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Donor-acceptor polymers by solid state eutectic melt reaction for optoelectronic applications

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ABSTRACT

We report, the synthesis of novel donor–acceptor conjugated polymers based on benzo[1,2-b:4,5-b′]dithiophene (**BDT**) donor and 4,7-bis(5-bromothiophen-2-yl)benzo[c] [1,2,5]thiadiazole (**DTBT**) acceptor by solvent-free eutectic melt polymerization reaction (**EMP**). The most important fact is, reaction between solid reactants actually proceeds through bulk liquid phases, due to the formation of eutectics between the reactants and product(s) and any evolution of heat. In the present study, crystalline solid with moderately high vapor pressure and low melting temperature such as naphthalene is explored for forming eutectics in melt polymerization reaction. The HOMO and LUMO energy levels of the polymer **P2** synthesized by **EMP** were found to be −5.30 eV and −3.77 eV. Optical bandgap was determined to be 1.53 eV. The solid-state reactions are important not only due to their high efficiency and selectivity but also for their more economical and eco-friendly procedures involved in the reaction.

1. Introduction

Solvent-free synthetic protocol in organic synthesis is gaining importance as a tool for the synthesis of a wide variety of useful and important compounds, with the number of reactions conducted under these conditions increasing. Originally, conventional methods have been utilized for solvent-free synthesis, but most recently there has been a shift in utilizing nonconventional energy sources, such as microwaves, ultrasound and mechanochemical mixing to increase the efficiency of the reactions [1–4]. Recently, the catalyst-free multi component reactions gained interest as alternative to the classical organic synthesis [5]. Taking into account that the most common procedures require large amounts of organic solvents, the presence of strong acidic reagents, long reaction times and complex work-up, the aim of solid state synthesis was to study more ecological and economic conditions, as green chemistry procedures, for the synthesis of these widespread ingredients with special interest focused on solvent-free methodologies [6–9].

It is well known that, in organic synthesis, avoiding the solvent leads to enhanced yields, milder conditions, increased safety and cost reduction [10]. There are also some reports on the synthesis of potential cosmetic ingredients in dry media [11,12]. Synthesis of nanocomposites of C_3N_4 with layers of MoS_2 and nitrogenated RGO, obtained by covalent cross-linking is reported in the literature [13,14]. In recent times, multicomponent reactions (MCRs) have been widely used as a green and powerful tool in organic synthesis. A mild and convenient L-proline catalyzed solid-state melt reaction for one-pot three-component condensation to afford highly substituted chromenopyridinone derivatives has been reported [15,16]. Although several melt reaction methods for the synthesis of polymers have been developed, more environmentally benign and efficient approaches are still desirable. In this regard, organocatalysts are suitable for the construction of a wide variety of structurally diverse heterocyclic molecules because of the mild reaction conditions, environmental benignity, atom economy, and functional group tolerance [17]. In addition, a solid-state melt reaction (SSMR) is an economically attractive and environmentally acceptable synthetic tool for the construction of a wide range of structurally diverse heterocyclic motifs without using toxic, flammable, expensive, and hazardous organic solvents [18,19].

The building blocks benzo[1,2-b:4,5-b′]dithiophene (**BDT**) [20,21] and 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]

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thiadiazole (**DTBT**) [22,23] have been proven to be excellent organic electronic materials. Eutectic systems, which are mixtures of chemical compounds or elements that melt and solidify at lower temperature than any of pure ingredients, have long been utilized in metallurgy to cast engineering alloys [24,25], but they were barely employed in polymerization. To the best of our knowledge, there are no reports on the synthesis of organic semiconducting polymers by naphthalene assisted eutectic reaction.

Herein, we report the synthesis of organic semiconducting polymers by eutectic melt polymerization reaction. To demonstrate the proposed concept, monomers used in our experiments includes alkyl chain substituted benzo[1,2-b:4,5-b′]dithiophene(**BDT**) and 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole(**DTBT**). Crystalline solid with moderately high vapor pressure and low melting temperature such as naphthalene, is utilized to form the eutectic mixture. Due to the lowered melting temperature, the polymerization by eutectic melting is highly applicable for a variety of organic molecules which originally have high melting temperature or/and insoluble in most organic solvents. The features of this developed protocol were improved reaction conditions, solvent-free and higher product yield. This solid state melt reaction provides an excellent choice for the construction of a variety of organic materials for electronic applications and development of new sensors. The solid-state reactions are important not only due to their high efficiency and selectivity but also for their more economical and eco-friendly procedures involved in the reaction. Furthermore the optoelectronic studies of the soluble polymer are suggesting the polymer to be promising candidate for organic electronics. The importance of solvent-free synthesis using nonconventional method is highlighted in the present article.

2. Experimental section

2.1. Materials and methods

Reagents tetrakis(triphenylphosphine)palladium, naphthalene, and solvents methanol, acetone, hexanes, chloroform are purchased from Aldrich. Unless otherwise stated all commercially available solvents and reagents were used without further purification. The monomers 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole [26] (**DTBT**), 2,6-bis(trimethyltin)-4,8-dimethoxybenzo[1,2-b:4,5-b′]dithiophene [27] (**BDT**) 2,6-bis(trimethyltin)-4,8-didodeyloxybenzo[1,2-b:4,5-b′]dithiophene [27] (**BDT**) were prepared by previously described methods. The synthesized compounds were characterized with ^{1}H NMR and ^{13}C NMR spectra obtained with a Bruker DPX-300 NMR spectrometer using commercial NMR solvents obtained from Aldrich with TMS as internal standard and chemical shifts are mentioned in δ ppm scale. UV–Vis spectroscopy were recorded using Lambda 20 (Perkin Elmer) diode array spectrophotometer at room temperature unless otherwise noted. All solution UV–Vis experiments were run in $CHCl_3$. Films were prepared by spin-coating $CHCl_3$ solutions onto quartz substrates. For the optical properties of **P2**, the thin films were prepared on quartz plates. Prior to deposition of polymer, plates were thoroughly cleaned with deionized water, chloroform and acetone followed by drying in the oven. The semiconducting polymer layer in chloroform solution was spin-coated with concentration of 6 mg mL^{-1}. The films were dried at 40 °C. Cyclic voltammetry experiment is carried out using Weis-500 work station. Cyclic voltammetry (CV), was used to investigate the electrochemical behaviour of the conjugated polymers and to estimate their HOMO and LUMO energy levels. For the electrochemical properties of **P2** as thin films were prepared on ITO, which is used as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode respectively. 0.1 M Bu_4NPF_6 used as electrolyte in acetonitrile solution with scan rate 50 mV s^{-1}. Based on CV, the onset oxidation and reduction potentials of the voltammogram correspond to HOMO and LUMO energy levels, respectively. The number and weight average molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with a TDA 302 detector and a PL-gel (Varian) column, using chloroform as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} with a Dupont 9900 analyzer. Elemental analyses were performed on a Vario III elemental analyzer.

2.2. *Poly[4,8-bis(4,8-dimethoxy)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-[4,7-bis(4-thiophen-2-yl)-benzo[c][1,2,5]thiadiazole (P1)*

2,6-Bis(trimethyltin)-4,8-dimethoxybenzo[1,2-b:4,5-b′]dithiophene (1a) (173 mg, 0.3 mmol), 4,7-bis(5-bromothiophen-2-yl) benzo[c][1,2,5]thiadiazole (2) (137 mg, 0.3 mmol), $Pd(PPh_3)_4$ (14 mg, 0.05 eq.) and naphthalene (400 mg, 3.0 mmol) were added to a 20 mL glass vial sealed with septum under argon atmosphere. The polymerization was carried out at 110 °C under argon protection. Naphthalene forms eutectic mixture with the starting material and acts as a melt liquid. After 12 h, the reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred methanol (15 mL). The polymer fibres were collected by filtration. The polymer precipitate was then subjected to Soxhlet extraction with methanol, acetone, hexanes, and chloroform. Finally, the polymer is filtered and dried in vacuo at 40 °C for 12 h. Polymer was obtained as dark blue powder (282 mg 75%). Molecular weight of polymer **P1** cannot be determined as the polymer is insoluble in organic solvents such as chloroform, chlorobenzene and dichlorobenzene. Anal. calcd: C, 57.12; H, 2.58; N, 5.12; S, 29.32%; found C, 54.68; H, 3.01; N, 4.64; S, 25.79%.

2.3. *Poly[4,8-bis(4,8-didodecyloxy)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-[4,7-bis(4-thiophen-2-yl)-benzo[c][1,2,5]thiadiazole (P2)*

2,6-Bis(trimethyltin)-4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene (1b) (265 mg, 0.3 mmol), 4,7-bis(5-bromothiophen-2-yl) benzo[c][1,2,5]thiadiazole (2) (137 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.05 eq.) and naphthalene (400 mg, 3.0 mmol) were added to a 20 mL glass vial with sealed with septum under argon atmosphere. The polymerization was carried out at 110 °C under argon protection. Naphthalene forms eutectic mixture with the starting material and acts as a melt liquid. After 12 h, the reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred methanol (15 mL). The polymer fibres were collected by filtration. The polymer was dissolved in chlorobenzene and precipitated again into methanol. The precipitate was then subjected to Soxhlet extraction with methanol, acetone, hexanes, and chloroform. The final polymers were obtained by evaporation of chloroform and precipitating in methanol. The polymer is filtered and dried in vacuo at 40 °C for 12 h. Polymer was obtained as dark blue shining powder (235 mg 58%). GPC analysis: $Mn = 22.5$ Kg/Mol, $Mw = 88.3$ Kg/mol, PDI = 3.7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.3–7.4 (br, 4H), 7.0–7.2 (br, 4H), 4.2 (br, 4H), 1.8 (br, 4H), 1.2–1.3 (br, 34 H). 0.8–0.90 (br, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 152. 0, 143.95, 140.62, 134.0, 132.20, 128.0, 125. 80, 73.6, 31.9, 30.5, 29.7,