

Aromatic nucleophilic substituted synthesis of high-molecular-weight poly(ether imide)s using bis(chlorophthalimide)s

YanLiu (刘妍), Xiaogang Zhao, Daming Wang, Hongwei Zhou, Chunhai Chen(陈春海)

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University(吉林大学), Changchun, 130012, China

Abstract : Poly(ether imide) (PEI) were prepared via aromatic nucleophilic substitution polymerization of bisphenol disodium salt and bis(chlorophthalimide)s. PEI show excellent solubility in a variety of organic solvents. The glass transition temperatures of PEI are 212°C, the 5% weight loss temperatures (T_{5%}) reach up to 417°C in N₂.

Key words: polycondensation; polyimides; aromatic nucleophilic substitution

Introduction:

Aromatic polyimides (PIs) are recognized as high-performance plastics, and they are used in a wide range of applications in advanced technologies.¹ The most important of polyimides are very likely the poly(ether imide)s which are soluble in organic solvents or melt-processable when fully imidized.² Generally, we used method for preparing PEIs is the imidization of polyamide acid.^{3,4} In this article, we report a new method for the syntheses of high-molecular-weight PEI by aromatic nucleophilic displacement polycondensation used bis(chlorophthalimide)s.

Experimental

Apparatus

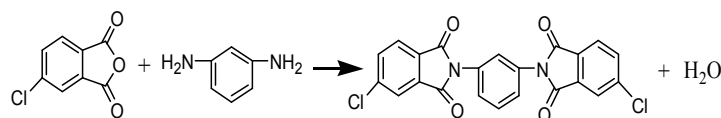
The Fourier transform infrared spectra (FT-IR) were obtained from a Thermo Nicolet 6700 FT-IR spectrometer, where the sample was prepared with KBr pellets. Thermogravimetric analysis was obtained from TGA instrument at a heating rate of 10°C/min under nitrogen (flow rate of 50ml/min). Differential scanning calorimetry (DSC) was carried out on a TA DSC at a heating rate of 10°C/min under nitrogen atmosphere with 50ml/min gas flow, and T_g was obtained at the middle of the thermal transition from the second heating.

Materials and monomers

m-phenylenediamine, bisphenol A (BPA), 4-chlorophthalic anhydride, and sodium carbonate were purchased from Shanghai Chemical Reagent Plant, Shanghai, China. N,N-Dimethylacetamide (DMAc), and xylene were purified by distillation over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of 1,3-bis[N-(4-chlorophthalimido) phenyl

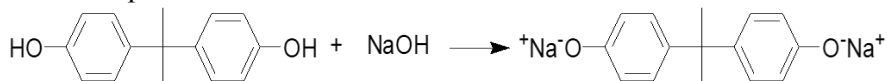
In a 500 ml round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, 4-chlorophthalic anhydride (36.49 g, 0.05 mol), xylene (15 ml) and N,N-Dimethylacetamide (300 ml) were added. The mixture was heated until 4-chlorophthalic anhydride was completely dissolved in N,N-Dimethylacetamide under nitrogen atmosphere. After addition of m-phenylenediamine (10.8 g, 0.10 mol), the mixture was refluxed for 12 hr, then cooled to room temperature. The pale yellow precipitate was collected by filtration, washed with ethyl alcohol, and then dried under vacuum at 100°C for 12 h. 1,3-bis[N-(4-chlorophthalimido) phenyl biphenyl was obtained at the yield of 91.2% (40.04 g).



Scheme 1. Synthesis of the 1,3-bis[N-(4- chlorophthalimido) phenyl

Synthesis of bisphenol disodium salt

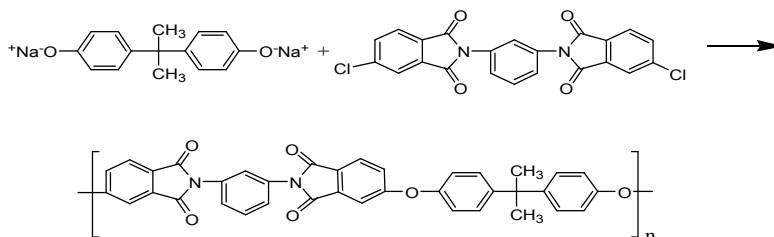
In a 300 ml round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, bisphenol A (7.98 g, 0.035mol) , xylene (10 ml) and N,N-Dimethyl acetamide (100 ml) were added. The mixture was heated until bisphenol A was completely dissolved in N,N-Dimethylacetamide under nitrogen atmosphere. After addition of sodium carbonate (3.67 g, 0.035mol), the mixture was refluxed for 5 h, then cooled to room temperature.



Scheme 2. Synthesis of the bisphenol disodium salt

Synthesis of polymers

The PEIs were prepared by the solution polycondensation in DMAc. A typical procedure for PIs (II) was carried out as follows: to a 300ml round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser, 1,3-bis[N-(4-chlorophthalimido) phenyl] (15.29 g, 0.035 mol), bisphenol disodium salt (9.52 g,0.035 mol), xylene (10 ml), and freshly distilled DMAc (100 ml) were added. A white solution was formed. When the temperature was raised to 150°C, color of the solution began to the yellow. The reactant was heated gradually to 160°C and allowed to react at this temperature for 12 h to finally obtain a viscous solution.



Scheme 3. Synthesis of the polymers

Results and discussion

Monomer synthesis

As shown in Scheme 1, 1,3-bis[N-(4- chlorophthalimido) phenyl] were prepared in our laboratory by directly reacting 4-chlorophthalic anhydride with m-phenylenediamine. Pale yellow monomer was obtained after washed with ethyl alcohol. DSC signals corresponding to the monomers are given in Fig. 1. DSC curve is a sharp unimodal, shows that the monomer we synthesized is pure . The data proved that the monomer was successfully prepared.

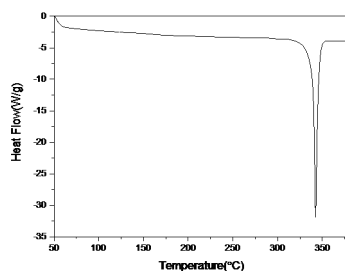


Figure 1 DSC curves of 1,3-bis[N-(4- chlorophthalimido) phenyl

Polymer synthesis

As shown in Figure 4, IR spectra of the polymers exhibited absorptions at 1787, 1729, 1343, 1103, and 779 cm^{-1} associated with the imide structure, and the absorptions at 1212 cm^{-1} associated with the ether bond. The FTIR spectrum of PI also indicated that during the polymerization, the imide rings did not change at all. The thermal stability of the polymers was examined by thermogravimetric analysis (TGA). TGA traces showed 5% weight losses at about 417°C. The glass-transition temperatures is 212°C

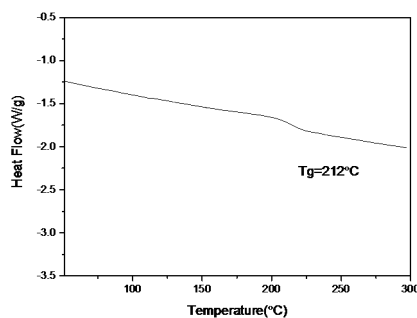


Figure 2 DSC curves of poly(ether imide)s

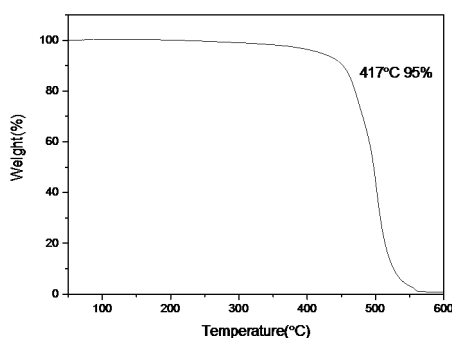


Fig 3. TGA curves of poly(ether imide)s

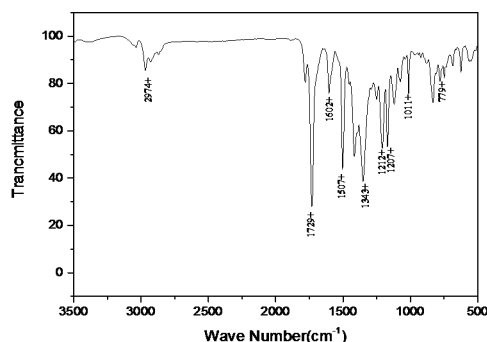


Fig 4. Typical FTIR spectrum of the polymer

Conclusion:

We have reported a Aromatic nucleophilic substituted method for the efficient syntheses of PEIs with high molecular weights from bis(chlorophthalimide)s and the disodium salt of bisphenol A. The polycondensations used aromatic nucleophilic substitution give us a new way to synthesize poly(ether imide)s

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