

Soluble polystyrenes with pyrrole pendant groups and their electroactive properties

Jin-Baek Kim *, Sung-Tek Lim

Department of Advanced Materials Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 201, Cheongryang, Seoul 130-650, Korea

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Summary

Four soluble styrenic polymers containing 3-substituted pendant pyrrole rings with ester or amide arm spacer were synthesized. Their electroactive characteristics were investigated by cyclic voltammetry. The chemical oxidation was accomplished by adding FeCl_3 into a solution of styrenic polymers dissolved in 1:1 mixture of dimethylformamide (DMF) and acetonitrile (ACN). The electrical conductivities of the chemically oxidized black powder of the styrenic polymers were in the range of 10^{-10} – 10^{-9} S/cm.

Introduction

It is well known that conducting polypyrrole can be prepared by the chemical oxidation in the presence of FeCl_3 . Several workers (1, 2) have studied the electrical properties of chemically oxidized polypyrrole. To get a higher conductivity, the structure of pyrrole is believed to consist of a linear planar chain with pyrrole rings alternating in opposite directions along the chain (3). Bryce et al. (4) reported soluble characteristics of the poly(3-acyl pyrroles) and poly(3-alkyl thiophenes). Both alkyl thiophenes and acyl pyrroles are susceptible to electrochemical oxidation, yielding polymers with conductivities in the range 10^{-2} – 10^3 S/cm. In this paper, the synthetic methods of soluble styrenic polymers containing 3-substituted pyrrole pendant groups and their oxidative coupling with FeCl_3 will be presented as a prerequisite step for the preparation of surface conducting particles. When a styrenic monomer containing 3-substituted pendant pyrrole ring, a conducting styrenic polymer can be prepared via radical polymerization and oxidative α – α' coupling between adjacent pendant pyrrole rings. The styrenic polymer bearing pendant pyrrole moiety in the side chain will have amphiphilic property due to the hydrophilic NH head of the pyrrole ring and the hydrophobic backbone of styrenic polymer. Therefore, surface conducting styrenic polymer particles having high conductivity can be easily obtained in emulsion medium when additional pyrrole monomers are coupled with the pendant pyrrole moiety. Kamogawa et al. synthesized the pyrrole derivatives bearing various styrenic groups at C-3 position of the pyrrole ring, however, homopolymerization of the styrenic monomers provided crosslinked insoluble polymers (5).

* Corresponding author

Experimental

Materials: p-Vinylbenzyl chloride and p-aminostyrene, purchased from Aldrich and Lancaster, respectively, were used without further purification. 2, 2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. LiClO_4 was dried in vacuo at 80°C for 10 h before use. Tetrahydrofuran (THF) and DMF were dried over sodium metal.

Measurements: $^1\text{H-NMR}$ spectra were recorded on a Bruker SY-200 spectrometer. FT-IR spectra were taken from a KBr pellet via a Bio-Rad Model FTS 165 spectrometer. UV-Vis spectra were measured on a Hewlett Packard 8453 spectrometer. Gel-permeation chromatograms (GPC) were obtained on a Waters 441 chromatograph. Substances were indicated by a Waters R401 differential refractometer. The molecular weight and molecular weight distributions were measured against polystyrene standards in DMF at 80°C . Glass transition temperature was measured by DSC on a DuPont 2100 instrument. Melting point was determined on a Thomas Hoover melting point apparatus (74T-7). Electrochemical oxidation by cyclic voltammetry was performed employing an EG&G PARC Model 362 potentiostat/279 digital coulometer. Electrical conductivity was determined by standard four-probe techniques on pressed pellet using Keithley 236 source and measure unit and Yokohama 2553 voltage and current device.

Synthetic scheme: Fig. 1 represents the synthetic route of styrenic monomers having pendant pyrrole rings, their homopolymers and their oxidized polymers. Two styrenic monomers (II-a, II-b) having pyrrole ring in the side chain were synthesized. Other compounds, I-ab, I-cd, II-c, II-d, III-c and III-d were also prepared according to the known procedure (6).

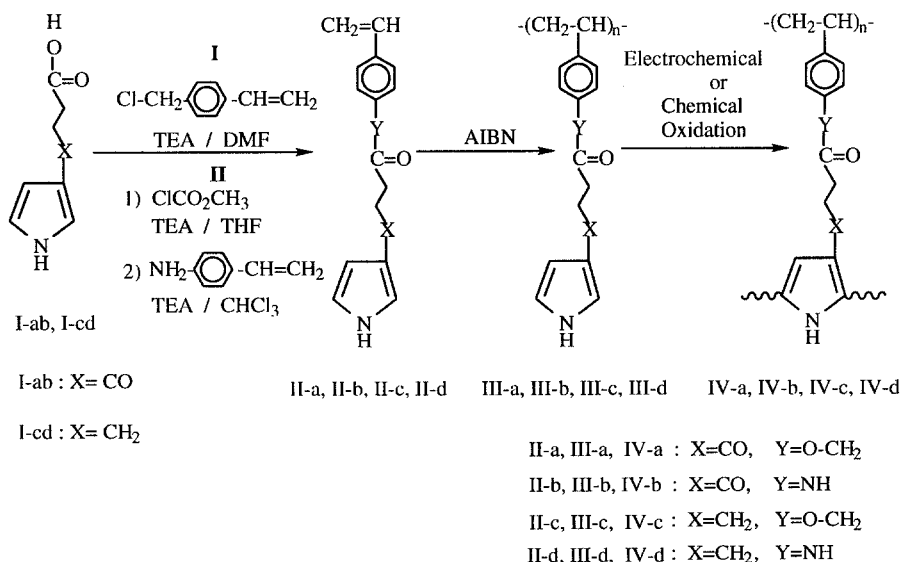


Fig. 1. Synthesis of styrenic monomers, their polymers and oxidized polymers.

***p*-Vinylbenzyl 4-(3-pyrrolyl)-4-oxobutyrate (II-a):** 20 mmol of *p*-vinylbenzyl chloride was added into a well-stirred solution of 4-(3-pyrrolyl)-4-oxobutyric acid (10 mmol) and triethylamine (TEA) (15 mmol) in 10 ml of DMF. The mixture was stirred at 20 °C for 36 h. The reaction mixture was poured into water and thoroughly extracted with ether. The organic layer was washed with 5% aqueous Na₂CO₃ and water, consecutively. Dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residual oil was chromatographed in a column of 60 mesh silica gel, eluting with 1:1 ethyl acetate-hexane to yield 1.85 g (66%) of II-a as an oil that tends to solidifies on standing. FT-IR (KBr) (cm⁻¹): 3316 -NH stretching, 3086 =C-H stretching, 2970 C-H antisymmetric and symmetric stretching, 1763, 1732 C=O stretching, 1649 C=C stretching, 1420 C-N stretching, 1161 C-O stretching, 992 =CH out-of-plane deformation, 755 =C-H out-of-plane bending. ¹H-NMR (CDCl₃, ppm): δ 2.90 (t, 2H, CH₂), 3.10 (t, 2H, CH₂), 5.15 (t, 1H, =CH), 5.30 (d, 2H, CH₂), 5.86 (s, 2H, CH₂=), 6.60~6.80 (m, 3H, H_{pyrrole}), 7.20~7.50 (m, 4H, H_{aromatic}), 8.95 (b, 1H, -NH).

***p*-Vinylphenyl 4-(3-pyrrolyl)-4-oxobutylamide (II-b):** Methyl chlorofomate (15 mmol) was gently added to a well-stirred solution of 4-(3-pyrrolyl)-4-oxobutyric acid (15 mmol) and TEA (15 mmol) in 40 ml of THF at 0 °C with vigorous shaking. Upon stirring for 10 min, a solution of *p*-aminostyrene (15 mmol) and TEA (15 mmol) dissolved in 30 ml of CHCl₃ was added at 0 °C with shaking, followed by stirring at this temperature for 1 h and subsequent stirring at 20 °C for 24 h. The reaction mixture was poured into water and extracted with CHCl₃. The organic layer was washed with water and dried over anhydrous MgSO₄ and concentrated at reduced pressure. Recrystallization from benzene-hexane (1:1) to give 1.35g (32%) of crystalline powder. mp 187-188 °C. FT-IR (KBr) (cm⁻¹): 3335, 3275 -NH stretching, 3139 =C-H stretching, 2959 C-H stretching, 1761, 1681 C=O stretching, 1650 C=C stretching, 992 =CH out-of-plane deformation, 763 =C-H out-of-plane bending. ¹H-NMR (Me₂SO-*d*₆, ppm): δ 2.68 (t, 2H, CH₂), 3.05 (t, 2H, CH₂), 5.15 (t, 1H, =CH), 5.70 (t, 2H, CH₂=), 6.40~6.80 (m, 3H, H_{pyrrole}), 7.30~7.60(m, 4H, H_{aromatic}), 10.01 (b, 1H, -NH), 11.41 (b, 1H, -NH).

Polymerization of styrenic monomers (III-a~III-b): The monomer and AIBN (2 mol% of monomer) were dissolved in DMF to afford 20 wt% monomer concentration. The solution was poured into a glass ampoule. Oxygen dissolved in DMF solution was evacuated via four freeze-pump-thaw cycles and then sealed in vacuo. Radical polymerization was carried out at 55 °C for 72 h. The contents were poured into ether and agitated to precipitate the polymer products.

III-a: FT-IR (KBr) (cm⁻¹) 3316 -NH stretching, 3086 =C-H stretching, 2970 C-H antisymmetric and symmetric stretching, 1763, 1732 C=O stretching, 1649 C=C stretching, 1420 C-N stretching, 1161 C-O stretching.

III-b: FT-IR (KBr) (cm⁻¹) 3335, 3275 -NH stretching, 3139 =C-H stretching, 2959 C-H stretching, 1761, 1681 C=O stretching, 1650 C=C stretching.

Cyclic voltammetry: The polymers were dissolved in DMF (20 wt%), and coated on the surface of the Pt electrodes and dried in vacuo at 40 °C for 12 h. Electrochemical oxidation of these polymers was carried out in a single compartment cell consisting of a Pt working

electrode that was coated with styrenic polymer solution and a Ag/AgNO₃ reference electrode in 0.1 M LiClO₄/ACN supporting electrolyte. The color of the film on the Pt electrode became dark brown. During the electrochemical oxidative polymerization of the pendant pyrrole moiety, the cyclic voltammetry measurements were conducted to investigate electroactive properties and the peak oxidation potentials of the styrenic polymers.

Chemical oxidation of styrenic polymers (IV-a~IV-d): Chemically oxidized polymers were obtained by adding FeCl₃ into a styrenic polymer solution. The styrenic polymer solution was made by dissolving the styrenic polymer in 1:1 mixtures of DMF and ACN. The initial molar ratio of oxidant against monomer unit of the styrenic homopolymer was fixed at 2.4 following the previous literatures (2, 7, 8). The reaction mixture was allowed to continue stirring for 5 h at room temperature. Immediately after adding of FeCl₃, the solution turned dark and became brownish black. The chemically oxidized polymers were precipitated by adding methanol. Collecting on a Büchner funnel by filtering, the resulting black powder was washed at Soxhlet extraction apparatus by refluxing with methanol until the filtrate became colorless. The powder was dried in vacuo at 40 °C for 24 h. For the measurement of the conductivity, the chemically oxidized polymer was pressed into thin circular pellets at a press.

Results and discussion

The monomers prepared according to the scheme in Fig. 1 are in good yield. The styrenic monomers having pendant pyrrole ring were subjected to polymerization with common radical initiator, AIBN. Radical polymerization of styrenic monomers took place in high conversion. The structure of the four styrenic monomers and polymers were confirmed by FT-IR and ¹H-NMR spectra. The properties of the polymers are summarized in Table 1.

Table 1. The properties of radical polymers having pendant pyrrole rings

Polymer	T _g (°C)	Conversion (%)	M _w (X 10 ⁴)	M _n (X 10 ⁴)	M _w /M _n
III-a	80.15	71	32.82	8.25	3.99
III-b	83.64	88	40.06	10.81	3.71
III-c	61.67	69	19.76	5.28	3.74
III-d	73.82	95	22.83	7.08	3.22

In FT-IR spectra, the absorption at 992 cm⁻¹ attributable to the vinyl group that was observed in all four styrenic monomers, no longer exist in the styrenic polymers. ¹H-NMR spectra of the polymers also show disappearance of vinyl proton signals of the monomers. Kamogawa et al. reported that the styrenic polymers with pyrrole pendant groups, III-c and III-d, were totally insoluble in any organic solvent due to the formation of cross-linked structure by coupling of reactive 2-position of pyrrole ring during the radical polymerization (5). However, all the polymers we prepared, III-a~III-d, were soluble in polar solvents

such as DMF and 1,1,1,3,3,3-hexafluoro-2-propanol (HF-2PrOH). The number and weight average molecular weights of the styrenic polymers by GPC in DMF were $19.76 \sim 40.06 \times 10^4$ and $5.28 \sim 10.81 \times 10^4$, respectively. In FT-IR spectra, the out-of-plane C-H bending intensities (in the vicinity of 760 cm^{-1}) of pyrrole groups of the polymers (III-a~III-d) remained unchanged during radical polymerization of those monomers (II-a~II-d). In the region between 250 nm and 280 nm of UV-Vis spectra, the absorption bands of each polymers were observed at the same region of those monomers. These absorption features indicate that the coupling of pyrrole ring did not occur during radical polymerization. The dissolved styrenic polymers were easily coated on the surface of glass and quartz. The glass transition temperatures of the four styrenic polymers examined by DSC were lower than that of polystyrene ($102 \sim 104 \text{ }^\circ\text{C}$). The lower glass transition temperature of four styrenic polymers are attributed to the long side chains. The conversions of the four polymers were high.

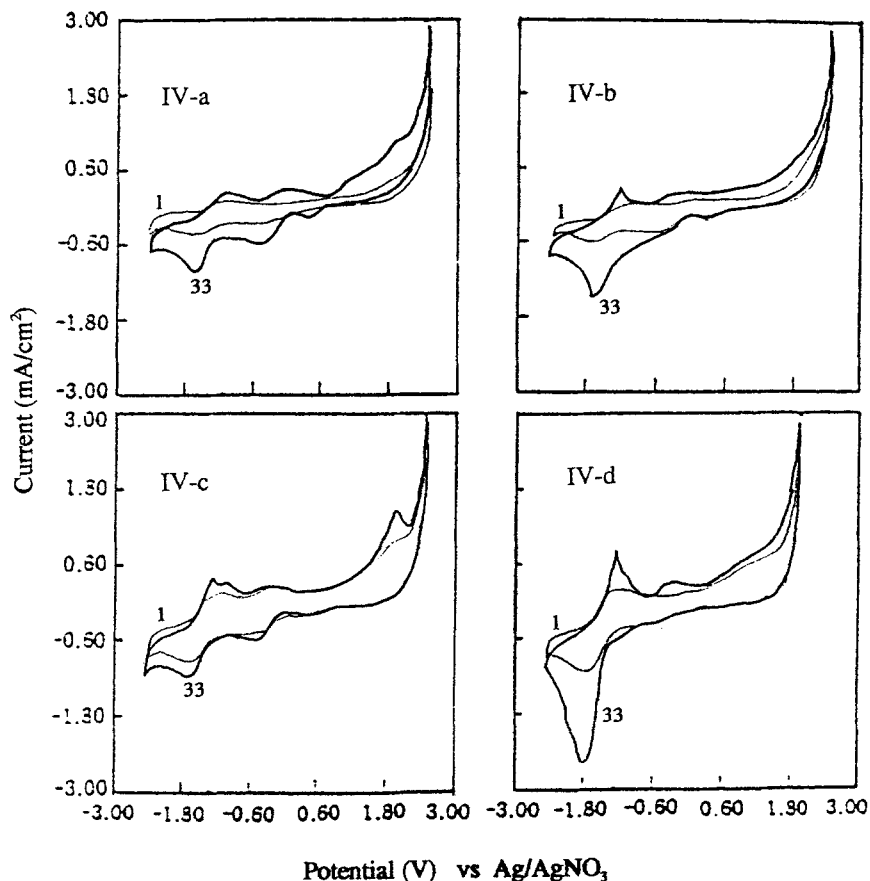


Fig. 2. Cyclic voltammograms of styrenic polymers bearing pendant pyrrole rings, 0.1M $\text{LiClO}_4/\text{ACN}$, Scan Rate: 100 mV/sec, Every 33 cycles are recorded.

Fig. 2 represent the cyclic voltammograms of the polymers. The multisweeps of the four polymers were similar in profiles. It revealed several anodic and cathodic peaks. These successive redox behaviors can be interpreted by the presence of conjugated pyrrole rings having different conjugation lengths. The 1st, 2nd and 3rd peaks are likely corresponding to the coupled polypyrrole with 3 or greater coupled pyrrole groups, dipyrrole and monopyrrole, respectively. The currents of the polymer at the first cycle were small, but the anodic and cathodic peak currents gradually increased. The saturated states were reached when 30 cycles were swept. The cyclic voltametry data of electrochemically oxidized polymers, IV-a, IV-b, IV-c and IV-d are shown in Table 2. The 1st oxidation (E_{pa}) and reduction (E_{pc}) potentials of IV-a and IV-b were higher than those of IV-c and IV-d. The higher potentials for the oxidized polymers of IV-a and IV-b may be due to the inductive effect of the carbonyl group which is attached to the pyrrole ring. The new peaks appeared and the redox currents increased due to α - α' coupling of neighboring pendant pyrrole rings in the side chain. The redox currents increased as the polypyrrole grows. It was impossible to measure the conductivities of the electrochemically oxidized styrenic polymers due to the difficulty of peeling off the coated film from the Pt electrodes.

Table 2. Cyclic voltametry data of electrochemically oxidized polymers

Polymer	IV-a	IV-b	IV-c	IV-d
E_{pa} [V]	-1.09	-1.21	-1.26	-1.29
E_{pc} [V]	-1.62	-1.63	-1.68	-1.78

The conductivities of chemically oxidized styrenic polymers (IV-a~IV-d), measured by four-probe techniques were in the range of 10^{-10} ~ 10^{-9} S/cm as shown in Table 3. These low conductivities are attributed to the steric effect due to long and bulky phenyl substituents at C-3 positions that prevent long conjugation length by the α - α' joining of the adjacent pyrrole rings. Moreover, deviation from coplanarity of pyrrole rings that are attached to styrenic polymers results in less electron delocalization and thereby leads to a drop in conductivity. In FT-IR spectra, the out-of-plane C-H bending intensities of pyrrole groups of the oxidized polymers (IV-a~IV-d) at 760 cm^{-1} , were considerably decreased when comparing with those of polymers (III-a~III-d). In the region between 350 nm and 450 nm, the insignificant broad absorption bands were observed in oxidized polymers (IV-a~IV-d), thus conforming the oxidation of styrenic polymers. In order to improve the conductivities of these polymers, the surface conducting polymer particles were studied and will be published in the separate papers (9).

Table 3. Electrical conductivities of the styrenic polymers

Polymer	IV-a	IV-b	IV-c	IV-d
Conductivity (S/cm)	8.70×10^{-10}	2.27×10^{-10}	1.17×10^{-9}	3.05×10^{-9}

Conclusions

The styrenic monomers (II-a, II-b) containing pyrrole pendant ring were synthesized from I-ab. Styrenic polymers (III-a~III-d) obtained from the monomers were soluble in an organic solvents such as DMF and HF-2PrOH. The electroactive properties of electrochemically oxidized polymers (IV-a~IV-d) were confirmed by cyclic voltammetry. We found that styrenic polymers having pendant pyrrole rings can be transformed into cross linked polymers by α - α' coupling of the adjacent pyrrole ring. The conductivities of the chemically oxidized styrenic polymers were 10^{-10} ~ 10^{-9} S/cm. The low conductivity may be attributed to the difficult formation of coplanarity and short conjugation length of polypyrrole due to the bulky substituents at C-3 position.

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