

A NEW METHOD ON THE CHEMICAL SYNTHESIS OF DOPED POLYPYRROLE INITIATED BY $\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}$ SYSTEM

ZHANG Jie* (张杰), SHE Yongbo (余永柏), LU Bin (陆斌),
ZHOU Yuliang (周岳亮) and FU Kejian (傅克坚)

(Institute of Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100080)

ABSTRACT

Our objectives were to develop a new chemical method for the polymerization of pyrrole. CuCl_2 dissolved in $\text{C}_2\text{H}_5\text{OH}$ solvent is primarily used for the initiation polymerization of pyrrole. The polymers with different yield and conductivity were obtained by varying the initial concentration of Cu^{2+} . The initial concentrations of Cu^{2+} varied from 1.2×10^{-4} mole to 6.48×10^{-3} mole Cu^{2+} with 2.16×10^{-2} mole pyrrole. The polypyrrole obtained was characterized with elemental analyzer, XPS, IR spectroscopy, Four-point probe and SEM.

INTRODUCTION

Polypyrrole (PPy) is one of the most important highly conductive organic polymer materials. Since the chemical method has many advantages for the synthesis of polypyrrole, especially for the doped polymer, the development of new chemical method becomes important. Some of chemical methods for the preparation of polypyrrole have been reported^[1]. The polypyrrole was obtained by the use of various oxidant, such as I_2 , H_2O_2 , AgClO_4 , CuClO_4 and FeCl_3 in aqueous or nonaqueous solution^[2-9]. Recently we find that the CuCl_2 dissolved in $\text{C}_2\text{H}_5\text{OH}$ can effectively initiate the polymerization of pyrrole (Py). As the CuCl_2 is not generally used as oxidant for the polymerization owing to its weak oxidation ability, the find on the CuCl_2 initiated polymerization of pyrrole probably suggests a new approach for the investigation of chemical synthesis of polypyrrole.

In this paper, we will report a new convenient chemical method for the polymerization of pyrrole. The doped polypyrrole obtained was characterized with IR spectroscopy, Four-point probe and SEM.

EXPERIMENTAL

Materials

Pyrrole was purchased from Aldrich Chem. Inc (purity > 99%) and distilled twice before use. CuCl_2 was purchased from Hong Xing Chemical Factory, Beijing (purity > 99%) the crystal water was removed before use. $\text{C}_2\text{H}_5\text{OH}$ was purchased from Beijing Chemical Factory (purity > 99%) and distilled once before use.

Chemical synthesis of polypyrrole

Pyrrole (1.5ml) was added to C_2H_5OH solution (19ml) containing $CuCl_2$ and the reaction is exposed to air. The polypyrrole was formed as a black precipitate and collected by removing the solvent. The yield of polypyrrole obtained increases with the increase of initial concentration of Cu^{2+} .

Physical measurement

The constitution (C, H, N, Cl and Cu) of polymer was analyzed with elemental analyzer (ST-02) and XPS. Sample for the measurement of IR spectrum was prepared by mixing measured quantities of polypyrrole powder with KBr and pressing pellet. The IR spectrum of sample was measured with Perkin Elmer spectrometer. The electrical conductivity of polypyrrole was determined by Four-point probe method. The surface structure of polypyrrole powder was analyzed with SEM(S-450, Hitachi).

RESULTS AND DISCUSSION

The polymerization of pyrrole initiated by $CuCl_2$ - C_2H_5OH system

The influence of initial concentration of Cu^{2+} on the yield of polypyrrole is shown in Table 1 and the yield of polypyrrole increases with the increase of initial concentration of Cu^{2+} . When the Cu^{2+} concentration reaches to 4.32×10^{-3} mole, the yield of polypyrrole is nearly 100%.

Table 1 The yield, conductivity and analytical data of PPy.

Polymer No.	[Py] (mol)	[Cu^{2+}] (mol)	Yield (%)	Conductivity (1/cm Ω)	C	H	N	Cl
PPy ₁	2.16×10^{-2}	1.2×10^{-4}	8	0.34	40.13	3.21	12.02	7.01
PPy ₂	2.16×10^{-2}	4.3×10^{-4}	16	0.55	38.92	3.03	11.56	6.74
PPy ₃	2.16×10^{-2}	8.6×10^{-4}	27	—	39.47	3.10	11.63	6.78
PPy ₄	2.16×10^{-2}	1.08×10^{-3}	43	2.4	40.89	3.56	12.02	6.96
PPy ₅	2.16×10^{-2}	4.32×10^{-3}	100	—	36.91	3.04	10.72	6.25
PPy ₆	2.16×10^{-2}	6.48×10^{-3}	100	3.7	—	—	—	—

This suggests that the polymerization proceeds in a step reaction rather than a chain reaction and the doping process is concomitant with the polymerization. At the initial stage of reaction, pyrrole radical cations are formed by a redox reaction between pyrrole and $CuCl_2$:



A deprotonation coupling occurs successively:



Further coupling reactions lead to the formation of high polymer. Besides the polypyrrole, some of contaminants such as chloride probably exist in the polymer.

In this experiment, we find that for the polymerization of pyrrole initiated by $CuCl_2$, the ratio of initial [Cu^{2+}] and [Py] is smaller than 1, whereas for the polymerization initiated by $FeCl_3$, previously reported^[9-10], the ratio of initial [Fe^{3+}] and [Py] is larger than 1.

In order to further explore the role of $CuCl_2$ - C_2H_5OH , we also investigated the

polymerization of pyrrole initiated by $\text{CuCl}_2\text{-CH}_3\text{OH}$, $\text{CuCl}_2\text{-DMF}$ and $\text{Cu}(\text{NO}_3)_2\text{-C}_2\text{H}_5\text{OH}$ systems under the same conditions. The polypyrrole was obtained by $\text{CuCl}_2\text{-CH}_3\text{OH}$, whereas no polypyrroles were obtained by $\text{CuCl}_2\text{-DMF}$, and $\text{Cu}(\text{NO}_3)_2\text{-C}_2\text{H}_5\text{OH}$. The result shows that the $\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}(\text{CH}_3\text{OH})$ is effective for the polymerization of pyrrole. At present we can not clearly explain the nature of $\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}$ initiated the polymerization of pyrrole, but we believe that the interesting result obtained in our experiment is probably helpful to understand the chemical synthesis of polypyrrole.

The characterization of polypyrrole

The total analysis values of C, H, N, Cl and Cu in polymer are measured with elemental analyzer and XPS, as shown in Table 1 together with reaction conditions. The C:N ratio is equated to 4:1 and the hydrogen content of every product was higher than that of pyrrole ring. This suggests that the polymer is probably hydrated. The XPS indicates that Cu and Cl also exist in the polymer and Cu:Cl ratio is 1:2.75. In accordance with the above results, Besides the hydrated polypyrrole and dopant, some of contaminants are also exist in the polymer.

The conductivity of polypyrrole measured in 273K is also obviously dependent on the initial concentration of Cu^{2+} (in Table 1) and increases with the increase of initial concentration Cu^{2+} . In fact, this also reflects the effect of dopant on the conductivity of polypyrrole. The influence of temperature (77-298K) on the conductivity of doped polypyrrole is shown in Figure 1. (sample no. PPy₆)

At high temperature, it can be approximated by the usual thermally activated temperature dependence given by:

$$\sigma = \sigma_{\infty} e^{-E/kT}$$

The conductivity observed for the obtained polymer was well explained by this equation at temperature between 190 and 290K (in Figure 2).

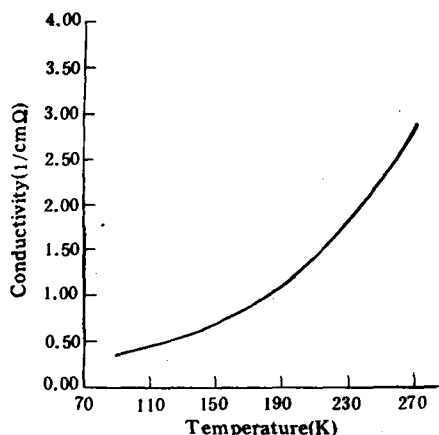


Fig.1 The effect of temperature on the conductivity of doped PPy. $[\text{Cu}^{2+}] = 6.48 \times 10^{-3}$ mole. $[\text{Py}] = 2.16 \times 10^{-3}$ mole. polymerization time 10 hours.

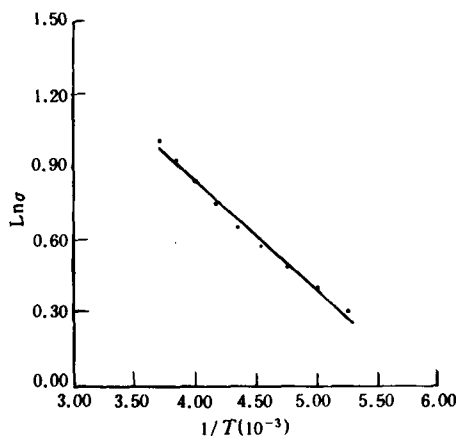


Fig.2 The relationship between conductivity and temperature in the region from 190 to 290K. Data is taken from Figure 1.

From the Arrhenius plot ($\ln$ against $1/T$), the highest room-temperature conductivity ($35.2 \text{ cm}^{-1} \Omega^{-1}$) and a lowest activation energy (5.01 J/mol) can be calculated.

The doped polypyrrole is black powder. The IR spectrum of polymer is shown in Figure 3. The $\text{CH}(3100 \text{ cm}^{-1})$ and $\text{NH}(3400 \text{ cm}^{-1})$ are not visible in the spectrum of doped polypyrrole obtained. This indicates that the polymer is not neutral polypyrrole as compared with the spectrum of neutral polypyrrole^[10]. In the region from 1700 to 500 cm^{-1} , several main bands (1710 , 1551 , 1296 , 1200 , 1050 , 933 , 791 and 416 cm^{-1}) were obviously observed that contain the pyrrole ring vibrations and chloride vibrations. These bands in both intensity and position are similar to that of polypyrrole perchlorate and different from that of neutral polypyrrole^[11].

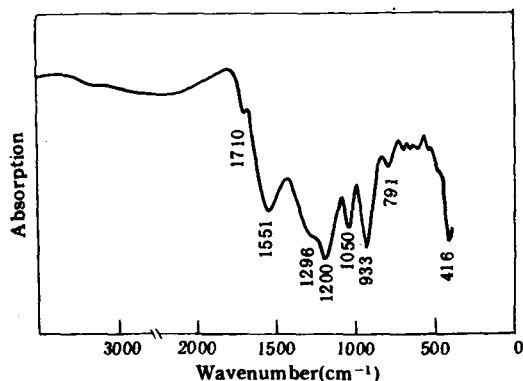


Fig.3 The IR spectrum of PPY

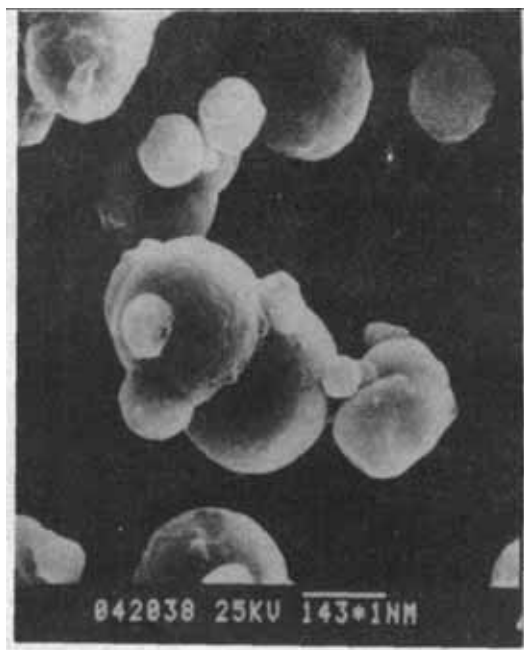


Fig.4 The SEM of PPY

SEM studies on the dried-down dispersive polypyrrole indicate a polydisperse spherical morphology with a particle diameter in the range of 400 — 200nm (in Figure 4).

CONCLUSION

The doped spherical particles of polypyrrole was synthesized by a new chemical method. The results indicate that $\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}$ is very efficient for the polymerization of pyrrole. The yield and conductivity of polypyrrole increase with the increase of initial concentration of Cu^{2+} . The advantages of this method are that the initiation efficiency of $\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}$ for the polymerization of pyrrole is much higher than those ever known initiation system. The new method developed is probably applicable for the oxidative polymerization of other monomer such as thiophene.

Keywords:

$\text{CuCl}_2\text{-C}_2\text{H}_5\text{OH}$ initiation system; Polymerization of pyrrole; Conductive polymer.

Acknowledgment This project was supported by National Natural Science Foundation of China, the Grant Term Fund for « Interaction of Laser and Condense Matter » and Beijing Zhong Guan Cun Associated Center of Analysis and Measurement.

REFERENCES

- [1] Street. G. B., "Handbook of Conducting Polymer" Vol. 8, Marcel Dekker Inc., New York, 1986.
- [2] Yoshino, K.; Hayashi, K. S. and Sugimoto, R., *Jap. J. Phys.*, 1984, 23, 1899.
- [3] Bocchi, V. and Gardai, G. P., *J. Chem. Soc. Chem. Commun.*, 1986, 148.
- [4] Kang E. F.; Neoh. K. G. and H. C. T., *Solid State Commun.*, 1986, 60, 457.
- [5] Mohammadi, A.; Lundstrom, I.; Salaneck, W. R. and Ingnas, O., *Synth. Met.*, 1987, 21, 169.
- [6] Armes, S. P. and Alsissi, M., *Synth. Met.*, 1990, 37, 137.
- [7] Castillo-Ortega, M. M.; Inoue, M. B. and Inoue, M., *Synth. Met.*, 1989, 28, C65.
- [8] Inoue, M. B.; Nebesny, K. W. and Fernando, Q., *Synth. Met.*, 1990, 38, 205.
- [9] Armers, S. P., *Synth. Met.*, 1987, 20, 365.
- [10] Lei, J. T.; Cai, Z. H and Martin, C. R., *Synth. Met.*, 1992, 46, 53.
- [11] Street, G. B.; Clarke, T. C.; Krounbi, M.; Kanazawa, K. K.; Lee, V.; Pfluger, P.; Scott, J. C. and Weiser, G., *Mol. Cryst. Liq. Cryst.*, 1982, 83, 253.