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Aspects of the Chemical Synthesis of PAni-DBSA and its Properties

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An investigation of the synthesis parameters (i.e., temperature and acid concentrations) in the chemical preparation of PAni-DBSA, was performed. The synthesis temperature was varied from 0° to 40°C, producing a strong effect on both the oxidation states during chain propagation stage and properties of polymers. DBSA molecules are incorporated in the PAni chain. The synthesis temperature has a strong influence on the properties of PAni-DBSA. PAni with a needle-like structure and compact morphology was obtained. The conductivity of polymers is dependent on the benzenoid/quinoid ratio in the polymer chain.

Keywords: chemical synthesis; dodecylbenzene sulphonic acid; polyaniline

INTRODUCTION

The conducting polymer polyaniline (PAni) has been widely studied. Since the first chemical synthesis by MacDiarmid [1] many investigations have been performed with the aim of improving the properties of the polymer. PAni can be prepared chemically or electrochemically and has been applied in numerous research and applied areas [2]. However, there are limitations to its use because of its low solubility in organic solvents and heating processibility. Many studies report the use of functionalized acids, such as dodecylbenzene sulphonic acid (DBSA) [3–5], in order to improve the solubility and processibility of PAni. Cao *et al.* [6] demonstrated that DBSA can act as a doping agent

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and surfactant for PAni and the resulting polymer could be processed and was water soluble. There are some discussions about the nature of the PAni-DBSA formation mechanism [7,8]. The main point of discussion is if the PAni formation occurs in or out of the micelle. It is well known that the synthesis temperature strongly influences the PAni polymerization process so, in the present study the influence of synthesis temperature and acid concentration on the chemical polymerization of PAni, in the presence of DBSA, is presented. All the PAni-DBSA precipitates were characterized by infrared spectroscopy, conductivity measurements and Scanning Electron Microscopy (SEM).

EXPERIMENTAL

The chemical syntheses of PAni-DBSA were performed as described by Habal *et al.* [3], using a DBSA solution (0.05 to 0.075 mol L^{-1}) that contained aniline (0.05 mol L^{-1}) and ammonium persulfate, (0.025 mol L^{-1} $(NH_4)_2S_2O_8$) as the oxidant. The polymerization was performed in the range of 0 to 40°C. The open circuit potential (E_{OC}) and the reaction temperature variation were recorded during each experiment. The $(NH_4)_2S_2O_8$ aqueous solution was introduced drop-wise to the DBSA solution containing aniline and the mixture was mechanically stirred. The PAni-DBSA precipitate was recovered by filtration and washed with distillated water. Finally, the polymer was dried at 60°C for 48 h under a dynamic vacuum. Infrared spectra (Bomem MB FTIR-spectrometer) were obtained using KBr disk method. Conductivity measurements were performed by the four-points technique and SEM micrographs were obtained using a microscope (Zeiss Leica model DSM 960).

RESULTS AND DISCUSSION

Effect of Synthesis Temperature

The curves obtained for E_{OC} during syntheses at different temperatures are shown in Figure 1.

The induction period is characterized by a rapid increase of E_{OC} and a maximum value of E_{OC} that corresponds to the pernigraniline oxidation state of PAni (auto catalytic mechanism) can be observed in the chain propagation stage. Following this, the finalization stage can be observed in which E_{OC} rapidly decreases to a constant value.

The increase of the synthesis temperature promotes a reduction in the chain propagation stage of PAni-DBSA and additionally, distinct stages can be observed. This can be indicative of different

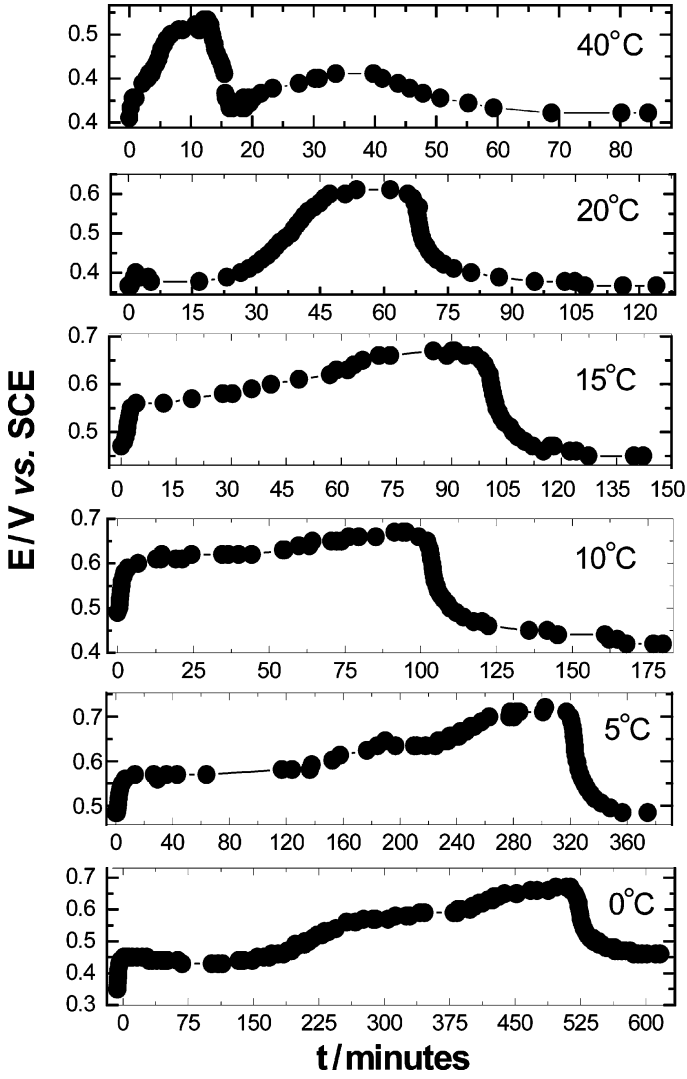

FIGURE 1 Potentiometric curves for PAni-DBSA prepared from the 1/1/0.5 ratio at different synthesis temperatures.

intermediary oxidation stages of polymers. The incorporation of DBSA in the PAni chain can promote a different organization of the monomer and/or a different reaction mechanism. The polymerization rate for PAni-DBSA increases with the synthesis temperature, due to the reduction of intermediary oxidation stages of the polymer.

In particular, at 40°C a second stage can be observed, which should be better investigated.

The anionic surfactants show an increase in solubility at the Kraft temperature [9], which is strongly influenced by factors such as ionic strength and the counter-ion. The value of the Kraft temperature for DBSA was not found in the literature however, for sodium dodecylsulfate (SDS) this temperature is close to 20°C [9]. Gil *et al.* [7], demonstrated that chemical syntheses of PAni in presence of SDS at 5°C promote a stable dispersion of the polymer. In this work, for all syntheses performed, PAni-DBSA was observed to precipitate and significant amounts of polymer were obtained at 20°C and so, it can be supposed that the DBSA Kraft temperature is very close to this value.

Influence of DBSA Content

The effect of DBSA concentration was investigated by performing the syntheses at 20°C and using DBSA concentrations of 0.05 to 0.075 mol L^{-1} in solutions containing aniline (0.05 mol L^{-1}) and $(NH_4)_2S_2O_8$ (0.05 mol L^{-1}). It was observed that increasing the DBSA concentration does not lead to an increase in the amount of polymer, which is indicative that the size of the PAni particles decreases due to the excess of DBSA in the reaction mixture. This is in agreement with the literature [8], where it is possible to find some models for the possible interaction between PAni chain and DBSA molecule.

Relation between Synthesis Temperature and Polymerization Time

In Table 1 the kinetic parameters obtained for synthesis of PAni-DBSA, under different conditions, are presented. Special attention was given to maximum values of temperature and E_{OC}.

TABLE 1 Kinetic Parameters Determined from Potentiometric and Calorimetric Curves of PAni-DBSA in Different Conditions

M/DBSA/O Ratio	T/°C	E_{oc}(max)/V	T_{max}/°C	t_{max}x/min	$t_{pol.}$/min
1/1/0.5	0	0.67	0.2	30935	616
	5	0.67	0.2	19036	374
	10	0.67	0.4	5960	180
	15	0.67	0.3	5791	142
	20	0.64	0.3	3935	124
	40	0.57	0.7	791	84.5
1/1.5/0.5	20	0.66	0.2	83	140

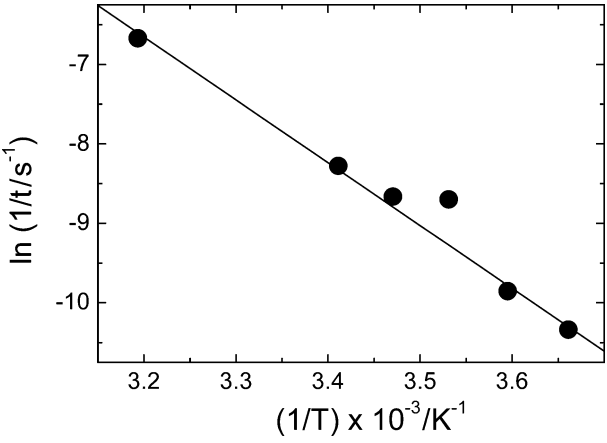

FIGURE 2 Application of the Arhenius equation to calculate the activation energy of PAni-DBSA polymers.

The maximum values of E_{OC} are similar, indicating that the pernigraniline oxidation state of PAni was obtained, independently of synthesis conditions. The dependence of the maximum temperature values ($T_{max.}$) on the time (Fig. 2), is described by the Arhenius equation [9]:

$$\ln\frac{1}{t} = (\ln A - \ln[M]) - \frac{E_a}{R} \times \frac{1}{T}$$

where the slope of a plot of $\ln 1/t$ as a function of $1/T$ is equal to $-E_a/R$. So, when R is $8.134\,J{\cdot}K{\cdot}mol^{-1}$, the activation energy (E_a) of PAni-DBSA system can be estimated. The average E_a value for the PAni-DBSA system is close to $66\,kJ{\cdot}mol^{-1}$. In spite of the fact that there is no data for this system in literature, the result is in agreement with those described for other PAni systems [2].

Infrared Spectra

In Figure 3 the infrared spectrum for PAni-DBSA obtained at 0°C from the aniline:DBSA:oxidant ratio of 1/1/0.5, is presented. This spectrum is representative of other polymers obtained under different conditions. The main vibrational bands attributed to PAni-DBSA can be observed at approximately 3280–3400 cm^{-1} (N–H stretch of aromatic amine); 2958–2852 cm^{-1} (vibrational of bending of CH_3 and aliphatic CH_2). These bands characterize the presence of DBSA in the polymer

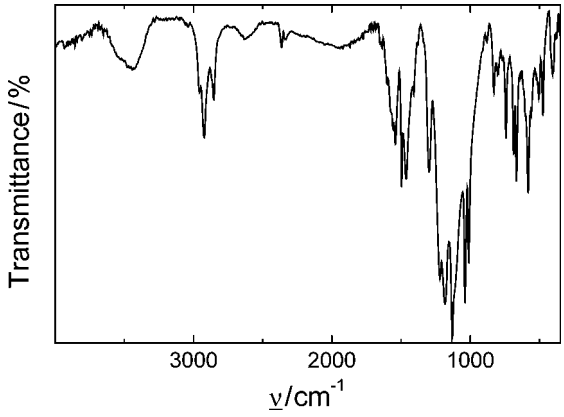

FIGURE 3 Infrared spectrum for PAni-DBSA obtained from syntheses in the ratio 1/1/0.5 at 0°C.

structure. The bands at 1463 and 1543 cm^{-1} correspond to benzenoid and quinoid rings; 1298 and 1182 cm^{-1} to vibrational C–N modes and C–H bending, respectively. The absorption bands between 1130–1110 cm^{-1} and 688 cm^{-1} are attributed to vibrational modes of sulfonic acid (S=O and SO_3 deformation). The vibrational aromatic C–H bending mode appears at around 829 cm^{-1}. The bands between 505 and 580 cm^{-1} correspond to out-of-plane N–H bending.

The infrared spectra PAni-DBSA are similar to PAni and they are in agreement with the literature [5,11,12]. From the spectra it is possible to conclude that the PAni-DBSA polymers present the structure of emeraldine salt (more conductive form).

Conductivity

The dependence of PAni-DBSA conductivity and the B/Q ratio obtained from the IR spectra on the synthesis temperature are shown in Figure 4. The same form is observed for both curves and it is interesting to observe that the conductivity increases when B/Q increases. The unitary value of the B/Q ratio is indicative that the PAni structure consists of equal fractions of benzenoid and quinoid units and the polymer is in its more conductive form. Due to either the influence of the synthesis temperature on the polymerization mechanism or the strong interaction of DBSA molecule with polymer structure, higher B/Q ratios did not promote a more conductive polymer.

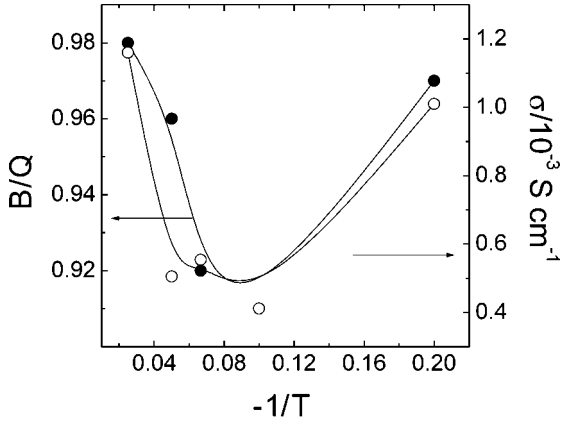

FIGURE 4 Dependence of conductivity (●) and of B/Q (benzenoid/quinoid ratio) (○) on the inversion of PAni-DBSA synthesis temperature.

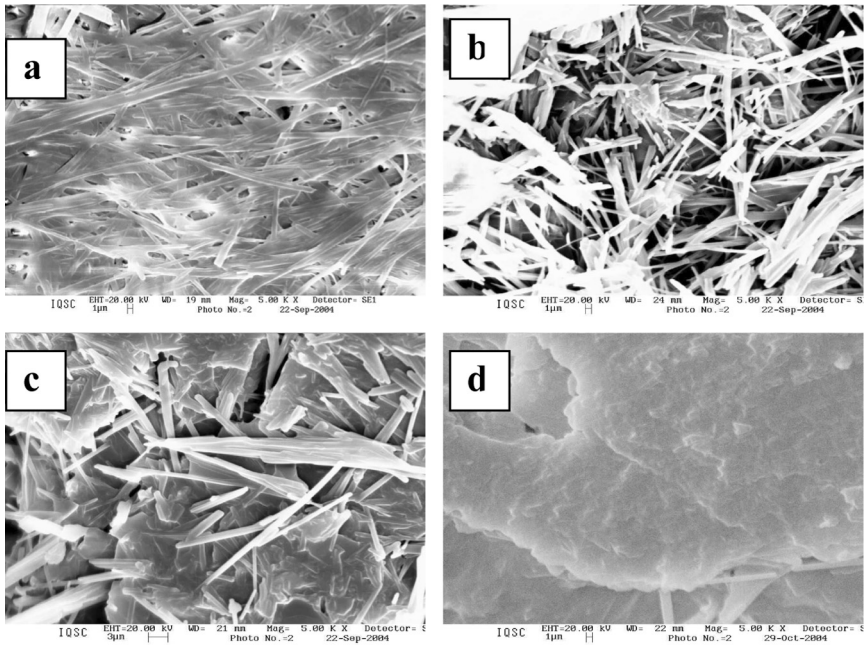

FIGURE 5 SEM micrographs of (a) aniline-DBSA complex and PAni-DBSA obtained at different synthesis temperatures, (b) 0°, (c) 20°, and (d) 40°C.

Surface Morphology

The SEM micrographs of PAni-DBSA obtained from a ratio 1/1/0.5, at different synthesis temperatures, are shown in Figure 5. The aniline-DBSA complex presents a needle-like structure in agreement with Cao *et al.* [6]. The PAni-DBSA obtained in the temperature range of 0° to 20° C keeps the structural characteristics of the aniline-DBSA complex. The polymers present particles in the form of needles and a homogeneous structure (Fig. 5(b) and (c)).

A more compact structure with small needle-like particles is obtained at 40°C (Fig. 5(d)). So, it is possible to conclude that the structure of PAni-DBSA is strongly dependent on the synthesis temperature.

CONCLUSIONS

PAni-DBSA can be prepared chemically at different synthesis temperatures. The strong influence of synthesis temperature can be observed from the open circuit potential monitored during the synthesis. The conductivity of PAni-DBSA is dependent on the B/Q ratio, which changes with the synthesis temperature. The morphology of the aniline-DBSA complex is maintained in the PAni-DBSA samples obtained. The homogeneous, needle-like structure of PAni-DBSA changes with increasing of synthesis temperature, forming a compact structure with small needles.

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