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Preparation of Poly(amic acid) and Polyimide via Microwave-Assisted Polycondensation of Aromatic Dianhydrides and Diamines

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Summary: A copolycondesation-type poly (amic acid) (PAA) was synthesized using pyromellitic dianhydride (PMDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) as dianhydride monomers, and 4,4′-oxydianiline (ODA) as a diamine monomer under microwave irradiation in dimethylformamide (DMF). PAA was then converted into a polyimide (PI) by an imidization. The structure and performance of the polymer were characterized by Fourier-transform infrared (FT-IR) spectroscopy, Proton nuclear magnetic resonance (^{1}H NMR) spectrometry, viscosity, X-ray diffraction (XRD), and thermogravimetric (TG) analyses. The results showed that under microwave irradiation, the intrinsic viscosity and the yield of PAA were increases, and the reaction time was shortened. The FT-IR spectra of the polymer revealed characteristic peaks for PI around 1778$^-$ and 1723 cm^{-1}. TG curves indicated that the obtained PI began to lose weight at 535 °C, and its 10% thermal decomposition temperature under N_2 was 587 °C.

Keywords: characterization; copolymerization; high performance polymers; microwave-assisted; polyimide

Introduction

It is well known that microwave irradiation is a special heating energy with significant advantages over conventional thermal methods. Studies have shown that, in comparison to reactions under conventional heating, reactions under microwave irradiation have the advantages of higher reaction rates and greater production yields within a shorter period of time; in other words, microwave irradiation can enhance the reactivity of reaction systems.[1–3] Therefore, microwave irradiation has inspired chemists. Recently, many researchers have focused on polymerization with microwave irradiation.[4–6] The use of microwave energy in polymer chemistry is an emerging field of research. Bogdal et al.[7] and Schubert and coworkers[8,9] have reviewed the application of microwave irradiation in polymer chemistry.

Aromatic polyimides (PIs) are class of high-performance polymers that posses many outstanding properties such as flexibility, low color, high glass transition temperature, excellent thermal stability, and radiation resistance.[10–12] There are a variety of applications for them which include electronics,[13,14] fuel cells,[15,16] membrane separation industries,[17,18] adhesives,[19] and so on.[20–21] PIs are usually prepared by the so-called two-step method in which a dianhydride and a diamine are allowed to undergo condensation polymerization to form a polyamic acid precursor, and subsequently the precursor is converted thermally or chemically into the final polyimide, but the reaction usually takes a long period. There have been some reports

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on the use of microwave irradiation for the synthesis of PIs.[22–24] Mallakpour et al. have detailed the use of microwave irradiation for the synthesis of PIs.[25–29] Using a Biotage microwave reactor fitted with a flask handling robot and a high-throughput approach, Groth et al. have optimized a copolyimide material with high T_g, while maintaining solution processability.[30] Typical examples also include PIs from dianhydrides and diamines[31–33] and PIs via polycondensation of dianhydrides and disocyanates.[34]

In our previous work, monodisperse thermoresponsive poly(styrene-*co*-*N*-isopropylacrylamide) particles with diameters in the range of 100–130 nm were prepared through emulsifier-free emulsion polymerization with microwave irradiation.[35] We also produced polystyrene microspheres with diameters of 200–500 nm by dispersion polymerization with microwave irradiation.[36–37] To our knowledge, there has been no report on the polycondensation of two different aromatic dianhydrides and amine by microwave irradiation.

Herein, we first report that the copolycondensation of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 4,4′-oxydianiline (ODA) under microwave irradiation (Figure 1).

Experimental Part

Materials

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (>98%) and pyromellitic dianhydride (>97%) were obtained commercially from Alfa Aesar (USA). They were recrystallized from acetic anhydride and sublimed under vacuum before use. 4,4′-Oxydianiline (ODA) was dried under vacuum for 24 h at 50 °C before use. *N*,*N*-Dimethylformamide (DMF) was also dried by sodium hydride (NaH), and then distilled under vacuum. ODA, DMF, and the other reagents such as N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), and tetrahydrofuran (THF) were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The water was deionized before use.

Apparatus

The apparatus used for the polycondensation was the XH-100A microwave oven which was purchased from Beijing Xianggu Science and Technology Development Co. Ltd. (2450 MHz and 100–1000 W). A 100 mL, four-necked, round-bottom flask equipped with a reflux condenser, a Teflon

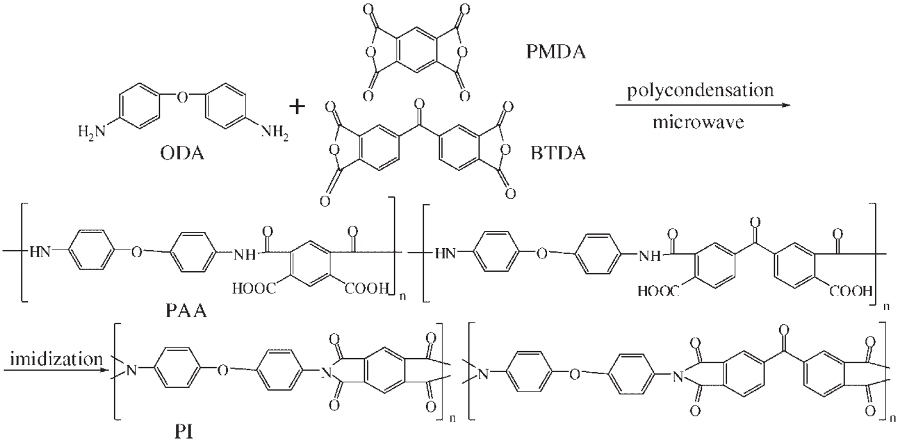

Figure 1.
Synthesis of polyamic acid and PI.

paddle stirrer, and a nitrogen gas inlet was in the microwave oven.

Characterization

The inherent viscosities were determined at a 0.5% concentration in NMP with an Ubbelohde capillary viscometer ($d = 0.6$ mm) at 30 ± 0.1 °C. Fourier-transform infrared (FT-IR) spectra were performed on a Spectrum One FT-IR spectrometer (Perkin–Elmer Co. Ltd., USA). The polymer powder was pulverized in a wet condition and mixed with KBr. The mixture was dried and pressed to form pellets, which were used to record the IR spectrum. ^{1}H NMR spectra (tetramethylsilane as an internal standard) were measured by a Varian Unity spectrometer at 600 MHz (USA); DMSO-d_6 was used as a solvent for the polymers. Thermogravimetric analyses (TGA) were obtained at a heating rate of 20 °C/min in N_2 atmosphere with a Perkin–Elmer DETLASERIES TGA7 thermogravimetric analyzer. A crystallographic study of PI was performed on an X-ray diffractometer (D/MAX-C, Japan). The X-ray diffraction (XRD) pattern was taken from 2° to 60° (2θ value) using Cu K_α radiation.

Synthesis

Microwave-Assisted Polycondensation (Method-A)

1) Preparation of polyamic acid (PAA-A)

   A typical polymerization procedure was as follows. A certain amount of BTDA and PMDA (mole ratio of n(BTDA): n(PMDA) = 1:1) was dissolved in DMF. The reaction vessel, which contained a mixture of a reactant and a solvent, was placed on the center of the turn table in the microwave oven. Nitrogen gas was introduced from the top of the reaction vessel through a thin Teflon tube to minimize danger of fire in the reaction system. A certain amount of ODA was then dropped into the reaction vessel. The reaction mixture was stirred and was irradiated with microwaves for a prescribed time at a low temperature (30 °C). Finally, the resultant viscous mixture was poured into 75 mL of water. The solid substance was separated from the liquid. The polymer was collected by filtration, washed with water and methanol, and dried under vacuum at 30 °C for 24 h. PAA-I was obtained as a grayish-yellow solid.

2) Preparation of polyimide (PI-A)

   PAA-I powder was set into the reactor under N_2 for 1 h and dehydrated under continuous microwave radiation. Temperatures were measured by setting a sensor into the polymerization system. PI-I was obtained by using microwave irradiation and was a yellow solid.

Conventional Solution Polycondensation (Method-B)

1) Preparation of polyamic acid (PAA-B)

   The general procedure consisted of adding ODA to a heated (30 °C) and stirred solution of BTDA and PMDA in DMF. The reaction mixture was stirred for certain time (1–24 h). The viscous solution was poured into 75 mL of water. The precipitated solid was filtered off, and then washed with water and methanol, and dried at 30 °C for 24 h under vacuum.

2) Chemical imidization: Preparation of polyimide (PI-B)

   PAA powder was dissolved in DMF and set into the reactor under N_2. It was then dehydrated with acetic anhydride and triethylamine, the reaction mixture was stirred for a certain time. The temperature was measured by a mercurial thermometer, which was set into the polymerization system. PI-II was obtained by a chemical imidization and was also a yellow solid.

Results and Discussion

Microwave-Assisted Polycondensation and Conventional Solution Polycondensation

To compare the microwave-assisted polycondensation method (A) with a conventional solution polycondensation method (B), the polymerization of ODA with aromatic dianhydrides (PMDA and BTDA) was

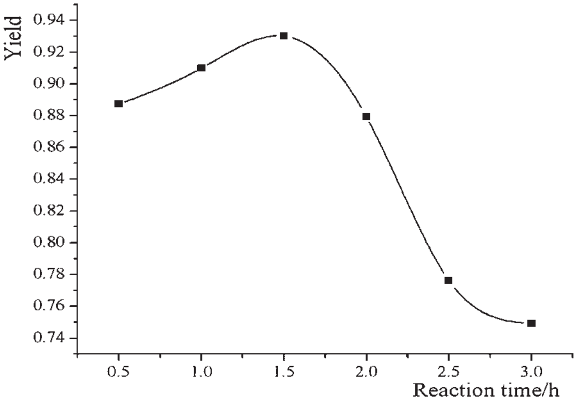

Figure 2.
The effect of microwave reaction (2450 MHz, 900 W) time on the yield of PAA-A (30 °C).

performed at the same reaction temperature. Figure 2 and Figure 3 illustrate the relative of yields of the prepared PAA to with regards to reaction time. The PAA yield (93.01%) obtained under microwave-assisted polycondensation is higher than the PAA yield (79.98%) obtained under conventional solution polycondensation in a period of 1.5 h. It can be concluded that microwave irradiation can accelerate the reaction rate. However, the decrease in yield of PAA after 1.5 h of MW irradiation might be due to depolymerization or decomposition of already formed PAA chains at longer irradiation.

Viscosity

To compare the inherent viscosity of the PAA prepared by the two methods, the polymerization was performed under the same reaction condition including magnetic stirrer, reaction temperature, solvent, and reaction time (1.5 h). The inherent viscosity (0.486 dL/g) of the PAA prepared by a conventional heating was lower than that (up to 0.598 dL/g) of the PAA prepared by microwave irradiation. That is to say, the molecular weights of the PAA prepared by conventional heating are lower than that of the PAA prepared by microwave irradiation.

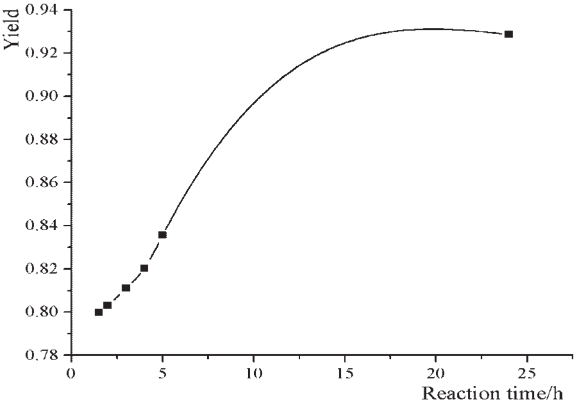

Figure 3.
The effect of conventional heating time on the yield of PAA-B (30 °C).

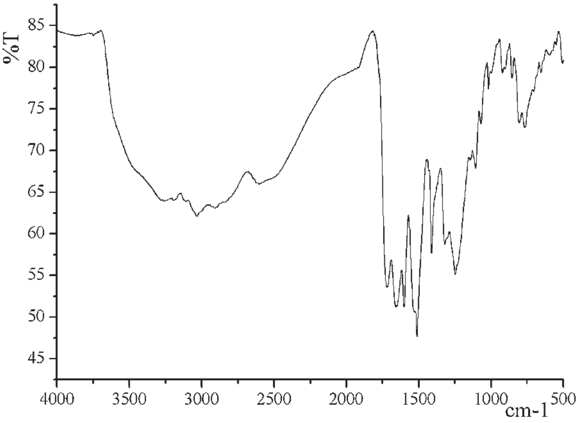

Figure 4.
The FT-IR spectrum of polyamic acid (PAA-A).

Infrared Spectroscopy

Figure 4 and 5 illustrate the FT-IR spectra of the prepared polymers. The IR spectrum of PAA-A (Figure 4) shows broad bands in the range of 3500–2500 cm^{-1}, which indicates the existence of –COOH and –NHCO– groups in the PAA-A, the peak at 1720 cm^{-1}(C=O stretching vibration) is representative of a C=O structure, and the peak around 1240 cm^{-1} indicates the existence of C–N bonds. That is to say, PAA-A has the structure of –CONH–. The FT-IR spectrum of this aromatic copolyimide (Figure 5) presents imide carbonyl peaks at around 1778 and 1723 cm^{-1}, and doesn't present amide carbonyl peaks at 1659 and 1544 cm^{-1}. The other characteristic absorption bands of the imide group are observed at 1381, 1239, and 739 cm^{-1}. The stretch vibration of the C=O of PI-A is expressed as the imidization degree, using the stretch vibration of C=C in the benzene ring as the reference.[38]

Proton Nuclear Magnetic Resonance Spectroscopy

The ^{1}H NMR spectrum (600 MHz) of PAA-A is depicted in Figure 6. By analyzing the ^{1}H NMR spectrum of PAA-A, the conclusion is drawn that a singlet at 6.63 ppm is assigned to the –NHCO–, a singlet at 7.04–8.31 ppm is

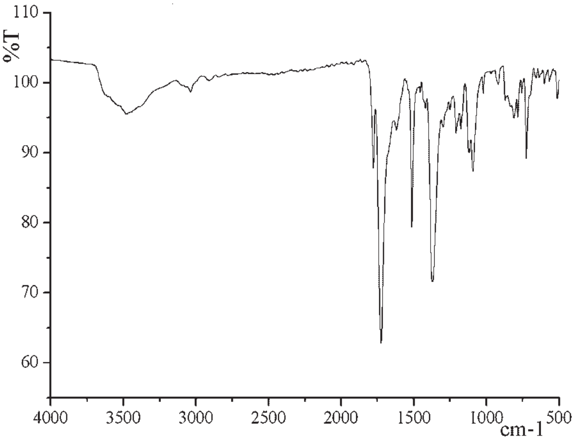

Figure 5.
The FT-IR spectrum of polyimide (PI-A).

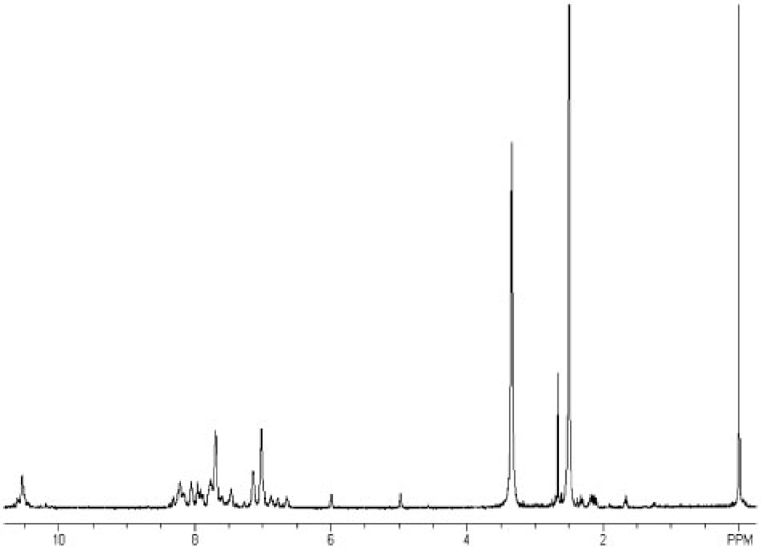

Figure 6.
The ^{1}H NMR spectrum of polyamic acid (PAA-A), solvent: DMSO-d_6.

assigned to the =CH– of benzene, and the singlet at 10.55 ppm is assigned to carboxylic acid protons. The results of this work combined with FT-IR results can clearly demonstrate that PAA is obtained.

X-Ray Diffraction

The *d*-spacing value was calculated with Bragg's equation by reported methods.[39,40] As first shown by Bragg et al., the Bragg equation can be expressed as follows:

$$n\lambda = 2d\sin\theta \; (n = 1,\ 2, \ldots\ldots) \qquad (1)$$

Here, the X-ray wavelength λ is 0.154 nm, θ is the Bragg angle in degrees, and *d* is the *d*-spacing of the polymer.

The *d*-spacing value of polyimide (PI-A) is 0.4756 nm. As shown in Figure 7, the diffraction maximum is sharp, which indicates a low-order aggregation morphology of the polymer. As reported in a previous study by Hsiao et al.,[41] the polyimide

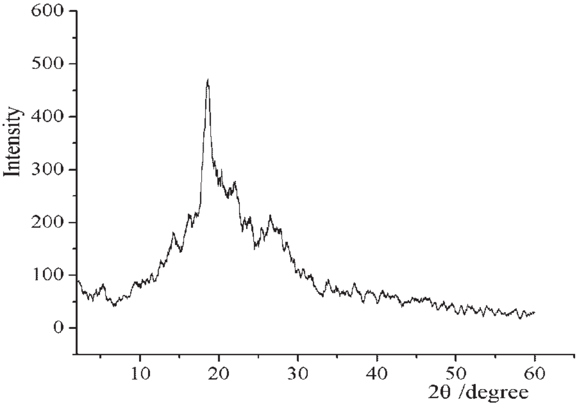

Figure 7.
X-ray pattern of polyimide (PI-A).

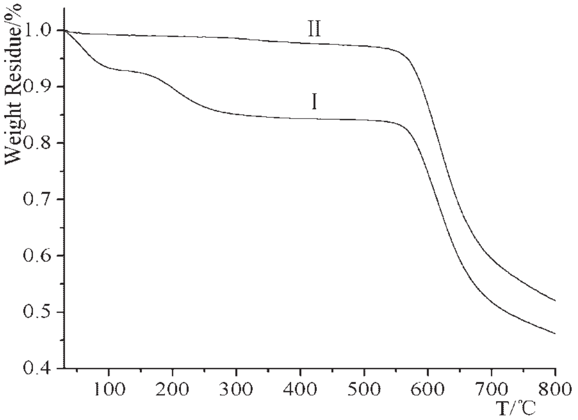

Figure 8.
Thermogravimetric (TG) curve of PAA (I) and PI (II) under N_2 atmosphere.

BTDA/ODA/MDA shows semicrystalline patterns.

Thermogravimetric Curve Analyses

Figure 8 illustrates the TGA curves of the prepared polymers (method A) at a heating rate of 20 °C/min from 25 to 800 °C under nitrogen flow.

Curve II shows that the copolyimide undergoes no weight loss up to 535 °C and is thermally stable with only 10% weight loss at 587 °C under N_2 atmosphere. The residual weight at 800 °C is above 54.9% under N_2. The high percentage of residual content at approximately 800 °C indicates the intrinsic fire-retardant properties of the polymer. Curve I shows that PAA shows an initial weight loss up to 160 °C. As described in the literature,[42,43] we suggest that the observed weight loss below 100 °C is mainly due to the volatilization of a low-molecular-weight substance, such as the solvent DMF and water. The weight loss at 160–275 °C may be attributed to cycloimidization of the PAA to PI (in a similar manner to the way in which PAA in converted into PI by a conventional heating polycondensation). There is a flat between 280 and 530 °C in curve I. The flat nature of the TGA curve between 280 and 530 °C indicates no weight loss and therefore no cycloimidization in this temperature range. Comparing curve I with curve II, we see that they are consistent with each other. All the results reveal that the copolymers keep their excellent thermal stability.

Solution Properties

The key reasons for insolubility and the non-melting character of the aromatic PIs are the lack of flexibility and strong interchain interations due to high symmetry and highly polar groups and also sometimes due to hydrogen bonding.[44]

One of the successful approaches to increase the solubility and processability of PIs without sacrificing their high thermal stability is the copolycondensation reaction. The solution properties of polymers

Table 1.
The solubilities of PAA-A and PI-A in different solvents (25 °C).

Polymer	Solvent						
	NMP	DMF	DMSO	THF	Chloroform	Cyclohexane	Ethanol
PAA-A	++	++	++	++	–	–	–
PI-A	+	+	+	+	–	–	–

++: Soluble; –: Insoluble; +: Partially soluble.

obtained by a copolycondesation of BTDA, PMDA and ODA have been studied (Table 1).

Table 1 shows that the PAA-A is soluble in most of polar aprotic solvents such as NMP, DMF, DMSO, DMAc and even in THF. PI-A is also partially soluble in organic solvents such as DMF, DMAc, NMP. But both PI-A and PAA-A are insoluble in solvents such as chloroform, cyclohexane, acetic acid, ethanol, and acetone.

Conclusions

The aim of this study is to describe a facile method based on the microwave-assisted synthesis of a co-polyimide prepared by polycondensation reaction. It also provides an easy way to control the temperature and time of the synthesis by using a given microwave oven. PI (BTDA-PMDA-ODA) is first synthesized with microwave-assisted polycondensation and conventional solution polycondensation. We have found that microwave irradiation can enable the rapid synthesis of aromatic polyimide by the direct polycondensation of aromatic diamine and aromatic dianhydride, compared with conventional heating. Experimental results show that the polymer obtained via microwave-assisted polymerization has superior inherent viscosity and yield in comparison to the polymer obtained via conventional solution methods. The TG result reveals that the polyimide began to lose weight at 535 °C with 10% weight loss at 587 °C in N_2 atmospheres. XRD spectrum demonstrates that obtained polyimide has low-order aggregation structure with a *d*-spacing of 0.4756 nm.

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