

Modified Triphenylmethane-based Polyimides with Improved Optical, Dielectric and Solubility Properties via Post-Polymerization Modification

Yan-Cheng Wu^{a*}, Guo-Tao Huang^a, Man-Yu Lian^a, Rui Liang^a, Hong-Lin Deng^a, Feng Gan^a, Yang-Fan Zhang^a, Ning-Bo Yi^a, Li-Yong Tian^a, Chun-Ping Ma^{a*}, and Yen Wei^{b*}

^a School of Textile Materials and Engineering, Wuyi University, Jiangmen 529020, China

^b Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing 100084, China

Electronic Supplementary Information

Abstract A family of new triphenylmethane (TPM)-based polyimides (PIs) containing bulky *tert*-butyldimethylsiloxy (TBS) side-groups (PI-TPMOSis) has been prepared by a post-polymerization modification via a simple silyl ether reaction of TPM-based PIs containing hydroxyl (OH) groups (PI-TPMOHs). The attachment of TBS side-groups in PI-TPMOSis can be achieved up to 100%, as confirmed by the ¹H-NMR and IR spectra. Due to the presence of the TPM structure, PI-TPMOSi films still display the excellent thermal stability with high glass transition temperature (*T*_g) of 314–351 °C and high degradation temperature (*T*_{d5%}) of 480–501 °C. It is quite remarkable that the introduction of TBS side-groups into PI-TPMOSi chains results in more superior optical, dielectric and solubility properties in comparison with the precursor PI-TPMOH films, probably due to the reductions of the packing density and charge-transfer complexes (CTCs) formation. The optical transmittance at 400 nm (*T*₄₀₀) of PI-TPMOSi films is significantly increased from 45.3%–68.8% to 75.4%–81.6% of the precursor PI-TPMOH films. The dielectric constant (*D*_k) and dissipation factor (*D*_f) at 1 MHz of PI-TPMOSi films are reduced from 4.11–4.40 and 0.00159–0.00235 to 2.61–2.92 and 0.00125–0.00171 of the precursor PI-TPMOH films, respectively. Combining the molecular design and simple preparation method, this study provides an effective approach for enhancement of various properties of PI films for microelectronic and photoelectric engineering applications.

Keywords Triphenylmethane-based polyimides; Post-polymerization modification; High *T*_g; High optical transparency; Low *D*_k

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INTRODUCTION

Polyimide (PI) materials, such as PI film,^[1] PI fiber,^[2] PI foam^[3] and so on, are a class of high-performance engineering plastics that have been extensively employed in many high-tech industries with electric, electronic, aerospace, and optical applications due to their desirable physical and chemical characteristics.^[4] Among these PI materials, PI films with outstanding comprehensive properties are the earliest, most mature and largest market-capacity commercial product, which are usually used as the dielectric layer in microelectronic industry,^[5,6] substrate in display devices,^[7] gas separation

membrane,^[8,9] film-based sensors,^[10,11] etc. With the rapid development of the microelectronics and optoelectronics industries, solution processible PI films with high glass transition temperature (*T*_g), low dielectric constant (*D*_k) and dissipation factor (*D*_f), and high optical transparency is urgently required to meet the requirements of high-temperature manufacturing processes and device usage.^[12–17] However, caused by their electron conjugated structures as well as the formation of intra- and inter-molecular charge-transfer complexes (CTCs) between electron-donating diamine and electron-accepting dianhydride fragments, the traditional aromatic PI films generally present some adverse characteristics of deep coloration, relatively high dielectric constant (*D*_k > 3.0) and poor solubility in organic solvents, especially in low boiling solvents.^[4] Therefore, the development of solution processible PI films with high *T*_g, low *D*_k and *D*_f and high light transmittance has been still needed.^[12,13,18,19]

In order to overcome some aforementioned deficiencies of PI films, many efforts have been devoted to modifying PIs at the molecular level by reduction or even elimination of CTCs

* Corresponding authors, E-mail: wyc@wyu.edu.cn (Y.C.W.)

E-mail: machunpingaa@126.com (C.P.M.)

E-mail: weiyen@mail.tsinghua.edu.cn (Y.W.)

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formation as well as breaking electron conjugation.^[6,7,20] The introduction of bulky side-groups into aromatic PI chains is one of an effective strategy to simultaneously improve the dielectric, optical and solubility properties of PI films.^[12,21–24] However, it is still a great challenge to keep a suitable balance between dielectric/optical/dissolving properties and other desirable properties, especially the thermal property.^[25–27] In addition, the method above has mainly focused on the design and synthesis of diamine monomers containing the bulky side-groups, which suffers from some defects, such as multistep synthesis, complicated purification process and low polymerization reactivity of the most synthesized monomers.^[12,21,25]

It was revealed that methylene-containing triphenylmethane-based (TPM-based) PI films show the outstanding combined properties with low D_k and D_f values, high light transmittance in the visible region and high solubility in organic solvents while preserving their excellent thermal stabilities and mechanical properties.^[28–34] This work focuses on the design and preparation of TPM-based PI containing bulky *tert*-butyldimethylsiloxy (TBS) side-groups (PI-TPMOSi). Obviously, the TPM-based core in PI main chains endows the resulting PI-TPMOSi films with high thermal stabilities and mechanical properties. And the introduction of TBS side-groups in to PI chains is expected to simultaneously improve the dielectric, optical and solubility properties of the resulting PI films. Contrary to the traditional preparation method, a post-polymerization modification *via* a simple silicon etherification reaction of easily prepared TPM-based PIs containing hydroxyl (OH) groups (PI-TPMOHs) is used to prepare PI-TPMOSi in this study (Scheme 1). The effect of replacing OH groups with bulky non-polar TBS groups in TPM-based PIs chain on the thermal, optical, dielectric and solubility properties of the resulting PI films was studied in detail.

EXPERIMENTAL

All involved reagents and characterizations are listed in the electronic supplementary information (ESI).

Synthesis of TPM-based Diamine Monomer Containing a Hydroxyl Group (TPMOH)

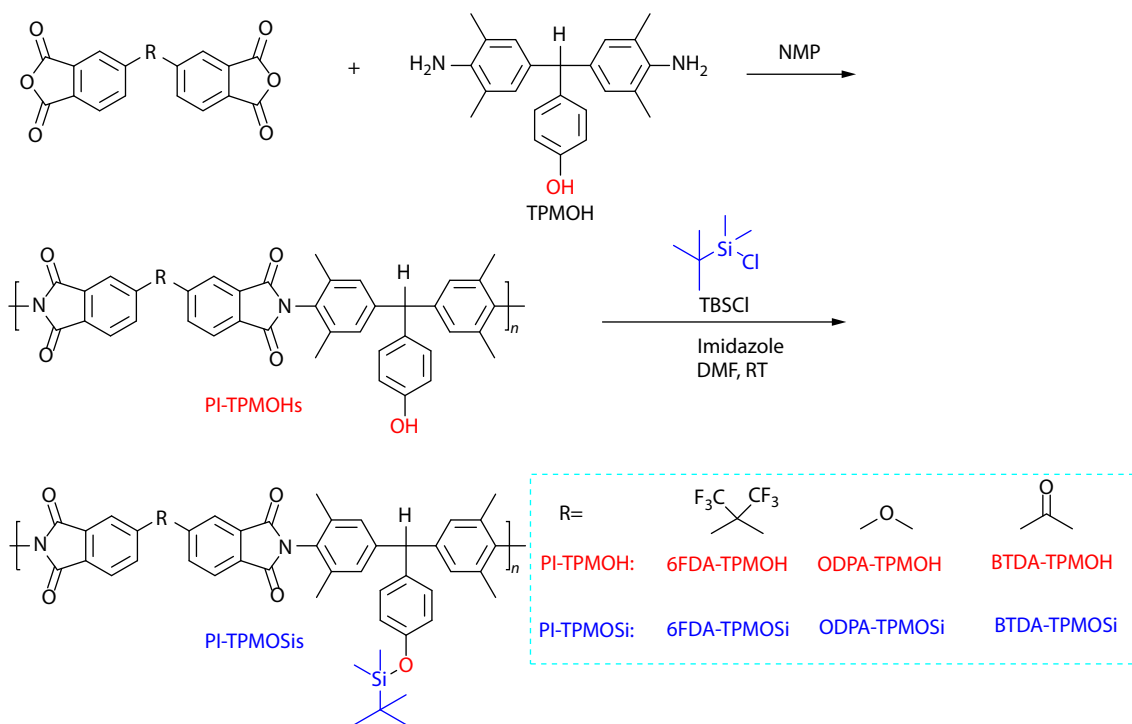
The diamine monomer TPMOH was synthesized by a condensation reaction as shown in Scheme S1 in ESI.^[33]

2,6-Dimethylaniline (48.47 g, 0.4 mol) was added to a 250 mL two-necked flask, which heated to 100 °C under N₂ atmosphere. Then a mixed solution of *p*-hydroxybenzaldehyde (12.21 g, 0.1 mol), 2-methoxyethanol (40 mL) and HCl (37 wt%, 8.3 mL) was added dropwise into the flask. The mixture was stirred at 125 °C for 12 h. After reaction, the homogeneous solution was slowly poured into the stirred methanol (500 mL). Then, using the saturated sodium bicarbonate solution adjust pH value to 9 to precipitate a pink crude product, which was filtered and washed thoroughly with deionized water. At last, the neat TPMOH was obtained by recrystallization using ethyl acetate.

TPMOH. Yield: 68.2%; ¹H-NMR (600 MHz, DMSO-*d*₆, δ , ppm): 9.11 (s, 1H, OH), 6.82 (d, *J*=8.5 Hz, 2H), 6.62 (d, *J*=8.5 Hz, 2H), 6.49 (s, 4H), 4.98 (s, 1H), 4.34 (s, 4H), 1.99 (s, 12H).

Synthesis of TPM-based PIs Containing Hydroxyl Groups (PI-TPMOHs)

Three PI-TPMOHs (named as 6FDA-TPMOH, ODPA-TPMOH and BTDA-TPMOH) were prepared *via* a one-step chemical imidization as shown in Scheme 1. The synthesis of 6FDA-TPMOH was taken as an example to illustrate the general synthetic route as follows. Under the protection of N₂, TPMOH (1.39 g, 4 mmol), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 1.78g, 4 mmol), and 20 mL of NMP were



Scheme 1 Schematic of polyimides synthesis step.

added to a 250 mL round-bottom flask and stirred at room temperature for 12 h. Then the reaction temperature was raised successively to 120 °C for 1 h and 180 °C for 3 h to achieve complete imidization. After reaction, the formed polymer resins were isolated by precipitation into ethanol. At last, the crude product dissolved in DMAc were re-precipitation into ethanol to give 6FDA-TPMOH resin.

The synthetic method of ODPa-TPMOH and BTDA-TPMOH resins was similar to 6FDA-TPMOH, and only 4,4'-oxydipthalic anhydride (ODPA) and benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) was used to replace 6FDA in the process, respectively.

6FDA-TPMOH. Yield: 91.5%; GPC data: number-average molecular weight (M_n) = 10.8×10^4 g·mol⁻¹, weight-average molecular weight (M_w) = 22.4×10^4 g·mol⁻¹, polydispersity index (\bar{D} , $\bar{D} = M_w/M_n$) = 2.07; ¹H-NMR (600 MHz, DMSO-d₆, δ , ppm): 9.33 (s, 1H), 8.15 (d, J =8.1 Hz, 2H), 7.91 (s, 4H), 7.03 (d, J =16.0 Hz, 6H), 6.74 (d, J =6.9 Hz, 2H), 5.48 (s, 1H), 2.05 (s, 12H).

ODPA-TPMOH. Yield: 90.3%; GPC data: M_n = 4.68×10^4 g·mol⁻¹, M_w = 12.3×10^4 g·mol⁻¹, \bar{D} =2.63; ¹H-NMR (600 MHz, DMSO-d₆, δ , ppm): 9.34 (s, 1H), 8.07 (d, J =8.2 Hz, 2H), 7.72 (s, 2H), 7.66 (d, J =8.0 Hz, 2H), 7.05 (s, 4H), 7.03 (d, J =8.9 Hz, 2H), 6.75 (d, J =7.6 Hz, 2H), 5.48 (s, 1H), 2.04 (s, 12H).

BTDA-TPMOH. Yield: 94.2%; GPC data: M_n = 7.23×10^4 g·mol⁻¹, M_w = 20.1×10^4 g·mol⁻¹, \bar{D} =2.75; ¹H-NMR (600 MHz, DMSO-d₆, δ , ppm): 9.36 (s, 1H), 8.48 (s, 2H), 8.41 (d, J =5.8 Hz, 2H), 8.14 (d, J =6.8 Hz, 2H), 7.08 (s, 4H), 7.06 (d, J =8.2 Hz, 2H), 6.77 (d, J =7.9 Hz, 2H), 5.51 (s, 1H), 2.08 (s, 12H).

Synthesis of TPM-based PIs Containing *tert*-Butyldimethylsiloxy Groups (PI-TPMOSiS)

Three PI-TPMOSiS (named as 6FDA-TPMOSi, ODPa-TPMOSi and BTDA-TPMOSi) were readily obtained by a post-modification reaction of PI-TPMOHs and *tert*-butyldimethylsilyl chloride (TBSCl) in the presence of imidazole as shown in Scheme 1. The synthesis of 6FDA-TPMOSi was taken as an example to illustrate the general synthetic route as follows. A reaction mixture of 6FDA-TPMOH (1.51 g, 2 mmol based on the repeating unit), TBSCl (0.60 g, 4 mmol), imidazole (0.27 g; 4 mmol) and 20 mL of DMF were added to a 50 mL round-bottom flask. The mixture was stirred at room temperature under N₂ for 24 h. After reaction, the resulted solution was poured into ethanol with stirring to precipitate the desired polymer resin, which was washed thoroughly with ethanol and dried in a vacuum oven at 100 °C. At last, the crude product dissolved in CHCl₃ were re-precipitation into ethanol to give 6FDA-TPMOSi resin.

The synthetic method of ODPa-TPMOSi resin and BTDA-TPMOSi resin was similar to 6FDA-TPMOSi resin, and only ODPa-TPMOH and BTDA-TPMOH resins was used to replace 6FDA-TPMOH resin in the process, respectively.

6FDA-TPMOSi. Yield: 95.4%; GPC data: M_n = 10.3×10^4 g·mol⁻¹, M_w = 19.7×10^4 g·mol⁻¹, \bar{D} =1.91; ¹H-NMR (600 MHz, CDCl₃, δ , ppm): 8.04 (d, J =8.0 Hz, 2H), 7.97 (s, 2H), 7.89 (d, J =7.3 Hz, 2H), 7.03 (d, J =8.4 Hz, 2H), 6.95 (d, J =6.0 Hz, 4H), 6.81 (d, J =8.4 Hz, 2H), 5.41 (s, 1H), 2.13 (s, 12H), 0.98 (s, 9H), 0.21 (s, 6H).

ODPA-TPMOSi. Yield: 95.7%; GPC data: M_n = 4.74×10^4 g·mol⁻¹, M_w = 11.0×10^4 g·mol⁻¹, \bar{D} =2.32; ¹H-NMR (600 MHz, CDCl₃, δ , ppm): 8.01 (d, J =8.1 Hz, 2H), 7.56 (s, 2H), 7.50 (d, J =8.1 Hz, 2H), 7.03 (d, J =8.4 Hz, 2H), 6.93 (s, 4H), 6.80 (d, J =8.4

Hz, 2H), 5.40 (s, 1H), 2.12 (s, 12H), 0.98 (s, 9H), 0.21 (s, 6H).

BTDA-TPMOSi. Yield: 93.8%; GPC data: M_n = 7.80×10^4 g·mol⁻¹, M_w = 22.7×10^4 g·mol⁻¹, \bar{D} =2.92; ¹H-NMR (600 MHz, CDCl₃, δ , ppm): 8.26 (s, 2H), 8.11 (q, J =8.2 Hz, 4H), 7.05 (d, J =8.5 Hz, 2H), 6.97 (s, 4H), 6.82 (d, J =8.4 Hz, 2H), 5.43 (s, 1H), 2.14 (s, 12H), 0.99 (s, 9H), 0.22 (s, 6H).

Preparation of PI Films

The obtained PI resins were dissolved in DMAc to afford a 10 wt% solution. The obtained homogeneous PI solution was smeared onto a horizontal clean glass plate, and then was dried under vacuum for 12 h at 50 °C to remove bubble and form a semi-dry film, and for additional 3 h at 100 °C, 3 h at 150 °C and 2 h at 200 °C to thoroughly remove the residual DMAc solvent. After cooling down to room temperature, PI film was stripped by immersing the glass plate in water.

RESULTS AND DISCUSSION

Synthesis and Characterization

The TPM-based diamine monomer containing a hydroxyl group (TPMOH) was successfully synthesized through a condensation reaction of *p*-hydroxybenzaldehyde and 2,6-dimethylaniline in the presence of HCl as the catalyst (Scheme S1 in ESI). The structure of TPMOH was well proved by ¹H-NMR spectrum (Fig. S1 in ESI). Specifically, the single-peak signals at 9.11, 4.98, 4.34 and 1.99 ppm attribute to the hydroxyl proton, methyldiylne proton of TPM core, amine protons and methyl protons, respectively. Furthermore, the integrals of all proton peaks are observed to be in good agreement with the theoretical values.

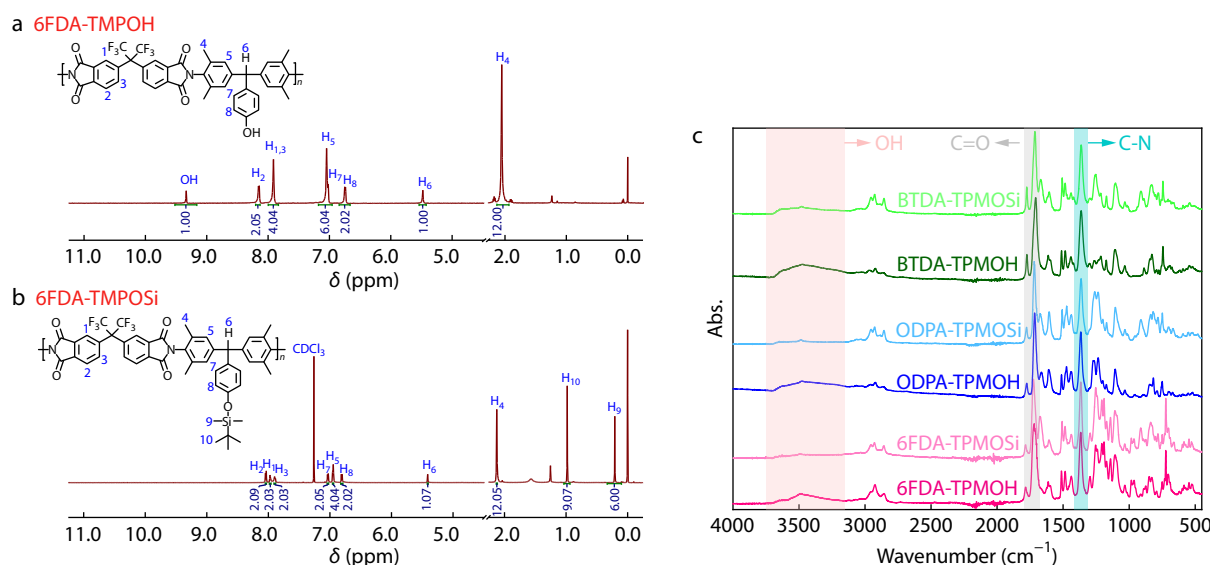
The TPM-based PIs containing hydroxyl groups (namely PI-TPMOHs, including 6FDA-TPMOH, ODPa-TPMOH and BTDA-TPMOH) were prepared *via* a one-step polymerization of a diamine, TPMOH, and three commercially available dianhydrides, 6FDA, ODPa and BTDA. The resulting PI-TPMOHs show high M_n of 4.68×10^4 – 10.8×10^4 g·mol⁻¹ with a polydispersity index of 2.07–2.75 (Table S1 in ESI). Based on successful preparation of the high molecular weight PI-TPMOHs, a simple and efficient silicon etherification reaction of PI-TPMOHs with TBSCl was employed to prepare TPM-based PIs containing TBS side-groups (namely PI-TPMOSiS, including 6FDA-TPMOSi, ODPa-TPMOSi and BTDA-TPMOSi). The post-polymerization modification on PI-TPMOHs mildly proceeded at room temperature to obtain the modified PI-TPMOSi resins. All OH groups in PI-TPMOHs almost completely switch to O-TBS groups, which was proved by the ¹H-NMR and IR spectra. The obtained PI-TPMOSi resins still possess high or even higher M_n of 4.74×10^4 – 10.3×10^4 g·mol⁻¹ with a polydispersity index of 1.93–2.92 (Table 1), indicating that the polymer backbone is not broken during the post-polymerization modification and allows it to prepare a flexible PI film.

The ¹H-NMR spectra of 6FDA-TPMOH (Fig. 1a) and 6FDA-TPMOSi (Fig. 1b) were used as the examples to prove the correct structure of three PI-TPMOHs and three PI-TPMOSiS. The ¹H-NMR spectrum of 6FDA-TPMOH shows the singlet proton signals at 9.33, 5.48 and 2.05 ppm corresponding to the proton of hydroxyl proton, methyldiylne proton of TPM core and methyl protons, respectively (Fig. 1a). The aromatic protons are present at 6.70–8.40 ppm with the precise integral ratio, indicating the 6FDA-TPMOH is successful synthesis *via* a one-

Table 1 Thermal and mechanical properties of the synthesized PI films.

PIs	$T_{5\%}$ ^a (°C)	$T_{10\%}$ ^a (°C)	R_w ^b (%)	T_g ^c (°C)	T_S ^d (MPa)	T_M ^d (GPa)	E_b ^d (%)
6FDA-TPMOH	477	514	68.8	346	—	—	—
6FDA-TPMOSi	501	530	70.1	314	71.6	1.42	9.7
ODPA-TPMOH	481	505	54.6	350	—	—	—
ODPA-TPMOSi	480	519	59.0	327	76.0	1.52	14.3
BTDA-TPMOH	476	513	63.8	386	—	—	—
BTDA-TPMOSi	492	518	64.7	351	71.0	1.35	18.3

^a The temperatures at 5% and 10% weight loss measured by TGA with 10 °C·min⁻¹ under N₂ flow; ^b Residual weight percentages at 800 °C under N₂ flow; ^c Measured by DSC with 40 °C·min⁻¹; ^d T_S : tensile strength; T_M : tensile modulus; E_b : elongation at break.

**Fig. 1** ¹H-NMR spectra of (a) 6FDA-TPMOH and (b) 6FDA-TPMOSi; (c) FTIR spectra of the synthesized PI films.

step, high-temperature solution polycondensation procedure. After the post-modification reaction of 6FDA-TPMOH, we find that the proton signal of OH disappear in the ¹H-NMR spectrum of 6FDA-TPMOSi, whereas two additional singlet proton signals appear at 0.21 (methyl protons of TBS group) and 0.98 ppm (*tert*-butyl protons of TBS group) with the precise integral ratio, due to the complete conversion (Fig. 1b). Similarly, successful synthesis of other two PI-TMPOHs (Figs. S2 and S3 in ESI) and PI-TMPOSis (Figs. S4 and S5 in ESI) was also proved by the ¹H-NMR spectra.

The structural confirmation of the synthesized PIs was also accomplished by FTIR spectra (Fig. 1c). All FTIR spectra of both series of PI films show the characteristic imide absorption bands at 1774–1784 cm⁻¹ (asymmetrical C=O), 1707–1725 cm⁻¹ (symmetrical C=O) and 1363–1366 cm⁻¹ (C–N). Besides, the disappearance of OH absorption broad band (Fig. 2) and blue-shift of the symmetrical C=O absorption band (Fig. S6 in ESI) are observed in the FTIR spectra of PI-TPMOSi films, indicating the successful synthesis of PI-TMPOSis by the post-modification on PI-TPMOHs.

Thermal and Mechanical Properties

Thermal properties of the synthesized PI films were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 2), and the results are summarized in Table 1. As shown in Fig. 2(a), the temperatures at 5% and 10% weight loss ($T_{d5\%}$ and $T_{d10\%}$) of three PI-TPMOH films are in the range of 476–481 and 505–514 °C, respectively. Meanwhile, PI-

TPMOH films show the high residual weight percentages (R_w) at 800 °C in N₂ of 54.6%–68.8%. Compared with the PI-TPMOH films, the $T_{d5\%}$ and $T_{d10\%}$ of three PI-TPMOSi films increase instead of decrease, which are increased to 480–501 and 518–530 °C, respectively. And the R_w at 800 °C in N₂ of PI-TPMOSi films also raise to 59.0%–70.1%. The higher heat resistance of PI-TPMOSi films is ascribed to the complete conversion to O-TBS groups from OH groups, which are more susceptible to thermal degradation.^[35]

Three PI-TPMOHs show high glass transition temperature (T_g) values of 346–386 °C measured by DSC (Fig. 2b), because OH groups in PI-TPMOH chains possess the strong intermolecular interaction by hydrogen bonding. For PI-TPMOSi, it is observed that their T_g values decrease slightly, due to the larger free volume associated with O-TBS groups and the reduced intermolecular attraction forces (hydrogen bonding) in PI-TPMOSi chains.^[36] Although the T_g values is reduced by the introduction of TBS group, the modified PI-TPMOSi films exhibit relatively high T_g values of 314–351 °C. The T_g values of both series of PI films are found to follow the order: 6FDA-based PI ≈ ODPA-based PI < BTDA-based PI, which basically consists with the rigidity of the dianhydride moieties. Additionally, $T_{d10\%}$ and T_g of the modified PI-TPMOSis in this study are higher than those of similar ref-PIs derived from analogue TPM derivative without OH group^[37,38] or with the pendant bulky side-groups^[25,39–42] and some ref-aromatic PI with the pendant bulky side-groups.^[26,43–45]

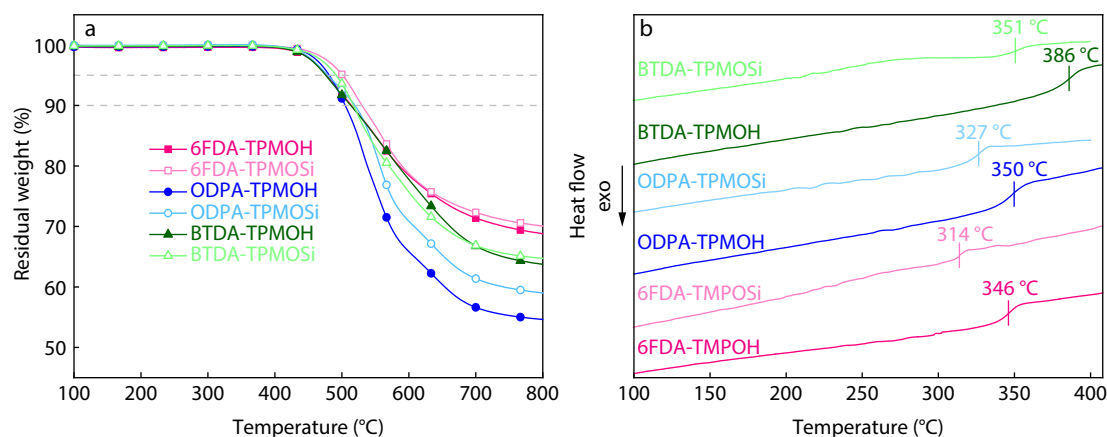


Fig. 2 (a) TGA and (b) DSC curves of the synthesized PI films.

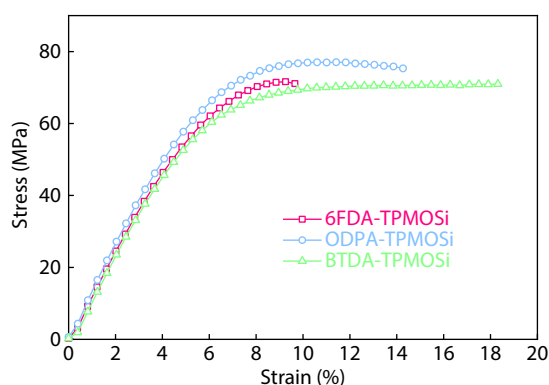


Fig. 3 Stress-strain curves of the modified PI-TPMOSi films.

Three modified PI-TPMOSis afforded good-quality films, and their mechanical properties were measured by tensile tests (Fig. 3). Three modified PI-TPMOSi films show tensile strength (T_s) of 71.0–76.0 MPa, tensile modulus (T_M) of 1.35–1.52 GPa, and elongation at break (E_b) of 9.7%–18.3%, which confirmed the successful preparation of high-molecular weight PI-TPMOSis via a simple post-modification reaction of PI-TPMOH.

Optical Properties

UV-Vis transmission spectra of the modified PI-TPMOSi films and

the precursor PI-TPMOH films for comparison were recorded (Fig. 4a) and the data, including cut-off wavelength (λ_0) and the optical transparency at 400 nm (T_{400}), are summarized in Table 2. Due to the formation of additional intermolecular hydrogen bonds by OH groups in PI-TPMOHs with the adjacent polymer chains, three PI-TPMOH films are still yellow in color (Fig. 4b). The λ_0 and T_{400} values of PI-TPMOH films are 311–367 nm and 45.3%–68.8%, respectively (Table 2). After post-modification reaction, PI-TPMOSi films demonstrate lighter color (Fig. 4b) and the improved optical transparency with the lower λ_0 values of 306–359 nm and higher T_{400} values of 75.4%–81.6% (Table 2), which exceed those of the corresponding PI-TPMOH films. The improved optical transparency of PI-TPMOSi films could be attributed to the effects of O-TBS group that replaces the OH groups on breaking the hydrogen bonds and reducing the packing density and intermolecular interactions. The interchain distance of PIs were calculated from XRD diffraction patterns (Fig. 5) according to Bragg equation.^[46] The broad XRD peaks indicate that all synthesized PI films present amorphous phases. Three PI-TPMOSi films display the larger interchain distance (6.15–6.20 Å, Table 2) compared with their corresponding precursor PI-TPMOH films (5.99–6.06 Å, Table 2).

Dielectric Properties and Water Absorption

The dielectric properties (Fig. 6), including dielectric constant (D_k) and dissipation factor (D_f), and water absorption of PI-

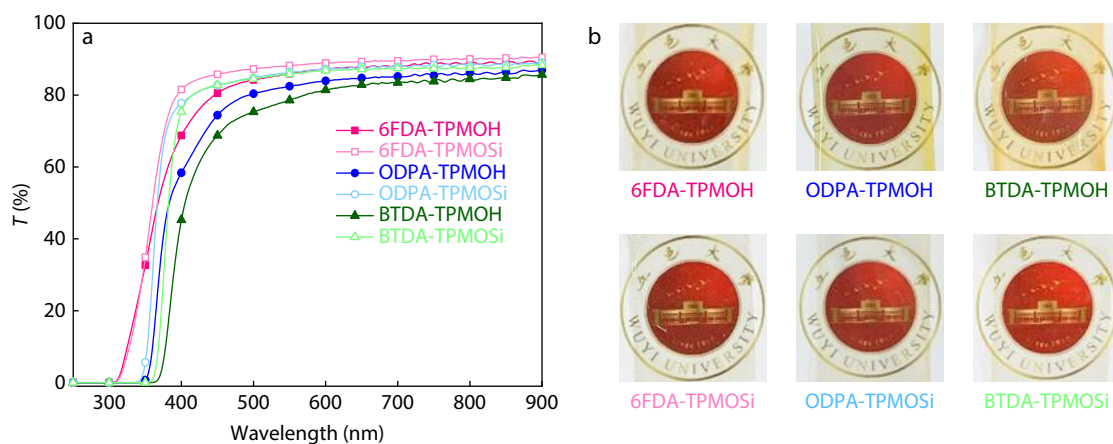
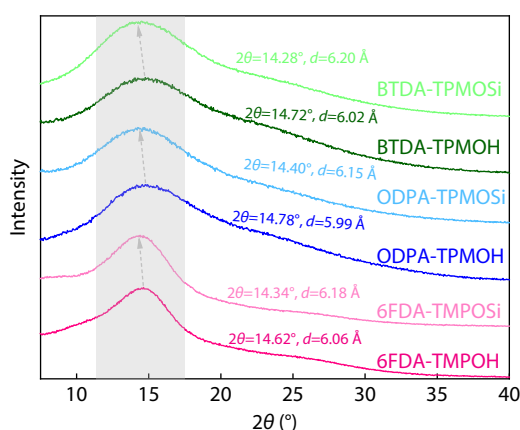


Fig. 4 (a) UV-Vis transmission spectra and (b) the photographs of the synthesized PI films, the thickness of the synthesized PI films of about 25 μm .

Table 2 Optical and dielectric properties, and water absorption of the synthesized PI films.

PIs	λ_0^a (nm)	T_{400}^a (%)	$2\theta^b$ (°)	d^b (Å)	D_k^c (1 MHz)	D_f^c (1 MHz)	W_a^d (%)
6FDA-TPMOH	311	68.8	14.62	6.06	4.11	0.00159	3.11
6FDA-TPMOSi	306	81.6	14.34	6.18	2.61	0.00125	0.51
ODPA-TPMOH	350	58.4	14.78	5.99	4.24	0.00235	3.36
ODPA-TPMOSi	342	77.7	14.40	6.15	2.85	0.00135	0.95
BTDA-TPMOH	367	45.3	14.72	6.02	4.40	0.00201	3.22
BTDA-TPMOSi	359	75.4	14.28	6.20	2.92	0.00171	1.19

^a λ_0 : cut-off wavelength; T_{400} : transmittances at 400 nm, the thickness of about 25 μm ; ^b 2θ : broad peaks center; d : the largest interlayer distance according to the Bragg equation; ^c Dielectric properties measured by the capacitance at 1 MHz; ^d W_a : Water absorption.

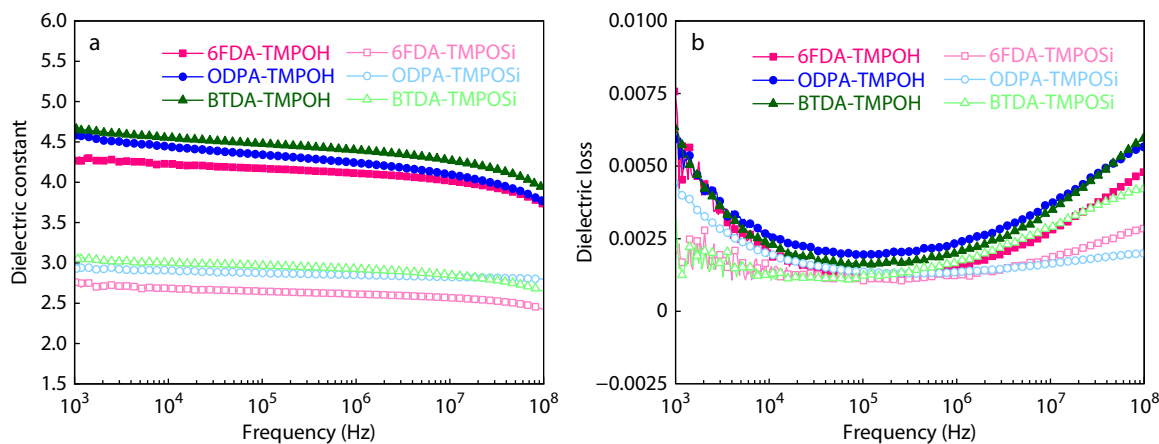
**Fig. 5** XRD profiles of the synthesized PI films.

TPMOSi films and the precursor PI-TPMOH films for comparison were measured, and the results are summarized in Table 2. Due to the existence of polar OH groups in PI-TPMOH chains, the precursor PI-TPMOH films show relatively higher D_k and D_f

values in the range of 4.11–4.40 and 0.00159–0.00235 at 1 MHz, respectively. As expected, the D_k and D_f values of the modified PI-TPMOSi films are significantly decreased to 2.61–2.92 and 0.00125–0.00171 at 1 MHz, respectively. The improved dielectric properties of PI-TPMOSi films could mainly be attributed to the bulky non-polar TBS groups that replace the OH groups in the polymer chains. The bulky non-polar TBS groups are expected to reduce the efficiency of polymer chain packing and eliminate of hydrogen bonding after conversion of OH groups, which are conducive to decreasing D_k and D_f values. On the other hand, the lower water absorption (W_a) of PI-TPMOSi films is also positive factor for decreasing D_k and D_f values. Three PI-TPMOSi films display a lower W_a in the range of 0.51%–1.19% compared with those of their corresponding precursor PI-TPMOH films in the range of 3.11%–3.36%.

Solubility

The dissolution behavior of the synthesized PIs in different solvents was tested and the results are listed in Table 3. It can be found that the precursor PI-TPMOHs possess better solubility in strong polar solvents (such as DMSO, DMF, DMAc and NMP). The good solubility in strong polar solvents of these PI-TPMOHs

**Fig. 6** (a) Dielectric constant and (b) dissipation factor of the synthesized PI films versus frequency.**Table 3** Solubility behavior of the synthesized PIs.^a

PIs	DMSO	DMF	DMAc	NMP	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
6FDA-TPMOH	++	++	++	++	++	±	±	++
6FDA-TPMOSi	+	++	++	++	++	++	++	++
ODPA-TPMOH	++	++	++	++	++	–	–	–
ODPA-TPMOSi	+	++	++	++	++	++	++	++
BTDA-TPMOH	++	++	++	++	±	–	–	–
BTDA-TPMOSi	+	++	++	++	++	++	±	±

^a Qualitative solubility was tested with 10 mg of a sample in 1 mL of solvent; ++, soluble at room temperature; +, soluble on heating; ±, partially soluble or swelling on heating; –, insoluble even on heating.

is due to the synergetic effects of the pendent phenyl moieties as well as the polar OH groups. However, due to the large polarity of OH groups in PI-TPMOH chains, PI-TPMOHs show poor solubility in low polar or non-polar solvents (such as CHCl_3 , CH_2Cl_2 and Acetone) according to the principle of similar compatibility.^[47] PI-TPMOSi display improved solubility in low polar or non-polar solvents (such as THF, CHCl_3 , CH_2Cl_2 and acetone) at room temperature. Meanwhile, the modified PI-TPMOSi maintain the good solubility in strong polar solvents except for DMSO. The enhanced solubility in low polar or non-polar solvents is mainly attributed to the introduction of the bulky and non-polar TBS groups, which reduce the packing density.^[26,46] The poorer solubility in DMSO with the strong polarity of PI-TPMOSi is mainly attributed to the greater dissimilarity of polarity between DMSO and the non-polar TPS groups in PI-TPMOSi chains.^[26]

CONCLUSIONS

A family of new TPM-based PIs containing TBS side-groups (PI-TPMOSi) were synthesized by the direct structural modification of TPM-based PIs containing OH groups (PI-TPMOHs). PI-TPMOSi films still maintain comparatively high thermal stabilities ($T_{d5\%} > 480^\circ\text{C}$ and $T_g > 314^\circ\text{C}$) and good mechanical properties ($T_g > 71.0\text{ MPa}$ and $E_b > 9.7\%$). The introduction of TBS groups into PI-TPMOSi chains reduce the packing density and CTCs formation to simultaneously improve the optical, dielectric and solubility properties of PI-TPMOSi films. PI-TPMOSi films show the excellently increased optical transparency (75.4%–81.6% at 400 nm), the decreased D_k and D_f values (2.61–2.92 and 0.00125–0.00171 at 1 kHz, respectively) and the improved solubility in low- or non-polar solvents (THF, CHCl_3 , CH_2Cl_2 and acetone) at room temperature. In summary, the incorporation of TBS groups into TPM-based PI chains by the post-polymerization modification can be used as a simple and effective way to simultaneously improve the optical, dielectric and solubility properties and maintain high thermostability of TPM-based PI films, which provided new guides to design and prepare the multifunctional PI films with outstanding comprehensive properties.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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