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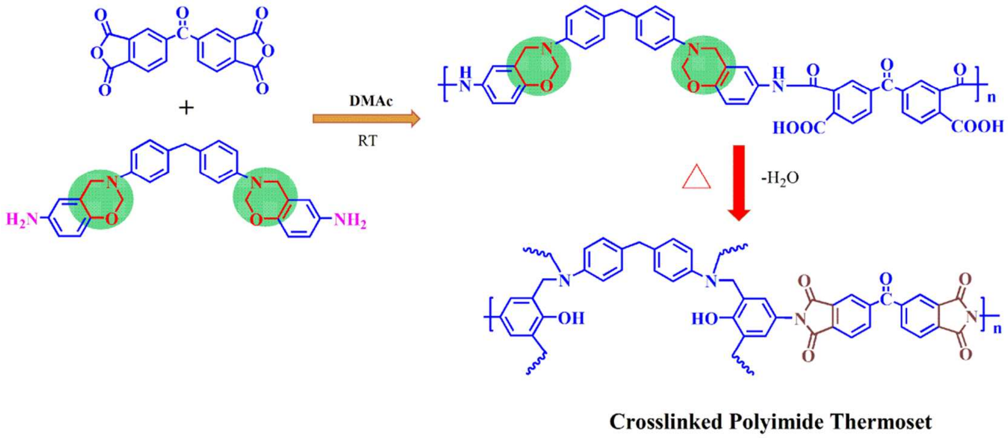
A novel approach has been developed to prepare thermosetting polyimides by incorporating benzoxazine structure as a repeating unit in the main chain. This method allows the crosslinked polyimide with excellent thermal and mechanical properties.



High Performance Crosslinked Polyimide Based on Main-Chain Type Polybenzoxazine

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Abstract

A main-chain type polybenzoxazines with amic acid and benzoxazine groups are repeating units in the main chain, termed as poly(benzoxazine amic acid) (poly(BZaa)), has been synthesized. It has been prepared by polycondensation reaction of primary amine-bifuctional benzoxazine with 3,3’,4,4’-benzophenonetetracarboxylic dianhydride using dimethylacetamide as solvent. Poly(BZaa) can undergo a crosslinking reaction to form a crosslinked polyimide (cPI) at 300 °C. Additionally, a model reaction is designed from the reaction of 3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-amine with phthalic anhydride. The structures of model compound are confirmed by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. Differential scanning calorimetry (DSC) and FTIR are also used to study crosslinking behavior of both model compound and polymers. Thermal properties of the crosslinked polymers are also studied by thermogravimetric analysis (TGA).

Introduction

Polyimide (PI) is an excellent polymer due to its advantages, including high thermal stability, chemical resistance and good mechanical properties. The high performance properties make it widely used as matrices of advanced composites for aerospace and aeronautical applications.[1] The structure of the PI backbone determines the heat resistance as well as the chemical resistance. The rigidity, originating from the combination of the imide structure with an aromatic structure results in polymers with a very high glass transition temperature (*Tg*). Moreover, the partial conjugation of the imide structure promotes a good oxidative stability.[2] However, the chemical structures that lead PI to very high thermal stability also causes processing difficulties. To solve this, the backbone can be diluted with other less stable structures. Therefore, the trade-off generally exists between the thermal resistance and processability.[3]

Polybenzoxazine is a newly developed thermosetting resin that have gathered wide attention over the past few decades on account of their unique properties, such as near-zero shrinkage during polymerization,[4-7] low water absorption upon saturation,[7] high glass transition temperature (ranging approximately from 160°C-400°C),[8,9] fast physical and mechanical property development,[10] very high char yield[9,11-15] and tremendous molecular design flexibility.[16-19] These properties make such material highly promising candidates for a diverse range of applications such as high performance composite matrix,[8,20-22] electronic packaging,[23,24] and coating and adhesives.[25,26] However, for some applications, brittleness, necessity of moderately high temperature for the ring-opening polymerization, and difficulty of processing into thin film from the typical monomers need to be overcome. One of the approaches consists of designing main-chain type polymers incorporating benzoxazine moieties either as a repeating unit in the main chain, terminal groups or pendant groups.

To improve the solubility and processibility of PIs and overcome the brittleness of polybenzoxazines, it appears worthwhile to study the effect of incorporating benzoxazine into polyimide structure. Benzoxazine resins with polyimide have been actively studied. Agag and Takeichi first reported benzoxazine group with imide structure, though their oxazine ring contained a carbonyl group, and this oxazinone group was not readily polymerizable.[27] Another approach with imide group is the formations of blends. Blend of benzoxazine resin with copolymers of dimethylsiloxane and fluorinated imide or ordinary polyimide were prepared to improve the toughness and thermal stability.[28-30] Zhao et al. reported the blend with polyetherimide to improve the thermal properties.[31] However, benzoxazine group has seldom been used as comonomer with imide group. One of the rare examples for this combination has been reported by Chen et al. where a siloxane dimer is used as the group that off-sets rigid benzoxazine-imide structure.[32] When benzoxazine group is used as a comonomer, the properties of the final product are usually different from the corresponding blends with similar chemical entities. It is this synergistic use of benzoxazine and imide as comonomers the current paper intending to exploit.

By combining the thermoplastic nature of linear polyimide and thermosetting nature of crosslinked polybenzoxazine, we created thermoplastic/thermoset crossover molecules that offer processibility and solubility of thermoplastics while adding to them are the improved thermal, chemical, and creep resistance of thermosetting resins. Thus, developing the current crosslinking polyimide has various advantages, in particular to balance various mechanical and physical properties that was lacking in traditional pure thermoplastic and thermosetting resins. [33,34]

In our previous work, we already reported the synthesis of primary amino-functional benzoxazines.[35] Based on the primary amino-functional benzoxazines which were developed in our laboratory, a type of main-chain type polybenzoxazines with amic acid and benzoxazine groups that are the repeating units in the main chain, termed as poly(benzoxazine amic acid) (poly(BZaa)), has been synthesized in this study. In addition, a model amic acid benzoxazine monomer was also studied. The properties of model compound and main-chain type polybenzoxazines as well as their thermosets will be discussed.

Experimental

Materials

p-Aminophenol, trifluoroacetic anhydride, sodium borohydride, phthalic anhydride, 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA) and paraformaldehyde (99%), were used as received from Sigma-Aldrich. 4,4’-Diaminodiphenylmethane (DDM) (98%), was purchased from Aldrich. Aniline was purchased from Aldrich and purified by distillation. Chloroform, hexane, methanol, xylenes, tetrahydrofuran, ethyl acetate, dimethylacetamide (DMAc) and sodium sulfate were obtained from Fisher scientific and used as received.

Preparation of 3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-amine (AP-a-NH_2) and 3,3’-(4,4’-Methylenebis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazin-6-amine) (P-ddm-NH_2)

Primary amine-monofunctional and bifunctional benzoxazine (AP-a-NH_2) and (P-ddm-NH_2) were prepared following the methods developed in our laboratory, which is published elsewhere.[35]

AP-a-NH_2: ^1H NMR ($CDCl_3$), ppm: $\delta = 3.39$ (s, NH_2), 4.5 (s, Ar-CH_2-N, oxazine), 5.30 (s, O-CH_2-N, oxazine), 6.37-7.28 (8H, Ar). FT-IR spectra (KBr), cm^{-1}: 3353 (N-H stretching), 1500 (stretching of trisubstituted benzene ring), 1224 (C-O-C asymmetric stretching), 1180 (C-N-C asymmetric stretching), 950 (out-of-plane C-H).

P-ddm-NH_2: ^1H NMR ($CDCl_3$), ppm: $\delta = 3.49$ (s, NH_2), 3.79 (s, CH_2), 4.48 (s, Ar-CH_2-N, oxazine), 5.24 (s, N-CH_2-O, oxazine), 6.33-7.15 (14H, Ar). FT-IR spectra (KBr), cm^{-1}: 3351 (N-H stretching), 1502 (stretching of trisubstituted benzene ring), 1222 (C-O-C asymmetric stretching), 1182 (C-N-C asymmetric stretching), 950 (out-of-plane C-H).

Preparation of benzoxazine amic acid model compound (BZaa).

Into a 50 mL round flask were added 20ml DMAc, AP-a-NH_2 (1 g, 4.4 mmol), and phathalic anhydride (0.66 g, 4.4 mmol). The mixture was stirred for 4 h in an ice bath. Then the mixture was poured into water. The precipitate was filtered and dried in a vacuum oven at 50 ^{o}C to give a brown crystal (yield ca. 85%). ^{1}H NMR ($CDCl_3$), ppm: δ = 4.58 (s, Ar-CH_2-N, oxazine), 5.32 (s, O-CH_2-N, oxazine), 6.61-8.21 (12H, Ar). IR spectra (KBr), cm^{-1}: 3227 (OH stretching of carboxylic acid), 1717 (carbonyl), 1657 (amide I), 1501 (stretching of trisubstituted benzene ring), 1255 (C-O-C asymmetric stretching), 933 (out-of-plane C-H).

Preparation of poly(benzoxazine amic acid) (poly(BZaa)) and crosslinked polyimide thermosets (cPI).

Into a 100 mL round flask were added 30 mL DMAc (g), P-ddm-NH_2 (2.6g, 5mmol), and BTDA (1.16 g, 5mol). The mixture was stirred for 12 h at room temperature to obtain poly(BZaa). Then, the viscous poly(BZaa) solution was cast on glass by an automatic film applicator and dried over night at 100 ^{o}C, then cured at 150 ^{o}C (1h), 200 ^{o}C (1h), 250 ^{o}C (1h) and 300 ^{o}C (1h), respectively to obtain cPI.

Characterization

^{1}H nuclear magnetic resonance (NMR) spectra were acquired on a Varian Oxford AS300 at a proton frequency of 300 MHz. The average number of transients for ^{1}H MNR measurement was 64. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Co addition of 32 scans was recorded at a resolution of 4 cm^{-1}. Transmission spectra were obtained by casting a thin film on a KBr plate for partially polymerized samples. A TA Instruments DSC model 2920 was used with a heating rate of 10°C/min and a nitrogen flow rate of 60 mL/min for all tests of differential scanning calorimetric (DSC) study. All samples were sealed in hermetic aluminum pans with lids. Dynamic mechanical analysis (DMA) was done on a TA Instruments Model Q800 DMA applying controlled strain tension mode with amplitude of 10μm and a ramp rate of 3 °C/min. Thermogravimetric analyses (TGA) were performed on a TA Instrument Q500 TGA with a heating rate of 10°C/min in a nitrogen atmosphere at a flow rate of 40 mL/min.

Result and discussion

Preparation of Primary Amino-Functional Benzoxazines and Model Compound

In our previous work, we have successfully synthesized amino-functional benzoxazines.[35] Here we no longer discuss the details about the preparation of amino-functional benzoxazines. The ^{1}H NMR spectra of AP-a-NH_2 and P-ddm-NH_2 are as shown in Figure 1.

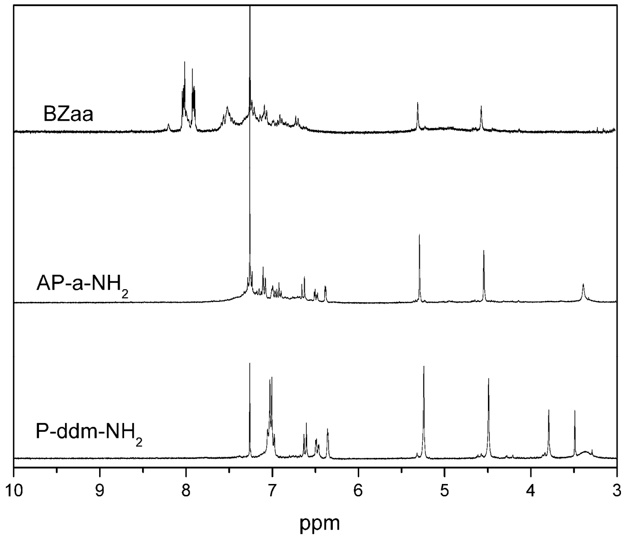
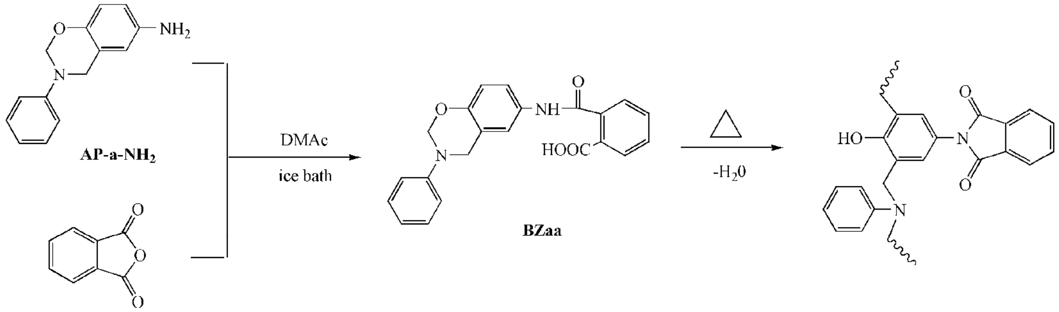


Fig. 1 ^{1}H NMR spectra of P-ddm-NH_2, AP-a-NH_2, and the model compound.

In order to study the reactivity of primary amino-bifunctional benzoxazine (P-ddm-NH_2) with BTDA, a model compound (BZaa) was synthesized from the model reaction between phthalic anhydride and AP-a-NH_2 as shown in Scheme 1. The chemical structure was confirmed by ^1H NMR and FTIR spectroscopy. Figure 1 shows the ^1H NMR spectra of BZaa. The disappearance of the NH_2 signal (3.39 ppm) supports the reaction of NH_2 and anhydride. FT-IR was used to further confirm the structure of BZaa. In Figure 2, the observation of a heavily overlapped broad band of carboxylic acid and NH group around 3227 cm^{-1}, a carbonyl absorption at 1717 cm^{-1} and the amide I mode at 1657 cm^{-1} supports the structure of amic acid. The peak at 933 cm^{-1} (the out-of –plane bending vibration of C-H) is weak due to the small amount of oxazine-rings opening. It is known that acid catalyzed the ring-opening of benzoxazine.[34]



Scheme 1 Preparation and thermal treatment of BZaa.

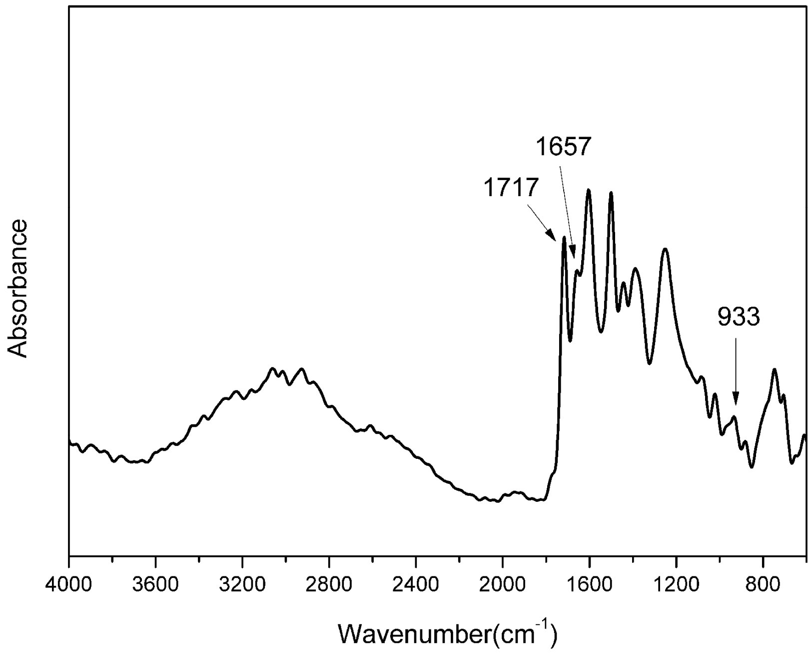


Fig. 2 FTIR spectra of the model compound.

Study of Polymerization Behavior of Benzoxazine Monomers by DSC and FTIR.

The effect of the presence of the aromatic amic acid linkage on the ring opening of benzoxazine in model compound was studied by DSC. Figure 3 shows DSC thermographs of P-ddm-NH_2, AP-a-NH_2 and model compound. As has been reported previously, the polymerization behavior of P-ddm-NH_2 and AP-a-NH_2 consists of multi thermal events, suggesting the catalytic interaction of the primary amine group with the benzoxazine structure.[35] The DSC thermogram of model compound shows a broad endothermic peak attributing to the solvent. To minimize ring-opening by the acid catalysis, we avoided removing the solvent completely, which requires heating the sample. Besides, the model compound shows a broad exothermic peak due to the endothermic behavior of imidization and exothermic behavior of polymerization overlap each other. However, we could not calculate the enthalpy for the ring-opening since the solvent evaporation and imidization changed the weight of sample during the DSC measurement.

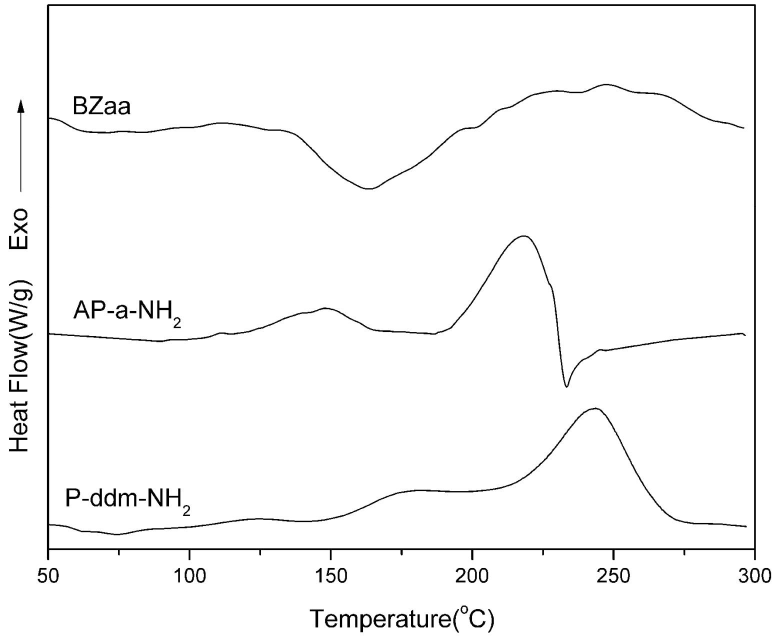


Fig. 3 DSC of thermograms of P-ddm-NH_2, AP-a-NH_2 and model compound.

In order to qualitatively study the structural evolution of the model compound during heating, FTIR analyses were carried out and the spectra are displayed in Figure 4.The characteristic absorption bonds at 1255 cm^{-1} (C-O-C asymmetric stretching modes) and 933 cm^{-1} (the out-of –plane bending vibration of C-H) gradually disappeared after the thermal treatment corresponding to the ring-opened of benzoxazine. Meanwhile, two new characteristic absorptions of imide at 1772 and 1376 cm^{-1} can be observed which is due to the imidization behavior of amic acid. The characteristic peaks at 1772 cm^{-1} is the typical peaks for imide, which is attributed to the imide C-C(=O)-C symmetric stretching. The peak at 1376 cm^{-1} is owing to the axial stretching of C-N bonding.[36,37]

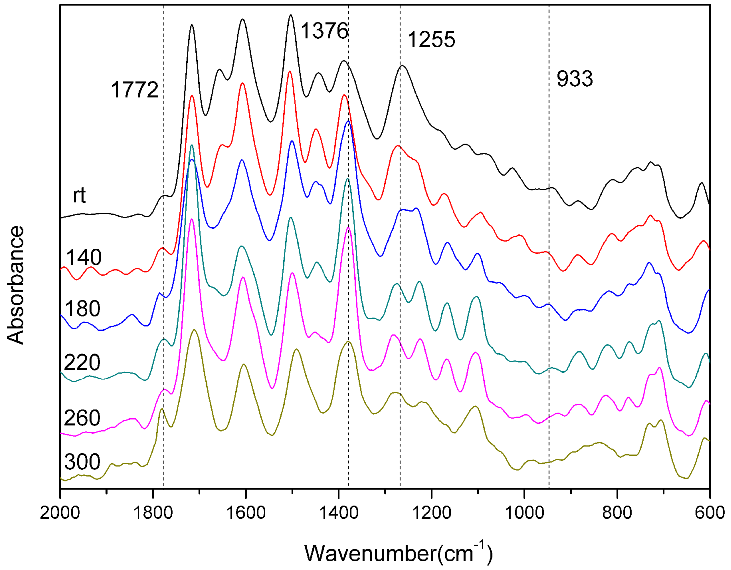
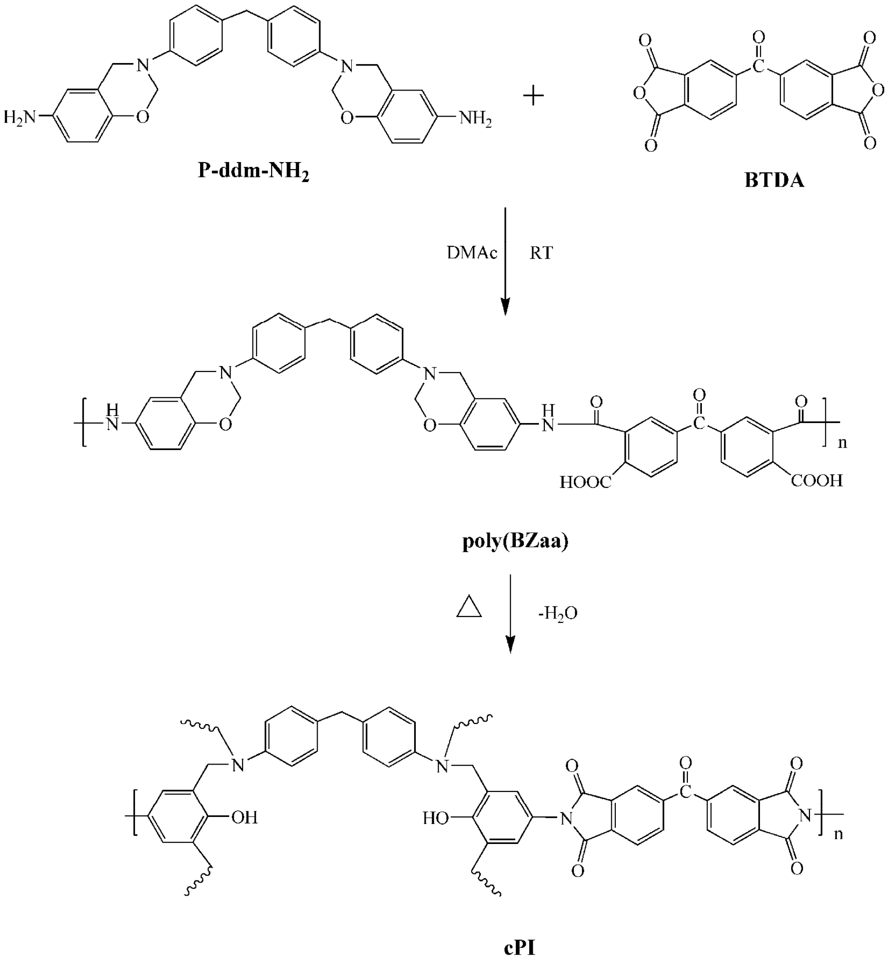


Fig. 4 FTIR of model compound after various thermal treatments at the designated temperature for 1 h.

Preparation of Poly(BZaa) and cPI.

The preparation of poly(BZaa) was performed by reacting P-ddm-NH_2 and BTDA with a molar ratio of 1:1 (Scheme 3). The mixture was reacted at room temperature to form poly(BZaa), followed by a thermal treatment to imidize and cross-link to form cPI. As suggested by the model reaction of BZaa, ring-opening of benzoxazine and thermal imidization of amic acid occurred after thermal treatment, leading to cPI thermosets.



Scheme 2 Preparation of poly(BZaa) and cPI.

DSC of Poly(BZaa) as a Functional of Heat Treatment.

The thermally accelerated crosslinking behavior of the main-chain type poly(BZaa) through ring-opening was also studied by DSC and FTIR. Figure 5 shows the DSC thermograms of the main-chain type poly(BZaa) after thermal treatment at 150, 200, 250 and 300 ^{o}C for 1 h at each temperature.

It is well known that 1,3-benzoxazine exhibits an exothermic ring-opening polymerization reaction mostly around 200-250 ^{o}C. However, the DSC results of poly(BZaa) show a totally different thermal behavior compared with the traditional benzoxazines. The broad endothermic peak was observed at 175 ^{o}C for poly(BZaa) without any thermal treatment, which is due the imidization. Meanwhile, the endothermic behavior of imidization overlapped with the exothermic ring-opening of benzoxazine, leading to difficulty of observing the exothermic peak. After thermal treatment at 150 °C for 1 h, the endothermic peak increased to 195 °C, but still no exothermic peaks could be observed. However, after thermal treatment at 200 °C, an exothermic peak can be observed at 239 °C, which is due to the ring-opening of benzoxazine. Besides, we can also infer that the imidization of amic acid has mostly completed after the thermal treatment at 200 °C. Moreover, the poly(BZaa) showed a small exothermic peak at 265 °C after thermal treatment at 250 °C. Finally, the product of poly(BZaa) showed a glass transition temperature (*Tg*) as high as 270 °C after further thermal treatment at 300 °C for 1 h.

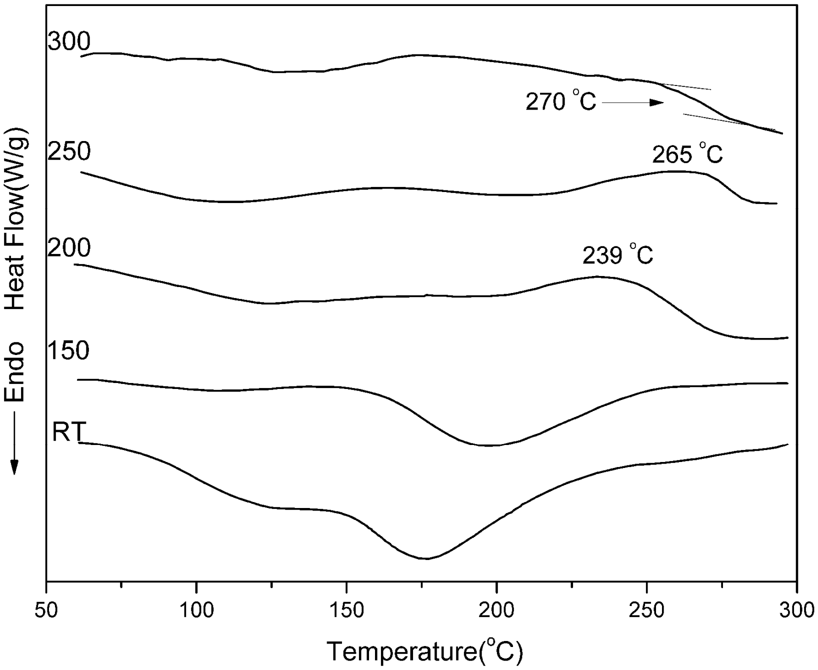


Fig. 5 DSC of poly(BZaa) after various thermal treatments.

In order to qualitatively study the structural evolution of poly(BZaa) during heating, FTIR analyses were also carried out and the spectra are displayed in Figure 6. The characteristic absorption bonds at1236 cm^{-1} (C-O-C asymmetric stretching modes) and 935 cm^{-1} (the out-of–plane bending vibration of C-H) gradually disappeared after the thermal treatment, indicating the ring-opened of benzoxazine. Meanwhile, new characteristic absorptions of imide at 1784 (C-C(=O)-C symmetric stretching) and 1375 (axial stretching of C-N bonding) cm^{-1} can be observed which is due to the imidization behavior of amic acid.

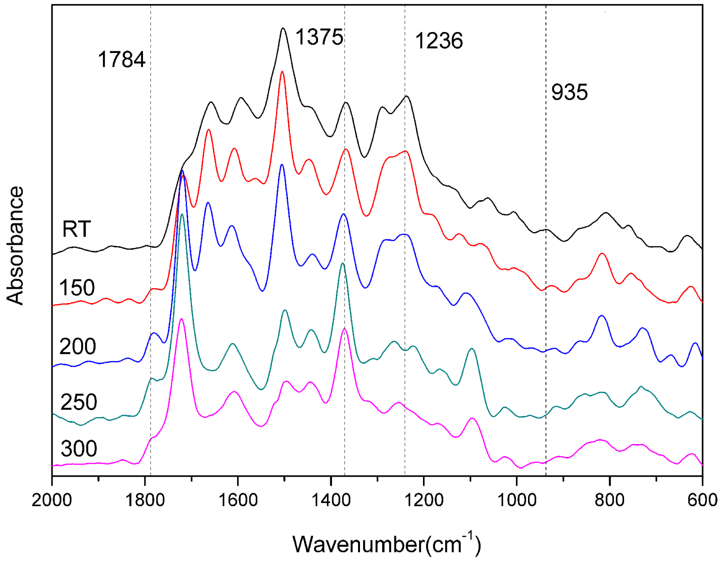


Fig. 6 FTIR spectra of poly(BZaa) after various thermal treatments

Thermal Properties of Crosslinked Polyimide Thermoset.

The results of dynamic mechanical analysis of the thermoset are shown in Figure 7 for the storage (E') modulus, loss (E") modulus, and tan δ. As shown in Figure 7, the *Tg* determined as the peak temperature of tan *δ* curve is around 304 °C whereas it is 285 °C with the E" peak method. A more rigorous determination of *Tg* usually uses E" peak and this value is in relatively good agreement with that measured by DSC in Figure 5. The differences could attribute to the machine sensitivity as well as different heating rate.

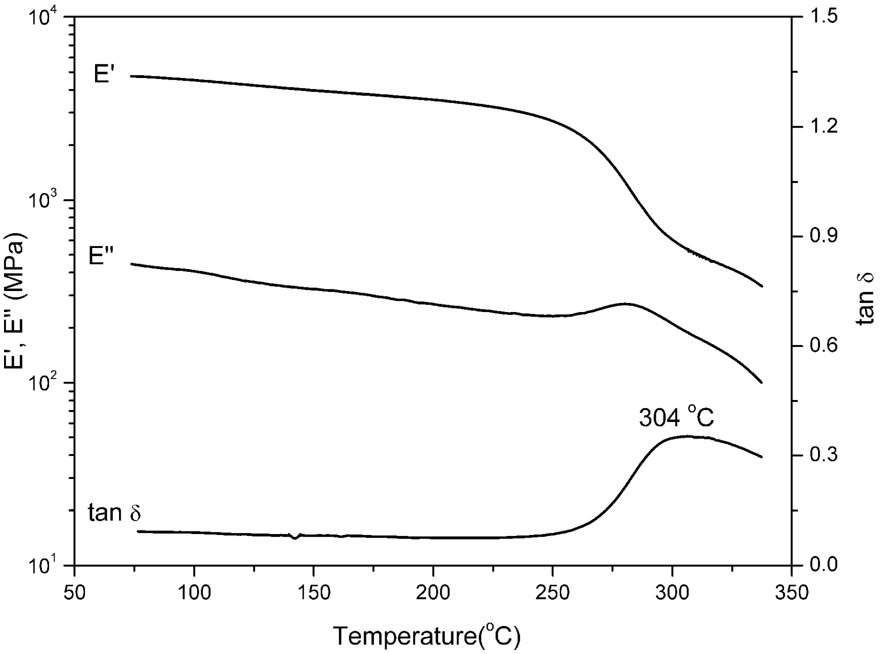


Fig. 7 Dynamic mechanical spectra of cPI.

It is well-established that the polymerization of benzoxazines occurs through oxazine ring-opening without producing any byproduct and the thermal degradation of polybenzoxazines starts over 300 °C. Thus it is reasonable to cross-link poly(BZaa) as high as 300 °C to obtain cPI. The thermal stability of cPI has been studied by TGA as shown in Figure 8. The initial decomposition temperatures of 5 and 10% weight losses (T_{d5} and T_{d10}) and the char yield at 800 °C under inert atmosphere are 407 °C, 486 °C and 65%, respectively. The data demonstrates the high thermal stability of cPI. Besides, the solubilities of main chain type polybenzoxazine poly(BZaa) in several organic solvents at 3.0% (w/v) were also studied. Remarkably, poly(BZaa) is easily soluble at room temperature in polar solvents such as N,N-dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO), which suggests the good processability of cPI.

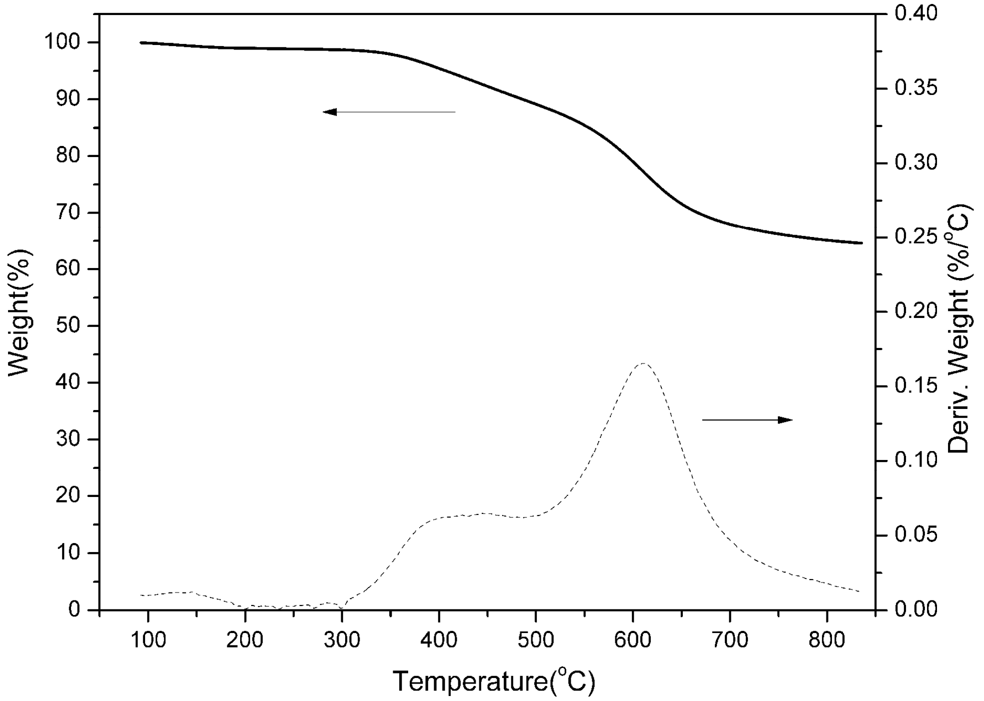


Fig. 8 Thermogravimetric analysis of cPI.

Conclusions

A novel approach has been developed to synthesize thermosetting polyimides by incorporating benzoxazine structure as a repeating unit in the main chain. For better understanding of synthesis and polymerization reaction, a model compound was also synthesized from the primary amino-functional benzoxazine with phthalic anhydride in dimethylacetamide as solvent. The structure of model compound was confirmed by FTIR and ^{1}H NMR. The crosslinked polyimide showed high Tg and good thermal stability appointing these material as a good candidate for high performance applications.

Acknowledgements

The author (K. Zhang) is indebted to the partial support of Chinese Scholarship Council (CSC) Program.

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