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THE CALORIMETRIC DETERMINATION OF THE CEILING TEMPERATURE FOR THE CHEMICAL POLYMERIZATION OF PYRROLE

Implications on the electrical conductivity

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Abstract

The previously found strong dependence of the polymerization enthalpy on the reaction temperature has been rationalized. The temperature dependence is to be ascribed to the existence of a 'ceiling temperature' for the polymerization process of the pyrrole monomer. The determined ceiling temperature has been $T \cong 350$ K when $FeCl_3$ was used as the oxidizing agent in CH_3CN solution. The existence of a ceiling temperature together with its already determined exoenthalpic nature allows to classify the polymerization reaction as an exoentropic one.

From the dependence of the yield of insoluble polymer on the reaction temperature, the trend of the relative mean numeral molecular mass M_n for the different obtained polymers has been determined. Measurements of electrical conductivity on pressed pellets of the different polymers allowed to establish a correlation between the M_n value and the conductivities. The dependence of the conductivity on the exposition time to the air allowed to do some essays on the aging behaviour of the obtained polypyrrole. By making some assumptions, an absolute calorimetric determination of the value of M_n of polypyrrole was tempted together with that of the related poly-N-vinilpyrrole.

Keywords: aging of polypyrrole, calorimetry of conducting polymers, conductivity of polypyrrole, numeral molecular weight of conducting polymers, polypyrrole

Introduction

The calorimetric and kinetic measurements made on the chemical polymerization of pyrrole and reported in a previous paper [1] were performed with the aim to give a contribution to the understanding of the quantitative balance of energy leading to the formation of the conjugated π-electrons system which is

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typical of most of the electroconducting polymers. The electroconductive properties are also to be ascribed to the onset of polarons and bipolarons [2, 3] when a charged doping ion counterbalances the apposite charge distributed on the backbone of the polymer. For these reasons, the nature of the chemical bonds formed between the 2- and 5-positions of adjacent pyrrole rings can be a very peculiar one and not easy to be studied by experimental methods due to the difficult tractability of the synthesized organic conducting polymers. On the other hand, the nearly complete lack of quantitative thermodynamic determinations on the polymerization process leading to the conducting material seemed to us a convincing incentive to go on with our efforts to give a deeper insight by the methods of calorimetry. The obtained results are given in the following of this paper together with some inferences regarding the possible relationships between the calorimetric data of polymerization and the mean numeral molecular weight M_n of the conducting polymer. By remembering the technological importance of the electroconductive behaviour of the materials so obtained, the transport properties have been studied by taking into account their possible utilizations in presence of the air of the environments and the necessity to clarify further the microscopic mechanisms determining the electrical conduction.

Experimental

Procedure and apparatus

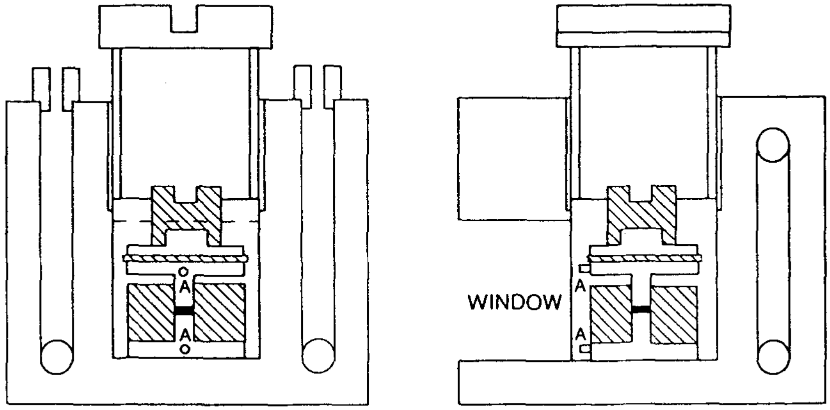
The materials, the calorimetric apparatus (Mettler RC1 reaction calorimeter), the chemical and physical treatment of the reagents and products have been exactly the same as described in the previous paper [1]. In particular, the concentration of pyrrole in acetonitrile (1.67×10^{-2} M) and the ratio $[Fe^{3+}]/[N]=2.5$ were held constant for all the carried out polymerizations. This time, we have tried to eliminate the air from the reaction medium by bubbling argon gas inside the RC1 apparatus before the beginning of the calorimetric measurements. In spite of these precautions, we are not sure to have been able of operating in the total absence of air due to the required very large volumes (600 ml) of solution. The samples used for the conductivity and aging studies were obtained in a separate and appropriate reaction vessel. The synthesis and the handling of the polymers have been then accomplished in a carefully controlled argon environment up to the predetermined exposition to the air.

The conductivity measurements have been performed on cylindrical pellets obtained at a constant pressure of five tons and having a diameter of 8.0 mm. The pellets were from 0.1 to 1.0 mm thick and the thickness was verified by a high precision nonius. The density, besides the geometrical sizes, was also considered with the aim to evaluate the spread of the conductivity values obtained for the same polymer due to a possible different compactness of the pellets. The conductivity σ values (in $\text{ohm}^{-1}\times\text{cm}^{-1}$, one ohm^{-1} being equal to one Siemens) were calculated from the formula

$$\sigma = \frac{1}{R} l / S \tag{1}$$

in which R is the resistance on ohm (Ω) of the pellet as measured between the two bases of the pellet, l is just the tickness in cm and S represents the area of the base in cm^2. It is clear that in so doing we have adapted a two-contacts method, the contact having been established by two golden-plated brass cylinders each of them having a surface base equal to that of the pellet. This configuration ensures the good quality of the contact and the achievement of the bulk resistance of the sample; this is an important requisite as when studying the aging of conducting polymers the effect of the exposure to the air is strictly linked to the diffusion processes of the gases inside the bulk of the sample. In other words, the aging process is not a surface one which could efficiently be investigated also by using the four-probes method [4]. The conductivity measurements were accomplished by applying a direct current electromotive force (*d.c.e.m.f.*) through a Schlumberger Mod. SL7071 Digital Multimeter. The applied *e.m.f.* was of the lowest possible value so that no electrochemical effect developed at the metal-polymer interface. This result was verified by the invariance of the displayed resistance value during the measurements.

The resistance measurements were carried out by the home-made apparatus shown in Fig. 1. It is essentially made by a bored teflon (polytetrafluoroethy-



FRONTAL VERTICAL SECTION

LATERAL VERTICAL SECTION

Fig. 1 Frontal and lateral vertical section of the home-made apparatus measuring the conductivity of pressed pellets (see text). The two A points are those with which the Schlumberger multimeter is connected. The cooling or heating serpentine is evidenced (see text). □ brass; ▧ PTFE; ■ pellet lene, PTFE) thick-walls cylinder placed inside the hole of a hallow brass cylindrical container. The bored teflon cylinder houses the sample pellet on which the two golden-plated brass contacts are pressed by the upper expressly built screw. The pressure is conveyed to the brass contacts by the interposed teflon transducer by taking advantage of the elasticity and autolubrificanting characteristics of this material. A window is open through the lateral surface of the brass container so that the teflon bored cylinder can be easily introduced and removed. The two electrical wires connecting the brass contacts with the digital multimeter come out from this same window. A serpentine is carved in the thick walls of the brass cylindrical container; a heating or refrigerating fluid can flow in this serpentine so that the temperature of the sample can be controlled when the whole apparatus is put inside an adiabatic vessel.

Results and discussion

Calorimetric measurements: the ceiling temperature

The results reported in the already cited previous paper [1] were obtained at only three temperatures, i.e. 288, 303 and 323 K. The anomalously large variation of the polymerization enthalpy in that temperature interval was not explained and the attempt of rationalizing it was postponed. Now, we have been able to obtain other enthalpy data on a more extended range of temperature, i.e. from 288 up to 338 K. All other experimental conditions were the same as before. Table 1 reports the values of the polymerization enthalpies determined at the different temperatures. Figure 2 shows the trend of the same enthalpies values as a function of the temperature. The uncertainty on these data has been estimated to amount to about 5% from the mean value of more than one independent measurement at each temperature. It is evident from the data reported in Fig. 1 that the enthalpy value tends linearly to zero at a temperature of about T=350 K. Therefore, when approaching that temperature the polymerization reaction is progressively prevented. In other and more precise words, at that temperature the rate of the polymerization reaction equals that of the depolymerization process. This means that at $T\cong 350$ K the free energy variation ΔG for the studied reaction becomes equal to zero. In the field of the polymerization chemistry the temperature T_c at which $\Delta G=0$ is called the 'ceiling temperature' [5]. Above this temperature it is not possible to polymerize a monomer while the polymerization degree *DP* (proportional to the mean numeral molecular weight M_n) decreases when T approaches T_c coming up from the lower temperatures. The value of T_c has been determined [6] for many usual insulating polymers and it has been a very useful parameter to optimize the achievement of a well characterized polymer particularly as regards the M_n value. At our knowledge, no other T_c value has been reported in the literature for a polymeric electroactive material. That is very surprising as, in our opinion, the awareness of the existence of an upper limiting polymerization temperature allows to better rationalize the frequently reported observation that the electroconductivity depends on the temperature at which the polymerization is carried out, all others variables having been held fixed. It was usually found that the electroconductivity is higher for polymers obtained at lower temperature [7, 8].

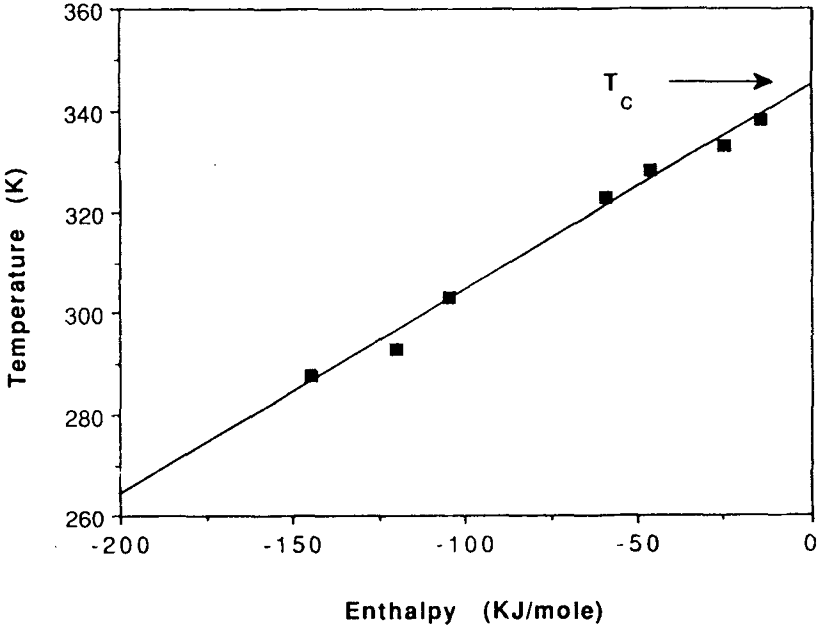


Fig. 2 The enthalpy values as a function of the temperature for the polymerization of pyrrole. The extrapolated ceiling temperature T_c is put in evidence by a linear best-fitting treatment

In the frame of a polymerization process determined by a value of T_c which is not so far from the room temperature, we can assert that those findings are to be related to values of M_n which are higher for polymers synthesized at room or lower temperature rather than at a higher one. It is not surprising that in these polymers the electroconductivity depends on the M_n value if we consider that the setting up to a conjugated π-electrons system is essential to give these materials their peculiar electroactive characteristics. Even if the accepted conductivity mechanisms are depicted as hopping processes between localized states represented by polarons and bipolarons [9], the associated charges and electrons have to be delocalized on a π-system involving four or more pyrrole rings [3]. We had also found, at least in the case of a polypyrrole-related polymer, the ladder poly-N-vinylpyrrole [10], that a threshold value of M_n exists above which the polymer is triggered from the insulating to the electroconductive state

Table 1. Experimental enthalpies (ΔH) for the oxidative chemical polymerization of pyrrole and gravimetric yields at different temperatures of synthesis

Reaction temperature T/K	Enthalpy ΔH/kJ·mol^{-1}	Gravimetric yield weight %
288	–144.8	–
293	–120.0	61.7
303	–104.4	55.5
323	–59.3	31.6
328	–46.0	23.7
333	–24.8	20.6
338	–14.0	8.9

[11]. We have verified that higher values of M_n are obtained when the polymerization is carried out at temperatures which are far from T_c, by evaluating the yield in polypyrrole. The yield is evaluated with respect to the monomer by weighting the quantity of polymer which remains on the filter at the end of the reaction. The polymer remained on the filter after washing is most likely the fraction at higher M_n value as the filtered solution appears dark brown couloured due to the presence of both partially soluble or passed through the paper filter oligomers at lower M_n value. The determined yields are reported in Table 1 for all the working temperatures.

The uncertainty on these data has been estimated to amount to about 6%. Figure 3 reports the dependence of the yield on both the temperature and the corresponding enthalpy values. The correlation between the yield and the temperature at which the polymerization has been carried out is extremely clear together with that between the yield and the enthalpy. It is even possible to obtain again the same value of $T_c \cong 350$ K by extrapolating the trend of the yield to the zero value. Therefore, the determination of the existence and of the value of the ceiling temperature can be of practical interest also for electroconducting polymers when the achievement of a high M_n value product has to be favoured. On the other hand, it must not be neglected the importance of T_c in gathering information on the thermodynamics of the polymerization process itself. This last point was not the main purpose of this work and we have the intention to develop it in a successive paper. For the moment we remark only that, from the definition of $T_c=\Delta H/\Delta S$, being $\Delta G=0$, the polymerization of pyrrole is exoentropic, i.e. ΔS must be negative having found that ΔH is also negative, see Table 1.

Electroconductive properties and aging

On some of the synthesized polypyrroles at different temperatures, conductivity measurements were carried out by the procedures and the apparatus al-

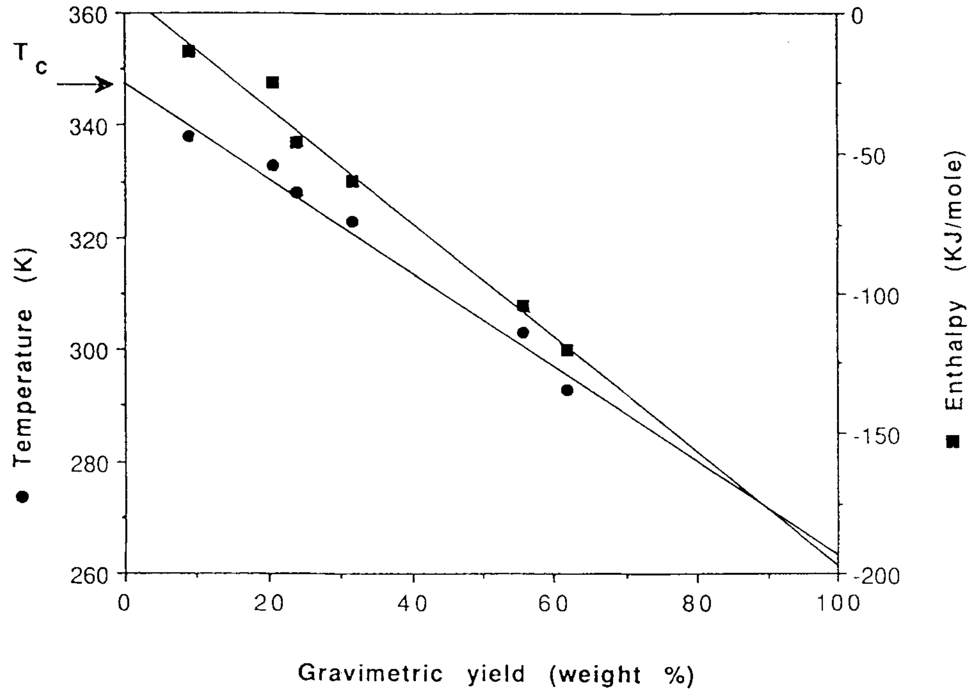


Fig. 3 The gravimetric yield in polypyrrole as a function of the temperature ● (left) and of the enthalpy ■ (right). The extrapolated ceiling temperature T_c is put in evidence by a linear best-fitting treatment

ready described. The uncertainty on the obtained data was evaluated to amount to about 10% by repeating conductivity determinations on different pellets of the same polymer prepared at a given temperature. The consideration of the density besides the geometrical sizes allowed to establish that also for variations of the density between 1.10 and 1.30 mgxmm^{-3} the limit of 10% was not exceeded. Figure 4 reports the values of the measured conductivities for samples synthesized at different temperatures. The measurements were carried out at a room temperature of 298 K. It is evident that the conductivity is lower for polymers obtained at higher temperature; it increases when the temperature of synthesis is lowered and remains constant starting from 323 K and lower. This trend, while confirming our previous finding that at higher temperatures the M_n value is too small to guarantee a good conductivity, puts in evidence that for polypyrrole an upper threshold value for M_n exists over which the conductivity seems to remain constant. This result is not surprising for us since, by totally different methods, we had already verified a similar effect in the ladder poly-N-vinylpyrrole [11]. A plausible and qualitative explanation of the existence of that threshold can be given. Indeed, it can be considered that very probably a too long conjugated π-electrons system (corresponding to high M_n values and hence to low temperatures of synthesis) is not essential to have the highest possible conductivity for that polymer; it can be only demanded the minimum M_n value corresponding to the conjugated π-electrons system necessary to stabilize the polaron or the bipolaron.

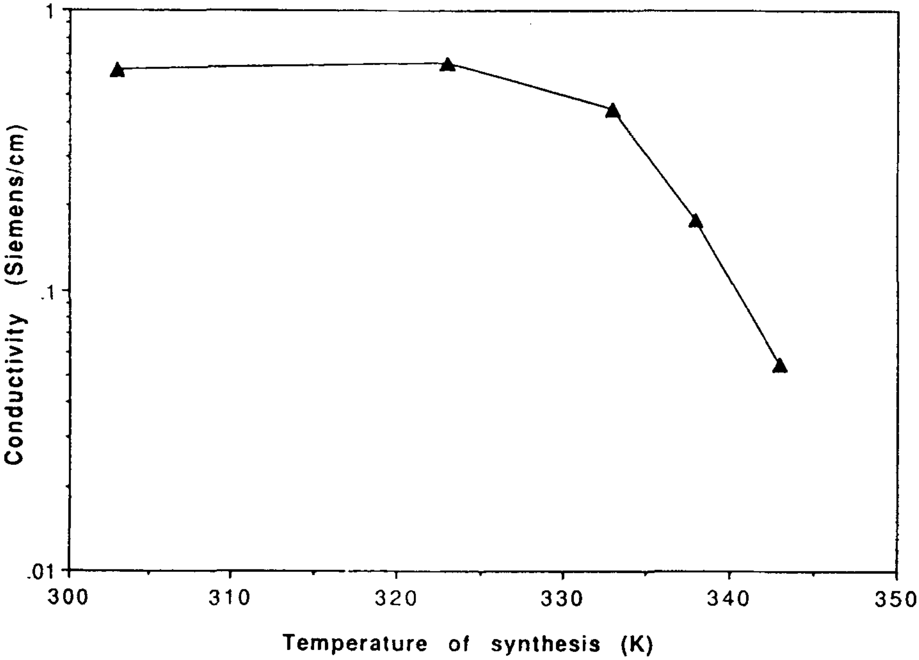


Fig. 4 The conductivities of polypyrroles synthesized at different temperatures (see text). The segments connecting the experimental points have been drawn to evidence the overall trend

Concerning the endurance of the electroconductive properties of polypyrrole when exposed to the surroundings and the decay of the conductivity because of the contact with air, we have verified that there is no difference in the decay of the polypyrroles synthesized at different temperatures. As a typical example, Fig. 5 shows the decrease in conductivity of the polypyrrole obtained at 303 K as a function of the exposure time to the air. During the time between two successive measurements, the pellet of polypyrrole was took off from the hole of the bored teflon cylinder of the measuring apparatus, Fig. 1, and totally exposed to the air. This was done to favour the diffusion of the gases in the bulk of the pellet. The trend reported in Fig. 5 seems to evidence that the uptake of oxygen is governed by at least two different processes. The first one is active at relatively short times while the second one becomes preponderant at longer times. We have not examined more carefully the aging process on these samples but we believe that studies on this subject are important for their technological

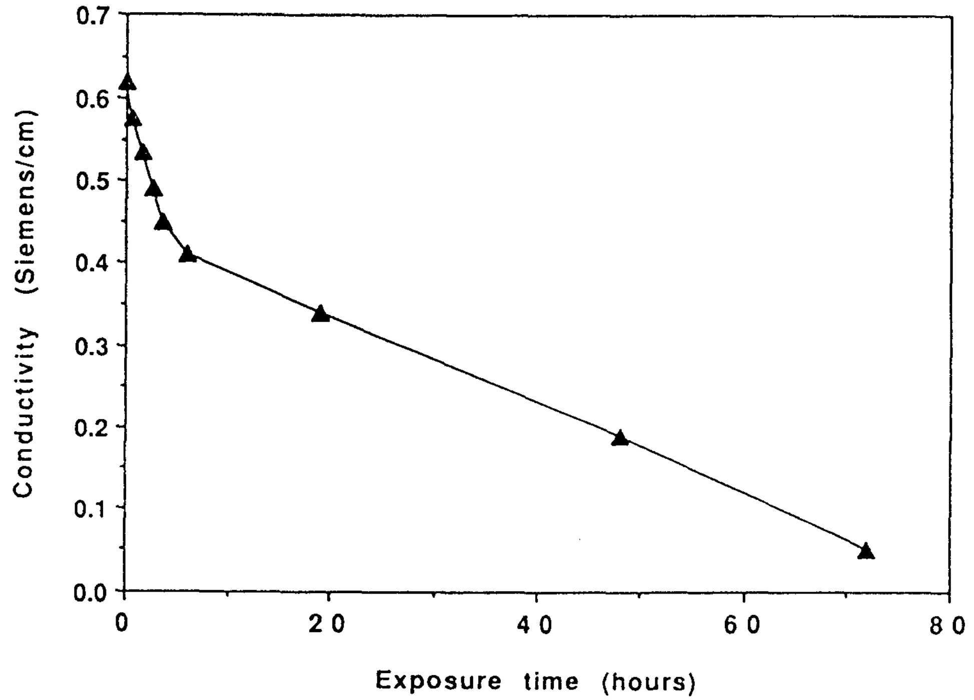


Fig. 5 The typical aging curve of a polypyrrole synthesized at 303 K when exposed to the air. The segments connecting the experimental points have been drawn to evidence the overall trend

impact on the practical applications of the conducting polymers. We are now doing combined ESR and conductivity measurements on polypyrrole and some related polymers with the aim to go deeper inside the mechanism of the aging process. Up to now we have verified [12] that at very short exposure times the uptake of oxygen is reversible as evidenced by the modification of the ESR signal. This result could be important for applications in the filed of gas sensors where the original characteristics of the conducting polymer should be renewed when the sensor carried out its function.

Some remarks on the possibility to gather information on the M_n value of conducting polymers

By considering the difficulties encountered in determining the M_n value of conducting polymers due to their poor tractability, it could be interesting to employ calorimetric determinations like those presented in this paper to gather some information on the degree of polymerization (*DP*) at a given temperature. In our opinion this may be possible, at least to have orders of magnitude or relative trends, if some assumptions and simplifying hypotheses are made. The first and more important assumption is that the chemical bond formed between the positions 2- and 5- during the polymerization of the pyrrole ring be characterized by an energy of, let us say, 100 kcal/mole, i.e. 418 kJ/mole. This seems to us a plausible assumption even if we consider the complexity of that bond when it is involved in a polaronic or bipolaronic system together with the necessary doping counterions. All other hypotheses, concerning for instance the possibility of neglecting a careful definition of the standard states, the insolubility enthalpy of the products and even the effect of the air, are to be considered of secondary importance. On these bases, if in Fig. 3 the trend of the gravimetric yield as a function of ΔH is linearly extrapolated up to a yield of 100%, an enthalpy value of $\Delta H \cong -200$ kJ/mole, i.e. $\Delta H \cong -50$ kcal/mole, can be estimated as the evolved heat if the polymerization were carried out at a temperature lower than 273 K. A yield of 100% means that all the monomer is converted to a polymer having a M_n value sufficiently high to remain entirely on the filter even if the *DP* is of the order of 50% as deduced from the obtained $\Delta H \cong -50$ kcal/mole enthalpy (half the value of the assumed energy bond). From Table 1 and Fig. 3 it can be consequently argued that at higher temperatures, for instance at $T=303$ K where a $\Delta H \cong -100$ kJ/mole, i.e. $\Delta H \cong -25$ kcal/mole was measured, the *DP* amounts to about 25% the yield being equal to about 55%. And so on at all other temperatures.

It must be recalled now that for the polypyrrole-related poly-N-vinylpyrrole (PNVP), obtained by radical polymerization of the vinylic double bond of the N-vinylpyrrole (NVP), a value of $M_n \cong 4500$ was determined [11]. The determination of M_n is possible in this case as the PNVP, an insulating polymer, is soluble and tractable in the usual organic solvents. The determined $M_n \cong 4500$ corresponds to about 48 pyrrole rings which are hanging and adjacent all along the backbone of PNVP. The PNVP can become an electroconducting material by treating it with $FeCl_3$ in CH_3CN. In so doing [10], bonds are formed between the 2- and 5-positions of the hanging pyrrole rings, giving origin to a conjugated system (ladder PNVP) which is very similar to that of polypyrrole. At 303 K and with $[Fe^{3+}]/[N]=2.5$ (the same conditions employed for polypyrrole), a calorimetric measurement on PNVP has been made in the frame of the present work and a value $\Delta H=-60.2$ kJ/mole, i .e. $\Delta H=-14.4$ kcal/mole, was found. If the considerations made for polypyrrole can be extrapolated to the ladder PNVP, this enthalpy value corresponds to a *DP* of about 14% with the consequence that on average seven pyrrole rings are polymerized. Therefore, the M_n value of the pyrrolic chain in the ladder PNVP amounts to about 470. At the same temperature, the M_n value for polypyrrole amounts to about 804 as the found $DP=25\%$ corresponds to twelve polymerized rings. This value of M_n at 303 K seems to be reasonable also at the light of the conductivity and enthalpy values reported in Fig. 4 and in Table 1, respectively. At $T=303$ K, the conductivity is at its saturation value as it could be expected with twelwe polymerized rings; the same can be said for a polypyrrole synthesized at T=323 K, for which about six polymerized rings can be expected. But, when the conductivity is markedly decreasing at T=333 and 338 K, the number of polymerized rings can be easily verified to be three and one point five, respectively. These two values are known to be too low to sustain a polaron or bipolaron [2, 3]. The threshold value of the conductivity found for the ladder PNVP as a function of the M_n value of the insulating precursor PNVP can also be treated by similar considerations. In fact, the ladder PNVP has been found to become insulating when the number of polymerized NVP monomers in the precursor PNVP becomes lower than about fifteen, corresponding to a M_n value of about 1500 [11]. A number of polymerized pyrrole rings in the ladder PNVP which is lower than three and which is not sufficient to assure the electroconductivity corresponds to this value.

Conclusions

We have shown how quantitative calorimetric measurements may help in getting a deeper insight into the thermodynamics of the polymerization reaction leading to electroconducting organic polymers. The determination of the ceiling temperature T_c for polypyrrole allowed us to rationalize the quantitative observations often reported concerning the effect of the temperature of synthesis on the electrical behaviour of conducting polymers. We suspect that its determination might also contribute to explain the different behaviour of the same conducting polymer but synthesized with different doping counterions. The different counterions can well influence the conductivity via their different electronic and/or steric characteristics but the variation of the value of T_c may include in itself the overall of the thermodynamic meaning of the formation of the conjugated π-electrons system sustaining polarons and dipolarons. From the thermodynamic expression of T_c it is easily verified that its value and that of DP are dependent on the concentration of the monomer [5, 6]. Some preliminary measurements have clearly shown that this is a very important point and it is for this reason that all the reported measurements have been carried out at a fixed concentration of pyrrole. T_c seems also to be strongly influenced by the different redox couples used to oxidize and polymerize the organic substrate. Again, preliminary results allowed to determine that the T_c value decreases from 350 to about 313 K when $CuCl_2$ is employed instead of $FeCl_3$.

On the basis of some assumptions we have discussed the possibility that calorimetric measurements may help in gathering information on the M_n value of the obtained conducting polymer. The M_n or DP value is a very difficult parameter to be determined for these usually untractable materials. It is for this reason that we hope that calorimetric methods like those described in this paper may be applied and refined in the future.

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Zusammenfassung — Es wird eine nüchterne Betrachtung der bereits festgestellten starken Abhängigkeit der Polymerisationsenthalpie von der Reaktionstemperatur angestellt. Die Temperaturabhängigkeit wird der Existenz einer "Höchsttemperatur" für den Polymerisationsprozeß des Pyrrolmonomers zugeschrieben. Die ermittelte Höchsttemperatur betrug $T \cong 350$ K, wenn $FeCl_3$ in CH_3CN-Lösung als Oxidationsmittel eingesetzt wurde. Die Existenz einer Höchsttemperatur zusammen mit ihrer bereits bestimmten Exoenthalpie-Natur erlaubt es, die Polymerisationsreaktion als exoentropische einzustufen.

Ausgehend von der Abhängigkeit der Menge an bei Reaktionstemperatur unlöslichem Polymer wurde der Trend der relativen mittleren Molekülmasse M_n der erhaltenen verschiedenen Polymere bestimmt. Messungen der elektrischen Leitfähigkeit an gepreßten Pellets der verschiedenen Polymere erlaubten die Feststellung einer Korrelation zwischen dem Wert für M_n und den Leitfähigkeitswerten. Die Abhängigkeit der Leitfähigkeit von der Dauer det Exposition mit Luft erlaubt einige Feststellungen über das Alterungsverhalten der erhaltenen Polymere. Unter Annahme einiger Voraussetzungen wurde eine absolute kalorimetrische Bestimmung des M_n-Wertes von Pyrrol und des entsprechenden Poly-N-Vinylpyrrols versucht.