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Cite this article as:

Wang Zhen-He, Chen Xing, Yang Hai-Xia, Zhao Jiang, Yang Shi-Yong. The In-plane Orientation and Thermal Mechanical Properties of the Chemically Imidized Polyimide Films[J]. *Chinese J. Polym. Sci.*, 2019, 37(3): 268-278. doi: 10.1007/s10118-019-2173-8

View online: <https://doi.org/10.1007/s10118-019-2173-8>

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The In-plane Orientation and Thermal Mechanical Properties of the Chemically Imidized Polyimide Films

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Electronic Supplementary Information

Abstract The thermal and mechanical properties of the chemically imidized polyimide (CIPI) films and thermally imidized polyimide (TIPI) films were investigated systematically. Experimental results indicated that the CIPI films show dramatically enhanced tensile strength and modulus with obviously reduced coefficient of thermal expansion (CTE) in comparison with TIPI films. These enhancements results from the high in-plane orientation and close packing of the CIPI backbones. Compared with thermal imidization which starts at about 140 °C, the chemical imidization activated by acetic anhydride and isoquinoline initiates the cyclization even at room temperature. The resulting imide rings restrict the mobility of polymer chains and lead to the in-plane orientation with solvent evaporation. Additionally, fewer small molecules remain in the films after treated at 120 °C by chemical imidization than by thermal imidization. The polymer chain plasticization caused by the evaporation of small molecules at high temperature is obviously restricted. Moreover, the partially imidized polymer inhibits the decomposition of mainchains that occurs at subsequent high temperature process, being beneficial to the formation of high molecular weight PI films. Hence, chemical imidization pathway shows apparent advantage to produce PI films with great combined properties, including high modulus, strength and toughness, as well as high thermal dimension stability etc.

Keywords Polyimide film; Chemical imidization; Thermal imidization; In-plane orientation; CTE

Citation: Wang, Z. H.; Chen, X.; Yang, H. X.; Zhao, J.; Yang, S. Y. The in-plane orientation and thermal mechanical properties of the chemically imidized polyimide films. *Chinese J. Polym. Sci.* 2019, 37, 268–278.

INTRODUCTION

Polyimide (PI) films have been widely used in electronic and aerospace industry as flexible boards for printed circuit and insulating layers for semiconductor devices, because of their outstanding chemical and physical properties, such as excellent mechanical strength, high thermal stability, good dielectric properties, radiation, and solvent resistance.^[1–3] To achieve the usage in electronic devices, PI films would be coated with other materials such as conductive metals, silicon or glass substrate. Hence, the matched coefficient of thermal expansion (CTE) and excellent mechanical properties are crucial to ensure the device performance and reliability.^[4,5]

The CTE values of commercial PI films generally exceed 30 ppm/K,^[6] which are higher than those of the common substrate materials such as copper (19 ppm/K), glass

(15 ppm/K), and silicon (6 ppm/K).^[7,8] There are three strategies reported for reducing the CTE of PI films. The first method is to stretch the partially imidized polymer films during the film production at high temperature.^[9–11] The orientation and regularity of polymer main chains can be induced by the mono- or biaxially stretching. The partially imidized films suitable for stretching are usually thermoplastic and have low glass transition temperature (T_g). The second method is to construct PI composite films by introducing inorganic nanoparticles with low CTE.^[12–14] However, the limited additions contribute little to reducing CTE because phase separation occurs at the inorganic content higher than 5%.^[15–18] The third method is to introduce rigid and rod-like segments into PI polymer backbones through co-polycondensation.

Previous researches have suggested that the rigid rod-like segments promote the in-plane orientation and ordered arrangement in film preparation, which enhance the thermal and dimension stability of the films.^[19–22] A lot of rigid rod-like diamines and dianhydrides are used to produce co-polyimides with reduced CTE. However, the introduction of rigid monomers generally results in the cracking of the par-

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Received August 11, 2018; Accepted September 18, 2018; Published online October 22, 2018

tially imidized polyimide films during thermal imidization process, and the resulting PI films cannot combine the excellent toughness and low CTE. Additionally, the preparation conditions also have obvious impacts on the film properties including CTE.^[23,24]

There are two pathways to produce PI films, namely thermal imidization and chemical imidization. The thermal imidized polyimide (TIPI) films are produced by a two-step film forming process.^[25–27] The polyimide precursor—poly(amic acid) (PAA) resin—is first synthesized by the polycondensation of aromatic diamines and aromatic dianhydrides in polar aprotic solvent, which is then cast on the surface of substrate and further treated thermally at high temperatures (300–450 °C) to give the fully imidized PI films. The chemically imidized polyimide (CIPI) films are produced by mixing PAA resin solution with a chemical imidizing agent firstly to give a chemically imidizable resin solution, which is then cast on the surface of substrate and treated thermally at high temperatures (300–450 °C) to complete the cyclization. During the conversion process of PAA into PI films, many factors such as solvent evaporation, imidization, cyclization, thickness reduction, and molecular chain mobility can affect the in-plane orientation of polymer backbones and birefringence of films.^[19,28] All of those changes have obvious effects on the combined properties of the fully imidized films.

There are many reports^[29–37] concerning the effect of film-forming parameters during thermal imidization process on the properties of resulting film. The solvent evaporation starts at temperature lower than 130 °C and the cyclization occurs at higher temperatures. The development of birefringence and enhancement of in-plane orientation are only induced by the solvent evaporation and thickness reduction, and the birefringence and in-plane orientation resulting from the more rigid and ordered molecular chains structures increase dramatically at temperatures higher than 150 °C.^[19] The PAA chain interruptions were observed at high temperature in thermal imidization.^[34,35] Recently, Unsal *et al.*^[36] and Chen *et al.*^[37] investigated the real time dynamics of the imidization reaction, which covers all the stages of thermal imidization. The results indicate that the evaporation of hydrogen-bonded solvents from PAA films will plasticize the polymer chains and disturb the ordered structures.

Although a lot of investigation results have been published regarding the thermal imidization, there are few reports concerning the chemical imidization. It has been demonstrated that the chemical imidization could start even at room temperature triggered by dehydrant and catalyzer,^[26,38] and the resulting imide rings will improve the degree of morphologic ordering and mechanic properties of final PI films.^[39,40] Compared with thermal imidization, chemical imidization with feature of low-temperature cyclization maybe provide an approach to fabricating PI films with high modulus and low CTE, which are suitable for microelectronic and optoelectric display applications. However, the film formation processes of chemical imidization and thermal imidization, especially their influences on aggregation structure and properties of PI films, are still unclear.

In this work, the chemical imidization process and thermal imidization process are monitored by variable-temperature FTIR spectroscopy from 40 °C to 400 °C. Then a series of fully imidized TIPI films and CIPI films are prepared respectively through a two-stage film formation process: the solvent evaporation stage (120 °C) and high temperature imidization stage (300–400 °C). The imidization degree, in-plane orientation, and residual solvents of films at the solvent evaporation stage are measured. Finally, the study is focused on the effects of imidization methods on the aggregation structure and properties of the resulting PI films.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA), 1,4-diaminobenzene (PPD), and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China). PMDA was dried in vacuum oven at 160 °C for 24 h prior to use. PPD and BAPP were used as received. *N,N*-dimethylformamide (DMF, Beijing Chemical Works Co., Beijing China) was distilled under reduced pressure (8 kPa) with calcium hydride at 80 °C. Acetic anhydride and isoquinoline supplied by Beijing Chemical Works Co., were used as received.

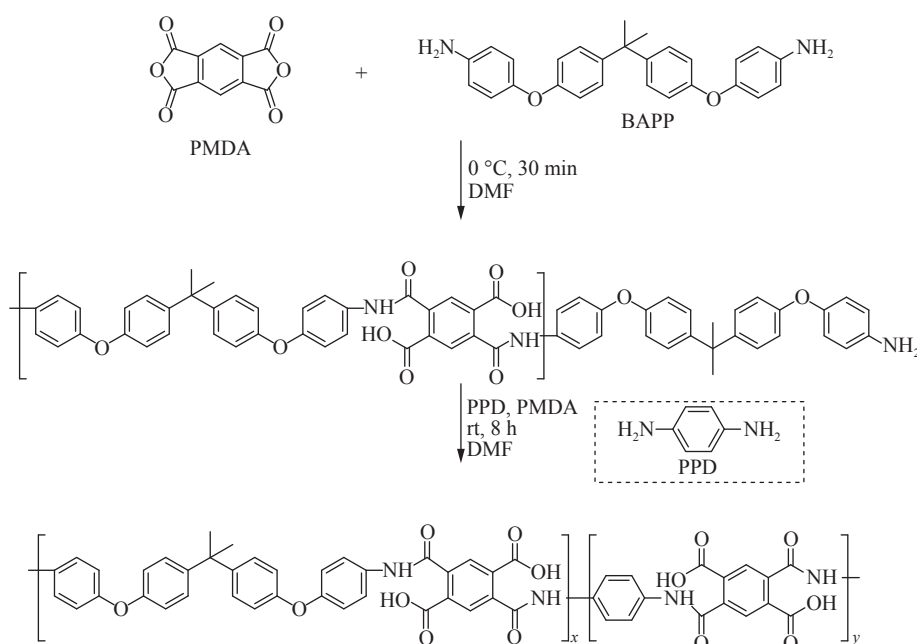
Synthesis of PAA Resins

PAA resin with block copolymer backbone of flexible segment and rigid segment was prepared from BAPP, PPD and PMDA at a 1:1 molar ratio of aromatic diamines to aromatic dianhydride by sequential copolymerization as shown in Scheme 1. The flexible segment was first synthesized with excessive BAPP and PMDA. PPD and PMDA were then added and polymerized to give the rigid segment. A series of PAA resins with different flexible segments were prepared and defined as PA-*X*, of which *X* represents the molar ratio of BAPP in the aromatic diamines (BAPP and PPD) used.

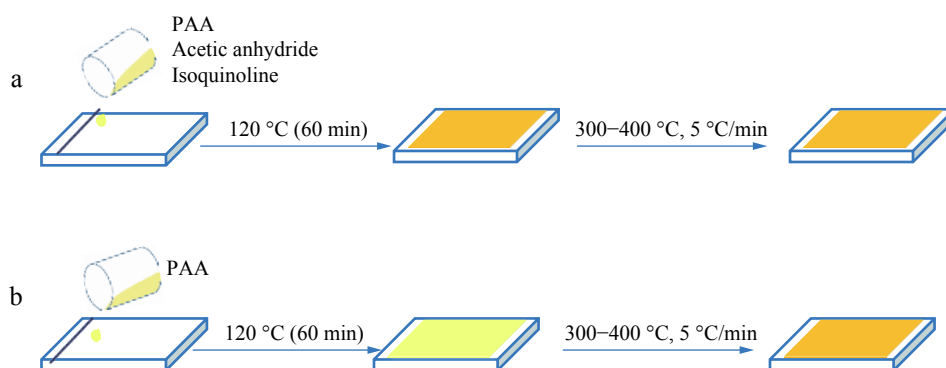
In a typical experiment, the resin PA-50 with molar ratio of PPD:BAPP = 50:50 and solid content of 15 wt% was synthesized. In a 250 mL three-necked flask equipped with a mechanical stirrer, BAPP (5.2279 g, 12.7351 mmol) was dissolved in DMF (46.19 mL) under nitrogen purge at room temperature, and PMDA (2.5000 g, 11.4616 mmol) was then added to the solution in one portion with mechanical stirring. The polycondensation proceeded at 0 °C for 30 min to produce a viscous resin comprising flexible segments, in which PPD (1.3772 g, 12.7351 mmol) and DMF (26.50 mL) were added respectively. After PPD was completely dissolved, a stoichiometric amount of PMDA (3.0556 g, 14.0086 mmol) was added gradually. The mixture was stirred mechanically for 8 h at room temperature to yield a viscous PAA resin solution, which was sealed and stored at 5 °C.

Preparation of the Fully Imidized PI Films

Scheme 2 shows the preparation processes of the fully imidized PI films by chemical and thermal imidization methods, respectively. It is well known that the high temperature (300–400 °C) treatment is essential for both chemical imidization and thermal imidization in order to



Scheme 1 The synthetic route to PAA resins



Scheme 2 Preparation of the fully imidized PI films by (a) chemical imidization and (b) thermal imidization

complete imidization and solvent extraction. Therefore, the key feature of chemical imidization is the addition of a chemical imidization agent (acetic anhydride and isoquinoline).

Specifically, for chemical imidization, the PAA resin was first diluted by DMF to a solid content of 11 wt%, in which the mixture of acetic anhydride (dehydrant) and isoquinoline (catalyzer) was added with molar ratio of PMDA:acetic anhydride:isoquinoline equal to 1:4:1. After deaerated for 5 min at a rate of 2200 r/min using THINKY MIXER ARE-310, the resin was cast onto a glass plate with a 700 μm depth blade. The resulting PAA wet film was treated at 120 $^{\circ}\text{C}$ for 1 h to remove some of the solvents and perform the pre-imidization. The formed gel film was then placed directly in an oven which was heated to 300 $^{\circ}\text{C}$ in advance and further heated from 300 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}/\text{min}$ for imidization. After cooled to below 100 $^{\circ}\text{C}$, the fully imidized PI film was obtained and defined as “CIPI- X ”, in which “ X ” represents the molar ratio of BAPP in the aromatic diamines (BAPP and PPD) used.

In comparison, a series of TIPI films were prepared by thermal imidization. The PAA resin was diluted by DMF to a solid content of 11 wt%, which was deaerated for 5 min at a rate of 2200 r/min using THINKY MIXER ARE-310, and then cast onto a glass plate with a 700 μm depth blade. The resulting PAA wet film was thermally treated at 120 $^{\circ}\text{C}$ for 1 h to remove some of the solvent. The formed gel film was then placed immediately in an oven which was pre-heated to 300 $^{\circ}\text{C}$ and further heated from 300 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}/\text{min}$. After cooled to below 100 $^{\circ}\text{C}$, the fully imidized PI film was obtained and defined as “TIPI- X ”, in which “ X ” represents the molar ratio of BAPP in the aromatic diamine (BAPP and PPD) used.

Measurements

The real-time FTIR measurement was performed on a Nicolet 6700 spectrometer. The sample in the specimen cell was heated from 40 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ with a heating rate of 2 $^{\circ}\text{C}/\text{min}$, and the spectra were continuously collected at an interval of 5 $^{\circ}\text{C}$. Attenuation total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a

TENSOR-27 spectrophotometer with the scanning range of 4000–400 cm^{-1} .

The relative molecular weight of the initial PAA resin was determined by gel permeation chromatography (GPC) on a Waters GPC system equipped with a Waters 1515 HPLC pump, three Styragel columns (HT-3, HT-4, and HT-5), and a Waters 2414 differential refractometer at 40 °C. Polystyrene standards were used for calibration and DMF containing 0.06 mol/L LiBr and 0.06 mol/L H_3PO_4 with a flow rate of 0.8 mL/min was employed as the eluting solution.

Wide angle X-ray diffraction (WAXD) measurements were carried out on a PANalytical/Empryan-1 diffractometer (40 kV, 200 mA) with Cu-K α ($\lambda = 0.154$ nm) radiation at room temperature. Data were collected by a continuous scan at a rate of 2 (°)/min over a range of $2\theta = 5^\circ$ – 35° . The d spacing was calculated from scattering angle (2θ) according to Bragg's law ($n\lambda = 2d\sin\theta$).

Mechanical tensile properties of PI films were measured at ambient temperature on the Instron-5848 Tensile Apparatus following GB 13022-91 with a gauge length of 80 mm and a crosshead speed of 2 mm/min. The theoretical thickness of PI films was designed to be 20 μm by adjusting the solid content of PAA resins to 11% and the gap of blade to 700 μm . The experimental thickness of PI films was measured by Labthink C640 Thickness Tester. At least seven specimens were tested for each PI film and results were averaged.

Thermogravimetric analysis (TGA) was performed on TA Q50 thermal analysis system from 40 °C to 760 °C at a heating rate of 20 °C/min under nitrogen atmosphere. Dynamic mechanical analysis (DMA) was recorded on TA Q800 thermal analysis system from 40 °C to 450 °C at a heating rate of 5 °C/min and a frequency of 1 Hz in nitrogen. The film tension mode was employed with the specimen size of 12 mm $\times$ 6.5 mm $\times$ 20 μm . Thermal mechanical analysis (TMA) was conducted on a TA Q400 thermal analysis system from 40 °C to 370 °C at a heating rate of 5 °C/min with a load of 0.02 N in a nitrogen flow. The coefficients of thermal expansion (CTE) with specimen's size of 16 mm $\times$ 4 mm $\times$ 20 μm were calculated in the range of 50–200 °C.

The refractive indices of the PI films formed on a 7.62 cm silicon wafer were measured at a wavelength of 633 nm at

room temperature with a Metricon 2010M Prism Coupler. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were determined using linearly polarized laser light polarizations parallel (transverse electric) and perpendicular (transverse magnetic) to the film plane, respectively.

RESULTS AND DISCUSSION

Imidization Degree (ID) as a Function of Temperature

In order to speculate the ID during the solidification of PAA resin, *in situ* FTIR spectroscopy (Fig. 1) was employed to monitor the imidization reaction from 40 °C to 400 °C with a heating rate of 2 °C/min, using PA-50 as a typical sample. In a chemical imidization, PA-50 resin solution mixed with acetic anhydride and isoquinoline was cast on KBr pellet for testing. For comparison, the pure PA-50 resin solution was used in thermal imidization. The band at 1375 cm^{-1} (stretching vibration of C–N) was selected for quantifying ID and the aromatic band at 1499 cm^{-1} (C–C stretching vibration of the benzene backbone) was used as internal standard.^[31,41] The intensity ratio of the peak at 1375 cm^{-1} to the peak at 1499 cm^{-1} was normalized by the fully imidized film at 400 °C. ID was calculated according to the following equation:

$$\text{ID} = \frac{(A_{1375}/A_{1499})_{\text{T}}}{(A_{1375}/A_{1499})_{400}} \times 100\% \quad (1)$$

where A is the area of specific absorption band of the film treated at particular temperature.

Fig. 2 compares the ID values as a function of temperature. The chemically imidized film shows ID of about 35% even at room temperature, which does not change until the temperature rises to 100 °C, indicating that the cyclization reaction can be activated by acetic anhydride and isoquinoline at room temperature. From 100 °C to 200 °C, ID increases from 35% to about 90%, and only 10% increment occurs at higher temperatures (> 200 °C). In comparison, the thermally imidized films do not show any imidization below 140 °C. Their IDs increase obviously with temperature rising from 140 °C to 250 °C in accordance with the previous works.^[42,43] The higher ID at low temperature for chemical imidization will have obvious impacts on depoly-

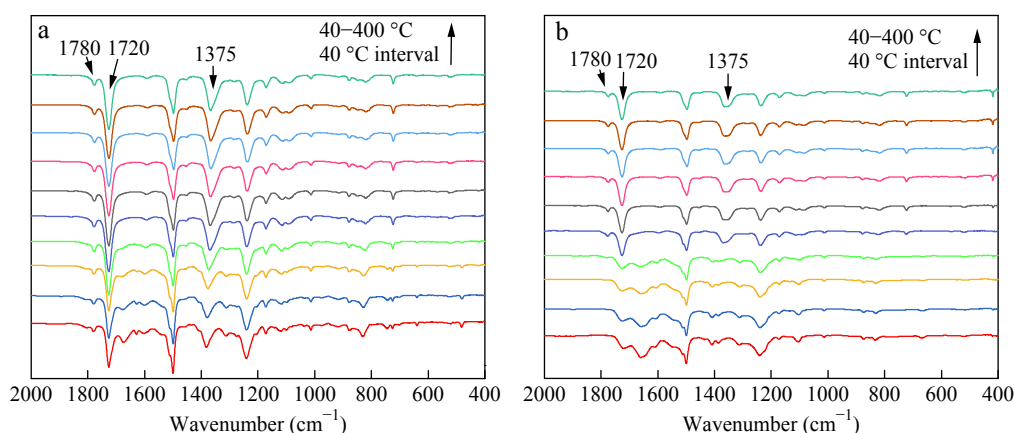


Fig. 1 The *in situ* FTIR spectra of PA-50 films fabricated by (a) chemical imidization and (b) thermal imidization as a function of temperature

merization, orientation, plasticization, and aggregation of the fully imidized PI films. Additionally, it is manifested that ID at 300 °C exceeds 99% and the value basically keeps constant from 300 °C to 400 °C for both chemical imidization and thermal imidization. The results indicate that the PI films can be fully imidized at 300 °C. However, the higher temperature (400 °C) was selected to promote molecular chain packing during preparation of PI film.

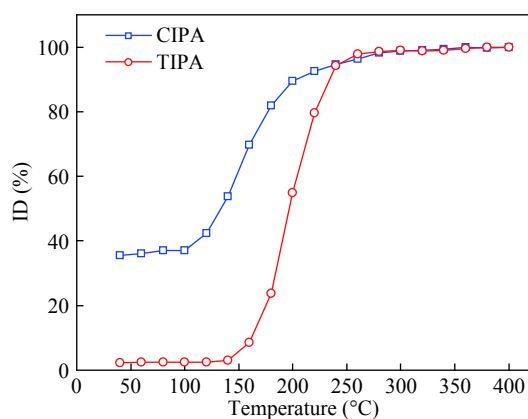


Fig. 2 ID of PA-50 films as a function of temperature (40 °C to 400 °C)

In-plane Orientation of Films at Evaporation Stage

According to the results of *in situ* FTIR (Fig. 2), the chemical imidization activated by acetic anhydride and isoquinoline initiates the cyclization even at room temperature. The resulting imide rings will directly affect the aggregation structure and the in-plane orientation of the partially imidized films. To identify the changes of in-plane orientation of polyimide chains in films at the stage of solvent evaporation, the real-time birefringence (Δn) of PA-50 films was calculated at 120 °C according to Eq. (2):^[44,45]

$$\Delta n = n_{TE} - n_{TM} \quad (2)$$

where n_{TE} and n_{TM} are the refractive index of films at in-plane orientation and out-of-plane orientation, respectively, which can be measured by Prism coupling device with 633 nm light.

Fig. 3(a) shows the real-time birefringence of the partially

imidized films by two different imidization methods at the solvent evaporation stage. The initial PAA films are solvent rich, thus the relaxation time is shorter and in-plane and out-of-plane refractive index values remain very close, where the birefringence is close to zero. With the increase of the standing time at 120 °C, solvents volatilize rapidly and birefringence increases simultaneously both in chemical and thermal imidizations. These results are in accordance well with the literatures.^[36,46] The partially imidized films by chemical imidization show higher birefringence than those by thermal methods do at the same baking time. For instance, the birefringence is 0.09 for CIPA-50 film aged at 120 °C for 30 min, compared to 0.04 for TIPA-50. The enhancement in birefringence is due to the high ID of CIPA-50 at solvent evaporation stage. Fig. 3(b) describes the IDs of TIPA-50 and CIPA-50 as a function of time at 120 °C, which were calculated using Eq. (1) according to the FTIR spectra (Fig. S3, in electronic supplementary information, ESI). The ID of CIPA-50 film exceeds 60% when standing time reaches 60 min at 120 °C. The resulting imide rings have higher intrinsic birefringence than that of PAA chains. Moreover, the rigid imide rings reduce the mobility of the polymer chains, which is favorable for the polymer chains to orientate in parallel to the film surface and the development of birefringence. In comparison, the ID of TIPA-50 is close to zero at solvent evaporation stage, and the flexible PAA molecular chains have weak force to promote the molecular orientation and the development of birefringence during thermal imidization process.

Residual Small Molecules in Films at Evaporation Stage

During the process of PI films formation, most of solvents escape from films at solvent evaporation stage (treated at 120 °C, 1 h). However, additional weight loss is observed at the high temperature imidization due to the evaporation of residual small molecules including hydrogen-bond solvents and water molecules generated from imidization reaction. It has been reported that the evaporation of small molecules would plastify polymer chains and disturb the ordered arrangement of PI films at high temperature.^[36] Fig. 4 depicts the weight loss of PA-50 films which have been treated at 120 °C for 1 h through thermal and chemical imidizations, respectively. It can be found that there are less residual small

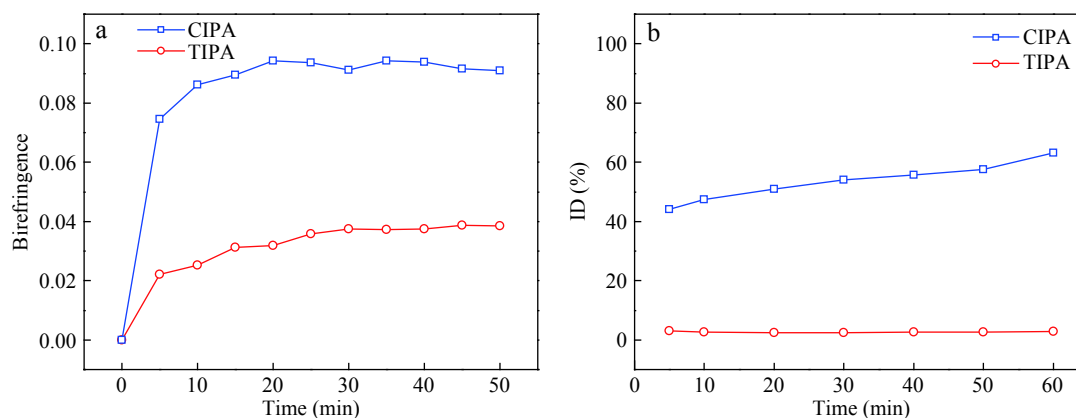


Fig. 3 (a) Birefringence and (b) imidization degrees of PA-50 films at the solvent evaporating stage (120 °C)

molecules in CIPA-50 film than TIPA-50 film after the solvent evaporation stage. As shown in Fig. 3(b), ID of CIPA-50 film exceeds 60% at the solvent evaporation stage. Different from PAA chains, the imide rings cannot combine with solvents through hydrogen bond as showed in Fig. 4 (inset picture). CIPA-50 releases more hydrogen-bonded solvents and water molecules generated from cyclization reaction due to high ID at the evaporation stage. Hence, fewer small molecules remain in CIPA-50 film and their plasticization effect on the polymer chains is obviously restricted at high temperature imidization. Furthermore, the rigid imide rings have better resistance to plasticization than PAA chains do. All of the factors helped to maintain the ordered arrangement of films during chemical imidization at the high temperature.

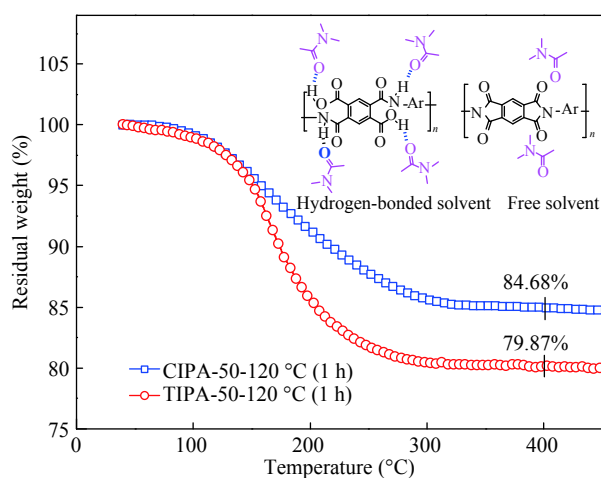


Fig. 4 TGA curves of PA-50 pre-treated at 120 °C for 1 h by the thermal (TIPA-50) and chemical imidizations (CIPA-50), respectively. The inset structures show hydrogen-bonded solvent in PAA and free solvent in PI.

Mechanical Properties of the Fully Imidized PI Films

Fig. 5 compares mechanical properties of the fully imidized PI films by chemical and thermal imidizations. The CIPI films show enhanced mechanical properties with the higher elastic modulus and tensile strength. For instance, the tensile modulus and tensile strength of CIPI-50 are 4.5 GPa and 160.4 MPa, respectively, 55.2% and 50.0% higher than those of TIPI-50. The obvious enhancement of the mechanical properties for CIPI films can be attributed to the aggregation phase structures of the PI films. As mentioned above, the chemical imidization results in higher ID and in-plane orientation degree at solvent evaporation stage. Hence, the CIPI films show the higher in-plane orientation degree and have more ordered molecular aggregation phase, which ensure the greater tensile strength and modulus. Additionally, the reduced volatilization of small molecules including the hydrogen-bond solvent and water molecules by-produced in high temperature imidization weakens the plasticization effect on molecular chain and contributes to maintaining the ordered structures (Fig. 4), accounting for more regular molecular arrangement and high tensile modulus and strength of CIPI films. It is also noted that CIPI films have

better toughness than the TIPI films do (Fig. 5c), especially the TIPI films with BAPP less than 40%, which are too brittle to give testing samples. For chemical imidization, the films consisting of 70% and 80% rigid component (PMDA-PPD) are still ductile. The improvement in toughness possibly results from the high stability of imide rings formed at the solvent evaporation stage in chemical imidization. Previous reports^[34,35] have identified the reduction of PAA molecular weight at high temperature in thermal imidization. Thus, the generated rigid PMDA-PPD segments and low molecular fragments cause the deterioration of toughness and stress cracking of films in the further imidization process. Although the generated anhydrides and amines can react again at high temperature and increase molecular weight and toughness, it cannot make up the influence caused by PAA chain interruption and the generated rigid PMDA-PPD segments. In contrast, the PAA molecular chains can convert into stable polyimide chains at the solvent evaporation stage in chemical imidization process, which have a great fracture resistance to the polymer chain depolymerization at high temperature. Therefore, the chemical imidization can simultaneously enhance the strength and toughness of the fully imidized PI films.

Aggregation Phase Structures of the Fully Imidized PI Films

Fig. 6 shows the wide-angle X-ray diffraction (WAXD) patterns of the PI films. A broad peak around 19° is observed in all PI films prepared by either chemical or thermal imidizations, indicating the PI films are all amorphous. From the scattering angles (2θ) at the center of the broad peaks, the corresponding d spacing was calculated according to Bragg's equation, and the values are plotted in Fig. 7. In general, the d spacing reflects the average distance between the polymer chain segments in linear polymers and is also indicative of the free volume. It has been widely used to characterize the packing density in amorphous polymer films.^[47,48] The d spacing ranges from 4.25 Å to 4.72 Å for the thermal imidized PI films and gradually enhances with increasing BAPP fraction in the polymer backbone. The similar tendency is also observed for the chemical-imidized PI films. It can be elucidated from the values of d spacing that the introduction of flexible BAPP segments with the large free volume fraction in the polyimide backbone will disturb the regular ordered structures and restrict the development of in-plane orientation of polymer chains. Both the large free volume of BAPP and low-ordered chains structure lead to high d spacing value. Additionally, the CIPI films have the smaller d spacing than TIPI films do (~4.65 Å for TIPI-50 film and ~4.44 Å for CIPI-50 film, respectively). Since d spacing depends greatly on the intrinsic structure of polymer, it is reasonable that the smaller d spacing of CIPI-50 film is induced by the higher ordered structures and closer chain packing, which is derived from the higher in-plane orientation at the solvent evaporation stage and decreased plasticization by volatilization of small molecules in the chemical imidization process.

Birefringence, the difference between the in-plane and out-of-plane refractive indices, has been used to characterize

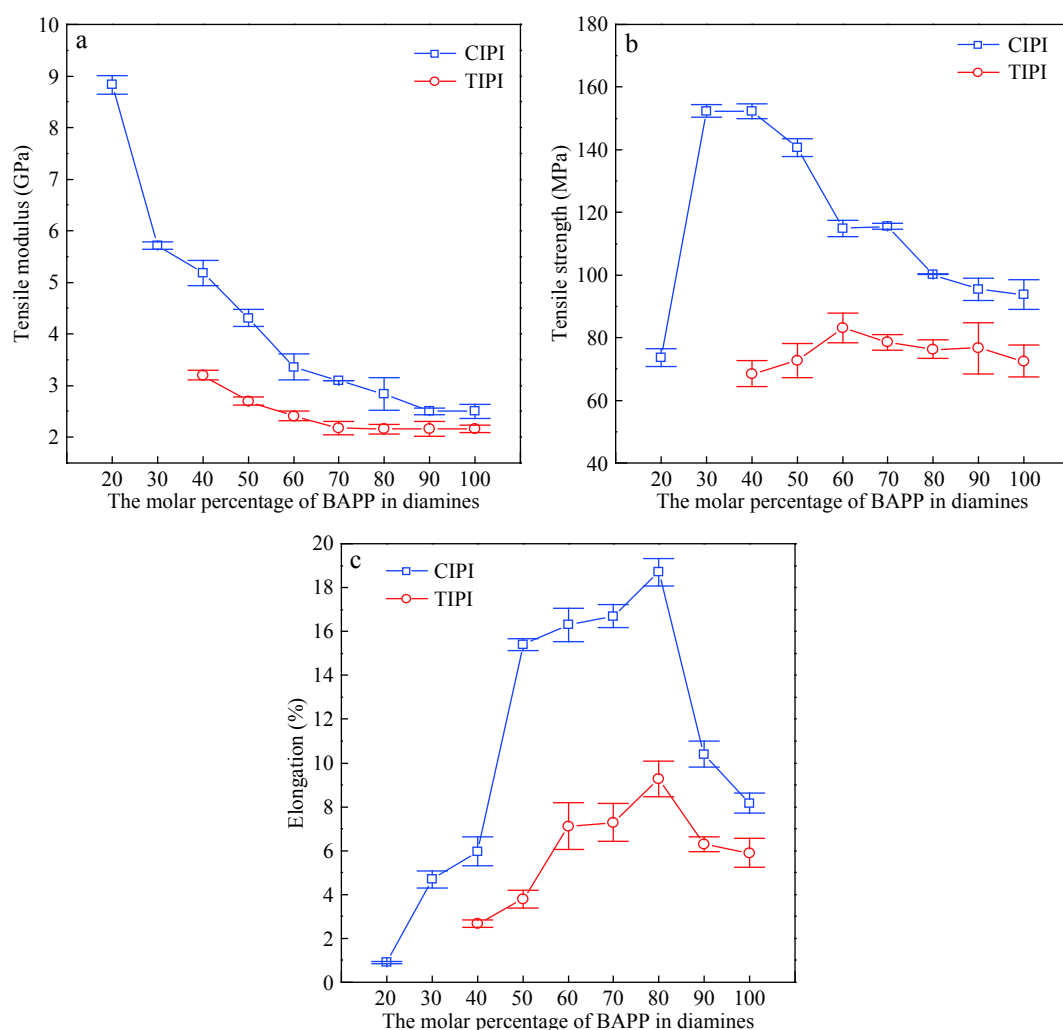


Fig. 5 Mechanical properties of PI films fabricated by the chemical and thermal imidizations: (a) tensile modulus; (b) tensile strength; (c) elongation at break

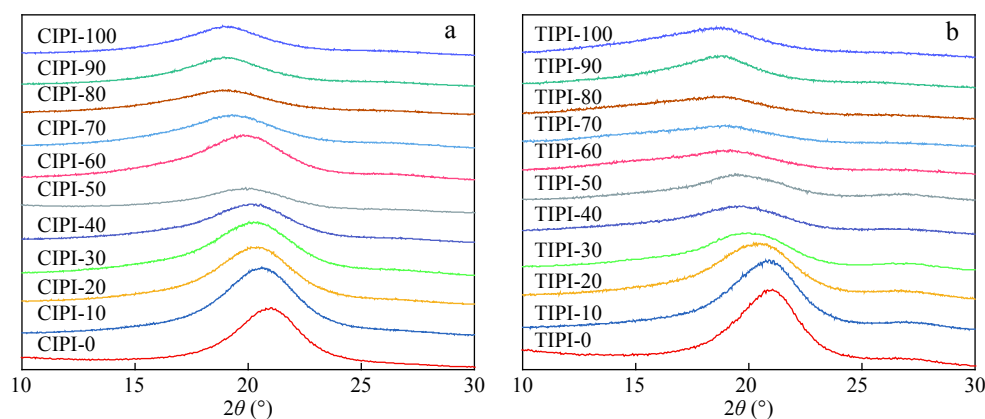


Fig. 6 WXR D patterns of the PI films fabricated by (a) chemical and (b) thermal imidizations

the in-plane molecular orientation. Fig. 8 compares the birefringence of the fully imidized PI films by the chemical and thermal imidizations, respectively. Obviously, the chemical imidization method can produce PI films with dramatically enhanced in-plane orientation than the thermal imidization one does, especially the PI films with flexible segment

contents higher than 40 mol%.

Thermal Properties of the Fully Imidized PI Films

The thermal stability of PI films was measured by TGA in nitrogen (Fig. S4, in ESI), and the results are summarized in Table 1. No weight loss is detected until the temperature is

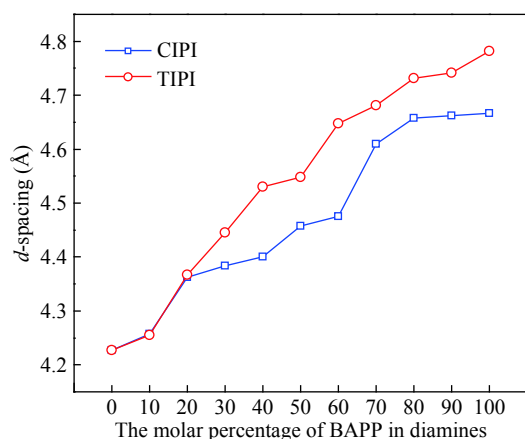


Fig. 7 The d -spacing of the PI films fabricated by the chemical and thermal imidizations

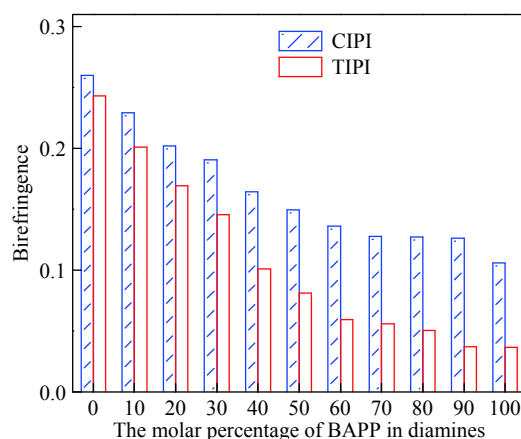


Fig. 8 Birefringence of the PI films fabricated by the chemical and thermal imidizations

Table 1 Thermal properties of the fully imidized PI films

	T_g^a (°C)		$T_{d,5\%}^b$ (°C)		CTE ^c (ppm/K)	
	CI ^d	TI ^e	CI	TI	CI	TI
PI-0	> 500.0	—	592.4	590.1	−9.1	—
PI-10	> 500.0	—	562.5	557.4	−4.1	—
PI-20	423.4	—	550.7	546.7	−1.6	—
PI-30	415.9	—	536.4	533.6	−0.9	21.7
PI-40	409.7	410.5	538.4	537.4	7.0	35.0
PI-50	401.6	402.1	532.3	533.6	9.8	44.9
PI-60	394.3	399.2	532.5	534.1	13.1	53.7
PI-70	389.6	390.5	532.7	527.8	17.8	59.6
PI-80	336.6	344.7	533.6	524.6	17.8	59.9
PI-90	334.0	335.3	528.5	521.0	18.9	61.2
PI-100	335.7	334.1	523.0	516.8	22.6	63.7

^a T_g , the glass transition temperature connected with $\tan\delta$ peak value obtained from DMA in nitrogen; ^b $T_{d,5\%}$, the decomposition temperature at 5% weight loss determined by TGA in nitrogen; ^c CTE, the in-plane linear coefficient of thermal expansion calculated from 50 °C to 250 °C; ^d CI, chemical imidization; ^e TI, thermal imidization; — The sample is too brittle to be measured.

up to 500 °C for all PI films and $T_{d,5\%}$ values of PI films decrease along with the increase of BAPP contents due to the low heat resistance of isopropyl. Furthermore, no obvious difference is found between CIPI films and TIPI films, which indicates that the polymer decomposition might be a direct consequence of the skeleton composition, independent of the aggregation structure. The glass transition temperatures (T_g) of PI films calculated by $\tan\delta$ of DMA curves (Fig. S5, in ESI) are presented in Table 1. It is manifested that the T_g values decline proportionally with the introduction of BAPP as a result of diminution in the chain packing degrees caused by the flexible molecular structure of BAPP. Unexpectedly, the CIPI films and TIPI films have similar T_g values despite of the higher in-plane orientation of CIPI films than TIPI films. This may be predominantly because the in-plane orientation can only enhance chain interactions parallel to the plane direction, while the chains perpendicular to the plane (thickness direction) are almost unaffected. Therefore, the approximative chain stacking in thickness direction endows CIPI films and TIPI films with the similar T_g values.

For the application of PI films in the production of flexible electronic substrate, good dimensional stability is highly desirable. The dimension changes of PI films as a function of temperature were evaluated by TMA (Fig. 9). The average

values of CTE from 50 °C to 250 °C are summarized in Table 1. The CTE values increase with the increasing contents of the flexible segment in PI backbones regardless of chemical or thermal imidizations. The TIPI films show CTE values of 21.7–63.7 ppm/K with increasing contents of the flexible segment from 30% to 100%. However, the PI films cannot be prepared if the flexible segment contents are lower than 30% because the films are too brittle. Hence, it is difficult to obtain the PI films with CTE less than 20 ppm/K with retaining appreciable toughness simultaneously using thermal imidization method. In comparison, the CIPI films show lower CTE values than the corresponding thermally imidized ones do at the same level of flexible segment content in the PI backbones. For instance, the CIPI-50 film shows a CTE of 9.8 ppm/K, much lower than that of the corresponding TIPI (CTE = 44.9 ppm/K). Obviously, the enhanced dimensional stability of the CIPI films is attributed to the higher in-plane orientation promoted by the more rigid imide rings formed at the solvent evaporation stage. Additionally, the reduced plasticization caused by volatilization of hydrogen-bond solvents and water molecules in the chemical imidization also contributes to the more ordered structures. Moreover, CTE of the CIPI films can be precisely adjusted in the range from −9.1 ppm/K to +22.6 ppm/K by con-

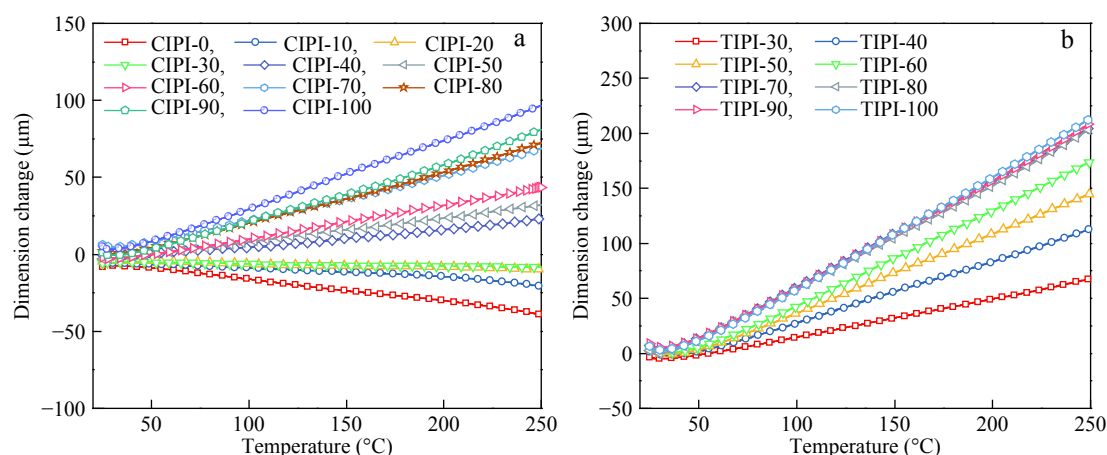


Fig. 9 TMA curves of (a) CIPI films and (b) TIPI films

trolling the flexible segment content in the PI backbones, being able to match with the requirements of different electronic substrate applications such as Si (~ 6.9 ppm/K) and Cu (~ 17.8 ppm/K), respectively.

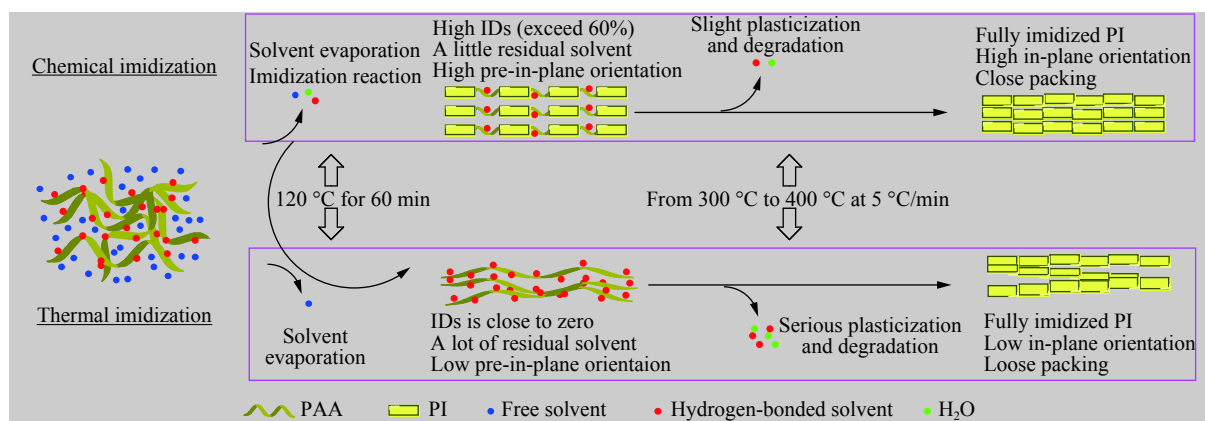
Overview of Chemical and Thermal Imidization Processes

In order to visually and comprehensively describe the effects of two imidization methods on the structure and properties of the fully imidized PI films, Scheme 3 depicts the physical and chemical changes of the polymer chains during entire chemical and thermal processes. Compared with thermal imidization which starts at about 140°C , the chemical imidization activated by acetic anhydride and isoquinoline initiates the cyclization even at room temperature. The high ID of partially imidized film achieved at the solvent evaporation stage will obviously affect the orientation and plasticization and depolymerization of the fully imidized PI films. Firstly, the imide rings are more rigid than PAA chains and can promote the in-plane orientation and development of birefringence. Secondly, the plasticization at high temperature imidization is restricted due to fewer small molecules remaining in the films after solvent evaporation stage during chemical imidization. Thirdly, the resulting imide rings possess better resistance to depolymerization than PAA chains do at high temperature imidization. All of

these factors will contribute to high in-plane orientation and close packing of fully imidized CIPI films.

CONCLUSIONS

Compared with thermal imidization, chemical imidization method can initiate the cyclization reaction of PAA resin in solution even at room temperature and the ID values of 60% can be achieved after thermally treating the wet resin films at 120°C for 1 h. The resulting imide rings contribute largely to the high in-plane orientation of the partially imidized polymer chains and inhibition of polymer chain degradation. Moreover, the plasticization effect caused by volatilization of hydrogen-bonded solvents and water molecules produced by the cyclization reaction is weakened, resulting in the formation of more ordered structure and closer packing of the fully imidized PI films as identified by the smaller d spacing and higher birefringence values. Therefore, chemical imidization method can dramatically enhance the mechanical properties and thermal dimensional stability of the fully imidized PI films with higher modulus, higher strength and toughness, as well as lower CTE, providing an advantaged pathway to produce advanced PI films with optimized properties for the flexible electronic substrate applications.



Scheme 3 Schematic diagram of physical and chemical changes in the PI film formation

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2173-8>.

ACKNOWLEDGMENTS

This work was financially supported by National Basic Research Program of China (No. 2014CB643604).

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