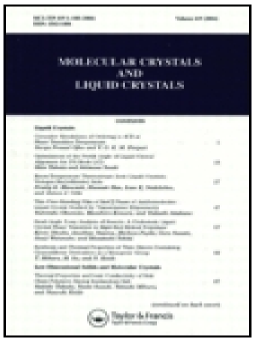

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Synthesis of Random Copolymers of Pyrrole and Aniline by Chemical Oxidative Polymerization

Doo Kyung Moon
Department of Materials Chemistry and Engineering, College of Engineering, Konkuk University, Gwangjin-gu, Seoul, Korea

Ju-Young Yun
Vacuum Center, Korea Research Institute of Standards and Science, Korea

Kohtaro Osakada
Takaki Kambara
Takakazu Yamamoto
Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan

Random copolymers have been synthesized in high yields (94%) by chemical oxidative polymerization of aniline/pyrrole comonomers using H_2O_2 in the presence of Fe catalyst. The oxidative polymerization proceeds via successive coupling that gives the copolymer structure similar to polyaniline and polypyrrole. The copolymers are black powders and soluble in dimethylsulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP). The weight–average molecular weight (M_w) of the copolymers was in a range, from 6200 to 15,000 g/mol.

Keywords: copolymer; polyaniline; polypyrrole

INTRODUCTION

π-Conjugated organic polymers having benzenoid or heterocyclic units (e.g., poly(*p*-phenylene) [1], polyaniline [2], polythiophene [3], and polypyrrole [4]) have attracted a great deal of attention as electrical conducting materials [5]. Among these polymers, polyaniline (PANI)

Address correspondence to Doo Kyung Moon, Department of Materials Chemistry and Engineering, College of Engineering, Konkuk University, 1, Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea. E-mail: dkmoon@konkuk.ac.kr

and polypyrrole have attracted special attention because of their easy preparation by chemical oxidative polymerization [2,4], and the presence of various application areas (e.g., corrosion protection, antistatic materials [6,7], plastic light emitting diodes [8] and gas or liquid separation [9]). However, both polymers do not have good solubility in organic solvents. Many works have been done to make PANI soluble in *N*-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) by using functionalized organic acids or dopants [10], introducing substitutent to the polymer, and designing new polymerization method.

We previously reported a new polymerization system of aromatic amines using H_2O_2 in the presence of Fe catalyst [11]. The polyamines including PANI showed high solubility in organic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP).

The polymerization is considered to proceed through redox reactions between Fe(II) and H_2O_2 to generate radicals like $^{\cdot}OH$ which abstract the NH hydrogen to give $^{\cdot}N$ radical that is considered to be responsible for preparation of the polymer chain. This method was mainly developed for polyaniline, and was also successfully extended to polyaromatic amines [12]. However, they gave lower electrical conductivity than usual insoluble polyaniline powder which was synthesized with ammoniumpersulfate as the oxidizing agent. As an extention of the preparation of poly(aryamine)s using the $Fe-H_2O_2$ oxidizing system, we have investigated similar oxidative polymerization of pyrrole. The oxidative polymerization of pyrrole has attracted interest for many years since the first report by Gardini who obtained pyrrole black [13]. Polypyrroles have been prepared by both chemical [14–18] and electrochemical [19–21] polymerization and utilized as electrodes of capacitors due to their high electrical conductivity. However, the structure of polypyrrole has not been well determined because of their insolubility in organic solvents and low stability toward air. Improvement of solubility and stability in air are required to determine molecular weight and structural analysis of polypyrrole. Many works have been carried out to obtain thin polyaniline film deposited on the surface of fibers, textile, glass etc. Ballav and Biswas showed different polymerization results of aniline and pyrrole in the presence of montmorillonite to give clay-polymer nanocomposites without solvent and oxidizing agents [22]. The reaction mixture was gradually heated and refluxed, and gave the polymer-clay composites. The composites showed chemical properties similar to those of polyaniline and polypyrrole, however, they had lower electrical conductivity.

In this paper we report the results of the copolymerization of pyrrole with aniline using the H_2O_2–Fe catalyst, which was previously applied in the polymerization of aniline and its derivatives [22,23].

EXPERIMENTAL

Materials

Pyrrole and aniline were purchased from Tokyo Kasei Kygyo Co. Ltd and purified by vacuum distillation and stored under argon in the dark. $FeSO_4$ and H_2O_2 (31% aqueous) were purchased from Koso Chem. Co. Ltd. and Mitsubishi Gas Chemical. Co. Inc., repectively.

Chemical Oxidative Polymerization of Pyrrole

To a dilute H_2SO_4 (0.15 M, 7.5 mmol) solution was added powdery $FeSO_4 \cdot 7H_2O$ (20 mg, 0.070 mmol) and pyrrole (1 mL, 15 mmol). On keeping the resulting mixture at 30°C, 31% H_2O_2 (0.74 mL, 6.7 mmol) was slowly added to the solution over a period of 2 h. The reaction mixture was agitated continuously for another 5 h under air at 30°C to cause precipitation of a black solid. The reaction mixture was quenched with ice water, and the solid product was collected on a glass filter and washed with methanol, and was dried in dynamic vacuum at room temperature to give polypyrrole as black powder (0.92 g, 95%).

Chemical Oxidative Random Copolymerization of Pyrrole and Aniline

Copolymerization of pyrrole and aniline was carried out similary to the polymerization of pyrrole. Molar ratios of pyrrole to aniline ranged from 5:1 to 1:9. Typical experimental procedure (aniline:pyrrole = 1:1) was as follows. Aniline (2.28 mL, 25 mmol) was added to a dil. H_2SO_4 (0.5 M, 0.05 mol) solution, which was soon followed by addition of pyrrole (1.75 mL, 25 mmol) with stirring. On keeping the resulting mixture at 30°C powdery $FeSO_4 \cdot 7H_2O$ (139 mg, 0.5 mmol) was added to the reaction mixture with vigorous stirring, and 31% H_2O_2 (7.5 mL, 68 mmol) was slowly added to the solution over a period of 3 h. The reaction mixture was agitated continuously for another 9 h under air at 30°C to cause precipitation of a black solid. The reaction mixture was quenched with ice water, and the solid product was collected on a glass filter, washed with methanol, and dried in dynamic vacuum at room temperature to give copolymer as a black powder (3.8 g, 95%).

Polymer Characterization

IR spectra were measured on a Jasco IR-810 spectrophotometer in KBr disks. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DT-30 thermal analyzer under nitrogen atmosphere at a constant heating rate of 10°C min^{-1}. UV-vis spectra were recorded on a Hitachi 200–20 spectrophotometer at room temperature. Gel permeation chromatography charts (GPC chart) were recorded on Toso HLC-810 apparatus at 25°C using 0.01 M LiBr/DMF as an eluent. The number-average (Mn) and weight-average (Mw) molecular weight were determined using polystyrene standards. The electrical conductivity (σ) was measured with pellets prepared by pressing the powder of the sample using a two-probe method with a Takeda Riken TR-8651 electrometer.

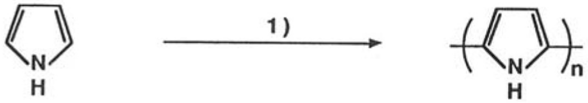
RESULTS AND DISCUSSION

Synthesis of Polypyrrole

Oxidative coupling of pyrrole using H_2O_2 in the presence of the Fe catalyst gave polypyrrole as shown in Scheme 1. Prepared powdery polypyrrole was slightly soluble in polar organic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP). Nos. 1 and 2 in Table 1 show results of the polymerization of pyrrole. The polymerization reaction with 0.5 mol of H_2O_2 per 1 mol of pyrrole was completed in 5 h to give 95% yield (No. 1). Use of 0.25 mol of H_2O_2 per 1 mol of pyrrole gives much lower yield (56%, No. 2 in Table 1). The C H N ratio of the homopolymer was close to the value of polypyrrole (C_4H_3N), although the absolute value of C, H, and N are considerably smaller than the proposed structure of polypyrrole; similar analytical data have been reported for the previously reported polypyrrole [13–21].

Synthesis of Random Copolymers of Pyrrole and Aniline

Copolymerization of pyrrole and aniline was carried out using H_2O_2 in the presence of Fe catalyst. Table 1 (Nos. 3–6) shows results of the



1) H_2O_2 and Fe^{2+}, at 30 °C in an aqueous H_2SO_4 solution

SCHEME 1 Polymerization of pyrrole.

TABLE 1 Chemical Oxidation Polymerization of Pyrrole and Copolymerization of Pyrrole and Aniline with H_2O_2 and Iron(II) Sulfate Catalyst

	Monomer (mmol)							
No.	Aniline	Pyrrole	H_2SO_4 (mmol)	$FeSo_4$ (mmol)	H_2O_2 (mmol)	Time (h)	Yields[2] (%)	Molecular weight[3] (Mw)
1	0	14	7.5	0.07	6.7	5	95	8000
2	0	14	7.5	0.07	3.4	3	56	–
3	8.3	42	50	0.50	18	1	85	–
4	25	25	50	0.50	68	9	94	6200
5	42	8.3	50	0.50	41	5	75	8400
6	45	5	50	0.50	68	15	70	15000

[1] Polymerization was carried out using H_2O_2 (31%) in the presence of the $FeSO_4{\cdot}7H_2O$ at 30°C.

[2] Yield = weight of polymer/(weight of pyrrole + weight of aniline).

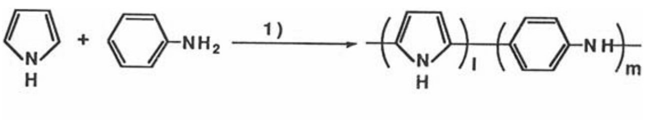
[3] Weight – average molecular weights (Mw) were evaluated by GPC (polystyrene standard, 0.01 mol L^{-1} LiBr/DMF solution as eluent).

copolymerization of pyrrole and aniline under various reaction conditions. The reaction proceeded smoothly by this catalyst system to give random copolymers of pyrrole and aniline as shown in Scheme 2.

Prepared powdery copolymers are black and slightly soluble in polar organic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP). The C:H:N ratio of the copolymer depends on the molar of the monomer. At the moment, it is not possible, from the analytical data, to determine whether the moiety from aniline in the copolymer contains the NH hydrogen or not. However, abstraction of rather strong IR absorption band at about 3500 cm^{-1} for the polymer (Fig. 1, vide infra) supports the presence of the NH hydrogen.

Characterization of Polypyrrole

Figure 1(a) shows the IR spectra of polypyrrle synthesize by H_2O_2–Fe catalyst. The IR spectra of polypyrroles already prepared by the other method strongly depend on the synthetic method [23]. The difference



1) H_2O_2 and Fe^{2+}, at 30 °C in an aqueous H_2SO_4 solution

SCHEME 2 Copolymerization of pyrrole and aniline.

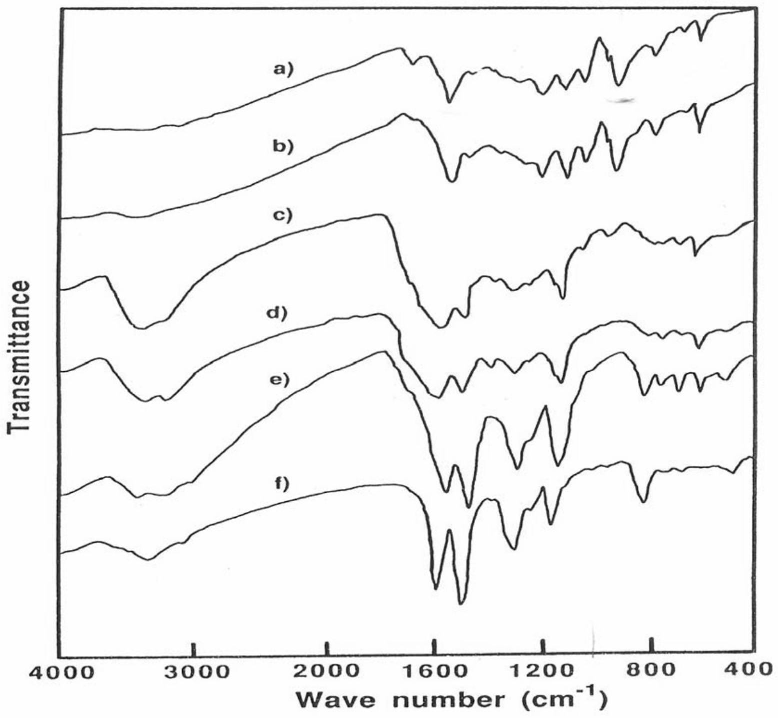


FIGURE 1 IR spectra of homopolymers {(a) polypyrrole, (f) polyaniline} and random copolymers {Synthesized as aniline/pyrrole molar ratio (b) 0.2, (c) 1, (d) 5 and (e) 9}.

has been explained in term of the interaction between the polymer and oxidant used for polymerization of pyrrole. The IR spectrum of the polypyrrole prepared by the present oxidation procedure is similar to that of the polymer obtained by oxidation polymerization of pyrrole using $FeCl_3$ [16,23a]. The spectrum shows bands at 1550 and 1460 cm^{-1} assigned to the stretching vibration of the pyrrole ring, the band at 1040 cm^{-1} to the C–H out of plane vibration, and the bands below 900 cm^{-1} to the C–H out of plane vibration. The bands at 1100 and 600 cm^{-1} are assigned to the sulfate anion according to assignment by Salmon [24]. The polymer shows a weak peak at 1700 cm^{-1}. The peak was also observed in polypyrrole prepared by $FeCl_3$ and was assigned to carbonyl C=O stretching due to pyrrolidone partly formed in the polymer structure [16,25]. Figure 2 (No. 6) shows the X-ray diffraction pattern of the powdery polymers. polypyrrole obtained by our catalytic system showed a broad peak at $2\theta =$ ca.

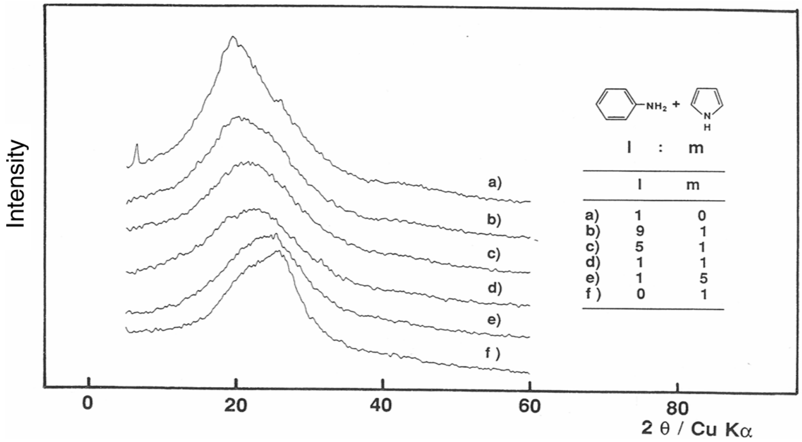


FIGURE 2 X-ray diffraction of homopolymers {(a) polyaniline (f) polypyrrole} and random copolymers {synthesized as aniline/pyrrole molar ratio (b) 9, (c) 5, (d) 1 and (e) 0.2}.

26°, with a shoulder at $2\theta =$ ca. 20°. The thermogravimetric scans of polypyrrole is shown in Figure 3. The weight loss of polypyrrole (Fig. 3f) starts at about 80°C, and becomes 38% at 600°C. The intial weight loss be due to elimination of the water absorbed to the polymer.

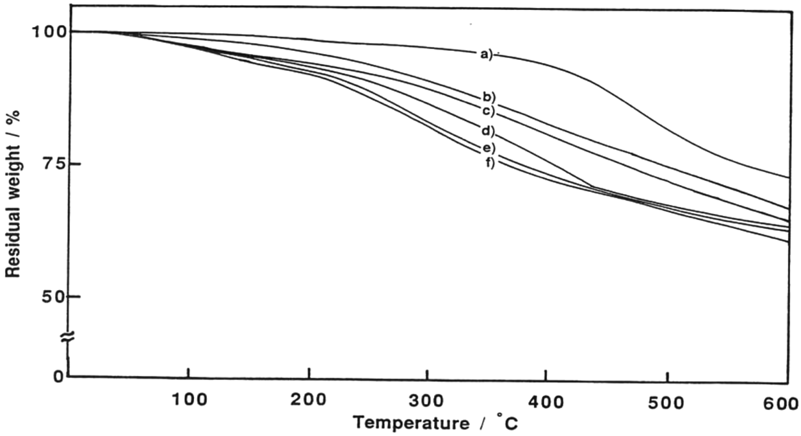


FIGURE 3 Thermogravimetric scan of homopolymers {(a) polyaniline (f) polypyrrole} and random copolymers {synthesized as aniline/pyrrole molar ratio (b) 9, (c) 5, (d) 1 and (e) 0.2}.

The molecular weight measurement of polypyrrole (soluble part in DMF) were carried out by gel permeation chromatography. Although the polypyrrole was not completely soluble in the solvent, the weight-average molecular weights (Mw) of a soluble part to DMF is about 8000.

Characterization of Random Copolymers of Pyrrole and Aniline

Figure 1 includes IR spectra of polyaniline [11,12] and the random copolymer synthesized with the H_2O_2-Fe catalyst system. Comparison of the spectra in Figure 1 reveals that the increase in molar ratio of aniline causes the increase in absorption bands at 3300, 1600, 1500, 1160 and 830 cm^{-1} that are not observed in polypyrrole. On the contrary, the band of polypyrrole at 1550 cm^{-1} decreases, and carbonyl absorption band at 1700 cm^{-1} is not observed in the copolymers. The C–H out-of-plane bending mode of copolymers show more complicated absorption bands than of polyaniline or polypyrrole. Figure 2 includes the X-ray diffraction patterns of the copolymers and polyaniline. X-ray pattern of the emeraldine base form polyaniline is shown in Figure 2 [21]. It consists mainly of one intense broad peak centered at $2\theta =$ ca. 19.5°, with a shoulder at $2\theta =$ ca. 30° and a weak peak at $2\theta =$ ca. 45°. These broad peak suggest low crystallinity of the polymer. X-ray diffraction patterns for the copolymers of pyrrole and aniline give rise to similar broad bands at intermediate positions between those of polyaniline (at $2\theta =$ ca. 19.5°) and polypyrrole (at $2\theta =$ ca. 26°). The thermogravimetric scans of the copolymers are included in Figure 3. TGA curves of the copolymers on the molar ratio of the monomers used. Increase in the molar ratio of aniline leads to higher thermostability. The molecular weight measurement of the copolymers (soluble part in DMF) was carried out by gel permeation chromatography. The weight-average molecular weights of copolymers are summarized in Table 1. Molecular weight and solubility increase with increase in the molar ratio of aniline, indicating that the copolymers with higher content of the aniline brings about high solubility and high molecular weight. The electrical conductivity of copolymers gave 10^{-5} S/cm by a two-probe method.

CONCLUSION

Polypyrrole and random copolymers of pyrrole and aniline were successfully obtained by chemical oxidative polymerization of the pyrrole and various mixtures of pyrrole and aniline with H_2O_2 in the presence of the Fe catalyst. They showed higher thermal stability and solubility than polypyrrole synthesized by other polymerization methods. The properties of the random copolymers depend on the molar ratio of aniline added to the reaction system.

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