The study on imidization degree of polyamic acid in solution and ordering degree of its polyimide film

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Abstract Polyamic acid (PAA) based on pyromellitic dianhydride and 4,4′-oxydianiline (PMDA–ODA) can be chemically converted to copolyamic acid-imide (PA-I) which is a partially converted PAA at ambient temperature by treatment with a mixture of acetic anhydride and pyridine. A systematic investigation by rotation viscometer and FT-IR revealed that phase separation in PA-I solution occurred when imidization degree was about 26%. Imidization degree of PA-I solution could be controlled by using adequate acetic anhydride amount, initial PAA concentration and imidization time. PA-I solutions with different imidization degree were converted to corresponding polyimide films by thermal imidization. WAXD showed that as imidization degree in PA-I solution increased, the degree of morphologic ordering of final PI film was improved, while tensile strength and modulus increased and ultimate elongation reduced slightly.

Introduction

Polyimide(PI) is an important polymeric material which have been applied in many technology fields, such as micro-electronic industry, mechanical industry and aerospace industry, etc. [1, 2]. It is well known that the earliest and most successfully used PI is synthesized from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA). However, its high glass temperature (which is over 673 K) caused by the rigid phenyl and imido ring impairs its solubility and meltability, resulting in poor processability [3–5]. Thus, it is important to prepare PI films by traditional two-step method. Precursor polyamic acid (PAA) differs from PI in that it is soluble in solvent with high boiling temperature such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAC). PAA solution cast on substrate can be converted into insoluble PI film by dehydrative cyclization [1, 2]. The process involves the simultaneous PAA imidization, solvent diffusion and the development of ordering aggregation [6–13]. Brekner and Feger built up the complexation between solvent NMP and PAA [6–8]. Hsu et al investigated imidization kinetics by isolating the processes of decomplexation between NMP and PAA and imidization [9]. Saraf indicated that solvent content after most of the imidization is complete is crucial in determining the ordering degree and texture in the film. The ordering degree was improved at higher heating rate and thicker film during imidization [10]. Bronnikov found different morphology in PI films prepared from PAA by thermal or chemical imidization [14]. The surface of the PI films prepared by thermal imidization showed micro-domains of a nearly spherical shape, and their size and packing depend on the heating temperature, while it exhibited net structure by chemical imidization. These discussions were focused on PI prepared from PAA solution, but the reports on PI film prepared from partially imidized PAA solution involved a little. The difference in chemical structure from PAA solutions with different imidization

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degree may influence properties of final PI films; therefore, the control of imidization degree in solution is especially important. PAA is converted into PI when the mixture of acetic anhydride and pyridine were added into PAA solution. The intermediate in imidization is a copolymer composed of amic-acid and imide, called copolyamic acid-imide (PA-I), whose solubility is directly relative to imidization degree (ID). There is a critical point of imidization degree (ID_c) below which solution of PA-I is homogenous and above which phase separation will occur immediately. Homogeneous copolymer solutions with different ID can be obtained before critical point of phase separation (CPPS) during imidization. Therefore, control of imidization degree of copolymer solution can provide us some routs to prepare PI films with required morphology and properties. Our work is focused on ID in PA-I solution based on PMDA–ODA in chemical imidization and the degree of morphologic ordering of final PI film.

Experimental

Materials and reagents

N-Methyl-2-pyrrolidinone (NMP), supplied by Qunli Chemical Co., Shanghai, China, was distilled under reduced pressure over phosphorous pentoxide. Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were supplied by Synthetic Resin Research Institute, Shanghai, China. PMDA was purified by sublimation and ODA was recrystallized from ethanol and dried under N_2 atmosphere before use. Other laboratory-grade reagents, as acetic anhydride, pyridine and ethanol, purchased from Chengdu Kelong Chemical Co., were used without further purification.

### Synthesis of polyamic acid (PAA) precursor

In a three-necked flask fitted with a mechanical stirrer and a nitrogen inlet tube, ODA was dissolved in NMP. PMDA was then added stepwise over 2 h. The reaction mixture was finally stirred for 12 h in ice bath to yield the PAA solutions (25 wt% initial PAA concentration) whose intrinsic viscosity was measured in NMP to be 0.365 m^3/kg. Then PAA was diluted to different initial concentration (3, 6, 9, 12, and 15 wt%) before used. Structure of PAA is showed in Scheme 1.

Imidization of PAA

PAA solution was chemically imidized in rotation viscometer. The structure of PI is showed in Scheme 1. When the effect of acetic anhydride amount on ID_c was investigated, different mole amount of acetic anhydride (100, 80, 60, 40, and 20 mol%) which is relative to original amino groups was added into PAA solutions with same initial PAA concentration. When the effect of initial PAA concentration on ID_c was investigated, 60 mol% acetic anhydride was added into PAAs with different initial PAA concentration (3, 6, 9, 12, 15, and 25 wt%).

Determination of critical point of phase separation

Insoluble gel would form when CPPS occurs. It was determined by an indirect method: phase separation is believed to occur when 0.05 cm^3 PA-Is solution could not be dissolved completely in 10 cm^3 solvent NMP in 1 min by fast stir at room temperature. At CPPS, sample (PA-I) was taken out and precipitated immediately from ethanol, and then was dried in a vacuum oven at 323 K before use.
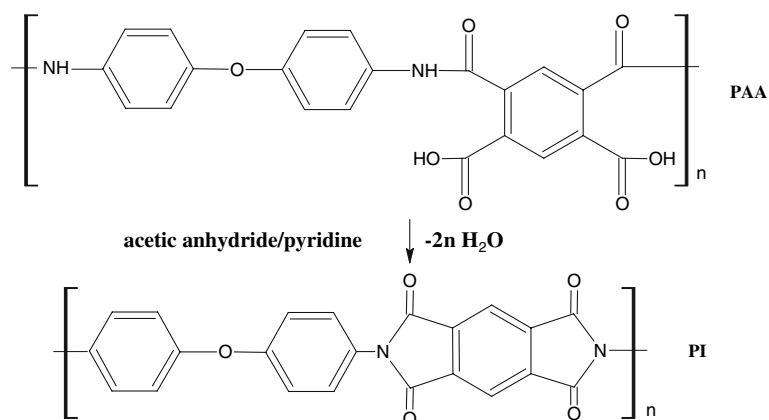
Scheme 1 Structure of PAA and PI based on PMDA–ODA

Preparation of PI film

The synthesized PA-I solutions were cast on glass substrate using doctor blade and dried in a vacuum oven at 323 K for 30 min. The soft-baked films were thermally imidized in an oven by an imidization process: 373 K for 30 min, 473 K for 1 h, 573 K for 1 h. The final PI films were cooled to room temperature and removed from the glass substrates. Their thickness was 11 ± 0.5 μm.

Measurements and characterization

Dynamic viscosities at different time during imidization were recorded before CPPS by rotation viscometer (Brookfield DV-α + PRO, USA). A viscosity was obtained every 1 min. ID of dried PA-I sample was determined by infrared spectrometer (Nicolet 560 type). Figure 1a was a FT-IR spectrum of PI prepared from PAA at 573 K for 3 h. The bands at 1,380 cm^{-1} (stretching vibration of C–N), 1,780 and 1,720 cm^{-1} (symmetric and asymmetric stretching vibration of C=O) which generally characterize PI could be seen obviously, but the band at 1,660 cm^{-1} (C=O in –COOH) which characterizes PAA was hardly observed. Thus, imidization was considered to be complete. Figure 1b was a FT-IR spectrum of PA-I at CPPS. The band of 1,380 cm^{-1} was least influenced by overlapping with other bands, and thus was selected for quantifying imidization degree. The aromatic band at 1,500 cm^{-1} (C–C stretching of the p-substituted benzene backbone) is usually selected as the internal standard. ID can be calculated using the equation [15]:

$$\text{ID}(\%) = \frac{(S_{1380}/S_{1500})_t}{(S_{1380}/S_{1500})_{t=\infty}} \times 100 \qquad (1)$$
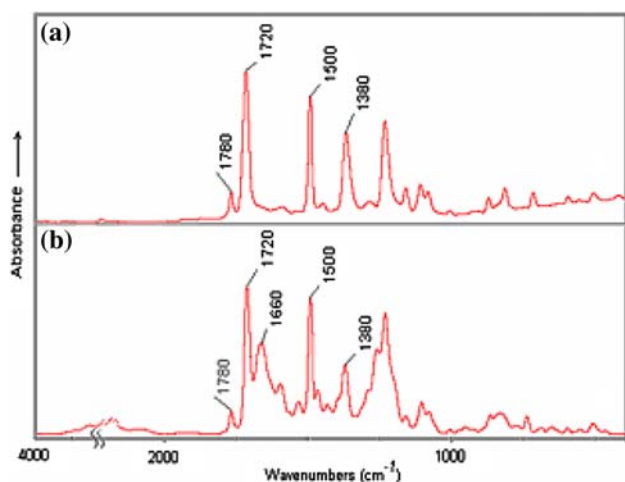

Fig. 1 FT-IR spectrum. (**a**) PI prepared from PAA at 573K for 3 h. (**b**) PA-I by chemical imidization

where S is the area of absorption band, t is imidization time, $t = \infty$ is taken as the time of completely imidized PI.

The characterization of degree of morphologic ordering of film. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature on a X-ray diffractometer (X'-Pert-MPD, Philip) with a graphite monochromator (operating at 40 kV and 40 mA) with nickel-filtered with Cu Kα radiation ($\lambda = 0.15418$ nm). Data were collected for a continuous scan at a rate of 2°/min over a range of $2\theta = 5°$–35°. Ordering degree is defined as [16]:

$$X(\%) = \frac{U_0}{I_0} \times \frac{I_X}{U_X} \times 100 \qquad (2)$$

where X is ordering degree, and U_0 and U_X denote the backgrounds of the reference sample and measuring sample while I_0 and I_X are integral intensities of diffraction lines of the reference sample and measuring sample, respectively.

Measurement of mechanical properties. Samples of PI film were cut into 50 mm × 10 mm strips. Mechanical tensile properties of PI films were performed at room temperature on a tensile tester (Instron Mechanical Tester, model No. 4320) with a gauge length of 20 mm and a crosshead speed of 5 mm/min. Average values of more than five measurements were taken for each sample. The experimental uncertainties in tensile strength and modulus were ±1 MPa and ±0.05 GPa, respectively.

Result and discussion

Effect of imidization condition on phase separation in PA-I solution

In addition to imido ring, isoimide is also usually formed in chemical imidization of PAA. The ratio of the two products is associated with dehydration catalyst. Two kinds of PAA isomers (1) and (2) are shown in Scheme 2. When nucleophilic substitution of –COOH– is going on, the nucleophilicity and steric hindrance of –NH– in (1) is greater than those of –OH– in (2). When dehydration catalyst is acetic anhydride/pyridine, its reactivity mainly depends on nucleophilicity of the group since steric hindrance of nucleophilic substitution of –COOH– in PAA is smaller. The reactivity of –NH– in (1) is larger than that of –OH– in (2) with –COOH– because of its higher nucleophilicity. Catalyst Pyridine makes the interchange isomerization move towards (1), and therefore PI would be the predominant imidization product. Obvious absorbance bands of PAA (1,660 cm^{-1}) and PI (1,780 and 1,380 cm^{-1}) were observed, but that of isoimide (1,800 cm^{-1})can was barely detectable in FT-IR spectrum of those partial
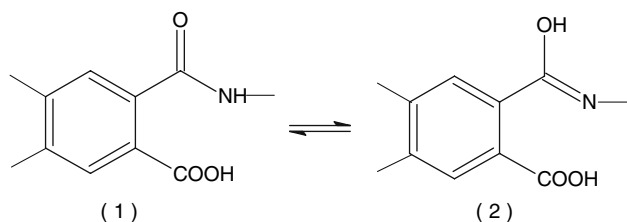
Scheme 2 Isomers of PAA

imidization samples obtained at CPPS as shown in Fig. 1b. Thus, the main imidization product obtained from chemical imidization was PA-I, and isoimide could be ignored.

As shown in Fig. 2, the viscosity of PA-I solution increased apparently with imidization time after acetic anhydride and pyridine were added into PAA. This is attributed to increasing conversion from PAA to PI. The rigidity of PI is greater than that of PAA due to the presence of imido ring, leading to imide chain mobility decrease in solvent. The curves of viscosity-time were similar to that in Fig. 2 when initial PAA concentration or acetic anhydride amount was different.

Effect of acetic anhydride amount

Acetic anhydride/pyridine is not only a dehydrating agent during imidization but also a diluter when it is just added into PAA solution. As shown in Fig. 3a, initial solution viscosity(η_0) was reduced as acetic anhydride amount increased. PA-I molecular chains can easily get together because of their strong interaction from increased PI component during imidization. Phase separation did not occur until ID was up to ID_c. Figure 3 showed that ID_c was
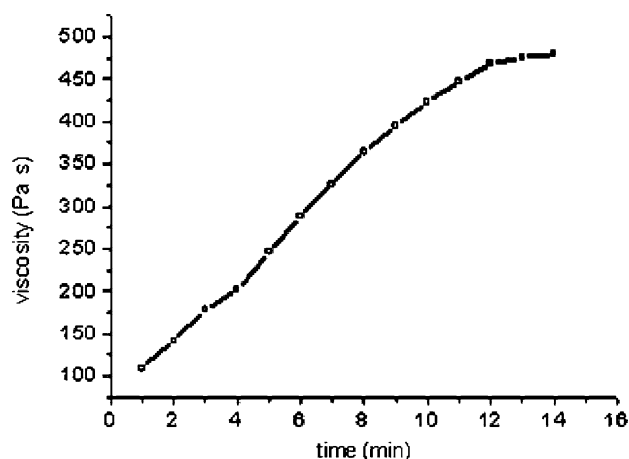

Fig. 2 Relationship between the viscosity of PA-I (15 wt% initial PAA concentration) solution and imidization time in imidizaon (60 mol% acetic anhydride) before phase separation
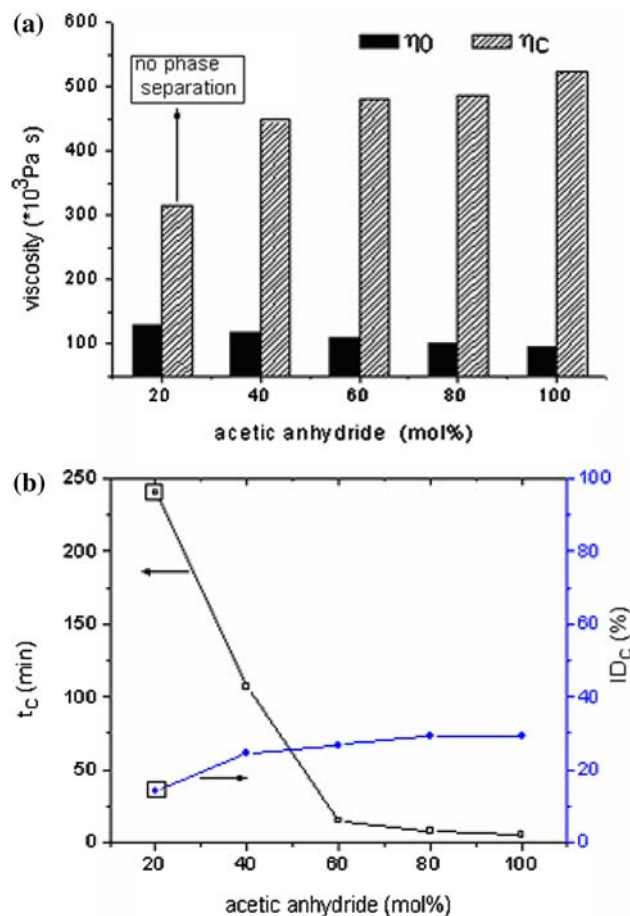

Fig. 3 The effects of acetic anhydride amount on viscosities, ID_c and t_c of PA-I solutions. Initial PAA concentration is 15 wt%. The data in rectangle were those determined at 4 h for which phase separation had not appeared

$27 \pm 2.5\%$ and viscosity of PA-I solution at CPPS (η_c) changed a little (in the range of 448–524 Pa s) when acetic anhydride increased from 40 to 100 mol%. Higher amount of acetic anhydride can accelerate phase separation due to faster imidization. Phase separation time (t_c) shortened by 102 min when acetic anhydride increased from 40 to 100 mol%. However, when acetic anhydride was 20 mol%, phase separation did not occur after imidization proceeded for 4 h because of lesser reactive centers. The final ID was only 14.03% at which PA-I could dissolve well in solvent.

Effect of initial PAA concentration

There was a great difference in t_c of PA-I for different addition of acetic anhydride. So, we chose 60 mol% acetic anhydride when we discussed the effect of initial PAA concentration on the phase separation of PA-I solution in order to observe and obtain a sample conveniently.

As shown in Fig. 4, η_0 and η_c increased while ID_c changed a little as initial PAA concentration was increased. ID_c was $25 \pm 2\%$ when initial PAA concentration increased from 3 to 25 wt%. Higher initial PAA concentration accelerates imidization, and therefore increased phase separation speed. On the other hand, relatively less solvent further sped up phase separation. t_c was shortened by 27 min when initial PAA concentration increased from 3 to 25 wt%. Experiment results showed that initial PAA concentration had a great effect on η_c and a little effect on ID_c. This may be attributed to different distribution of areas of macroscopically homogenous solution before phase separation. Lower initial PAA concentration was beneficial to intramolecular cyclization and could suppress intermolecular reaction; therefore, the whole area exhibited a homogenous solution. While for higher initial PAA concentration, the two reactions proceeded simultaneously and the solubility of partial area was better due to intermolecular reaction, thus, solution was macroscopically homogenous.
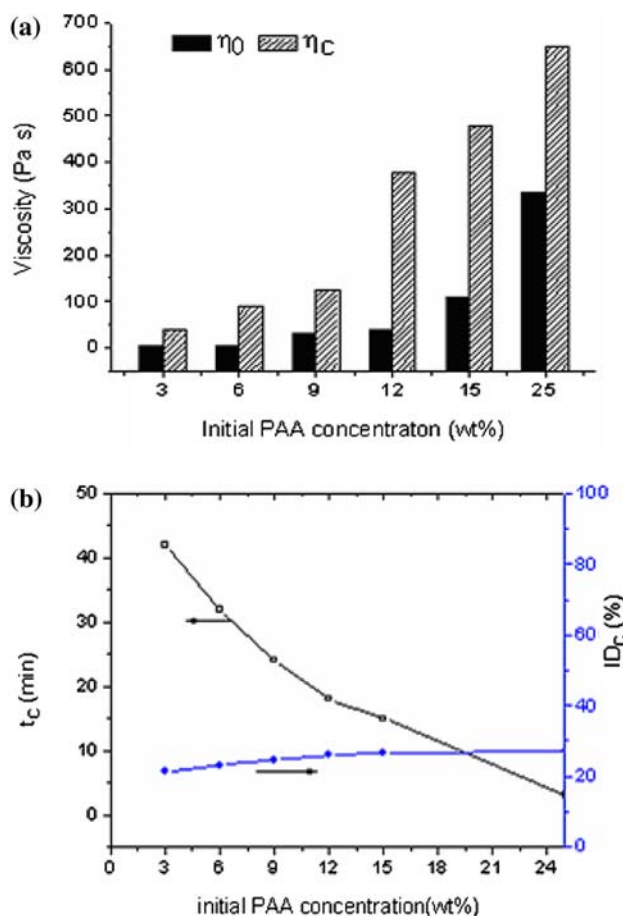

Fig. 4 The effects of initial PAA concentration on viscosities, ID_c, and t_c of PA-I solutions (acetic anhydride: 60 mol%)

Control of imidization degree of PA-I solution

The degree of morphologic ordering and properties of final PI films depend on the ID of PA-I solution. Thus, it is important to control the ID of PA-I solution before PI film was prepared. As shown in Fig. 5, the 3D diagram of acetic anhydride–ID_c–t_c was plotted according to Fig. 3b in order to clearly understand the control of ID of PA-I solution by acetic anhydride amount and imidization time. Curve ABCDEF represented the maximum ID and phase separation time with different acetic anhydride amount. Thus, plane 1, plane 2, plane 3, plane 4, and plane 5 denoted phase separation interface, before which the region was a homogeneous one, and after which, the region on the top of plane 6, plane 7, plane 8, plane 9, and plane 10 was a two-phase one. Specifically, the meaning of line AB was different from that of curve BCDEF since the minimum acetic anhydride amount was 40 mol% when phase separation occurred in our experiment. Therefore, line AB denoted the maximum ID of homogenous PA-I solution when acetic anhydride amount was less than 20 mol%, and the region on the top of plane 6 was nonexistent in solution. Depending on the imidization time, the same value of ID in PA-I solution could be obtained with different amount of acetic anhydride in homogeneous region, and the viscosity in this region was 93.6–524 Pa s. Thus, it is convenient to control ID of PA-I solution by using adequate acetic anhydride amount and imidization time.
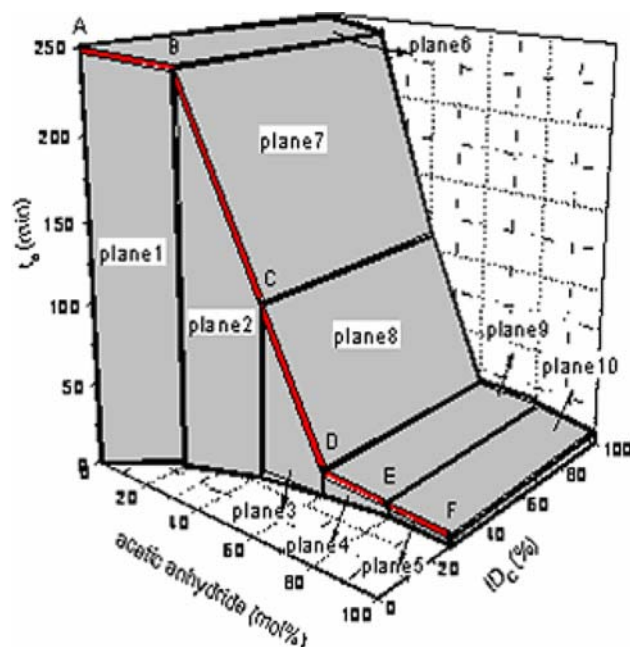

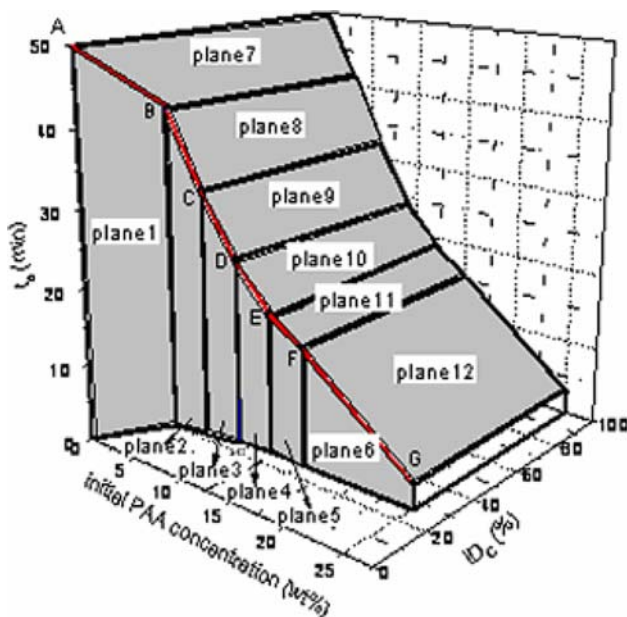Fig. 5 3D diagram of acetic anhydride–ID_c–t_c

Fig. 6 3D diagram of initial PAA concentration–ID_c–t_c (60 mol% acetic anhydride)

As shown in Fig. 6, the 3D diagram of PA–ID_c–t_c was plotted on the basis of Fig. 4b to distinctly know the control of ID of PA-I solution by initial PAA concentration and imidization time. Curve ABCDEFG represented the maximum ID and phase separation time with different initial PAA concentration. Thus, plane 1, plane 2, plane 3, plane 4, plane 5, and plane 6 represented phase separation interface, before which the region was a homogeneous one, and after which, the region on the top of plane 7, plane 8, plane 9, plane 10, plane 11, and plane 12 was a two-phase one. In homogeneous region, a same value of ID in PA-I solution could be obtained with different initial PAA concentration by controlling the imidization time, and the viscosity in this region was 1.8–648 Pa s. Thus, it is facilitated to control ID of PA-I solution by choosing appropriate initial PAA concentration and imidization time.

Effect of imidization degree of PA-I solution on ordering degree and property of PI film

In order to investigate the effect of ID in PA-I solution on morphologic structure and properties of PI films, we subjected PA-I with partial chemical conversion to thermal imidization. On the basis of Figs. 5 and 6, some solutions with different ID were prepared, as listed in Table 1. Sample 1 was PAA solution; samples 2 and 3 were PA-I solutions whose IDs were 8.07% and 19.11%, respectively, by adding 20 and 60 mol% acetic anhydride into 10 wt% PAA solutions, and correspondingly reacting for 1 h and 15 min. The three reacted solutions were cast on glass substrate and were thermally imidized as following imidization process: 323 K for 30 min, 373 K for 1 h, 473 K for 1 h, 573 K for 1 h. Though IDs of PA-I solutions were different before thermal imidization, IDs of final PI films were almost the same (100%), as shown in Table 1. Table 1 lists tensile properties of three PI films. With IDs of PA-I solutions increasing, tensile strength, and modulus of PI films increased, while elongation decreased slightly. This was attributed to different degree of morphologic ordering of final PI films. WAXD and ordering degree of three PI films are shown in Fig. 7. The different shape and intensity of peaks indicated the difference in the degree of morphologic ordering of final PI films. PA-I solution with higher ID showed sharper and stronger peak in their WAXD, and resulted in higher ordering degree. This may be related to regularity of molecular arrangement in initial PA-I solution. As ID increased, PA-I chain mobility decreased in solution because of the restriction of rigid imido rings increased gradually. This implied that reduction of molecular chain mobility was helpful to improve the molecular arrangement in solution. Moreover, the regularity of molecular arrangement in PA-I solution was mostly preserved and somewhat improved by thermal imidization. Therefore, PI film prepared from solution with higher ID has more regular molecular arrangement and greater tensile strength and modulus. From above discussion, we can infer that the

Table 1 IDs and tensile properties of PI films based on PA-I solution with different ID

Sample	Types of PA-I solution[a]	ID of PA-I solution (%)	ID of PI film (%)	Tensile properties of PI film[b]		
				Strength (MPa)	Modulus (GPa)	Elongation (%)
1	PAA	0	100	104.70	2.087	15.95
2	PAA + 20 mol% acetic anhydride, 3 h	8.07	99.43	115.40	2.182	14.60
3	PAA + 60 mol% acetic anhydride, 15 min	19.11	99.86	125.40	2.579	13.15

[a] 10 wt% initial PAA concentration

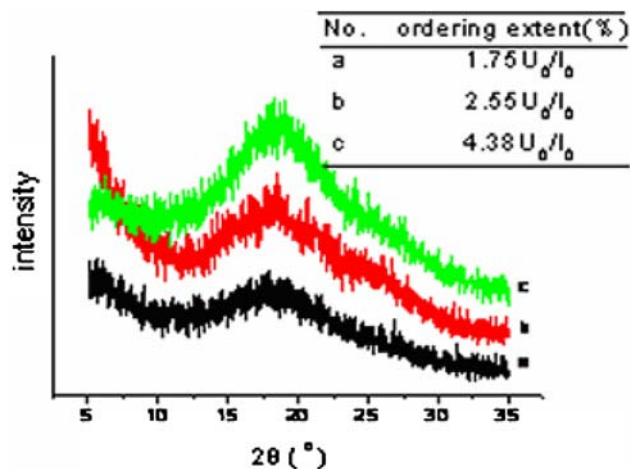[b] Curing process: 323 K/30 min, 373 K/1 h, 473 K/1 h, 573 K/1 h

No.	ordering extent(%)
a	$1.75 U_0/I_0$
b	$2.55 U_0/I_0$
c	$4.38 U_0/I_0$

Fig. 7 WAXD of PI films from different solutions. Curing process: 323 K/30 min, 373 K/1 h, 473 K/1 h, 573 K/1 h. (**a**) PAA. (**b**) PAA and 20 mol% acetic anhydride reacted for 1 h. (**c**) PAA and 60 mol% acetic anhydride reacted for 20 min

degree of morphologic ordering and mechanical properties of final PI films are dependent on ID of PA-I solution before thermal imidization and are not relative to ID of final PI film after thermal imidization.

Conclusion

PAA based on PMDA–ODA can be chemically converted to the corresponding copolyamic acid-imide (PA-I) at ambient temperature by treatment with a mixture of acetic anhydride and pyridine. During imidization, decreasing solubility of PA-I in solvent resulted in phase separation, and homogeneous PAA solution was converted into heterogeneous PA-I solution. Phase separation occurs when the ID of PA-I solution is about 26%. Phase separation time is shortened as acetic anhydride amount or initial PAA concentration increased. ID of PA-I solution can be controlled conveniently by adjusting acetic anhydride amount, initial PAA concentration and imidization time. PI films prepared from PA-I solutions with different ID by thermal imidization differ in their degree of morphologic ordering and properties. With the ID of PA-I solution increasing, the ordering of molecular arrangement of the corresponding PI film was improved, and tensile strength and modulus of the film increased. Thus, a series of PI films with different degree of morphologic ordering and properties can be obtained by PA-I solution with different imidization degree.

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