



Short communication

Bio-based adenine-containing high performance polyimide



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ABSTRACT

Because of the unique conjugated heterocyclic structure and the presence of reactive groups, adenine which can be obtained from biomass may be an ideal bio-based alternative structure of petroleum-based aromatic/heterocyclic structures. In this paper, the adenine was introduced into mainchain of polyimide (API) for the first time to evaluate the feasibility of replacing petroleum-based aromatic/heterocyclic structures by adenine. Systematic studies showed that the API possesses outstanding solubility, thermal and mechanical properties (glass transition temperature (T_g): 363 °C, weight residual of 95%: 513 °C (N₂); 506 °C (Air), tensile strength: 144 MPa). Systematic studies indicated that hydrogen-bonding interaction could be a significant cause of these unique thermal and mechanical properties.

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1. Introduction

The rapid development of the petroleum industry has promoted the development of technology and the progress of the human society. Meanwhile, it also comes with many troubles, such as the greenhouse effect, environmental pollution problems, the diminishing of fossil reserves. In order to solve these problems, scientists and industries have focused on developing renewable bio-based materials which can replace petroleum-based materials. Currently, the researches of bio-based polymers are mainly focused on the traditional aliphatic polymers, such as polylactic acids, cellulose, Lignin, starch, chitosan and furan compounds [1–11].

High performance polymers (HPP) such as wholly aromatic polyamide (aramide) [12], polyimide (PI) [13] and phthalonitriles [14] have received much attention over the past decades because of their unique properties such as superior thermal stability, mechanical properties and chemical resistance, a variety of applications have been found in high-tech fields such as aerospace and microelectronics. Recently, functionality of HPP and their applications are emerging areas in the field of polymer electronic memories, gas separation membranes, electrochromic, polyelectrolyte films for fuel cell, smart materials, etc. [13,15–19] Although big advances have been achieved, combination of good thermal and

mechanical properties and unique functionality for HPP is still a big challenge. One attempted approach to obtain the combined properties is structure modification, such as the introduction of heterocyclic units bearing functional groups [13,15–19].

Adenine, as an amine substituted purine, is known as an important building block of DNA with double helix supramolecular structure, which is constructed with multiple hydrogen bonds. It has attracted many attentions of pharmacologists for its unique bioactivity and molecular tailor ability [20,21]. Many works have shown that adenine can be obtained from biomass [22–27]. Previously, the studies on adenine are mainly concentrated on medicine [28–30]. Recently, owing to the unique aromatic heterocyclic structure, adenine has attracted many researchers to study its application in functional materials, e.g. Andrew J. Steckl et al. reported that adenine can be used as a novel hole-injection layer of OLEDs [31–33]. Because of the unique and stable aromatic heterocyclic structure and flexible molecular tailor ability, adenine is a potential building-block and molecular platform for designing high-performance polymers.

In this communication, adenine was introduced into the backbone of polyimide (a representative of HPP) for the first time. The fundamental thermal, mechanic and electric properties of adenine-containing polyimide (API) were evaluated by TGA, DSC, DMA, etc. Preliminary studies showed that the API possessed excellent combination of properties compared with other analogous polyimides. The studies implied that these outstanding properties were probably closely related to the hydrogen-bonding interaction originated from the unique chemical and supramolecular structure

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of adenine building block. Furthermore, because of stable aromatic heterocyclic structure and the existence of both proton donor (-NH-, =CH-) and proton acceptor (=N-, C=O) hydrogen bonding and functional sites of API, comprehensive research will be further introduced to study its applications in structure and functional materials, such as high performance fiber [34], proton exchange membranes [35], removal of heavy metal ions [36] and flexible supercapacitors [37]. Adenine is a building block from nature and we believe the subsequently systematic study on this system will provide much more insights into the molecular design of high performance polymers, in addition to the view of resources.

2. Experimental details

2.1. Materials

Adenine and isoquinoline were purchased from Chengdu Best Reagent Co., Ltd., 4-Chloronitrobenzene and *m*-Cresol were purchased from Shanghai Kefeng Chemical Reagent Co., Ltd., and *m*-Cresol was purified by distillation under reduced pressure over phosphorus pentoxide. Ethanol and methanol were purchased from Shanghai Fine Chemical Reagent Co., Ltd. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from Zigong Tiansheng New Material Technology Co., Ltd., and it was dried in the vacuum oven at 170 °C for 12 h. Chromatographic grade of tetrahydrofuran (THF) was purchased from Aladdin Industrial Corporation, Dimethyl sulfoxide (DMSO), *N,N*-Dimethylformamide (DMF), *N*-Methyl-2-pyrrolidone (NMP), potassium carbonate, palladium on carbon (Pd/C, 5%), hydrazine hydrate and other chemicals were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. and were all used as received.

2.2. Measurements

Elemental analyses (EA) were performed on an Italy CARLO ERBA 1106 elemental analyzer. ¹H NMR (300 MHz) was measured on a Bruker Avance-300 NMR spectrometer with DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet FTIR-380 Fourier transform infrared spectrometer by KBr pellet. In-situ IR of API film (about 9 μm thick) was recorded with a Nicolet FTIR-380 Fourier transform infrared spectrometer, and the film was placed into a temperature control instrument utilizing a heating cell. Thermal gravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out from 40 °C to 800 °C using a TA instrument Q500 thermogravimetric analyzer in flowing nitrogen and flowing air (60 mL/min) at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) were performed on a TA instrument Q200 differential scanning calorimeter under nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min. Mechanical properties of API films were tested on INSTRON 5567 Universal Strength Tester with a strain rate of 5 mm/min. Measurements were performed at room temperature (about 10 °C) with film specimens (about 34 μm thick, 10 mm wide and 60 mm long) and the fixture span of tests was set as 30 mm. Inherent viscosities (η^*) of the API were measured with an Ubbelohde viscometer at 30 °C in DMAc at a concentration of 0.5 g/dL. Gel permeation chromatography (GPC) analysis was performed in DMF at a flow rate of 0.4 mL/min using a Tosoh HLC-8320GPC (Column: TSK gel Super AWM-H) with Polymethylmethacrylate as standard and DMF as the eluent. Dynamic mechanical analysis (DMA) was recorded on a TA instrument DMA Q800 at a heating rate of 5 °C/min with a load frequency of 1 Hz in air (Specifications of API film: 0.0371 mm thick, 6.0600 mm wide and 14.7528 mm long). X-ray Diffractometer (Philips X'Pert Pro MPD DY129) was used for measuring morphology of PI thin films. Cu Ka ($\lambda = 1.5406$

Å) radiation was used and filtered by monochromator. X-ray generator was run at 40 kV × 40 mA. The density data were measured with an electronic densimeter (Quarrz, AU-120SLM) at 17 °C in water.

2.3. Syntheses of 9, 10-bis(4-aminophenyl) adenine (*p*-APA)

2.3.1. Synthesis of compound 9, 10-bis(4-nitrobenzene) adenine (*p*-NBA)

To a 1000 mL, three-necked flask was added adenine (13.51 g), DMSO (480 mL), toluene (200 mL) and K₂CO₃ (42.00 g). The reaction was heated and refluxed for 4 h. Then steamed out toluene by raising temperature and the 4-Chloronitrobenzene (32.90 g) was added when the reaction system was cooled to 60 °C, and then the temperature of the reaction system was increased to 162 °C and held at this temperature for 6 h. After reaction system was cooled to room temperature, the reaction mixture was poured into 5000 mL deionized water, the solution was filtered and the precipitate was washed three times with 3000 mL deionized water each time. The resulting filter cake was dried at 80 °C for 8 h under vacuum. Then the filter cake was washed four times with 500 mL DMF each time. The insoluble part, namely *p*-NBA, was leached with a small amount (about 20 ml) of alcohol after washed with DMF, and then the compound *p*-NBA was dried at 80 °C for 12 h under vacuum. Yield: 11.10 g, 29.4%. IR (KBr, cm⁻¹): 3341 (N-H stretching), 1576 (NO₂ asymmetric stretching), 1324 (NO₂ symmetric stretching). ¹H NMR (300 MHz, DMSO-*d*₆, δ): 10.88 (s, 1H, N-H), 9.11 (s, 1H, C-H), 8.68 (s, 1H, C-H), 8.50 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.39 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.33 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.25 (d, *J* = 8.7 Hz, 2H, Ar-H). EA: found: C, 54.10; N, 26.63; H, 3.29. Calcd for C₁₇H₁₅N₇: C, 54.12; N, 25.99; H, 2.94%.

2.3.2. Synthesis of compound *p*-APA

To a 250 mL, three-necked flask was added compound *p*-NBA (17.25 g), palladium-charcoal (Pd/C (5%), 1.725 g), ethanol (45.90 mL), and DMAc (as an auxiliary solvent, 69.00 mL). And then the solution of hydrazine hydrate (57.27 g) was added dropwise (3–5 s per drop, as slowly as possible). The reaction mixture was reacted at 80 °C for 4 h after the solution of hydrazine hydrate was completely added. Then the hot reaction mixture was filtered, and the filtrate was washed with 1200 mL deionized water, then the solution of water was filtered again and the precipitation was washed with 1000 mL deionized water for three times. The resulting filter cake was dried at 80 °C for 12 h under vacuum. The crude product (12.8 g) was purified by pouring dry HCl gas into DMF solution (130 mL), producing hydrochloric acid salt precipitate, which was collected by filtration and then neutralized using ammonia water (Redistilled water: 500 mL, ammonia water (25.0%–28.0% v): 30 mL). Yield: 11.50 g, 79.2%. IR (KBr, cm⁻¹): 3413 (N-H stretching), 3312 and 3205 (N-H stretching). Melting points: 254 °C. ¹H NMR (300 MHz, DMSO-*d*₆, δ): 9.44 (s, 1H, N-H), 8.42 (s, 1H, C-H), 8.26 (s, 1H, C-H), 7.43 (dd, *J* = 17.2, 8.7 Hz, 4H, Ar-H), 6.71 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.55 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.39 (s, 2H, N-H), 4.90 (s, 2H, N-H). EA: found: C, 64.94; N, 30.95; H, 4.97. Calcd for C₁₇H₁₅N₇: C, 64.34; N, 30.90; H, 4.76%.

2.4. Synthesis of polyimide (adenine containing polyimide API)

To a solution of 1.0783 g (3.4 mmol) of *p*-APA in 25 mL of *m*-methylphenol, dianhydride 6FDA (1.5096 g, 3.4 mmol) was added in one portion, the reaction solution was stirred at room temperature for 3 h to afford a viscous solution (poly(amic acid), PAA). The PAA was subsequently converted to polyimide (API) via a thermal imidization process by the addition of isoquinoline 10 drops. After heated to reflux (about 202 °C) for 5 h, the solution was cooled to

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