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New diphenylamine-based donor–acceptor-type conjugated polymers as potential photonic materials

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ABSTRACT

A new series of donor–acceptor-type conjugated polymers (**P1** and **P2**) carrying a diphenyl amine moiety were synthesized via Wittig condensation technique. The polymers structures were well established by FT-IR, ^{1}H NMR, elemental analysis and gel permeation chromatographic techniques. They exhibited good thermal stability with an onset decomposition temperature of approximately 325 °C under nitrogen atmosphere. The optical and electrochemical properties of the polymers were studied by UV–vis, fluorescence emission spectroscopy and cyclic voltammetry. They exhibited good fluorescence in dilute solutions and showed solvatochromic behavior in various polar solvents. The electrochemical studies revealed that the polymers possess low-lying LUMO energy levels that ranging from −3.47 to −3.73 eV and high-lying HOMO energy levels that ranging from −5.57 to −5.81 eV. The thirdorder nonlinear optical properties of the polymers were investigated using the Z-scan technique. The effective two-photon absorption (TPA) coefficients (β) of the polymers were found to be 0.645×10^{-10} and 0.212×10^{-10} m/W.

1. Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers because of their intriguing properties, such as electrical conductivity [1], electroluminescence [2], photovoltaic [3] and chemical-sensing [4] properties. Additionally, conjugated polymers have been extensively studied for nonlinear optical (NLO) applications [5–7], such as electro-optical (EO) modulation, optical switches, optical power limiting and frequency doubling, because of their large optical nonlinearity, fast response time, and easy processability for integrated assembly [8–10].

Many conjugated polymeric systems that carry aromatic heterocyclic rings are known to exhibit an increased hyperpolarizability compared to those that carry benzenoid systems [11–13]. This increase in the hyperpolarizability occurs because the delocalization energy of hetero-aromatics is lower than that of benzenoid systems. Active chromophores that contain aromatic heterocycles such as thiophene [14–16], thiazole [17,18] benzothiazole [18,19] or their derivatives are among the most studied systems. Recently, a donor–acceptor (D–A) approach has been adopted to tune the nonlinear properties of conjugated polymers [20]. According to this concept, the incorporation of alternate electron-acceptor and electron-donor units along the main polymer chain would significantly increase the NLO properties, mainly due to an enhancement of the hyperpolarizability. The desired optical properties can be achieved when polymer backbones are tailored with different heterocyclic systems that allow the fine-tuning of important physical and/or photophysical properties.

An extensive literature survey reveals that the incorporation of a 3,4-dialkoxythiophene moiety along the backbone of a polymer enhances the polymer's dopability and decreases its band gap. Furthermore, the incorporation of a highly electron-withdrawing oxadiazole ring along the conjugation path increases the charge-carrying properties of the polymer [21,22], which may alter its NLO properties. In addition, the introduction of vinylene linkages increases the planarity of the polymer chain by reducing the torsional interactions between the hetero-aromatic rings, which leads to a decrease in the band gap [21]. A pyridine ring is also a highly electron-withdrawing moiety that exhibits good electron-transporting abilities and optical properties when it is introduced into the polymer main chain. The presence of a nitrile (CN) substituent on the pyridine ring further enhances the charge-carrying properties of the resulting polymer [23]. Because of the fluorescent nature of cyanopyridine, its presence in a polymer chain would improve the optical properties. Conjugated polymers carrying cyanopyridine are also known to exhibit good optical-limiting properties [24].

In general, the NLO properties of conjugated polymers can be further enhanced either by doping the polymer with a NLO chromophore (guest–host) or covalently incorporating an NLO moiety

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onto the polymer backbone [22]. The guest–host method has some fatal disadvantages, such as the low solubility of the chromophore in the polymer host, the fast decay of NLO activity due to orientational relaxation and sublimation of the chromophore. However, the method of covalent incorporation of an NLO chromophore leads to an enhancement of the chromophore density without phase separation and is therefore advantageous over the guest–host method. Among the various classes of NLO chromophores reported in the literature, triphenylamine and diphenylamine derivatives are good candidates because of their multifunctional properties, such as good solubility, two-photon absorption, and hole-conducting properties [23,24]. Therefore, the diphenylamine moiety can be conveniently connected with a strong acceptor system through ethylene-conjugated bridges to produce large first-molecular hyperpolarizability in the resulting molecules.

Against this background, we have designed two new D–A type conjugated polymers, **P1** and **P2**, by introducing the highly electron-donating diphenylamine moiety into the polymer network. In the synthetic design of the new polymer **P1**, alkoxythiophene and diphenylamine moieties were connected as electron donors, and an oxadiazole ring was connected as an electron acceptor. In polymer **P2**, a diphenylamine group was attached as the electron donor, and a cyanopyridine ring was used as the electron acceptor. In addition, phenylene vinylene units were incorporated as conjugated spacers in both **P1** and **P2** to enhance the conjugation path length, which in turn enhances their optical properties. In the present work, the required monomers have been prepared from simple thiodiglycolic acid through multistep reactions. The structures of the new **P1** and **P2** polymers have been established by spectral techniques, and their electrochemical, linear and nonlinear optical properties have been evaluated to investigate the influence of their structure on the properties.

2. Experimental

2.1. Materials and methods

3,4-Ditetradecyloxythiophene-2,5-dicarboxylate (structure **8**) was synthesized according to the reported procedure [21]. All chemicals used in the present work were procured from Sigma–Aldrich and Lancaster (UK). All solvents were of analytical grade; they were purchased and used without further purification.

2.2. Instrumentation

Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 5700 FTIR (Thermo). The UV–visible and fluorescence spectra were recorded on a GBC Cintra 101 and a JASCO FP-6200 spectrofluorometer, respectively. ^{1}H NMR spectra were obtained on a Bruker 400 MHz FT-NMR spectrometer using the TMS/solvent signal as an internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). Mass spectra were recorded on a Jeol SX-102 (FAB) mass spectrometer. Electrochemical studies were performed using an AUTOLAB PGSTAT30 electrochemical analyzer. Molecular weights of the polymers were determined with a gel permeation chromatograph (GPC) against polystyrene standards with THF as the eluent.

2.3. Synthetic plan

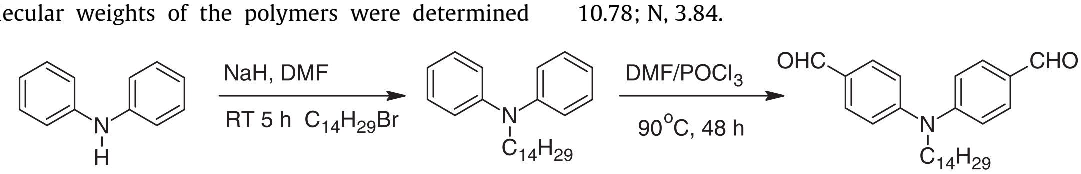
Schemes 1 and 2 show the synthetic routes for the preparation of new monomers and their polymerization to the target polymers. In Scheme 1, compound **1** was alkylated using tetradecyl bromide in the presence of sodium hydride to produce alkylated diphenylamine **2**, which was later converted into the corresponding dialdehyde **3** via the Vilsmeyer–Haak reaction. In Scheme 2, the required chalcone **4** was prepared from tolualdehyde and 4-methylacetophenone using the Claisen–Schmidt reaction. The product was then cyclized to cyanopyridine **5** by reaction with malononitrile in the presence of sodium methoxide. Further, two methyl groups of compound **5** were brominated via the Wholzigler method using NBS and BPO. The resulting dibromo derivative **6** was conveniently converted to phosphonium Wittig salt **7**, which, upon treatment with dicarboxaldehyde **3** in ethanol–chloroform medium, yielded polymer **P2** in good yield.

As shown in Scheme 2, the diesters of 3,4-ditetradecyloxy thiophene were readily converted to 3,4-ditetradecyloxythiophene-2,5-carboxydihydrazides **9** by the action of hydrazine hydrate in alcoholic medium. This dihydrazide was tolylated to yield 3,4-bis(tetradecyloxy)-N′2,N′5-bis(4-methylbenzoyl)thiophene-2,5-dicarbohydrazide **10**, which, upon treatment with phosphorus oxychloride gave 5,5′-(3,4-bis(tetradecyloxy) thiophene-2,5-diyl)bis(2-p-tolyl-1,3,4-oxadiazole) **11** [25] in good yield. This bisoxadiazole compound **11** was then Wohl–Ziegler brominated using N-bromo succinimide (NBS) in carbon tetrachloride, and the resulting 5,5′-(3,4-bis(tetradecyloxy)thiophene-2,5-diyl)bis(2-(4-(bromomethyl)phenyl)-1,3,4-oxadiazole) **12** was further converted to 5,5′-(3,4-bis(tetradecyloxy)thiophene-2,5-diyl)bis(2-(4-triphenylphosphonionmethyl)phenyl)-1,3 ,4 oxadiazole) **13** upon treatment with triphenylphosphine in the presence of DMF. The reaction of compound **13** with diphenylaminedicarboxaldehyde **3** in ethanol–chloroform medium yielded polymer **P1**.

2.4. Syntheses of intermediates, monomers and polymers

2.4.1. Synthesis of N-tetradecyl diphenylamine *2*

Sodium hydride (0.7185 g, 29.5 mmol) was added to the solution of diphenylamine **1** (5 g, 29.5 mmol dissolved in 50 ml of DMF) and the resulting mixture was stirred for approximately 30 min. 1-Bromo tetradecane (8.29 g, 29.5 mmol) was then slowly added to the reaction mixture, and the mixture was stirred for 5 h at room temperature. After completion of the reaction, the resulting mixture was extracted with ethyl acetate/brine and then dried with Na_2SO_4. The solvent was removed by evaporation. The resulting crude product was purified by column chromatography using hexane and ethyl acetate. Yield: 8.8 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.36–7.04 (m, 10H, aromatic protons), 3.83 (t, 2H, —NCH_2), 1.74 (m, 2H, —NCH_2CH_2—), 1.34–1.24 (m, 24H, —CH_2CH_2), 0.87 (t, 3H, CH_3). FTIR (cm^{-1}): 2920, 2852, 1590, 1494, 1309, 891, 743. Anal. Calcd for $C_{26}H_{39}N$: C, 85.42; H, 10.75; N, 3.83. Found: C, 85.45; H, 10.78; N, 3.84.



Scheme 1. Synthesis of N-substituted diphenylamine dialdehyde.