Preparation of Poly(amic acid) and Polyimide Derived from 3,3′,4,4′-Benzophenonetetracarboxylic Dianhydride with Different Diamines by Microwave Irradiation

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ABSTRACT: Polycondensation-type poly(amic acid) (PAA) was synthesized with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride as a dianhydride monomer and 4,4′-diaminodiphenylmethane and 4,4′-oxydianiline as diamine monomers under microwave irradiation in dimethylformamide. Then, PAA was used to make polyimide (PI) by imidization at a low temperature. The structure and performance of the polymers were characterized with Fourier transform infrared (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), viscosity, X-ray diffraction (XRD), and thermogravimetry (TG) curve analyses. The FTIR spectra of the polymers showed characteristic peaks of PI around 1779 and 1717 cm^{-1}. The ^{1}H-NMR spectrum of PAA indicated a singlet at 6.55 ppm assigned to —NHCO— and a singlet at 10.27 ppm assigned to carboxylic acid protons. The XRD spectrum demonstrated that the obtained PI had a low-order aggregation structure with a d-spacing of 0.5453 nm. The TG results revealed that the PI was thermally stable with 10% weight loss at 565°C in an N$_2$ atmosphere. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 797–802, 2008

Key words: copolymerization; high performance polymers; polyimides; synthesis; thermal properties

INTRODUCTION

It is well known that microwave irradiation is a special kind of heating energy with significant advantages over conventional thermal methods. Studies have shown that, in comparison with 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.[4–7] Bogdal et al.[8] reviewed the applications of microwave irradiation in polymer chemistry.

Aromatic polyimides (PIs) are considered high-performance polymers for a variety of applications in electronics,[9,10] fuel cells,[11,12] membrane separation,[13] and so on.[14,15] In comparison with common polymers, PIs possess many outstanding properties such as low color, flexibility, a high glass-transition temperature, excellent thermal stability, and radiation resistance.[16–19] PIs are usually prepared by a so-called two-step method in which a dianhydride and a diamine are allowed to undergo condensation polymerization to form a poly(amic acid) (PAA) precursor, and the precursor is subsequently converted thermally or chemically to the final PI, but the reaction takes a long time. There have been a few reports on the use of microwave irradiation for the synthesis of PIs.[20–22] Mallakpour and coworkers reported in detail the use of microwave irradiation for the synthesis of PIs. Typical examples also include poly(ether imide)s and poly(amide imide)s from diacid chlorides[23–27] and PIs from dianhydrides and diamines.[28–30]

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.[31] We also produced polystyrene microspheres with diameters of 200–500 nm by dispersion polymerization with microwave irradiation with poly(N-vinylpyrrolidone) as a steric stabilizer and 2,2′-azobisisobutyronitrile as a radical initiator in an ethanol/water medium.[32,33]

Here we report for the first time the copolycondensation of 3,3′,4,4′-benzophenonetetracarboxylic

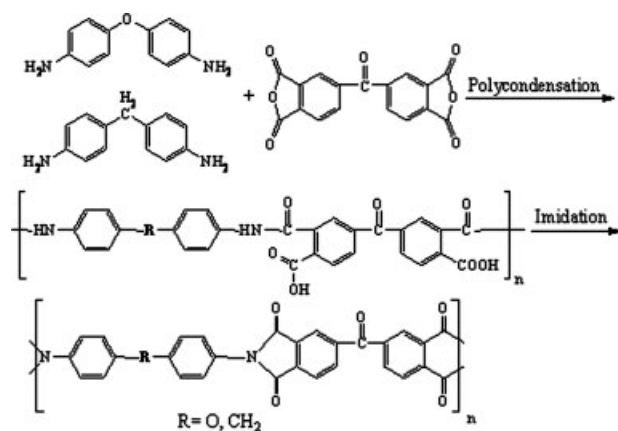WILEY InterScience®
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Figure 1 Synthesis of PAA and PI.

dianhydride (BTDA), 4,4′-diaminodiphenylmethane (MDA), and 4,4′-oxydianiline (ODA) under microwave irradiation (Fig. 1).

EXPERIMENTAL

Materials

BTDA (>98%) was obtained commercially from Sigma–Aldrich (Milwaukee, WI). It was recrystallized from acetic anhydride and sublimed *in vacuo* before use. MDA and ODA were dried *in vacuo* for 24 h at 50°C before use. *N,N*-Dimethylformamide (DMF) was also dried with sodium hydride (NaH) and then distilled *in vacuo*. MDA, ODA, DMF, and other reagents were analytical-grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The water was deionized before use.

Apparatus

The inherent viscosities were determined at a 0.5% concentration in *N*-methyl-2-pyrrolidinone (NMP) with an Ubbelohde capillary viscometer ($d = 0.6$ mm) at 25 ± 0.1°C. Fourier transform infrared (FTIR) spectra were performed on a Spectrum One FTIR spectrometer (PerkinElmer Co., Ltd., Waltham, MA). 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. Proton nuclear magnetic resonance (¹H-NMR) spectra (tetramethylsilane as an internal standard) were measured with a Varian (Palo Alto, CA) Unity spectrometer at 600 MHz; dimethyl sulfoxide-d_6 was used as a solvent for the polymers. Thermogravimetric analysis (TGA) was obtained at a heating rate of 20°C/min in an N_2 atmosphere with a PerkinElmer Delta series TGA7 thermogravimetric analyzer. A crystallographic study of PI was performed on a D/MAX-IIIC X-ray diffractometer (Akishima-shi, Tokyo, Japan). The X-ray diffraction

(XRD) pattern was taken from 2 to 60° (2θ value) with Cu Kα radiation. The apparatus used for the polycondensation was an XH-100A microwave oven purchased from Beijing Xianggu Science and Technology Development Co., Ltd. (2450 MHz and 100–1000 W, Beijing, China). A 250-mL, four-necked, round-bottom flask equipped with a reflux condenser, a Teflon paddle stirrer, and a nitrogen gas inlet was in the microwave oven. The reaction apparatus is schematically presented in Figure 2.

Microwave-assisted polycondensation (method I)

Preparation of PAA-I

A typical polymerization procedure was as follows. A certain amount of ODA and MDA [n(ODA)/n(MDA) = 1.05:0.95 mol/mol] was dissolved in the solvent DMF. The reaction vessel, containing a mixture of a reactant and a solvent, was placed on the center of the turn table in the microwave oven, and then nitrogen gas was introduced from the top of the reaction vessel through a thin Teflon tube to minimize the danger of fire in the reaction system. Then, a certain amount of BTDA was dropped into the reaction vessel. The reaction system was irradiated with microwaves for a prescribed time at a low temperature. At last, the resultant viscous mixture was poured into 50 mL of water. The solid substance was separated from the liquid. The polymer was collected by filtration, washed with water and methanol, and
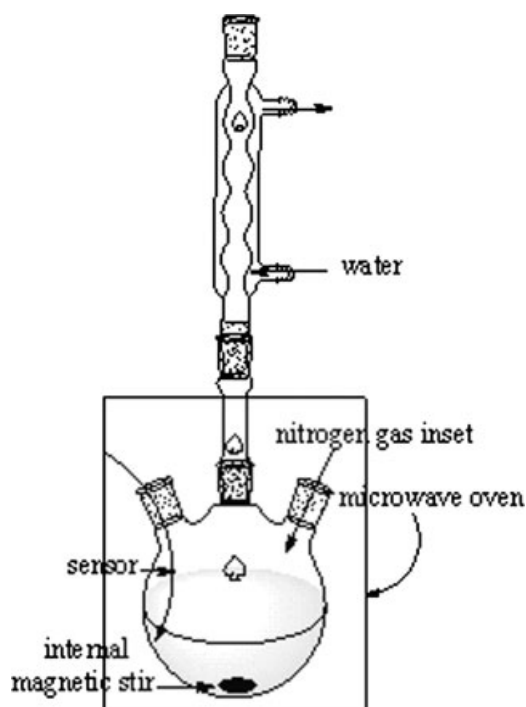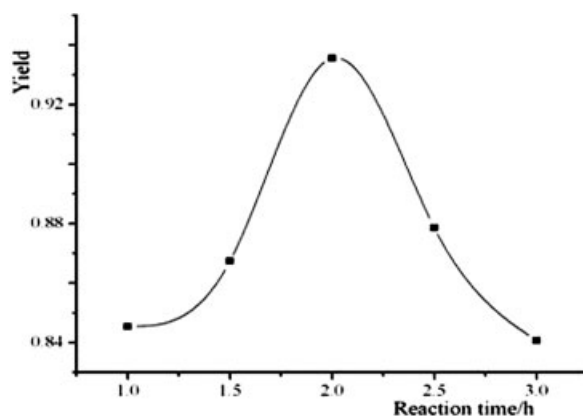

Figure 2 Sketch of the reaction apparatus for microwave irradiation.

Figure 3 Effect of the microwave irradiation time on the yield of PAA.

dried *in vacuo* at 40°C for 18 h. PAA was obtained and was a grayish-yellow solid.

Preparation of PI-I

PAA powder was set into the reactor under N_2 for 1 h and dehydrated under continuous microwave radiation. Temperatures were measured by a sensor being set into the polymerization system.

Conventional solution polycondensation (method II)

Preparation of PAA-II

The general procedure consisted of adding BTDA to a heated (15°C) and stirred solution of ODA and MDA in the solvent DMF. The reaction mixture was stirred for a certain time (2–10 h). The viscous solution was poured into 50 mL of water. The precipitated solid was filtered off, then was washed with water and methanol, and dried at 40°C for 18 h *in vacuo*.

Chemical imidization: Preparation of PI-II

PAA powder was dissolved in the solvent DMF, set into the reactor under N_2, and dehydrated with acetic anhydride and triethylamine; the reaction mixture was stirred for a certain time. The temperature was measured with a mercury thermometer, which was set into the polymerization system.

RESULTS AND DISCUSSION

#### Microwave-assisted polycondensation and conventional solution polycondensation

To compare microwave-assisted polycondensation (method I) with conventional solution polycondensa-

tion (method II), the polymerization of BTDA with aromatic diamines (ODA and MDA) was performed at the same reaction temperature. Figures 3 and 4 illustrate the yields of the prepared PAA. The PAA yield (93.56%) obtained under microwave-assisted polycondensation was higher than the PAA yield (77.50%) obtained under conventional solution polycondensation in a period of 2 h. It can be concluded that microwave irradiation can accelerate the reaction rate.

The decrease in the yield of PAA after 2 h of microwave irradiation might have been due to depolymerization or decomposition of already formed PAA chains at longer irradiation. Hence, we present the inherent viscosity of PAA obtained at different microwave irradiation times to explain the decrease in the yield of PAA at higher microwave irradiation times.

Figure 5 illustrates the effect of microwave irradiation time on the inherent viscosity of PAA. The reaction conditions, including the reaction temperature and solvent, were fixed. The results show that there was a decrease in the inherent viscosity of PAA at higher microwave irradiation times. This was consistent with the effect of the microwave irradiation time on the yield of PAA.

To compare the inherent viscosity of the PAA samples prepared by the two methods, the polymerization was performed under the same reaction conditions, including the magnetic stirrer, reaction temperature, solvent, and reaction time (2 h). The inherent viscosity (0.468 dL/g) of the PAA prepared by conventional heating was lower than that (up to 0.615 dL/g) of the PAA prepared by microwave irradiation. That is, the molecular weights of the PAA prepared by conventional heating were lower than those of the PAA prepared by microwave irradiation. The results also indicate that microwave irradiation can accelerate the reaction rate.
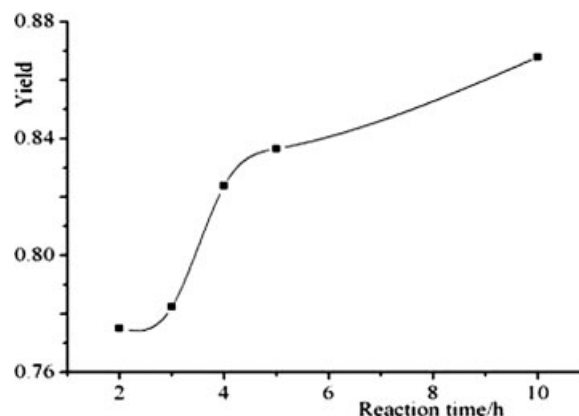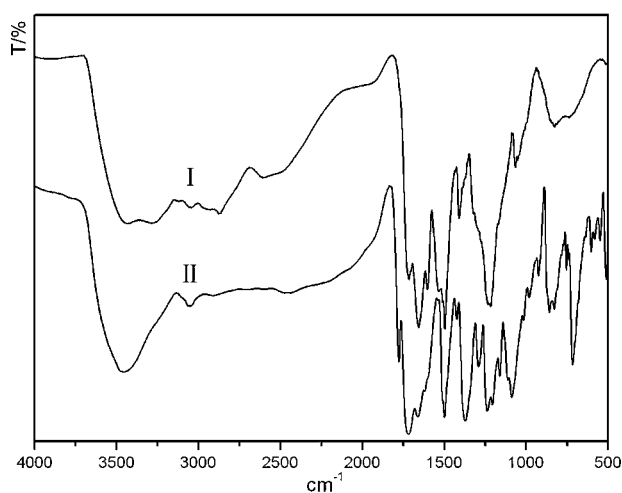

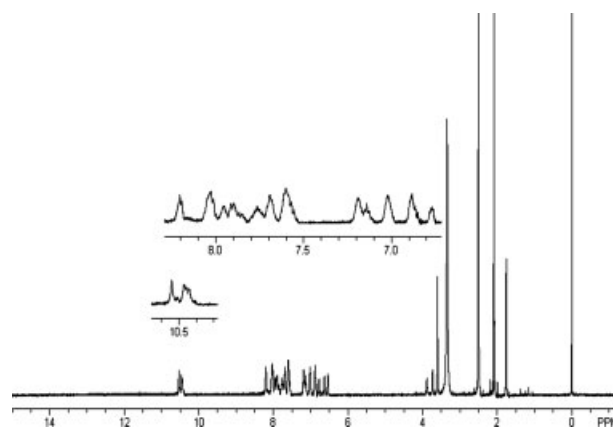**Figure 4** Effect of the conventional heating time on the yield of PAA.
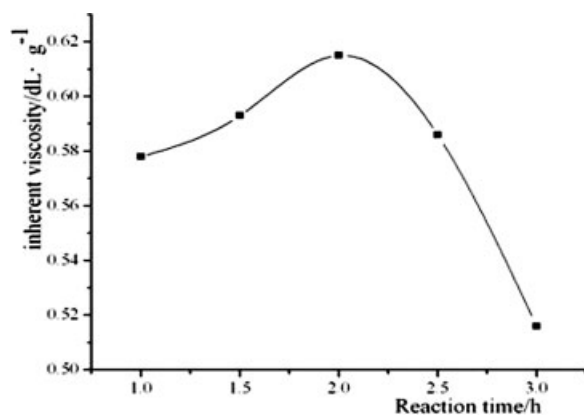
Figure 5 Effect of the microwave irradiation time on the inherent viscosity of PAA.

IR spectroscopy

Figure 6 illustrates the FTIR spectra of the prepared polymers (method I). The IR spectrum of PAA [Fig. 6(I)] can be interpreted as follows: the peak around 3437 cm^{-1} indicates the existence of the N—H bond medium, the broad bands at 3270 and 3074 cm^{-1} indicate the existence of —COOH end groups, the peak at 1716 cm^{-1} (bending) is representative of a C=O structure, and the peak around 1217 cm^{-1} indicates the existence of C—N bonds. That is, PAA has the structure of —CONH—. FTIR spectra of this aromatic copolyimide [Fig. 6(II)] show imide carbonyl peaks around 1779 and 1718 cm^{-1} and do not show amide carbonyl peaks at 1655 and 1533 cm^{-1}. The other characteristic absorption bands of the imide group can be observed at 1372, 1238, and 739 cm^{-1}. The stretching vibration of C=O of PI is expressed as the imidization degree, with the stretching vibration of C=C in a benzene ring used as a reference.[34]

Figure 7 ^{1}H-NMR spectrum of PAA.

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectrum (600 MHz) of PAA (method I) is depicted in Figure 7. By an analysis of the ^{1}H-NMR spectrum of PAA, the singlet at 6.55 ppm can be assigned to —NHCO—, and the singlet at 10.27 ppm can be assigned to carboxylic acid protons. The results of this work combined with FTIR results clearly demonstrate that PAA was obtained.

Thermogravimetry (TG) curve analyses

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

Curve I shows that the copolyimide began to experience weight loss up to 500°C and was thermally stable with 10% weight loss at 565°C in an N_2 atmosphere. The residual weight at 800°C was above 54.9% under N_2. The high percentage of residual content at approximately 800°C indicated the intrinsic fire-retardant properties of the polymer. Curve II

Figure 6 FTIR spectra of PAA-I and PI-II.
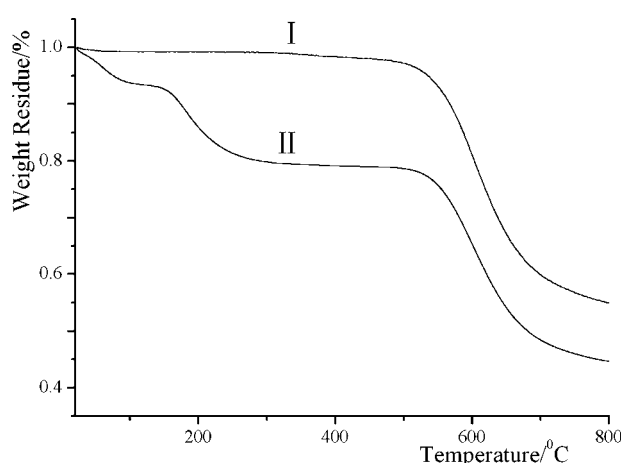
Figure 8 TG curves of PAA-II and PI-I under an N_2 atmosphere.
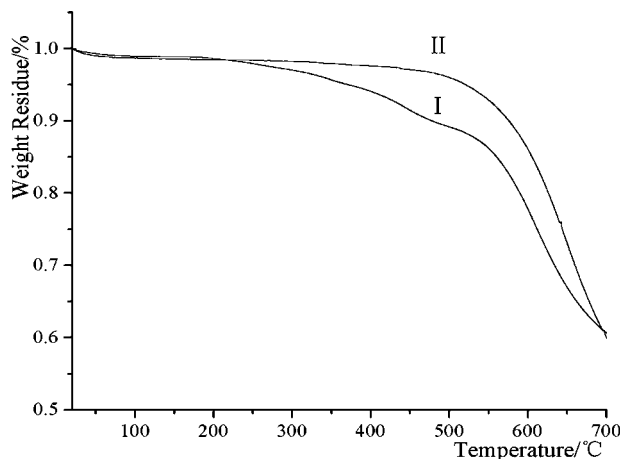
Figure 9 TG curve of PI-I and PI-II under an N_2 atmosphere.

shows that PAA began to experience weight loss up to 150°C. As described in refs 35 and 36, we suggest that the observed weight loss below 150°C was mainly due to the volatilization of low-molecular-weight substances, such as the solvent DMF and water; and the weight loss at 175–275°C may be attributed to cycloimidization of PAA to PI. PAA became PI by conventional heating polycondensation. There is a plateau between 280 and 500°C in curve II. The flat nature of the TGA curve at 280–500°C indicates no weight loss and therefore no cycloimidization in this temperature range. Comparing curve I with curve II, we know that they are consistent with each other. All the results reveal that the copolymers kept their excellent thermal stability.

Figure 9 illustrates the TGA curves of the prepared polymers (method II) at a heating rate of 20°C/min from 20 to 700°C under a nitrogen flow.

Curve I shows that the copolyimide began to experience weight loss up to 200°C and was thermally stable with 10% weight loss at 477°C in an N_2 atmosphere. The reason was that when the reaction time was fixed (1 h), the chemical imidization was incomplete (the reaction time was too short), but the imidization under microwave irradiation was basically complete, as shown in Figure 8. When the reaction time was prolonged (20 h), the chemical imidization was also basically complete. Curve II shows that PI obtained by this method had almost the same TGA trace in comparison with Figure 8.

XRD

The d-spacing value was calculated with Bragg's equation by reported methods.[37,38] As first shown by Bragg et al., the Bragg equation can be expressed as follows:

$$n\lambda = 2d \sin \theta, n = 1, 2, \ldots \tag{1}$$

where X-ray wavelength λ is 0.154 nm, θ is the Bragg angle (°), and d is the d-spacing of the polymer.

By calculation, the d-spacing value is 0.5453 nm. As shown in Figure 10, the diffraction maximum is sharp, and this indicates low-order aggregation morphology for the polymer. As reported in a previous study by Hsiao and Chen,[39] the PI BTDA/ODA/MDA (method I) showed semicrystalline patterns.

Solution properties

The key reasons for the insolubility and nonmelting character of aromatic PIs are a lack of flexibility and strong interchain interactions due to high symmetry, highly polar groups, and also sometimes hydrogen.[40,41]

One of the successful approaches to increasing the solubility and processability of PIs without sacrificing their high thermal stability is the copolycondensation reaction. To compare microwave-assisted polycondensation (method I) with conventional solution polycondensation (method II), the polymerization of BTDA with aromatic diamines was performed under the same reaction conditions, including the reaction temperature, reaction time, and magnetic stirrer. The solution properties of polymers obtained by the copolycondensation of BTDA, ODA, and MDA have been studied (Table I).

PAA-I was soluble in most polar aprotic solvents such as DMF, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), NMP, and even tetrahydrofuran (THF). PI-I was also partially soluble in organic solvents such as DMF, DMAc, and NMP. However, both PI and PAA were insoluble in solvents such as chloroform, cyclohexane, acetic acid, ethanol, and acetone. As can be seen in Table I, we can conclude that the solubilities of the polymers prepared by the two methods were almost the same.
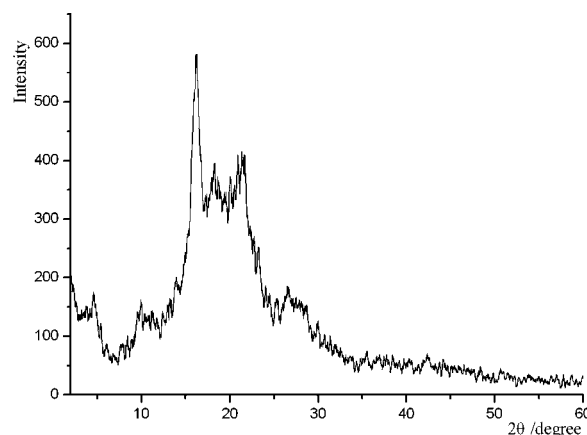
Figure 10 X-ray pattern of PI.

TABLE I
Solubility of PAA and PI in Different Solvents (25°C)

Solvent	NMP	DMF	DMSO	THF	Chloroform	Acetone	Ethanol
PAA-I	++	++	++	++	−	−	−
PI-I	+	+	+	+	−	−	−
PAA-II	++	++	++	++	−	−	−
PI-II	+	+	+	+	−	−	−

++ = soluble; − = insoluble; + = partially soluble.

CONCLUSIONS

In this article, we report a facile method for the rapid synthesis of PI. We also provide an easy way to control the temperature and time of the synthesis by the use of a given apparatus. PI (BTDA/ODA/MDA) was first synthesized with microwave-assisted polycondensation and conventional solution polycondensation. We found that microwave irradiation could enable the rapid synthesis of aromatic PI by the direct polycondensation of an aromatic diamine and an aromatic dianhydride in comparison with conventional heating. Experimental results showed that the polymer obtained via microwave-assisted polymerization had superior inherent viscosity and yield in comparison with the polymer obtained via the conventional solution method. The TG results revealed that the PI was thermally stable with 10% weight loss at 565°C in an N_2 atmosphere. The XRD spectrum demonstrated that the obtained PI had a low-order aggregation structure with a d-spacing of 0.5453 nm.

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