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Soluble conjugated copolymers based on poly(1,4-phenylenevinylene)

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Abstract

Soluble conjugated copolymers containing 2-methoxy-5((4-(4-methoxyphenylazo) phenyloxy) hexyloxy) -1,4-phenylenevinylene (MHPV) and 2-methoxy-5-*n*-butoxy-1,4-phenylenevinylene (MBPV) units were prepared via a dehydrochlorination route. The copolymers were characterized by FTIR, ^{1}H NMR, GPC cyclic voltammetry, UV–Visible and photoluminescence spectroscopies. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Poly(phenylenevinylene) (PPV) is one of the most interesting electroactive polymers which has demonstrated high conductivity, relatively large third-order nonlinear optical (NLO) activity, and electroluminescent activity [1–4]. In recent years, PPV derivatives and their copolymers have been paid great attention to improve their solubility, electrical conductivity and other properties [5–7]. In the previous paper, we have reported a novel PPV derivative with an azobenzene side chain [8]. We selected (4(4-methoxyphenylazo) phenyloxy) hexyloxy group for the functionalization of PPV for two reasons:

1. The azobenzene has been widely used as mesogenic group in liquid crystalline polymers [9,10]. The functionalized polymer with the azobenzene might exhibit liquid crystal behavior, hence it would exhibit an anisotropic conductivity and give rise to improving the physical properties.
2. Azobenzene derivatives are photochromic and possess second NLO properties [11,12]. So the functionalized polymer might be not only a third-order NLO polymer but also a second-order NLO and photochromic polymer.

Here the synthesis and characterization of the copolymers containing 2-methoxy-5((4-(4-methoxyphenylazo)phenyloxy) hexyloxy) -1,4-phenylenevinylene (MHPV) and 2-methoxy-5-*n*-butoxy-1,4-phenylenevinylene (MBPV) units are reported.

2. Experimental

2.1. Materials and reagents

All the reagents used in this work are commercial products of high grade employed as received. Potassium *tert*-butoxide was prepared according to the literature [13].

2.2. Measurements

^{1}H NMR spectra were recorded with a Varian Unity 400 spectrometer (400 MHz), using deuteriated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a BIO-RAD FTS-7 spectrometer; the samples for study were pressed tablets with KBr. The molecular weights of the copolymers were determined by gel permeation chromatography (Waters 410 GPC) with styragel columns relative to polystyrene standards using tetrahydrofuran (THF) as eluent. Cyclic voltammetry experiment was carried out in a three-electrode compartment cell with a total volume of electrolyte solution (0.1 M Bu_4NClO_4 in acetonitrile), using a SCE as reference electrode, a platinum wire as counter electrode, and a platinum disc (effective area 0.5 cm^2) as working electrode, on which the thin polymer was coated by dipping. The cyclic voltammetry experiment

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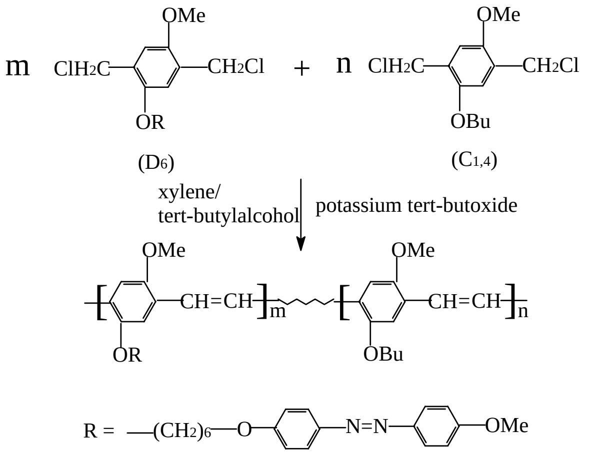

Fig. 1. Synthetic route to the copolymers.

was performed using a HPD-1A model potentiometer under nitrogen atmosphere. UV–Vis spectra were measured with a Shimadzu UV-3100 UV–Vis spectrophotometer. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301 PC spectrofluorometer.

2.3. Copolymer synthesis

The synthetic strategy is shown in Fig. 1. The synthesis of the compound D_6 and $C_{1,4}$ have been described elsewhere [14,15].

Copolymer 1: *N*-(-(4-methoxyphenylazo) phenyloxy)-hexyloxy-(-methoxy-2,5-bis(chloromethyl))benzene D_6 (0.106 g, 0.0002 mol), 2-methoxy-5-*n*-butoxy-α, α′-dichloro-*p*-xylene $C_{1,4}$ (0.166 g, 0.0006 mol), potassium *tert*-butoxide (0.224 g, 0.002 mol), *tert*-butylalcohol 5 ml, xylene 10 ml were placed in a three-necked flask equipped with a thermometer, stirrer and reflux condenser. The mixture was kept at reflux for 2 h in a nitrogen atmosphere. Following the start of the reaction, the viscosity of the medium increased and the color changed from yellow to fluorescent yellow and then to red. After the prescribed time, the mixture was cooled to room temperature, filtered. The red solution was poured into plenty of methanol and a red precipitate was obtained from the solution. Then the product was filtered, washed with water and methanol, and dried in vacuum at 60°C. The yield was 65%.

Copolymer 2 was synthesized using the same method with different amount of D_6 (0.319 g, 0.0006 mol) and $C_{1,4}$ (0.055 g, 0.0002 mol).

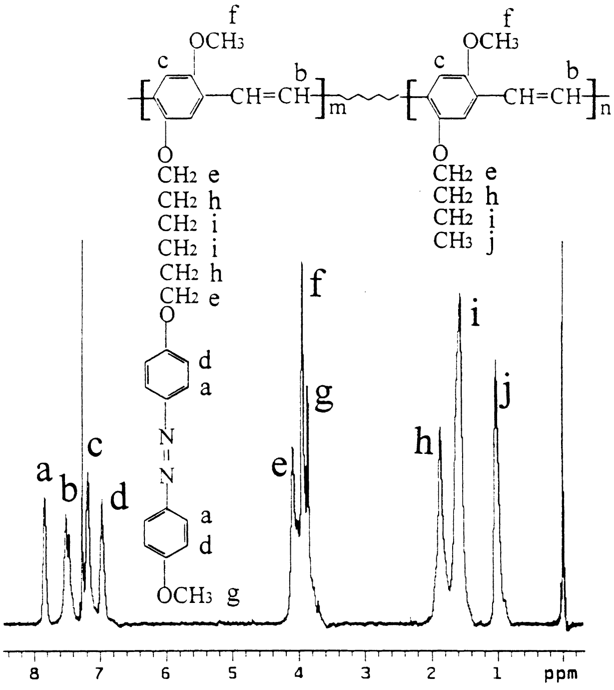

Fig. 2. ^{1}H NMR spectrum of copolymer 1.

3. Results and discussion

3.1. Synthesis

The approach to PPV formation has involved either polymers that are insoluble in their final form and are prepared via processible precursor polymers, or material that are soluble in their conjugated form [16]. In recent times much of the emphasis has rested on the soluble polymers because of their relative ease of processing into single-layer devices and their high luminescence yields [17,18]. In this work, the copolymers have been synthesized via a dehydrochlorination route, induced by potassium *tert*-butoxide in xylene and *tert*-butylalchol, which are soluble in organic solvents such as xylene, chloroform, THF and so on. This method is simple for its short reaction time and moderate reaction condition. The molecular weights of the copolymers 1 and 2 were determined to be $M_n = 3.04 \times 10^4$ and 2.16×10^4 by GPC, respectively. The molecular weight distributions (M_w/M_n) for the copolymers 1 and 2 were 3.56 and 2.61, respectively.

3.2. H NMR spectra

^{1}H NMR spectrum of copolymer 1 is shown in Fig. 2. One doublet peak assigning to the absorption of protons of *trans*-1,2-disubstituted olefin is observed at $\delta \approx 7.5$ ppm ($J = 18.4$ Hz), which indicates that the prepared copolymer 1 possessed *trans*-structure. The ratio of the MHPV and MBPV units in the copolymer can be determined by the following equation:

$$m/n = 3(\mathrm{Aa} + \mathrm{Ad})/8\mathrm{Aj}$$

where Aa, Ad and Aj are the integral areas of protons a, d and j, respectively. According to the equation, the ratio of the MHPV and MBPV units in copolymers 1 and 2 were 1:3.7 and 2.0:1, respectively.

^{1}H NMR spectrum of copolymer 2 is similar to that of copolymer 1, while the couple constant of the protons of *trans*-1,2-disubstituted olefin is 17.6 Hz, which is lower

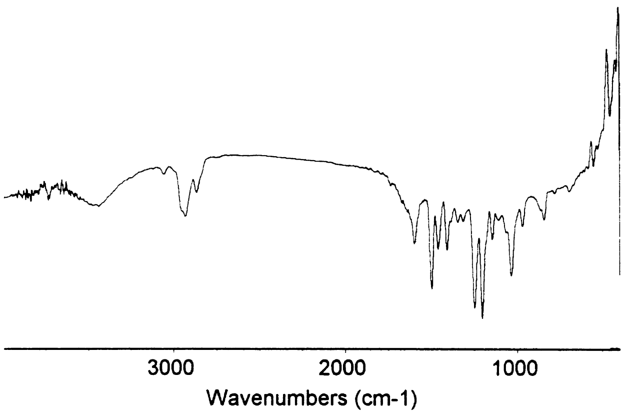

Fig. 3. FTIR spectrum of copolymer 1.

than that of copolymer 1 because of the increase of the amounts of MHPV units. The couple constants of poly(MHPV) and poly(MBPV) were 17.6 and 22.4 Hz, respectively [8,15].

3.3. FTIR spectra

FTIR spectrum of copolymer 1 is shown in Fig. 3. The valence bands of the aliphatic C–H groups are seen between 3000 and 2800 cm^{-1}. The aromatic ring vibrations and deformation vibrations of the side chains appear in the finger-print region between 1600 and 1300 cm^{-1}. The strong band at 1250 and 1205 cm^{-1} are attributed to the asymmetric Ar–O–C vibration. The strong band at 1036 cm^{-1} is attributed to the symmetric Ar–O–C vibration. The out-of-plane vibration of the aromatic hydrogen shows a medium absorption at 843 cm^{-1}. It should be noticed that there is one weak band at 3057 cm^{-1}, which is attributed to C–H stretching vibration of an olefin. A medium absorption corresponding to an out-of-plane C–H binding vibration of a *trans*-1,2-disubstituted olefin is observed at 964 cm^{-1}, which indicates that the synthesized copolymer possessed *trans*-structure. FTIR spectrum of copolymer 2 is similar to that of copolymer 1.

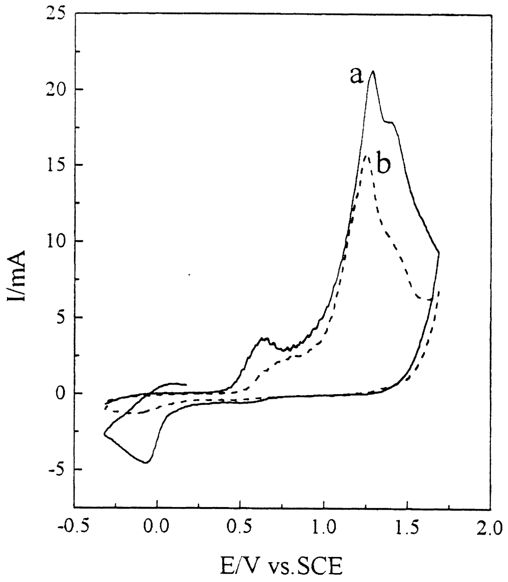

Fig. 4. Cyclic voltammograms of (a) copolymer 1 and (b) copolymer 2 films, scan rating: 50 mV/s.

3.4. Cyclic voltammetry

The electrochemical behavior of the copolymers was studied by cyclic voltammetry. The cyclic voltammograms of the copolymers 1 (curve a) and 2 (curve b) are shown in Fig. 4, which resemble the one observed for poly(MHPV) with two oxidation peaks [8]. The oxidation peaks at 0.7 and 1.3 V are attributed to the oxidation of the polyconjugated system and the azo dye, respectively, and the redox couples are both irreversible. From curves a and b, it can be seen that the oxidation peak related to the oxidation of the polyconjugated system of copolymer 1 is clearer than that of copolymer 2, as is caused by that the ratio of MBPPV of copolymer 1 is higher than that of copolymer 2.

3.5. UV–Vis and PL spectra

The UV–Vis and PL spectra of the copolymers 1 and 2 in chloroform are given in Fig. 5. Curves a and b are the UV–Vis spectra of the copolymers 1 and 2, respectively. Copolymer 1 exhibits two absorption bands centered at 360 and 478 nm, which are related to the π–π^* transitions of *trans* configuration of azobenzene moiety and the highly conjugated PPV units, respectively. While the copolymer 2 exhibits two absorption bands centered at 360 and 472 nm. It had been found that the poly(MHPV) also exhibited two absorption bands centered at 360 and 467 nm [8], and the poly(MBPV) exhibited one absorption band centered at 478 nm [15]. From the above, it can be concluded that the maximum absorption related to highly conjugated PPV units of copolymers increases with the increase of the ratio of MBPV unit in the copolymers. Curves c and d are the PL spectra of the copolymers 1 and 2 (excited at 470 nm), respectively, which show the maximum emissions of the copolymers are both at 550 nm. The maximum emissions of poly(MHPV) and poly(MBPV) in chloroform were also at 550 nm [8,15]. Hence it can be seen that the introduction of the azo benzene side chain into polyconjugated system has little effect on the PL of the PPV derivatives.

4. Conclusions

Soluble conjugated copolymers based on PPV have been designed and synthesized by combining 2-methoxy-5((4-(4-methoxyphenylazo) phenyloxy) hexyloxy) -1,4-phenylenevinylene (MHPV) and 2-methoxy-5-*n*-butoxy-1,4-phenylenevinylene (MBPV) units via a dehydrochlorination route. The prepared copolymers exhibited two absorption bands corresponding to the π–π^* transitions of *trans* configuration

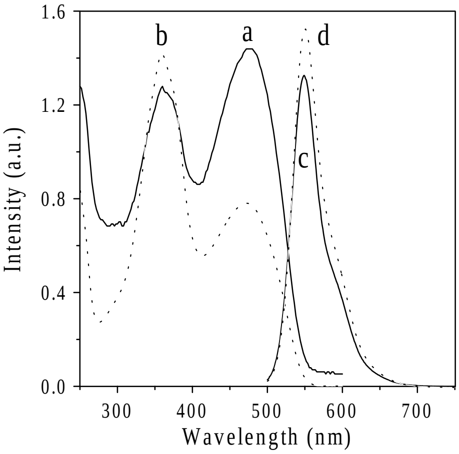

Fig. 5. UV–Vis spectra of: (a) copolymer 1; (b) copolymer 2 and PL spectra of: (c) copolymer 2; (d) copolymer 2 in $CHCl_3$.

of azobenzene moiety and the highly conjugated PPV units, respectively. The electrochemical behavior of the copolymers showed two oxidation peaks related to the oxidation of the polyconjugated system and the azo dye, respectively. The PL spectra of the copolymers in chloroform showed maximum emissions both at 550 nm. The third-order and second-order NLO and photochromic properties of the copolymers will be discussed later with its other properties.

Acknowledgements

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