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Synthesis and Properties of Benzocyclobutene-Functionalized Perylene Bisimide

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Benzocyclobutene-functionalized perylene bisimide (PBI 4) has been synthesized *via* Suzuki coupling reaction and its structure was characterized by FTIR, MS and NMR. The thermal and optical properties have been determined by thermogravimetric analyses, differential scanning calorimetry, UV/VIS and fluorescence spectroscopy. The results showed that PBI 4 has thermopolymerization property, which can react either with itself or the appropriate dienophiles to form the corresponding polymers under appropriate temperature. The polymer resin possessed good film planarization in the white-light interferometry photo and the process of oligomer curing on a wafer was no fusion and flow. These results indicated that PBI 4 is a promising film material.

Key Words: Perylene bisimide, Benzocyclobutene, Synthesis, Thermopolymerization.

INTRODUCTION

Perylene bisimides (PBIs) have received considerable attention owing to their favorable properties such as light resistance, intense photoluminescence and outstanding *n*-type semiconductive properties[1], so more and more interesting investigation has been focused on the systems containing perylene bisimides[2-13]. However, few papers are published on the benzocyclobutene-perylene system. Benzocyclobutene (BCB) is a reactive intermediate which can react either with itself or the appropriate dienophiles to give the corresponding Diels-Alder products under appropriate temperature[14,15]. When heated to *ca.* 200 °C (Fig. 1), benzocyclobutene (**1**) opens the cyclobutene ring and forms a highly reactive *o*-quinodimethane intermediate **2**. If dienophile is present, this intermediate can react to form stable Diels-Alder adducts **3**. On the other hand, intermediate **2** can also form an unstable spirodimer **4** which rearranges to polymer[16].

In this paper, we designed and synthesized benzocyclobutene-functionalized perylene bisimide(N,N'-didocananyl-1,6,7,12-tetra(4-benzocyclobutenyl)perylene-3,4,9,10-tetracarboxylic acid bisimide) (**Scheme-I**). This approach is quite promising as it allows incorporation of those two classes of compounds that possess the thermal polymerization property of benzocyclobutene and optical properties of perylene bisimide within a single easily accessible material.

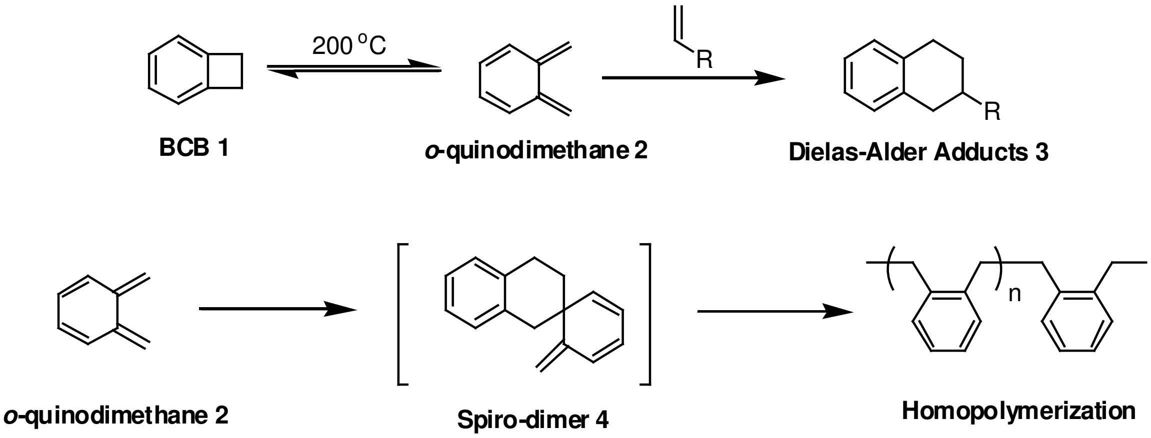
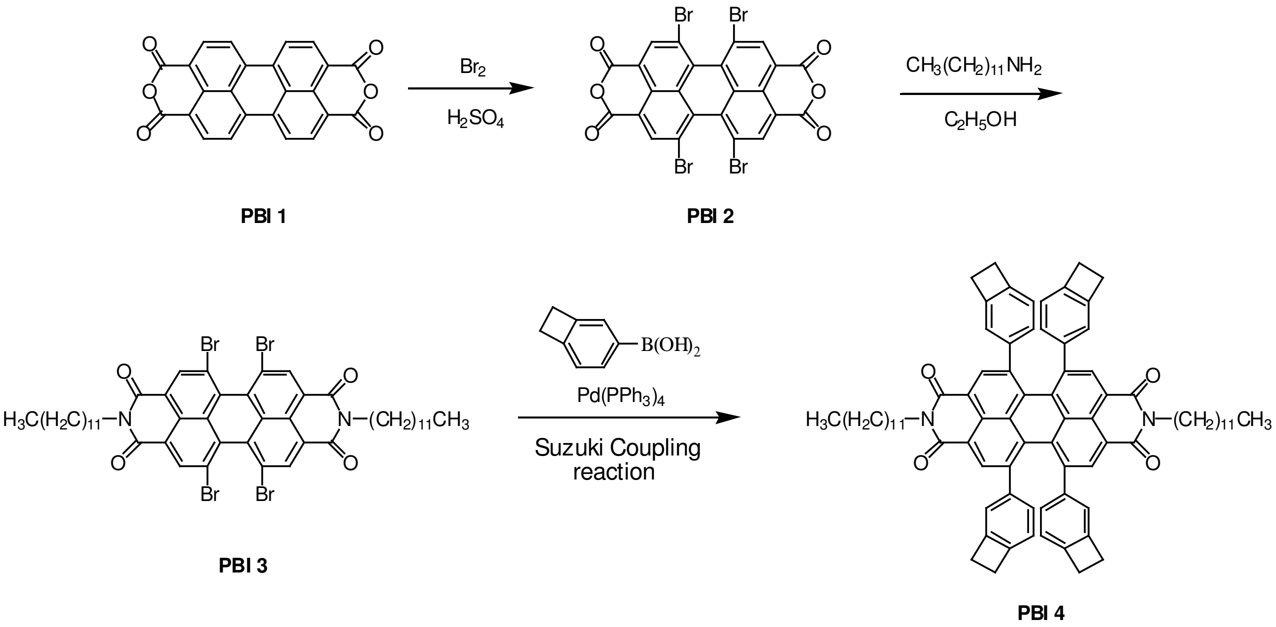


Fig. 1. Reactions of benzocyclobutene



Scheme-I: Route for preparation of PBI 4

EXPERIMENTAL

The chemicals and reagents, unless otherwise specified, were purchased from Aldrich, Acros and TCI Chemical Co. and used as received. All the solvents were further purified before use. ^{1}H and ^{13}C NMR spectra were recorded on Brucker NMR spectrometers in CDCl$_3$ and chemical shifts were obtained relative to tetramethylsilane. Mass spectra were recorded on VG Autospec 3000 for ESI MS. Fourier transform infrared (FTIR-on line) spectra were recorded on NICOLET-6700 with a liquid film method at a heating rate of 20 ºC/min from 20-250 ºC and keeping 250 ºC for 0.5 h.

General procedure: PBI 2 and PBI 3 were synthesized according to the literature[17].

N,N'-Didocananyl-1,6,7,12-tetra(4-benzocyclobutenyl) perylene-3,4,9,10-tetracarboxylic acid bisimide (PBI 4): PBI 3 (320 mg, 0.3 mmol, 1 equiv.), phenylboronic acid (450 mg, 3 mmol, 10 equiv.), cesium fluoride (460 mg, 3 mmol, 10 equiv.), silver(I) oxide (350 mg, 1.5 mmol, 5 equiv.), *tetrakis*(triphenylphosphine)palladium (52 mg, 0.045 mmol, 15 % equiv.) was added with a gentle flow of nitrogen and DME (15 mL) were added in flask. After three freeze-pump-thaw cycles, the reaction mixture was stirred at 80 ºC for 24 h with vigorous stirring. After being cooled to room temperature, the crude product was purified by silica gel column chromatography (dichloromethane/petroleum ether = 2:1) to obtain blue-purple solid (230 mg, 45 %). ^{1}H NMR (600 MHz, CDCl$_3$, 25 ºC, TMS): δ: 8.25 (s, 4H), 6.68 (d, 4H), 6.54 (s, 4H), 6.39 (s, 4H), 4.19 (m, 4H), 3.01 (d, 16H), 1.85 (s, 4H), 1.44 (m, 4H), 1.38 (m, 4H), 1.23 (m, 28H), 0.88 (t, 6H); ^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC, TMS): δ: 163.83, 145.15, 143.11, 139.36, 133.76, 132.02, 131.39, 128.32, 125.69, 121.99, 40.61, 33.72, 31.92, 30.16, 29.70, 29.64, 29.59, 29.46, 29.42, 29.35, 28.26, 27.22, 26.73, 22.69, 14.10 ppm; MS (FAB$^+$): m/z: calcd. (%) for $C_{80}H_{82}N_2O_4$ 1135.6352; found (%): 1135.6362.

RESULTS AND DISCUSSION

Synthesis and solubility: The drawback of perylene bisimides is the inherent low solubility, which prevented the utilization. Driven by their use in the 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 positon). A docananyl group is appended at the terminal imide, primarily to enhance solubility. Benzocyclobutenyl groups are introduced to the bay region, which not only influences solubility and optical property, but also leads the new product to possess thermal polymerization property. These substitutions offered the desired molecule N,N'-didocananyl-1,6,7,12-tetra(4-benzocyclo butenyl)perylene-3,4,9,10-tetracarboxylic acid bisimide (PBI 4) (Fig. 2). The solubility of PBI 4 was determined by the dissolution of 10 mg of solid PBI 4 in 1 mL of organic solvent at room temperature. The results showed that PBI 4 was highly soluble in conventional solvents, such as toluene, chloroform, dichloromethane and tetrahydrofuran. Because PBI 4 exhibits good solubility in organic solvents, purification and full characterizations are easy to perform.

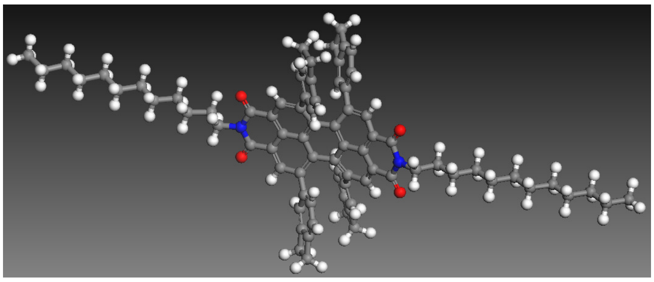


Fig. 2. Chemical structure and three-dimensional stereostructure of PBI 4

Optical properties: Fig. 3 shows the UV-VIS absorption spectra of compounds PBI 3 and PBI 4 in CHCl$_3$. PBI 3 shows the maximum absorption at 531 and 440 nm as well as the

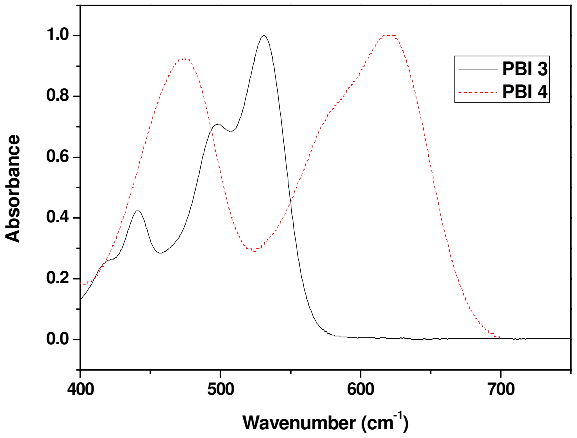


Fig. 3. UV/VIS absorption of PBI 3 and PBI 4

shoulder absorption at 496 nm. In case of PBI 4, the maximum absorptions appear at 624, 579 (shoulder absorption) and 474 nm, respectively. Compared with PBI 3, the absorption bands of PBI 4 undergo a significant bathochromic shift along with considerable band broadening, especially for the longest absorptions. The result could be attributed to the steric twisting of the perylene core.

Fig. 4 shows the normalized emission spectra of PBI 3 and PBI 4 in $CHCl_3$ with the maximum emission located at 564 and 518 nm. In comparison to PBI 3, displacement of bromines by benzocyclobutene groups causes the blue shift of the emission band. The result could be attributed to the conjugate effect and the stack of PBI.

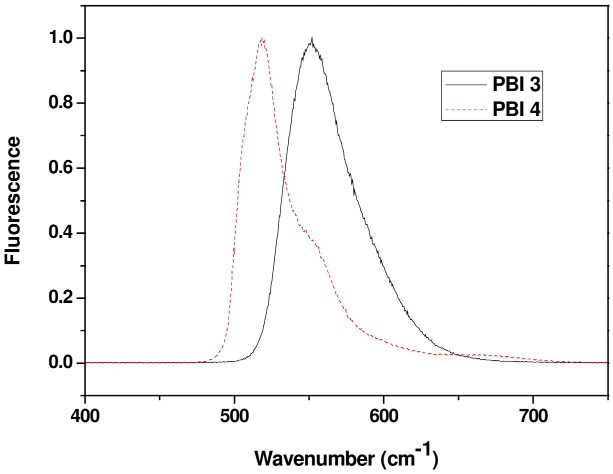


Fig. 4. Fluorescence emission spectra of PBI 3 and PBI 4

Thermal properties of PBI 4: It is known that benzocyclobutene can open the cyclobutene ring to react either with itself or the appropriate dienophiles to produce the corresponding products under appropriate temperature, so the thermal properties of PBI 4 were investigated by thermogravimetric analyses and the differential scanning calorimetry. It is found from Fig. 5 that PBI 4 possesses excellent thermal stability. The initial decomposition temperature is about 389 °C, meanwhile, over 800 °C there are still 30 %. The DSC spectrum of PBI 4 is shown in Fig. 6. The initial ring opening temperature occurs at about 228 °C and the maximum ring opening temperature of cyclobutene peaks is about 251 °C.

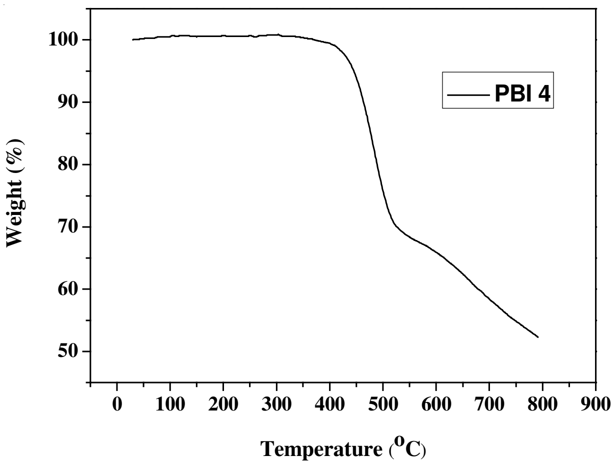


Fig. 5. Thermogravimetric analysis of PBI 4

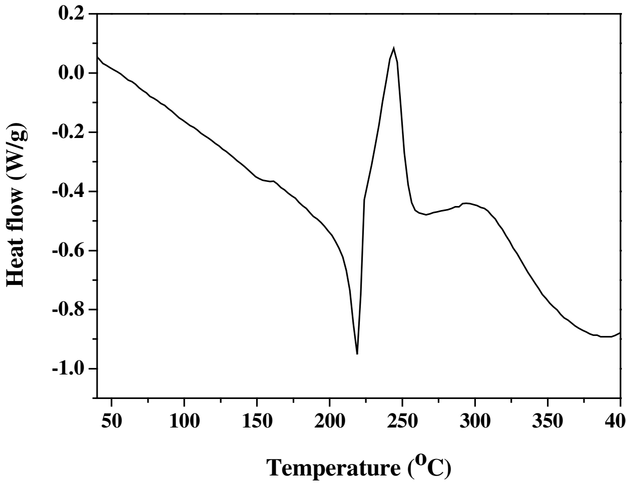


Fig. 6. DSC analysis of PBI 4

Thermopolymerization property of PBI 4: When heated to around 250 °C, PBI 4 opens the cyclobutene ring and forms stable polymer resin. The IR spectra of PBI 4 and polymer resin from PBI 4 are depicted in Fig. 7. The peak at 1467 cm^{-1} is assigned to the vibration of $-CH_2-$ from alicyclic moiety, however, the peak of polymer resin is at 1493 cm^{-1}. FTIR-on line analysis indicated that the peak areas of 1467 and 1493 cm^{-1} were changing under the condition from 20-250 °C at a heating rate of 20 °C/min and keeping at 250 °C for 0.5 h. With the temperature increasing, the intensity of the peak at 1467 cm^{-1} reduces and the peak at 1493 cm^{-1} appears and increases. At the same time we can find that the peak at 1467 cm^{-1} did not disappear completely, which indicated that under the condition of FTIR-on line, in the polymer there were still traces or a little amount of four member ring.

Preparation of polymer film: PBI 4 was heated in 1,3,5-trimethylbenzene to form oligomer at 180 °C for *ca.* 72 h. Alternatively, the oligomer was prepared to be the film on the glass through spin-coating technique. Then the oligomer film was placed in polymerization tube and heated to be polymer film at 250 °C for 6 h. The film was measured by white-light interferometer and the array size is 736 μm × 480 μm. As shown in Fig. 8, Ra is 11.56 nm, Rq is 14.52 nm and Rt is 195.80 nm, separately. During the heating polymerization process, we did not find the fusing or flowing phenomenon. It indicated that

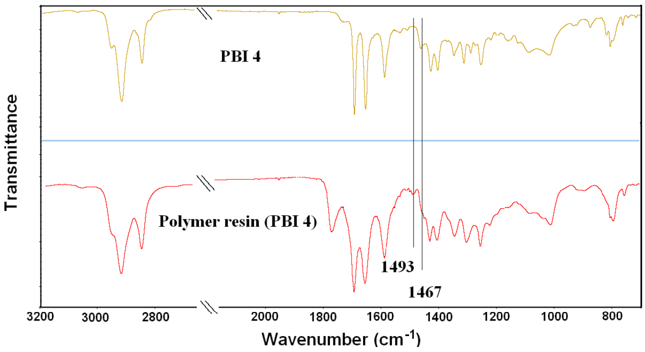


Fig. 7. IR spectra of PBI 4 and polymer resin (PBI 4)

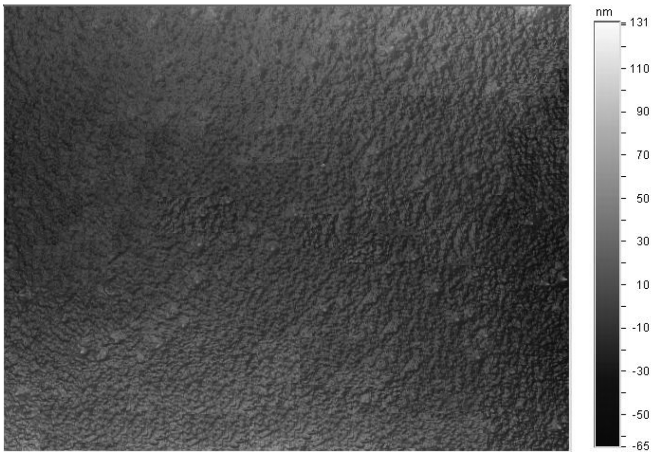


Fig. 8. White-light interferometry photo of polymer resin (PBI 4)

the oligomer with lower crosslinking degree had been formed. Moreover, due to crosslinking reaction, polymer resin is difficult to dissolve in any solvent and has no glass transition temperature (T_g).

Conclusion

Fourfold benzocyclobutene-functionalized perylene bisimide has been synthesized *via* Suzuki coupling reaction and PBI 4 has the thermopolymerization property. The thermopolymerization behaviour was studied and our study showed that it can react either with itself or the appropriate dienophiles to form the corresponding products under appropriate temperature. Further investigation and the related benzocyclobutene-functionalized perylene bisimide materials are still underway.

ACKNOWLEDGEMENTS

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