



Development of high dielectric polyimides containing bipyridine units for polymer film capacitor



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ABSTRACT

Polymer dielectrics with high dielectric constant, low dielectric loss, high breakdown strength, and high temperature capability are attractive for applications such as capacitive energy-storage. Commercially available polymer dielectrics such as biaxially oriented polypropylene (BOPP), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), polycarbonate (PC), and poly(vinylidene) fluoride (PVDF) can be just operated below 200 °C. Great effort has been put into exploring high temperature polymer dielectrics to fulfill the demand of high temperature applications, such as the aerospace and military power supply. In this study, a series of polyimides containing bipyridine units with good dielectric performance and high temperature capability were prepared by using a newly synthesized diamine monomer, (5,5'-bis [(4-amino) phenoxy]-2,2'-bipyridine (BPBPA)). These polyimides possessed high dielectric constant of the *as*-synthesized polyimides can be up to 7.2, the dielectric loss was <0.04, and the energy density was up to 2.77 J/cm³. Furthermore, the polyimides exhibited high glass transition temperature (T_g) of 275–320 °C and tensile strengths of 175–221 MPa. These obtained polyimides promise potential applications in high temperature flexible polymer film capacitor operated at high temperature.

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1. Introduction

Dielectric materials with not only high dielectric constant, low dielectric loss, and high breakdown strength, but also excellent mechanical flexibility, high operating temperature and good chemical resistance, are highly desired for advanced electrical applications such as film capacitors, electroactive actuators and gate dielectrics, especially for the high temperature field [1–4]. Polymer dielectrics are the ideal candidates due to their inherent advantages in mechanical flexibility, easy processing, low cost, and high breakdown strength [5–9]. However, most polymers show a low dielectric constant and relative low operating temperature (*i.e.*, low glass transition temperature and/or melt temperature). For example, the commercially available polymers biaxially oriented polypropylene (BOPP), polyester (PET), polycarbonate (PC), polyphenylenesulfide (PPS), polyurea and polyurethane, possess the dielectric constant ranging from 2.2 to 6.7 at 1 kHz, and the maximum operating temperature was limited to 200 °C [10–14]. Especially, poly(vinylidene) fluoride (PVDF) and its random copolymers P(VDF-TrFE) and P(VDF-TrFE-CFE) (TrFE: trifluoroethylene; CFE: chlorofluoroethylene) have super high dielectric constant in the range of 12–60 because of their high dipole density; unfortunately, these ferroelectric polymers exhibit not only the high dielectric constant but also

the high dielectric losses and low glass transition temperature (~40 °C) and melting points (<170 °C) [8,15–17].

Polyimides (PIs) are a class of high performance polymer with excellent mechanical properties, good chemical resistance, superior thermal stability, low dielectric losses and high breakdown strength [18–20]. However, the dielectric constant of PIs typically ranges from 3–5, which limits the application of high dielectric materials [20,21]. Recently, great effort has been put into increasing the dielectric constant of polyimides by rationally designing the chemical structures [22–24]. Rui Ma et al. [22] reported a series of polyimides with high dielectric constants by adjusting the backbone of polyimide with different —NH—, —C(=O)—, and —O— groups. The highest dielectric constant they achieved was up to 7.8 and energy density of ~15 J/cm³; but they also exhibit a low glass transition temperature (T_g < 175 °C). In our previous work, we prepared a novel polyimide containing bipyrimidine units with high dielectric properties, high thermal stability and excellent mechanical properties by using a newly home-synthesized diamine monomer, 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyrimidine. The *as*-synthesized PI showed high dielectric constant of 7.1 (100 Hz), low dielectric loss below 0.04, and glass transition temperature as high as 291 °C [24]. However, the synthesis of the 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyrimidine is complicated and time consuming, which significantly limits the large-scale preparation.

In this work, a new diamine, (5,5'-bis [(4-amino) phenoxy]-2,2'-bipyridine (BPBPA)), which containing bipyridine units was synthesized facilely; and four kinds of polyimides were prepared by using

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this diamine polymerized with four dianhydrides (*i.e.*, PMDA, BPDA, BTDA, and ODPDA). The *as*-synthesized polyimides had excellent dielectric constant of up to 7.2, low dielectric loss (<0.04) and high breakdown strength, as well as high glass transition temperature of 275–320 °C and tensile strengths of 175–221 MPa.

2. Experimental

2.1. Materials

2,2'-bipyridine (99.0%), 4-aminophenol (99.0%), bromine (99.5%), 1,2,4,5-benzenetetracarboxylic anhydride (PMDA, 99%), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 99.0%), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, 99.0%), and 4,4'-oxydiphthalic anhydride (ODPA, 99.0%) were purchased from J&K Chemical Ltd. All other chemicals and solvents were obtained from China National Pharmaceutical Group Corporation. 1-methyl-2-pyrrolidinone (NMP) and *N,N*-diethylacetamide (DMAc) were purified using CaH₂ and then distilled under reduced pressure and then stored in the presence of 4 Å molecular sieves.

2.2. Synthesis of 5,5'-dibromo-2,2'-bipyridine

2,2'-bipyridine (**1**, 4.99 g, 0.032 mol) and bromine (10.24 g, 0.064 mol) were first added in a hydrothermal reaction container and heated to 150 °C and annealed for 15 h. Then, the mixture was cooled and the hard solid was powdered and following treated with Na₂SO₃ solution to remove the unreacted bromine. Finally it was basified with sodium hydroxide and filtered. The white solid product 5,5'-dibromo-2,2'-bipyridine was obtained by the chromatography on silica (CH₂Cl₂). 5,5'-dibromo-2,2'-bipyrimidine, 8.64 g (86%), m.p. 221.6–222.1 °C. ¹H-NMR (400 MHz, CDCl₃, δ): 7.95 (d, 2H), 8.28 (s, 2H), 8.71 (d, 2H); ¹³C-NMR (100 MHz, CDCl₃, δ): 121.47 (C5), 122.25 (C3), 139.64 (C4); 150.28 (C6), 153.64 (C2); IR (KBr): 3049 (C–H, stretching), 1562, 1453, 1356 (Ar, stretching), 636 (C–Br, stretching). Anal. calcd for C₁₀H₆N₂Br₂: C 38.22, H 1.91, N 8.92, Br 50.95; found: C 38.26, H 1.94, N 8.90, Br 50.97.

2.3. Synthesis of 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyridine (BPBPA, **4**)

5,5'-dibromo-2,2'-bipyridin (**2**, 6.28 g, 0.02 mol) and 4-aminophenol (**3**, 5.23 g, 0.048 mol) were dissolved in 100 mL NMP. Anhydrous K₂CO₃ (2.73 g, 0.02 mol) was added to the solution, and the mixture was heated at 175 °C for 12 h. After cooling to room temperature, the mixture was poured into 5 wt% sodium hydroxide solution, and stirred for 1 h. The solution was filtered, and the filter cake was washed repeatedly with distilled water. The white crystals of 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyrimidine (BPBPA, **4**) was recrystallized from H₂O/ethanol. 6.44 g (87%), m.p. 204.0–204.6 °C. ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 5.06 (s, 4H), 6.61 (d, 4H), 6.85 (d, 4H), 7.29 (d, 2H), 8.21 (s, 2H), 8.29 (d, 2H). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ): 114.89 (C3'), 120.82 (C2'), 123.92 (C3, C4), 138.43 (C6), 144.75 (C4'), 146.04 (C1'), 148.84 (C2), 155.36 (C5); FTIR (KBr): 3396, 3302 (N–H, stretching), 1633, 1558, 1503, 1455 (Ar, stretching). Anal. calcd for C₂₂H₁₈N₄O₂: C 71.35, H 4.86, N 15.14, O 8.65; found: C 71.31, H 4.89, N 15.11, O 8.70.

2.4. Preparation of polyimides containing bipyridine units

Four kinds of polyimides containing bipyridine units (PI-**7a**, PI-**7b**, PI-**7c**, PI-**7d**) were prepared from the diamine (BPBPA, **4**) and aromatic dianhydrides (BPDA, PMDA, BTDA, OPDA) via a conventional two-step thermal imidization method. The synthesis of PI-**7a** is used as an example to illustrate the general synthetic route used to produce the polyimides. BPBPA (3.70 g, 0.01 mol) and BPDA (2.94 g, 0.01 mol) were added to 63.7 g of DMAc and the mixture was reacted for 12 h at

room temperature. The resulting polyamic acid (PAA, **6a**) solution with 9.44 wt% was diluted into 8 wt% with DMAc and casted into PAA films. The PAA films was imidized into PI (**7a**) in a high temperature furnace according to the following protocol: (1) heating to 160 °C at a rate of 10 °C/min and annealing at 160 °C for 2 h to remove the residual solvent, (2) heating at a rate of 10 °C/min and annealing at 250 °C for 15 min, (3) heating at a rate of 5 °C/min and annealing at 350 °C for 2 h to complete the imidization process.

2.5. Measurements

Proton and carbon (¹H- and ¹³C-NMR) nuclear magnetic resonance spectra were measured at 400 MHz and 10⁵ Hz, respectively on a Bruker Avance-400 spectrometers. The intrinsic viscosities were measured (Ubbelohde viscometer) in DMAc at 25 °C. FTIR spectra were obtained with Perkin-Elmer SP one FTIR. Elemental analyses were determined by a Perkin-Elmer model 2400 CHN analyses. Thermal gravimetric analysis (TGA) was performed with 6–8 mg film samples with a Perkin-Elmer Pyris 1 TGA in nitrogen at a heating rate of 10 °C/min. The glass transition temperature was determined by a Perkin-Elmer Diamond dynamic thermomechanical analysis (DMA) instrument. During the test, a load of 10 g (stress, 0.125 MPa) and a heating rate of 10 °C/min in air were applied. Tensile tests of polymer films were performed using SANS CMT8012 (Shenzhen, China) instrument at 5 mm/min on strips (0.5 cm wide, 2 cm long, and about 0.05 mm thick). The dielectric properties were measured on an Agilent E4980 LCR electrometer at different frequencies and conductive tapes were served as electrodes to clamp our samples with 10 mm in diameter and thickness of about 20 μm. Dielectric breakdown strength was tested using an electric breakdown strength test machine (DDJ-20 kV, China) under DC high-voltage power with 200 × 200 mm and thickness of below 3 mm. Scanning electron microscope (SEM, TESCAN vega3) were employed to obtain the films thickness.

3. Results and discussion

3.1. Synthesis of 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyridine (BPBPA)

Scheme 1 shows the preparation of BPBPA. The synthesis process includes two steps. 2,2'-bipyridine (**1**) is brominated using liquid Br₂ to give 5,5'-dibromo-2,2'-bipyridine (**2**) under high temperature and pressure. In the second step, the 5,5'-dibromo-2,2'-bipyridine (**2**) was reacted with 4-aminophenol (**3**) in NMP to produce the 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyridine (**4**). All the molecules were characterized by the elemental analysis, FTIR, ¹H-NMR, and ¹³CNMR spectroscopic techniques and complete data is presented in the experimental section. The ¹H- and ¹³C-NMR spectra of important compounds (**2**) and (**4**) are given in the supporting information (Figs. S1–S4). Detailed assignments of protons and carbons are given in the figures, confirming the molecular structure.

3.2. Polymerization

Scheme 2 shows the synthesis of PIs. The novel PIs (**7**) were prepared by polymerizing the BPBPA (**4**) with aromatic dianhydrides (**5**) via a two-step method. The polymerization was reacted in the solvent DMAc for 12 h at room temperature to yield the PI precursors solutions, polyamic acids (PAA, **6**); and the obtained PAA solutions were used to prepare PI thin films by solution casting and heating process (thermal imidization). The intrinsic viscosity of the precursors (PAA, **6**) was 2.0–2.5 dL/g (2.5, 2.2, 2.0, and 2.3, respectively for PAA-6a, PAA-6b, PAA-6c, and PAA-6d). The high intrinsic viscosity corresponds to a high molecular weight, which is helpful for making high performance PI films with good mechanical properties. Fig. 1 shows the FT-IR spectra of PAAs and PIs. The characteristic peaks of PAAs (Fig. 1a) appears a big absorption bands from 2500 to 3600 cm⁻¹ (corresponding to the O–H

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