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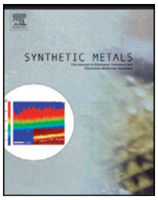

Polystyrene functionalized carbazole and electrochromic device application

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ABSTRACT

Polystyrene (PS) functionalized carbazole macromonomer was synthesized and polymerized by electrochemical oxidative polymerization on the ITO-glass surface. The structure of the macromonomer was elucidated by ^{1}H NMR, FT-IR, UV–Vis and cyclic voltammetry (CV). The spectro-electrochemical and electrochromic properties of the polymer film were investigated. Also the greenish blue colored film converted to dark blue color by the applying potential. Polystyrene-carbazole/polyethylenedioxythiophene (PS-Carb/PEDOT) electrochromic device was assembled in sandwich configuration: ITO-coated glass/anodically coloring polymer (PS-Carb)//gel electrolyte//cathodically coloring polymer (PEDOT)/ITO-coated glass. According to kinetic studies of this device, the optical contrast $\Delta T\%$ at 640 nm between −1.0 and +2.0 V with a residence time of 10 s was found to be 38% and switching time was measured as 1.1 s.

1. Introduction

Since discovery of photoconductivity of PVK by Hoegl, carbazole containing polymers have great importance in photo-electronic technology [1]. Due to ease of formation of relatively stable radical cations (holes), high charge carrier mobilities, high thermal and photochemical stabilities, these polymers have been used in electrochromic devices, hole transport layers, electro-xerography, microcavity photoconduction, and as photovoltaic components that provide a very efficient matrix as a current carrier transport. Carbazole could also be easily functionalized at (3,6) [2,3], (2,7) [4], or N-positions [5], and then covalently linked into polymeric systems, both in the main chain as building blocks [6] and in a side chain as pendent groups [7].

Studies in electrochromic devices began with inorganic compounds such as tungsten trioxide (WO_3), iridium dioxide (IrO_2). Electrochromic conducting polymers have several advantages over inorganic compounds such as their potential for structurally controllable HOMO-LUMO band gap, fast switching speeds, high contrast ability, and easy processing [8–11]. The color is determined by the band gap, defined as the onset of the π–π^* transition [12]. Because of this, band gap control is the most important parameter that the construction of dual-polymer-based electrochromic devices where a low band gap (cathodically coloring) polymer is matched with a high band gap (anodically coloring) polymer to obtain a high degree of contrast during the switching process [13]. For these reasons, ECPs have received increasing attention for two decades.

Polystyrene is well known one of the commercial polymers. Various physical and chemical properties of the polystyrene have been improved for more using various purposes. Some methods have been applied for these aims such as, synthesis of copolymer with polar monomer such as acetonitrile and anchoring some functional groups [14–20] modified several electro-active groups such as, thiophene [21], fluorine [22], carbazole [23–26] and pyrrole [27], and thus can be gained useful properties for the various applications [28].

In this study, we achieved to attach carbazole molecule onto polystyrene and to synthesize electrochromic conducting polymer via electrochemical polymerization of PS-Carb. Also, we have prepared dual-polymer-based electrochromic devices containing cathodically coloring PEDOT, anodically coloring poly(PS-Carb). For this purpose, polystyrene was firstly brominated and than functionalized with carbazole according to Ullmann coupling reaction process [29]. Finally this macromonomer was directly polymerized onto ITO/glass surface by the electro-oxidative process, which gives uniform films that exhibit electrochromism.

2. Experimental

2.1. Materials

All chemicals purchased from Aldrich, Merck and Fluka and used without further purification. PS (M_w: 2.5×10^5) was supplied from Petkim A.Ş. (İzmir).

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2.2. Bromination of polystyrene

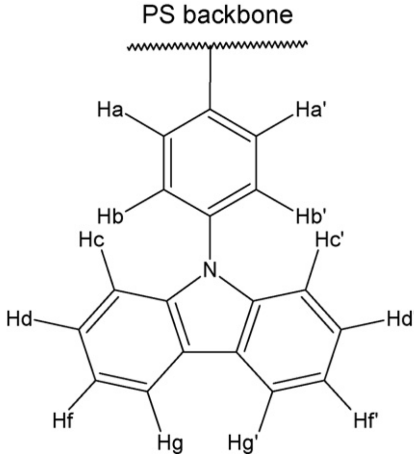
PS (4.24 g, 40 mmol) was added to 100 ml of DCM. Then, the mixture was stirred at room temperature for 30 min; iodine (0.280 g, 1.10 mmol) was added to the reaction mixture and stirred for an additional 1 h at room temperature. Solution of the bromine (2.4 ml, 44 mmol) in DCM was added drop wise into the reaction flask over 1 h and stirred for 24 h at room temperature. The mixture was then poured very cautiously into methanol (250 ml) and the precipitate was filtered off. The crude product was washed with methanol and used without further purification. Yield: 5.47 g, 74%.

UV–Vis (λ_{max}, nm) ($CHCl_3$): 210, 235 and 269; FT-IR (cm^{-1}): 3148, 3029 (C–H aromatic); 2931, 2859 (C–H aliphatic); 1487, 1447 (C=C phenyl); 818 (C–Br).

2.3. Synthesis of PS-Carb macromonomer

CuI (0.057 g, 0.3 mmol), 18-crown-6 (0.026 g, 0.1 mmol), K_2CO_3 (1.66 g, 12 mmol), carbazole (1 g, 6 mmol) and N, N′-dimethylacetamide (DMA) (15 ml) were added to a round-bottom flask and vigorously stirred at 165 °C under argon. After 2 h, PS-Br (2.22 g, 12 mmol) was dissolved in DMA (50 ml) and slowly added into the mixture. The final mixture was heated to reflux for 30 h. The crude product solution was poured into 500 ml of methanol to precipitate the crude product, which was collected and dried under vacuum (yield: 2.14 g, 66%).

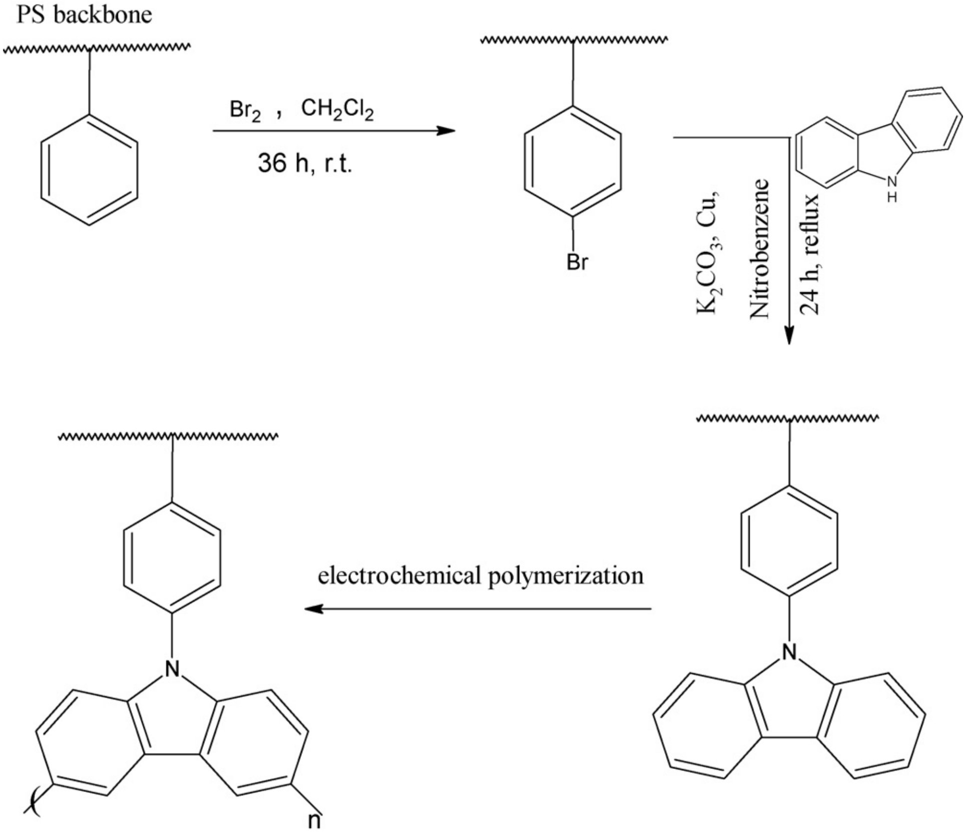
UV–Vis (λ_{max}, nm) ($CHCl_3$): 206, 215, 256 and 292. FT-IR (cm^{-1}): 3073, 3058, 3017 (C–H aromatic); 2921, 2850 (C–H aliphatic); 1589, 1514, 1485 (C=C phenyl); 1230 (C–N). ^1H NMR ($CHCl_3$-*d*): δ ppm, 6.33, (br, 2H, Ar-$H_{aa'}$); 7.18, (br, 2H, Ar-H_{bb}′); 7.42 (d, 2H, Ar-H_{cc}′); 7.25, (m, 4H, Ar-H_{ee}′, Ar-H_{ff}′); 8.09, (d, 2H, Ar-H_{gg}′); 1.66 and 1.24 (br, 4H, PS-backbone) (Scheme 1).



Scheme 1.

2.4. Electrochemical polymerization and characterization

Electrochemical synthesis and cyclic voltammetric measurements were performed using CH instruments 660C cyclic voltammetry. The polymer was synthesized from a reaction medium containing 2.0×10^{-3} M PS-Carb macromonomer and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in DCM via repetitive cycling at a scan rate of 100 mV/s. The polymer was coated on platinum (0.02 cm^2) or indium–tin oxide (ITO, 8–12 Ω, 0.8 cm × 5 cm). A platinum wire was used as a counter electrode and Ag/AgCl in 3 M KCl (aq.) solution as a reference. The potentials were calibrated to the ferrocene redox couple $E^\circ(Fc/Fc^+) = +0.38$ V in dichloromethane (DCM). After coating



Scheme 2.