Electroactive Polymeric Materials for Battery Electrodes: Copolymers of Pyrrole and Pyrrole Derivatives with Oligo(ethyleneoxy) Chains at the 3-Position

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ABSTRACT: The electrochemical polymerization of pyrrole derivatized at the 3-position with an oligo(ethyleneoxy) group was investigated. Two monomers were synthesized, namely, 3-(3,6-dioxaheptyl)pyrrole (DHPy) and 3-(3,6,9-trioxadecanyl)pyrrole (TDPy), and homopolymerized in a $LiClO_4$/propylene carbonate medium. The electrical conductivity of poly[3-(3,6-dioxaheptyl)pyrrole] (PDHPy) and poly[3-(3,6,9-trioxadecanyl)pyrrole] (PTDPy), measured by the four-point probe method, was 0.08 and 15 S cm^{-1}, respectively. Electrochemical copolymerization of both oligo(ethyleneoxy)-substituted pyrroles with pyrrole led to good quality films which displayed considerably higher electrical conductivity than the homopolymers. The conductivity of the copolymer with DHPy was in the range from 8 to 10 S cm^{-1} and that with TDPy in the range from 20 to 100 S cm^{-1}. The cyclic voltammogram of both homopolymers and of the copolymers gave current–potential curves with larger areas (ca. 3 times) than PPy. The copolymer of TDPy and pyrrole showed that it was capable of supplying the same current for a longer period of time than polypyrrole itself. No stability problems were observed with the copolymers in contrast to the homopolymer films, and the samples charged and discharged smoothly. In scanning electron micrography, copolymers showed larger nodules than the homopolymer which entirely cover the surface of the compact layer. The results of the copolymer systems show that they have a high potential as materials for polymeric battery electrodes.

Introduction

Recently, π-conjugated organic polymers having benzenoid or heterocyclic units, such as poly(*p*-phenylene),[2] polyaniline,[3] polythiophene,[4] and polypyrrole,[5] have attracted a great deal of attention as electrical conducting materials,[6] including the development of new conducting polymers by modification of the monomer.[7] However, the longstanding goal of developing an all-polymer battery system suitable for secondary commercial cell applications has not been achieved to date due to the lack of appropriate polymer electrodes. Polymer electrolytes of the poly(ethyleneoxy) type containing a lithium salt are currently being used to develop practical secondary lithium batteries of the following type:

$$- \text{Li/polymer electrolyte } (Li^+)\text{/cathode } +$$

Currently the cathodes of choice are Ti_2S or V_6O_{13} with Li^+ intercalated into its van der Waals gap. Major improvements of such polymer electrolyte batteries could be obtained by the use of mixed ionic and electronic conducting polymers as the electrodes of such cells, because the interface between the electronically conducting polymer and the nonaqueous electrolyte, usually a lithium salt in an ethylene oxide solvent, presents a substantial barrier.[8]

In this work, we propose to minimize this barrier by attaching oligo(ethyleneoxy) groups to the electrically conducting polymer. We chose pyrrole (Py) as the electronically active nucleus and will incorporate oligo(ethyleneoxy) units onto the polypyrrole (PPy) polymer backbone. A reasonably straightforward method to synthesize such polymers is by the synthesis and polymerization of oligo(ethyleneoxy)-substituted pyrroles. The 3-position appears to be the position of choice based on previous experience with substituted pyrroles, because it leaves the 2- and 4-positions open for the electrochemical polymerization. The covalent graft of the ether chains on the conjugate system is expected to exhibit an effect on both the electronic and the ionic conductivity. Therefore, this concept is of great potential interest for the design of ion-selective electrodes or for interfacing conducting polymers with ionic conductors such as oligo(ethyleneoxy) in all solid-state batteries.[9]

Very few derivatives of PPy with a polyether chain at the 3-position have been synthesized to date due to the difficult synthesis of the monomer. Recently, one of these 3-oligo(ethyleneoxy) derivatives of polypyrrole, poly[3-(3,6-dioxaheptyl)]pyrrole, has been reported by Delabouglise and Garnier.[9a]

In this paper, a new synthetic route for pyrroles substituted at the 3-position with a polyether functionality is described. We also describe the successful electrochemical oxidative polymerization of 3-(3,6-dioxaheptyl)pyrrole (DHPy) and 3-(3,6,9-trioxadecanyl)pyrrole (TDPy) and the electrochemical copolymerization of both oligo(ethyleneoxy)-substituted pyrroles with pyrrole. The structure and electrochemical property relationships are investigated by electrical conductivity, cyclic voltammetry, charge and discharge tests, and scanning electron micrography.

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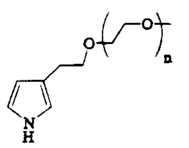


DHPy n=1
TDPy n=2

Experimental Section

Materials. Pyrrole and chloroacetyl chloride, purchased from Aldrich, were purified by distillation and stored a nitrogen atmosphere. Propylene carbonate, used as solvent for polymerization, was distilled over molecular sieves (5 Å) prior to use and stored under nitrogen. $LiClO_4$ and the other reagents were used as reagent grade without further purification.

Synthesis of the Monomers. Most procedures for the preparation of the monomers were carried out according to modified literature methods.[9a,10] However, the key intermediate for this synthesis, 3-(chloroacetyl)-1-tosylpyrrole, was performed by direct Friedel–Crafts acylation with chloroacetyl chloride.

3-(Chloroacetyl)-1-tosylpyrrole. To a suspension of anhydrous $AlCl_3$ (5.32 g, 40 mmol) in 50 mL of 1,2-dichloroethane at 25 °C was added dropwise chloroacetyl chloride (4.52 g, 40 mmol). The resulting solution was stirred at 25 °C for 1 h, and a solution of *N*-tosylpyrrole (4.43 g, 20 mmol) in 30 mL of 1,2-dichloroethane was added. The mixture was stirred at 25 °C for another 1 h. The reaction was quenched with 0.5 N HCl, and the product was extracted with dichloromethane. The extracts were washed with brine, 0.1 N NaOH, and brine, dried over Na_2SO_4, and concentrated at reduced pressure. Chromatography on a column of silica gel (70–230 mesh), eluting with 4:1 hexane/ethyl acetate, followed by recrystallization from methanol, gave 77% yield. Mp: 116–118 °C. ^1H NMR ($CDCl_3$): δ 2.43 (3H, CH_3), 4.43 (2H, CH_2Cl), 6.76 (1H, C_4H), 7.15 (1H, C_5H), 7.80 (1H, C_2H), 7.34–7.37 (2H, m), 7.79–7.84 (2H).

3-[(2-Methoxyethoxy)acetyl]pyrrole and 3-(3,6-dioxaheptyl)pyrrole (DHPy) were synthesized according to modified literature methods.[9a,10] To a 100-mL three-neck flask, fitted with a thermometer, a condenser with a bubbler, and an argon inlet were added 3.42 g (11.5 mmol) of 3-(chloroacetyl)-*N*-tosylpyrrole, 50 mL of 2-methoxyethanol, and 1.3 g (35 mmol) of lithium bromide. The solution was heated to reflux (145 °C) under argon for 24 h. After cooling 20 mL of 5 N aqueous sodium hydroxide was added, and the mixture was stirred for 24 h. Brine (20 mL) was added, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, and dried over sodium sulfate. The solvent was evaporated, and the crude product (2.82 g) was dissolved in a small amount of methanol. The product was purified by column chromatography on silica (60–200 mesh) using 1:1 hexane/ethyl acetate as eluent. The product, 3-[(2-methoxyethoxy)-acetyl]pyrrole, crystallized upon cooling. Yield: 0.62 g (30%). Mp: 69 °C ^1H NMR ($CDCl_3$): δ 7.75 (m, 1H), 6.94 (m, 1H), 6.82 (1H), 4.73 (s, 2H), 3.9 (m, 2H), 3.77 (m, 2H), 3.55 (s, 3H).

Lithium aluminum hydride (0.58 g, 15 mmol) was added to 20 mL of tetrahydrofuran, distilled over sodium under an argon atmosphere. A solution of 3-[(2-methoxyethoxy)acetyl]-pyrrole (0.55 g, 3 mmol) in 30 mL of dry THF was added slowly at room temperature. The mixture was heated to reflux for 1.5 h, cooled, and quenched slowly with brine under argon. The resulting precipitate was filtered off and washed with THF. THF was evaporated, and the resulting aqueous mixture was extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 0.55 g of crude product. The latter is distilled at 1.5 mmHg to give 0.4 g (80% yield) of DHPy as a colorless liquid. ^1H NMR ($CDCl_3$): δ 8.0 (m, 1H), 6.56 (m, 1H), 6.47 (m, 1H), 5.95 (m, 1H), 3.5 (m, 6H), 3.25 (s, 3H), 2.67 (t, 2H). IR (KBr): 3370, 2895, 1118, 1095, 1071 cm^{-1}.

3-[[(2-Methoxyethoxy)ethoxy]acetyl]pyrrole and 3-(3,6,9-trioxadecanyl)pyrrole (TDPy) were synthesized in the same manner as described above in higher combined yields (50% than DHPy (30%), as a colorless viscous liquid. Bp: 160–170 °C/1.5 mmHg. ^1H NMR ($CDCl_3$): δ 2.79 (2H, CH_2), 3.4 (3H, CH_3), 3.55 (2H, CH_2O), 3.65 (8H, CH_2, CH_2O), 6.08 (1H), 6.6 (1H), 6.7 (1H).

Electrochemical Homopolymerization. The electrochemical polymerizations were performed in the presence of a magnetic stirrer in a one-compartment cell with a platinum plate as the working electrode, a platinum wire as the counter electrode, and a sodium saturated calomel electrode (SSCE) as the reference electrode. All the electrode potentials cited in this paper were referenced to SSCE. Typically, a reaction vessel contained 0.5 M monomer(s) and 0.1 M Bu_4NClO_4 or 0.1 M $LiClO_4$ in propylene carbonate solvent. The solution containing electrolyte and monomer was purged with nitrogen for about 30 min before polymerization. The thickness of the prepared film was measured by observations with a scanning electron microscope. The samples were exposed to laboratory atmosphere when they were transferred to the measurement equipment, washed with fresh electrolyte and acetone, and characterized by elemental analysis. However, the samples for the charge and discharge test were kept in a fresh electrolyte solution under a nitrogen atmosphere at all times.

Electrochemical Copolymerization. Electrochemical copolymerizations of Py with DHPy or TDPy were carried out in a one-component cell as described above.

Cyclic Voltammetry. Cyclic voltammograms were recorded in a one-compartment cell with a platinum plate (0.5 × 0.5 cm) as the working electrode, a platinum wire as the counter electrode, and a sodium saturated calomel electrode (SSCE) as the reference electrode under a nitrogen atmosphere. The solution for the cyclic voltammograms was 1 M $LiClO_4$ in propylene carbonate. The solution was purged with nitrogen for about 30 min before use, and a positive pressure of nitrogen was maintained throughout the experiment.

Charge and Discharge Test. Charge and discharge tests were carried out in a on-compartment cell with three electrodes in a drybox under constant argon flow. The electrolyte consisted of 0.1 M $LiClO_4$ in 25 mL of propylene carbonate. Excess oxygen was burned using a palladium catalytic heater. The heater kept the temperature inside the drybox at a constant 30 °C. Lithium ribbon was used as the counter and reference electrodes. The electrodes were kept parallel to each other, and the working electrode was placed between the counter and reference electrodes through manual manipulations in the cell. The sample was first charged, using 100 μA, to a given potential and then open-circuited for 30 s. After this, the sample was discharged at a rate of 500 μA. Data were then collected via a GPIB interface with an IBM compatible computer.

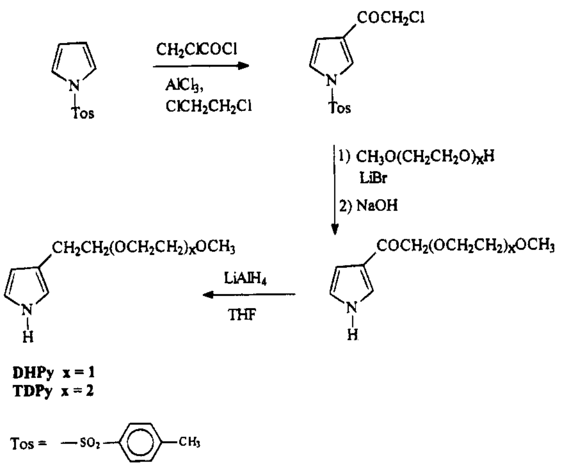
Scanning Electron Micrographs (SEM). The samples were scraped off the platinum foil and viewed both without being charged and discharged and after being charged and discharged. The scraping process destroyed the sample. Thus, a before and after analysis was not possible.

Polymer Characterization. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 983 infrared spectrophotometer. NMR spectra in solution were taken at ambient temperature on a Bruker WM-250 NMR spectrophotometer. The electrochemical polymerization and cyclic voltammetry were performed using a Bioanalytical System SP-2 potentiostat and a CU-1B cyclic voltammograph, respectively. Elemental analyses were performed by Desert Analytics, Tucson, AZ. The electrical conductivity of doped samples was measured with films prepared by electrochemical polymerization (*vide ante*) using the four-point probe method at room temperature (ca. 25 °C). The equipment used for the charge and discharge test consisted of a Keithley 274 programmable current source and a Keithley 175A digital voltage meter. The scanning electron microscopy (SEM) of the samples was observed with a Jeol JSM 840 A.

Results and Discussion

Syntheses of the Monomers. Scheme 1 shows the synthesis route for the pyrroles containing an oligoether chain (n = 1, 2), DHPy and TDPy.

Scheme 1



The synthetic method for DHPy has been described in the literature. The key intermediate, 3-(chloroacetyl)-1-tosylpyrrole, was previously obtained by selective chlorination of 3-acetyl-*N*-tosylpyrrole using 2,3,4,5,6,6-hexachlorohexa-2,4-dien-1-one.[9a] However, we obtained 3-(chloroacetyl)-*N*-tosylpyrrole successfully by a one-step direct acylation of *N*-tosylpyrrole with chloroacetyl chloride in high yield (77%).

A new monomer having a longer ethyleneoxy chain ($n = 2$), TDPy, was synthesized using the same synthesis route. TDPy was obtained in higher yield than DHPy. The monomers were purified by Kugelrohr distillation under high vacuum.

Homopolymerization. The electrochemical polymerizations were carried out in the presence of a magnetic stirrer in a one-compartment cell with a platinum plate as the working electrode, a platinum wire as the counter electrode, and a sodium-saturated calomel electrode (SSCE) as the reference electrode. Electrochemical oxidation polymerization of Py, DHPy, and THPy gave good quality blue–black films.

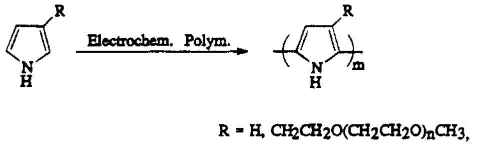
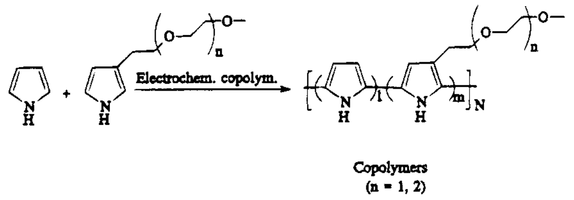


Table 1 summarizes the results of the preparation of polypyrrole (PPy), poly[3-(3,6-dioxaheptyl)pyrrole] (PDHPy), and poly[3-(3,6,9-trioxadecanyl)pyrrole] (PTDPy). The solutions used for the preparation of good quality films typically contained 0.05 M of the appropriate monomer with 0.1 M electrolyte in propylene carbonate. The electrochemical polymerization proceeded smoothly without any color change of the polymerization solution. The film thickness was controlled by the polymerization time. Films of sufficient quality to measure electrical conductivity were obtained.

Microanalysis and conductivity values of the obtained homopolymers are also presented in Table 1. Microanalysis of these films showed some excess oxygen weight percent due to some overoxidation of the pyrrole ring, even though the polymerizations were carried out under low applied potentials (under 0.45 V *vs* SSCE). Overoxidation of pyrrole in the chemical and electrochemical polymerization has already been reported in the literature.[11] However, the excess oxygen could also be due to covalently bound oxygen from the presence of traces of water present during the electropolymerization or from incorporation of oxygen as a molecular complex due to exposure to laboratory air.[12] The ratios of the obtained C, H, and N for the homopolymers are close to the calculated values even though the absolute calculated values for C, H, and N are considerably smaller. This is due to the high counterion content present in the polymer film. These microanalysis results and counterion content in polypyrrole are in good agreement with previously reported results.[13] If we assume that chlorine exists in the form of perchlorate ions in the polypyrrole, then there is approximately one anion per three pyrrole rings. In the case of the homopolymers of the two derivatives, higher doping levels were obtained of approximately one anion per 2.5 monomer units.

The room-temperature electrical conductivity of the ClO_4^--doped polypyrrole was 60 S cm^{-1} as measured by the four-point probe method. The homopolymers of the pyrrole derivatives prepared in the same polymerization conditions showed lower conductivity values than polypyrrole itself. PDHPy gave a lower value 0.08 S cm^{-1} than reported in the literature[9a] (2.2 S cm^{-1}), while PTDPy, polymerized at 1 mA in the 0.3–0.45 V range, gave a much higher electrical conductivity (15 S cm^{-1}) than PDHPy.

Electrochemical Copolymerization. Electrochemical copolymerizations of DHPy or TDPy with Py were carried out using the same method in a one-compartment cell as described above at 0.05 M total monomer concentration and the results are summarized in Table 2.



The electrochemical copolymerization proceeded smoothly and gave good quality films. Microanalysis and conductivity values of the obtained copolymers are also presented in Table 2. Comparison of the microanalysis results reveals that decreasing the molar ratio of pyrrole in the monomer feed leads to a decrease of the pyrrole moiety in the copolymer. The upper limit for incorporation of the comonomer seems to be about 30 mol % (50 wt %) for DHPy and only about 8 mol % (23 wt %) for TDPy. It is interesting to compare the conductivities of homopolymers and copolymers. All copolymers had higher electrical conductivity than the homopolymers. The conductivity (σ) of the DHPy copolymers were in the range from 8 to 10 S cm^{-1} and the TDPy copolymers in the range from 20 to 100 S cm^{-1}. These conductivity values of the TDPy copolymers are nearly the same as the PPy value reported in the literature.

Cyclic Voltammogram. The cyclic voltammograms were carried out in the same electrochemical system as used for the electrochemical polymerization. Figures 1 and 2 show the cyclic voltammograms of PPy and PTDPy films of the same thickness in a propylene carbonate solution of 1 M $LiClO_4$, respectively. CVs of the obtained polymer films were measured in ranges from −1 to +1.2 and −0.5 V to +1.2 V *vs* SSCE, respectively. The difference between PPy and PTDPy arose from the shape of the CV curves. Delabouglise and Garnier reported that PDHPy was a more reversible

Table 1. Electrochemical Homopolymerization of Pyrrole Monomers[a]

monomer[b]	potential (V)	current (mA)	time (h)	microanalysis C %	H %	N %	Cl %	thickness (10^{-3} cm)	conductivity[c] (S cm^{-1})
Py	0.36−0.4	2	5	42.59	3.13	13.23	12.19	4.6	60
DHPy	0.45	2	4.5	50.59	5.27	6.20	4.08	8.4	0.08
TDPy	0.3−0.45	1	4	50.32	6.30	5.53	5.77	1.7	15

[a] Electrochemical polymerization carried out in a one-compartment cell containing 0.05 M monomer and 0.1 M $LiClO_4$ in propylene carbonate. [b] Py = pyrrole; DHPy = 3-(3,6-dioxaheptyl)pyrrole; TDPy = 3-(3,6,9-trioxadecanyl)pyrrole. [c] Electrical conductivity measured by the four-point probe method.

Table 2. Results of the Copolymerization[a]

Py/comonomer feed (M)	potential (V)	current (mA)	time (h)	microanalysis C %	H %	N %	Cl %	mol % comon[b]	wt % comon[b]	conductivity[c] (S cm^{-1})
DHPy										
0.045/0.005*	0.40−0.36	2−5	3	47.78	3.18	10.16	9.29	11.5	24.8	8.6
0.035/0.015*	0.40	2−6	4	41.92	4.04	8.57	10.62	31.0	53.3	
0.025/0.025*	0.40	2−4	3	41.37	4.07	8.54	9.91	29.2	51.2	10.0
0.025/0.025	0.24	1−2	4	42.69	3.72	8.72	10.82	31.2	53.6	9.2
TDPy										
0.025/0.025	0.36	2−3	3	43.85	4.05	9.24	9.38	8.5	23.0	20−50
0.035/0.015	0.36	2−4	2.5	44.72	3.62	9.60	8.77	7.2	19.9	100
0.045/0.005	0.36	2−4	3	42.83	3.60	9.75	9.76	5.1	14.7	30−50
0.100/0.025	0.36	2−4	1	51.83	3.24	11.71	6.56[d]	4.8	13.9	30

[a] The electrochemical copolymerization was carried out in a one-compartment cell containing 0.1 M $LiClO_4$ in propylene carbonate except when indicated by an asterisk (0.3 M $LiClO_4$). [b] mol % and wt % comonomer in films are calculated from the elemental analysis results. [c] Electrical conductivity was measured by a four-point probe method; if a range is given, the conductivity was measured on several samples. [d] After discharge test.

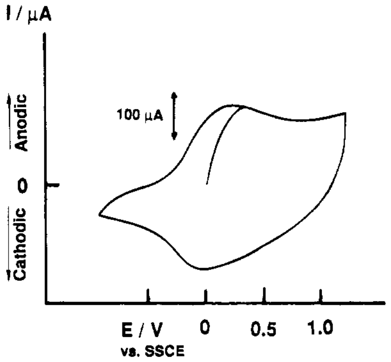


Figure 1. Cyclic voltammogram of a polypyrrole film on a platinum plate in a 1 M $LiClO_4$ propylene carbonate solution. Sweep rate: 200 mV/s.

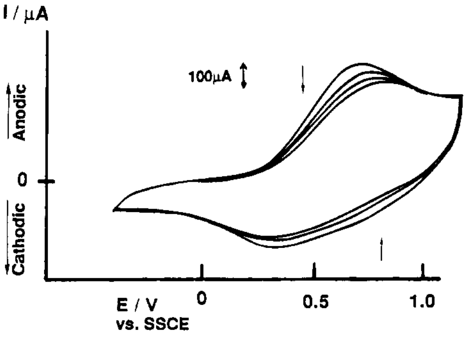


Figure 2. Cyclic voltammogram of a poly[3-(3,6,9-trioxadecanyl)pyrrole](PTDPy) film on a platinum plate in a 1 M $LiClO_4$ propylene carbonate solution. Sweep rate: 100 mV/s.

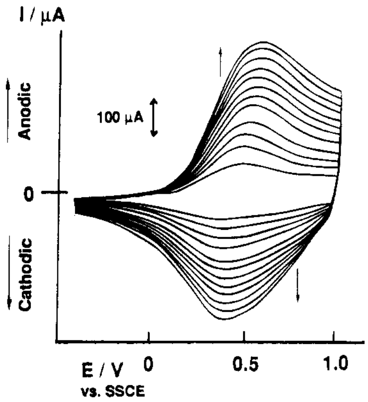


Figure 3. Cyclic voltammogram of a copolymer film of 3-(3,6-dioxaheptyl)pyrrole and pyrrole on a platinum plate in a 1 M $LiClO_4$ propylene carbonate solution at different sweep rates: 25, 35, 45, 55, 70, 80, 90, 100, 110, 120, 130, 140 mV/s.

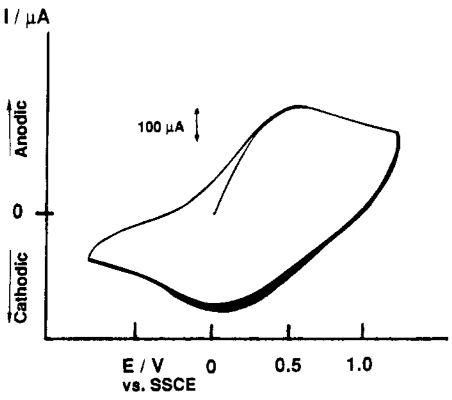


Figure 4. Cyclic voltammogram of a copolymer film of 3-(3,6,9-trioxadecanyl)pyrrole and pyrrole on a platinum plate in a 1 M $LiClO_4$ propylene carbonate solution. Sweep rate: 200 mV/s.

redox system than PPy.[9a] The derivative gave a larger area (ca. 3 times) of the current−potential curves in the cyclic voltammogram than PPy as shown in Figures 1 and 2. These results can be explained by a higher mobility of the electrolyte in the polymer matrices. The substitution of the ether chains on the 3-position of pyrrole enhanced the surface area and reversibility of the films. The doping and undoping process of PDHPy could be repeated for 50 cycles without any observable change in the CV curves, whereas PTDPy showed unstable CV curves when it was recycled as shown in Figure 2.

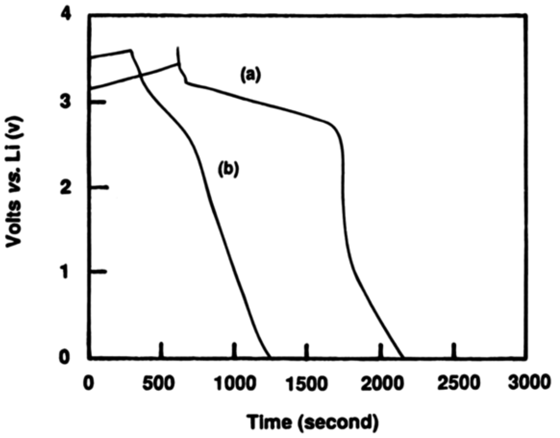


Figure 5. Charge and discharge curves of (a) poly[3-(3,6-dioxaheptyl)pyrrole] and (b) polypyrrole in a 1 M $LiClO_4$ propylene carbonate solution.

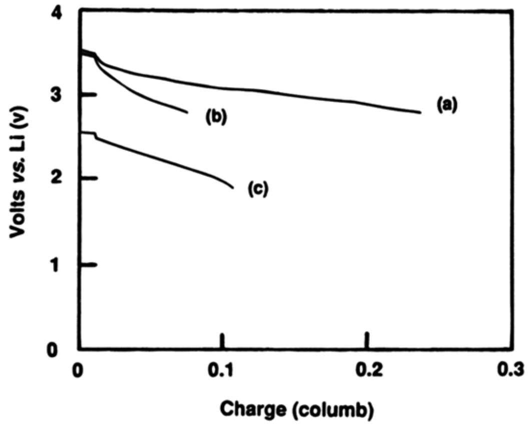


Figure 6. Charge and discharge curves of the copolymer of (a) 3-(3,6,9-trioxadecanyl)pyrrole and pyrrole, (b) polypyrrole, and (c) poly[3-(3,6,9-trioxadecanyl)pyrrole] in a 1 M $LiClO_4$ propylene carbonate solution.

Figure 3 shows the cyclic voltammogram of the copolymer of DHPy with Py. The redox pattern of the copolymer showed only one redox peak at 0.4−0.6 V *vs* SSCE (sodium-saturated calomel electrode) at different sweep rates, and faster scans resulted in smaller surfaces, as would be expected. The anodic and cathodic peak currents are essentially proportional to the scanning rate as shown in Figure 3. CV of both copolymers gave a larger area of the current−potential curves than the homopolymers of the derivatives, indicative of larger current densities in the copolymers.

The doping−dedoping process can be repeated for 50 cycles without any observable change in the cyclic voltammogram curves for both polymers. Especially, the copolymer of TDPy with Py gave a very stable CV, even though PTDPy was unstable in the CV, as shown in Figure 4. These results suggest that the introduction of ether chain and incorporation of the pyrrole in the copolymer systems increased the current density and the stability.

Charge and Discharge Curve. Figure 5 shows discharge curves of PPy and PDHPy. The samples were charged at 100 μA to 3.6 V and then open-circuited for 30 s. The samples were then discharged to 0 V at 500 μA. PDHPy exhibited stability problems, as is evidenced in the sudden jump in the potential; however, the discharge curves all resembled those shown in Figure 5. In this figure it is seen that PDHPy is capable of providing a greater energy/power density; however, the stability remains a question.

Figure 6 shows the result of the charge and discharge test of PPy, PTDPy, and the copolymer of TDPY with Py. In this figure the discharge has been converted to coulombs by multiplying the discharge current (500 μA) by the time over which the discharge occurred. In this case PTDPy could not be charged above 2.6 V; therefore, it was discharged to a lower potential, 1.9 V, to keep the voltage ranges comparable. Additionally, the sample was unstable in the repeated charge and discharge tests. However, the copolymer with TDPY and Py showed very interesting properties. The copolymer sample was charged to 3.6 V and the Py sample to 3.5 V. These potentials were the maximum values for each experiment. Both these samples were discharged to 2.8 V. From these curves it is clear that the copolymer was capable of supplying the same current for a longer period of time, as indicated by the polypyrrole's steeper slope. Additionally, no stability problems were observed with the copolymers in contrast with the homopolymer films; i.e., the samples charged and discharged smoothly, while the film's composure remained sound.

Scanning Electron Micrographs (SEM). The surface of the obtained films was analyzed by scanning electron micrography both in the virgin state (without being charged and discharged) and after being charged and discharged. The scanning electron micrographs of perchlorate-doped PPy, the homopolymers of the derivatives, and the copolymers showed a wide variation of surface morphology. PPy gave the traditional morphology reported in the literature as shown in Figure 7. However, homopolymers of the pyrrole derivatives gave

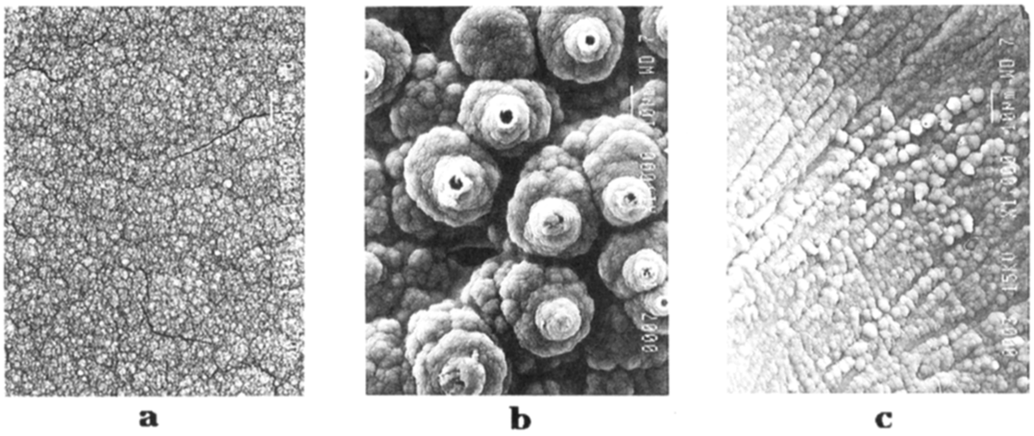

a b c

Figure 7. Scanning electron micrographs (SEM) of the surface of (a) polypyrrole films, (b) poly[3-(3,6-dioxaheptyl)pyrrole] films, and (c) poly[3-(3,6,9-trioxadecanyl)pyrrole] films.

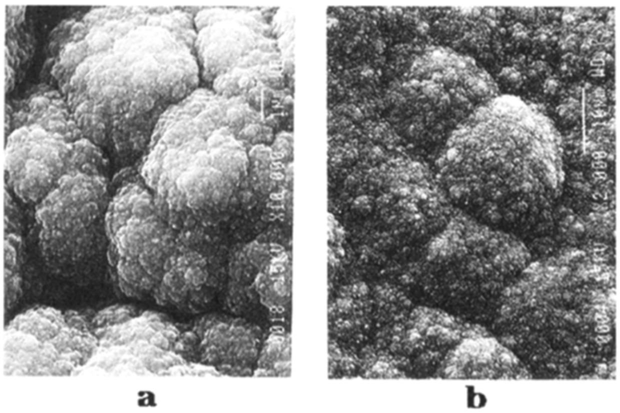


Figure 8. Scanning electron micrographs (SEM) of the surface of copolymer films of (a) 3-(3,6-dioxaheptyl)pyrrole and pyrrole and (b) 3-(3,6,9-trioxadecanyl)pyrrole and pyrrole.

different morphologies as shown in parts b and c of Figure 7. Both derivative films exhibit the influence of the polymer chains on polymer growth. The total surface areas of these films are clearly much larger than that of the polypyrrole film. These increased surface areas of the derivatives resulted in the higher current densities observed in the CVs.

PTDPy gave more compact morphology than PDHPy as shown in parts b and c of Figure 7. It seemed as if PDHPy films were grown in a perpendicular direction, while the PTDPy films were grown parallel to the surface of the platinum plate. The higher conductivity of the PTDPy compared to PDHPy can be ascribed to this more compact morphology reminiscent of polypyrrole.

Figure 8 shows the surface morphology of the copolymers. The copolymers showed larger nodules entirely covering the surface. Despite the differences observed in the surface morphology depending on feed ratios, the composition and conductivity were nearly the same, as shown in Table 2.

No specific morphological texture changes were observed on the surface of polypyrrole before or after discharge tests. However, the homopolymers of the derivatives and the copolymers showed different morphologies after the discharge test. They displayed a more porous surface. The microanalysis of the TDPy copolymer gave a 3% reduced Cl value after the discharge test (up to 1.9 V) without great change of the conductivity as indicated in Table 2. It is assumed that the dopant anion moved easily through the porous structure of the polymer matrix; however, sufficient anions remained to yield conductive samples.

The copolymers showed larger nodules entirely covering the surface. The morphology of these films is illustrated by the SEM of the copolymer films as shown in Figure 8.

Conclusion

In conclusion, monomeric pyrrole was derivatized at the 3-position with a poly(ethyleneoxy) group separated from the pyrrole ring by an ethylene group. Poly[3-(3,6-dioxaheptyl)pyrrole], poly[3-(3,6,9-trioxadecanyl)pyrrole], and copolymers of both poly(ethyleneoxy)-substituted pyrrole with pyrrole have been synthesized by electrochemical polymerization. These films are of high quality and have moderate conductivity and electrochemical activity. In both copolymer systems, electrical conductivity was greatly increased compared to the homopolymers. The copolymer systems gave larger current density and stability in the cyclic voltammograms and charge and discharge test.

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References and Notes

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