

New Catalytic Polymerization of Pyrrole

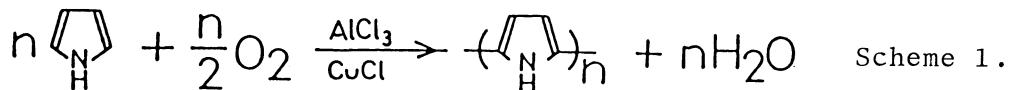
Naoki TOSHIMA* and Jun-ichi TAYANAGI

Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Pyrrole can be easily polymerized to produce polypyrrole by using an $\text{AlCl}_3\text{-CuCl-O}_2$ catalytic system. The yield of polypyrrole was very high and more than 600% based on the amount of CuCl used. The conductivity of the pressed polypyrrole was $10^{-2} \text{ S cm}^{-1}$.

Polypyrrole (PPY) is one of the most attractive functional polymers from the viewpoint of its electronical conductivity and stability.¹⁾ The preparation methods of PPY from pyrrole can be devided into two, electricchemical and chemical polymerization.¹⁾ Most of the investigations on PPY have been carried out about that prepared by the electrochemical method. Recently highly electroconductive PPY was prepared chemically by using a Fe(III) or Cu(II) metal salt such as FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$, CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ ²⁻⁴⁾ or using halogen such as I_2 , Br_2 , and Cl_2 .⁵⁻⁷⁾ These chemicals are called "catalysts" in the reports. However, they are consumed stoichiometrically. Thus, these methods require a large amount of chemicals for the mass production which should be an advantage for a chemical method compared with the electrochemical method.

Recently we have reported that poly-1,4-phenylene can be prepared from benzene at high yield by using only a small amount of AlCl_3 and CuCl under O_2 .⁸⁾ Toluene can also be polymerized by the same catalytic system with or without an appropriate solvent.⁹⁾ In the present letter, we would like to report that PPY can be prepared from pyrrole at high yield by using only a small amount of AlCl_3 and CuCl in an appropriate solvent under oxygen (Scheme 1).



Typical experimental procedure was as follows: 1.5 g (1.1 mmol) of AlCl_3 , 1.1 g (1.1 mmol) of CuCl and 30 cm^3 of acetonitrile (as a solvent)

Table 1. Polymerization of pyrrole catalyzed by an $\text{AlCl}_3\text{-CuCl-O}_2$ system^{a)}

Run	Solvent	Yield / %		Elemental Analysis ^{d)}
		$\text{CuCl}^b)$	Py ^{c)}	
1	p-Xylene	1300	130	$\text{C}_{8.25}\text{H}_{9.85}\text{N}_{1.00}\text{Cl}_{0.02}\text{O}_{1.76}$
2	MeNO_2	1200	120	$\text{C}_{5.17}\text{H}_{3.84}\text{N}_{1.00}\text{Cl}_{0.04}\text{O}_{1.35}$
3	PhNO_2	1300	130	$\text{C}_{6.35}\text{H}_{4.92}\text{N}_{1.00}\text{Cl}_{0.02}\text{O}_{0.84}$
4	MeCN	700	70	$\text{C}_{4.54}\text{H}_{3.86}\text{N}_{1.00}\text{Cl}_{0.22}\text{O}_{0.36}$

a) Charged molar ratio of AlCl_3 : CuCl : pyrrole : solvent was 1 : 1 : 5 : 50. Reactions were carried out at room temperature for 24 h.

b) Based on the amount of CuCl used.

c) Based on the amount of pyrrole used.

d) Based on nitrogen.

were placed in a 200 cm^3 Kjeldahl flask and the mixture was stirred at room temperature under N_2 for 1 h. Then 3.9 cm^3 (5.5 mmol) of pyrrole was added and the mixture was further stirred for 2 h. The polymerization reaction was carried out by replacing the atmosphere of the reaction mixture with oxygen and stirring the mixtures at room temperature for 24 h. Then the reaction mixture was filtrated and the remaining solid was repeatedly washed with a HCl solution, pure water and methanol. The black solid obtained was dried overnight under vaccum at 80 °C.

The yields and elemental analyses of PPYs prepared in various solvents are summerized in Table 1. The yields are based on the amount of CuCl and pyrrole used, respectively. The former yield corresponds to the turn over number of CuCl as a catalyst. In each run the yields based on CuCl are more than 100%, which suggests that CuCl works effectively as a real catalyst. When p-xylene, nitromethane and nitrobenzene are used as a solvent (run 1, 2, and 3, respectively), the yields based on pyrrole can be calculated to be higher than 100% and the results of elemental analyses are far from the value calculated for PPY ($\text{C}_4\text{H}_3\text{N}$). These results suggest that these solvents react with pyrrole to some extent in the presence of AlCl_3 and CuCl , and are involved in the polymeric products. The conductivities of PPYs prepared in these solvents are lower than $10^{-10} \text{ S cm}^{-1}$.¹⁰⁾ On the contrary, when acetonitrile is used as a solvent, the elemental analysis of the polymeric product is close to the value calculated for PPY. By using acetonitrile as a solvent the conductivity of PPY increases up to the order of $10^{-2} \text{ S cm}^{-2}$.¹⁰⁾ Moreover, the IR spectrum of this product (Fig. 1(b)) is also close to that of PPY prepared by the reaction with FeCl_3 in water (Fig. 1(a)).²⁾ These results indicate that acetonitrile is the best among

these solvents for the pyrrole polymerization by using an $\text{AlCl}_3\text{-CuCl}_1\text{-O}_2$ system and that the polymer obtained in acetonitrile mainly consists of the pyrrole unit.

The elemental analysis in Table 1 shows the contamination of a small amount of Cl and O in the PPy obtained in acetonitrile. Electron spectroscopy for chemical analysis (ESCA) spectrum of Cl 2p shown in Fig. 2(a) clearly indicates the presence of Cl, at least two kinds of Cl, in the product. If the product is treated with an aqueous NH_3 solution (undoping treatment), the Cl peak at the lower energy disappears (Fig. 2(b)). These results demonstrate that the product contains both a chloride anion as a dopant and a chlorine atom covalently bound to the pyrrole ring carbon. As shown in the IR spectrum of the product treated with an aqueous NH_3 solution (Fig. 1(c)), the broad absorption from 4000 to 1600 cm^{-1} , which is generally observed in PPy prepared by chemical methods,

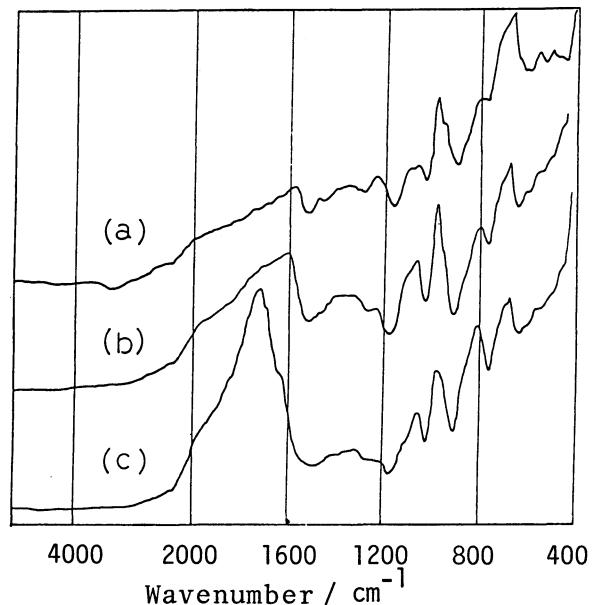


Fig. 1. IR spectra of polypyrrole prepared (a) by FeCl_3 in H_2O , (b) by an $\text{AlCl}_3\text{-CuCl}_1\text{-O}_2$ system in CH_3CN , and (c) by treatment of the sample (b) with aq. NH_3 .

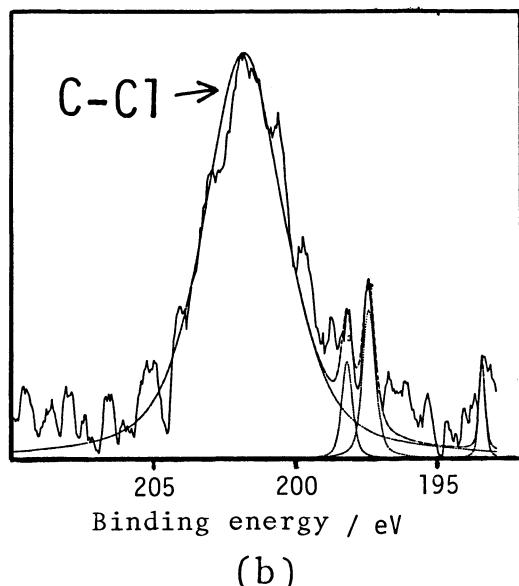
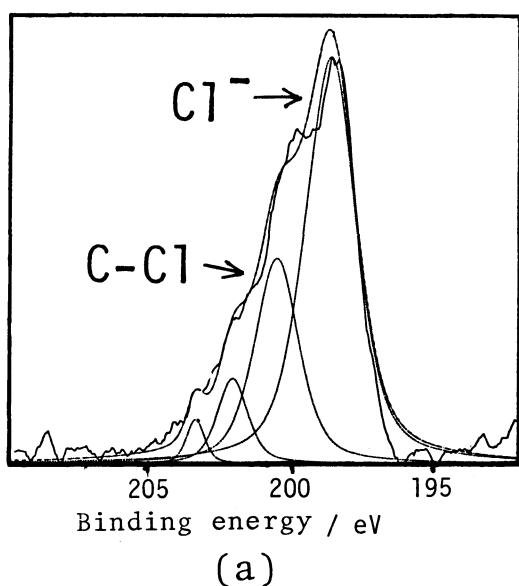


Fig. 2. ESCA Cl 2p spectrum of polypyrrole prepared in acetonitrile.

decreases as the result of the treatment with NH_3 and the shoulder peak appears at 1600 cm^{-1} . This shoulder peak can be assigned as a carbonyl or carboxyl group. ESCA spectrum of C 1s (Fig. 3) also shows the presence of both a carbonyl (286.6 eV) and a carboxyl group (288.4 eV). Therefore, the product obtained in acetonitrile mainly consists of the pyrrole unit and contains a small amount of C-Cl, carbonyl and carboxyl groups not only at the 2,5-position of the terminal ring but also at the 3,4-position of the pyrrole in polymer chain. It can be reasonably proposed that the former groups are the result of chlorination of the pyrrole ring by AlCl_3 and the latter oxidation of the primary product by oxygen. Thermogravimetric analysis of the product was carried out at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ under nitrogen. The weight loss of the product was about 50% at $1200 \text{ }^{\circ}\text{C}$, which indicates the high thermostability of the polymeric product.

References

- 1) N.C.Billingham and P.D.Calvert, *Adv. Polym. Sci.*, 90 (1989); N.Toshima and J.Tayanagi, *Kino Zairyo*, 10, No.5, 11 (1990).
- 2) S.Rapi, V.Bocchi, and G.P.Gardini, *Synth. Met.*, 24, 217 (1988).
- 3) T.H.Chao and J.March, *J. Polym. Sci. A, Polym. Chem.*, 26, 743 (1988).
- 4) M.M.Castisso-Ortega, M.B.Inoue, and M.Inoue, *Synth. Met.*, 28, C65 (1989).
- 5) E.T.Kang, T.C.Tan, K.G.Neoh, and Y.K.Ong, *Polymer*, 27, 1958 (1986).
- 6) E.T.Kang, K.G.Neoh, T.C.Tan, and Y.K.Ong, *J. Macromol. Sci.-Chem.*, A24, 631 (1987).
- 7) K.G.Neoh, T.C.Tan, and E.T.Kang, *Polymer*, 29, 553 (1988).
- 8) N.Toshima, K.Kanaka, A.Koshirai, and H.Hirai, *Bull. Chem. Soc. Jpn.*, 61, 2551 (1988).
- 9) N.Toshima, K.Kanaka, N.Ishiyama, and H.Hirai, *Bull. Chem. Soc. Jpn.*, 62, 2201 (1989).
- 10) The conductivity of the polymeric product was measured by a two probe method under vaccum. The polymeric product was pressed under vaccum at 3000 kg cm^{-2} resulting in a pellet of 1 cm in diameter upon heating by heat gun, and then two gold electrodes were deposited onto the pellet.

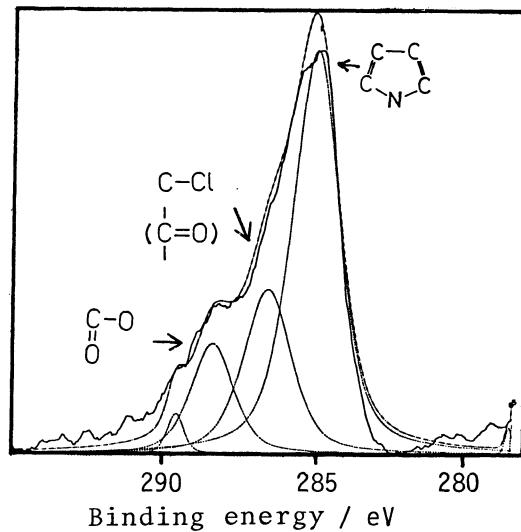


Fig. 3. ESCA C 1s spectrum of polypyrrole prepared in CH_3CN .

(Received May 7, 1990)