

THE POLYMERIZATION THERMOKINETICS OF PYRROLE IN THE PRESENCE OF IRON TRICHLORIDE

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ABSTRACT

The polymerization thermokinetics of pyrrole in the presence of iron trichloride are studied by using a Calvet microcalorimeter. The apparent activation energy, the pre-exponential constant and reaction order of this reaction in the temperature range of 25.2—37 °C are $34.5 \text{ kJ} \cdot \text{mol}^{-1}$, $10^{2.74} \text{ s}^{-1}$ and 1 respectively. The activation free-energies of this reaction at 25.2 °, 30 ° and 37 °C are 91.8, 92.9 and 94.2 $\text{kJ} \cdot \text{mol}^{-1}$ respectively.

INTRODUCTION

Polypyrrole is capable of conducting electricity and used as a semiconductor. Its synthesis, chemical structure and electrical properties have been reported^[1-7]. However, the polymerization thermokinetics of pyrrole in the presence of iron trichloride have not been reported. In this paper, the synthesis of polypyrrole and the fundamental parameters for the polymerization reaction, including the rate constant (k), the reaction order (n), the apparent activation energy (E), the pre-exponential constant (A) and the activation free-energy (ΔG°) obtained by means of a Calvet microcalorimeter, were studied. These parameters will provide a scientific basis for technological processing of polymer synthesis.

EXPERIMENTAL

Materials

The iron trichloride used as a catalyst and the pyrrole used as a monomer were of chemical purity. A solution of 6.0400g of FeCl_3 (30% wt.) in 14.0038g of distilled water (Solution A) and a solution of 3.5526g of pyrrole (10% wt.) in 31.9054g of benzene (Solution B) were prepared. In our experiments, the molar ratio of Solution A to Solution B was 1:1.

Preparation of the Polypyrrole

Mix Solution A and Solution B in a sealed reactor at room temperature, and then stand or stir until the polymerization reaction comes to the end. Filter and wash the polypyrrole with distilled water until the washing liquid is colorless, and then dry it. Finally, a black powdered (or platelike) polypyrrole was obtained.

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Experimental equipment and conditions

The thermokinetics of the polymerization reaction of pyrrole were measured by using a microcalorimeter, type E. Calvet from SETARAM, France, which had a sensitivity of $66.5 \mu\text{V}/\text{mW}$ and was equipped with two 15 mL-vessels. The microcalorimeter was calibrated by the Joule effect and the calibration was repeated after each experiment. The precision of enthalpy measurement is 2%. The measurements of the title reaction were carried out at 25, 2, 30 and 37 °C. The device used for the study of the polymerization reaction is shown in Fig. 1. The electrical conductivity and IR spectrum for polypyrrole were determined by the voltageshortened compaction method and the Perkin-Elmer Model 180 IR spectrophotometer respectively.

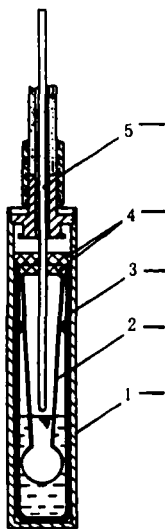
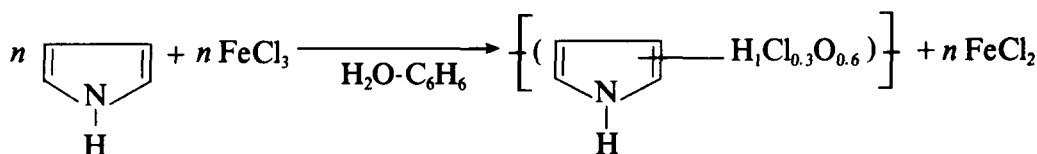


Fig. 1 Device used for the study of polymerization
1. Calorimetric cell; 2. adding tube containing pyrrole solution; 3. adding tube containing FeCl_3 solution; 4. silicone rubber cover; 5. glass rod (On depressing the rod, the bottom of tube, 2, is broken. The two solutions mix together in the tubes 1 and 2.)

(see Figs. 2 and 3). The results determined by the oxidation-reduction method showed that Fe^{+++} ion in the original solution (i. e. Solution A) was changed into Fe^{++} ion in the mother solution. This fact showed that the polymerization of pyrrole in the presence of iron trichloride was an oxidation-reduction reaction, which could be represented as follows:

RESULTS AND DISCUSSION

The polypyrrole yield and Fe^{++} content in the mother solution increased with the increase of the molar ratio of FeCl_3 to pyrrole



The IR spectra of polypyrrole (see Fig. 4) did not show any $\text{C}=\text{O}$ absorption, but $-\text{CH}_2$, $\text{N}-\text{H}$ and ether bond absorption appeared.

The composition of polypyrrole prepared by the above mentioned method was determined to be $\text{C}_{4.107}\text{H}_{4.107}\text{N}_{0.929}\text{O}_{0.559}\text{Cl}_{0.263}$ by elemental analysis. It was different from the published data ($\text{C}_{4.045}\text{H}_{3.066}\text{N}_{1.0}\text{Cl}_{0.39}$ ^[3]; and $\text{C}_4\text{H}_{3.05}\text{N}_{1.06}\text{O}_{1.66}$ ^[7]).

At room temperature the electrical conductivities of the polypyrroles prepared by the reaction of FeCl_3 and pyrrole with the molar ratio 0.1 : 1, 1 : 1 and 1.25 : 1 were 4.7×10^{-6} , 1.4×10^{-5} and $5.1 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$ respectively. These values were 100 — 100,000 times higher than that of the polypyrrole published in literature[7].

The typical thermokinetic (TK) curves of the polymerization reaction of pyrrole in the presence of iron trichloride were shown in Fig. 5. The original data obtained from

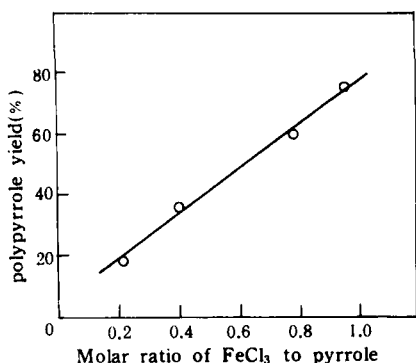


Fig.2 The relationship between the molar ratio of FeCl₃ to pyrrole and the polypyrrole yield

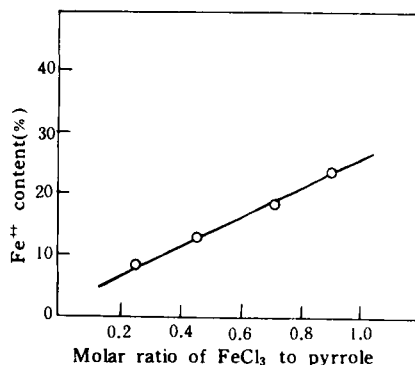


Fig.3 The relationship between the molar ratio of FeCl₃ to pyrrole and the Fe⁺⁺ content in the mother solution

the TK curves were shown in Table 1. These experimental data were put into Equation (1) obtained by the equation of the reaction of the n th order and the relation^[8] between the energy change of a reacting system and the extent of reaction by linear least-squares method.

$$\ln \left(\frac{1}{H_0} \frac{dH_t}{dt} \right) = \ln k + n \ln \left(1 - \frac{H_t}{H_0} \right) \quad (1)$$

where H_0 is the total reaction heat (corresponding to the global area under the TK curve); H_t is the reaction heat in a certain time (corresponding to the partial area under the TK curve); dH_t/dt is the exothermic rate at time t ; k is the rate constant of polymerization; n is the reaction order.

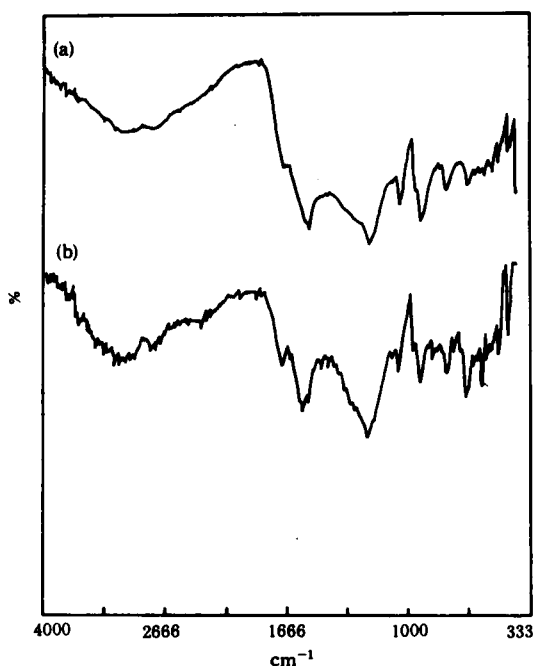


Fig.4 IR spectra of the polypyrrole prepared by reaction of a 10% pyrrole benzene solution with (a) 30% FeCl₃ aqueous solution and (b) 3% FeCl₃ aqueous solution at room temperature

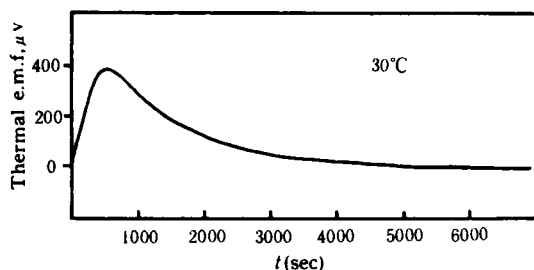


Fig.5 Typical thermokinetic curve of the polymerization reaction of pyrrole in the presence of iron trichloride

The values of k and n obtained by Eq. (1) and the values of E , A and $\Delta G_{\ddagger}^0$ obtained by Eqs. (2) and (3) are all listed in Table 2.

$$\ln k = \ln A - (E/RT) \quad (2)$$

and

$$\Delta G_{\ddagger}^0 = RT \ln (RT/Nhk) \quad (3)$$

where A is the pre-exponential constant; E is the apparent activation energy; R is the gas constant; T is the absolute temperature; $\Delta G_{\ddagger}^0$ is the activation free-energy; N is the Avogadro number; h is Planck's constant.

The results in Table 2 clearly indicated that the higher the temperature of polymerization reaction, the faster the rate of polymerization, and the title reaction was of the first order. The apparent activation energy of the polymerization reaction was estimated to be $34.5 \text{ KJ} \cdot \text{mol}^{-1}$. The pre-exponential constant of the polymerization reaction was $10^{2.74} \text{ s}^{-1}$. The values of E , $\Delta G_{\ddagger}^0$ and A were very low.

Table 1 Thermographic data of the polymerization reaction of the pyrrole in the presence of iron trichloride

t s	25.2 °C		30.0 °C		37.0 °C	
	$(dH/dt)_i \cdot 10^3$	H_i/H_0	$(dH/dt)_i \cdot 10^3$	H_i/H_0	$(dH/dt)_i \cdot 10^3$	H_i/H_0
	$\text{mJ} \cdot \text{s}^{-1}$		$\text{mJ} \cdot \text{s}^{-1}$		$\text{mJ} \cdot \text{s}^{-1}$	
600					5370	0.3012
900	1300	0.3957	3910	0.3528	4030	0.4662
1200	962	0.4963	3110	0.4730	2910	0.5891
1500	764	0.5726	2460	0.5690	2140	0.6800
1800	636	0.6351	2010	0.6472	1600	0.7497
2100	523	0.6857	1670	0.7112	1260	0.8043
2400	453	0.7283	1370	0.7647	1030	0.8486
2700	396	0.7658	1140	0.8154	799	0.8834
3000	339	0.7983	1030	0.8475	685	0.9121
3300	297	0.8267	828	0.8795	542	0.9355
3600	255	0.8521				
3900	226	0.8746				
4200	198	0.8951				

Table 2 The values of k , n , A and $\Delta G_{\ddagger}^0$ for the title reaction

T K	Eq. (1)			Eq. (2)			Eq. (3)
	$k \cdot 10^4$ s^{-1}	n	r^*	E $\text{KJ} \cdot \text{mol}^{-1}$	$\log A$ s^{-1}	r^*	$\Delta G_{\ddagger}^0$ $\text{KJ} \cdot \text{mol}^{-1}$
298.4	5.223	1.05	0.993				91.8
303.2	6.211	0.91	0.996	34.5	2.74	0.995	92.9
310.2	8.816	0.98	0.993	(25.2 — 37 °C)			94.2

* r , The correlation coefficient.

These facts showed that the title reaction easily took place in the temperature range of 25.2 — 37 °C, but the rate of polymerization was low.

CONCLUSIONS

(1) The composition of the polypyrrole prepared by our laboratory was C₄H_{4.107}N_{0.929}O_{0.559}Cl_{0.264}. The electrical conductivity of the polypyrrole prepared by the reaction of FeCl₃ and the pyrrole with a molar ratio 1 : 1 was $1.4 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$. The title reaction took place easily at room temperature, however the rate of polymerization was low.

(2) On the basis of experimental and calculated results, the polymerization rate of pyrrole in the presence of iron trichloride in the studied temperature range was found to be of the first order.

(3) The observed activation energy and pre-exponential constant of the title reaction in the temperature range of 25.2 — 37 °C were 34.5 KJ · mol⁻¹ and 10^{2.74}s⁻¹, respectively.

(4) The activation free-energy of the title reaction at 25.2, 30 and 37 °C was 91.8, 92.9 and 94.2 KJ · mol⁻¹, respectively.

Keywords :

Thermokinetics ; Pyrrole ; Polypyrrole ; Polymerization

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