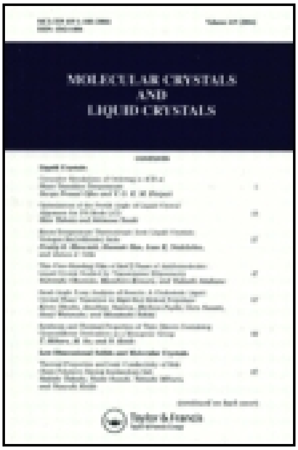

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Effects of LiCl and MgCl2 in the Synthesis Solution on the Kinetics and Properties of Polyaniline

P. Sbaite [a] , A. J. Motheo [a] , B. Siefert [b] & D. Huerta-Vilca [b]

[a] DFQ, IQSC-USP, P.P. 780, CEP 13560-97-, São Carlos, SP, Brazil

[b] TU Clausthal, ABKO, Clausthal-Zellerfeld, D-38678, Germany

To cite this article: P. Sbaite, A. J. Motheo, B. Siefert & D. Huerta-Vilca (2004): The Effects of LiCl and MgCl2 in the Synthesis Solution on the Kinetics and Properties of Polyaniline, Molecular Crystals and Liquid Crystals, 415:1, 239-245

To link to this article: http://dx.doi.org/10.1080/15421400490482231

Mol. Cryst. Liq. Cryst., Vol. 415, pp. 239–245, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490482231

THE EFFECTS OF LiCl AND MgCl$_2$ IN THE SYNTHESIS SOLUTION ON THE KINETICS AND PROPERTIES OF POLYANILINE

P. Sbaite and A. J. Motheo
DFQ, IQSC–USP, P.P. 780, CEP 13560-97-, São Carlos-SP, Brazil

B. Siefert and D. Huerta-Vilca
ABKO, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany

The effects of salt additions, LiCl and MgCl$_2$, into the aniline-bearing HCl solutions have been studied during the oxidative polymerization with ammonium persulphate. To assess both protonic and ionic effects, LiCl or MgCl$_2$ was added maintaining the chlorine concentration constant. Three polymerization parameters were recorded: T_{max}, E_{max} and t_{max}($v = 1/t_{max}$). T_{max} and v have been correlated with [H^+] and [cation]/[H^+]. The conductivity as a relevant property of the polymer depends on its preparation history. The present study shows a positive effects of salt additions to the conductivity, which increases following the trend HCl < LiCl < MgCl$_2$ when [Cl^-] > 2.0 M.

Keywords: chemical synthesis; conductivity; polyaniline; reaction kinetics; salts

INTRODUCTION

Since the first chemical synthesis of pure polyaniline (PAni), reported by MacDiarmid *et al.* [1], many studies have been performed to establish the polymerization mechanism [2–4] and to propose different applications [5–7]. The main goal of many studies has been to increase the conductivity of PAni, which was achieved by synthesis at low temperatures and addition of great amounts of LiCl [8]. The PAni conductivity is that it is related with the crystalline structure and the crystallization degree of PAni increases at low synthesis temperature and in the presence of strong acid electrolytes [9].

The financial support of FAPESP (Processes 99/11621-7 and 00/02674-9) is gratefully acknowledged.

Address correspondence to A. J. Motheo, DFQ, IQSC–USP, P.P. 780, CEP 13560-97-, São Carlos-SP, Brazil. E-mail: artur@iqsc.usp.br

Morales *et al.* [10] found that high amounts of chloride in the deposition electrolyte leads to an incorporation of this anion into the PAni. The polymerization rate increased with the concentration of chloride between 0.1–1 M, but decreased for concentrations between 1–6 M. At high chloride concentrations, the conductivity also decreased. The same authors found chloride in the polymer chain by FTIR-measurements [11].

In this work, we focus the influence of salt additions, LiCl and $MgCl_2$, on the kinetics and conductivity of PAni. The conductivity was discussed in terms of structure and morphology.

EXPERIMENTAL

The chemical synthesis was performed in a 250 mL glass reactor with monitoring of (a) the open circuit potential of a platinum wire against a reference electrode (saturated calomel electrode (SCE)) and (b) the temperature inside the reactor with a Pt-100 resistor. Solutions were HCl (0.4–2.51 M) containing 0.1 M aniline plus LiCl or $MgCl_2$ maintaining the total amount of chloride constant. The oxidant agent (0.1 M $(NH_4)_2S_2O_8$) was added to the reactor after conditioning at 0°C. The reagents were of analytic grade (HCl 37% and salts from Merck). Aniline 99.5% (Aldrich, A.C.S. reagent) was distilled under vacuum at 155°C, in the presence of zinc powder to remove the oxidation products. Aqueous solutions were prepared by using Milli-Q water. A total of 25 syntheses were performed. Each process was characterized by potentiometric and quasi-calorimetric time-dependent curves. The resulting PAni (emeraldine base, EB) powders were dedoped with 0.1 M NH_4OH, filtered and dried under vacuum. The EB powders were characterized by conductivity measurement (four points method), infrared spectroscopy (BOMEM MB-102 FTIR), X-ray diffraction (Rigaku-Rotaflex RU 200-B diffractometer) and Scanning Electron Microscopy (LEO Cambridge 440).

RESULTS AND DISCUSSION

Figure 1 depicts the parameters controlled during the chemical synthesis of PAni: temperature and potential. It is evident that polymerization is an exothermic process as indicated by a temperature rise inside the cell whit the external temperature maintained at 0°C. The open circuit potential during the formation of the polymer first, increases fast due to the initial nucleation and then, slowly to a maximum (E_{max}) that is coincident to the maximum in the temperature (T_{max}). This maximum polymerization potential corresponds to the situation where the polymer exists in its

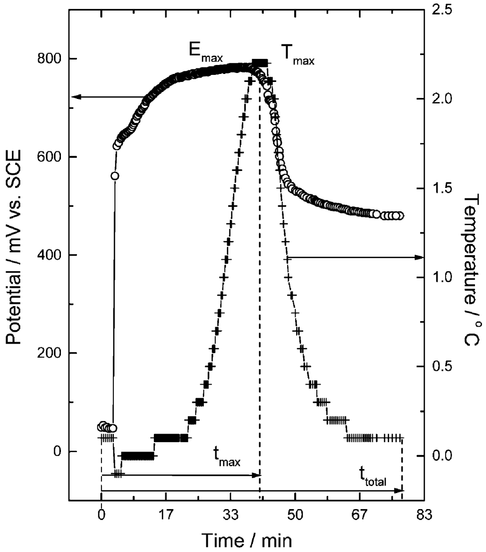

FIGURE 1 Monitored parameters during the chemical synthesis of PAni as a function of time of polymerization to emeraldine salt. Electrolyte: 0.4 M HCl + 0.1 M aniline.

oxidized state (pernigraniline). After some time, the open circuit potential decreases continuously by formation of the emeraldine salt reaching a near stationary value. In order to perform the analysis of the curves corresponding to the different solutions, some additional definitions have been introduced: $\mathbf{t_{total}}$, time to reach the oxidation state of emeraldine salt (total synthesis time); $\mathbf{t_{max}}$, the time to reach the maximum temperature and/or the inflexion point of the potential curve. This parameter characterizes the polymerization reaction rate, defined as $v = 1/t_{max}$. According to Manohar *et al.* [3], the point (E_{max},t_{max}) corresponds to the formation of oligomers and pernigraniline.

Figure 2 shows changes in the polymerization heat and the reaction rate (T_{max} and $1/t_{max}$) as a function of the proton concentration at constant chloride concentrations of 0.4 M in the presence of salts. A decrease in the proton concentration leads to a decrease in both the polymerization amounts and reaction rates. This behavior is similar to that observed for pure HCl solutions. A presence of Mg^{2+} in the solution makes the process more exothermic compared to Li^{+}. On the reaction rate, the higher influence of Mg^{2+} ions over Li^{+} is observed rather when the proton concentration is equal or higher than 0.2 M.

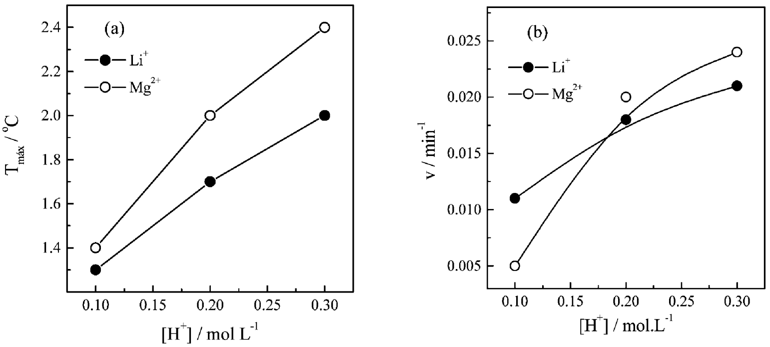

FIGURE 2 The dependence on the solution ionic force of (a) T_{max} and (b) v, at constant chloride concentration $[Cl^-] = 0.4\,M$.

A more significant influence of the ionic force and cation addition at high chloride concentration on the reaction rate can be obtained using the [cation]/[proton] ratio, as shown in Figure 3. The presence of Mg^{2+} increase the polymerization rate more drastically than Li^+.

The infrared spectroscopy was used to detect whether chloride enters or not into the benzenic ring to give characteristic peaks as formulated by Morales *et al.* [10]. Figure 4 shows the region of the FTIR-spectra where chlroride bound to the polymer was localized in the results of Barbero *et al.* [11]. Indeed, chloride peaks can be observed for concentrations 1.81 and 2.51 M. The characteristic bands for chloride bound to the aromatic ring appear at 1041 and $918\,cm^{-1}$.

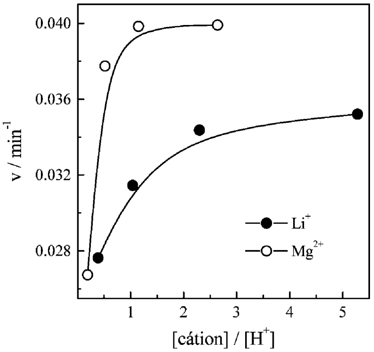

FIGURE 3 Reaction rate as a function of the ratio $[cation]/[H^+]$, at constant $[Cl^-] = 2.51\,M$.

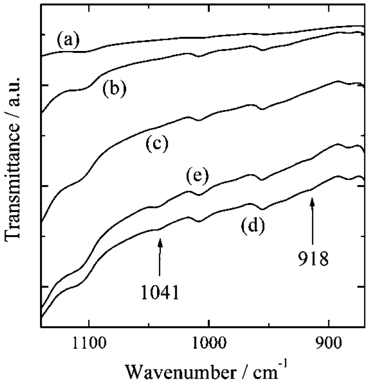

FIGURE 4 Expanded FTIR spectra for PAni prepared from 0.1 M aniline containing (a) 0.4, (b) 0.76, (c) 1.23, (d) 1.81 and (e) 2.51 M HCl.

The Debye-Scherrer patterns (Fig. 5) characteristic peaks of PAni as-synthesized (doped) and the peaks were indexed according to Peugeot *et al.* [12]. No differences in the XRD-patterns were observed for PAni synthesized in 0.4 as well as in 2.51 M chloride, in the presence or absence of different cations.

The SEM micrographies (Fig. 6) show cauliflower structure in 0.4 M and chip structure in 2.51 M HCl. The addition of MgCl$_2$ to a high chloride

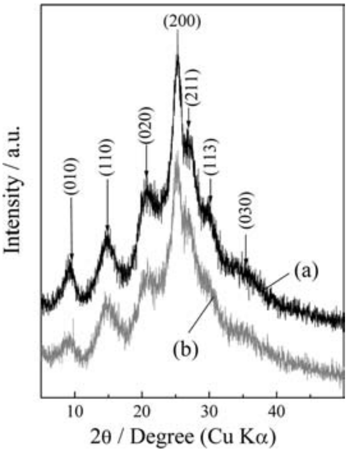

FIGURE 5 X-ray diffraction patterns at grazing angle of PAni deposited at constant chloride concentration of 2.51M and different salts, (a) 1.81M HCl + 0.7 M LiCl + 0.1 M aniline and (b) 1.81 M HCl + 0.35 M MgCl$_2$ + 0.1 M aniline.

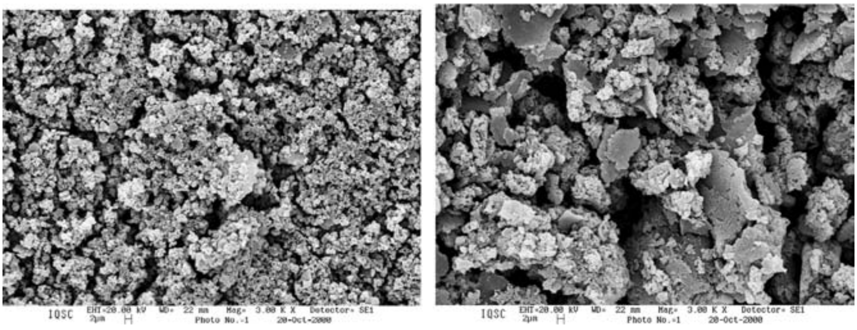

FIGURE 6 SEM-micrographies of PAni prepared from 0.1 M aniline in (a) 0.4 and (b) 2.51 M HCl. Magnification: 3000x.

solution of 1.81 M HCl refined the structure and increased the conductivity drastically. In general, the conductivity of PAni with a chip structure is rather lower than with a cauliflower or refined features.

As shown in Figure 7, the positive effects of salt additions on the conductivity are manifested at chloride concentrations higher than 2.0 M, increasing in the order HCl $<$ LiCl $<$ $MgCl_2$. The advantage of chloride salt addition on the conductivity might be attributed to the presence of cations in the polymer.

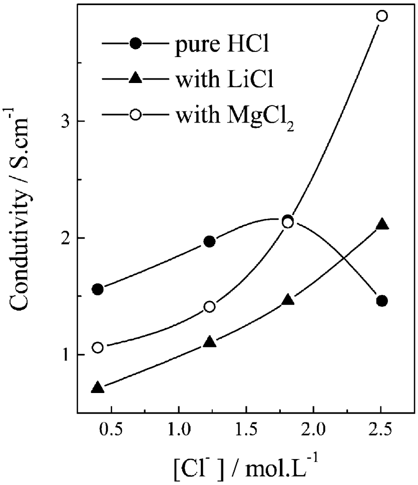

FIGURE 7 Conductivity as a function of the total chloride concentration in the reactional medium.

CONCLUSIONS

The present study demonstrated that the salt additions to the synthesis electrolyte have influence in the polymerization kinetics and the conductivity of the resulting polymer. In the specific range of concentrations used, the following conclusions are drawn:

1. A clearly positive role played by salt addition in the solutions can be first observed at high chloride concentration (1.81 M or higher).
2. Chloride bound to the aromatic ring was found by FTIR-analysis, but a mechanism cannot be drawn.
3. At high chloride concentrations, salt addition can enhance the chloration of the monomer making faster its polymerization. A second effect is the increase of the conductivity, increasing in the order HCl $<$ LiCl $<$ $MgCl_2$.
4. PAni with a chip-structure shows lower conductivity than cauliflower-structure. $MgCl_2$ refines the structure of PAni during the synthesis at high chloride concentrations.

REFERENCES

[1] Huang, W. S., Humphrey, B. D., & MacDiarmid, A. G. (1986). *J. Chem. Soc. Faraday Trans.*, *I 82*, 2385.

[2] Mattoso, L. H. C. (1996). *Quimica Nova*, *19*, 388.

[3] Manohar, S. K., MacDiarmid, A. G., & Epstein, A. J. (1991). *Synth. Met.*, *711*, 41–43.

[4] Ahmad, N. & MacDiarmid, A. G. (1996). *Synth. Met.*, *78*, 103.

[5] Maia, D. J., De Paoli, M. A., & Alves, O. L. (2000). *Quimica Nova*, *23*, 204.

[6] Ohtani, A., Abe, M., Ezoe, M., Doi, T., Miyata, T., & Miyake, A. (1993). *Synth. Met.*, *55*, 3696.

[7] Moraes, S. R., Huerta-Vilca, D., & Motheo, A. J. (2002). *Mol. Cryst. Liq. Cryst.*, *374*, 391.

[8] Adams, P. N., Laughlin, P. J., Monkman, A. P., & Kenwright, A. M. (1996). *Polymer*, *37*, 3411.

[9] Stejskal, J., Riede, A., Halavatá, D., Prokes, J., Helmstedt, M., & Holler, P. (1998). *Synth. Met.*, *96*, 55.

[10] Morales, G. M., Llusa, M., Miras, M. C., & Barbero, C. A. (1997). *Polymer*, *38*, 5247.

[11] Morales, G. M., Miras, M. C., & Barbero, C. A. (1999). *Synth. Met.*, *101*, 687.

[12] Pouget, J. P., Jósefowicz, M. E., Epstein, A. J., Tang, X., & MacDiarmid, A. G. (1991). *Macromolecules*, *24*, 779.