Electrochemical Synthesis of Processible Conducting Graft Copolymers of Styrene - Pyrrole, N- Methylpyrrole and Aniline:

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ABSTRACT

The insolubility and infusibility of classical conducting polymers make their processing difficult and limit their applications. One way to improve the solubility is to synthesize copolymers of conducting polymers with soluble classical polymers.

We describe the synthesis of 2- vinylpyrrole, N-methyl-2- vinylpyrrole and p-aminostyrene via Wittig methodology, and copolymerization of these compounds with styrene.

The monomers pyrrole, N-methylpyrrole and aniline are grown on resulting random copolymers via electrochemical oxidative polymerization.

Key Words
polypyrrole, poly (N-methylpyrrole), polyaniline, conducting polymer, electropolymerization

INTRODUCTION

As in the case of electronic properties, physical properties are a strong function of the macromolecular structure of conducting polymers. Just as many attempts have been made to improve the electronic properties, so too has considerable effort gone into improving physical properties. One of these physical properties is the ability to dissolve in common solvents.

The most common way to increase the solubility of these compounds is to add a substituent to the monomeric units. A number of substituted polythiophenes [1,2] and polypyrroles [3] are known. Nevertheless, it has been shown that these substituents may also have a negative influence on the doping stability because of the easier twisting of the conjugated chain arising from steric hindrance. In particular the thermal stability seems to be substantially decreased by substitution. Moreover, in the doped state, most of them become insoluble.

The other way to improve the solubility is to synthesize block or graft copolymers with a
conducting polymer and a soluble classical polymer. Aldissi [4] produced block copolymers by polymerizing acetylene at the ends of chains of anionic polyisoprene after conversion of the anionic chain ends to Ziegler centers. The polymers appeared to be soluble, with the polyacetylene segments having molecular weight of 1500 to 1900 as do similar block copolymers of polystyrene and polyacetylene [5]. Stowell et al. [6] synthesized acetylene-styrene block copolymers by an anionic to metathesis conversion of polystyrene chain ends. The same authors have also described block copolymers of acetylene and cyclopentene, prepared by sequential addition of two monomers to a living metathesis catalyst [7].

Armes et al. [8] reported synthesis of isoprene-acetylene block copolymer by reaction of anionic polyisoprene with CoCl₂ to make an analogue of the Luttinger catalyst attached to the chain end.

Poly(methyl methacrylate) side chains have been grafted to polyacetylene by treating sodium-doped polyacetylene with the MMA monomer [9]. A graft copolymer with polyacetylene side chains on a polybutadiene backbone has also been reported as soluble [10].

Francois et al. [11] have reported the synthesis of soluble polystyrene-poly(p-phenylene) diblock copolymer. The same authors [12], have also described polystyrene-graft polythiophene comb-like copolymers as a soluble precursor for polythiophene. Li et al. [13] described a method for graft polymerization of aniline in an aqueous solution of poly (p-aminostyrene) with HCl as a protic acid. Huang et al. [14] reported the synthesis of random (block) copolymer of 3-methyl thiophene and methyl methacrylate as an example of solution processible polymer. By considering these ideas, we describe the synthesis of conducting graft copolymers of pyrrole, N-methyl pyrrole and aniline via electrochemical oxidative polymerization. The obtained copolymers are soluble in common solvents.

EXPERIMENTAL

IR spectra were measured as liquid film from CHCl₃ on KBr or as KBr pellets on a 408 IR Shimadzu. UV spectra were measured for CHCl₃ solution on a UV-2100 Shimadzu instrument. Cyclic voltamograms were measured on a Polarecord E506 combined with VA-scanner E612 and a Hewlett Packard 7015 A X-Y recorder.

Synthesis of Monomers

- **Methyl bromide**: This colorless liquid (bp=4.5 °C) was prepared from a previously reported procedure [15].

- **Methyl triphenyl phosphonium bromide (MTPB)**: This compound was prepared from a previously reported procedure[16] and oven dried at 100 °C and stored in a desiccator over P₂O₅ (90% yield; mp=232 °C).

- **2- Vinyl pyrrole and N-methyl-2-vinyl pyrrole**: These compounds were prepared with modification of reported procedures [17,18].

  MTPB (40.2g (0.112 mol)) was stirred with sodium ethoxide (from 2.6 g Na in dry tetrahydrofuran (250 mL) for 15 minutes at 20 °C under nitrogen. The appropriate formyl pyrrole (0.1 mol) in dry THF (50 mL) was added dropwise, and the mixture was stirred for 30 minutes at 20 °C and then heated under reflux for 24 hours. Then the solvent was removed under vacuum and water (50 mL) was added to the residue. The crude vinyl pyrrole was extracted from the aqueous mixture with ether (2 x 40 mL) and the extract was washed successively with aqueous sodium metabisulfite (30%, 4 x 100 mL), aqueous sodium carbonate (20%, 3 x 100 mL) and water (40 mL). The dried (MgSO₄) ethereal extracts were evaporated, and any residual triphenyl phosphine oxide was removed by filtration. Distillation under vacuum gave vinyl pyrrole.

  N-Methyl-2-vinyl pyrrole (61% yield) bp=64 °C (14 mmHg) and 2-vinyl pyrrole (42% yield) bp=67 °C (18 mmHg).

  N-Methyl-2-vinyl pyrrole IR: 3050, 2950, 1630, 990 cm.

- **p-Nitrobenzyl bromide (PNB)**: This compound was prepared from reported procedure (60% yield,
p-Nitrobenzyl triphenyl phosphonium bromide (PNBTPB): Equimolar amounts of PNB and triphenyl phosphine were dissolved in chloroform and heated under reflux for 30 minutes, then cooled and precipitated with addition of ether. The product filtered and dried under vacuum (90% yield, mp=275 °C) [20].

p-Nitro styrene (PNS): PNBTPB (75 g, 0.155 mmol) was suspended in 300 mL of 40% formaldehyde. While stirring vigorously, 30 g of sodium carbonate in 100 mL water were added in a slow and discontinuous way. Each quantity was added only after the dark red color of the intermediate phosphorane disappeared. The suspension was stirred 4 additional hours. The crude PNS was extracted from aqueous mixture with ether (3 x 40 mL). The dried (Na₂SO₄) ethereal extracts were evaporated and the residue was purified by chromatography on a short and broad column of alumina using n-hexane as an eluent (80% yield, mp=20-21°C) [20].

IR: 3050, 1610, 1520, 1350, 990, 860, cm.

p-Amino styrene (PAS): To a solution of 7 g (0.05 mol) of PNS in 75 mL of acetone was added a solution of 5 g of ammonium chloride in 20 mL of water. The mixture was heated to boiling on a water bath. The bath was removed and 10 g of zinc dust was added in small portions to maintain a moderate reaction. After the zinc was added and the reaction subsided, five additional grams of zinc dust was added and the mixture was refluxed on the water bath for 30 minutes. The solution was then filtered while hot and the precipitate was washed twice with acetone. The combined washing and filtrate was concentrated in the water bath. Then 100 mL benzene was added and the organic phase separated.

Dried (Na₂SO₄) benzene phase is evaporated in vacuum and crude PAS was distilled in vacuum over 0.5 g hydroquinone (62% yield, bp=74-77 °C (2 mm Hg)) [21].

IR: 3450, 3350, 3200, 3050, 1605, 1620, 990, 830 cm.

Backbone Random Copolymer Synthesis
Polymerization was carried out in apparatus shown in Figure 1.

Poly (2-vinyl pyrrole-co-styrene) (PVPCS): Into a polymer tube was placed 3 g (0.032 mol) of 2-vinyl pyrrole, 3.33 g (0.032 mol) of styrene, 0.01 g (6.4 E-5 mol) azobisisobutyronitrile (AIBN) and 3 mL benzene. After sealing under vacuum the tube was immersed in a 60°C water bath for 4 days. A very viscous liquid was obtained; 10 mL of benzene was added and the resulting solution was poured into a beaker containing 100 mL of methanol. The white solid was collected, washed with methanol and dried under vacuum to yield 40% of white solid.

IR: 3400, 3050, 3100, 2900, 1600, 1490, 1450, 1030, 700 cm.

UV: (CHCl₃) max= 249, 283 nm.

Poly (N-methyl-2-vinyl pyrrole-co-styrene) (PNMPCS): This polymer was prepared by dissolving 3 g (0.028 mol) N-methyl-2-vinyl pyrrole, 2.9 g (0.028 mol) styrene, and 0.001 g (5.6 E-5 mol) AIBN in 5 mL benzene.

After pouring the mixture into a polymerization tube which was subsequently evacuated and sealed, it was heated at 60 °C for 6 days. A viscous liquid was obtained, and 5 mL benzene was added and the resulting solution was added to a beaker containing 100 mL of methanol. The white solid was collected, washed with methanol and dried to
yield 55% of white solid.
IR: 3080, 3000, 2900, 1600, 1490, 1440, 1290, 1080, 690 cm.
UV: (CHCl₃) max=242.4, 290 nm.

Poly[p-aminostyrene-co-styrene] (PASCS): Synthesis of this polymer was accomplished by placing 2 g (0.0168 mol) of p-aminostyrene, 1.8 g (0.0168 mol) styrene, 0.014 g (8.4 E-5 mol) AIBN and 5 mL benzene in a polymer tube. The polymerization tube was evacuated, sealed under vacuum and placed into a water bath at 60°C for 6 days. The viscous solution was poured into a beaker containing 100 mL methanol, the resulting solid was collected; washed with methanol and dried to yield 10% pale yellow solid.
IR: 3450, 3350, 3200, 3010, 2900, 1620, 1600, 1510, 1450, 1340, 1090, 700, cm.
UV: (CHCl₃) max=243.4, 285 nm.

Electrochemical Graft Polymerization
In all experiments Pt disc, Pt wire and saturated calomel electrode were used as working, auxiliary and reference electrodes respectively. Tetrabutyl ammonium perchlorate in acetonitrile (0.1 M) and perchloric acid in distilled water were used as supporting electrolyte. For graft polymerization all solutions were deaerated by N₂ bubbling.

-Cyclic Voltametry Method (A)
Grafting of N-methyl pyrrole to PNMPCS: A solution of 1 wt% of PNMPCS in chloroform was prepared and working electrode was coated with this polymer via dip coating method. Then this electrode along with the auxiliary and reference electrode were placed in a single compartment cell containing tetrabutyl ammonium perchlorate (0.1 M) and N-methyl pyrrole (0.1 M) in acetonitrile (15 mL). Then potential was scanned between 0 to 1000 mV. In the latter step the working electrode was washed with acetonitrile and placed in supporting electrolyte solution (0.1 M) without monomer. Again the potential was swept between 0 to 1000 mV.
Grafting of pyrrole to PVPCS: The above procedure was repeated, but this time potential was swept between - 500 to 1500 mV.

Grafting of aniline to PASCS: The above procedure was repeated, but this time perchloric acid (1 M) was used as the supporting electrolyte and water as solvent. The potential was swept between - 200 to 1200 mV.

-Galvanostatic Method (B)
In a single compartment cell two Pt electrodes (2 cm²), were placed 1 cm distance apart, as anode and cathode. The anode electrode was coated with 1 wt% solution of backbone copolymer. The cell contained tetrabutyl ammonium perchlorate (0.1 M) in acetonitrile for pyrrole (0.1 M) and N-methyl pyrrole (0.1 M) electropolymerization and perchloric acid (1 M) in water for aniline (0.1 M) electropolymerization. Then solutions were deaerated with N₂ bubbling and stirred vigorously during the reaction. Then 0.1 mA/cm² current was applied through a potentiostat for 10 minutes.

RESULTS AND DISCUSSION
The synthesis of random copolymers of styrene with 2-vinyl pyrrole, N-methyl-2-vinyl pyrrole and p-aminostyrene was performed and their structures were confirmed by UV and IR spectra. The corresponding vinylic compounds were prepared via Wittig methodology and copolymerized with styrene.

Two electrochemical methods of cyclic voltametry and galvanostatic were used for growth
of desired monomers onto the backbone of random copolymers.

Fig. 2(a). CV-gram of coated Pt with PVPCS in acetonitrile as solvent, tetrabutyl ammonium perchlorate (0.1M), N-methylpyrrole (0.1M), \( V = 100 \) mV/s.

Fig. 3(a). CV-gram of coated Pt with PNMPCS in acetonitrile as solvent, tetrabutyl ammonium perchlorate (0.1M), N-methylpyrrole (0.1M), \( V = 100 \) mV/s.

Fig. 4(a). CV-gram of coated Pt with PASCS in water as solvent, perchloric acid (1M), aniline (0.1M), \( V = 100 \) mV/s.
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**Fig. 2(b).** CV-gram of graft polypyrrole in supporting electrolyte (0.1 M), V=50, 100, 200, 300, 400, 500 mV/s.

**Fig. 3(b).** CV-gram of graft poly N-methylpyrrole in supporting electrolyte (0.1M) in V=50, 100, 200, 300, 400, 500 mV/s.

**Fig. 4(b).** CV-gram of graft polyaniline in supporting electrolyte (1M) V=50, 100, 200, 300, 400, 500 mV/s.

- Cyclic voltammetry method: In this method the working electrode was coated with 1 wt% solution of desired random copolymer by the dip coating method. Then, this electrode, along with auxiliary and reference electrode, were placed in a single compartment cell containing supporting electrolyte and desired monomer in appropriate solvent. Electropolymerization was carried out by sweeping potential in appropriate range as shown in Figures 2(a), 3(a), 4(a). After washing the working electrode on which the polymeric film was deposited with acetonitrile or water, it was transferred to a solution of supporting electrolyte in desired solvent without monomer.

The potential was swept again between desired range according to the kind of polymer at different scan rate as was shown in Figures 2(b), 3(b), 4(b). A linear relationship was observed for Ipa versus scan rate for the growth of desired monomer on bare Pt or coated Pt with appropriate backbone copolymer. This difference is due to the lower...
Fig. 5(a). Anodic peak current vs. scan rate for electropolymerization of N-methyl pyrrole.

Fig. 5(b). Anodic peak current vs. scan rate for electropolymerization of pyrrole.

Fig. 5(c). Anodic peak current vs. scan rate for electropolymerization of aniline.

electrode was placed in a beaker containing 10 mL of chloroform. After dissolution of copolymer, its UV spectra was measured, (Figures 6(a), 6(b), 6(c)).

CONCLUSION

Soluble graft copolymers have been synthesized by electrochemical polymerization (cyclic voltametry and galvanostatic methods) of N-methyl pyrrole onto (PNMPCS), pyrrole onto (PVPCS) and aniline onto (PASCS). Cyclicvoltamograms show the complete growth of monomers on electroactive site of the backbone copolymers. UV spectra of graft copolymers show a band over 500 nm that is absent in backbone copolymers. This band characterizes a conjugated system in graft copolymers.

REFERENCES

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Fig. 6(a). UV spectra of graft polypyrrole in chloroform.

Fig. 6(b). UV spectra of graft poly N-methyl-pyrrole in chloroform.

Fig. 6(c). UV spectra of graft polyaniline in chloroform.

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