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OXIDATIVE CHEMICAL POLYMERIZATION OF PYRROLE

Calorimetric and kinetic measurements

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A reaction calorimeter has been used to determine at three different temperatures the enthalpy values for the polymerization of pyrrole dissolved in acetonitrile, by using $FeCl_3$ as the oxidative agent. From the calorimetric data it has been found that the reaction is first-order with respect to the pyrrole. The rate constants at the same temperatures have also been determined. By using the Arrhenius equation we have obtained the activation energy for the formation of this electroconducting polymer.

Keywords: calorimetry of conductive polymers, conducting polymers, kinetics of polypyrrole, polypyrrole, thermodynamics of polypyrrole

Introduction

Though a great deal of both experimental and theoretical effort has been devoted to evaluate the characteristics of polypyrrole [1, 2], no thermodynamic studies on it seem to be available. As a matter of fact, the C-C bonds formed between the α-α' positions of different pyrrole rings during an oxidative polymerization do not seem to be 'normal' bonds. Instead, they are part of a quinoid structure distributed all along the polymeric backbone where positive charges are also present. Such a charge and electronic distribution has been called

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'polaron' if and unpaired electron besides a positive charge is present or 'bipolaron' of two positive charges only are present [3].

As polarons and bipolarons are thought to be involved in the electrical conductive properties of this organic polymer [4], they have been particularly studied by taking into account the most remarkable characteristics of polypyrrole, that is its important technological applications in the field of electric conductivity. On the other hand, the polymerization process leading to the formation of the α-α' bonds, and hence to the polarons and bipolarons, has not been satisfactorily ascertained. A better knowledge of the energy balance during the polymerization process might give a deeper insight into the mechanism of the reaction.

To gather information on the polymerization reaction and the thermodynamic stability of the species obtained, we have carried out some calorimetric and kinetic measurements on the chemical oxidation of pyrrole dissolved in acetonitrile. The oxidative agent was $FeCl_3$, the ratio Fe^{3+}/N being 2.5 (N is the nitrogen of the pyrrole ring). The negative counterion, the so-called 'doping ion', of the positively charged polymeric backbone was therefore the chloride ion. It has been found [2, 5] that the nature of the counterion markedly influences the electrical conductivity of the polymeric species obtained. By the methods here employed we intend to further investigate the formation of polarons and bipolarons in the same polypyrrole, but with different counterions. Furthermore, a relationship between thermodynamic stability of the different polarons and bipolarons and the electrical conductivity (to be measured in the future) could be expected.

Experimental

Materials

Acetonitrile and pyrrole are 'Fluka' pure grade. The latter has been freshly distilled at reduced pressure, under nitrogen. RLE grade C. Erba sublimated anhydrous ferric chloride has been used.

Apparatus and procedure

The calorimetric measurements have been accomplished by using a 'Mettler RC1' reaction calorimeter equipped with an AP01 glass reactor, upflow propeller stirrer and baffles. The reaction temperature was automatically settled by an 'IBM PS2/80' on-line computer controlling all functions of the apparatus. The same computer provides for the data acquisition and handling.

The oxidative agent $FeCl_3$ ($2.5\cdot10^{-2}$ moles) has been firstly solubilized in acetonitrile (600 ml) and its solution heat determined. Redistilled pyrrole (10^{-2}

moles) has been then added under vigorous stirring (500 r.p.m.). In order to evaluate the heat evolved during the polymerization reaction, the heat capacity of the overall mass (solution, suspended polymer and internal glass inserts) and its overall heat tranfer coefficient have also been automatically detected by the RC1-PS2/80 system after each experimental run.

The polymerization reaction and the subsequent working up of the polypyrrole have been done in air. At the completion of the reaction, the black insoluble amorphous product has been filtered, washed with acetonitrile and water to eliminate the iron ions and dried under vacuum. A simple testing with an ohmmeter has shown that the obtained polymer is electrically conductive even if quantitative measurements are planned for the future.

Results and discussion

Calorimetric measurements to obtain the enthalpies of the polymerization reaction have been executed at three temperature values, i.e. at 288, 303 and 323 K. Different temperatures have been considered since previous measurements had shown that the electrical conductivity of polypyrrole is strongly dependent on the temperature at which the polymerization is carried out [6]. The conductivity is usually higher for polymers synthesized at lower temperature. This has been attributed to a better morphological order inside the polymer [6, 7].

Accordingly, our research has been focoused to verify if the thermodynamic factors related to polarons and bipolarons can be also important to establish the conductivity of polypyrrole.

Table 1 Experimental enthalpies (ΔH) for the oxidative chemical polymerization of pyrrole at three different temperatures

Reaction temperature (T / K)	Enthalpy[a] (ΔH / kJ·mol^{-1})
288	–144.8±7.2
303	–104.4±5.2
323	– 60.0±3.0

[a] Each reported enthalpy value is the mean value of three different independent measurements. The uncertainties have been consequently determined.

Table 1 reports the values of the polymerization enthalpies determined at the different temperatures, all other conditions being constant, namely the concentration of pyrrole in acetonitrile ($1.67 \cdot 10^{-2} M$) and the ratio $Fe^{3+}/N = 2.5$.

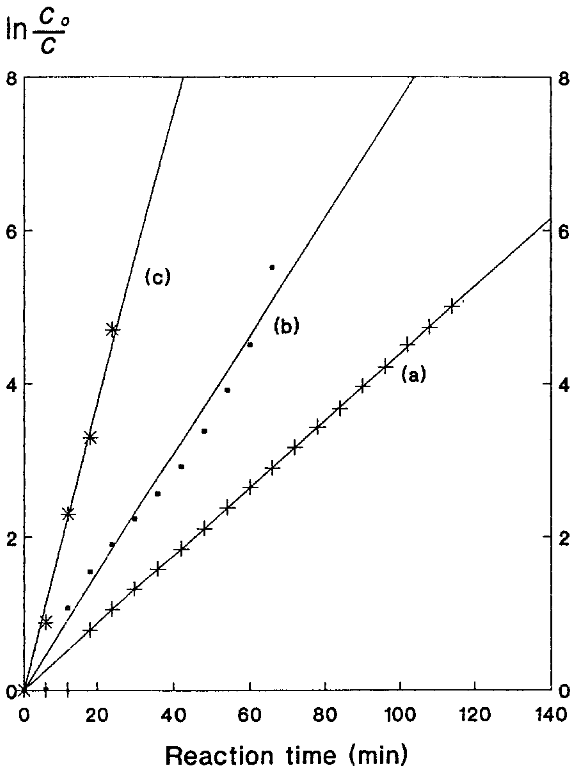

Fig. 1 Experimental behaviour of the pyrrole polymerization reaction as a function of the integral heat evolved (kJ) *vs.* the reaction time (min): (*a*) = 288 K; (*b*) = 303 K; (*c*) = 323 K

Figure 1 reports the trend of the heat evolved during all the reaction course, at the three different temperatures.

It must be stressed that the enthalpy values reported in Table 1 show an anomalously large variation within a temperature range of 35 K only (from 288 to 323 K). For other polymers, totallly different from polypyrrole and not electroconductive [8], the variation of enthalpy with temperature is not so significant.

So far, since we do not have accurate data on the electrical conductivities of the polypyrroles obtained at the three different temperatures, it is untimely to draw definite conclusions from the results of Table 1. In the near future, however, we intend to produce further data by using different counterions as well as other oxidative agents, such as $CuCl_2$, and to carry out the related conductivity measurements. Presently, we have confirmed the validity of the calorimetric data reported in Table 1 by using the well known formula:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p \qquad (1)$$

(T_2–T_1) is the difference between the two temperatures at which the enthalpy values ΔH_2 and ΔH_1 have been determined, being $T_2 > T_1$. ΔC_p is the difference between the heat capacities of products and reagents for the reaction under investigation. If the three values of ΔH in Table 1 are alternatively introduced in Eq. (1), the three obtained values of ΔC_p are nearly constant and average to 2.44 ± 0.26 kJ·mol^{-1}·K^{-1}. We assume this result as a good indication of the reliability of the data of Table 1, on the ground that the heat capacity can be considered invariant for small changes of temperature. Furthermore, the positive value of ΔC_p is taken simply as an evidence that the heat capacity of the products is larger than that of the reagents.

The trends of curves in Fig. 1 clearly evidence how temperature affects the rate of the polymerization reaction. In Fig. 2 these trends become satisfactorily linear when the logarithm of the ratio between the initial concentration of the pyrrole (C_o) and its concentration at a given reaction time (C) is reported *vs.* the same reaction time. This means that, by using a 2.5 fold excess of $FeCl_3$, the polymerization reaction shows to be first-order with respect to the pyrrole,

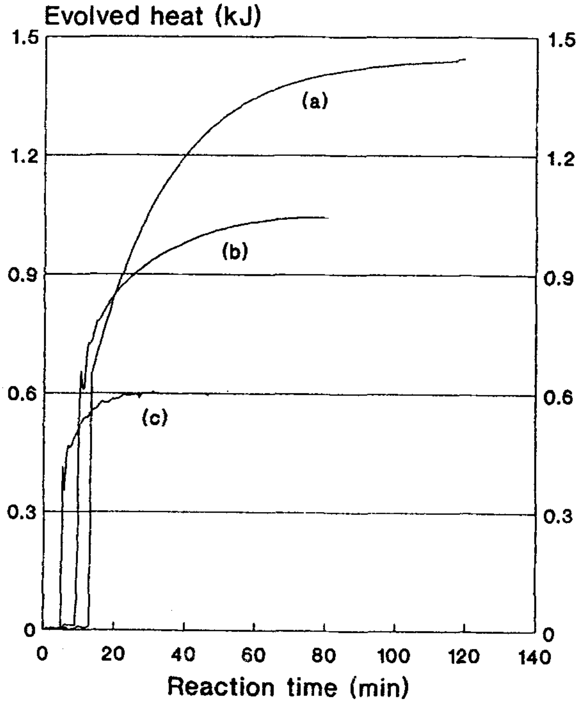

Fig. 2 Experimental reaction trend (marks) and first-order reaction behaviour (solid lines) at different temperatures: (*a*) = 288 K; (*b*) = 303 K; (*c*) = 323 K

despite the complexity of its overall mechanism. In fact, according to the most recent reports [2, 9], the first step of the above reaction should involve the oxidation of pyrrole to a radical-positive ion by the $FeCl_3$ and simultaneous reduction of the latter to $FeCl_2$. Due to the activation effect of the pyrrole nitrogen, the positive charge is mainly located in the α ring position and two pyrrole oxidized molecules link themselves producing the first α - α' bond. Further reaction of new oxidized monomeric species leads to the formation of the polypyrrole.

The first order rate constants k_1 at the three choosen temperatures are obtained as the angular coefficients of the related linear trends, as show in Fig. 2. Table 2 reports the obtained rate constants together with the half-life reaction time of pyrrole.

Table 2 First-order rate constants (k_1) and related half-lives[a] ($t_{1/2}$) for the oxidative chemical polymerization of pyrrole, at three different temperatures

Reaction temperature (T / K)	Rate constant (k_1/min^{-1})	Half-life[a] ($t_{1/2}$/min)
288	0.044±0.001	15.75±0.37
303	0.077±0.004	9.00±0.49
323	0.188±0.004	3.69±0.08

a $t_{1/2} = \ln 2 / k_1$

From the three rate constants k_1 of Table 2 it is possible to obtain the activation energy ΔE by using the well-known Arrhenius equation:

$$\ln k_1 = \ln A - \Delta E / RT \qquad (2)$$

$\Delta E/R$ represents the angular coefficient of the straight-ine $\ln k_1 = f(1/T)$. The gas constant value being $R = 8.314$ J· mol^{-1}·K^{-1}, the activation energy results $\Delta E = 32 \pm 5$ kJ/mole (of pyrrole).

The obtained ΔE value gives further insight on the course of the polymerization reaction, although it does not allow for definite conclusions as far as the thermodynamic aspects of the process are concerned. Probably its significance will become more relevant when obtained for the same reaction, by using other different counterions and oxidative agents, as planned.

Conclusions

Reaction calorimetry has been used to investigate the chemical preparation of a conductive polymer, i.e. polypyrrole. This technique has shown its usefulness to obtain simultaneous thermodynamic and kinetic data.

Although the reported results are rather preliminary, we hope they will contribute to the understanding of the complex thermodynamic and kinetic behaviour of the formation of the electrically conductive polypyrroles. To this end the temperature range will be extended when some technical problems will be solved. Moreover, these results are part of a research project under development on the polypyrrole and related conducting polymers. In our opinion, these species have not been investigated enough by the methods outlined above.

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Zusammenfassung — Mittels eines Reaktionskalorimeters wurden bei drei verschiedenen Temperaturen die Enthalpiewerte der Polymerisation von in Acetonitril gelöstem Pyrrol, unter der Anwendung von $FeCl_3$ als Oxidationsmittel bestimmt. Aus den kalorimetrischen Daten ergibt sich, daß es sich bezogen auf Pyrrol um eine Reaktion erster Ordnung handelt. Bei den gleichen Temperaturen wurden auch die Geschwindigkeitskonstanten bestimmt. Unter Anwendung der Arrhenius'schen Gleichung haben wir auch die Aktivierungsenergie der Bildung dieses elektronenleitenden Polymers ermittelt.