Novel Catalytic Oxidative Synthesis of Soluble Conductive Polymers of Poly(3-butoxycarbonyl-4-methylpyrrole)

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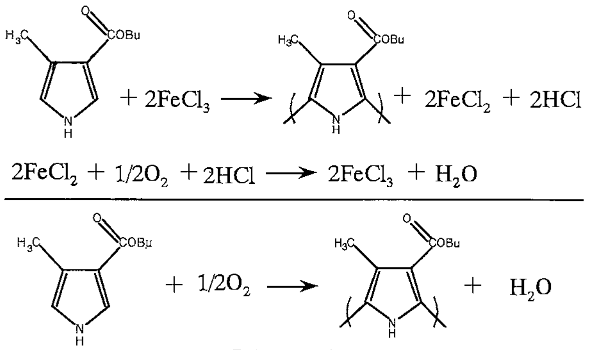
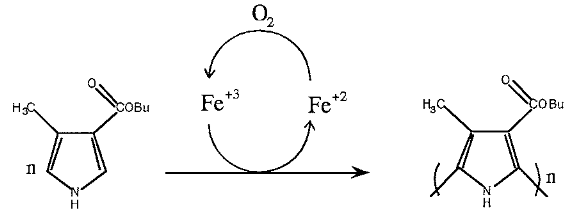
A soluble conductive polymer, poly(3-butoxycarbonyl-4-methylpyrrole) was synthesized by catalytic oxidative polymerization of 3-butoxycarbonyl-4-methylpyrrole, where only a small amount of iron (III) chloride as a catalyst, and enough amount of oxygen as an oxidant were used. Addtion of $BF_3 \cdot Et_2O$ to the reaction system can make the yield of the polymer remarkably increase.

Polypyrrole is well known as one of the typical conductive polymers,[1-8] but mostly insoluble in most organic solvents. This makes the processing difficult and limits the application as conductive polymer. The polymers of pyrrole derivatives having ester and/or alkyl groups in the pyrrole ring were reported to be easily soluble in the solvent like tetrahydrofuran (THF) and N-methylpyrrolidone (NMP). 3-Butoxycarbonyl-4-methylpyrrole (BMP) can be polymerized by chemical oxidation of BMP with enough amount of $FeCl_3$ as an oxidant to form soluble polymer.[9] Synthesis of conductive polymers by an ordinary chemical oxidative polymerization method, however, requires a large quantity of oxidizing reagent. It causes not only an increase in the production cost of conductive polymer but also an increase in trouble in processes after the synthesis. Moreover, it may lead environmental problems because the by-product may produce a large quantity of effluent. We have synthesized poly(*p*-phenylene), polypyrrole and polyaniline by a catalytic oxidative polymerization method, in which relatively small quantity of metal salts are used as a catalyst and enough quantity of molecular oxygen as an oxidizing reagent.[10-18] In this method the metal salts are recycled and only oxygen is consumed with producing water as a by-product in its ideal case. Here we want to report the successful polymerization of BMP by the catalytic oxidative polymerization method to produce a soluble conductive polymer.

Catalytic polymerization of BMP was carried out as follows (Scheme 1 and 2): BMP[19] 1 cm^3 (5.64×10^{-3} mol) and $FeCl_3$ 0.18 g ($1/5 \times 5.64 \times 10^{-3}$ mol) were dissolved into the mixed solvent of 10 cm^3 of chloroform and 10 cm^3 of butyl acetate, stirred at room temperature for 24 h under oxygen atmosphere. After the reaction for 24 h, the solid product was separated by filtration. Blackish brown colored filter cake was dispersed into 21 cm^3 of methanol, and the mixtures were stirred for 30 min after addition of 1.8 cm^3 of 80% hydrazine. After filtrartion, the cake was again dispersed into 18 cm^3 of water, and then 2.5 cm^3 of 98% sulfuric acid was added to the mixtures, keeping the stirr for 30 min. After filtration, cake was repeatedly washed with pure water, and dispersed into 23 cm^3 of water. To the mixtures, 0.7 cm^3 of 80% hydrazine was added, and the resulting mixtures were stirred for 30 min. After filtration, cake was washed with water, and finally washed with 5 cm^3 of methanol, and then dried at 60 °C under vacuum. Yield was 0.24 g (the yield based on the charged BMP was 24%). For reference, polymerization of BMP was performed by an ordinary chemical oxidative polymerization method as well. The procedures were as follows: BMP 1 cm^3 (5.64×10^{-3} mol) and $FeCl_3$ 2.74 g ($3 \times 5.64 \times 10^{-3}$ mol) were dissolved into the mixed solvent of 10 cm^3 of chloroform and 10 cm^3 of butyl acetate, and the mixtures were stirred at room temperature for 4 h under a flow of nitrogen. After the reaction, the same procedures were applied as in the case of the catalytic polymerization method mentioned above. The yields of the polymers by both methods, i. e., chemical oxidative polymerization and catalytic oxidative polymerization are summarized in Table 1. Turnover number is defined as the polymer yield in percent against the calculated yield of the polymer based on charged amount of $FeCl_3$, meaning how many times $FeCl_3$ is repeatedly used as a catalyst.



Scheme 1.



Scheme 2.

In run 3 (an ordinary oxidative polymerization), the yield of polyBMP is 39% on the basis of the charged amount of BMP. In this case 26% of charged amount of $FeCl_3$ are used for the polymerization because the polymerization of 1 mole of BMP requires 2 moles of $FeCl_3$ as an oxidant. In run 1, on the other hand turnover number is 120% when the relatively small amount of $FeCl_3$ (mole ratio of $FeCl_3$ to BMP is 0.2) is used under oxygen. This means that some of $FeCl_3$ are repeatedly used as the catalyst. If the reaction time is extended to 24 h from 4 h, the turnover number increases to 240% (run 2). Apparently $FeCl_3$ is used as the catalyst for the polymerization of BMP. If the chemical oxidative polymerization (mole ratio of $FeCl_3$/BMP=3) was carried out under air and oxygen, the yield of polyBMP increases to 68% and 87%, respectively. This means that some $FeCl_3$ may play a role of catalyst under oxygen.

The above results suggest that the reaction of $FeCl_3$ with O_2 is a rate-determining step in the catalytic oxidative polymerization of BMP in the present system. Thus, the reaction was followed by the signal resulting from Fe^{3+} in electron spin resonance spectra. The intensity of the Fe^{3+} signal increased after addition of oxygen, from which the rate of conversion of Fe^{2+} to Fe^{3+} is proved to be 4.3%/h. The reaction rate of this elementary reaction has been really confirmed to be very late.

Both polymers, obtained by catalytic oxidative polymerization and ordinary chemical oxidative polymerization, are easily soluble in THF and NMP. The structures of polymers synthesized by two polymerization methods were compared in infrared absorption spectra (IR), ^1H and ^{13}C nuclear magnetic resonance spectra (NMR), gel permeation chromatography (GPC), scanning electron microscopy (SEM), and elementary analysis. No difference between both polymers was observed in IR and ^1H and ^{13}C NMR spectra. From the result of GPC measurement weight average molecular weight (M_w) of polymers prepared by catalytic oxidative polymerization was 45000-58000, meanwhile M_w of those by chemical oxidative polymerization was 61000-115000, Thus, the latter was revealed to be higher molecular weight than the former. Dispersibility of molecular weight (M_w/M_n) was recognized to be little difference, namely 2.12-2.38 in catalytic polymerization, and 2.00-2.38 in chemical polymerization. Globular particles of relatively equal size were observed in polymers prepared by the catalytic method, while distinct globular particles were not recognized in chemically polymerized polymers by SEM measurement. The elementary analysis has shown the existence of chlorine in polymers prepared by the chemical oxidative method, but the absence of chlorine in those by the catalytic oxidative method. Physical properties of both polymers, prepared by two different methods, were compared by the conductivity measured by a four-probe technique. The conductivity of polymers prepared by the catalytic oxidative method was about 4.6×10^{-5} S cm^{-1}, and those by the chemical oxidative method was 1.4×10^{-4}-5.0×10^{-5} S cm^{-1}, which means that there is little difference in electroconductivity in both polymers.

Last but not least is unique and interesting effect of an additive upon the polymer yield. Since the yield of polypyrrole can be improved by addition of $AlCl_3$ as Lewis acid in the catalytic oxidative polymerization,[13] we have tried to add soluble $BF_3\cdot Et_2O$ in the present system. The yield of polymers has increased remarkably by the addition of $BF_3\cdot Et_2O$. The results are shown in Table 2. When the quantity of $BF_3\cdot Et_2O$ is gradually increased from 0.2 mol to 2.0 mol per 1 mol of BMP, the yield suddenly increases at 0.5 mol of $BF_3\cdot Et_2O$, and the highest yield of 66% was achieved by the addition of 1.0 mol of $BF_3\cdot Et_2O$. The turnover number is 660%, which is 2.7 times larger than that without $BF_3\cdot Et_2O$. The yield of 66% is very high and almost the same as the yield of polymers prepared by chemical oxidative polymerization using 3 mole of $FeCl_3$ under air. When the sum of molar number of $FeCl_3$ and $BF_3\cdot Et_2O$ was fixed to 1.2 mol per 1 mol of BMP and the ratio of $FeCl_3$ to $BF_3\cdot Et_2O$ was changed, the high yield of 66-77% was achieved almost independently of the ratio. Although it is not clarified yet how $BF_3\cdot Et_2O$ is concerned with the catalytic oxidative polymerization reaction in the present system,[20] this is the first report that an additive to the catalytic system can really increase the yield remarkably. This kind of method can provide a new approach to the catalytic oxidative polymerization to produce conductive polymers.

Table 1. Comparison of the yield of polymers prepared by two kinds of polymerization methods

Run	Molar ratio ($FeCl_3$/BMP)	Reaction time/h	Atmosphere	Yield /%	Turnover number/%
1[a]	0.2	4	O_2	12	120
2[a]	0.2	24	O_2	24	240
3[b]	3	4	N_2	39	(26)[c]
4[b]	3	4	air	68	(45)[c]
5[b]	3	4	O_2	87	(58)[c]

[a]Catalytic oxidative polymerization. [b]Chemical oxidative polymerization. [c]Apparent turnover number although $FeCl_3$ is not used as a catalyst because of enough amounts of $FeCl_3$ in these cases.

Table 2. Effect of $BF_3\cdot Et_2O$ on the yield of BMP polymers prepared by catalytic oxidative polymerization

Run	Molar ratio ($BF_3\cdot Et_2O$/$FeCl_3$/BMP)	Yield /%	Turnover number /%
2[a]	0 / 0.2 / 1.0	24	240
6	0.2 / 0.2 / 1.0	29	290
7	0.5 / 0.2 / 1.0	56	560
8	1.0 / 0.2 / 1.0	66	660
9	2.0 / 0.2 / 1.0	56	560

[a]without $BF_3\cdot Et_2O$

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19 BMP was kindly offered by Nippon Soda Co., Ltd.
20 A referee suggests that $BF_3\cdot Et_2O$ may keep the catalytic activity of $FeCl_3$ by depressing the formation of iron(III) hydroxide by hydration of $FeCl_3$.