

Microwave-Assisted Synthesis of High-Molecular-Weight Poly(ether imide)s by Phase-Transfer Catalysis

Changlu Gao, Suobo Zhang, Lianxun Gao, Mengxian Ding

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; Changchun, 130022, People's Republic of China

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ABSTRACT: A facile and rapid polycondensation reaction of disodium bisphenol A with bis(chlorophthalimide)s was performed with a domestic microwave oven in *o*-dichlorobenzene by phase-transfer catalysis. The polymerization reactions, in comparison with conventional heating polycondensation, proceeded rapidly and were completed within 25 min. The polymerizations gave the corresponding poly(ether imide)s with inherent viscosities of 0.55–0.92 dL g⁻¹.

The effects of various factors on the polymerization, such as the amount of the catalyst, the reaction time, and the microwave power were studied. The properties of the polymers were briefly characterized. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2415–2419, 2004

Key words: polycondensation; polyimides; phase transfer catalysis

INTRODUCTION

Aromatic polyimides (PIs) are considered high-performance polymers, and they are used in a wide range of applications in advanced technologies.¹ The chemistry of PIs during the last few years has been directed toward novel linear species that are soluble in organic solvents or melt-processable when fully imidized.² The most important of them, on the basis of production figures, are very likely the poly(ether imide)s (PEIs),³ which are prepared with several methods. A widely used method for preparing PEIs is the reaction of dianhydrides with diamines.^{3,4} Other approaches involve the nucleophilic displacement reactions of bisimide and diphenoxide.^{5–8}

Microwave technology has been used in organic synthesis since 1986.⁹ Some organic reactions can be accelerated dramatically and completed in a few minutes, and the yields are enhanced in comparison with those from conventional methods.^{9,10} There have been a few reports on the use of microwave irradiation for the synthesis of PIs. Recent examples include poly(ester imide) and poly(amide imide) from diacid chlorides¹¹ and PIs from dianhydrides and diamines.¹²

In this article, we report a facile method for the rapid syntheses of high-molecular-weight PEIs by aromatic nucleophilic displacement polycondensation with a domestic microwave oven, and we compare the

results with those of conventional heating polycondensation.

EXPERIMENTAL

Apparatus

¹H-NMR spectra were measured at 300 MHz on a Bruker AV300 spectrometer (Germany). CDCl₃ was used as a solvent for the monomers. Fourier transform infrared (FTIR) spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer (Cambridge, MA). Elemental analyses were performed on a Flash EA-1112 series elemental analyzer (Norwalk, CT). The inherent viscosities were determined at a 0.5% concentration in *N,N*-dimethylacetamide (DMAc) with an Ubbelohde capillary viscometer at 30 ± 0.1°C. The melting points were determined on an RY-1 melting-point apparatus (Tianjin, China) and were uncorrected. The apparatus used for the polycondensation was an LG domestic microwave oven (Tianjin, China) (2450 MHz and 800 W), as shown in Figure 1.

Materials and monomers

4-Chlorophthalic anhydride (99.2%), 3-chlorophthalic anhydride (99.8%), 4,4'-oxydianiline, 4, 4'-diaminodiphenylmethane, 2,2'-bis(4-hydroxyphenyl)propane (bisphenol A), and *o*-dichlorobenzene were used as received.

4,4'-Bis(4-chlorophthalimido)diphenyl ether (**1a**) was prepared from 4-chlorophthalic anhydride and 4,4'-oxydianiline (ODA) with the procedure described in the literature.^{5a} The product was a yellow solid (88%, 23.3 g).

Correspondence to: S. Zhang (sbzhang@ciac.jl.cn).

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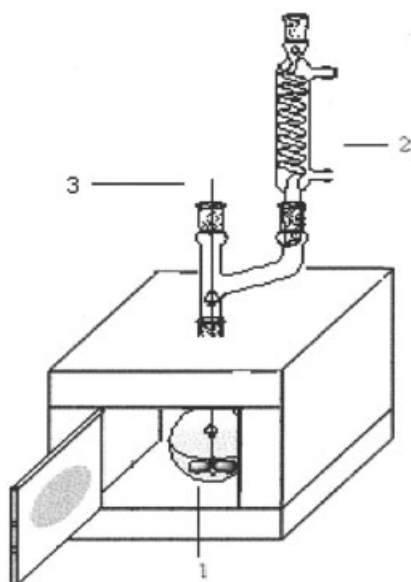


Figure 1 Microwave reactor modified from a domestic microwave oven: (1) Pyrex, (2) condenser, and (3) stirrer.

mp: 238–240°C (literature^{5a} 238–240°C). ¹H-NMR (CDCl₃, δ): 7.94 (2H, d, *J* = 1.6 Hz), 7.93–7.90 (2H, d, *J* = 8 Hz), 7.78–7.76 (2H, dd, *J* = 1.6, 8 Hz), 7.43–7.41 (4H, dd, *J* = 2, 6.8 Hz), 7.2–7.18 ppm (4H, dd, *J* = 2, 6.8 Hz). IR: 1777, 1718 (C=O of imide), 1393 (C–N stretching), 736 cm⁻¹ (C=O bending). ANAL. Calcd for C₂₈H₁₄O₅N₂Cl₂: C, 63.53%; H, 2.66%; N, 5.29%. Found: C, 63.23%; H, 2.76%; N, 5.13%.

4,4'-Bis(3-chlorophthalimido)diphenyl ether (**1b**) was prepared from 3-chlorophthalic anhydride and ODA as previously described. The product was a yellow solid (90%, 23.8 g).

mp: 259–260°C. ¹H-NMR (CDCl₃): 7.95–7.89 (6H, m), 7.50–7.53 (4H, d, *J* = 8.8 Hz), 7.24–7.27 ppm (4H, d, *J* = 8.8 Hz). IR (KBr): 1774, 1718 (C=O of imide), 1387 (C–N stretching), 737 cm⁻¹ (C=O bending). ANAL. Calcd for C₂₈H₁₄O₅N₂Cl₂: C, 63.53%; H, 2.66%; N, 5.29%. Found: C, 63.14%; H, 2.50%; N, 5.33%.

4,4'-Bis(4-chlorophthalimido)diphenyl methane (**1c**) was prepared from 4-chlorophthalic anhydride and 4-4'-diaminodiphenylmethane (MDA) as previously described. The product was a light yellow solid (91%, 24.0 g).

mp: 257–259°C. ¹H-NMR (CDCl₃): 7.95 (2H, d, *J* = 1.6 Hz), 7.93–7.91 (2H, d, *J* = 6.8 Hz), 7.77–7.75 (2H, dd, *J* = 1.6, 6.8 Hz), 7.47–7.29 (8H, m), 4.12 ppm (2H, s). IR: 1777, 1718 (C=O of imide), 1393 (C–N stretching), 736 cm⁻¹ (C=O bending). ANAL. Calcd for C₂₉H₁₆O₄N₂Cl₂: C, 66.15%; H, 3.07%; N, 5.32%. Found: C, 66.23%; H, 2.96%; N, 5.23%.

4,4'-Bis(3-chlorophthalimido)diphenyl methane (**1d**) was prepared from 3-chlorophthalic anhydride and MDA as previously described. The product was a yellow solid (92%, 24.2 g).

mp: 244–246°C. ¹H-NMR (CDCl₃): 7.91–7.87 (2H, m), 7.74–7.72 (4H, m), 7.42–7.28 ppm (8H, m). IR (KBr): 1774, 1718 (C=O of imide), 1387 (C–N stretching), 737 cm⁻¹ (C=O bending). ANAL. Calcd for C₂₉H₁₆O₄N₂Cl₂: C, 66.15%; H, 3.07%; N, 5.32%. Found: C, 66.03%; H, 3.12%; N, 5.26%.

Bisphenol disodium salt hexahydrate was prepared with the described procedure,⁸ and the yield was 80%. Hexaethyl guanidinium bromide was prepared with the described procedure,¹³ and the yield was 50% (mp = 175–176°C, literature¹³ 174–175°C).

Preparation of PEIs

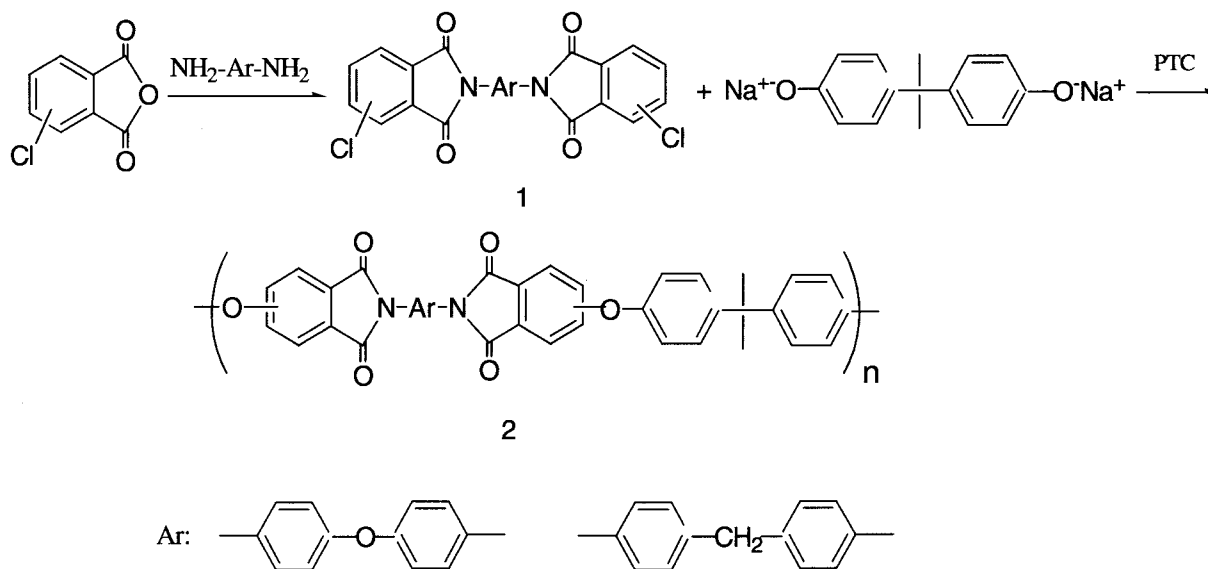
The polymerization reaction was performed through the reaction of bisphenol disodium salt with different bis(chlorophthalimide)s via two methods.

Solution polymerization

A mixture of 100 mL of *o*-dichlorobenzene and 6.13 g (16.12 mmol) of the product of bisphenol hexahydrate was heated under nitrogen at 200°C to distill off the water of hydration along with about 40 mL of *o*-dichlorobenzene. A mixture of 20 mL of *o*-dichlorobenzene and bis(chlorophthalimide)s (8.53 g, 16.12 mmol) was then added, and distillation was continued until an additional 20 mL of *o*-dichlorobenzene had been removed. Then, 173 mg (0.56 mmol) of hexaethyl guanidinium bromide was added to the reaction mixture. The mixture was stirred at 200°C for 4 h. The resultant viscous mixture was diluted with 40 mL of DMAc and poured into 400 mL of methanol. The polymer was collected by filtration, washed with methanol, and dried *in vacuo* at 150°C for 12 h.

Microwave-assisted polymerization

In this method, a mixture of 100 mL of *o*-dichlorobenzene and 6.1322 g (16.12 mmol) of the product of bisphenol hexahydrate was heated under nitrogen at 200°C to distill off the water of hydration along with about 40 mL of *o*-dichlorobenzene. A mixture of 20 mL of *o*-dichlorobenzene and bis(chlorophthalimide)s (8.53 g, 16.12 mmol) was then added, and distillation was continued until an additional 20 mL of *o*-dichlorobenzene had been removed. Then, the sample cell was placed in the center of the microwave cavity with 20% power for 25 min after 173 mg (0.56 mmol) of hexaethyl guanidinium bromide was added to the reaction mixture. The resultant viscous mixture was diluted with 40 mL of DMAc and poured into 400 mL of methanol. The polymer was collected by filtration, washed with methanol, and dried *in vacuo* at 150°C for 12 h.



Scheme 1 Synthesis of PEI by phase-transfer catalysis.

RESULTS AND DISCUSSION

Preparation of bis(chlorophthalimide)s

According to the literature, four aryl dichlorides (**1a–1d**) were prepared in high yields. The structures of the monomers were confirmed with elemental analyses and IR and NMR spectroscopy.

Preparation of the polymers

PEIs were prepared by phase-transfer catalysis with two methods (Scheme 1). For the determination of optimal conditions for the polymerization, polymer **2b** was studied in detail in the presence of a phase-transfer catalyst. The amount of the solvent found to be appropriate for the reaction was a 12–15% concentration of the polymer in *o*-dichlorobenzene. A more concentrated system would lead to almost no stirring during the late period of the polymerization. The effect of the amount of the catalyst on the polycondensation is shown in Figure 2. The added catalyst—3.5 and 6.0 mol % with respect to the monomer—was effective under microwave irradiation and conventional heating, respectively. Upon the further addition of the catalyst, the inherent viscosities of the polymers were not obviously enhanced. The effect of the microwave power on the inherent viscosity of the resultant polymer was also investigated. The polycondensation at 20% total power gave the highest value. Higher power led to a large amount of *o*-dichlorobenzene being distilled off.

Figure 3 shows the courses of the polymerizations in terms of the inherent viscosities of the resultant polymers. More rapid polymerizations proceeded within a few minutes, and higher molecular weight polymers

were obtained under microwave heating. In contrast, polymerizations by conventional heating produced polymers with lower molecular weights. These results indicate that microwave heating could accelerate the reaction rate. After ion exchange, the nucleophilic ion pair $\text{ArO}^-\text{C}[\text{N}(\text{C}_2\text{H}_5)_2]_3^+$ is a highly polar species. When the species is subjected to an oscillating microwave field, the orientation of the species changes with each alternation. The strong molecular agitation, provided by the reorientation of the species, causes intense internal heating, which can accelerate the phenol ion to rapid transfer and then attack the substrate (chlorophthalimide) effectively. However, microwave irradiation could pass through the walls of the vessel rapidly and heat only the reactants and solvents. The

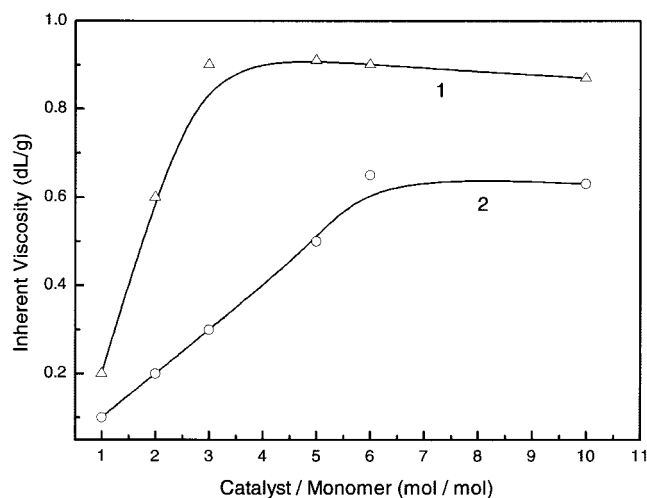


Figure 2 Effect of the amount of the catalyst (16 mmol of the monomer and 60 mL of *o*-dichlorobenzene).

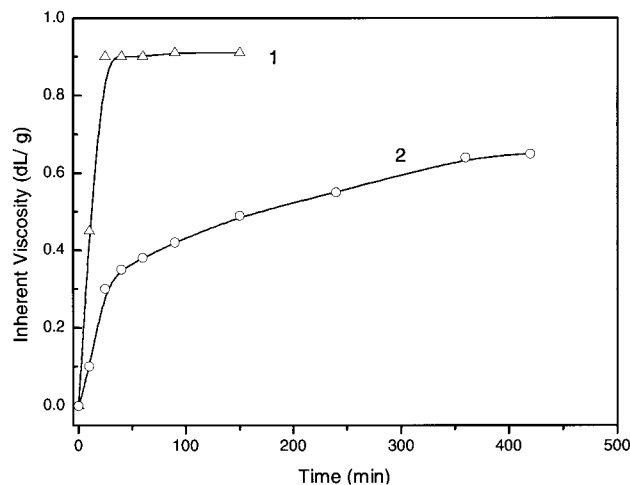


Figure 3 Course of the polymerizations in terms of the inherent viscosities of the polymers (16 mmol of the monomer, 0.1 mmol of the catalyst, and 60 mL of *o*-dichlorobenzene) by phase-transfer catalysis: (1) microwave heating and (2) conventional heating.

temperature increase will be uniform throughout a sample, and this can lead to an increase in the polymer molecular weight in an equal system. In contrast, conventional heating techniques are rather slow, and a temperature gradient can develop within a sample; local overheating can lead to some unexpected side reactions, which can result in the reduction of the polymer molecular weight.

Polymer characterization

The results from the various studies are summarized in Table I. PEIs with inherent viscosities of up to 0.92 dL g⁻¹ under microwave heating could be obtained in shorter reaction times. These polymers were con-

TABLE I
Preparation of PEIs 2a–2d

Monomer		Polymer					
Method	Time (min)	Yield (%)	η_{inh} (dL/g)	T_g (°C)	T_5^c (°C)		
1a	MW ^a	25	2a	97	0.55	217	456
1a	Δ^b	240	2a	95	0.44	218	452
1b	MW	25	2b	98	0.92	238	462
1b	Δ	240	2b	97	0.65	237	454
1c	MW	25	2c	95	0.60	227	467
1c	Δ	240	2c	97	0.52	227	458
1d	MW	25	2d	96	0.58	235	465
1d	Δ	240	2d	97	0.45	234	459

η_{inh} = inherent viscosity; MW = microwave heating; Δ = conventional heating.

^a 20% microwave power.

^b 200°C.

^c 5% weight loss.

TABLE II
Elemental Analysis of PEIs 2a–2d

Polymer	Method	Formula		Elemental analysis (%)		
				C	H	N
2a	MW	(C ₄₃ H ₂₈ N ₂ O ₆) _n	Calcd	75.43	4.12	4.09
2a	Δ	(684.70) _n	Found	74.60	4.16	3.99
2b	MW	(C ₄₃ H ₂₈ N ₂ O ₆) _n	Calcd	75.43	4.12	4.09
2b	Δ	(684.70) _n	Found	74.91	4.03	4.16
2c	MW	(C ₄₄ H ₃₀ N ₂ O ₆) _n	Calcd	77.41	4.43	4.10
2c	Δ	(682.73) _n	Found	76.99	4.38	4.02
2d	MW	(C ₄₄ H ₃₀ N ₂ O ₆) _n	Calcd	77.41	4.43	4.10
2d	Δ	(682.73) _n	Found	76.60	4.24	4.15

MW = microwave heating; Δ = conventional heating.

firmed to be PEIs by elemental analysis and IR spectroscopy. Their elemental analysis values are listed in Table II.

As shown in Figure 4, IR spectra of all the polymers exhibited absorptions at 1776, 1717, 1373, 1103, and 742 cm⁻¹ associated with the imide structure. The FTIR spectrum of PI also indicated that during the polymerization, the imide rings did not change at all.

Thermal properties

The thermal stability of the polymers was examined by thermogravimetric analysis (TGA). For comparison, polymer 2b was prepared by the conventional heating method. Typical traces of polymer 2b are shown in Figure 5. The PEIs prepared by the two methods had almost the same TGA traces and showed 5% weight losses at about 450°C. The glass-transition temperatures (T_g 's) from differential scanning calorimetry are summarized in Table I. The polymers derived from bis(3-chlorophthalimide)s showed higher T_g 's than those from their isomers.

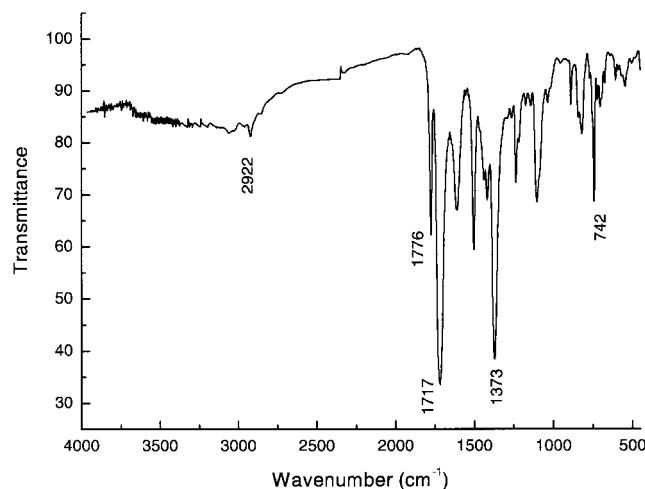


Figure 4 Typical FTIR spectrum of the polymer.

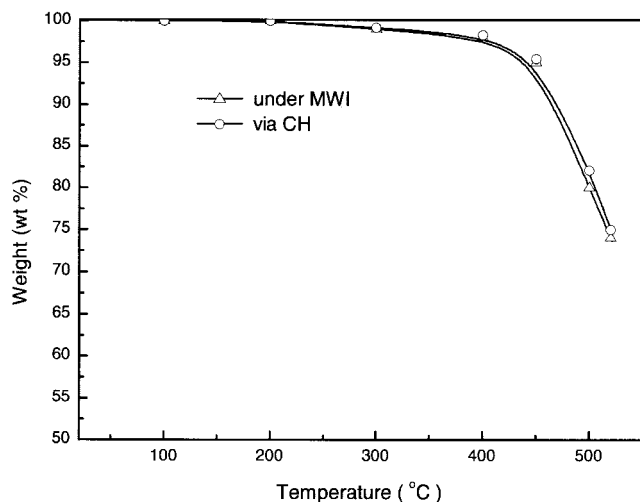


Figure 5 TGA curves of polymer 2b.

CONCLUSIONS

We have reported a microwave method for the efficient syntheses of PEIs with high molecular weights from bis(chlorophthalimide)s and the disodium salt of bisphenol A by phase-transfer catalysis. In comparison with conventional heating, microwave heating could accelerate the phenol ion to attack the substrate. The polycondensations under microwave heating gave polymers with higher molecular weights in a few minutes.

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