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Synthesis of star-shaped pyrrole and thiophene functionalized monomers and optoelectrochemical properties of corresponding copolymers

Metin Ak[a,b], Levent Toppare[a,*]

[a] Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey
[b] Pamukkale University, Department of Chemistry, 20020 Denizli, Turkey

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ABSTRACT

Star-shaped thiophene and pyrrole functionalized monomers namely 2,4,6-tris(4-(1H-pyrrol-1-yl)phenoxy)-1,3,5-triazine (TriaPy) and 2,4,6-tris(4-(1H-pyrrol-1-yl)phenoxy)-1,3,5-triazine (TriaTh) were synthesized from 2,4,6-trichloro-1,3,5-triazine, thiophen-3-ylmethanol and 4-(1H-pyrrol-1-yl)phenol. Electrochemical copolymerization of monomers with thiophene and pyrrole was achieved in tetrabutylammonium tetrafluoroborate/acetonitrile (TBAFB/AN). Resulting copolymers were characterized by Fourier transform infrared (FTIR) spectrometer, cyclic voltammetry (CV) and conductivity measurements. Spectroelectrochemical analysis reflected that copolymer films have low λ_{max} for π–π^* electronic transitions accompanied with a rather high band gap compared to polythiophene and polypyrrole. Switching abilities of copolymer films were evaluated by a kinetic study via measuring the transmittance (%*T*) at the maximum contrast.

1. Introduction

Polymers containing 1,3,5-triazine units have been widely used in industry [1–3] due to their high thermal stability. In recent years, some new types of polymers containing 1,3,5-triazine units have been reported [4–12]. These organic materials possess good optical and electrical properties, and are expected to have applications in liquid-crystalline materials [8,10], magnetic materials [11], and organic light-emitting diodes (OLEDs) [5,7,12]. The 1,3,5-triazine unit possesses structural symmetry and high electron affinity [9], introducing such a unit into the main chain of conjugated polymers may contribute good electrochemical and optical properties to the polymers [13]. Especially for OLED applications, such p-conjugated polymers containing 1,3,5-triazine units in the main chain would be favored for improving the electron injection and transportation [5,7,12].

Star-shaped polymers, which are composed of multiple polymer chains emanating from junction points, have received significant attention over the past decade due to their unique three-dimensional shape. They have possible processing advantages due to their compact structure in comparison with linear analogues [14]. Conducting polymers (CPs) contain a π-electron backbone, which is responsible for their unusual electronic properties such as electrical conductivity, low-energy optical transitions, low ionization potential and high electron affinity. This extended conjugated system of CPs has single and double bonds alternating along the polymer chain. The high electrical conductivity obtained in such organic polymers have led to the name “synthetic metals”. Recent advances in the field of these conducting polymers has led to the production of a variety of materials with a greater potential for practical applications such as batteries [15], electronic devices [16], sensors and capacitors [17], electromagnetic radiation shielding, antistatic coatings, gas separation membranes, nonlinear optical and electrochromic devices (ECDs) [18–21]. Building super-structured CPs are of great interest because of the novel properties that could arise from such structures [22,23]. Branched conducting polymers with electronically connected nodes are excellent candidates among this family of super structured CPs; with such polymers, there should be no need for inter-chain coupling or inter-chain electronic transfer to ensure high electronic conductivity [24,25]. Moreover, this type of material possesses a three-dimensional structure which could also improve the conductivity [26].

In this study, we synthesized star-shaped thiophene and pyrrole functionalized monomers namely 2,4,6-tris(4-(1H-pyrrol-1-yl)phenoxy)-1,3,5-triazine (TriaPy) and 2,4,6-tris(thiophen-3-ylmethoxy)-1,3,5-triazine (TriaTh). Electrochemical copolymerization of TriaPy and TriaTh was achieved in acetonitrile using tetrabutylammonium tetrafluoroborate (TBAFB) as the supporting electrolyte. The resultant copolymers were characterized by cyclic

* Corresponding author. Tel.: +90 3122103251; fax: +90 3122103200.
E-mail address: toppare@metu.edu.tr (L. Toppare).

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