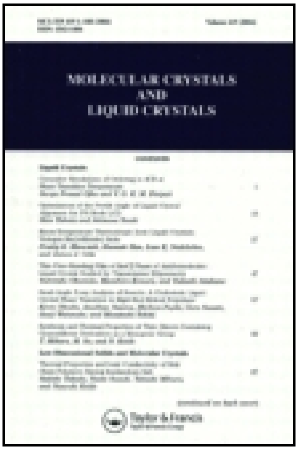

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Electrochemical Properties of Poly(Vinyl Carboxy Ethyl Ether)-g-Poly(Pyrrole)s with Different Length and Number of Branches

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Electroactive graft copolymers with different length and number of branches, poly(vinyl carboxy ethyl ether)-g-poly(pyrrole)s [PVCEE-g-(PPy)s] were able to be prepared according to the following steps; PVCEE was synthesized by reacting poly vinyl alcohol (PVA) with 3-chloloropropionic acid (CPA). Poly(vinyl pyrrolyl propanone ether) (PVPPE) was synthesized by fully or partially substituting carboxyl groups of PVCEE via carbonyl chloride groups with carbonyl pyrrolyl groups. Fully or partially substituted pyrrolyl groups in PVPPE act as the nuclei for electrochemical polymerization of pyrrole. Electroactive graft copolymers with different number of branches and length of pyrrolyl groups were finally obtained by keeping the total number of repeating groups of all branches constant on electrochemical polymerization of pyrrole on pyrrolyl groups of PVPPE. The differences of electrochemical properties and electroconductivity of these PVCEE-g-(PPy)s were investigated using cyclic voltammetry (CV) and chronoamperometry (CA). Synthesis of PVCEE-g-(PPy)s was characterized using FT-IR spectroscopy and ^{1}H-NMR.

Keywords: conducting graft copolymer; electrochemical polymerization; electrochemical properties; polypyrrole

1. INTRODUCTION

Conducting polymers have been applied to various fields such as in chemical sensor [1], light emitting diode [2], EMI shielding [3], electrochromic display device [4], rechargeable battery [5,6], photovoltaic cell [7] etc. They have good electrical properties but usually have poor

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environmental stability, physical properties, and processibility. To overcome these defects, various methods such as reforming the monomers of the conducting polymers and preparing copolymers [8–10] and composites [11] have been reported.

Previously the authors synthesized already poly(vinyl carboxy ethyl ether)-g-poly(pyrrole) (PVCEE-g-PPy) [10]. In this study, the authors have prepared various [PVCEE-g-(PPy)s] with different number of branches and length of pyrrolyl groups and have investigated the differences of electrochemical properties and electroconductivity of these graft copolymers.

2. EXPERIMENTAL

2.1. Chemicals

Pyrrole (Aldrich) and dimethyl sulfoxide (DMSO) (Aldrich) were dried over CaH_2 and distilled under reduced pressure. Poly(vinyl alcohol) (PVA) with the molecular weight of 50,000 g/mol (Aldrich) was used without further purification and potassium hydride (Aldrich) was used after removing mineral oil. Other chemicals were purchased from Aldrich and used without further purification.

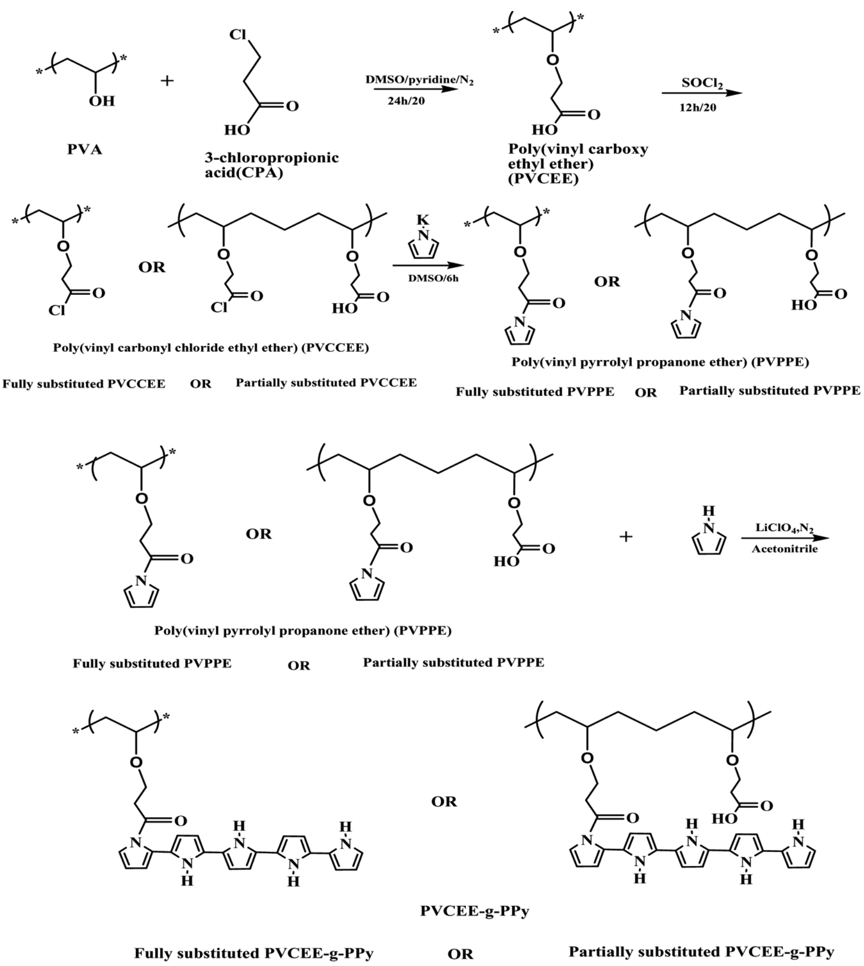
2.2. Synthesis of PVCEE-G-(PPy)s

PVCEE-g-(PPy)s were synthesized through the following procedures and the schematic routes are shown in Scheme 1.

PVCEE was first synthesized by reacting PVA with 3-chlolopropionic acid (CPA) for 24 hrs at room temperature under N_2 atmosphere in DMSO. PVCEE was precipitated by pouring the solution to methanol/water mixture. The precipitate was filtered and dried at 80°C under vacuum.

The precursor polymer, poly(vinyl pyrrolyl propanone ether) (PVPPE), was synthesized from PVCEE through the following two steps; Poly(vinyl carbonyl chloride ethyl ether) (PVCCEE) was synthesized by reacting PVCEE with exact mole concentration of $SOCl_2$ for intended degree of substitution for 12 hrs at room temperature under N_2 atmosphere in DMSO. The PVCCEE solution was then added to a flask which contains potassium pyrrole salt solution in DMSO at room temperature. The reaction was continued for 8 hrs at room temperature under N_2 atmosphere. PVPPE powder was obtained by pouring the solution to methanol and drying at 60°C under vacuum.

Finally, PVCEE-g-(PPy)s with different length and number of branches were synthesized on an electrode coated with PVPPE by



SCHEME 1 Synthetic routes for preparing fully or partially substituted PVCEE-g-PPy.

applying intended potential using potentiostat (EG&G 273A) in the electrolyte solution consisting of 0.1 M pyrrole monomer and 0.1 M lithium perchlorate in acetonitrile. In this electrolysis, a standard three-electrode cell was employed, where a square-type ($1 \times 1\,\mathrm{cm}^2$) platinum working and counter electrodes and an Ag/AgCl reference electrode were used. The applied potential range for electrochemical polymerization was $-2 \sim 2\,\mathrm{V}$ (vs. Ag/AgCl) and the scanning rate was 50 mV/sec.

The chemical structure of synthesized PVCEE-g-(PPy)s was characterized using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy.

Electrical conductivity was measured by a four-probe method (Fluke, Model 73°C Multimetry).

3. RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCEE-g-PPy and (c) one fourth substituted PVCEE-g-PPy. As shown in Figures 1(a), (b) and (c) the appearance of

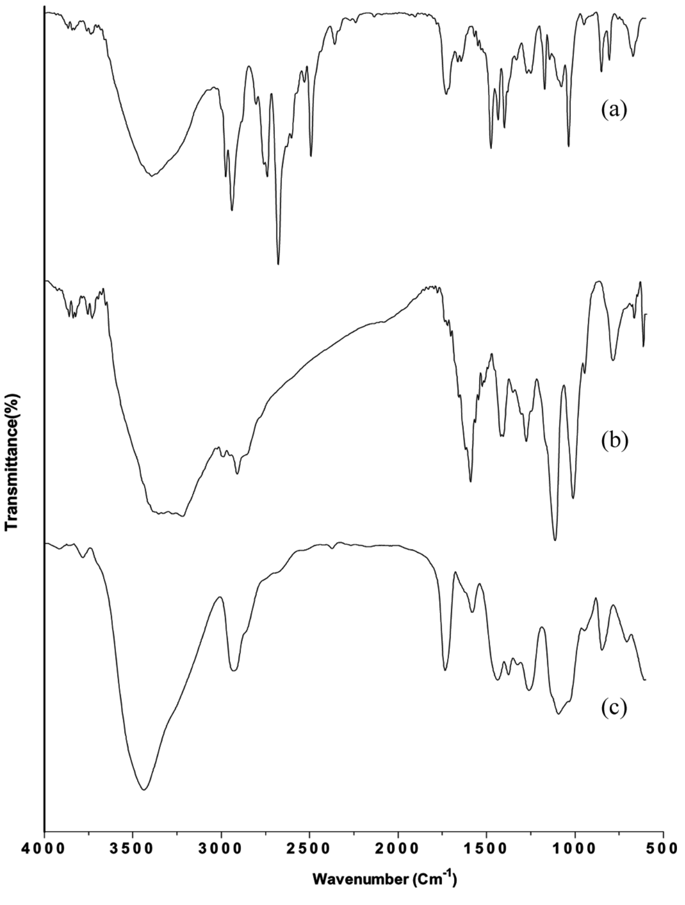
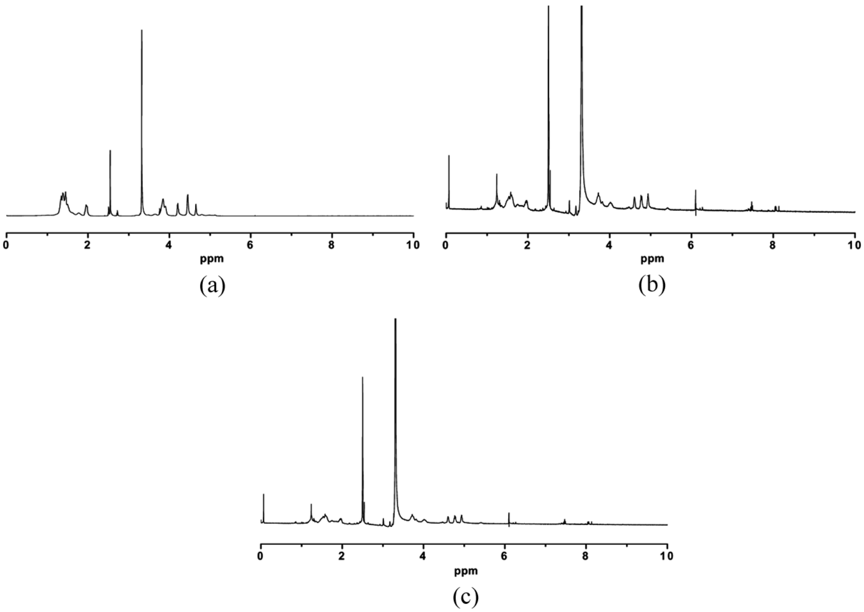


FIGURE 1 FT-IR spectra of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCCE-g-PPy and (c) one fourth substituted PVCEE-g-PPy.

the peaks at 1440–1490 cm^{-1} and 1030–1090 cm^{-1} are due to C=C and C-N stretching of the pyrrolyl groups, respectively and the strong peaks at 3250–3350 cm^{-1} shown in Figures 1(b) and (c) remain due to partial substitution of carboxyl groups with pyrrolyl groups.

Figure 2 shows the ^{1}H-NMR spectra of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCEE-g-PPy and (c) one fourth substituted PVCEE-g-PPy. The peaks at 4.2–4.7 ppm Shown in Figures 2(a), (b) and (c) are due to the protons of pyrrolyl groups but the peaks at 7.5–8.5 ppm shown in Figures 2(a) and (b) are due to the protons of carboxyl groups. From the results of Figures 1 and 2 it could be supposed that the carboxyl groups of PVCEE are fully or partially substituted with carbonyl pyrrolyl groups and consequently fully or partially substituted PVCEE-g-PPy could be prepared as it was intended.

Figure 3 shows the cyclic voltammograms obtained during the process of preparing fully substituted PVCEE-g-PPy and partially substituted PVCEE-g-PPy with 0.1 M pyrrole and 0.1 M lithium perchlorate in acetonitrile. As shown in Figure 3 the current peaks of half substituted PVCEE-g-PPy copolymer are higher than those of

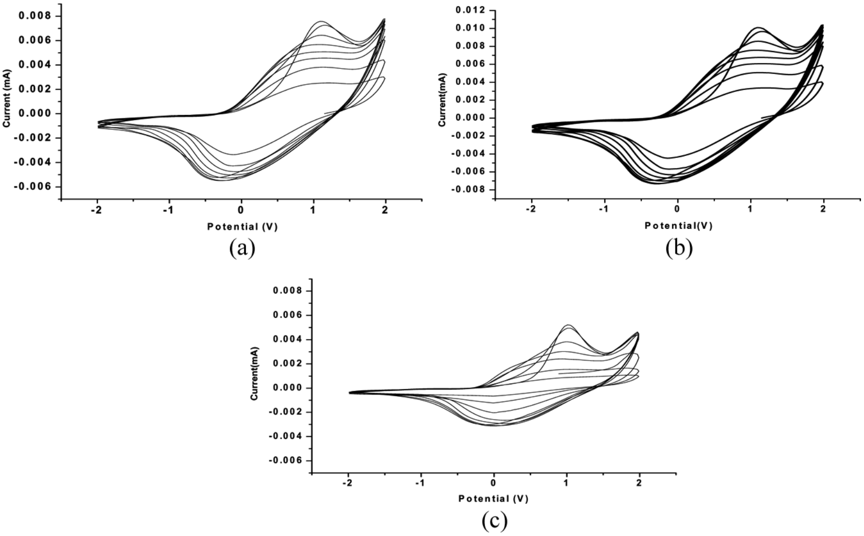


(a)

(b)

(c)

FIGURE 2 ^{1}H-NMR spectra of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCCE-g-PPy and (c) one fourth substituted PVCEE-g-PPy.



(a) (b)

(c)

FIGURE 3 Cyclic voltammograms of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCCE-g-PPy and (c) one fourth substituted PVCEE-g-PPy in 0.1 M pyrrole and 0.1 M lithium perchlorate electrolyte solution in acetonitrile at 50 mV/s scan rate.

the other PVCEE-g-PPy copolymers. From the results of Figure 3 it may be concluded that the optimum number of electroconductive branches are needed for higher electrochemical activity when the total number of electroconductive repeat unit of all branches in the graft copolymers is same. A plausible explanation is that under the same total number of electroconductive repeat unit of all branches, the more the number of branches the shorter the length of electroconductive branches and the less the number of branches the longer the length of electroconductive branches, both cases result in the more discontinuity between electroconductive neighboring branches than the case with optimum number of electrocunductive branches in the bulky graft copolymers.

Figure 4 shows chronoamperograms of fully substituted PVCEE-g-PPy and partially substituted PVCEE-g-PPy copolymers that were polymerized for 1 hr under the constant potential of 0.7, 0.9, 1.1, 1.3 and 1.5 V using PVPPE as the precursor. As shown in Figure 4, when half substituted PVCEE-g-PPy was synthesized, the oxidation current flows much more and polymerization proceeds more rapidly at the same potentials than when the other PVCCE-g-PPy copolymers were synthesized. The higher oxidation current and faster polymerization

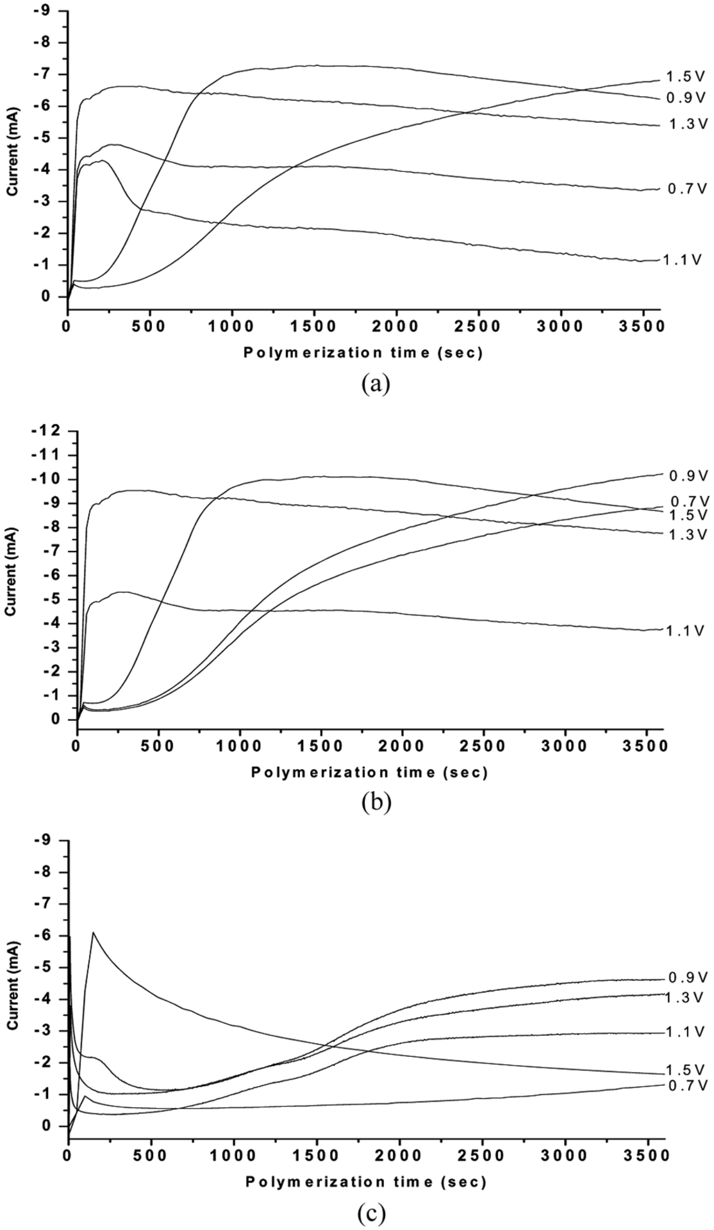


FIGURE 4 Chronoamperograms of (a) fully substituted PVCEE-g-PPy, (b) half substituted PVCCE-g-PPy and (c) one fourth substituted PVCEE-g-PPy at constant potentials of 0.7, 0.9, 1.1, 1.3 and 1.5 for 1 hr.

of PPy in the half substituted PVCEE-g-PPy are also resulted from the optimum number of electroconductive PPy branches in PVCEE-g-PPy.

The conductivities of fully substituted PVCEE-g-PPy, half substituted PVCEE-g-PPy and one fourth substituted PVCEE-g-PPy prepared for 1 hr under the constant potentials of 0.5 V were 1.70×10^{-1}, 2.84×10^{-1} and 1.58×10^{-1} S/cm, respectively. This electrical activity is also consistent with the results of electrochemical activities. The explanation for these results is the same as mentioned of the electrochemical activities. That is, fully substituted PVCEE-g-PPy has shorter distance between electroactive branches but has shorter length of electroactive branches. One forth substituted PVCEE-g-PPy has longer distance between electroactive branches but longer length of electroactive branches. Both structures may not be satisfied for continuous contacts of the electroactive branches. However, half substituted PVCEE-g-PPy may have optimum structure for the continuous contacts of the electroactive branches which result is higher electrochemical and electrical activities.

4. CONCLUSION

Fully and partially substituted PVCEE-g-PPy copolymers can be synthesized by the electrochemical polymerization of pyrrole using the precursor, PVPPE which has fully or partially substituted carbonyl pyrrolyl groups.

The half substituted PVCEE-g-PPy copolymer showed higher electrochemical and electrical activities compared to other PVCEE-g-PPy copolymers. The electrical conductivity of the half substituted copolymer was 2.84×10^{-1} S/cm. The higher electrochemical activities and conductivity are resulted from the optimum number of electroconductive branches of pyrrolyl groups in bulky PVCEE-g-PPy graft copolymer.

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