chem Rev.* **2010**;110(1):56–110.
- [5] Kohl PA. Low-dielectric constant insulators for future integrated circuits and packages. *Annu Rev Chem Biomol Eng.* **2011**;2:379–401.
- [6] Tang Z, Chang C, Bao F, et al. Feasibility of predicting static dielectric constants of polymer materials: a density functional theory method. *Polymers-Basel.* **2021**;13(2):284.
- [7] Ling M, Yu K, Wang J, et al. Synthesis and properties of low dielectric constant phenolphthalein-based poly (aryl ether) resin containing isopropyl groups. *Mater Lett.* **2022**;311:131547.
- [8] Pu Z, Zheng X, Xia J, et al. Novel low-dielectric-constant fluorine-functionalized polysulfone with outstanding comprehensive properties. *Polym Int.* **2020**;69:604–610.
- [9] Li X, Huang Y, Ye X, et al. Low dielectric resins derived from hyperbranched carbosilane oligomers functionalized by benzocyclobutene groups. *Des Monomers Polym.* **2021**;24(1):362–370.
- [10] Wang Z, Zhang X, Weng L, et al. Low dielectric constant and high toughness epoxy resin based on

- hyperbranched polyester grafted by flexible chain modified. *J Mater Sci.* **2019**;30(6):5936–5946.
- [11] Lu M, Liu Y, Liang L, et al. Synthesis and characterization of easily degradable acrylate-epoxy resin with superior dielectric properties and high transmittance. *Polym.* **2020**;202:202.
- [12] Chen M, Li J, Chen L, et al. Methyl-substitution affects dielectric, thermal, mechanical properties, and shrinkage of fluorinated epoxy. *Polym.* **2022**;253:253.
- [13] Li J, Chen M, Wang Y. Preparation and properties of a fluorinated epoxy resin with low dielectric constant. *J Appl Polym Sci.* **2022**;139:19.
- [14] Liu W, Tian P, Huang Y, et al. A novel UV-curable epoxy resin modified with cholic acid for high-frequency dielectric packaging. *Prog Org Coat.* **2022**;167. DOI:10.1016/j.porgcoat.2022.106849
- [15] Zhang X, Liu M, Chen Y, et al. Epoxy resin/hollow glass microspheres composite materials with low dielectric constant and excellent mechanical performance. *J Appl Polym Sci.* **2022**;139:33.
- [16] Zhou X, Liu X, Cui Z, et al. Design and development of HMS@ZIF-8/fluorinated polybenzoxazole composite films with excellent low-k performance, mechanical properties and thermal stability. *J Mater Chem C.* **2020**;8(22):7476–7484.
- [17] Huangfu MG, Shen DX, Zhi XX, et al. Preparation and characterization of electrospun fluoro-containing poly (imide-benzoxazole) nano-fibrous membranes with low dielectric constants and high thermal stability. *Nanomaterials (Basel).* **2021**;11(2):537.
- [18] Ma Q, Wang H, Zhan G, et al. Preparing multifunctional high-performance cross-linked polybenzoxazole aerogels from polybenzoxazine. *ACS Appl Polym Mater.* **2021**;3(5):2352–2362.
- [19] Yu Z, Wu S, Li C, et al. Ultra-low dielectric constant fluorinated graphene/polybenzoxazole composite films with excellent thermal stabilities and mechanical properties. *Compos Part A Appl Sci Manuf.* **2021**;145. doi:10.1016/j.compositesa.2021.106387.
- [20] Ma Y, Xu L, He Z, et al. Tunable dielectric and other properties in high-performance sandwich-type polyimide films achieved by adjusting the porous structure. *J Mater Chem C.* **2019**;7(24):7360–7370.
- [21] Pu L, Huang X, Wang W, et al. Strategy to achieve ultra-low dielectric constant for polyimide: introduction of fluorinated blocks and fluorographene nanosheets by in situ polymerization. *J Mater Sci.* **2019**;30(15):14679–14686.
- [22] Cao X, Wen J, Song L, et al. Polyimide hollow glass microspheres composite films with low dielectric constant and excellent thermal performance. *J Appl Polym Sci.* **2021**;138:25.
- [23] He JJ, Yang HX, Zheng F, et al. Dielectric properties of fluorinated aromatic polyimide films with rigid polymer backbones. *POLYMERS-BASEL.* **2022**;14(3):649.
- [24] Li Y, Ma B, Zhang R, et al. Mechanically strong, thermal-insulated, and ultralow dielectric polyimide aerogels with adjustable crosslinking methods. *Polym.* **2022**;253:253.
- [25] Liu Y, Qian C, Qu L, et al. A bulk dielectric polymer film with intrinsic ultralow dielectric constant and outstanding comprehensive properties. *Chem Mater.* **2015**;27(19):6543–6549.
- [26] Kuo C-C, Lin Y-C, Chen Y-C, et al. Correlating the molecular structure of polyimides with the dielectric constant and dissipation factor at a high frequency of 10 ghz. *ACS Appl Polym Mater.* **2020**;3(1):362–371.
- [27] Kim MP, Lee Y, Hur YH, et al. Molecular structure engineering of dielectric fluorinated polymers for enhanced performances of triboelectric nanogenerators. *Nano Energy.* **2018**;53:37–45.
- [28] Liu B, Hu W, Chen C, et al. Soluble aromatic poly(ether ketone)s with a pendant 3,5-ditrifluoromethylphenyl group. *Polym.* **2004**;45(10):3241–3247.
- [29] Wang Z, Zhang M, Han E, et al. Structure-property relationship of low dielectric constant polyimide fibers containing fluorine groups. *Polym.* **2020**;206:122884.
- [30] Wang Z, Zhang J, Niu H, et al. Structure-property relationship of polyimide fibers with high tensile strength and low dielectric constant by introducing benzimidazole and trifluoromethyl units. *Macromol Mater Eng.* **2021**;306(7):2000705.
- [31] He X, Zhang S, Zhou Y, et al. The “fluorine impact” on dielectric constant of polyimides: a molecular simulation study. *Polym.* **2022**;254:125073.
- [32] Boufflet P, Bovo G, Occhi L, et al. The influence of backbone fluorination on the dielectric constant of conjugated polythiophenes. *Adv Electron Mater.* **2018**;4(10):1700375.
- [33] Jia XE, Liu G, Chen S, et al. Backbone fluorination of polythiophenes improves device performance of non-fullerene polymer solar cells. *ACS Appl Energy Mater.* **2019**;2(10):7572–7583.
- [34] Jia M, Zhou M, Li Y, et al. Construction of semi-fluorinated polyimides with perfluorocyclobutyl aryl ether-based side chains. *Polym Chem.* **2018**;9(7):920–930.
- [35] Matsumoto K, Xu P, Nishikimi T. Gas permeation of aromatic polyimides .1. Relationship between gas permeabilities and dielectric-constants. *J Membr Sci.* **1993**;81(1–2):15–22.
- [36] Peng W, Lei H, Qiu L, et al. Perfluorocyclobutyl-containing transparent polyimides with low dielectric constant and low dielectric loss. *Polym Chem.* **2022**;13(26):3949–3955.
- [37] Li S, Cao Q, Wang C, et al. Studies on the dielectric properties of laterally fluorine-substituted multiphenylacetylene-type liquid crystal compounds at microwave region. *J Mol Liq.* **2021**;337:116600.
- [38] Xia J, Pu Z, Zheng X, et al. Dielectric properties of polyethersulfone copolymers containing bisphenol S and six fluorine hexafluorobisphenolA (6AF) segments. *J Polym Res.* **2020**;27(9):1–8.
- [39] Dhara MG, Banerjee S. Fluorinated high-performance polymers: poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups. *Prog Polym Sci.* **2010**;35(8):1022–1077.
- [40] Zhang Y, Zhao C, Liu J, et al. Preparation and characterization of ultralow dielectric and fibrous epoxy thermoset cured with poly(arylene ether ketone) containing phenolic hydroxyl groups. *Eur Polym J.* **2018**;109:110–116.
- [41] Niu Y, Zhu X, Liu L, et al. Synthesis and characterization of poly(aryl ether ketone) with trifluoromethyl-substituted

- benzene in the side chain. *React Funct Polym.* **2006**;66(5):559–566.
- [42] Sun H, Lv Y, Zhang C, et al. Materials with low dielectric constant and loss and good thermal properties prepared by introducing perfluorononyl pendant groups onto poly(ether ether ketone). *RSC Adv.* **2018**;8(14):7753–7760.
- [43] Geng Z, Lu Y, Zhang S, et al. Synthesis and characterization of novel adamantane-based copoly(aryl ether ketone)s with low dielectric constants. *Polym Int.* **2014**;63(2):333–337.
- [44] Liu Y, Zhang Y, Guan S, et al. Synthesis and properties of soluble fluorinated poly(ether imide)s with different pendant groups. *Polym.* **2008**;49(25):5439–5445.
- [45] Song N, Shi K, Yu H, et al. Decreasing the dielectric constant and water uptake of co-polyimide films by introducing hydrophobic cross-linked networks. *Eur Polym J.* **2018**;101:105–112.
- [46] Kong Q, Li Z, Ren X, et al. The surface morphology and dynamic impact properties with rebounding and splashing of water droplet on phase separation and breath figure assisted electrospinning films. *Des Monomers Polym.* **2021**;24(1):162–172.
- [47] Wu K, Zhang S, Liu Q, et al. Poly(arylene ether sulfone) containing diphenyl-bipthalazin-dione moieties with excellent thermal resistance. *Polym.* **2022**;243:124653.
- [48] Ling M, Yu K, Wang J, et al. Design and synthesis of novel phenolphthalein-based poly (aryl ether) resin containing isopropyl groups. *J Mater Res Technol.* **2022**;21:153–160.
- [49] Xie X, Wang Z, Zhang K, et al. Novel phosphorous–nitrogen containing poly(aryl ether ketone)s: synthesis, characterization, and thermal properties. *Des Monomers Polym.* **2012**;16(1):38–46.