



Chemically oxidative polymerization of aromatic diamines: The first use of aluminium-triflate as a co-catalyst

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ARTICLE INFO

Article history:

Received 21 August 2012

Received in revised form

6 November 2012

Accepted 28 November 2012

Available online 4 December 2012

Keywords:

Aluminium-triflate

Diamines

Oxidative polymerization

ABSTRACT

Aromatic diamine monomers, including *o*-phenylenediamine (*o*PD), *p*-phenylenediamine (*p*PD), 4,4'-diaminodiphenylmethane (DADPM) and benzidine (BZN), were polymerized by chemical oxidation using sodium persulfate, potassium persulfate, and ammonium persulfate as oxidant catalysts. Aluminium-triflate ($\text{Al}(\text{OTf})_3$) was also used for the first time as a co-catalyst under various polymerization conditions. The homopolymers obtained are characterized by FT-IR, ^1H and ^{13}C NMR, GPC, WAXD, DSC and TGA. The yield, solubility, structure and molecular weight of the polymers are significantly dependent on the oxidative catalyst and polymerization conditions. The polymers show different molecular structures, good thermal stability and decompose above 400 °C in nitrogen.

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1. Introduction

Chemically oxidative polymerization has produced various functional polymers. Typical polymers include polyaniline, polytoluidine, polypyrrole, polyaminopyridine, polyaminonaphthalene, polyaminoquinoline, polymethylquinoline and polyphenylenediamine, which are used in the production of rechargeable batteries, electrocatalysts, smart windows, microelectronic and electrochromic devices, sensors, and actuators. Novel multifunctionality, which includes good redox reversibility, variable conductivity, strong electroactivity, colorful electrochromism, adsorption of heavy metal ions and good environmental stability has enabled the use of diamine polymers in various technological applications [1–11].

Polyphenylenediamines are considered to be conductive polymers which have attracted attention lately because they display high gas separation ability [12,13] and lyotropic liquid crystallinity [14,15]. Furthermore, it is reported that polyphenylenediamines produced by chemically oxidative polymerization with sodium, potassium, or ammonium persulfate as oxidants show ladder and ladder-like structures having highly aromatic nitrogenous heterocycles and show unusually high thermostability [16–22]. The nitrogenous heterocyclic ladder structure is considered to be of great benefit to the preparation of advanced air separation

membranes [23]. Moreover, the solubility of the polyphenylenediamines in most of the common organic solvents is low and depends on solvent composition and on the oxidant that was used for polymerization [24,25]. Only a few studies on oxidative homopolymerization of three phenylenediamine isomers have been described [16–22,26–29].

Chemically oxidative polymerization of *p*-phenylenediamine (*p*PD) was first reported as an additive of aniline (AN) polymerization in order to increase the rate and yield of polymerization [30]. Chan, Rawat, and coworkers reported the chemically oxidative polymerization of different aromatic diamines with persulfate as the oxidant in acidic aqueous solution from 0 °C to room temperature [18,31]. Improvements in synthetic techniques, characterization of structure and properties lead to the design of functional materials of the polymers [2,32–34].

Metal triflates have received wide attention for their role as Lewis acids in a number of reactions [35–38]. Water-tolerant metal triflates are especially attractive from both an economical and environmental perspective as they can be recycled easily and repeatedly [39]. Thus, aluminiumtriflate ($\text{Al}(\text{OTf})_3$) is a reusable catalyst, which tolerates water effectively and is stable in aqueous medium [40]. $\text{Al}(\text{OTf})_3$ has not been explored as extensively as other metal triflates, for example the rare earth metal triflates in particular, despite it being comparatively more affordable [40,41]. $\text{Al}(\text{OTf})_3$ was used in our study as co-catalyst to polymerize different phenylenediamines instead of protic acids which are normally used for polymerizations. $\text{Al}(\text{OTf})_3$ showed an improvement on the yield and had different effects on the molecular weight

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of phenylenediamine polymers, compared to polymerization reactions in which protic acids were used.

This article reports the chemically oxidative polymerization and characterization of a series of aromatic diamines, including *o*PD, *p*PD, 4,4'-diaminodiphenylmethane (DADPM) and benzidine (BZN), using different oxidants and acidic co-catalysts.

2. Experimental section

2.1. Materials

The *o*PD, *p*PD, DADPM, BZN and all other solvents and reagents were obtained from Aldrich or Fluka and were used as received.

2.2. General polymerization procedure

The oxidative polymerization was generally accomplished according to Ref. [19]. A typical procedure for the preparation of polymers was as follows: Phenelynediamine monomer (1.7 g) (*o*PD, *p*PD, DADPM or BZN) was added to an acidic solution (150 ml of HCl, glacial acetic acid or water) in a 500-ml glass flask in an oil bath at certain temperatures (Table 1) and was magnetically stirred. In a separate flask, the oxidative catalyst or co-catalyst (4.0 g) (sodium persulfate, potassium persulfate, ammonium persulfate or Al(OTf)₃) was dissolved in 20 ml of water. The polymerization reaction was started by steadily adding oxidant solution dropwise into the monomer solution at a rate of one drop every 3 s over a period of 30 min. The dropwise addition of oxidant solution produced polymers with a relatively high molecular weight and narrow molecular weight distribution, as the highly exothermic nature of the polymerization reaction could then be effectively controlled. Immediately after the addition of the first few drops of oxidant, the color of the reaction solution changed as shown in Table 1. The reaction mixture was vigorously stirred for at least 8 h. Thereafter, the reaction mixture was filtered and washed several times with an excess of distilled water to remove the oxidant and

oligomers. Finally, the resulting powder products were left to dry in ambient air for one week.

2.3. Equipments

Fourier transform infrared spectroscopy (FT-IR) was used to characterize the molecular structure of aromatic diamine polymers. Infrared spectra of the samples were recorded on a Bruker VERTEX 80 FT-IR spectrometer at room temperature. The analysis was performed between 500 and 4000 cm⁻¹, the resolution used was 2 cm⁻¹ and the results were based on an average of 22 scans.

¹H and ¹³C nuclear magnetic resonance spectroscopy (¹H and ¹³C NMR) spectra were recorded at room temperature on a 600 SB Ultra Shield™ Plus NMR spectrometer equipped with an Oxford magnet (14.09 T), operating at 600 MHz. Samples (20–30 mg) for NMR analyses were dissolved in deuterated dimethyl sulfoxide (DMSO-d₆).

Gel permeation chromatography (GPC) was used to determine weight average molecular weight (\overline{M}_w) and molecular weight distribution (MWD). Samples were analyzed with a PL-GPC 220. A flow rate of 1.0 ml/min was used. The analyses were carried out in dimethylacetamide (DMAC).

Wide-angle X-ray diffraction (WAXD) analysis was performed on a Bruker AXS D8 Advance diffractometer at room temperature with filtered CuK α radiation. All samples were scanned at 2 θ angles, ranging from 0° to 80°, with a sampling width of 0.02°, where 2 θ is the diffraction angle.

Differential Scanning Calorimetry (DSC) analysis was performed on a TA Instruments Q100 DSC. All measurements were conducted under a nitrogen atmosphere, at a purge gas flow rate of 50 ml/min. Three cycles were performed for each sample. First the samples were heated in crimped aluminium pans from 25 °C to 450 °C at a rate of 10 °C/min. Samples were then cooled from 450 °C to 25 °C. Finally, the samples were heated for a second time at rate of 10 °C/min to 450 °C.

Thermogravimetric analysis (TGA) measures the change in the weight of polymer sample as a function of temperature which was

Table 1
Shows preparation and properties of the polymer powders from aromatic diamines by chemically oxidative polymerization under various conditions using different catalysts.

Run	Polymer	Powder color	Acid/solvent	T ^a [°C]	Time [h]	Oxidant/catalyst	Yield [wt%]	M _w	PD ^b
1	PoPD ^c	—	Glacial CH ₃ COOH	118	72	None	0.0	—	—
2	PoPD	—	CH ₃ COOH/H ₂ O	100	8	None	0.0	—	—
3	PoPD	Black	Glacial CH ₃ COOH	118	72	(NH ₄) ₂ S ₂ O ₈	34.0	16,365	2.28
4	PoPD	Orange	HCl/H ₂ O	0–2	72	(NH ₄) ₂ S ₂ O ₈	8.0	4816	1.10
5	PoPD	Dark	H ₂ O	100	8	(NH ₄) ₂ S ₂ O ₈	85.0	5573	1.91
6	PoPD	Orange	HCl/H ₂ O	30	24	K ₂ S ₂ O ₈	6.0	4252	1.11
7	PoPD	Orange	HCl/H ₂ O	30	24	Na ₂ S ₂ O ₈	12.0	4576	1.10
8	PoPD	—	Al-triflate/H ₂ O	100	24	None	0.0	—	—
9	PpPD ^d	Black	Glacial CH ₃ COOH	118	72	None	16.0	1010	1.04
10	PpPD	—	CH ₃ COOH/H ₂ O	100	8	None	0.0	—	—
11	PpPD	Black	Glacial CH ₃ COOH	118	72	(NH ₄) ₂ S ₂ O ₈	44.0	9882	2.32
12	PpPD	Black	HCl/H ₂ O	0–2	72	(NH ₄) ₂ S ₂ O ₈	56.0	—	—
13	PpPD	Dark	H ₂ O	100	8	(NH ₄) ₂ S ₂ O ₈	93.0	—	—
14	PpPD	Black	HCl/H ₂ O	30	24	K ₂ S ₂ O ₈	53.0	16,992	2.86
15	PpPD	Black	HCl/H ₂ O	30	24	Na ₂ S ₂ O ₈	54.0	26,445	1.17
16	PpPD	Purple	Al-triflate/H ₂ O	100	24	None	15.0	—	—
17	PDADPM ^e	Brown	H ₂ O	100	8	(NH ₄) ₂ S ₂ O ₈	91.0	—	—
18	PDADPM	Brown	HCl/H ₂ O	30	24	(NH ₄) ₂ S ₂ O ₈	38.0	—	—
19	PDADPM	—	Al-triflate/H ₂ O	100	24	None	0.0	—	—
20	PBZN ^f	Brown	H ₂ O	100	8	(NH ₄) ₂ S ₂ O ₈	98.0	—	—
21	PBZN	Brown	HCl/H ₂ O	30	24	(NH ₄) ₂ S ₂ O ₈	95.0	14,258	2.73
22	PBZN	Gray	Al-triflate/H ₂ O	100	24	None	82.0	850	1.03

^a Reaction temperature.

^b Polydispersity.

^c Poly(*o*-phenylenediamine).

^d Poly(*p*-phenylenediamine).

^e Poly(diaminodiphenylmethane).

^f Poly(benzidine).

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