Highly solvent-stable polyimide ultrafine fibrous membranes fabricated by a novel ultraviolet-assisted electrospinning technique via organo-soluble intrinsically negative photosensitive varnishes

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Abstract. A novel fabrication methodology for polyimide (PI) UFM s based on soluble PIs with high solvent durability was developed. As fiber-forming agents, a series of intrinsically negative photosensitive polyimides (PSPIs) with solubility in organic solvents were synthesized by the one-step thermal polymerization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) with three *ortho*-alkyl-substituted diamine monomers, namely, 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane (TMDA, for PI-1), 3,3'-dimethyl-5,5'-diethyl-4,4'-diaminodiphenylmethane (DMDEDA, for PI-2), and 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (TEMDA, for PI-3), respectively. Electrospun UFM s were prepared by both traditional electrospinning (PI UFM s) and the novel ultraviolet-assisted electrospinning (UVAES) method (PI-UV UFM s). The effects of the fabrication method on the physical and chemical properties of the electrospun UFM s were investigated systematically. High-efficiency photoinduced crosslinking reactions under ultraviolet (UV) radiation provided the PI-UV UFM s with considerable thermal dimensional stability with the 5% weight loss temperature over 440 °C. Meanwhile, the derived PI-UV UFM s showed excellent resistance against a polar aprotic solvent, *N,N*-dimethylacetamide (DMAc).

Keywords: polymer membranes, photosensitive polyimides, electrospinning, thermal stability, solvent resistance

1. Introduction

Electrospinning is one of the most versatile and convenient technologies for preparing polymeric ultrafine fibrous membranes (UFMs) based on fibers with diameters on the scale from sub-nanometres to micrometers [1]. The electrospinning process, which involves the application of an electrostatic force, can produce continuous fibers with both high specific surface areas and ultralow fiber diameters [2]. In recent decades, the electrospinning principle has been fully demonstrated, and new applications have gradually emerged in various areas, including fibrous membranes for filtration, biomedical tissues,

nanotube templates, sponges, fiber-reinforced composites, responsive fibers, actuators, and flexible electronics [3–9]. Owing to the physical nature of the main fiber-shaping mechanism, the diameter and surface properties of electrospun ultrafine fibers can be easily adjusted by controlling apparatus parameters such as electric field intensity, spinneret-to-collector distance, and injector flux [10]. In addition, the morphological quality of the electrospun fibers can be further influenced by the properties of the polymer solution, such as viscosity, conductivity, polymer molecular weight and distribution, and surface tension. Moreover, new spinning strategies such as

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coaxial electrospinning, multi-spinneret spinning, and microfluid spinning can be applied to build up fibrous materials with various morphologies, including core-shell structures and vertically or horizontally aligned fibers [11–13]. A variety of raw polymeric materials can be subjected to electrospinning; however, commonly used polymeric spinning sources, such as polystyrene (PS), polyvinyl alcohol (PVA), and polyurethane (PU), have disadvantages such as poor heat tolerance and poor chemical stability, which have limited their applications tremendously [14]. To date, considerable attention has been paid to the fabrication of UFM s using a special series of aromatic heterocyclic polymers, namely, polyimides (PIs) [15]. Nonwoven fibrous PI materials with one-dimensional structures have been considered attractive for several decades owing to their favorable advantages of high specific surface areas, ultralow fiber diameters, high environmental stability, and good mechanical properties. Such materials have been used in filtration, oil/water separation, clarification, and other high-tech applications [16–22]. Typically, PI UFM s have been fabricated via electrospinning using either PI precursors or soluble PI resins. In the precursor electrospinning approach, the use of precursors such as poly(amic ester) (PAE) or poly(amic acid) (PAA) requires the heat treatment of the accumulated fibers at temperatures over 300 °C to achieve conversion to PI by thermal cyclodehydration. The PI UFM s prepared by this process usually exhibit excellent mechanical properties and good chemical stability owing to a high imidization rate and the formation of a thermally crosslinked structure. However, the high-temperature process always causes severe yellowing of the fibers. Moreover, common structural damage, such as microvoid-like defects formed by the evaporation of the generated water by-products, combined with the fusion of fibers can extensively deteriorate the physical and chemical properties of PAA-derived PI UFM s [23–28]. The disadvantages for PAA-derived PI UFM s promote us to develop new approaches for producing PI UFM s. As a more advanced alternative, soluble PI electrospinning allows PI UFM s to be fabricated directly using pre-imidized PI solutions without subsequent high-temperature imidization treatment. Advantageously, this process has a lower energy cost, and the obtained fibers are paler in color with smooth surfaces. Nevertheless, there are limitations to this process because few soluble PI resins can be directly implemented

and the solvent resistance of the spun PI fibers is vastly degraded by the lack of an inter- or intra-molecular crosslinked structure; these disadvantages have impeded the development of UFM s based on soluble PI resins [29–32]. To obtain ultrafine fibers with both of enhanced environment stability and favorable morphologies, the development of new soluble PI resins and electrospinning techniques is imperative.

It has been clearly established that a crosslinked structure plays an important role in enhancing the solvent resistance of polymers [33, 34]. Among the variety of methodologies for fabricating polymeric materials with crosslinked structures, photoinduced crosslinking under ultraviolet (UV) irradiation is considered a suitable method for preparing electrospun UFM s with crosslinked topological structures. For instance, Zhu *et al.* [35] developed bio-based and photo-crosslinked electrospun antibacterial nanofibrous membranes with PVA and chitosan, and evaluated their applicability to air filtration. Meanwhile, Thielke *et al.* [36] used the thiol-ene reaction to modify electrospun polybutadiene fibers and simultaneous crosslinking under UV irradiation to obtain fibrous mats with superhydrophilic properties. Thus, photo-crosslinking reactions can be considered as a potential approach for improving the performance of materials based on ultrafine PI fibers. The high specific surface area and small diameter of the fibers produced by electrospinning should provide sufficient exposure to the UV irradiation source. Thus, both phase separation and the elongation of polymeric filaments could occur simultaneously with chemical crosslinking reactions to produce a highly crosslinked structure with enhanced environmental stability [37, 38].

Previously, we reported an early attempt to combine *in-situ* UV-induced crosslinking and electrospinning for fabricating PI UFM s with improved stability against organic solvents using 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and diamines with benzene substituents [39]. However, such UFM s suffered from deterioration in solvent resistance because of the increased free molecular volume by lateral bulk benzene side substituents. In the current work, the ultraviolet-assisted electrospinning (UVAES) technique was applied to photocurable PI solutions as the fiber-forming resources. For this purpose, a series of soluble intrinsically negative photosensitive polyimides (PSPIs) consisting of benzophenone (BP) and *ortho*-alkyl-substituted units were synthesized. These pre-imidized soluble PSPI resins

were developed in the 1980s and applied for photolithography for semiconductor fabrication [40–44]. The intrinsic PSPIs of this type are auto-photosensitive to UV radiation at the wavelength of 365 nm (i-line) without extra initiating additions. The obtained photo-patterns can maintain its high resolution even heated into high temperature, expressed benign thermal stability and photosensitivity [45–47]. Such PSPIs function via a negative mechanism, where the exposed area undergoes photoinduced crosslinking reactions and maintains the photo-pattern after development in organic solvents [48]. In this study, three different *ortho*-alkyl-substituted diamine monomers were used to synthesize PSPI resins, whose physicochemical properties were evaluated for subsequent electrospinning. Then, the three PSPI resins were electrospun into UFMs using conventional electrospinning and UVAES procedure. The influences of UV irradiation during electrospinning and such type of PSPI resins on the morphology, thermal properties, optical properties, and solvent resistance were investigated systematically.

2. Experimental

2.1. Materials

The dianhydride BTDA was purchased from Evonik Industries AG (Frankfurt, Germany) and dried under a vacuum at 180 °C for 10 hour before use. The diamine 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane (TMMDA) was purchased from POME Sci-tech Co. (Beijing, China), whereas the other two diamines, 3,3'-dimethyl-5,5'-diethyl-4,4'-diaminodiphenylmethane (DMDEDA) and 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (TEMDA), were obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). All the diamines were purified by recrystallization from absolute ethanol before use. The organic solvents *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich China, Shanghai, China) were distillation with calcium hydride (CaH₂) and phosphorus pentoxide (P₂O₅) (Sinopharm. Co. Ltd., Shanghai, China), respectively, and stored with 4 Å molecular sieves before use. All other commercially available reagents were used as received without further purification. The UV source (BILON Co. Ltd., Shanghai, China) is consisted of a high-pressure mercury lamp with an emission wavelength of 365 nm (i-line) and covered with a quartz cooling shell using water as the coolant. The electrospinning device (Yongkang Leye Co.,

Ltd., Beijing, China) had a drum with a fixed size (30 cm in length and 10 cm in diameter) and was covered with a layer of aluminum foil as a collector.

2.2. Synthesis of the intrinsic PSPI resins

The intrinsically negative PSPI resins with solubility in organic solvents were synthesized via the one-step thermal polycondensation of BTDA with aromatic diamines using isoquinoline, NMP, and toluene as the catalyst, solvent, and dehydrating agent, respectively. A typical procedure for synthesizing the PSPI resins is described here using PI-1 (BTDA-TMMDA) as an example. In a 1000 mL three-necked flask equipped with a mechanical stirrer and a Dean-Stark apparatus under a nitrogen atmosphere, TMMDA (25.4370 g, 100 mmol) was dissolved in NMP (226.7 g) to give a clear solution. Then, BTDA (32.2240 g, 100 mmol) was added to the mixture as well as an additional amount of NMP (100.0 g). Isoquinoline (0.5 g) was then added, and the mixture was stirred for 1 h under nitrogen. Subsequently, toluene (250 ml) was added and the mixture was heated to 180 °C for 3 h to complete the imidization reaction. During the heating process, the water generated by the reaction was continuously removed from the system at the temperature of 130–140 °C via its azeotrope with toluene and then collected in the Dean-Stark trap. The dehydration process proceeded for 5–6 h until no azeotrope was visually observed in the trap. After the completion of the reaction, the reaction system was cooled to room temperature. The obtained dark yellow viscous solution was slowly poured into a beaker containing an excess amount of ethanol to give a pale brown precipitate. The entire reaction process was conducted in a dark environment under a black cloth to prevent exposure to sunlight. The collected PI-1 resin was dried under vacuum at 80 °C for 24 h. Yield: 52.4 g, 97.0%. ¹H-NMR (DMSO-*d*₆, ppm): 8.31–8.18 (m, 6H), 7.16 (s, 4H), 3.91 (s, 2H), and 2.07 (s, 12H).

The other two PSPI resins were synthesized using similar methods with BTDA and the diamine DMDEDA for PI-2 (55.2 g, 97.0%) and TEMDA for PI-3 (57.9 g, 97.0%), respectively. In summary, the TMMDA-, DMDEDA-, and TEMDA-based PSPI resins were denoted as PI-1, PI-2, and PI-3, respectively.

PI-2. ¹H-NMR (DMSO-*d*₆, ppm): 8.32–8.19 (m, 6H), 7.23–7.18 (m, 4H), 3.99 (s, 2H), 2.40–2.38 (m, 4H), 2.06 (s, 6H), and 1.06–1.02 (m, 6H).

PI-3. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 8.32–8.20 (m, 6H), 7.24 (s, 4H), 4.04 (s, 2H), 2.38 (s, 8H), and 1.07–1.02 (m, 12H).

2.3. Fabrication of the PSPI ultrafine fibrous membranes

The UFM fabrication route is shown in Figure 1. Each synthesized PSPI resin was dissolved in DMAc at a solid content of 15 wt%. The PSPI solutions were filtered through a 0.50 μm Teflon filter to remove the undissolved contaminations and avoid the formation of obstructions during the spinning procedure. Each prepared PSPI solution was then poured into a 5 ml syringe equipped with a 21# stainless steel spinneret (0.5 mm inner diameter). The same parameters were used for both of the traditional electrospinning and UVAES procedures (applied voltage between syringe and collector: 15 kV, flow rate of pumping system: 0.1 ml/h, the distance between spinneret and rotary drum: 20 cm, collection speed: 5 rpm, clockwise rotation, and relative humidity: $30\pm 2\%$). The primary difference between these two methods was that the high-pressure mercury lamp (maximum wavelength: 365 nm) at a fixed temperature of $3-4^\circ\text{C}$ by the ice-water cooling was located 5 cm above the collector drum during the UVAES procedure. Continuous UV exposure was applied during the entire spinning process.

2.4. Characterization methods

The absolute viscosity of the synthesized PSPI resins was measured using a Brookfield DV-II+ Pro viscometer (Middleboro, USA). An Ubbelohde viscometer with 0.5 g/dl NMP solutions was used for determining the inherent viscosities of the resins at 25°C . A Shimadzu gel permeation chromatography (GPC) system (Kyoto, Japan) with NMP as the mobile phase (flow rate: 1.0 ml/min) was utilized for determining the weight-average molecular weight (M_w) and the number-weight molecular weight (M_n) of the PIs. The solubility of the synthesized resins

was determined as follows: 1.5 g of each PSPI resin was dissolved in 8.5 g of different test solvents (solid content: 15 wt%) and then allowed to stand for 24 h in black at room temperature. The solubility was divided into three levels: completely soluble (++), partly soluble (+), and insoluble (–). Complete solubility was defined as a homogeneous and clear solution in which no precipitation, gel formation, or phase separation was observed.

The chemical structures of the PSPI resins were confirmed by hydrogen nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy using a Bruker Avance II 400 spectrometer (Karlsruhe, Germany) with deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as the solvent at 400 MHz. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy using a Thermo Fisher Scientific Nicolet 6700 spectrometer (Waltham, USA) was used to evaluate the photochemical reaction mechanism and the functional group composition of the PI UFM. The crosslinking degree was calculated using the internal standard method according to Equation (1):

$$\text{Crosslinking degree} = \frac{\left(\frac{A_{1680}}{A_{1485}}\right)_{\text{PI}}}{\left(\frac{A_{1680}}{A_{1485}}\right)_{\text{PI-UV}}} \cdot 100 \quad (1)$$

where A_{1680} is the strength of the carbonyl group absorption in BTDA, whereas the A_{1485} is the absorption strength of $\text{C}=\text{C}$ in the benzene unit, which was used as the internal standard. The subscripts ‘PI’ and ‘PI-UV’ refer to the UFM. s prepared by traditional electrospinning and UVAES, respectively.

The photosensitivity of the derived PSPI was evaluated by an i-line (365 nm) photolithography procedure using a photolithographic machine (MA-6, SUSS MicroTec, Garching, Germany). The PI-1 solution (solid content: 10 wt%, viscosity: 3200 mPa·s) was spin-coated onto a 3 inch silicon wafer at the speed of 2000 rpm for 20 s and then dried on a hot plate at 70°C for 90 s. Then, the wafer was exposed to ultraviolet light with a wavelength of 365 nm (i-line) for 70 s using the photolithography machine. After exposure, the wafer was developed in pure *N,N*-dimethylformamide (DMF) for 3 min at room temperature. Then, the wafer was sprayed with butyl acetate for 30 s at room temperature. At last, the wafer was post-baked at 300°C for 30 min in nitrogen. The photolithography patterns of PI-1 were observed with the field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F, Tokyo, Japan).

Figure 1. The fabrication route for the PI and PI-UV UFM. s

The micro-morphologies of the obtained microfibers were observed by field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F, Tokyo, Japan) with an acceleration voltage of 10 kV. A thin layer of Pt/Pd was sputtered on the surface of the membranes. The Image-J software was used for the statistical analysis of the fiber diameters, and the average values were calculated from 100 single fibers. To determine the heat resistance characteristics of the UFM, Thermal gravimetric analysis (TGA) was conducted using a TA Instruments TGA Q50 analyzer (New Castle, USA) at the heating rate of 20 °C/min from 50 to 750 °C under nitrogen. The glass transition behavior of the UFM was evaluated using a Netzsch DSC 204 HP (Selb, Germany) differential scanning calorimetry (DSC) system at a heating rate of 10 °C/min up to 400 °C under nitrogen. The water contact angles (WCAs) of the PI fibers were measured using a Dataphysics OCA40 Micro automatic video microcontact angle measuring instrument (Stuttgart, Germany). For the WCA measurements, 5 µl of deionized water was dropped onto the flat surface of the fibrous membrane, and the static value was determined from the average of five measurements. The reflectance of each PI UFM was measured by ultraviolet-visible (UV-Vis) spectroscopy using a Hitachi U-3210 spectrophotometer (Tokyo, Japan) at room temperature. An X-rite Ci 7860 spectrophotometer (Grand Rapids, Michigan, USA) was used to determine the whiteness index (WI) of the PI UFM. The WI values were calculated using Equation (2):

$$WI = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (2)$$

where L^* is the lightness of the UFM, and a^* and b^* are the color parameters of the samples, respectively. The solvent resistance of the fabricated PI UFM was evaluated via immersion tests, as follows. Each UFM was cut to a size of 35 mm (length) by 25 mm (width) by 0.2 mm (thickness) and then gradually immersed in a glass vessel containing 50 ml of the

aprotic polar organic solvent DMAc. Once completely submerged, the UFM was allowed to soak for 30 s. Subsequently, the solvent resistance of the UFM was evaluated based on both SEM images and visual observations.

3. Results and discussion

3.1. Polymer synthesis

Three organic-soluble PSPI resins were synthesized by a one-step direct polycondensation reaction between BTDA and various *ortho*-alkyl-substituted diamine monomers, as shown in Figure 2. The designed PI structures are expected to possess good solubility, high thermal stability, and auto-photosensitivity owing to the combination of an aromatic heterocyclic ring structure and active carbonyl groups.

The molecular weights and inherent viscosities of the PI resins are summarized in Table 1. The prepared PSPI resins all had high M_n values of 50 639–106 604 g/mol with polydispersity indices (PDI; M_w/M_n) of 1.77–1.98, indicating that the resins possessed both a relatively high polymerization degree and a narrow distribution. The inherent viscosities of the PI resins were in the range of 1.00–1.29 dl/g at room temperature (25 °C) in NMP (Table 1), which suggested moderate to high molecular weights of the PI resins.

Figure 2. Synthesis of the PI resins.

Table 1. Absolute molecular weight and solubility of the PSPIs.

PI	Dianhydride	Diamine	$[\eta]_{inh}^a$ [dl/g]	Molecular weight [g/mol]		
				M_n	M_w	PDI
PI-1	BTDA	TMDA	1.00	50 639	89 827	1.77
PI-2	BTDA	DMDEDA	1.29	106 604	203 937	1.91
PI-3	BTDA	TEMDA	1.18	86 247	170 910	1.98

^aInherent viscosities measured with a PI resin at a concentration of 0.5 g/dl in NMP at 25 °C.

Solution electrospinning is an important method for the fabrication of PI UFM, in which the solubility of PI resins is a crucial factor. High solubility is usually ascribed to the strong interactions between the polymer and solvent, which allowing benign swelling and disentanglement of the polymer chains. Sufficiently high solubility in organic solvents is a necessary requirement for PIs to achieve ultrafine fibers with suitable morphologies and adequate optical properties. The solubility was largely controlled by the molecular weight and the molecular structure of the PI resins. Herein, the solubility of the negative PSPI resins was evaluated using seven typical solvents, including the polar solvents DMAc, DMF, and NMP as well as the less polar solvents, cyclopentanone (CPA), tetrahydrofuran (THF), CHCl_3 , and γ -butyrolactone (GBL), as shown in Table 2. All the PSPI resins exhibited good solubility in the polar aprotic solvents (NMP, DMF, and DMAc), with clear and homogeneous solutions obtained at a solid content of 15% at room temperature for 24 h. The resins were also completely or mostly soluble in CPA and THF. The PI resins only showed inferior solubility in CHCl_3 and GBL.

The production of UFM with good morphologies and reasonable fiber diameter distributions was highly dependent on the balance between Coulombic forces, surface tension, and the viscoelasticity of the polymers. To obtain relatively thin and uniformly distributed fibers required the determination of appropriate spinning parameters for the PI fiber-forming agents, such as solvent solubility, viscosity, concentration, spinneret-collector distance, and spinning voltage. Suitable solvents and solid contents for the PIs should be determined for the fabrication of the UFM. When considering the solution properties of the fiber-forming agents, the solid content and viscosity of the polymer solution should be investigated comprehensively. Suitable solution properties favor the fabrication of ultrafine fibers with good surface morphologies and appropriate diameters. The high

Figure 3. Relationship between absolute viscosities and solid contents of PI resins.

viscosity of the polymer solution can result in the formation of excessively thick fibers. On the contrary, if the concentration is too low, the rapid evaporation of the solution and weak entanglement between the molecular chains make it difficult for the PI resins to overcome the Rayleigh instability from the electric field, which can lead to fibers with bead defects. As shown in Figure 3, an apparent increase in the viscosity occurred as the solid content of the PI solution increased. This is because the mobility of the polymer chains was reduced by chain entanglement at higher solution concentration, which impeded the re-ordering of the molecular chains and thus increased the solution viscosity. Furthermore, an obvious change in the slope of the plots was observed when the solid content increased from 15 to 20 wt %, which corresponds to the beginning of cohesion between the PI molecular chains. Owing to the preliminary entanglement and the interactions between molecular chains, the jetted polymer could maintain a sufficient tension to protect its structure from damage when passing through the high-voltage electric field. It has been demonstrated that a solid content near where the change in slope was observed will provide polymer jets with a suitable viscosity for electrospinning thin and bead-free ultrafine

Table 2. Solubility in organic solvents of the PSPIs.

PI	Dianhydride	Diamine	Solvent ^a						
			NMP	DMAc	DMF	GBL	CPA	THF	CHCl_3
PI-1	BTDA	TMDMA	++ ^b	++	++	–	++	++	–
PI-2	BTDA	DMDEDA	++	++	++	–	++	++	+
PI-3	BTDA	TEMDA	++	++	++	–	+	++	–

^aGBL: γ -butyrolactone; CPA: cyclopentanone; THF: tetrahydrofuran;

^b: ++: Wholly soluble at room temperature, +: Partially soluble, –: Insoluble.

fibers. Hence, for UFM fabrication, a solid content of 15 wt% was used for all three PI solutions as fiber-forming agents.

3.2. Structure and photochemical mechanism of the UFM

The soluble intrinsically negative PSPI resins (PI-1–PI-3) were fabricated into UFM by traditional electrospinning and UVAES procedure. The chemical structures of the PI UFM were confirmed using ATR-FTIR and ^1H -NMR spectroscopy, respectively. In the ATR-FTIR spectra shown in Figure 4, the absorption peaks at 2980 and 2920 cm^{-1} correspond to the asymmetric and symmetric vibrations of the methyl ($-\text{CH}_3$) groups in the polymers. Furthermore,

Figure 4. ATR-FTIR spectra of PI and PI-UV UFM.

the absorption peak at 2870 cm^{-1} , which corresponds to the symmetric vibration of $-\text{CH}_2-$ structures, confirmed the existence of ethyl ($-\text{CH}_2\text{CH}_3$) groups in PI-2 and PI-3. The characteristic absorption peaks at 1780 and 1720 cm^{-1} are attributed to the asymmetric and symmetric stretching vibration of carbonyl moieties, respectively. In addition, the absorption peak at 1378 cm^{-1} , which corresponds to C–N–C stretching vibrations, provides evidence for successful imide formation.

More importantly, the intensity of the absorption peak at 1680 cm^{-1} , which represents the ketone carbonyl group of BTDA units in PI UFM (labelled as pentagram in Figure 4), showed an apparent decrease in all of the PI-UV UFM, as can be illustrated in Figure 5. This phenomenon provides sufficient evidence for the occurrence of photoinduced crosslinking. As shown in Figure 5b, this mechanism of the photochemical crosslinking reaction for auto-sensitive PSPI has been well established [40–44]. Following UV irradiation, the activated triplet ketone carbonyl can abstract a hydrogen from an adjacent *ortho*-substituted alkyl group in the diamine moiety, leading to the formation of free radicals that subsequently generate a crosslinked structure by inter/intramolecular reactions of the polymer chains. This mechanism was confirmed by monitoring the absorption intensity of the carbonyl group from the benzophenone moiety (Figure 5b). According to Equation (1), the calculated crosslinking degree is 99.1% for

Figure 5. (a) ATR-FTIR spectra of PI and PI-UV UFM in the range of 1500 to 1800 cm^{-1} and (b) photo-crosslinking mechanism of the intrinsic negative PSPIs.

PI-1(UV), 68.6% for PI-2(UV), and 75.7% for PI-3(UV), respectively. Thus, the UV exposure in electrospinning process indeed induced the occurrence of the photo-crosslinking reaction of the PSPIs although the exposure time was quite short, which is on one hand due to high sensitivity of the PSPI to i-line exposure, and on the other hand due to the high specific surface area and ultrathin fiber diameters of the thin PSPI fibers. This offered sufficient contact between the electrospun microfibers under UV irradiation during the transitory time from the spinneret to the collector. In practical UVAES fabrication, the PI molecular chains in the charged micro-jet are expected to be in a partially extended state because of the induced plastic stretching; therefore, the majority of photochemical reactions are likely to result in intermolecularly crosslinked structures, although the occurrence of intra-molecular crosslinking cannot be neglected. The realization of effective photopolymerization during the electrospinning process confirms the UVAES procedure as a practical method for fabricating PI UFMs with *in-situ* crosslinked structures.

To further understand the photosensitivity of the PI resin solution, the photolithography behaviors of the typical PI-1 resin solution were evaluated and the patterns were shown in Figure 6. It can be clearly observed that the PI-1 solution exhibited good photosensitivity to i-line (365 nm) UV light. The photolithography patterns with the resolution around 20 μm were achieved. The good photosensitivity of the current PI solution made it possible to fabricate high quality PI UFMs vis UVAES procedure.

The good solubility of the PI UFM in polar solvents DMSO made it possible to confirm the chemical

structures of the PI UFM with NMR measurements. In the ^1H -NMR spectra of the polymers, all of the hydrogen proton signals were in good accordance with the designed molecular structures. The absorptions of the aromatic protons in the PIs all appeared at the farthest downfield (chemical shift: 7.0~8.5 ppm) in the spectra, owing to the strong electron-withdrawing carbonyl groups in the dianhydride moiety. On the contrary, the aliphatic protons, such as the ones in $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_3$, or $-\text{CH}_3$ showed absorptions at the farthest upfield (chemical shift: 1.0~4.2 ppm) in the spectra. These results demonstrate that the target PSPI resins were successfully synthesized and fabricated into PI UFM.

3.3. Morphology of the ultrafine fibers

Representative morphologies of the fabricated PI UFM are shown in Figure 7. Highly random aligned microfibers with smooth surfaces were obtained by both of normal electrospinning and UVAES procedures. The fiber diameters could be further controlled by adjusting parameters such as the injection speed, electric field intensity, and ejection distance. No pin-hole-like defects or bead structures were observed in the SEM images of the fibers, which can be explained by the balance achieved between the surface tension, viscoelastic force, and electrostatic repulsion in the spinning system. When a suitable solid content of a PI resin is used, the viscoelastic force, as the prominent force of the jet, aids in the formation of bead-free fibers with good surface appearance. The UFM consist of loose porous multilayers with net-shaped structures formed from fibers with a uniform diameter distribution. The fiber diameters increased from 249 to 426 nm as the content of alkyl side chains

Figure 6. Patterns of the PI-1 by i-line photolithography procedure. (a) Top-sectional view, (b) cross-sectional view.

Figure 7. FE-SEM images of PI and PI-UV UFMs. (a) PI UFMs; (b) PI-UV UFMs.

increased from PI-1 to PI-3 (Figure 7a). Although the PI-2 resin had the highest viscosity, the diameter of the PI-2 fibers was lower than that of the PI-3 fibers. Furthermore, the fibers of PI-2 and PI-3 showed uniform diameter distributions, whereas the diameter distribution of PI-1 was broader. These phenomena showed that unlike ordinarily spun PI polymers, for this type of soluble intrinsically PSPI, the diameters of the spun fibers were not only affected by the viscosity of the polymers but also by the chemical structure of the PI resin. Moreover, the uniformity coefficient of the diameter of the spun fibers was mainly controlled by the viscosity of the PI resins. UV irradiation had no obvious influence on the surface morphology of the PI fibers, with the exception of a slight increase in the average diameter (Figure 7b).

This increase can be attributed to the enhancement in molecular chain entanglement among the PI-UV UFMs caused by photocrosslinking, which increased the surface tension of the spray jet and led to a larger diameter.

3.4. Thermal properties of the PI UFMs

The thermal properties of the PI and PI-UV UFMs were investigated by TGA and DSC, respectively and the data are summarized in Table 3. According to the TGA plots shown in Figure 8a, the UFMs prepared by both of traditional electrospinning and UVAES procedures all exhibited good heat resistance with thermal decomposition temperatures ($T_{5\%}$, corresponding to the temperature at which 5% weight loss occurs) in the range of 443.8–481.3 °C and residual

Table 3. Thermal properties of PI UFMs.

	T_g^a [°C]	$T_{5\%}^b$ [°C]	$T_{10\%}^b$ [°C]	R_{w740}^c [%]
PI-1	320.5	481.3	506.4	57.6
PI-1(UV)	null	448.9	499.1	56.7
PI-2	304.8	453.9	489.1	60.2
PI-2(UV)	null	443.8	486.6	59.9
PI-3	285.4	471.5	494.1	59.4
PI-3(UV)	null	463.7	498.9	57.4

^a T_g : Glass transition temperature measured by DSC;

^b $T_{5\%}$, $T_{10\%}$: Temperatures at 5 and 10% weight loss, respectively;

^c R_{w740} : Residual weight ratio at 740 °C in nitrogen.

weight ratios of 56.7~60.2 wt% at 740 °C. In addition, the TGA results revealed a slight decrease in the thermal stability of the UV-irradiated UFMs, as the $T_{5\%}$ values decreased slightly for the PI-UV UFMs, mainly because of a change in the molecular structure of the fibers caused by the transformation of benzophenone into benzhydrol, which is less thermally stable. Despite this slight deterioration, the thermal stability of the PI-UV UFMs remains sufficiently high for high-temperature applications because of the successful photoinduced crosslinking reaction.

The glass transition temperature (T_g) values of one polymer indicate its heat durability and reliability, which is also a critical indicator for the temperature range in which the current PI UFMs can be applied. Below T_g , PI UFMs are in a glassy state without obvious chain motions. Above T_g , the provided energy is sufficient to overcome intermolecular attraction, and the resulting chain motion breaks the fibrous structure and causes the deterioration of the mechanical properties of the UFMs. The T_g values of the PI UFMs, as determined by DSC curves shown in Figure 8b, were between 285.4~320.5 °C and showed

an obvious decrease as the amount of alkyl side chains in the diamine increased. This tendency can be ascribed to the increased number of alkyl branches occupying a larger molecular free volume and weakening the interactions between PI molecular chains. However, the T_g values of the PI-UV UFMs were not clearly observed in the investigated temperature range. This result indicates that the thermal movement of the molecular chains was effectively hindered by the photo-crosslinking reaction, thus providing the UV-exposed fibers with improved thermal dimensional stability.

3.5. Optical properties of the PI UFMs

The optical properties of the UFMs were investigated using UV-Vis spectroscopy, and WI measurements and the data are tabulated in Table 4. As shown in the UV-Vis spectra of the PI UFMs (Figure 9a), for both of conventionally spun and UVAES spun UFMs, the reflectance values increased rapidly from 300 to 400 nm and then increased more slowly, reaching a stable value above 550 nm. The reflectance at 457 nm (R_{457}), known as the blue-ray whiteness, is typically used to evaluate the color properties of fibrous membranes. The R_{457} values of the PI UFMs were all higher than 75% but decreased as the fiber diameter increased, which was attributed to thinner fibers providing more cavities for light to reflect from the membrane surface. The PI-UV UFMs also exhibited decreased R_{457} values compared with the corresponding PI UFMs, which might be attributed to a color transformation derived from the photo irradiation process [49].

To further understand the optical properties of the membranes, the WI values were determined, as shown

Figure 8. Thermal properties of PI ultrafine fibrous membranes. (a) TGA; (b) DSC.

in Figure 9b. The WI values of the PI-UV UFMs fabricated using PI-1, PI-2, and PI-3 were 81.75,

78.19, and 80.02, respectively. All of these values were lower than those of the UFMs fabricated by traditional electrospinning, indicating that an obvious yellowing phenomenon occurred. The darker color of the PI-UV UFMs was attributed to charge transfer (CT) reactions caused by the irradiation of the PI fibers [50, 51]. As the high-pressure mercury light source can emit UV irradiation at different wavelengths, in addition to photopolymerization of the polymer chains, some side reactions, such as the direct decomposition of the benzophenone units and

Table 4. Optical properties of PI and PI-UV UFMs.

PI	R_{457}^a	L^*	a^*	b^*	WI ^b
PI-1	87.0	91.98	-1.31	6.34	89.69
PI-1(UV)	75.4	92.46	0.31	16.61	81.75
PI-2	76.7	89.44	-0.81	9.26	79.15
PI-2(UV)	69.1	90.56	-1.35	19.61	78.19
PI-3	75.8	88.73	-0.46	9.34	85.36
PI-3(UV)	67.3	89.59	-0.91	17.03	80.02

^a R_{457} : Reflectance at 457 nm measured with membranes;

^bWI: whiteness index.

Figure 9. The optical properties of the PI ultrafine fibrous membranes. (a) UV-Vis spectra; (b) WI values.

the photo-oxidation of the PIs, can also simultaneously occur, which are responsible for the deterioration of the WI values for the PI-UV UFMs.

3.6. Wettability of the PI UFMs

The surface energy of the fibrous membranes has been demonstrated to be negatively correlated with the contact angle of liquids, and a lower surface energy tends to impart materials with self-cleaning properties. The WCA values measured for the prepared PI and PI-UV UFMs are shown in Figure 10. The WCA values of all the UFMs were relatively high, ranging from 130.9 to 135.1°, indicating that these membranes are essentially hydrophobic. A possible explanation for the high WCA values is that the spun fibers with smooth surfaces and ultrathin diameters have a high surface tension, which can drive the water droplets away. Comparatively, the WCA values of the PI thin films (unfibrous membranes) were only 89.6° for PI-1, 92.3° for PI-1, and 92.1° for PI-3. The WCA of the PI-3 UFM was slightly higher than those

of the other two samples, indicating that microfibers with a certain diameter can form a rougher membrane surface and thus increase the contact area between the air and the droplet, resulting in a higher WCA. Conversely, fibers with excessively small diameters will form membranes with decreased roughness, thus enlarging the contact surface between the gas and liquid phases and decreasing the WCA. The WCA values of the PI-UV UFMs were slightly lower than those of the PI UFMs owing to the benzhydrol moieties generated by photoinduced crosslinking. The lone pair of oxygen in the generated hydroxyl unit can form hydrogen bonds with hydrogen from the water molecules, which decreases the hydrophobicity of the PI-UV fibers. Interestingly, despite the decreased WCA values of the PI-UV samples, these membranes were still hydrophobic (WCA > 130°) owing to the microfibrous structure. These high WCA values indicate that the prepared PI and PI-UV UFMs are potential materials for developing self-cleaning cloth with applications in body protection and wearable devices.

Figure 10. The water contact angle of PI ultrafine fibrous membranes. (a) Experiment schematic diagram of WCA; (b), (c), (d) WCA of UFMs conventionally and UVAES spun from PI-1 to PI-3, respectively.

3.7. Solvent resistance of the PI UFMs

Finally, the solvent resistance of the fabricated UFMs was evaluated using immersion tests according to the process shown in Figure 11a with pure DMAc as the test solvent. Both of the PI and PI-UV UFM had a fibrous appearance and adhered well to the aluminum foil substrates before immersion. During the immersion process, the PI UFM dissolved immediately upon immersion in DMAc. In contrast, the PI-UV UFM only swelled owing to solvent absorption but did not dissolve in the solvent, even when completely immersed. After soaking in DMAc for 30 s, visual observations indicated that the fibrous structure of the PI UFM disappeared completely with the aluminum foil substrate completely exposed. In contrast, the PI-UV UFM maintained their shape with a small amount of shrinkage. The PI-UV UFM was then dried and observed in more detail using SEM (Figure 11b). The PI-UV UFM obtained from PI-1 and PI-3 both maintained good fibrous structures, indicating that they were completely insoluble in DMAc. In PI-UV sample obtained from PI-2, some partial bonding of the fibers was observed as well as the loss of the original structure, but dissolution was restricted to the surface of the membrane. These results demonstrate that the tremendous decrease in molecular free volume caused by successful photo-initiated cross-linking impeded the movement of the molecular chains, making the PI-UV UFM insoluble.

4. Conclusions

In summary, a UVAES technology utilizing intrinsically soluble pre-imidized negative PSPIs as a fiber-shaping agent was successfully developed. The PSPI resins were synthesized by the one-step thermal polycondensation of the dianhydride BTDA with *ortho*-substituted diamines TMDA, DMDEDA, or TEMDA, respectively. The UVAES method combined the advantages of traditional electrospinning with a photocrosslinking reaction to realizing the facile fabrication of UFM with highly cross-linked structures. The application of UV irradiation during the electrospinning process resulted in successful in situ photocrosslinking of the PI fibers at relatively high efficiency. The average diameters of the UVAES-fabricated fibers increased slightly compared with the corresponding conventionally spun fibers. Despite the UVAES process causing a slight deterioration in the thermal decomposition temperatures, optical properties (R_{457} and WI), and hydrophobic performance of the PI-UV UFM, and the thermal dimensional stability of the fibers was improved. The PI-UV UFM exhibited high solvent resistance against the organic solvent DMAc. The good comprehensive properties of the PI-UV UFM indicate the potential of UVAES as a strategy for obtaining ultrafine PI fibers with high environmental stability for use in various high-tech applications.

Figure 11. The solvent resistance test of the PI ultrafine fibrous membranes. (a) Schematic diagram of the testing procedure; (b) SEM images of the PI UFM after immersion in DMAc.

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