Chinese Chemical Letters 25 (2014) 1367–1370

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Synthesis and thermal polymerization of perylene bisimide containing benzocyclobutene groups

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ARTICLE INFO

Article history:
Received 14 January 2014
Received in revised form 31 March 2014
Accepted 10 April 2014
Available online 30 April 2014

Keywords:
Perylene bisimide
Benzocyclobutene
Thermopolymerization
Optical properties

ABSTRACT

Fourfold benzocyclobutene-functionalized perylene bisimide (PBI 4) has been synthesized and its structure was characterized by FTIR, MS and NMR. PBI 4 can react either with itself, or the appropriate dienophiles to form the corresponding products under appropriate temperature. The polymer film obtained from the reaction of PBI 4 with methyl vinyl silicone rubber possessed excellent film forming properties including flatness. The optical properties of PBI 4 and polymer film obtained from the reaction of PBI 4 and methyl vinyl silicone rubber have been determined by UV/vis and fluorescence spectroscopy.

1. Introduction

Perylene bisimides (PBIs) have attracted great interest due to their intense luminescence, high chemical stability and thermal stability [1–4]. Consequently, more and more interesting investigations have been focused on the modification of perylene bisimide structures through high-yield synthetic routes to improve the chemical and physical properties [5–11]. Although considerable research has been conducted on the systems containing PBIs [12–18], studies on the benzocyclobutene–perylene system have rarely been reported.

Benzocyclobutene (BCB) is a reactive intermediate which can react either with itself, or the appropriate dienophiles to obtain the corresponding Diels–Alder products at appropriate temperatures [19,20]. When heated to approximately 200 °C, the cyclobutene ring of BCB opens and forms a highly reactive *o*-quinodimethane intermediate. If a dienophile is present, the *o*-quinodimethane intermediate can react to form stable Diels–Alder adducts. On the other hand, the intermediate can also form an unstable spirodimer which rearranges to a polymeric material. The BCB group can also be incorporated into polymers through other functional groups to provide reactive sites [21].

The preparation of most functional materials is based on the simple mixing of the required functional components [22,23]. In this letter, we synthesize the molecule which contains four benzocyclobutene units tethered to a perylene bisimide dye and the result demonstrate that the benzocyclobutene units can undergo Diels–Alder polymerization and cross-linking reactions by thermal isomerization to form a polymeric network. This approach seems to be quite promising as it allows incorporation of two classes of compounds that possess the thermal polymerization properties of benzocyclobutene [24,25] and optical properties of perylene bisimide [26,27] within a single, easily accessible material.

2. Experimental

The 1,6,7,12-tetrabromoperylene-3,4:9,10-tetracarboxylic acid bisanhydride (PBA 2) and *N*,*N*′-didodecyl-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisimide (PBI 3) were synthesized according to the literature [7].

Preparation of *N*,*N*′-didodecyl-1,6,7,12-tetra(4-benzocyclobutenyloxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (PBI 4): PBI 3 (0.32 g, 0.3 mmol), 4-benzocyclobutenol (0.36 g, 3 mmol) and potassium carbonate (0.4 g, 3 mmol) were stirred in 40 mL *N*-methyl-2-pyrrolidone under N_2 at 90 °C for 72 h. After being cooled to room temperature, 10% hydrochloric acid (100 mL) was added, and the precipitate was collected, washed with water and methanol. The crude product was purified by silica gel column

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http://dx.doi.org/10.1016/j.cclet.2014.04.022
1001-8417/

chromatography (petroleum ether:dichloromethane = 2:1) to yield PBI 4 as a red-brown solid (0.23 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.12 (s, 4H), 6.95 (d, 4H, J = 7.6 Hz), 6.79 (d, 4H, J = 7.4 Hz), 6.68 (s, 4H), 4.09 (s, 4H), 3.11 (d, 16H, J = 9.9 Hz), 1.65 (s, 4H), 1.24 (m, 36H), 0.86 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 163.46, 156.57, 154.49, 146.89, 141.82, 132.77, 124.00, 122.41, 120.04, 119.55, 119.35, 119.11, 115.51, 40.62, 31.89, 29.70, 29.59, 29.51, 29.31, 29.05, 28.95, 28.09, 27.11, 22.66, 14.09; MS (FAB$^+$) (m/z): calcd. for $C_{80}H_{82}N_2O_8$: 1198.6071; found: 1198.6101.

3. Results and discussion

The drawback of perylene bisimides is the inherent low solubility, so the utilization is hindered. Driven by the demands in applications, the structure of perylene bisimides has been modified by introducing substituent groups either to the imide nitrogen atoms, or at the bay positions (*i.e.*, 1,6,7,12 position) [8,28–30]. A dodecyl group is appended at the terminal imide, primarily to enhance solubility. Benzocyclobutenyloxy groups are introduced in the bay region, and, as a result, not only the solubility and optical properties are influenced, but also allows the new product to possess thermal polymerization properties. These substitutions yield the desired molecule *N*,*N*′-didodecyl-1,6,7,12-tetra(4-benzocyclobutenyloxy)perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI 4) (Scheme 1). The solubility of PBI 4 was determined by the dissolution of 10 mg of solid PBI in 1 mL of organic solvent at room temperature. PBI 4 is highly soluble in conventional solvents, such as toluene, chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF), and partially soluble in some organic solvents, such as *N*-methyl-2-pyrrolidone (NMP), acetone and dimethylformamide (DMF). Due to the good solubility of PBI 4, purification and full characterization are easy to perform.

It is known that benzocyclobutene can react either with itself, or the appropriate dienophiles to produce the corresponding products by opening the cyclobutene ring under appropriate temperatures, so the thermal properties of PBI 4 were investigated by thermogravimetric analysis and differential scanning calorimetry. Based on Fig. 1, PBI 4 possesses excellent thermal stability with the initial decomposition temperature of about 344 °C. Meanwhile, at over 800 °C, the char yield is still 30%. The DSC spectrum of PBI 4 is shown in Fig. 2. The initial ring opening

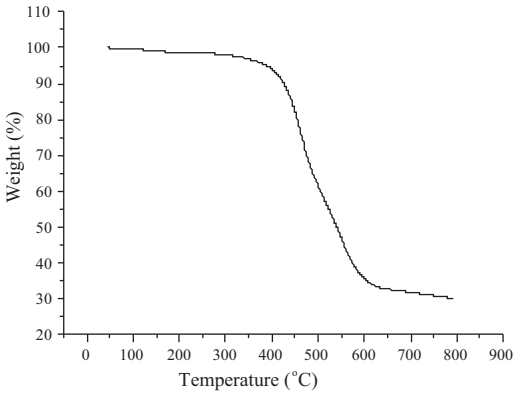


Fig. 1. TGA curve of PBI 4.

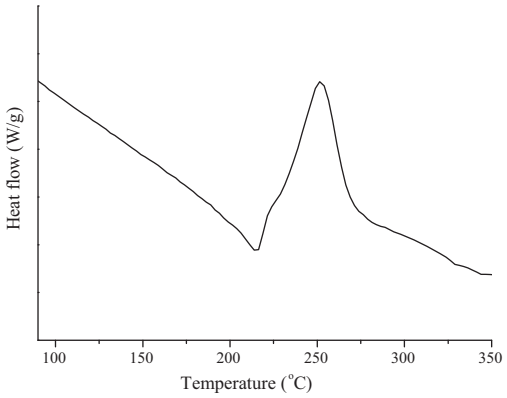
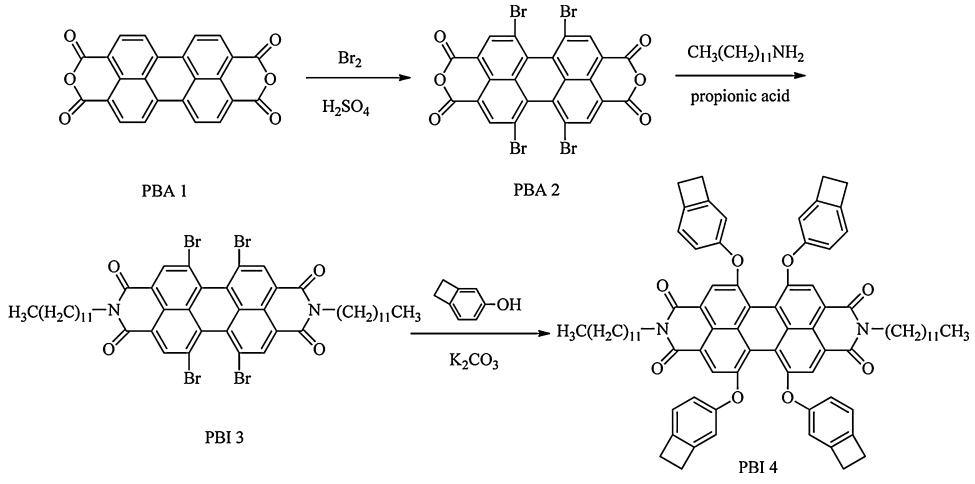


Fig. 2. DSC analysis of PBI 4.

temperature occurs at about 228 °C, and the maximum ring opening temperature of cyclobutene peaks at about 250 °C.

PBI 4 can also react with itself to form a polymeric network under appropriate temperature. Polymer resin (PBI 4) was obtained in a polymerization tube, which was sealed under N_2 and heated at 250 °C for 6 h after three freeze–pump–thaw cycles. The IR spectra are depicted in Fig. 3. The peak at 1465 cm^{-1} is assigned to the vibrations of –CH_2– of the alicyclic moiety. When heated to around 250 °C, the cyclobutene ring of PBI 4 opens and forms a stable polymer resin (the peak at 1492 cm^{-1}) with itself. At



Scheme 1. The route for preparation of benzocyclobutene-functionalized perylene bisimide.