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Conducting Copolymers of 3-Methylthienyl Methacrylate and p-Vinylbenzyloxy Poly(ethyleneoxide) and Their Electrochromic Properties

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Abstract: A random copolymer (CP) containing 3-methylthienyl methacrylate (MTM) and *p*-vinylbenzyloxy poly(ethyleneoxide) (PEO-VB) units was synthesized. Further graft copolymerization of CP with pyrrole (Py) and thiophene (Th) were achieved in H_2O - sodium dodecyl sulfate (SDS), H_2O - *p*-toluenesulphonic acid (PTSA) and acetonitrile (AN) - tetrabutylammonium tetrafluoroborate (TBAFB) solvent electrolyte couples via constant potential electrolyses. Characterization was performed by cyclic voltammetry (CV), nuclear magnetic resonance spectroscopy (NMR), and fourier transform infrared spectroscopy (FTIR). The morphologies of the films were examined by scanning electron microscopy (SEM). Conductivities of the samples were measured by using four-probe technique. Moreover, spectroelectrochemical and electrochromic properties of the copolymer obtained from thiophene were investigated by UV-Vis spectrometry and colorimetry.

1. Introduction

Interest in conducting polymers is largely due to the wide range of possible applications because of their facile synthesize good environmental stability and long-term stability of electrical conductivity. Despite the short history, they have found a place in various application areas such as rechargeable batteries, nonlinear optics, gas separation membranes, gas sensors, enzyme immobilization and electrochromic devices. Conducting polymers were synthesized by either chemical or electrochemical polymerization methods [1-3]. Electropolymerization has several advantages over chemical methods. Using electropolymerization, reactions are performed at room temperature and thickness of the films can be controlled. Polymer films are directly formed at the electrode surface and it is possible to obtain homogeneous films[4-7]. Although conducting polymers are used in several application areas, these applications are limited due to the poor mechanical properties and processabilities of conducting polymers. To improve mechanical properties of the films, graft or block copolymers with conventional and conducting sequences were synthesized. For this, polymeric precursors with functional groups within or at end of the chain are used. In these processes, electrochemically polymerizable thiophene moieties are incorporated into polymers by means of various polymerization methods [8-11].

Conducting polymers exhibit a change in their optical spectra when they are exposed to a dopant. Electrochromism is reversible and the visible change in the absorbance of a material as a result of an electrochemical oxidation or reduction is closely related with the band gap of polymer. Electronic band gap could be controlled structurally which in turn controls the redox and optical properties of the materials. The incorporation of electron-donating substituents onto a conjugated chain is a commonly employed strategy to decrease a polymer's oxidation potential by raising the energy of the valance band electrons, thus decrease the energy of the band gap. Copolymerization by introducing new groups changes the existing structure and band gap leading to absorbance at different wavelengths and colors. Among all conjugated polyheterocyclic polymers polythiophenes are of particular interest as electrochromic materials[12-17].

In this study, a random copolymer (CP) of 3-methyl thienyl methacrylate (MTM) and *p*-vinylbenzyloxy poly(ethyleneoxide) (PEO-VB), was synthesized chemically. Then, graft copolymer films of CP with pyrrole (CP/PPy) and CP with thiophene (CP/PTh) were synthesized. CP/PPy was synthesized in aqueous media using p-toluene sulphonic acid (PTSA) and sodium dodecyl sulfate (SDS) as supporting electrolytes. CP/PTh was synthesized in acetonitrile (AN) using tetrabutylammonium tetrafluoroborate (TBAFB) as the supporting electrolyte. The characterizations were done by Fourier transform infrared spectroscopy (FTIR), cyclic voltammetry (CV), scanning electron microscopy (SEM). The electrochromic and spectroelectrochemical behavior of the copolymers were also studied.

2. Experimental

Chemicals

Commercial reagents were purified according to usual procedures. Tetrahydrofuran (THF) was refluxed and distilled over sodium wire. Chloroform was dried over phosphorous pentaoxide and distilled over calcium hydride. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The reagents used for anionic polymerization of ethylene oxide (EO) and its end-capping, were purified and dried by the usual procedure using a vacuum line (10^{-5} mmHg), and sealed in ampoules fitted with breakable seals. EO was purified by repeated trap-to-trap distillations over calcium hydride and finally distilled over sodium mirror. 2-Methoxyethanol (Fluka, 99%) was dried and distilled under vacuum. *p*-Vinylbenzyl chloride (VBCl) was distilled over calcium hydride and stocked as THF solutions for end-capping reaction.

Triethylamine (TEA) (Merck), dichloromethane (DCM) (Merck), acetonitrile (AN) (Merck), chloroform (Merck), boron fluoride-ethylether (Aldrich) and methanol (Merck) were used without purification. Pyrrole (Aldrich) and thiophene (Aldrich) were distilled before use. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), sodium dodecyl sulphate (SDS) (Sigma) and p-toluene sulfonic acid (PTSA) (Sigma) were used as received.

Synthesis of 3-methylthienyl methacrylate (MTM)

3-Methythienyl methacrylate (MTM) was synthesized according to the following procedure: 3 Thiophene methanol, 5.7 g (50 mmol), triethylamine, 7.3 g (71 mmol) and a small amount of CuCl were dissolved in 35 mL of dry ethyl ether. Freshly distilled methacryloyl chloride, 5.35 g (51 mmol), in 35 mL of dry diethyl ether were added slowly at 0°C. The mixture was stirred for two hours. Triethylammonium chloride was filtered off through a silica gel column. After solvent evaporation, the residue was stirred overnight in 1:1 mixture of methylene chloride and 2 M NaOH. The organic layer was separated, washed twice with water and dried over $CaCl_2$. Following solvent evaporation residue was distilled in a vacuum over a Vigreux column.

b.p. (1mm-Hg) : 90°C; yield 70 %.

^{1}H-NMR ($CDCl_3$) : 1.9 (s, 3H, CH_3), 5.1 (d, 2H, OCH_2), 5.5 (d, 2H, vinyl H), 6.1 (d, 2H, vinyl H), 7.06 (m, 2H, ring H), 7.2 (m, 1H, ring H)

Synthesis of p-vinyl benzyloxy polyethylene oxide (PEO-VB)

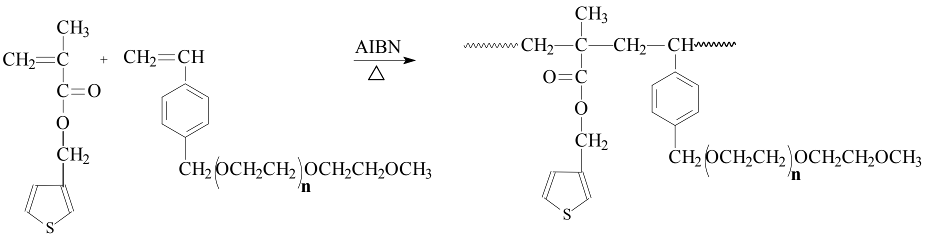
PEO macromonomers bearing *p*-vinylbenzyl end-group was prepared by a conventional high vacuum line technique[18]. 13.5 mmol of 2-methoxyethanol, 6 mmol of potassium naphthalene in THF, 295 mmol of EO and THF, each in an ampoule with a breakable seal, were fitted into a flask, baked under vacuum and sealed off from vacuum line. 2-Methoxyethanol and THF were introduced into a dried flask and then reacted with potassium naphthalene in THF. The dark green color due to potassium naphthalene almost immediately disappeared. Then, EO, chilled by dry ice/isopropanol, was introduced to the flask and polymerized at 40°C over 3 nights. Then the flask was fitted into a vacuum line with the ampoules containing 50 mmol of *p*-vinylbenzyl chloride (VBCl) and 15 mmol of triethylamine (TEA). After evacuation, the system was sealed off and the contents were mixed to terminate the poymerization by breaking the seals. The reaction took place immediately to a cloudy appearence indicating formation of KCl and Et_3NHCl. The mixture was poured into a large amount of acetone (700 mL) to precipitate the salts, which were filtered off. The filtrate was concentrated by a rotary evaporator under a reduced pressure to about 70 mL and poured into a large amount of hexane (700 mL). The macromonomer was collected by filtration and freeze-dried from hexane. The yield was almost quantitative.

^{1}H-NMR ($CDCl_3$) : 3.3 (s, 3H, OCH_3), 3.8 (m, 80H, OCH_2CH_2), 4.5(s, 2H, OCH_2), 6.7 (t, 1H, vinyl H), 5.4 (t, 1H, vinyl H), 5.6(t, 1H, vinyl H), 7.2 (m, 2H, ring H), 7.4 (m, 2H, ring H).

Synthesis of random copolymer (CP) of 3-methylthienyl methacrylate (MTM) and p-vinyl benzyloxy polyethylene oxide (PEO-VB)

PEO-VB (0.2 g) was dissolved in 1 mL dichloromethane. To this solution, 0.10 g ($5.5x10^{-4}$ mol) of 3-methylthienyl methacrylate was added. After adding AIBN, the tube was degassed by three freeze-pump-thraw cycles and sealed under vacuum. Polymerization was performed at 80°C for 3 hours. After the reaction time, the mixture was poured into n-hexane. The precipitated polymer was filtered off and dried in a vacuum oven. (Composition of MTM:PEO-VB = 91:9; Mn = 14000; Mw/Mn = 1.14 via GPC using PS standards)

^{1}H-NMR ($CDCl_3$) : 0.9 (s, 3H, CH_3), 1.2 (m, 2H, vinyl H), 1.3 (m, 2H, vinyl H), 2.2 (m, 1H, vinyl H), 3.3 (s, 3H, OCH_3), 3.6 (m, 80H, OCH_2CH_2) ,4.5 (s, 2H, CH_2), 4.8 (m, 2H, OCH_2), 6.8 (m, 2H, benzyl ring H), 6.9 (m, 2H benzyl ring), 7.1 (m, 1H, thienyl ring), 7.15 (m, 1H, thienyl ring), 7.2 (m, 1H, thienyl ring).



Scheme 1. Synthesis route of random copolymer (CP) of 3-methylthienyl methacrylate and p-vinylbenzyloxy poly(ethyleneoxide).

Cyclic voltammetry

The oxidation / reduction behavior of the random copolymer CP in the presence of thiophene and pyrrole was investigated by cyclic voltammetry (CV). The system consists of a potentiostat (Wenking POS 2), and X-Y recorder and CV cell containing platinum foil working and counter electrodes and a Ag/Ag^+ reference electrode. Measurements were carried out in AN-TBAFB solvent – electrolyte couple under nitrogen atmosphere at room temperature.

Synthesis of copolymer of CP with thiophene (CP/PTh)

A Wenking POS 73 potentiostat was used for the supply of a constant potential in the electrochemical polymerization. Electrolysis were performed under nitrogen atmosphere in conventional three-electrode cell by using platinum electrodes as the working and counter electrodes. Ag/Ag^+ was utilized as the reference electrode.

For the synthesis of copolymer of CP with thiophene, 15 mg of CP was dissolved in 15 mL of AN and 20 µL of thiophene was added into 15 mL of AN. The supporting electrolyte was TBAFB. Constant potential was run at 2.0 V for one hour at room temperature under inert atmosphere. Films were washed with AN to remove excess TBAFB after electrolysis.

Synthesis of copolymers of CP with pyrrole (CP/PPy)

Electrolysis was performed in two different media; water-PTSA and water-SDS solvent – electrolyte couples under nitrogen atmosphere. In both media, CP was coated onto the working electrode surface from its (1 %, w/v) dichloromethane solution. SDS and PTSA were used as the supporting electrolytes. Electrolyses were done at 1.1 V versus Ag/Ag^+ reference electrode. After electrolyses, films were washed several times with water to remove supporting electrolytes adsorbed on the films.

FT-IR spectroscopy

The FT-IR spectra of the pristine CP polymer and the copolymers of CP with thiophene and pyrrole were recorded on a Nicolet 510 FT-IR spectrometer.

Scanning electron microscopy

The morphologies of the copolymer films were investigated by scanning electron microscopy studies (SEM). SEM micrographs were obtained for the electrode side and solution side of the copolymer films. JSM 6400 scanning electron microscope was used for this purpose.

Electrochromic and spectroelectrochemical analysis

Electrochromic and spectroelectrochemical analyses experiments were done on an HP 8453 Diode-array UV–Vis Spectrophotometer. For spectroelectrochemistry studies, copolymer films were electrochemically synthesized on indium tin oxide (ITO) coated glass slides in a strong Lewis acid, boron fluoride ethyl ether, BF_3Et_2O (BFEE) by potentiostatic methods. In this case, ITO, Pt and Ag/Ag^+ were used as working, counter and reference electrodes respectively. The anodically coloring film was switched between the fully oxidized and fully reduced states. In order to ensure the access to maximum doping level, UV-Vis spectra of the film was recorded at various potentials in AN/TBAFB (0.1 M).

Colorimetry analysis was run in order to visually monitor the sample. To assign a quantitative scale color measurements, the CIE color spaces 1976 L*a*b system was used. The film prepared for spectroelectrochemical studies was switched in AN/TBAFB (0.1 M) and its colors at fully reduced and oxidized states were determined by Gretag-Macbeth Color-Eye XTH.

Results and Discussion

Cyclic voltammetry

The pristine CP polymer is not electroactive. However, after introducing Py into the solution, an increasing redox peaks showing the increase in electroactivity with increasing scan number were observed. When voltammogram of CP in the presence of Py was compared with the voltammogram of pure PPy, two important differences were observed. The redox peaks of CP/PPy system were more narrower than that of pure PPy. Also the first few scans did not reveal any electroactivitiy. These events show us that electro copolymerization between CP and Py is occuring and the product (graft copolymer of CP/PPy) does not behave like the pure PPy in voltammograms.

A similar trend was seen upon addition of Th into the solution that contains CP. When the voltammogram of CP/PTh system was compared with the voltammogram of pure Th system, it is seen that the redox peaks of CP/PTh were narrower than that of pure Th and a tilt was observed for the redox couple on the voltammogram of CP/PTh. These differences reveal that a reaction between CP and Th occurs (Figure 1).

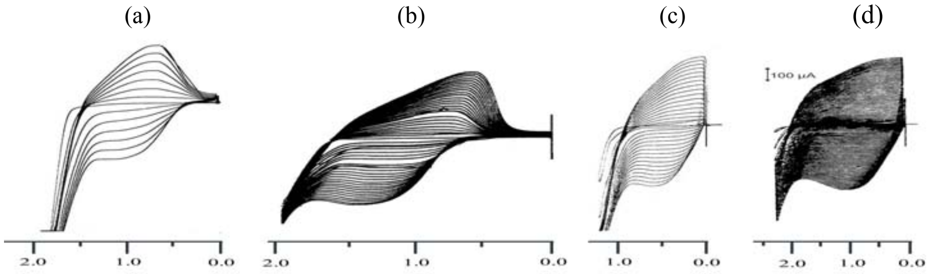


Figure 1. Cylic voltammogram of (a) PTh; (b) CP/PTh; (c) PPy; (d) CP/PPy.

FT-IR spectroscopy

Characteristic C-O-C asymmetric stretching peaks were detected at 1146 cm^{-1}, 1114 cm^{-1}, and 1061 cm^{-1}. The peaks at 1230 cm^{-1} and 1241 cm^{-1} are due to O=C-O-C stretching. The sharp intense peak at 1726 cm^{-1} can be attributed to carbonyl stretching vibrations. The peaks of CH_α stretching and CH_β stretchings of Th moieties are at 786 cm^{-1} and 842 cm^{-1} respectively. Also the peak at 1467 cm^{-1} is due to the aliphatic CH_2 vibrations.

FTIR spectra of electrochemically synthesized copolymers of SDS doped CP/PPy revealed a peak 1715 cm^{-1} belonging to the carbonyl group. In addition, O=C-O-C and C-O-C stretchings are at 1256 cm^{-1} and 1084 cm^{-1} respectively. Also the peak at 1627 cm^{-1} was due to the pyrrole chains. These data prove that CP/PPy copolymerization occured successfully.

In the FTIR spectrum of PTSA doped CP/PPy, carbonyl group at 1736 cm^{-1} is present. The peak at 1441 cm^{-1} belongs to pyrrole ring. The peaks at 1237 cm^{-1} and 1124 cm^{-1} are coming from O=C-O-C and C-O-C stretchings respectively.

FTIR spectrum of BF_4^- doped CP/PTh showed a characteristic peak of C-O-C at 1124 cm^{-1}. O=C-O-C stretching gave a peak at 1397 cm^{-1}. The peak at 871 cm^{-1} belongs to thiophene group. Moreover, the characteristic peak of carbonyl group at 1676 cm^{-1} was observed. This spectrum supports the synthesis of CP/PTh copolymers.

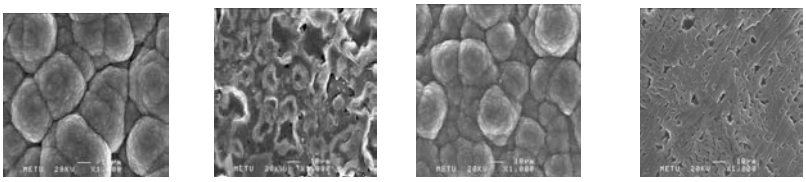
Scanning electron microscopy

The morphology of the solution side of CP/PTh films does not exhibit standard cauliflower structure. This provides yet another evidence that a new copolymer was synthesized.

The morphologies of the solution sides of CP/PPy copolymer synthesized in water-SDS and water-PTSA media, have cauliflowerlike structure.Yet, they have more compact globules than that of pure PPy (Figure 2).

Conductivities of the copolymer films

Conductivities of the copolymer films were measured by using four-probe technique. Conductivities of the solution and electrode sides of the copolymer films were found to be the same. Conductivities of the copolymers (doped with TBAFB, PTSA and SDS) were 0.4 ; 0.5; 0.8 s/cm respectively. This indicates the homogeneity of free-standing films



(a) (b) (c) (d)

Figure 2. SEM micrographs of (a) solution side of CP/PPy; (b) electrode side of CP/PPy in water-SDS medium. (c) solution side of CP/PTh; (d) electrode side of CP/PTh in AN-TBAFB medium.

Spectroelectrochemistry

In order to obtain information on the spectroelectrochemical and electrochromic properties of the resulting graft copolymers, films were prepared by performing the related polymerization on ITO-coated glass slides in BFEE potentiostatically at 1.4 V. At different potentials, a series of UV-Vis spectra were run. The λ_{max} values for the Π-Π^* transitions in the neutral state of CP/PTh was found to be 510 nm (Table 1). For comparison, the values for the PTh under the same conditions, 495 nm, is also given the Table 1. The electronic band gaps defined as the onset energy for the Π-Π^* transition, are at 1.92 eV for PTh and at 1.97 eV for CP/PTh, also included in Table 1.

This film was switched between the neutral (red color) and fully oxidized (blue color) states. With the applied voltage, the evolution of new absorption band ; the polaron charge carrier band at 770 nm was observed, while the intensity of the 510 nm band decreases. As the charge carrier bands at longer wavelengths (lower energy) increase in intensity with the application of increasing positive potentials with suitable increments, the Π-Π^* transitions currently decrease. This strong shift of the maximum absorption upon applied voltage is related to the electrochromic property of the polymer. The spectra for PTh and CP/PTh are similar but different in the ratio of polaron charge states accessed in the fully oxidized polymers (Figure 3).

Colorimetry measurements were performed for the films in an electrolyte solution of TBAFB (0.1 M)/ AN/ BFEE and films were synthesized in BFEE. The relative luminescence (L) and the a,b- values (CIE color space) were measured at the fully oxidized and neutral states. The color of the copolymer film switches from transmissive blue in the oxidized form to brick red in the reduced (neutral) form.

Table 1. Electrochemical, electronic and electrochromic properties of PTh and CP/PTh.

	λmax (nm)	*L*	*a*	*b*	*Eg(eV)*
PTh	495	(ox) 57	(ox) – 7	(ox) –2	1.92
		(red) 51	(red) 52	(red) 46	
CP/PTh	510	(ox) 34	(ox) – 5	(ox) – 7	1.97
		(red) 44	(red) 19	(red) 13	

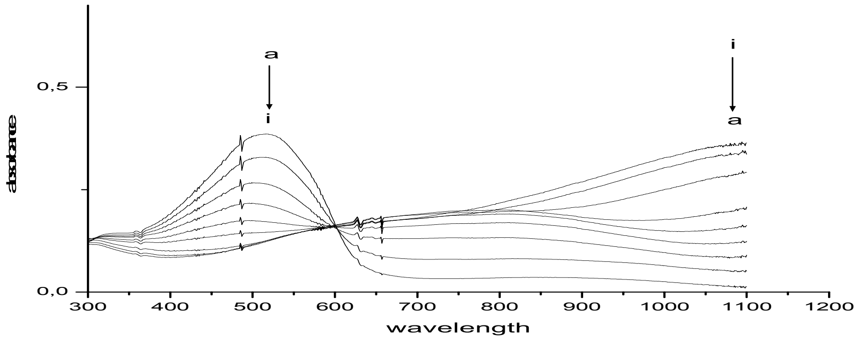


Figure 3. Spectroelectrochemical spectrum of CP/PTh (a: 0.2 V, b: 0.4 V, c: 0.5 V, d: 0.6 V, e: 0.7 V, f: 0.8 V, g: 1.0 V, h: 1.2 V, i: 1.4 V)

Conclusion

A random copolymer (CP) of 3-methylthienyl metacrylate and *p*-vinylbenzyloxy poly(ethyleneoxide) was synthesized. The syntheses of graft copolymers of CP with thiophene in AN-TBAFB solvent electrolyte couple and graft copolymers of CP with pyrrole in water-SDS and water-PTSA solvent-electrolyte couples were achieved by constant potential electrolysis.

It is shown that CP can be further graft polymerized in BFEE to yield homogeneous polymer films. The spectroelectrochemistry of the films synthesized in BFEE shows the accessibility and reversibility of both oxidized and reduced states. Coupled with colorimetry, this film is observed to exhibit distinctive and aesthetically pleasing color changes between blue to brick red.

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