

Synthesis and characterization of polyimides from triphenylamine-based diamine monomers with fluorene

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ABSTRACT

A series of novel polyimides with a fluorene chromophore in the backbone were prepared from a newly synthesized diamine monomer, 4,4-diamino-9,9-dimethyl-fluorenyl – triphenylamine, and various commercially available tetracarboxylic dianhydrides via a conventional two-step procedure. These polyimides were readily soluble in many organic solvents and could afford flexible and dimension stable films. They had useful levels of thermal stability with glass-transition temperature in the range of 289-374°C and 5% weight loss temperature in excess of 520°C. The cyclic voltammetry studies of the polymer films revealed a reversible redox couples at half-wave potential of 1.05 V.

Keywords: Polyimides; Synthesis; Triphenylamine; Fluorene

Introduction

Aromatic polyimides are well-known for high-performance polymers that have excellent thermal, mechanical, electrical and outstanding chemical resistance properties.¹⁻⁴ However, most of them have high melting or softening temperature and are insoluble in most of organic solvents because of the strong interchain interaction. To overcome this drawback, various efforts have been centered on improving processability and solubility through the synthesis of new diamine or dianhydride monomers.⁵⁻¹⁰ The incorporation of bulky substituents or bulky pendant groups into rigid backbones was very successful, which hinder the chain packing but do not affect the glass transition temperature.

Triarylamine derivatives are well known as photo and electroactive properties that find optoelectronic applications as organic photoconductor, electroluminescence, electrochromic and nonvolatile memory devices.¹¹⁻¹³ Electron-rich triarylamine can be easily oxidized to form stable radical cations, and the process is always associated with a noticeable change of coloration. Therefore, the introduction of triphenylamine units into the polymer backbone would not only enhance the solubility in organic solvents, but also allow them to be used as potential electrochromic or hole-transporting materials.

Fluorene and its derivatives have been widely used as blue-light-emitting materials with extremely high photoluminescence, quantum yields, and thermal and oxidative stability.¹⁴ In recent years, fluorene derivatives have attracted increasing interest in the fabrication of various electronic devices such as organic light-emitting diodes (OLEDs)¹⁵⁻¹⁸ and solar cells¹⁹⁻²⁰. There are a vast number of fluorene derivatives that have been reported in the literature, and among them, the fluorene-containing triarylamine generally exhibit both hole-transporting and emitting properties; therefore, they can be used as hole-transporting emitters in the fabrication of OLEDs.²¹⁻²⁴

In view of the attractive properties associated with the fluorene and triarylamine units, herein, we synthesized a novel triphenylamine-based novel diamine monomers and their derived polyimides containing electron-rich triphenylamine groups. The general properties such as solubility, thermal and electrochemical properties of these polymers will be described.

Experimental

2.1. Materials

All the reagents were purchased from commercial sources and used as received. 2-amino-9,9-dimethylfluorene (Acros), 4-fluoronitrobenzene (Acros), 10% palladium on charcoal (Pd/C, TCI), and hydrazine monohydrate (TCI) were used as received. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropaned dianhydride (6FDA) and 3,3',4,4'-Diphenylsulfonetetracarboxylic dianhydride (DSDA) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd, and these aromatic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuum at 150°C for 10 h prior to use. Dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMAc) were purified by vacuum distillation over CaH₂ and stored over 4 Å molecular sieves prior to use. The other commercially available reagents and solvents were used without further purification.

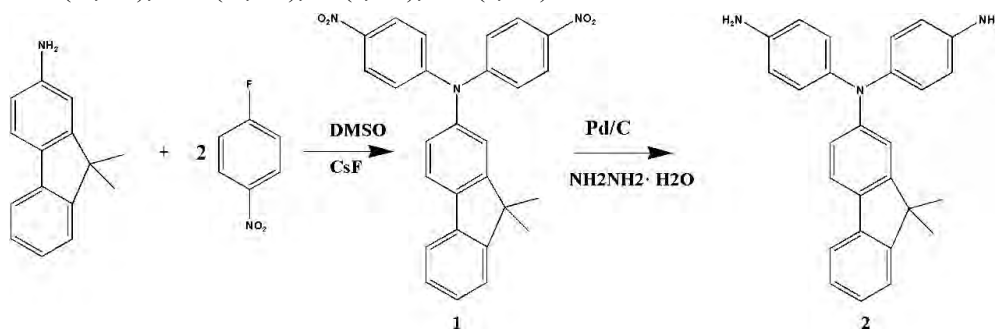
Synthesis of monomers

1、Synthesis of 4,4-dinitro-9,9-dimethyl-fluorenyl – triphenylamine

In a 250ml three-neck round-bottom flask equipped with a stirring bar, a mixture of 12.0g (0.057mol) of 2-amino-9,9-dimethylfluorene, 12.8g (0.12mol) of 4-fluoronitrobenzene, and 13.7g (0.12mol) of CsF in 100mL of dried dimethyl sulfoxide (DMSO) was heated with stirring at 130°C for 12h under nitrogen atmosphere. After cooling, the mixture was poured into 500 mL stirred ethanol slowly and the yellow precipitate was collected by filtration and washed thoroughly by ethanol and hot water. The crude product was filtered and recrystallized from glacial acetic acid to afford 21.2g in 80% yield; mp=195°C; IR (KBr): 1308 cm⁻¹, 1577 cm⁻¹ (NO₂ stretch). ¹H NMR (300MHz, DMSO-d₆, δ, ppm): 8.21(d, 2H), 7.95(m, 1H), 7.86(m, 1H), 7.55(m, 1H), 7.51(m, 1H), 7.37(m, 1H), 7.34(m, 1H), 7.27(m, 1H), 7.24(m, 1H), 1.42(s, 6H).

2、Synthesis of 4,4-diamino-9,9-dimethyl-fluorenyl – triphenylamine

In a 500-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 20g (0.044mol) of dinitro compound 1 and 2g 10% Pd/C were dissolved in 250ml ethanol. The suspension solution was heated to reflux, and 50 mL of hydrazine monohydrate was added slowly to the mixture, then, the solution was stirred at reflux temperature. After a further 12h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled under a nitrogen flow to grow crystals. The crystals were collected by filtration and dried in vacuo at 80°C; yield= 14.2g(80%), mp=239-241°C; IR (KBr): 3445 cm⁻¹, 3362 cm⁻¹ (NH₂ stretch). ¹H NMR (300MHz, DMSO-d₆, δ, ppm): 7.58(d, 1H), 7.43(d, 1H), 7.42(d, 1H), 7.26(t, 1H), 7.17(t, 1H), 6.85(d, 2H), 6.75(s, 1H), 6.57(m, 1H), 6.53(m, 2H), 5.0(s, 4H), 1.28(s, 6H).



Scheme 1. Synthetic route to the target diamine monomer 2

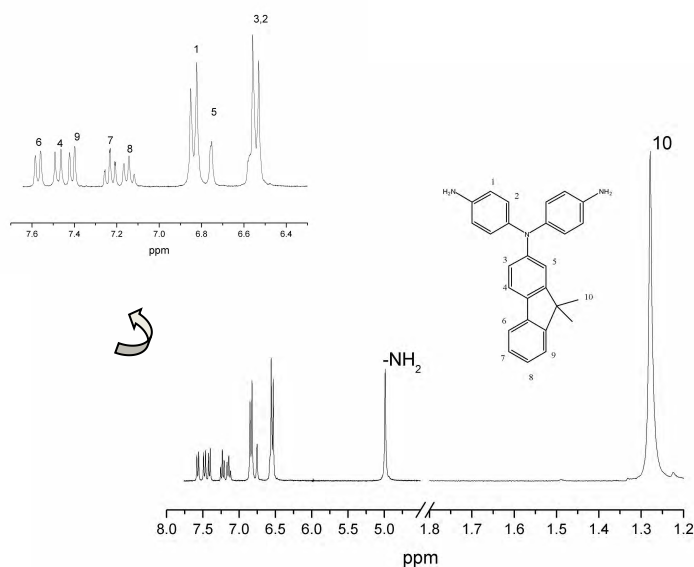


Figure 1. ^1H NMR spectra of the diamine **2**

Synthesis of polyimides

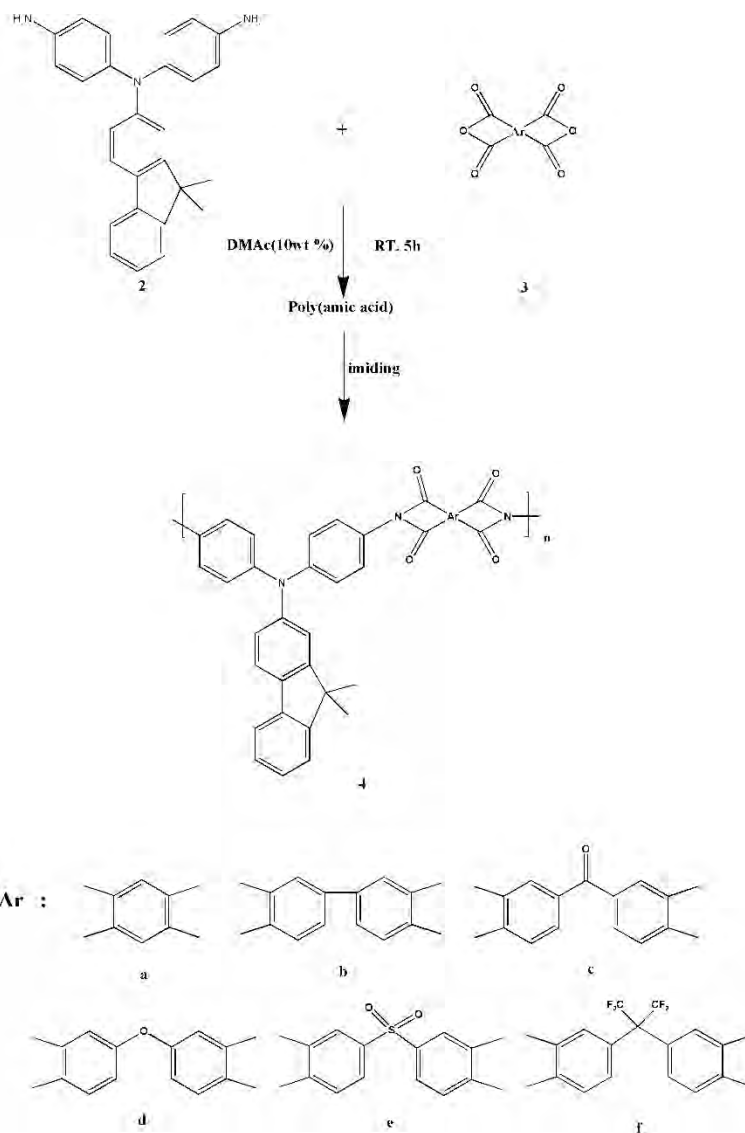
A typical procedure is as follows. The diamine monomer was dissolved in 10 ml DMAc in a 50mL round-bottom flask. Then dianhydride was added to the diamine solution in one portion. Thus, the solid content of the solution is approximately 10wt%. The mixture was stirred at room temperature for about 5h to yield a viscous poly(amic acid) solution. The poly(amic acid) film was obtained by casting from the reaction polymer solution onto a glass Petri dish and drying at 80°C overnight, and then was converted to polyimide by successive heating under vacuum at 100 for 1h, 200 for 1h, 300 for 1h.

For the chemical imidization method, 4 mL of acetic anhydride and 2mL of pyridine were added to the poly(amic acid) solution obtained by a similar process as above, and the mixture was heated at 100 for 1 h to effect a complete imidization. The homogenous polymer solution was poured slowly into 400mL ethanol giving rise to yellow precipitate that was collected by filtration, washed thoroughly with hot water and ethanol, and dried.

Measurements

Inherent viscosities (η_{inh}) of PAA were measured with an Ubbelohde viscometer with a 0.5g/dL of DMAc solution at 20°C. Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-300 spectrometer at 300 MHz for ^1H NMR in deuterated dimethyl sulfoxide. FTIR spectra were recorded on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1} . All spectra were measured at room temperature and represented the average of 128 scans. Differential scanning calorimetric (DSC) analysis was performed on a TA instrument DSC Q100 at a scanning rate of 10°C/min in a nitrogen flow of 50 mL/min. Thermo gravimetric analysis (TGA) was conducted with the TA 2050, with a heating rate of 10°C/min under nitrogen atmosphere. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.8*1.25 cm^2) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference

electrode.



Scheme 2 Synthesis of fluorene-based polyimides

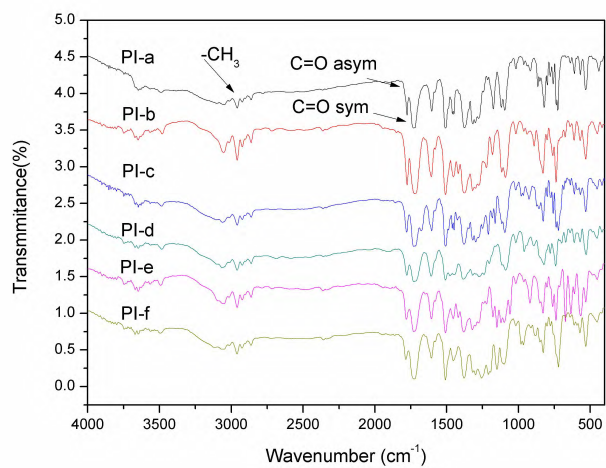


Figure 2. FTIR spectra of the PIs.

Results and Discussion

Monomer synthesis

The fluorene-containing diamine monomer **2** was synthesized by the synthetic route outlined in Scheme 1. The new aromatic diamine, 4,4-diamino-9,9-dimethyl-fluorenyl-triphenylamine, was successfully synthesized by the amination reaction of 2-amino-9,9-dimethylfluorene with 4-fluoronitrobenzene followed by hydrazine Pd/C-catalytic reduction. IR and ^1H NMR spectroscopic techniques were used to identify the structures of the intermediate compounds **2** and the diamine monomer **3**. The transformation of nitro to amino functionality could be monitored by the change of IR spectra. The nitro groups of compounds **2** gave two characteristic bands at around 1308 and 1577 cm^{-1} ($-\text{NO}_2$ asymmetric and symmetric stretching). After reduction, the characteristic bands of the nitro group disappeared and the amino group shows the typical N-H stretching absorption bands at around 3445 and 3362 cm^{-1} . Figure 1 illustrates the ^1H NMR spectra of the diamine monomer **2**. Assignments of each proton are assisted by the NMR spectra, and the spectra agree well with the proposed molecular structure of the diamine. The ^1H NMR spectra confirm that the nitro groups have been completely transformed into amino groups by the high-field shift of the aromatic protons and by the resonance signals at around 5.0 ppm corresponding to the amino protons.

Polymer Synthesis.

A series of novel polyimides **4a-4f** with fluorenylamine units were prepared in conventional two-step method by the reactions of equal molar amounts of diamine **2** with various aromatic dianhydrides (**3a-3f**) to form poly(amic acid)s, and followed by the thermal or chemical cyclodehydration (Scheme 2). As shown in Table 1, the inherent viscosities of the poly(amic acid) precursors derived from aromatic dianhydrides **3a-3f** were in the range 0.50-1.23 dL/g. The molecular weights of these poly(amic acid)s were sufficiently high to permit the casting of flexible and tough poly(amic acid) films, which were subsequently converted into tough polyimide films by stage-by-stage heating to elevated temperatures. The transformation from poly(amic acid) to a polyimide could also be carried out via chemical cyclodehydration by using acetic anhydride and Py. Structural features of these polyimides were by IR analysis. IR spectra of these polyimides are presented in the Figure 2. All polyimides exhibited characteristic imide group absorption around 1780 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretch), 1380 cm^{-1} (C-N stretch). The disappearance of amide and carboxyl bands indicates a virtually complete of the poly(amic acid) precursor into polyimide.

The solubility properties of polyimides **4a-4f** in some selected organic solvents at 2%(w/v) are also displayed in Table 1. The solubility behavior of these polyimides depended on their chain packing ability and intermolecular interactions that was affected by the rigidity, symmetry and regularity of the molecular backbone. These polyimides exhibited high solubility in polar aprotic organic solvents such as N-methyl-2-pyrrolidinone (NMP), DMAC and DMF. The resulting polyimides PI-f were soluble not only in polar aprotic organic solvents but also in less polar solvents such as tetrahydrofuran (THF) and Toluene. The excellent solubility can be attributable to the existence of the hexafluoroisopropylidene structure which limit the CTC formation and reduce the intermolecular interactions.

Table 1. Solubility Behavior of Polyimides

Solvent	NMP ^a	DMAc	DMF	DMSO	CHCl ₃	THF	Toluene
PI-a	+-	+-	+-	--	+-	+-	--
PI-b	+-	+-	+-	+-	++	--	--
PI-c	+-	--	+-	--	+-	+-	--
PI-d	+-	+-	+-	--	++	--	--
PI-e	++	++	++	+-	++	++	--
PI-f	++	++	++	++	++	++	++

soluble at room temperature; +-, partial soluble; --, insoluble.

^a Qualitative solubility tested with 4 mg of sample in 2mL of solvent.

Thermal Properties

The thermal stability and phase-transition temperatures of these polyimides were recorded by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal behavior data are summarized in Table 2. The DSC and TGA curves of these polyimides are illustrated in Figure 3 and 4. These polyimides exhibit excellent thermal properties, the decomposition temperature at a 10% weight-loss in nitrogen were recorded in the range of 524-575°C and the amount of carbonized residue (char yield) of these polymers was more than 55% at 800°C in nitrogen. The high char yields of these polymers can be ascribed to their high aromatic content. The glass-transition temperatures (T_g) of all the polymers were observed in the range of 289-374°C and decreased with decreasing rigidity of the tetracarboxylic dianhydride used. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms and this result supports the amorphous nature of these triphenylamine-containing polymers.

Table 1 The thermal behavior of Polyimides

Polyimides	η_{inh} (PAA) (dL/g) ^a	T _g (°C) ^b	T10% (°C) ^c	R _w (%) ^d
PI-a	0.50	374	548	66.7
PI-b	1.23	320	575	58.5
PI-c	0.51	303	576	56.8
PI-d	0.74	289	545	69.7
PI-e	0.69	318	524	61.5
PI-f	0.87	305	547	55.4

^aInherent viscosities of PAA was measured at 20°C with a concentration of 0.5 g/dL.

^bObtained at the baseline shift in the second heating DSC traces, with a heating rate of 10°C/min under N₂.

^c10% weight loss temperatures measured by TGA at a heating rate of 10°C/min under N₂.

^dResidual weight retention at 800°C by TGA at a heating rate of 10°C/min under N₂.

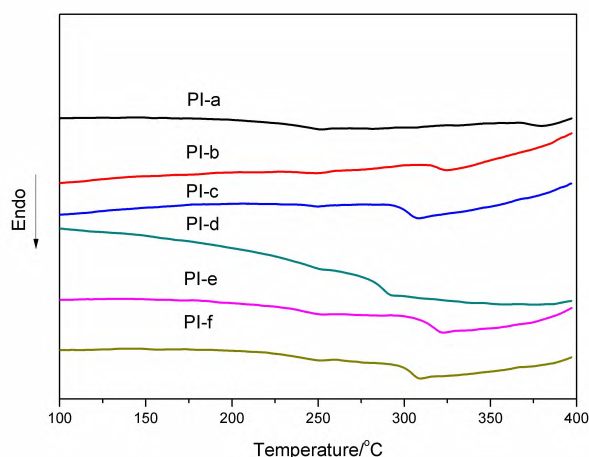


Figure 3.DSCcurves of PI films

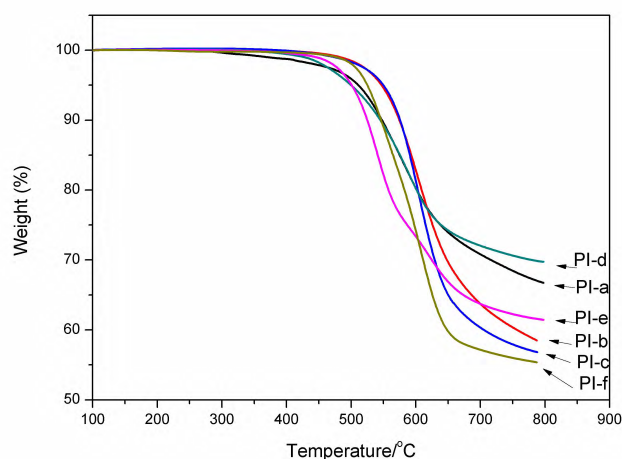


Figure 4. TGA curves of PI films.

Electrochemical Properties

The electrochemical behavior of these polyimides was investigated by cyclic voltammetry conducted by film cast on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH₃CN) in oxidation 0.1 M of TBAP as an electrolyte under nitrogen atmosphere respectively. The typical cyclic voltammograms for PI-e revealing reversible redox couples are depicted in Figure 5. The half-wave potentials ($E_{1/2}$) of PI-e was 1.05V, corresponding to TPA oxidation with the color of the polyimides film changed from colorless to deep blue because of electrochemical oxidation of the polymer.

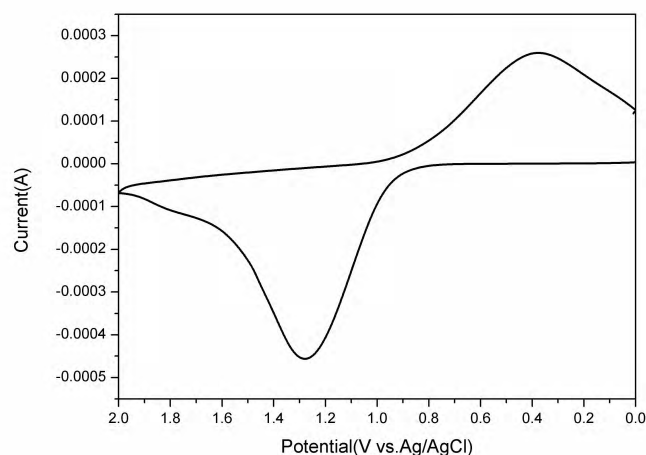


Figure 5. PI-e films on the ITO-coated glass substrate in 0.1M TPAB at a scan rate of mV/s.

Conclusions

A series of novel fluorene-containing polyimides have been prepared from a newly synthesized diamine monomer, 4,4-diamino-9,9-dimethyl-fluorenyl – triphenylamine, with various commercially available tetracarboxylic dianhydrides via a conventional two-step procedure. All the polymers could form morphologically stable and uniform amorphous films. In addition to good solubility, high T_g and thermal stability, the polymers also revealed reversible redox couples and interesting electrochromic characteristics with color changed from yellow neutral state to deep blue oxidized state. Thus, these polyimides may find optoelectronic applications as new electrochromic materials.

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