



Colorless polyimides derived from isomeric dicyclohexyl-tetracarboxylic dianhydrides for optoelectronic applications

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ARTICLE INFO

Article history:

Received 18 September 2017

Received in revised form

3 November 2017

Accepted 19 November 2017

Available online 24 November 2017

Keywords:

Isomeric dicyclohexyl-tetracarboxylic dianhydrides

Alicyclic polyimides

Isomer effect

ABSTRACT

Two isomers of conventional *cis*-dicyclohexyl-3,3',4,4'-tetracarboxylic dianhydride (4,4'-HBPDA), i.e. dicyclohexyl-2,3',3,4'-tetracarboxylic dianhydride (3,4'-HBPDA) and dicyclohexyl-2,2',3,3'-tetracarboxylic dianhydride (3,3'-HBPDA), were prepared through a four-step procedure. The data from single crystal X-ray diffraction revealed that 3,3'-HBPDA possessed higher structural rigidity/linearity than 4,4'-HBPDA. The one-step polycondensation of isomeric HBPDAs with commercial diamines enabled the synthesis of alicyclic polyimides. The isomer effects of the dianhydrides on the properties of resulting polyimides were studied in detail. For certain diamines, 3,3'-HBPDA-derived polyimides possessed higher glass transition temperatures (T_g) and better dimensional stability compared with those from 4,4'-HBPDA and 3,4'-HBPDA. These phenomena could be attributed to the higher structural rigidity/linearity of 3,3'-dicyclohexyl-tetracarboxydiimide, and restricted rotation of 3-substituted cyclohexylimide. Owing to the asymmetric structures and suppressed rotation of 3-substituted cyclohexylimides, 3,4'-HBPDA-based polymers exhibited higher T_g , improved dimensional stability, and enhanced solubility compared with 4,4'-HBPDA-based ones. Furthermore, all the isomeric HBPDA-derived polyimides were essentially colorless with excellent optical transparency in the UV–Visible region. The excellent overall properties of polyimides from 3,3'-HBPDA and 3,4'-HBPDA made them promising candidate materials for optoelectronic applications.

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1. Introduction

Heat-resistant optically transparent polymers are extensively investigated for the applications in electronic and optoelectronic fields due to their several distinct advantages over inorganic glass, such as lightness, flexibility, and good processability. These polymers are expected to offer several critical features including high heat resistance, excellent optical transparency, essential colorlessness, good dimensional stability, outstanding mechanical properties, and solution processability [1–4]. Due to their low T_g , traditional engineering plastics, such as polyesters, polycarbonate, and polysulfones, do not fulfill the requirements for high temperature manufacturing in electronics industry, where long-term service temperature of 270 °C (for lead-free solder reflowing) and short-term service temperature of 400 °C (for silicon-based TFT

fabrication) are required. Hence, it is still challenging to develop polymers with T_g of higher than 300 °C without sacrificing their excellent optical transparency [5,6].

Aromatic polyimides have been widely used for various applications due to their extremely high T_g , outstanding thermal stability, favorable chemical resistance, and good dielectric and mechanical properties [7–14]. However, the intra- and intermolecular charge transfer (CT) interactions between the electron-withdrawing dianhydride residues and electron-donating diamine residues yield their yellow to deep brown colors and strong absorption in the UV–visible region [15–20]. Consequently, usage of aromatic polyimides as optical and optoelectronic materials is hampered by their intrinsic discoloration. To overcome these limitations, tremendous research efforts have been devoted to improving polyimides' optical transparency through rational structural modification [21–28]. One efficient approach to colorless polyimides is to incorporate alicyclic moieties, which could interrupt the electron conjugation, loosen chain packing, and reduce or even eliminate the formation of CT complexes [29–32]. Alicyclic

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polyimides also exhibit enhanced solubility in organic solvents and low dielectric constants when compared with aromatic polyimides. The latter can minimize crosstalk and maximize signal propagation in electronics packaging [33–35]. Matsumoto [36] prepared polyalicyclic dianhydrides through Diels-Alder reactions and subsequent palladium-catalyzed methoxycarbonylation of double bonds. The polycondensation between these dianhydrides and commercial diamines produced polyimides with high T_g and thermo-oxidative stability, excellent optical transparency, and low refractive indices. These features could be explained by the rigid alicyclic architectures, and the presence of multi-bonds. Nonetheless, the mechanical properties and dimensional stability of these polyimides were inferior to those of aromatic polyimides. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA) and its methyl-substituted analogues are ideal monomers to produce colorless polyimides because of their high reactivity towards diamines, and high structural linearity/rigidity [37]. Polyimides derived from rigid diamines and CBDA exhibited combined properties of low coefficients of thermal expansion (CTE) and high T_g [38–42]. However, their film ductility and solubility in organic solvents are still inadequate for practical applications [43].

Polyimides from isomeric dianhydrides have attracted considerable attentions because of their significant advantages over traditional polyimides, including higher T_g , and enhanced solubility/processability [44]. The structure-property relationship of isomeric aromatic polyimides was well established by Yokota et al. [45–47] and our group [48–50]. However, only a few reports dealing with the isomer effects of alicyclic dianhydrides on polyimides properties are so far published. Hasegawa et al. [51–55] reported alicyclic polyimides from three isomers of hydrogenated pyromellitic dianhydride: 1S,2R,4S,5R-cyclohexanetetracarboxylic dianhydride (HPMDA), 1S,2S,4R,5R-cyclohexanetetracarboxylic dianhydride (H'PMDA), and 1R,2S,4S,5R-cyclohexanetetracarboxylic dianhydride (H''PMDA). They found that the different ring strains and steric structures of the isomers imparted varied polymerizability towards diamines, following the order of HPMDA << H'PMDA < H''PMDA. For given diamines, H'PMDA-derived polymers exhibited the lowest CTE among the counterparts from hydrogenated pyromellitic dianhydrides. Shiotani and co-workers [56] reported the synthesis and characterization of polyimides derived from the isomers of hydrogenated 4,4'-biphenyltetracarboxylic dianhydride (4,4'-BPDA): 1R,1'S,3R,3'S,4R,4'S-dicyclohexyl-3,3',4,4'-tetracarboxylic dianhydride (*trans*-4,4'-HBPDA) and 1R,1'S,3R,3'S,4S,4'R-dicyclohexyl-3,3',4,4'-tetracarboxylic dianhydride (*cis*-4,4'-HBPDA). Polyimides from *trans*-4,4'-HBPDA had higher T_g , tensile strength and modulus but lower elongation at break when compared with those based on *cis*-4,4'-HBPDA.

In this study, we report the synthesis and characterization of alicyclic polyimides from *cis*-dicyclohexyl-2,2',3,3'-tetracarboxylic dianhydride (3,3'-HBPDA) and dicyclohexyl-2,3',3,4'-tetracarboxylic dianhydride (3,4'-HBPDA), the two isomers of 4,4'-HBPDA. These polyimides were characterized according to their solubility, and thermal, mechanical, and optical properties, and the isomer effects of dianhydride monomers on the properties of the resulting polyimides were elucidated.

2. Experimental

2.1. Materials

4,4'-Oxydianiline (ODA), *p*-phenylenediamine (*p*-PDA), 1,4-bis(4-aminophenoxy)benzene (APB), and 4,4'-bis(4-aminophenoxy)biphenyl (BAPB) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China), and were

purified by sublimation under vacuum prior to use. 4,4'-Methylene bis(cyclohexylamine) (MBCHA, a mixture of *cis/trans* isomers, 97%) and boron trifluoride diethyl etherate were obtained from Xiya-Reagent (Chengdu, China). MBCHA was purified by distillation under vacuum. Rhodium on carbon (5 wt% loading) and *trans*-1,4-Cyclohexanediamine (*t*-CHDA) were purchased from Beijing Inno-Chem Science & Technology Co., Ltd (Beijing, China). *cis*-4,4'-HBPDA was provided by Rongcheng K&S Chemical Co., Ltd (Weihai, China), and its single crystal was grown from its acetic anhydride solution by slow evaporation at room temperature. All the other chemicals were purchased from JK Scientifics and used without further purification. 2,3',3,4'-Biphenyltetracarboxylic dianhydride (3,4'-BPDA) and tetramethyl 2,2',3,3'-biphenyltetracarboxylate (2,2',3,3'-BPTME) were synthesized according to literature procedures [44].

2.2. Monomer synthesis

2.2.1. Tetramethyl 2,3',3,4'-biphenyltetracarboxylate (2,3',3,4'-BPTME)

3,4'-BPDA (100.00 g, 0.340 mol), methanol (350 mL), and boron trifluoride diethyl etherate (80 mL) were placed into a 1 L three-necked flask under nitrogen atmosphere. The reaction was refluxed at 80 °C for 7 h. Then excess methanol and boron trifluoride diethyl etherate were removed by rotatory evaporation. The mixture was dissolved in ethanol (300 mL), and then poured into ice water. The resulting precipitate was collected by filtration, and recrystallized from ethanol to afford 2,3',3,4'-BPTME (120.00 g, Yield: 91%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 4.0 Hz, 1H), 7.73 (m, 2H), 7.67 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 3.93–3.74 (m, 9H), 3.63 (s, 3H).

2.2.2. Tetramethyl dicyclohexyl-2,3',3,4'-tetracarboxylate (2,3',3,4'-HBPTME)

2,3',3,4'-BPTME (5.00 g), tetrahydrofuran (THF, 40 mL), and rhodium on carbon (5 wt% loading, 0.5 g) were placed into a 250 mL autoclave. Hydrogenation was performed at 100 °C with hydrogen pressure of 4 MPa. After 8 h, the mixture was filtrated off to remove the catalyst, and THF was removed by rotatory evaporation to yield 2,3',3,4'-HBPTME as viscous liquid. The crude product was directly used for hydrolysis without further purification. ¹H NMR (400 MHz, CDCl₃): δ 3.72–3.59 (m, 12H), 3.36–3.18 (m, 2H), 2.57–2.37 (m, 2H), 2.36–2.13 (m, 2H), 1.97 (m, 1H), 1.93–1.88 (m, 1H), 1.88–1.62 (m, 3H), 1.58–1.37 (m, 3H), 1.37–1.13 (m, 3H), 0.89 (dd, *J* = 8.8, 2.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 173.92, 173.67, 173.29, 172.74, 51.31, 51.20, 50.78, 45.67, 45.29, 43.19, 42.75, 40.90, 40.84, 39.15, 39.04, 28.07, 27.68, 26.03, 25.95, 25.14, 23.62, 23.49.

2.2.3. Dicyclohexyl-2,3',3,4'-tetracarboxylic acid (2,3',3,4'-HBPTA)

2,3',3,4'-HBPTME (5.00 g) was dissolved in methanol (25 mL), and sodium hydroxide aqueous solution (20 wt%, 40.5 g) was added in one pot. After the solution became clear, methanol was removed by distillation. The reaction was refluxing with stirring at 100 °C for 28 h. Upon cooling to room temperature, the solution was neutralized using concentrated HCl (30 g). The solution was then extracted with diethyl ether (100 mL X 3 times). The organic layers were combined, washed with DI water, and dried over magnesium sulfate. Diethyl ether was depleted by rotatory evaporation to afford 2,3',3,4'-HBPTA as a white solid (3.92 g, 89%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.06 (s, 4H), 3.18–2.94 (m, 2H), 2.46–2.20 (m, 2H), 2.07 (m, 1H), 1.97–1.81 (m, 1H), 1.83–1.40 (m, 6H), 1.40–1.13 (m, 5H), 0.98–0.54 (m, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 175.51, 175.40, 175.15, 174.51, 45.37, 43.07, 42.76, 41.04, 28.67, 28.54, 28.26, 26.64, 26.49, 25.41, 24.02, 23.68.

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