

Catalysis and Inhibition of Benzimidazole Units on Thermal Imidization of Poly(amic acid) *via* Hydrogen Bonding Interactions^{*}

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Abstract The effect of benzimidazole units on thermal imidization was studied when they were introduced into the main chain of poly(amic acid) (PAA). The thermal imidization process of PAA-PABZ synthesized by 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2-(4-aminophenyl)-5(6)-aminobenzimidazole (PABZ) was studied by TGA, DSC, DMA, FTIR and *in situ* FTIR. The results of FTIR and *in situ* FTIR indicate benzimidazole units act as an “*in situ*” catalyst to accelerate thermal imidization of PAA to polyimide (PI) when the temperature is lower than 170 °C. FTIR and ¹H-NMR results demonstrate that *in situ* catalysis is caused by the hydrogen bonding interactions between C=N of benzimidazole and —NH— in —CONH— of PAA and the semi-ionization of the H in imidazole ring of benzimidazole. However, when the imidization temperature is higher than 170 °C, the thermal imidization process is inhibited. DMA and *in situ* FTIR results illustrate that the decreased mobility of PI-PABZ macromolecular chains and the reduced reactive ability of anhydride formed during the intramolecular breakdown of polymer chains lead to the inhibition of thermal imidization process.

Keywords: Benzimidazole; Hydrogen bonding; Catalysis; Inhibition; Polyimide.

INTRODUCTION

Aromatic polyimides (PIs) are an important member of aromatic heterocyclic polymers, which are well known for their outstanding thermal stability, chemical resistance, mechanical properties, dielectric, dimensional stability and good resistance to irradiation^[1–4]. Because of these excellent properties, PIs have been widely used in many applications such as in the aerospace, optoelectronics, microelectronics industries and so on^[5–9]. However, the properties of polyimides, especially the mechanical properties, are still need to be highly improved in order to meet the requirements for the application in the severe environment.

For most of PIs, there is no hydrogen bonding interactions between PI chains when the thermal imidization has been completely finished, which is not conducive to the improvement of the properties of PIs. Introducing hydrogen bonding into PI main chains by molecule design is an available method to significantly enhance the overall performance of PI, such as mechanical properties, thermal properties, dimensional stability and so on^[10–12]. The research of polyimide contains 2-(4-aminophenyl)-5(6)-aminobenzimidazole (PABZ) has been focused in recent years since PABZ involves both proton donor (—NH—) and proton acceptor (=N—) simultaneously, the benzimidazole units can not only increase the rigidity of PI polymer backbone but also form strong intermolecular and intramolecular hydrogen bonding (H-bonding) interactions in PI chains even when the

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thermal imidization has been completely finished, which is different from the traditional polyimides. For example, Gao^[13, 14] introduced the diamine containing benzimidazole moieties into PMDA/ODA PI system, when the diamine ratio of 2-(4-aminophenyl)-5-aminobenzimidazole was 70%, the tensile strength reached 1.53 GPa, which was almost three times over that of the PMDA/ODA PI fibers. Wang^[15] prepared a series of PI films containing benzimidazole, the tensile strength and modulus of films were up to 234 MPa and 5.6 GPa, respectively and the thermal stability of the films had also been improved, the T_g of PIs could reach up to 425 °C. Song^[16] and his co-workers found that the in-plane CTE value of benzimidazole-based PI film was negative when cured at 350 °C (contract upon heating) and the value of CTE turned positive when cured at 400 °C. Our previous article^[17] found the especial “sudden crystalline” behavior in benzimidazole-based PI compared to the “gradual crystallization” process of conventional PI. Thus, the benzimidazole-based PIs have become a hot research fields on high-performance PI material in recent years.

Polyimides are usually synthesized by a two-stage process^[18]. In the first stage, the soluble precursor polyamic acid (PAA) is obtained by dianhydride reacting with diamine in a polar solvent such as dimethylacetamine (DMAc) and *N*-methylpyrrolidone (NMP), then the PAA is cyclized into infusible and insoluble PI through thermal imidization. The thermal imidization of PAA is a complicated physicochemical process, there is a set of series-parallel reactions besides the main thermal imidization reaction, such as the solvent evaporation, water evaporation, decomplexation of PAA/solvent, PAA hydrolysis, intramolecular breakdown, re-polymerization and so on^[19]. The changes happened during the process of thermal imidization have a prominent effect on the structure and properties of polyimides, so the research of thermal imidization process is an important issue for improving the properties of PIs^[20]. In previous references^[21–23], it is well known that the hydrogen bonding interactions between solvent and PAA play an crucial role in the thermal imidization process. Because of the versatile structure of benzimidazole, new types of hydrogen bonding interactions can be formed when it is introduced into the main chain of PI, which would affect the thermal imidization.

Previous researches about the thermal imidization process found that the cyclization of the precursor polyamic acid (PAA) to PI could be accelerated when imidazole small molecules were blended in PAA^[19, 24–26]. Mikitayev^[19] found that adding of tertiary amines imidazole or benzimidazole small molecules led a higher degree of imidization. Nelson^[25] found that PAA had a faster imidization rate when blended with polybenzimidazole (PBI) than without PBI. The catalysis effect of imidazole units on the thermal imidization when they are blended with PAA is obvious, now the curious thing is that what kind of effect would produce if they are introduced into the main chain of PAA by polymerization.

In this paper, we comparatively study the thermal imidization process of benzimidazole-based PI (PI-PABZ) and benzoxazole-based PI (PI-BOA). The only difference between benzimidazole and benzoxazole units is that the $-\text{NH}-$ in the five-member ring of benzimidazole is replaced by $-\text{O}-$ in benzoxazole. Without hydrogen proton, H-bonding can not be formed in PI-BOA. The effect of H-bonding interactions on thermal imidization is discussed in detail. We find the *in situ* catalysis behavior of imidization below 170 °C and inhibition behavior above 170 °C in PI-PABZ. This situation that benzimidazole units have different effects on the thermal imidization process of PAA at different temperatures is a new discovery that has never been reported, which would have a guiding significance on the research of polyimide materials.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP), obtained from Shanghai Qunli Chemical Company, was distilled over P_2O_5 under reduced pressure before used. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) was supplied by Changzhou Sunlight Pharmaceutical Co., Ltd (Changzhou, China), and dried in an oven at 200 °C for 10 h at least prior to use. 2-(4-Aminophenyl)-5(6)-aminobenzoxazole (BOA) and 2-(4-aminophenyl)-5(6)-aminobenzimidazole (PABZ) were provided by Changzhou Sunlight Pharmaceutical Co., Ltd (Changzhou, China) and used as received. Phthalic anhydride (PA) was obtained from Chengdu Kelong Chemical Co. Ltd. and used as received.

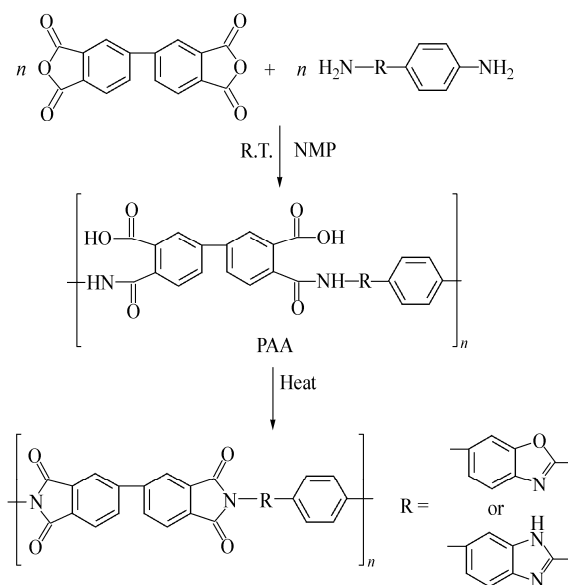
Synthesis of Poly(amic acid)s and Model Compounds

The poly(amic acid)s (PAAs) were synthesized through the polycondensation between 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) with 2-(4-aminophenyl)-5(6)-aminobenzoxazole (BOA) or 2-(4-aminophenyl)-5(6)-aminobenzimidazole (PABZ) in stoichiometric balance. For example, 14.0792 g (0.06285 mol) PABZ and 200 mL NMP were added into a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet-tube and an outlet-tube, after the diamine was dispersed uniformly, 18.4789 g (0.06285 mol) BPDA was added into the solution in two portions of 85% and 15%. The reaction mixture was stirred at room temperature for 48 h under dried nitrogen atmosphere in an ice bath. The solid content of benzimidazole-based PAA (PAA-PABZ) and benzoxazole-based PAA (PAA-BOA) solutions were both 14%.

The model compound (PA-PABZ) of PAA-PABZ was synthesized by PABZ and PA, PABZ and PA were added into distilled NMP in a 1:2 mole ratio to make a 15% by weight solution. The solution was stirred at room temperature for 8 h under flowing N_2 , then ethanol was added and solution was filtered under vacuum. The filtered powder was washed with more ethanol and filtered again, this procedure was repeated several times and finally the filtered powder was dried in an oven for 8 h at 60 °C.

Preparation of PI Fibers

The PAA solutions were filtered and degassed at room temperature under reduced pressure for 48 h prior to spinning. The precursor fibers were prepared *via* wet spinning. The PAA solutions were extruded through a spinneret of 50 holes with a diameter of 100 μ m, and then entered into the first coagulation bath followed by the second coagulation bath, at last they were collected on a rotating spool. Then the PAA fibers were dried in vacuum oven for 6 h at 50 °C immediately after spinning, and then they were converted to PI fibers through thermal imidization at different temperatures without tension under vacuum at a heating rate of 6–8 K/min. The reaction process of synthesis is shown in Scheme 1.



Scheme 1 The preparation process of polyimide

Preparation of PAA and PAA/PI Films

The PAAs were first cast onto clean and dry glass plates and were subsequently imidized by heating at 80 °C for 1 h, 150 °C for 1 h, 220 °C for 1 h and 300 °C for 1 h in a vacuum oven. So the PAA/PI films of thermal imidization at different temperatures were obtained. The PAA films were obtained by drying in vacuum oven for 6 h at 50 °C.

Characterization

Thermogravimetric analysis (TGA) was carried out on a TGA-2950 TA instrument under N_2 atmosphere at a heating rate of 5 K/min in the range of 30–300 °C. Differential scanning calorimetry (DSC) data was obtained with a DSC Q200 thermal analyzer at a scanning rate of 10 K/min from 40 °C to 450 °C. Dynamic mechanical analysis (DMA) was performed on a TA instrument DMA Q800 under N_2 atmosphere, scanning from room temperature to 550 °C at a heating rate of 10 K/min, the load frequency applied was 1 Hz. Fourier transform infrared (FTIR) spectra of PI fibers were recorded on a Nicolet Magna 650 Fourier transform spectroscope from 4000 cm^{-1} to 400 cm^{-1} , the resolution was 4 cm^{-1} . *In situ* FTIR spectra were collected with a Nicolet 560 spectrometer equipped with a deuterated triglycine sulfate detector, the spectral resolution was 4 cm^{-1} and the number of scans of each spectrum was 40. The *in situ* FTIR spectra were collected from 100 °C to 300 °C with a constant heating rate of 5 K/min under the protection of dried high-purity nitrogen gas during measurement. Proton nuclear magnetic resonance (^1H -NMR) spectroscopy of the model compound was recorded on a Bruker Fourier Transform AC200 spectrometer at 400 MHz.

RESULTS AND DISCUSSION

The Additional Hydrogen Bonding Interactions in PAA-PABZ

The solvent *N*-methylpyrrolidone (NMP) can form hydrogen bonding (H-bonding) with carboxyl and amide groups of PAA^[22, 23]. With the increase of heat temperature, the hydrogen bonding interactions between NMP and carboxyl and amide groups are destroyed, followed by the decomplexation of NMP molecules from PAA and then the imidization reaction between adjacent $-COOH$ and $-CONH-$ starts^[19]. Thermogravimetric analysis (TGA) is usually used to investigate the liberation process of solvent in PAA solutions. The TGA curves of two PAA solutions are illustrated in Fig. 1. The significant weight loss is due to the liberation of NMP solvent molecules. As the weight-temperature curves show, both of the PAA-PABZ and PAA-BOA solutions display a large weight loss during the heat treatment at 30–150 °C. The maximum rate of the weight loss for PAA-PABZ happens at 105 °C, which is much lower than that of PAA-BOA at 130 °C. This result indicates that the decomplexation of NMP molecules from PAA-PABZ solutions is easier than that from PAA-BOA.

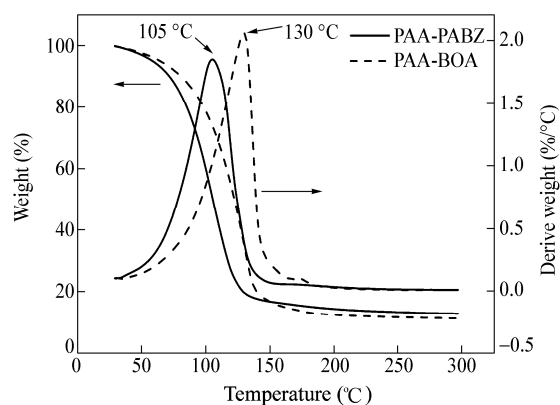


Fig. 1 The TGA curves and the corresponding differential curves of PAA-PABZ (solid curves) and PAA-BOA (dashed curves)

The same result can also be obtained by DSC as shown in Fig. 2, the endothermic peak at 130–140 °C in both of the two curves is mainly caused by the volatilization of NMP molecules and a small amount of water generated by the thermal imidization of PAA to PI^[23]. The onset of volatilization for PAA-PABZ appears at around 100 °C and the endothermic peak reaches the maximum at 131 °C, but that for PAA-BOA does not appear until 125 °C and the endothermic peak centers at 137 °C. The results show that the volatilization of NMP solvents for PAA-PABZ occurs at a lower temperature, which is consistent with the TGA results.

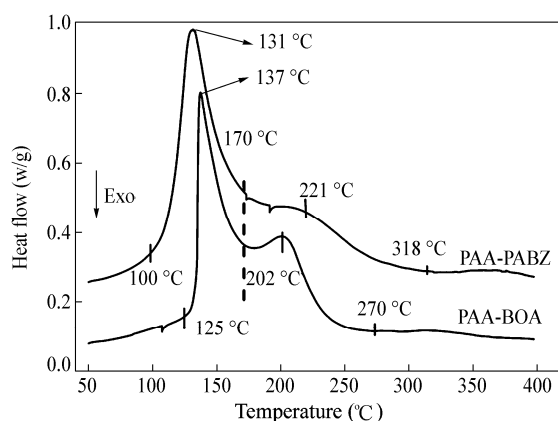


Fig. 2 The DSC curves of PAA-PABZ and PAA-BOA

The different volatilization behavior of NMP solvent molecules in PAA-PABZ and PAA-BOA solutions with the same solid content could be caused by the specific effect of $C=N$ in benzimidazole on the hydrogen bonding between PAA and NMP molecules. The unshared electron pairs of the N atom of $C=N$ in benzimidazole and benzoxazole endue them with basic property. It has been reported that benzimidazole is alkaline^[27] whose pK_a is 5.4, while NMP is a weak base in PAA whose pK_a is smaller than 2.0^[28]. Due to its higher basicity, benzimidazole is totally capable of competing with small NMP molecules in formation of interchain interactions with carboxyl and amide groups of PAA, as shown in Fig. 3. Compared to benzimidazole, benzoxazole does not have the ability to compete with NMP molecules because the pK_a of oxazole is small, which is 0.8 or 1.2^[29], and the pK_a will decrease as a result of the conjugation when the benzene ring linked to form a benzoxazole^[30]. Therefore, the NMP molecules are partial replaced by benzimidazole units and more small NMP molecules become “free” in PAA-PABZ, which is proven by the fact of the faster volatilization of NMP from PAA-PABZ in the results of TGA and DSC.

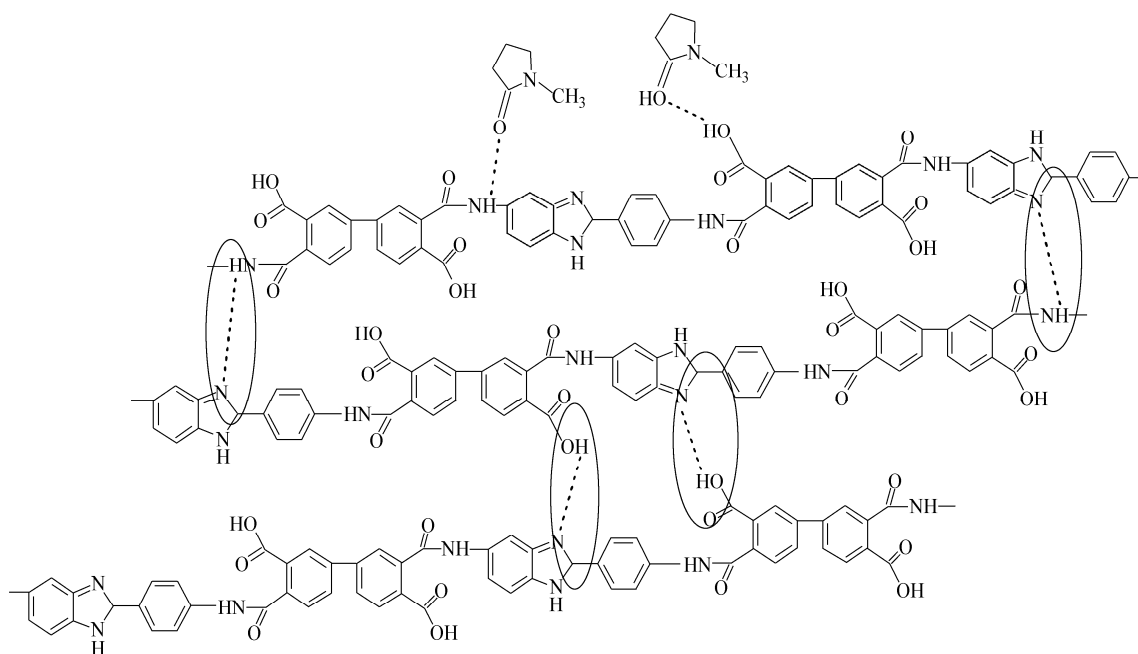


Fig. 3 The schematic diagram of hydrogen bonding interactions between $C=N$ of benzimidazole and $-CONH-$ and $-COOH$ of PAA-PABZ

The additional hydrogen bonding interactions between C=N in benzimidazole and $-\text{COOH}$ and $-\text{CONH}-$ groups in PAA-PABZ can be investigated by the frequency shifts of the C=N. When C=N in benzimidazole forms hydrogen bonding with $-\text{COOH}$ and $-\text{CONH}-$, the frequency of the C=N will shift with the change of the degree of imidization. The FTIR curves of PI-PABZ fibers and PI-BOA fibers in $1300\text{--}1550\text{ cm}^{-1}$ at different temperatures are shown in Fig. 4. The characteristic absorption of C=N group in benzimidazole/benzoxazole units is at $1470\text{--}1480\text{ cm}^{-1}$ ^[31, 32]. With the annealing temperature increasing from $80\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$, the C=N stretching band position of benzimidazole units obviously shifts from 1470.5 cm^{-1} to 1477.8 cm^{-1} . This blue shift confirms the existence of H-bonding interactions between C=N in benzimidazole units and PAA. However, the C=N stretching band position of benzoxazole units at 1479 cm^{-1} is almost unchanged with the increase of temperature, indicating that C=N of benzoxazole units does not take part in forming H-bonding interactions^[17].

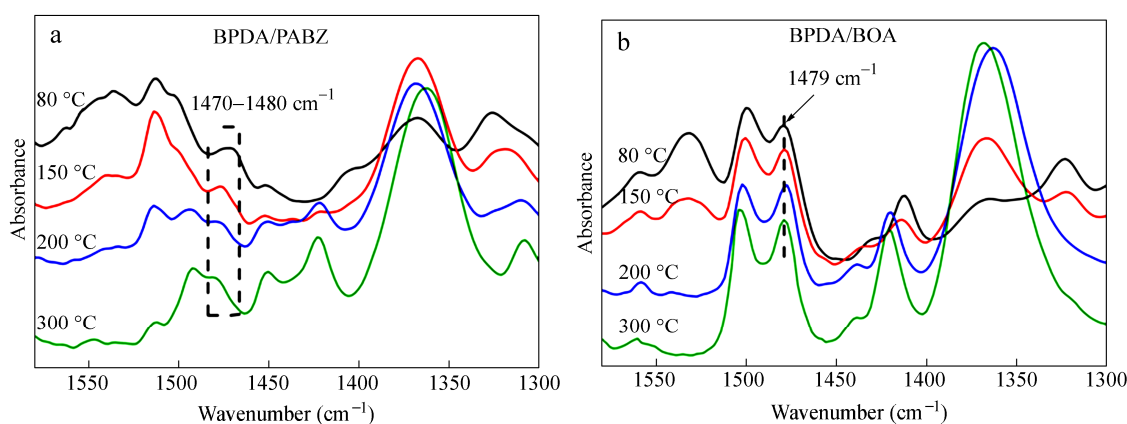


Fig. 4 The shift of C=N in (a) BPDA/PABZ and (b) BPDA/BOA PAA-PI fibers at different temperatures

***In situ* Catalysis on Thermal Imidization of PAA-PABZ**

To investigate further whether the interactions would affect the thermal imidization process of PAA to PI, *in situ* FTIR is applied to track the changes of the rate of imidization of the two systems in the continuous imidization process. Figure 5 shows the changes of the absorbance peak of the two types of PAA-PI films at a heating rate of 5 K/min during $100\text{--}300\text{ }^{\circ}\text{C}$. As shown in Fig. 5, the absorption intensity of the characteristic peaks of amide bond ranging from $1600\text{--}1700\text{ cm}^{-1}$ decreases gradually while the absorption intensities of the imide ring at 1775 cm^{-1} , 1720 cm^{-1} and 1360 cm^{-1} increase with the rise of imidization temperature. To study the characteristics of the rate of imidization under continuous imidization process, the relatively absorbance intensity I_{1775}/I_{840} is calculated to monitor the thermal imidization process, I_{1775} is the intensity of carbonyl vibration of the imide ring at 1775 cm^{-1} , and the C—H bending vibration in the benzene ring around 840 cm^{-1} is selected as the internal standard because the intensity of the peak remains unchanged during the temperature from 100 to $300\text{ }^{\circ}\text{C}$. The change of the relatively absorbance intensity (normalized absorbance intensity) with the temperature rises is shown in Fig. 6. When the temperature is lower than $140\text{ }^{\circ}\text{C}$, the relatively absorbance intensity is weak for both PAA-PABZ and PAA-BOA as there is only minor imidization process accomplished. However, the imidization rate increases significantly after $140\text{ }^{\circ}\text{C}$ since most of the imidization process takes place from this temperature.

The imidization rates of PAA-PABZ and PAA-BOA are calculated by the following equation to investigate whether the hydrogen bonding interactions between $-\text{COOH}$ and $-\text{CONH}-$ groups of PAA and C=N of benzimidazole unit could affect the imidization process:

$$\nu = dc/dt \quad (1)$$

where ν is the imidization rate, the higher of the value of ν is, the faster of the rate of imidization will be, c is the concentration of the polyimide generated, t is the reaction time in minute.

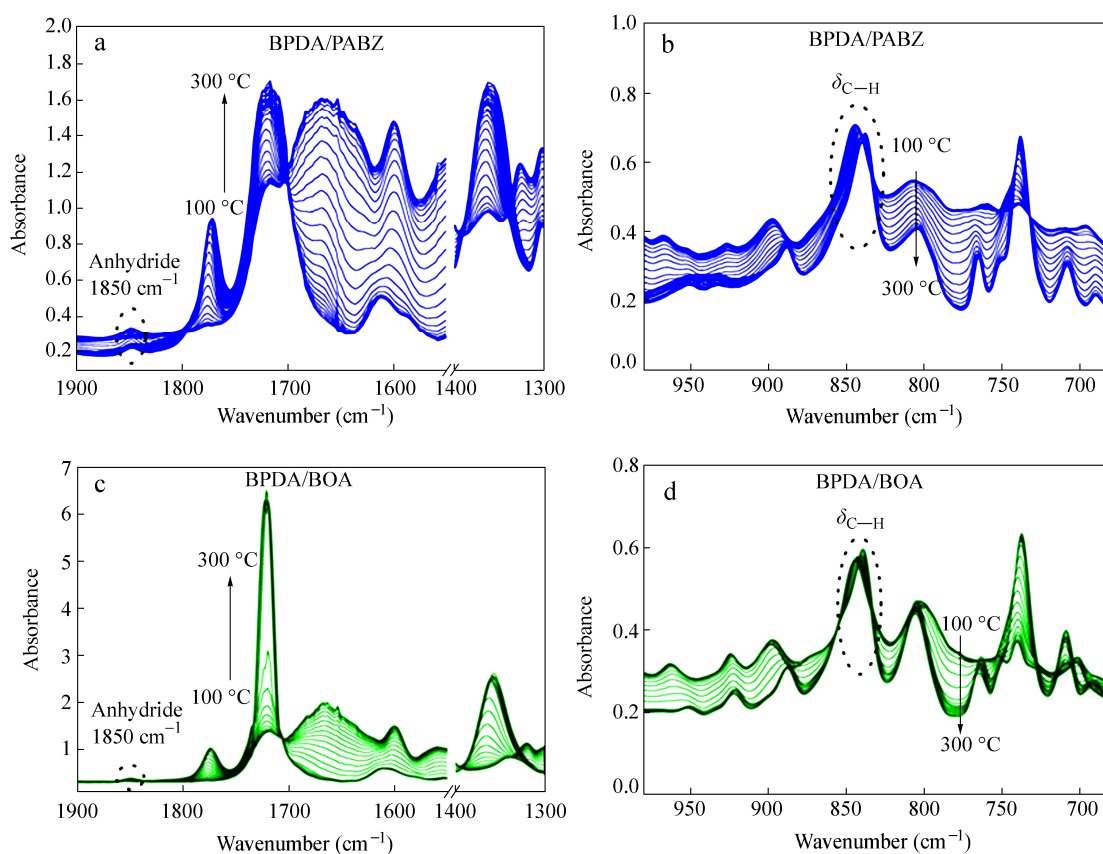


Fig. 5 The *in situ* FTIR spectra curves of (a) (b) BPDA/PABZ PAA-PI films and (c) (d) BPDA/BOA PAA-PI films

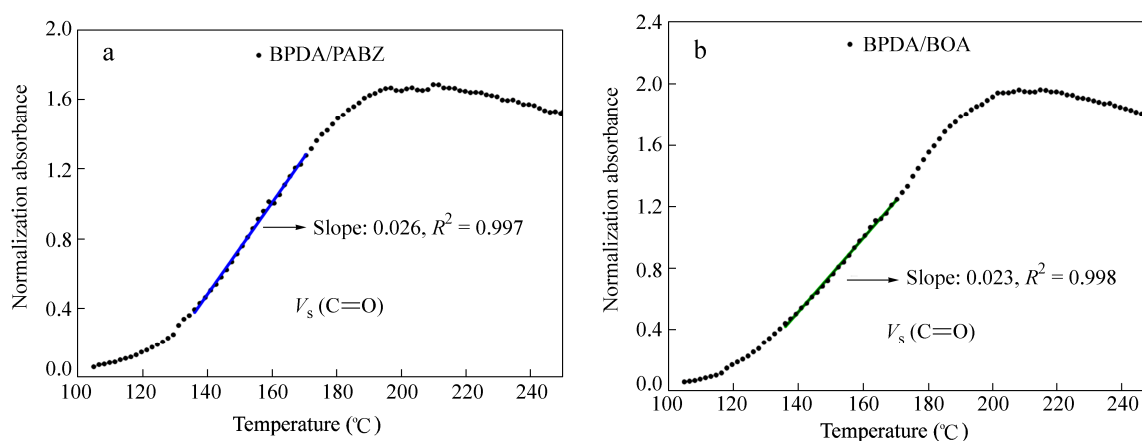


Fig. 6 The normalized absorbance fitting curves of BPDA/PABZ and BPDA/BOA PAA-PI films

As shown in Fig. 6, the normalized absorbance intensity of the imide ring at 1775 cm^{-1} increases linearly between $140\text{ }^{\circ}\text{C}$ and $170\text{ }^{\circ}\text{C}$ both in BPDA/PABZ and BPDA/BOA systems. To calculate the imidization rates of the two systems, we transform the temperature to the time by their relationship with the heating rate. During the

calculation, we set the moment when the temperature is 140 °C as the start time, the heating rate is 5 K/min, so the time t and the concentration of the polyimide generated c can be replaced by expressions (2) and (3):

$$t = (T - 140) \quad (2)$$

$$c = I_T / I_{\max} \quad (3)$$

where I_T is the normalized absorbance intensity at the temperature T , $I_{\max}$ is the normalized absorbance intensity when PAA is completely imidized, and it is 2.52 and 2.96 for BPDA/PABZ PI and BPDA/BOA PI, respectively. Bring these into Eq. (1), the following expression can be obtained:

$$\nu = d(I_T / I_{\max}) / d\{(T - 140)/5\} \quad (4)$$

Then we can obtain the value of ν by expression (4), they are 0.0516 min⁻¹ and 0.0389 min⁻¹ for PI-PABZ and PI-BOA, respectively, suggesting that PAA-PABZ has a faster rate of imidization during continuous imidization process than PAA-BOA when the temperature is lower than 170 °C. This indicates that benzimidazole unit has a positive effect on the thermal imidization process when the temperature is lower than 170 °C, and previous researches defined this as the catalysis effect of benzimidazole^[24–26].

Furthermore, FTIR is used to determine the degree of imidization (DOI) of PI fibers at different temperatures. Figure 7 shows the FTIR spectra for BPDA/PABZ and BPDA/BOA PAA-PI fibers, the two kinds of PAA fibers were treated at 80 °C, 150 °C, 200 °C, 250 °C, 300 °C and 320 °C respectively for 1 h before tested by FTIR. Generally, the DOI of PI is acquired by calculating the ratio between the area of the characteristic peaks corresponding to the imide ring and the area of the internal standard peak corresponding to the C=C stretching in the benzene ring which does not change during the imidization process. The calculation is undertaken on the assumption that PI fibers are fully 100% imidized when the calculated ratio is constant, so the DOI of PIs at different temperatures represents the relative values. In this work, the peak area of the phthalimide carbonyl stretching bands at 1780 cm⁻¹ is used to calculate the DOI, and the peak of C=C in the benzene ring at 1500 cm⁻¹ is used as the internal standard band. The formula for calculating the degree of imidization is:

$$w = \frac{(A_{1780}/A_{1500})_T}{(A_{1780}/A_{1500})_{\max}} \quad (5)$$

where w is the degree of imidization, $(A_{1780}/A_{1500})_T$ is the area ratio of the symmetric stretching vibration C=O in the imide ring (A_{1780}) and the C=C vibration in the benzene ring (A_{1500}) at temperature T , $(A_{1780}/A_{1500})_{\max}$ is the area ratio of the two bands when the imidization is fully completed. The maximum value of A_{1780}/A_{1500} is at 300 °C for PAA-BOA and it is at 320 °C for PAA-PABZ.

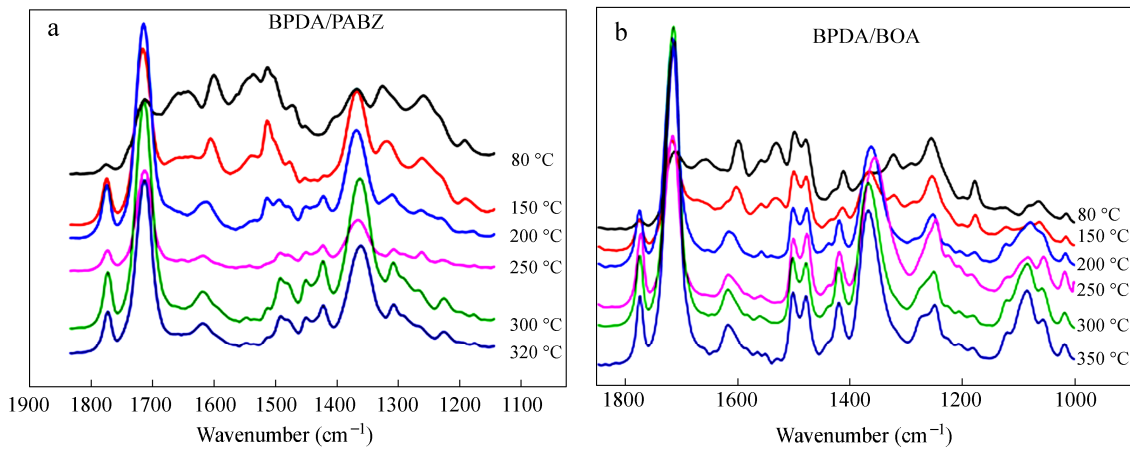


Fig. 7 FTIR spectras for (a) BPDA/PABZ and (b) BPDA/BOA PAA-PI fibers

The degree of imidization against the cure temperature with 1 h annealing at each temperature is shown in Fig. 8. When the temperature is lower than 170 °C, the DOI of PAA-PABZ fiber is higher than that of PAA-BOA fiber at the same temperature, suggesting the catalysis effect of benzimidazole unit on the thermal imidization process of PAA-PABZ, which is consistent with the result of *in situ* FTIR.

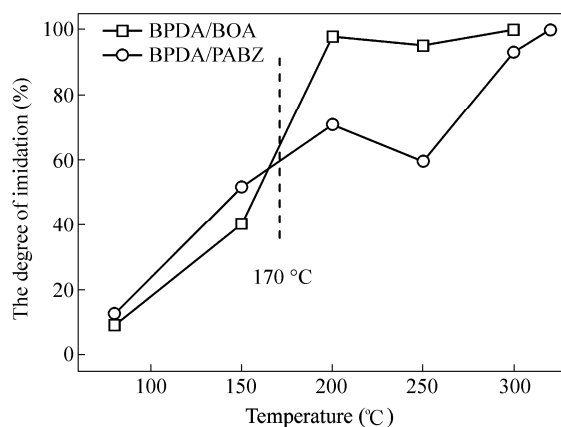


Fig. 8 The degree of imidization of two PAA-PI fibers at different temperatures

As discussed above, the imidization rate of PAA-PABZ is promoted when C=N in benzimidazole unit replaces C=O in NMP molecule to form hydrogen bonding with PAA, which means that the hydrogen bonding interactions between C=N of benzimidazole unit and $-\text{COOH}$ or $-\text{CONH}-$ of PAA could catalyze the imidization process when the temperature is lower than 170 °C.

However, even though there is also a C=N bond in benzoxazole ring of BOA, it could not catalyze the thermal imidization process of corresponding PAA as the C=N in benzimidazole ring of PABZ does. This difference could be interpreted in two aspects. First, as mentioned above, the pK_a value of BOA is lower than that of NMP molecule, which makes BOA could not compete with NMP to form hydrogen bonding with $-\text{COOH}$ and $-\text{CONH}-$ of PAA. Second, H in imidazole ring of benzimidazole is semi-ionization^[33] which can be confirmed by proton nuclear magnetic resonance (^1H -NMR) spectroscopy. The chemical shift δ of $-\text{NH}-$ in R_2NH is 0.4–3.5 usually. However, the $-\text{NH}-$ signal of imidazole ring shifts downfield to 12.71 as the ^1H -NMR spectra of the model compound PA-PABZ shows in Fig. 9, which is close to the δ of H in $-\text{COOH}$ (13.06), meaning that the atom H in $-\text{NH}-$ of imidazole ring is semi-ionization. The charge density of the

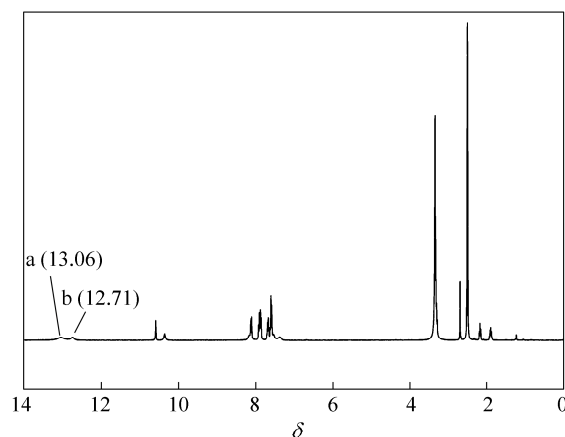
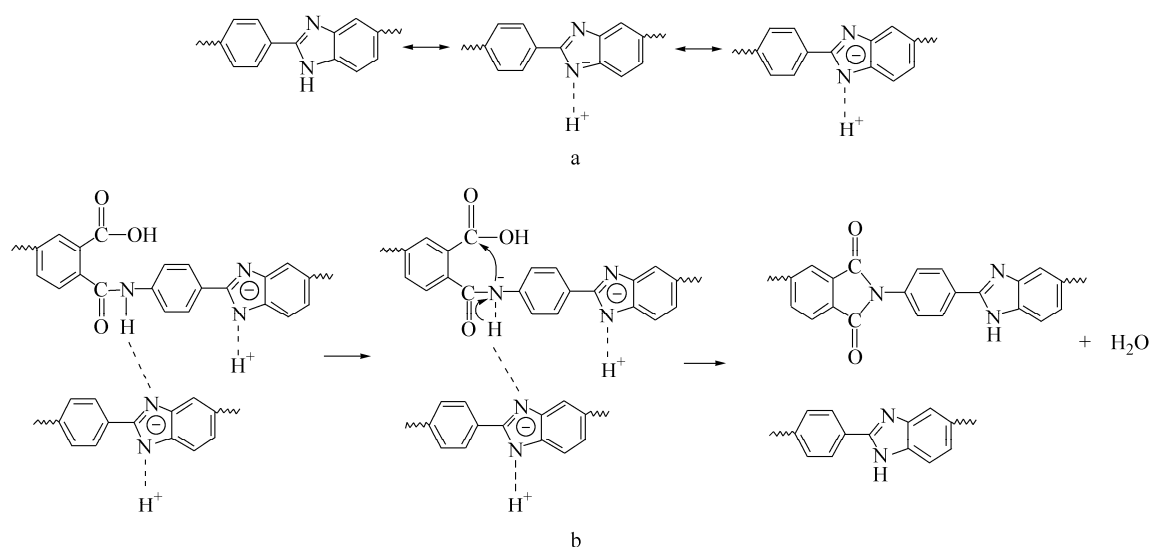


Fig. 9 ^1H -NMR spectrum of the model compound PA-PABZ

imidazole ring in benzimidazole unit increases because the increased electronegativity of N atom in —NH— caused by the semi-ionization of benzimidazole, the charge density of the atom N in C=N will also increase correspondingly as shown in Scheme 2(a). Therefore, C=N in benzimidazole could compete with NMP molecules to form hydrogen bonding with —CONH— and —COOH in PAA. When it attracts the H atom in —CONH— of PAA to form hydrogen bonding, there will form an active complex of amido acid fragment with the imidazole ring of the neighboring chain, the electron cloud density and the nucleophilicity of the N atom in —CONH— would increase correspondingly, which is conducive to the imidization process of PAA to PI as shown in Scheme 2(b). However, the O atom in oxazole ring does not have the ionization tendency and could not increase the charge density of N atom in oxazole ring, so there is no hydrogen bonding between BOA and PAA, and BOA could not catalyze the thermal imidization of PAA as a result.



Scheme 2 (a) The semi-ionization of H in imidazole ring of PABZ; (b) Benzimidazole as a base catalyst in the imidization process

Inhibition Effect of Benzimidazole Units on Thermal Imidization

However, when the temperature is higher than $170\text{ }^{\circ}\text{C}$, most of the PAA have been cyclized to PI, the hydrogen bonding interactions between C=N of benzimidazole and —CONH— and —COOH of PAA would decrease, the catalysis effect of benzimidazole would disappear correspondingly, and the thermal imidization process will be different. As can be seen in Fig. 2, the endotherm caused by imidization process starts from $170\text{ }^{\circ}\text{C}$ in PAA-BOA, and there is a sharp peak at $202\text{ }^{\circ}\text{C}$, while the endothermic peak of PAA-PABZ fibers is not very clear. Besides, the fully imidized temperature for PAA-BOA is $270\text{ }^{\circ}\text{C}$, far lower than $318\text{ }^{\circ}\text{C}$ for PAA-PABZ. The result of FTIR also shows that PAA-BOA has a higher degree of imidization than PAA-PABZ at the same temperature when the temperature is higher than $170\text{ }^{\circ}\text{C}$ as shown in Fig. 8. Both of the results indicate that comparing with the PAA-BOA, the rate of imidization of PAA-PABZ is lower when the temperature is higher than $170\text{ }^{\circ}\text{C}$ and it needs a higher temperature for the final completion of the thermal imidization for PAA-PABZ. In other word, the thermal imidization process of PAA-PABZ is inhibited by benzimidazole units when the temperature is higher than $170\text{ }^{\circ}\text{C}$, which is absolutely different from previous reported results^[19, 26].

The inhibition effect of benzimidazole on thermal imidization process could be explained by the following two reasons. First, when the temperature is higher than $170\text{ }^{\circ}\text{C}$, the mobility of PI-PABZ macromolecular chains weakens because the increased rigidity of the main chains with the formation of strong hydrogen bonding interactions between —NH— of imidazole ring and C=O of imide ring in PI-PABZ, leading the polymer chains cannot realize the conformation sterically favorable for imidization reaction. As for PI-BOA, there is no such

kind of hydrogen bonding interactions since BOA has no —NH— in oxazole ring^[17]. The mobility of polymer chains can be characterized with the glass transition temperature (T_g) of fully imidized PI fibers. Usually, the lower the T_g is, the better the mobility of the polymer chains will be. As shown in Fig. 10, the T_g of PI-BOA is 59 K lower than that of PI-PABZ, suggesting that the chains of PI-BOA can move more easily than that of PI-PABZ, so the imidization will be more difficult for PABZ system than for BOA system. Second, as the thermal imidization process can be reversed during the temperature of 200–300 °C, the anhydrides generated by the break of macromolecular chains could synthesize with diamine to form PAA accompanied with the thermal imidization, so the ability of the re-polymerization of anhydrides will affect the thermal imidization rate of PAA. The chemical reactions that take place after the solvents have been removed completely at 200–300 °C are solid-phase reaction, so the mobility of macromolecular chains will be the main reason that affects the imidization rate. The hydrogen bonding formed between the —NH— of benzimidazole and the C=O of newly-formed anhydride would further decrease the mobility of polymer chains and inhibit the re-polymerization process as a result even though it could enhance the electrophilicity of the anhydride toward amine. As shown in Fig. 5, the characteristic peak of anhydride at 1850 cm^{-1} disappears at higher temperature in PAA-PABZ system than in PAA-BOA system also confirms the decreased ability of re-synthesis of anhydride. The subsequent thermal imidization process would be inhibited correspondingly with the decreased reaction ability of anhydride.

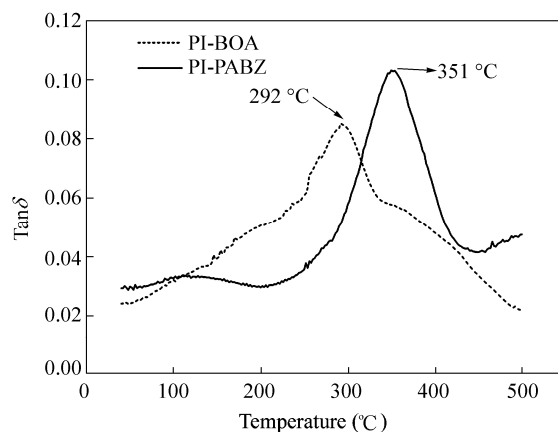


Fig. 10 The DMA curves of PI-PABZ and PI-BOA fibers

CONCLUSIONS

The effect of benzimidazole on the thermal imidization process was studied. The results show that benzimidazole units can catalyze the incipient thermal imidization of PAA-PABZ. But when the temperature is higher than 170 °C, the imidization process is inhibited and PAA-PABZ needs a higher temperature to finish the thermal imidization completely.

When the thermal imidization temperature is lower 170 °C, as benzimidazole unit of PABZ has a higher pK_a than the solvent NMP and the H in imidazole ring is semi-ionization, C=N in imidazole ring and —NH— in —CONH— of PAA can form hydrogen bonding interaction, which could increase the electronegative of N atom in —CONH— and improve the reactivity of cyclization of PAA. And that makes PAA-PABZ fibers have a faster rate of evaporation of NMP molecules and a faster rate of imidization than that of PAA-BOA. In other words, benzimidazole has the “*in situ* catalysis” effect on the thermal imidization process before 170 °C. However, when the thermal imidization temperature rises to more than 170 °C, the strong hydrogen bonding interactions between —NH— of benzimidazole and C=O of imide ring decrease the mobility of PI-PABZ main chains and the hydrogen bonding between —NH— of benzimidazole and C=O of the anhydride generated during the intramolecular breakdown of polymer chains can decrease the reactive ability of newly-formed anhydride to hinder the re-polymerization, the conversion of PAA to PI in BPDA/PABZ is inhibited.

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