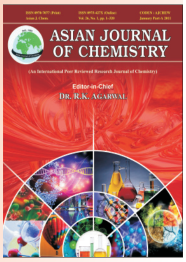
Asian Journal of Chemistry; Vol. 26, No. 20 (2014), 6993-6996

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17650



Synthesis and Properties of Polyimides Based on BTDA/BPDA and Diamine Monomer

Yanfei Lan, Yong Qian*, Shizhen Dai and Yuting Liao

Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, Department of Materials Science and Engineering, East China Institute of Technology, Nanchang, 330013, Jiangxi Province, P.R. China

*Corresponding author: Tel./Fax: +86 791 83897912; E-mail: yqianecit@163.com

Received: 22 March 2014; *Accepted*: 21 May 2014; *Published online*: 25 September 2014; AJC-16053

A series of high molecular weight polyimide precursors with different intrinsic viscosity were synthesized *via* changing the ratio of dianhydrides (BTDA/BPDA) acted with diamine monomer at the low temperature polycondensation. The as-obtained polyamic acids were then thermal imidized to form polyimide (PI). The structures and properties of polyimides were studied by using IR, UV-visible, TG, mechanical test and contact angle (CA) measurement. The results show that the properties of the polyimides vary with the different ratio of BTDA/BPDA components. A higher ratio of BTDA component in the polyimide is related to a good UV-visible transmission. In reverse, the polyimide with higher ratio of BPDA exhibits better thermal stability as well as higher tensile strength and elastic modulus. Furthermore, all of the polyimide films possess excellent hydrophobic properties.

Keywords: Polyimide, Low temperature polycondensation, Mechanical properties, Thermal properties.

INTRODUCTION

Aromatic polyimides (PIs) exhibit a series of excellent comprehensive perfomances due to their special structure which contain aromatic and heterocyclic ring. They possess outstanding mechanical strength, low dielectric constant, wear resistance, radiation shielding capability, chemical stability, adhesive properties and they are difficult to volatilize under high vacuum[1-3]. Therefore, they are widely applied in the aerospace, electronic industries and gas separation in the forms of films and moldings, such as interlayer dielectrics in microelectronics applications[4]. And polyimide resins are well-known as important high-performance polymers[5-8]. The polyimide was synthesized by Bogert for the first time in 1908, a series of polyimides have synthesized in succession[9]. The main synthetic methods of polyimide include one-step method, two-steps method, three-steps method and gas phase deposition method[10-12]. In one-step method, dianhydride and diamine were mixed together and dissolve in the high boiling point solvents to generate soluble polyimide at 150-220 °C by solution polycondensation. Two-steps method is the simplest and most common method for polyimide synthesis. It includes two steps. Firstly, the polyamic acid (PAA) precursor was prepared by the condensation polymerization of diamine and dianhydride in the polar aprotic organic solvent (such as DMAc, NMP) at low temperature. Then the corresponding polyimide was obtained through chemical imidization method or thermal imidization approach. Three-steps method is a novel method which prepared polyimide through polyisoimide. Gas phase deposition method is as follows: dianhydride and diamine transport in the mixer for mixing in the form of airflow under the high temperature and produce films by the monomer directly.

In this work, a series of polyimides were synthesized successfully through thermal imidization of polyamic acids which produced by polycondensation of two dianhydrides (BTDA/BPDA) and diamine monomer (MDA) at the low temperature. The structures and properties of the polyimides which vary with the different ratio of BTDA/BPDA component were characterized. A higher ratio of BTDA component in the polyimide is related to a good UV-visible transmission. On the other hand, the polyimide with higher ratio of BPDA component posesses better thermal stability, higher tensile strength and elastic modulus. Furthermore, all of the polyimide films possess excellent hydrophobic properties.

EXPERIMENTAL

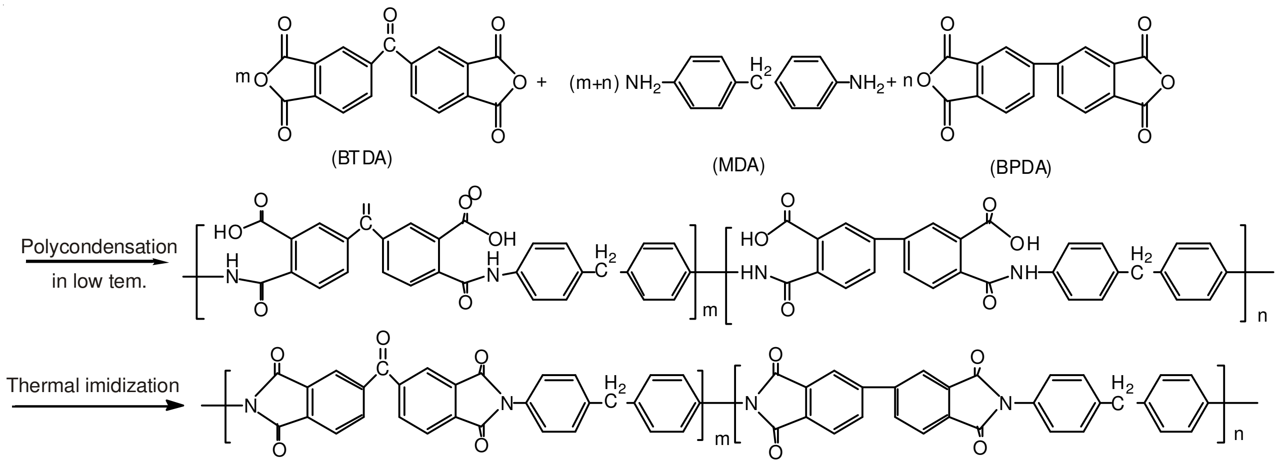
3,3',4,4'-Benzophenone tetracarboxylic dianhydride-(BTDA) 4,4-methylenedianiline (MDA) and 3,3',4,4'-biphenyl teracarboxylic dianhydride (BPDA) (Shanghai Guchuang Chem. Co.) were purified by sublimation N,N-dimethylacetamide (DMAc) (Shanghai Haoshen Chem. Co.) was distilled over CaH_2 under reduced pressure prior to use. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant.

Inherent viscosities of polyimide precursor polyamic acid (BTDA/BPDA and MDA) were determined using an Ubbelohde Viscometer at 20 °C and the polymer concentration was 0.5 g/dL in DMAc. Molecular weight measurements of polyamic acid were determined by gel permeation chromatography (GPC). The samples were dissolved in DMAc (10 mg/mL) and filtered through a 0.20 μm Telflon filter. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin-Elmer 782 Fourier transform spectrophotometer. UV-visible spectra were measured with a Shimadzu UV-2550 spectrometer in the transmittance mode. The mechanical properties were measured using SANS CMT-8102 stretching tester at a speed of 5 mm/min using thin films of about 5-10 μm thickness. At least five specimens were used for each sample in the tensile test. Thermogravimetric analysis (TGA) was analyzed under an N_2 atmosphere at a heating rate of 10 °C/min (Q50, TA Instrument). The water contact angle of different samples was determined using a JC2000C contact angle meter (Zhongchen, China) at ambient conditions. The averaged values of at least five repeated measurements for each sample were obtained.

Preparation of the polyimide films: All polyimides were prepared *via* conventional two-step procedure in DMAc in this study. An equimolar amount of dianhydride and diamine monomers was used in all cases. The representative polymerization procedures are described as following: 5 mmol BTDA (1.6111 g) and 5 mmol BPDA (1.4711 g) were dissolved in 50 mL anhydrous DMAc in a 100 mL of three-necked flask fitted with a nitrogen inlet pipet and mechanical stirrer and 10 mmol diamine monomer (0.9913 g) was added to the solution with stirring, then the reaction was allowed to carry through 24 h at between -2 and 2 °C to yield a viscous polyamic acid (PAA) solution. Next, the polyamic acid solution was coated to a clean glass plate and heated according as temperature procedure of 100 °C/2 h, 150, 200, 250 and 300 °C/1 h, a polyimide film was obtained by full imidization. The films were collected from the glass plates soaked in water at room temperature for a couple of days.

RESULTS AND DISCUSSION

Synthesis of polyimides: As shown in **Scheme-I**, the polyimides are synthesized *via* a conventional two-step method. The resulting polymers were isolated by the precipitation of the reaction mixture into ethanol and were purified by extracting with ethanol in a Soxhlet extractor. The experimental data of the samples are shown in Table-1. The yields of as-obtained polyimides are greater than 90 % and the inherent viscosity values of these polyamic acids (polyimide precursor) are in the range of 1.46-1.76 dL/g, which indicates clearly formation of high molar masses. This was consistent with the fact that tough and flexible (Table-1) films could be obtained by casting and thermal imidation of polyamic acid. The elemental analysis data of the resulting polyimides also agreed well with the calculated values. These results demonstrate that the diamine and dianhydride polymerized well to form polyimides *via* typical two step synthetic method.



Scheme-I: Synthetic outline for the preparation of polyimide copolymers

TABLE-1
EXPERIMENTAL DATA OF FOUR POLYIMIDES

Polyimide (m:n)	Yield (%)	$\eta_{inh}{}^{a}$ (dL/g)	Elemental Analysis (%)		
			C	H	N
PI-1 (100/0)	91.3	1.46	Calcd: 74.38 Found: 74.35	3.31 3.26	5.79 5.86
PI-2 (75/25)	92.2	1.61	Calcd: 74.84 Found: 74.96	3.35 3.26	5.87 5.77
PI-3 (50/50)	90.7	1.69	Calcd: 75.32 Found: 75.60	3.40 3.36	5.96 5.81
PI-4 (25/75)	90.9	1.63	Calcd: 75.81 Found: 75.93	3.46 3.39	6.05 6.13
PI-5 (0/100)	93.1	1.76	Calcd: 76.32 Found: 76.26	3.51 3.61	6.14 6.15

[a] Inherent viscosity of PAA (PI precursor) measured at a concentration of 0.5 g/dL at 20 °C

IR analysis: The structures of polyamic acids and polyimides were confirmed by IR spectra and elemental analysis. According to the IR spectroscopy in Fig. 1, polyamic acid-3 gave broad bands at 3500-3000 cm^{-1} (-N-H and -OH stretching). After imidization, the broad absorption is disappear. And polyimide-3 exhibits characteristic absorption bands for the imide ring at 1789-1780 and 1730-1726 cm^{-1}, which showed asymmetric and symmetric stretching vibrations of imide ring C=O. The absorption bands of C-N stretching vibration (1379-1370 cm^{-1}), N-H stretching vibration (3410-3370 cm^{-1}) and imide-ring deformation vibrations (1156-1152 and 751-732 cm^{-1}) indicated that the expecting polyimides prepared herein accorded with the proposed structure.

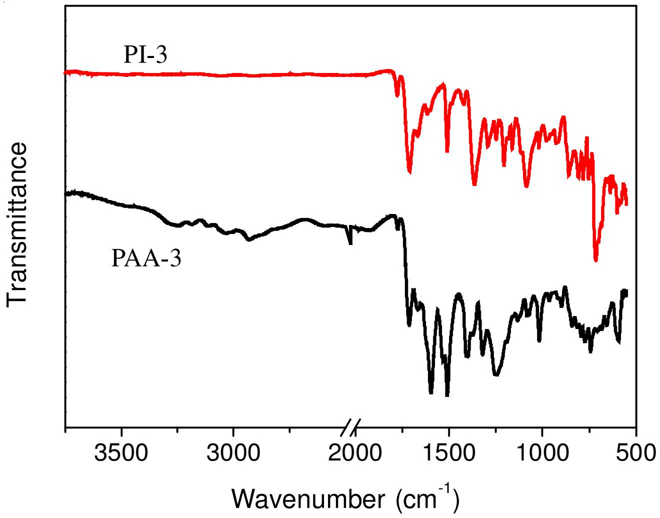


Fig. 1. IR of PAA-3 and polyimides-3

Optical properties: UV-visible transmission spectra of polyimide films are shown in Fig. 2. All of the polyimide thin films have good transparency in the visible light region with and transmission of 80 %. In our system, polyimide film based on dianhydride BTDA/BPDA and diamine diamine monomer, which is nonfluorinated and wholly aromatic, exhibits excellent optical properties. The cutoff wavelength of polyimide-1 at 400 nm is lowest among the polyimides. Furthermore, the polyimide-1 film presents more excellent optical properties and broad wavelength range than others.

Meachanical properties: The representative stress-strain curves of the neat polyimides with various structural units are shown in Fig. 3 and the parameters of mechanical properties are listed in Table-2. All of the films are tough and flexible. Obviously, both the tensile strength and Young's modulus of the polyimide films increase with the raising of BPDA units, while the elongation at break reduces relatively. When the mole ratio of BTDA/BPDA is 0/100, the composites exhibit the greater tensile strength (122.9 MPa) by 39.5 % and higher Young's modulus (2.1 GPa) by 31.3 % than those of ratio 100/0. In addition, the value of the elongation-at-break decreased to 8.72 % (the ratio of BTDA/BPDA 0/100) compared with 11.94 % (the ratio 100/0). The significant reinforcement effect can be mainly attributed to the special structure of BPDA which contains two rigid phenyl rings connecting directly to form π-π stacking without polar carbonyl in the break.

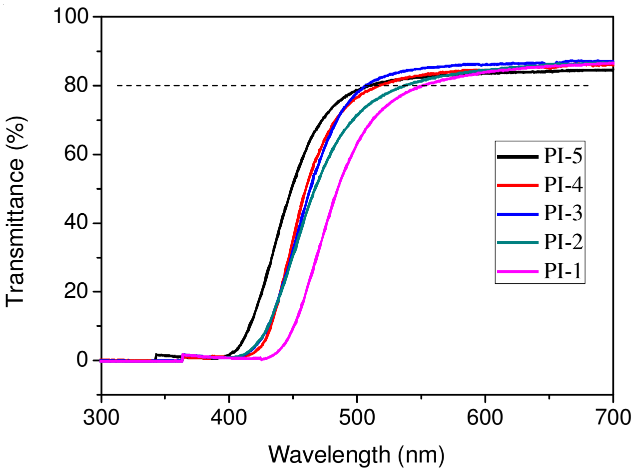


Fig. 2. UV-visible of polyimides films with various structural units

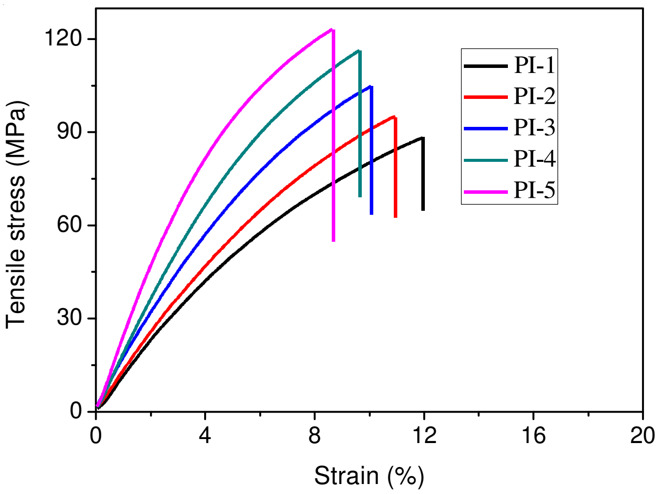


Fig. 3. Typical stress-strain curves of pure polyimides films with various structural units

Thermal properties: Thermal stability is one of the important properties of polyimide materials because of potentially high-performance engineering plastics in relatively high temperature applications. The thermal stability of polyimides

TABLE-2
MECHANICAL PROPERTIES AND THERMAL STABILITY OF POLYIMIDES

Polyimides film^{a}	Film properties	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	T_d^{b} (°C)	T_d^{c} (°C)
PI-1 (100/0)	Tough flexible	88.1 ± 13.67	1.6 ± 0.25	11.94 ± 2.3	500	540
PI-2 (75/25)	Tough flexible	95.2 ± 13.96	1.8 ± 0.26	10.96 ± 2.6	508	547
PI-3 (50/50)	Tough flexible	104.9 ± 14.35	1.9 ± 0.23	10.06 ± 2.4	516	554
PI-4 (25/75)	Tough flexible	116.2 ± 16.01	1.9 ± 0.21	9.69 ± 2.2	525	560
PI-5 (0/100)	Tough flexible	122.9 ± 15.88	2.1± 0.22	8.72 ± 2.1	535	566

[a]Cast from 5 % (w/v) DMAc solutions, [b]Decomposed temperature at 5 % weight loss, [c]Decomposed temperature at 10 % weight loss

was estimated by TGA under nitrogen atmosphere, as shown in Fig. 4. All the films showed excellent thermal stability. Moreover, the decomposition temperature (5 and 10 % weight loss) is greater than 500 °C. Both the initial degradation temperature and maximum mass loss temperature gradually shifted to higher temperature with increasing BPDA fraction as shown in the inset of Fig. 4 and the experimental data of thermal stability of polyimides are listed in Table-2. The 5 and 10 % weight loss temperature of polyimide-1 (100 % BTDA: 0 % BPDA) is 500 and 540 °C, respectively. The weight loss temperature enhance with the content of the monomer BPDA increased. When dianhydride monomer is pure BPDA (polyimide-5), the 5 and 10 % weight loss temperature increased to 535 and 566 °C compared with that of polyimide-1 film. The significant improvement of thermal stability can be mainly ascribed to the special structure of BPDA which contains two rigid phenyl rings connecting directly.

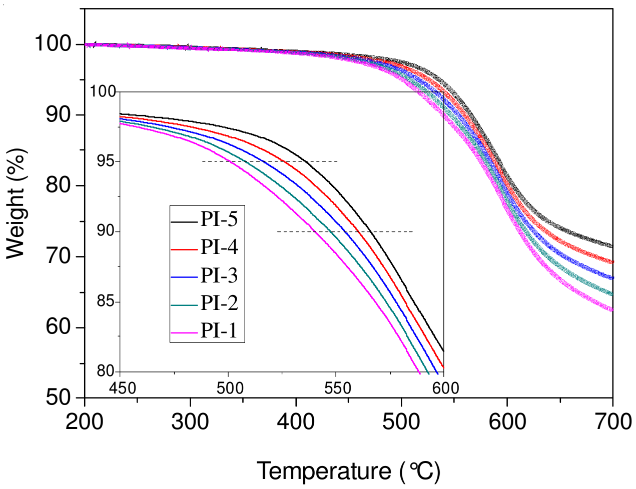
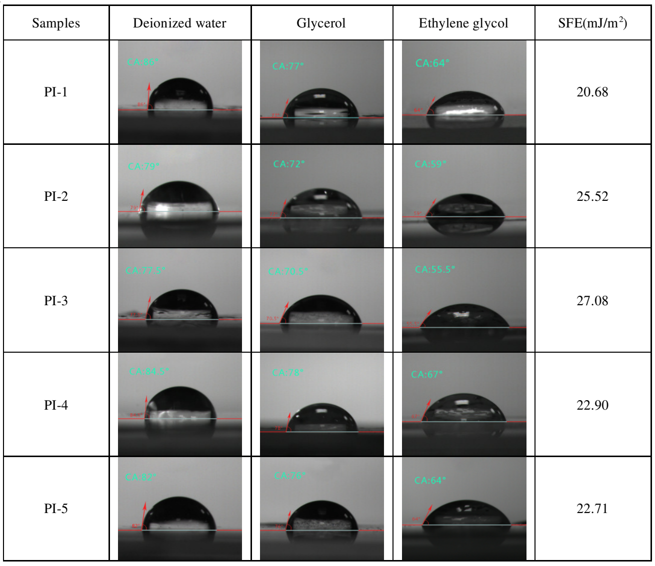


Fig. 4. TGA curves of polyimide with various BPDA contents at a heating rate of 10 °C/min. Inset: magnification of the turning section

Surface wettability: The contact angle (CA) measurement provides tremendous information about the surface wettability of polyimide films. Fig. 5 shows contact angles and surface free energies (SFE) of polyimide films with various BPDA contents in the solvents of water, glycerol and ethylene glycol and the surface free energies values of the polyimide films were calculated by the Young-Good-Girifalco-fowkes Equation. It can be seen that the SFE value ranges of polyimide films are 20.68-27.08 mJ/m^2. The SFE values are far less than that of water (72.8 mJ/m^2). As we all known, the smaller surface energy, the better hydrophobicity. The result reveals that polyimide films (BTDA-MDA-BPDA) have very excellent hydrophobicity. And the polyimide film's surface wettability with water was becoming difficult.

Conclusion

In summary, a series of polyimides were synthesized successfully by polycondensation of two dianhydride (BPDA/BTDA) and diamine monomer (MDA) at the low temperature and thermal imidization subsequently. The as-synthesized polyimides was characterized by IR, UV-visible, TG, mechanical test and contact angle measurement. The effect of BTDA/BPDA ratio on the properties of the polyimides was investigated.



Samples	Deionized water	Glycerol	Ethylene glycol	SFE(mJ/m^2)
PI-1	CA:86°	CA:77°	CA:64°	20.68
PI-2	CA:79°	CA:72°	CA:59°	25.52
PI-3	CA:77.5°	CA:70.5°	CA:55.5°	27.08
PI-4	CA:84.5°	CA:78°	CA:67°	22.90
PI-5	CA:82°	CA:76°	CA:64°	22.71

Fig. 5. Contact angle of water, glycerol and ethylene glycol droplets over the different polyimide films

The polyimides with higher ratio of BPDA component exhibit better thermal stability as well as higher tensile strength and elastic modulus due to the special structure of BPDA which contains two rigid phenyl rings connecting directly to form π-π stacking without polar carbonyl in the break. On the other hand, a higher ratio of BTDA component in the polyimide is related to a good UV-visible transmission. All of the polyimide films possess excellent hydrophobic properties.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No. 21264001), Natural Science Foundation of Jiangxi Province (20114BAB213010), Young Scientist Foundation of Jiangxi Province (20133BCB23020), the Open Project Foundation of the Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense of China (2011RGET07, RGET1310) and the Open Project Foundation of Nuclear engineering technology research center of Ministry of Education (HJSJYB2011-17).

REFERENCES

1. Y.H. Zhang, Y.Q. Li, G.T. Li, H.T. Huang, H.L.W. Chan, W.A. Daoud, J.H. Xin and L.F. Li, *Chem. Mater.*, **19**, 1939 (2007).
2. C.M. Leu, Y.T. Chang and K.H. Wei, *Chem. Mater.*, **15**, 3721 (2003).
3. Y.C. Xiao, L. Shao, T.S. Chung and D.A. Schiraldi, *Ind. Eng. Chem. Res.*, **44**, 3059 (2005).
4. T. Strunskus, M. Grunze, G. Kochendoerfer and C. Wöll, *Langmuir*, **12**, 2712 (1996).
5. S. Osaki and K. Tashiro, *Macromolecules*, **31**, 1661 (1998).
6. C.F. Cheng, H.H. Cheng, P.W. Cheng and Y.J. Lee, *Macromolecules*, **39**, 7583 (2006).
7. K.W. Lee, S.P. Kowalczyk and J.M. Shaw, *Langmuir*, **7**, 2450 (1991).
8. C. Wang, Q.H. Wang and T.M. Wang, *Langmuir*, **26**, 18357 (2010).
9. M.T. Bogert and R.R. Renshaw, *J. Am. Chem. Soc.*, **30**, 1135 (1908).
10. M.A. Shahram and B.B. Naeemeh, *Iran. Polym. J.*, **2**, 95 (2008).
11. H. Deligöz, S. Özgümüs, T. Yalçinyuva, S. Yildirim, D. Deger and K. Ulutas, *Polymer*, **46**, 3720 (2005).
12. C. Zhang, M. Zhang, H. Cao, Z. Zhang, Z. Wang, L. Gao and M. Ding, *Compos. Sci. Technol.*, **67**, 380 (2007).