

## Synthesis and characterization of novel poly(amide-imide)s derived from N,N'-Bis(p-aminophenyl) terephthalamide

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### Summary

An aromatic diamine monomer, N, N'-bis (p-aminophenyl) terephthalamide (PTP) was synthesized by employing sodium hydride as catalyst, 1,4-phenyleneamine (PDA) and dimethyl terephthalate (DMT) as starting materials. The structure of monomer was characterized by FT-IR, <sup>1</sup>H-NMR and elemental analysis. A series of new poly(amide-imide)s (PAIs) having inherent viscosities of 1.85-2.07dL/g were synthesized from aromatic diamine PTP with various commercially available aromatic dianhydrides using a standard two-stage process with thermal imidization of poly(amic-acid) (PAA) films. The structure of polymers was respectively investigated by FT-IR. The WAXD patterns indicated an amorphous morphological structure of these polymers. All the new PAIs had good thermal stability with the glass transition temperature of 234-248°C, the temperatures of 5% and 10% weight loss in nitrogen were in the range of 518-541°C and 543-564°C respectively. All PAIs were found to hold outstanding mechanical properties with the tensile strengths of 267.83-326.14 Mpa and Young's modulus of 4.67-5.83GPa.

### Introduction

Aromatic poly (amide-imide)s (PAIs) are an important class of thermoplastic materials, which offer high thermal stability, good chemical resistance, low dielectric constants and robust mechanical properties [1-10]. As a result, PAIs have been investigated for various applications. For example, PAIs have been applied to fingermounted tactile sensors [11], cold valves for superfluid helium [12], membranes for separation and purification of fluid mixtures [13], alignment surfaces for liquid crystals [14], and as an organic host for inorganic materials [1]. PAIs have a chemical structure similar to polyimides, which have found common use in integrated optic [15] and microelectromechanical devices [16]. The inherent stability and mechanical robustness [17] of PAI may make it superior for certain microdevice

applications, besides widely used in encapsulation, machine, aviation and separation, etc. [18-19].

M.C.E.J. Niesten et al. [20] described the synthesis of segmented copolymers having aramid units of uniform length. They referred to the simple synthesis of N, N'-Bis(p-aminophenyl) terephthalamide (PTP). The reaction was carried out with diphenyl terephthalate which was synthesized by themselves, PDA and sodium methanolate as the catalyst under 200°C, but they didn't report the yield and the purity. We followed their methods and found the yield and the purity were both low. So we modified the way. First we used dimethyl terephthalate instead of diphenyl terephthalate since the former was more active than the later and the former was more common in the market. Second, we employed sodium hydride as the catalyst which nobody was applied in this reaction and decreased the temperature to 40°C. In this way, we avoided the reaction under high temperature when diamine was rather easy to be oxidated. On the other side, our method was easier to manipulate. Moreover, the yield was increased and the product was more pure.

In the work reported here, PTP was synthesized in our new way and a series of new PAIs were successfully synthesized from PTP with various commercially available aromatic dianhydrides using a standard two-stage process with thermal imidization of the precursor poly(amic-acid)(PAA) films. These PAIs could afford good quality films via thermal-imidization, due to the rigidity of chain structure derived from PAIs because of the phenyl rings, hydrogen bonds and symmetry of the molecular structure. As a result of the outstanding mechanical properties and thermal stability, these PAIs have a widely applied prospect in high-powered materials.

## Experimental

### *Materials and Measurements*

1,4-phenyleneamine (PDA), dimethyl terephthalate(DMT) was purchased from Beijing Chemical Reagents Corp, China, and were recrystallized from ethanol and dried in vacuum at 80°C for 10h prior to use. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 3,3',4,4'-Biphenyl teracarboxylic dianhydride(BPDA) (Beijing Chemical Reagents Corp.) were purified by sublimation before use. N, N-dimethylacetamide (DMAc) (Shanghai Jinwei Chem. Corp.) purified by distillation under reduced pressure over calcium hydride and were stored in the presence of 5Å° molecular sieves. <sup>1</sup>H-NMR spectra were performed on a Bruker Vance 400 MHz in dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>). Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were recorded on a Pyris-I series thermal analysis system in nitrogen at a heating rate of 20°C /min. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin-Elmer 782 Fourier transform spectrophotometer. Wide-angle X-ray diffraction patterns were obtained for the thin film specimens. The mechanical properties were measured using SANS CMT-8102 stretching tester at a speed of 5mm/min using thin films of about 6-8µm thickness. Inherent viscosity was carried out with an Ubbelohde viscometer in NMP at 25°C.

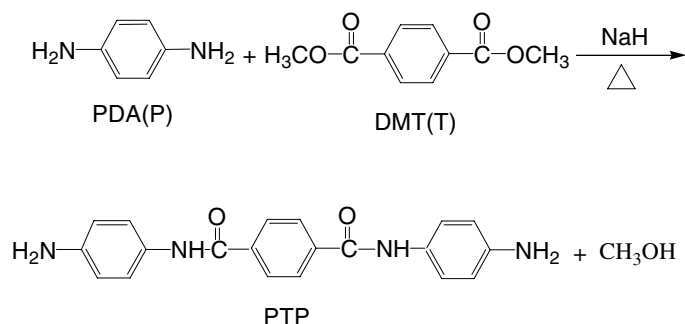
### *Monomer synthesis*

A mixture consisting of PDA (64.8g, 0.6mol), DMT (19.4g, 0.1mol), sodium hydride (2.88g, 0.12mol) was added to a 500ml of four-necked round-bottom flask equipped

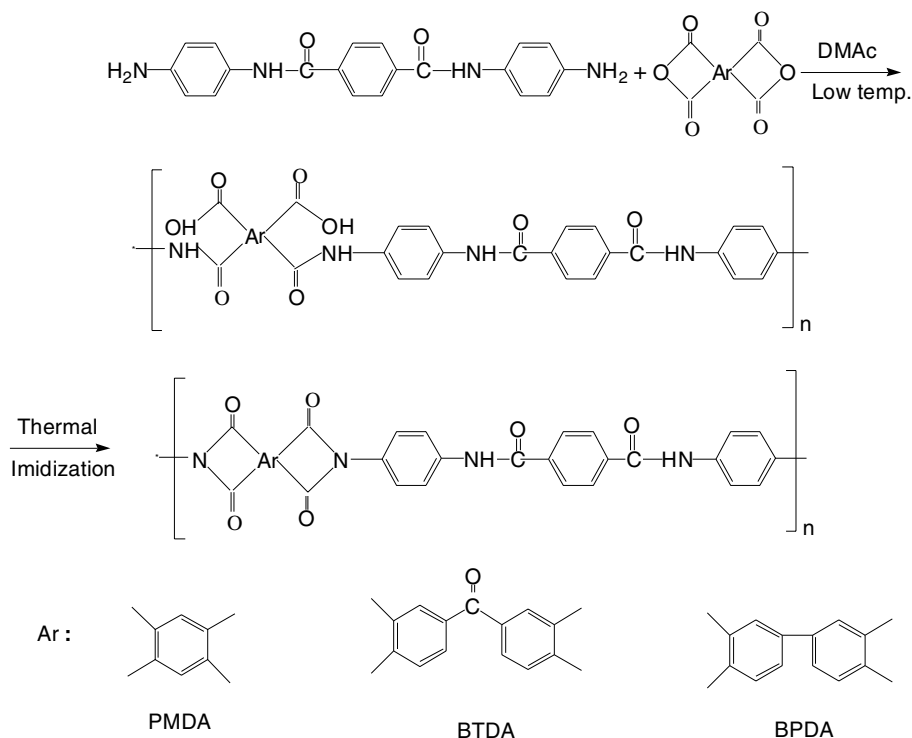
with thermometer, reflux condenser with drying tube and mechanical stirrer in nitrogen. To which, freshly anhydrous DMAc (200 ml) was added by injector until the mixture was dissolved completely. The mixture was slowly heated at 40°C for 6h under nitrogen. Then, the part of the solvent (DMAc) was removed by vacuum distillation, cooling, and the reaction mixture was poured into 3000 ml of distilled water. The precipitate formed was collected by filtration, washed with distilled water, ethanol and ether, and dried in vacuum at 60°C. The process was showed in scheme 1. The resulting crude product was recrystallized from DMAc, also dried in vacuum at 120°C to give yellow powder (almost 11.9 g, yield: 51%), the melting point was 302.5°C, tested by DSC. C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> (Molecular weight=346.384): Calculated: C=69.345%, H=5.238%, N=16.179%, O=9.238%; Found: C=69.364%, H=5.202%, N=16.185%, O=9.249%.

#### Polymer synthesis

Utilizing N,N'-bis(p-aminophenyl)terephthalamide(PTP) as diamine monomer, three kinds of novel PAIs were synthesized by low temperature polycondensation of PTP with PMDA, BTDA and BPDA respectively, and the resulting PAIs were abbreviated to PTP/PMDA, PTP/BTDA, PTP/BPDA, successively. In a typical experiment, PTP/BPDA, which derived from PTP and BPDA was prepared as follows: PTP (3.464 g, 0.01mol) was dissolved in 25 ml anhydrous DMAc in a 100 ml of four-necked flask fitted with a nitrogen inlet pipet and mechanical stirrer, then BPDA (2.702g, 0.01mol) was added to the solution with stirring, then the reaction was allowed to carry through 72h at between -2 and 2°C to yield a viscous poly (amic-acid)(PAA) solution with 10% of solid content. PAA solution was gradually converted into PAI by thermal imidization, the PAA solution was coated to a clean glass plate and heated according as temperature procedure of 100°C /2h, 150°C /1h, 200°C /1h, 250°C /1h, 300°C /1h, a PAI film was obtained by full imidization. PTP/PMDA and PTP/BTDA, were synthesized from the polymerization of 1 equiv. PTP and 1 equiv. of PMDA, BTDA respectively, at 10% solid content in DMAc in the same method as PTP/ BPDA. The process was showed in scheme2.



**Scheme 1.** Synthesis of diamine monomer N,N'-bis(p-aminophenyl)terephthalamide(PTP)

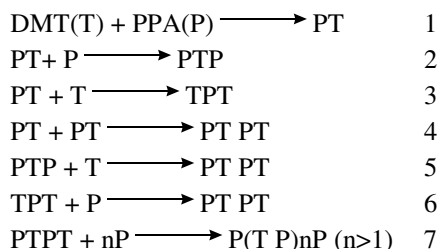


**Scheme 2.** Synthesis of PAI based on diamine monomer

## Results and discussion

### Synthesis of monomer

The diamine monomer PTP was prepared by the reaction as shown in Scheme 1. First, PTP was synthesized from DMT and PDA using a solvent of DMAc, and employing NaH as a catalyst. The influence of reaction conditions on yield was studied. Both of the endgroups of PPA and DMT exhibited good activity of the reaction, therefore, it was vital important to control the reaction conditions during the process. Otherwise, many side-products would appear. For example, many different products would be come forth like 1-7 with the difference of the amounts of reactants and the reaction conditions. Optimal reaction condition was found according to *monomer synthesis*. When using the mole ratio 6 : 1 of PDA/DMT, employing NaH as the catalyst and reacting at 40°C for 6h, the diamine monomer with high purity (99.6%) and good yield (51.2%) would be obtained.



For the resulting PTP, the composition and structure were confirmed by FT-IR,  $^1\text{H-NMR}$ , and elemental analysis methods. The elemental analysis data presented in the above experimental section had indicated that diamine monomer PTP held the composition of  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$  and that found were correspond to that calculated. Figure 1 was FT-IR spectra of the resulting PTP, the absorption bands presented at  $3412\text{ cm}^{-1}$  and  $3325\text{ cm}^{-1}$  resulting from asymmetric and symmetric stretching vibration of  $-\text{NH}_2$  group, the  $\text{C}=\text{O}$  group was presented at  $1727\text{ cm}^{-1}$ .  $1600\text{ cm}^{-1}$ ,  $1533\text{ cm}^{-1}$ ,  $1515\text{ cm}^{-1}$  were the absorption bands of framework vibration of phenyl rings,  $1326\text{ cm}^{-1}$ ,  $1266\text{ cm}^{-1}$  were the absorption bands of stretching vibration of  $\text{C-N}$ ,  $834\text{ cm}^{-1}$  was the absorption bands of phenyl group of 1,4-substitution. The FT-IR spectra showed that the chemical reaction of PDA and DMT was taken place.

The chemical shift of proton of the PTP was presented in  $^1\text{H-NMR}$  spectra (Figure 2). All of the proton peaks in Figure 2 could find their belongs in the structure of the expecting product. The ratio of peak areas was  $\text{Ha} : \text{Hb} : \text{Hc} : \text{Hd} : \text{He} = 2 : 1 : 2 : 2 : 2$ ,

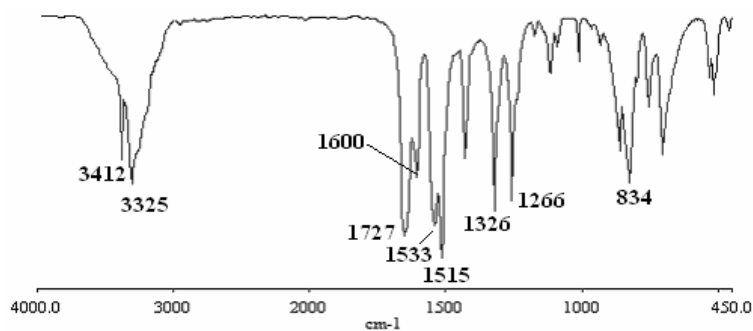


Figure 1. FT-IR spectra of diamine monomer (PTP)

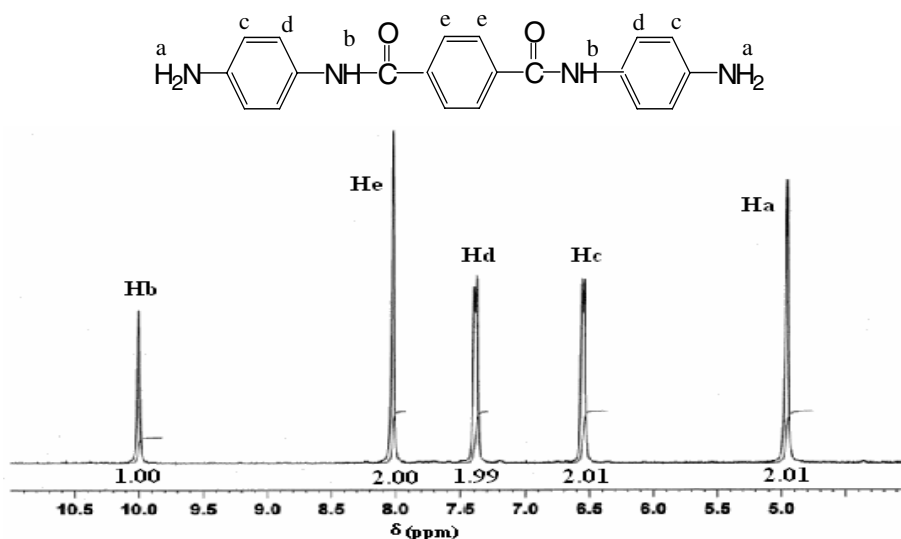
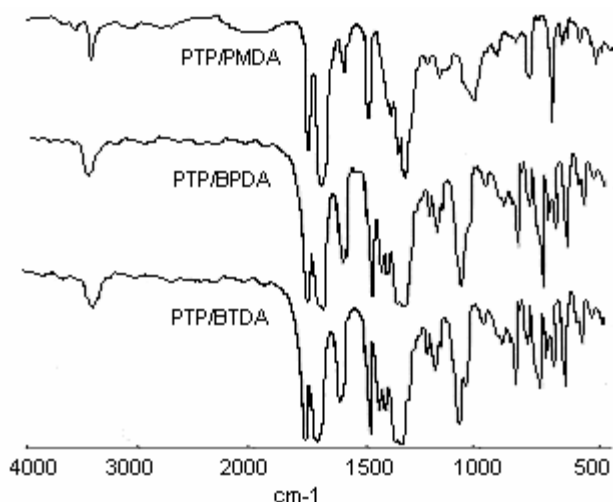


Figure 2.  $^1\text{H-NMR}$  spectra of diamine monomer (PTP)

coincident with the number ratio of various protons. This approved that the structure of diamine monomer was the same with the expecting one.

#### *Synthesis of PAIs*

When PTP was employed as diamine monomer, the polycondensation of it with dianhydride monomer of PMDA, BTDA and BPDA would form three kinds of new PAIs, i.e. PTP/PMDA, PTP/BTDA and PTP/BPDA. Table 2 showed that the resulting PAIs could attain yields of 83.7–90.0%, the thin films were all yellow and the inherent viscosities of the three kinds of precursors (PTP/PMDA–PAA, PTP/BTDA–PAA and PTP/BPDA–PAA) were 2.03 dL/g, 1.85 dL/g, 2.07 dL/g respectively. FT-IR spectra (Figure 3) of the resulting PAIs exhibited characteristic absorption bands for the imide ring at 1780–1789  $\text{cm}^{-1}$  and 1726–1730  $\text{cm}^{-1}$ , which showed asymmetric and symmetric stretching vibrations of imide ring C=O. The absorption bands of C–N stretching vibration (1370–1379  $\text{cm}^{-1}$ ), N–H stretching vibration (3370–3410  $\text{cm}^{-1}$ ) and imide-ring deformation vibrations (1152–1156  $\text{cm}^{-1}$  and 732–751  $\text{cm}^{-1}$ ) indicated that the expecting PAIs containing hydrogen bond had gotten by polycondensation of novel diamine monomer PTP with aromatic dianhydrides through the general two-stage process, as shown in Scheme2.



**Figure 3.** FT-IR spectra of the resulting PAIs

#### *Thermal properties of PAIs*

Figure 4 and Figure 5 are TGA and DSC curves of the resulting PAIs, and the corresponding data of thermal analysis were listed in Table 1. The TGA curves and data in Table 1 showed that there were not weight loss before 500°C, the temperature of 5% weight loss was at 518–541°C (in  $\text{N}_2$ ), while that of 10% weight loss was at 543–564°C (in  $\text{N}_2$ ), and their  $T_g$  values have reached to 234–248°C (Figure 5). The results of thermal analysis demonstrated that the resulting PAIs should hold excellent thermal stability and melting fluidity, for the structure units of these PAIs contained

hydrogen bonds and phenyl rings, besides the molecular structure was symmetric. These would be suitable to their application and processing.

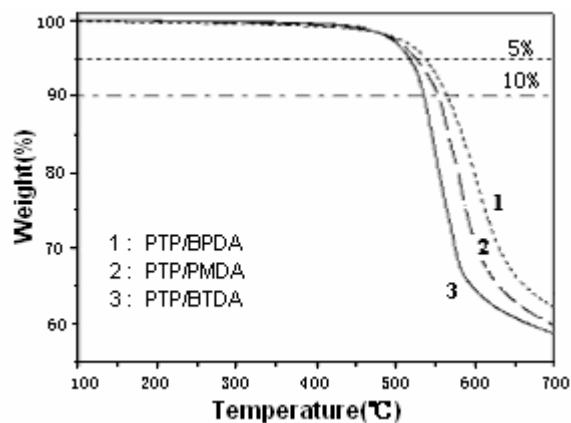


Figure 4. TGA curves of three PAIs

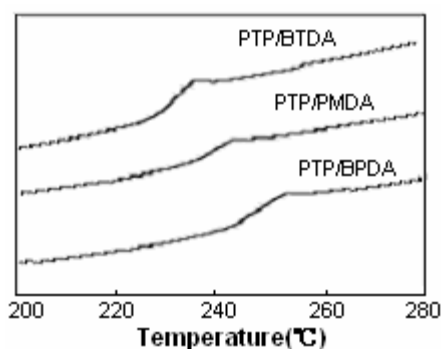


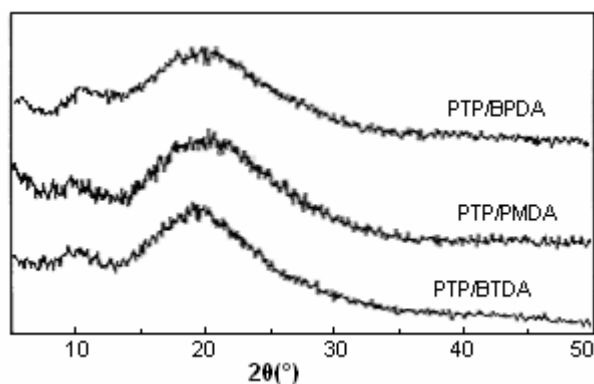
Figure 5. DSC curves of three PAIs

Table 1. The data of thermal analysis of PAI films

PAI/No	Glass transition temp. (DSC, °C)	Temp. at 5% weight loss (TG, °C)	Temp. at 10% weight loss (TG, °C)
PTP/BTDA	234	518	543
PTP/PMDA	241	529	556
PTP/BPDA	248	541	564

#### Morphologies of PAIs

The measurement of wide-angle X-ray diffraction of the thin film samples confirmed that there was only one broad peak. It indicated that they were all in amorphous morphology, as shown in Figure 6. This showed that the molecular chains of these PAIs arranged irregularly.



**Figure 6.** Wide-angle X-ray diffraction patterns of three PAIs

#### *Mechanical properties of PAIs*

The mechanical properties of the thin films from the resulting PAIs were summarized in Table 2. The PAIs films measured in this experiment were non-tropism or low-tropism. When the molecular weight of PAIs was almost the same, the main factor influenced the mechanical properties of these thin films was molecular structure. The data indicated that the resulting PAIs could afford good quality films by thermal-imidization, due to rigidity of chain structure derived from PAIs because of the phenyl rings, hydrogen bonds and symmetry of the molecular structure. According to Table 2, the tensile strength and Young's modulus of the films from PTP/BPDA reached 326.14MPa and 5.83GPa, better than the other two PAIs. While its elongation to break was only 5.67%, this thin film was relatively brittle, the worst of the three. The data exhibited that the resulting PAIs held good mechanical properties. The inherent viscosities of the resulting PAIs showed that their molecular weights could also satisfy easily the requirement for engineering materials.

**Table 2.** Mechanical properties of three PAIs

PAI/No	Yield (%)	Inherent viscosity ( $\eta_{inh}$ , dL/g)	PAI thin film color	Tensile strength (MPa)	Young's modulus (GPa)	Elongation to break (%)
PTP/PMDA	90.0	2.03	Yellow	304.19	5.45	7.21
PTP/BTDA	83.7	1.85	Yellow	267.83	4.67	10.19
PTP/BPDA	92.4	2.07	Yellow	326.14	5.83	5.67

#### **Conclusions**

A novel aromatic diamine monomer was successfully synthesized by employing sodium hydride as catalyst, PDA and DMT as starting materials. And three kinds of PAIs were prepared by low temperature polycondensation of PTP with PMDA, BTDA and BPDA. The glass transition temperature of the PAIs was in the range of 234–248°C. Temperatures of 5% and 10% weight loss in nitrogen were in the range of 518–541°C and 543–564°C respectively. The tensile strengths reached 267.83–326.14MPa,



Young's modulus arrived at 4.67–5.83GPa. All PAIs were found to be amorphous and held distinguished mechanical properties and excellent thermal stability.

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