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Synthetic Metals 156 (2006) 135–140

SYNTHETIC METALS

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Synthesis and characterization of a low band gap polymer with an aromatic oxadiazole moiety as the side chain

Qinghui Zhang[a], Mujie Yang[b,*], Peng Wu[b], Hui Ye[b], Xu Liu[b]

[a] *Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*
[b] *Department of Optic Science and Engineering, Zhejiang University, Hangzhou 310027, China*

Received 20 October 2004; received in revised form 25 October 2005; accepted 25 October 2005
Available online 7 December 2005

Abstract

A novel low band gap polymer with an electron deficient oxadiazole side chain, poly[(α-bithiophene-5,5′-diyl) (5′-(2″-phenyl-1″,3″,4″-oxadiazole-5″-phenylidene))-block-(α-bithiophene (2″-phenyl-1″,3″,4″-oxadiazole-5″-phenylidene)quinodimethane-5, 5′-dily)] (PBTBQ-Oid), was synthesized. The polymer was soluble in common organic solvents, such as THF, chloroform and xylene. The structure of the polymer was confirmed by FT-IR, ^{1}H NMR. The optical spectrum revealed that it had maximum absorption among 600–700 nm. The electrochemical analysis showed that it had good electron-transporting properties and a low band gap of ∼1.10 eV.

Keywords: Conjugated polymer; Low band gap; Oxadiazole

1. Introduction

Recently, design and synthesis of low band gap polymers have attracted a great deal of attention due to their intrinsic electronic, optoelectronic, optical and non-linear optical properties [1–3]. Due to their wide visible absorption and good film-forming ability, they were expected to extend the photoactive spectral region of polymer solar cells and emit red light in organic light-emitting diodes (OLEDs) [4,5]. While like common conjugated polymers, most low band gap polymers were p-type semiconductors, facilitating the transport and inject of holes. So how to realize the balance of charge inject and transport was an important way to improve the efficiency.

Here, a novel low band gap polymer, PBTBQ-Oid, was designed and synthesized. It had good electron-transporting oxadiazole units as side chain, and conjugated poly(heteroarylene methines) as main chain.

2. Experimental

2.1. Materials

p-Methyl benzoic acid, *N*-bromosuccinimide (99%) (NBS), thionyl chloride ($SOCl_2$), phosphorus oxychloride ($POCl_3$), 85% hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$), benzoyl chloride and sodium acid carbonate ($NaHCO_3$) were purchased from domestic chemical company and used without further purification. 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) and benzoyl peroxide (BPO) were recrystallized from ethanol. α-Bithiophene was prepared according to the literature [6]. All of the solvents were commercially obtained and purified by standard distillation methods. All of the following reactions were carried out under argon atmosphere.

2.2. Synthesis of monomers [7,8]

2.2.1. Ethyl p-methyl benzoate (1)

Thionyl chloride (22 mL, 0.3 mol) was added dropwise to a solution of (27.2 g, 0.2 mol) of *p*-methyl benzoic acid in 350 mL of dry ethanol at 0 °C under vigorous stirring. The mixture was then heated to room temperature and stirred for 12 h. After the solvent was removed by rotary evaporation, the mixture was poured into water and extracted with dichloromethane

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[*] Corresponding author. Tel.: +86 571 8795 2444; fax: +86 571 8795 2444.
E-mail address: yangmj@cmsce.zju.edu.cn (M. Yang).

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doi:10.1016/j.synthmet.2005.10.014

three times. The extraction was washed with water twice and dried with anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by silica-gel column chromatography using petroleum ether as the eluent. Yield: 95%. FT-IR (film on NaCl, cm^{-1}): 1717.6 (vs, γC=O), 1277.1 and 1175.8 (s, γC–O), 844.9 (m, δC–H, 1,4-substituted phenyl). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84 (2H), 7.17 (2H), 4.30 (2H), 2.36 (3H), 1.30 (3H).

2.2.2. 4-Methyl benzoyl hydrazine (2)

A mixture of (26.6 g, 0.16 mol) of compound 1, (30 mL, 0.5 mol) of 85% hydrazine hydrate and 100 mL of ethanol was heated to 60 °C and was stirred for 4 h. Then, the mixture was cooled, poured into 500 mL water and extracted with dichloromethane three times. The organic layer was dried with unhydrous magnesium sulfate. After the solvent was removed by rotary evaporation, the residue was purified by silica-gel column chromatography using petroleum ether as the eluent. Yield: 40%. FT-IR (film on NaCl, cm^{-1}): 3304.0, 3224.2 and 3025.3 (s, γN–H), 1660.0, 1612.2, 1562.2 and 1506.7 (s, δN–H, NH), 1296.2 (m, γC–N, CONH), 828.7 (m, δC–H, 1,4-substituted phenyl). ^1H NMR (500 MHz, $CDCl_3$, ppm): 58.11 (1H), 7.82 (2H), 7.23 (2H), 4.30 (2H), 2.35 (3H), 1.98 (2H). Anal. Calcd. for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.02; H, 6.69; N, 18.60.

2.2.3. 1-(4′-Methylbenzoyl)-2-benzoyl-hydrazine (3)

Benzoyl chloride (43.3 mL, 0.12 mol) was added dropwise to a solution of 3 (14.3 g, 0.09 mol) in 86 mL of dry pyridine at 0 °C under vigorous stirring. The mixture was heated to reflux for 2 h. The most solvent was removed by distillation. After cooled, the residue was poured on ice. The precipitate was collected by filtration, washed with water and dried under vacuum. The crude product was purified by recrystallization from ethanol to afford a white solid. Yield: 67%. mp 114–116 °C. FT-IR (KBr pellet, cm^{-1}): 3205.1, 3006.5 (s, γN–H), 1667.8, 1633.8, 1574.8 and 1534.7 (s, δN–H), 1281.1 (m, γC–N, CONH), 836.5 (m, δC–H, 1,4-substituted phenyl). Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.86; H, 5.53; N, 11.07.

2.2.4. 2-(4′-Methylphenyl)-5-phenyl-1,3,4-oxadiazole (4)

(18.9 g, 67 mmol) of compound 3 was dispersed in 224 mL of $POCl_3$ at room temperature. The mixture was refluxed for 7 h. After cooling, the reaction mixture was poured into ice. The precipitate was collected by filtration, washed with water and dried under vacuum. The crude product was purified by recrystallization from ethanol to afford a white solid. Yield: 83.6%. mp 116–118 °C. FT-IR (KBr pellet, cm^{-1}): 3056.1, 2917.9, 1956.0, 1613.5 (m, γC=N), 1549.6, 1487.5, 1446.6, 1311.8, 1270.9, 1175.9, 1072.1, 1020.3, 966.7, 925.2, 823.9, 776.0, 695.1. Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.19; H, 5.08; N, 11.85.

2.2.5. 2-(4′-Bromomethyl phenyl)-5-phenyl-1,3,4-oxadiazole (5)

(13.0 g, 55 mmol) of 4, (9.8 g, 55 mmol) of NBS, a catalytic amount of benzoyl peroxide (BPO) and 130 mL of carbon tetrachloride were refluxed for 5 h. As the reaction proceed, succinimide was precipitated and the reaction progress was monitored by TLC on silica plate. The warm reaction mixture was filtered under suction and washed with hot CCl_4. After the solvent was evaporated, the crude product was purified by recrystallization from ethanol to afford a white solid. Yield is 70%. mp 171–173 °C. FT-IR (KBr pellet, cm^{-1}): 3160.7, 3059.8, 3029.4, 2973.2, 1773.5, 698.6, 1609.9 (m, γC=N), 1581.3, 1548.8, 1489.2, 1445.7, 1418.2, 1268.0, 1227.1, 1188.5, 1070.1, 965.2, 923.4, 846.5, 816.3, 774.3, 744.4, 708.9, 688.6. Anal. Calcd. for $C_{15}H_{11}N_2BrO$: C, 57.17; H, 3.52; N, 8.89. Found: C, 57.19; H, 3.49; N, 8.87.

2.2.6. 2-Phenyl-1,3,4-oxadiazole-5-phenyl aldehyde (6)

(10.5 g, 0.03 mmol) of 5, and (26.6 g, 0.32 mol) of $NaHCO_3$ were placed in a 500 mL round-bottom flask, and 200 mL of DMSO was added. The mixture was heated to 115 °C for 24 h. After cooling, the reaction mixture was poured into water. The precipitate was filtered, dissolved in dichloromethane, washed with water and dried under vacuum. After the solvent was evaporated, the crude product was purified by silica-gel column chromatography using petroleum ether:ethyl acetate as the eluent. mp 143–145 °C. FT-IR (KBr pellet, cm^{-1}): 3061.1, 2836.1, 1703.8 (b, C=O, CHO), 1666.5, 1610.2 (m, γC=N), 1578.7, 1547.7, 1487.2, 1447.1, 1419.7, 1389.6, 1299.6, 1269.3, 1240.6, 1075.3, 1025.9, 8340, 733.4, 705.6, 687.9. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.11 (1H), 8.32 (2H), 8.15 (2H), 8.05 (2H), 7.54–7.59 (3H). Anal. Calcd. for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03; N, 11.19; O, 12.79. Found: C, 71.98; H, 4.05; N, 12.82.

2.3. Synthesis of pre-polymer and polymer [9,10]

2.3.1. Poly[(α-bithiophene-5,5′-diyl) (2″-phenyl-1″,3″,4″-oxadiazole-5″-phenylidene)] (PBTB-Oid)

(0.789 g, 4.8 mmol) of α-bithiophene, (1.345 g, 5.4 mmol) of 5 and 10 mL of *p*-dioxane were added to a 25 mL round-bottom flask. The mixture was heated to 85 °C and 0.10 mL of 98% H_2SO_4 was added dropwise. Then, it reacted at same temperature for 24 h. The reaction mixture was poured into methanol. The precipitate was filtered, reprecipitated in THF/methanol twice and vacuum dried at 50 °C. The product is blue/black solid. FT-IR (KBr pellet, cm^{-1}): 3064.5, 1715.6, 1611.9, 1549.3, 1488.8, 1448.5, 1417.5, 1270.3, 1178.3, 1107.6, 1066.9, 1018.1, 961.0, 839.3, 798.0, 711.3, 689.3.

2.3.2. Poly[(α-bithiophene-5,5′-diyl) (5′-(2″-phenyl-1″,3″,4″-oxadiazole-5″-phenylidene))-block-(α-bithiophene (2″-phenyl-1″,3″,4″-oxadiazole-5″-phenylidene)quinodimethane-5, 5′-dily)] (PBTBQ-Oid)

The reaction mixture was (0.717 g, 1.8 mmol) of PBTB-Oid, (0.245 g, 1.1 mmol) of DDQ and 25 mL of unhydrous THF. The reaction temperature was maintained at 50 °C for 10 h. A dark blue polymer was recovered in stirring methanol, dissolved in THF, recovered in methanol, extracted with hot methanol in a Soxhlet apparatus, and dried in a vacuum oven at 60 °C for 12 h.