Influence of electropolymerization conditions on the molecular weight of polyaniline

L. H. C. Mattoso* and R. M. Faria
Instituto de Física e Química de São Carlos, DFCM, CP 369, São Carlos 13560-970, SP, Brazil

and L. O. S. Bulhões
Departamento de Química, UFSCar, São Carlos, SP, Brazil

and A. G. MacDiarmid
Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA
(Received 16 November 1993; revised 18 March 1994)

Successful attempts to produce high-molecular-weight polyanilines via electrochemical synthesis are reported. A systematic study of the influence of electropolymerization conditions on the weight-average molecular weight (M_w) showed that M_w of polyaniline varied only between about 22 000 and 40 000 g mol^{-1}, even for a wide range of conditions. Significant increases in M_w are only obtained when a neutral salt is added to the electrolyte. M_w can be increased up to 160 000 g mol^{-1} by increasing the LiCl concentration to about 6 M. This salt effect on M_w is consistent with electrostatic charge screening effects.

(Keywords: polyaniline; electrochemical synthesis; molecular weight)

INTRODUCTION

In recent years there has been growing interest in the study of the molecular weight and molecular-weight distribution of conducting polymers, for the properties of these polymers may depend strongly on their molecular weight. For instance, the mechanical properties as well as the electrical conductivity are usually improved by increasing the molecular weight.

Polyanilines can be prepared by either electrochemical[1–6] or chemical[7–14] methods. Chemical synthesis has the advantage of producing high-molecular-weight polyanilines, which allows the preparation of flexible and conductive films. The molecular weight of electrochemically synthesized polyanilines[2–6], however, is much lower than those attained in the chemical synthesis[8,10–14]. The weight-average molecular weight (M_w) usually ranges from 1000 to 50 000 g mol^{-1} depending on the conditions of electropolymerization and/or on the methods for polymer solubilization and molecular-weight determination. Another problem faced in studies of molecular weight is that polyaniline is generally not completely soluble. In this respect, several solubilization techniques have been employed in order to maximize the soluble fraction of polyaniline. Different solvents, such as 20% aqueous NaOH–tetrahydrofuran (THF) solution[2,5], dimethylformamide (DMF)[3,6], *N*-methylpyrrolidinone (NMP)[4], have been used, some of which also include ultrasonic field to increase the polymer solubility[5,6]. In addition, the molecular weight distribution exhibits a polymodal pattern in gel permeation chromatography (g.p.c.). The choice of an adequate solvent is certainly important to have complete polymer dissolution, as recently reported by Tang[11] where the use of 0.5% LiCl–NMP led to a unimodal molecular-weight distribution for polyanilines.

In this work, we attempt to obtain high-molecular-weight polyaniline via electropolymerization. For this purpose, we performed a systematic study to determine the main electrochemical synthesis conditions affecting the molecular weight of the polyaniline produced. We also build upon previous studies[15,16] where the presence of neutral salts in the chemical synthesis of polyaniline was shown to increase remarkably the molecular weight of the polymer.

EXPERIMENTAL

Aniline (Aldrich Chemical Co.) was distilled under reduced pressure prior to polymerization. *p*-Phenylenediamine (PPDA), poly(vinylsulfonic acid, sodium salt) (PVS) and 1-methyl-2-pyrrolidinone (NMP; h.p.l.c. grade) were purchased from Aldrich Chemical Co., and LiCl, $LiNO_3$, KCl, $CaCl_2$, HCl, $HClO_4$ and NH_4OH were analytical grade from Fisher; all were used as received.

The electrochemical studies were performed with a PARC model 173 Potentiostat/Galvanostat connected to a PARC model 175 Universal Programmer. A standard three-electrode cell was used and all potentials were measured against a saturated calomel electrode (SCE). The working electrode was a platinum foil with a

---

* To whom correspondence should be addressed

0032-3861/94/23/5104-05

geometric area of 1.9 cm^2. A glass tube ended by a fritted glass disc was employed to separate the platinum foil counter-electrode from the cell compartment. The polyaniline (PANI) film deposited on the working electrode was kept in the solution with aniline for 15 min after the polymerization was concluded. This allowed the stabilization of the open-circuit potential (V_{oc}) of the polymer to a constant value of approximately 0.42 V (SCE), which is characteristic of the emeraldine oxidation state. The polymer was then washed with acetone to eliminate monomers. The deprotonation step was carried out by stirring the polymer in a 0.1 M ammonium hydroxide solution for 10 h.

The molecular weight was determined by gel permeation chromatography calibrated with monodisperse polystyrene standards with molecular weights ranging from 3250 to 2 950 000 g mol^{-1}. Gel permeation chromatography was performed on a Waters GPC model IIA equipped with a model 590 programmable solvent delivery module, a differential refractometer as detector and an Ultrastyragel linear column (Waters/Milipore Co.). The polyaniline samples in the base form were dried for 16 h under dynamic vacuum prior to the preparation of the solution. They were then dissolved in the mobile phase (0.5% LiCl–NMP, w/v) in order to prepare a ~0.5 g l^{-1} solution. The temperature of the g.p.c. column and detector was kept at 30°C and the flow rate was 0.44 ml min^{-1}.

In order to investigate the influence of electrochemical synthesis parameters (applied potential, polymerization time, temperature, aniline concentration, electrolyte nature and ionic strength) on the molecular weight of polyaniline, the following initial conditions were used: polymerization potential of 0.7 V applied during 2.0 min in a 1.0 M HCl aqueous solution containing 0.5 M of aniline. The polymerization was performed at 25°C.

RESULTS AND DISCUSSION

Effect of synthesis conditions

In contrast to several previous studies[2–6] a unimodal g.p.c. chromatogram was obtained for all samples analysed in this paper. A unimodal chromatogram is in agreement with recent results of Tang[11], who identified the solvent mixture 0.5% LiCl–NMP as the most appropriate for g.p.c. measurements. It is proposed that under these conditions entanglements and/or residual charges in the polymer are eliminated by the salt and complete polymer solubilization is promoted.

The effect of the potential applied during the polymerization on M_w was investigated in the range of 0.70 to 0.95 V (SCE). As shown in *Table 1*, the molecular weights of the polyaniline films obtained at various potentials (keeping the other conditions constant) are slightly different. When the potential is increased to values more positive than 0.75 V, a small decrease in the molecular weight is observed, despite the larger electrical charge observed during the polymerization. This fact might be associated with a larger number of new chains at this higher potential rather than with an increase of repeat units in each individual chain. For electropolymerization at potentials higher than 0.85 V the solubility of the polymer in 0.5% LiCl–NMP is not complete, indicating that crosslinking reactions must have been favoured. The polydispersity factor (M_w/M_n) did not change significantly for these conditions.

Table 1 Molecular weight of PANI (g mol^{-1}) as a function of polymerization potential (E): polymerized in 1.0 M HCl with 0.5 M aniline; polymerization time = 2 min; T = 25°C

E (V, SCE)	M_w	M_n	M_w/M_n
0.70	26 700	14 500	1.8
0.75	26 500	14 800	1.8
0.85	24 700	13 500	1.8
0.95	25 900	13 500	1.9

Table 2 Molecular weight of PANI (g mol^{-1}) as a function of polymerization time (t): polymerized in 1.0 M HCl with 0.5 M aniline; at 0.7 V; T = 25°C

t (min)	M_w	M_n	M_w/M_n
2	26 000	14 500	1.8
5	34 300	16 700	2.0
15	34 100	16 200	2.1
60	33 600	15 900	2.1

Table 3 Molecular weight of PANI (g mol^{-1}) synthesized at different temperatures: polymerized in 1.0 M HCl with 0.5 M aniline; at 0.7 V; t = 2 min

T (°C)	M_w	M_n	M_w/M_n
0	20 500	12 600	1.6
25	26 500	14 800	1.8
44	40 800	24 000	1.7

In *Table 2* we show the molecular weight of polyaniline synthesized at a constant potential as a function of the polymerization time (up to 60 min). From 2 to 5 min of polymerization an increase of 30% in the molecular weight is obtained, after which it remains constant. It is interesting to note that the polymer molecular weight is constant despite the increased number of coulombs observed with increasing polymerization time. The material resulting after 60 min of polymerization gave an elemental analysis of C 78.0% (theory 79.5%), H 4.7% (5.0%), N 15.0 (15.5%) in the base form. This result is satisfactory since this long polymerization time could, in principle, favour side reactions.

An increase in the molecular weight is observed when the temperature of polymerization is varied from 0 to 44°C as shown in *Table 3*. The increase in M_w with temperature suggests a greater temperature dependence of the coupling propagation rate as compared to the termination rate and/or a greater dependence of the propagation rate as compared to the initiation rate. Higher temperatures of polymerization also lead to the appearance of an insoluble, possibly crosslinked, polymer fraction.

The influence of aniline concentration on the molecular weight, under constant supporting electrolyte concentration and applied potential, is shown in *Table 4*. An increase of 52% in the weight-average molecular weight was obtained when the aniline content is changed from 0.1 to 0.5 M. However, a drastic decrease of M_w was observed with 1.0 M aniline, the resulting film being completely soluble in acetone when deprotonated. At

Table 4 Molecular weight of PANI (g mol^{-1}) as a function of aniline concentration: polymerized in 1.0 M HCl; at 0.7 V; $t = 15$ min; $T = 25°C$

[Aniline] (M)	M_w	M_n	M_w/M_n
0.1	22 500	13 600	1.7
0.5	34 300	16 700	2.0
1.0	<3000	<3000	–

Table 5 Molecular weight of PANI (g mol^{-1}) as a function of electrolyte nature: polymerized in 1.0 M HCl with 0.5 M aniline; at 0.7 V; $t = 5$ min; $T = 25°C$

	Electrolyte^a	M_w	M_n	M_w/M_n
(i)	1.0 M HCl	34 100	16 200	2.1
(ii)	1 mM PPDA + 1.0 M HCl	40 600	20 900	1.9
(iii)	2.3 M $HClO_4$	46 600	26 300	1.8
(iv)	1.0 M PVS + 1.0 M HCl	53 000	20 800	2.6
(v)	2.0 M LiCl + 1.0 M HCl	90 600	34 500	2.6

^{a} Similar synthesis conditions were used in (ii) ref. 4, (iii) ref. 3 and (iv) ref. 12

1.0 M monomer concentration the number of initiation sites of new chains may be greatly increased as compared to propagation sites, hindering chain growth. The polydispersity increased from 1.7 to 2.0 with increasing monomer concentration from 0.1 to 0.5 M, probably associated with the smaller uniformity of polymer chain growth promoted by the higher polymerization rate. An increase of polydispersity was also observed under other conditions that involved higher polymerization rates. The smallest polydispersity value (1.6) was obtained at low temperature where the polymerization rate was also the lowest one. A polydispersity of around 2 was obtained, as well, for poly(3-hexylthiophenes) electrochemically synthesized under various conditions[1]. However, further work is required to correlate polydispersity with mechanisms of polymerization.

The results thus far reported show that for the whole range of variables studied the M_w can be changed only from ~20 000 up to ~40 000 g mol^{-1}, still below the values obtained for chemically synthesized polyanilines. This is not a significant improvement on molecular weight, in particular if one considers that some of the conditions investigated were already a limiting point, since the polymer solubility started to decrease. The decrease in solubility may be an indication of the increase in the rate of side reactions such as chemical crosslinking.

Synthesis in the presence of neutral salts

In an attempt to obtain high-molecular-weight polyanilines and building upon previous studies[3,4,12,15], we decided to investigate the effect of the supporting electrolyte on the molecular weight. Electropolymerization was carried out in five different types of electrolyte, as shown in *Table 5*. The molecular weight of polyaniline can be varied significantly depending on the nature of the compound present in the electrolyte. Increases of M_w were observed for PPDA, $HClO_4$ and PVS solutions up to a maximum of 1.54 times for the case of PVS. These electropolymerization conditions were previously used in the literature[3,4,12] to obtain polyanilines with higher molecular weights. A greater increase of about 2.6 times the molecular weight was obtained when 2.0 M LiCl was added to the solution containing 1.0 M HCl. Since the molecular weight of polyaniline has been shown to be highly dependent on the addition of salts to the electrolyte, further attempts were made to obtain still higher-molecular-weight polymers.

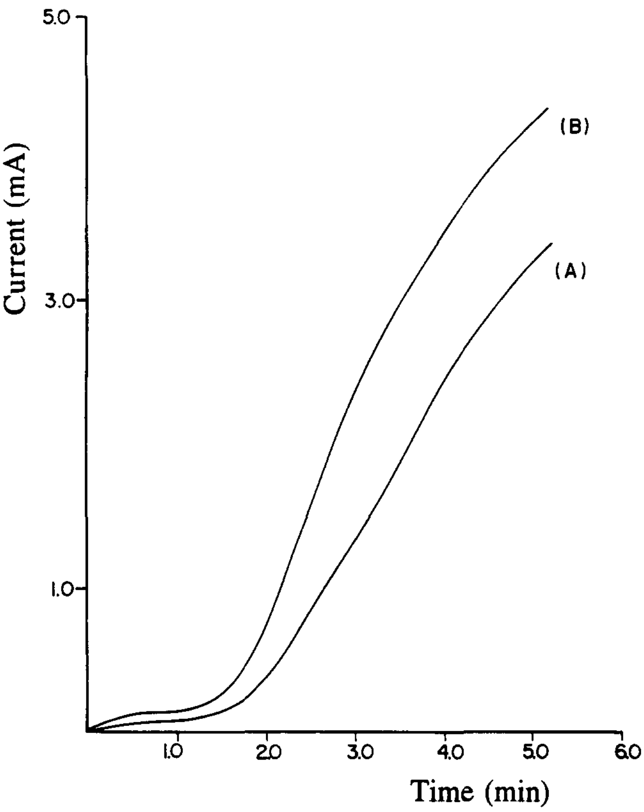

Figure 1 Current *versus* time curves for the electrochemical polymerization of 0.5 M aniline at 0.7 V with 1.0 M HCl and without/with LiCl: [LiCl] = 0 M (a) and 2 M (b)

Figure 1 shows the polarization curve during the electropolymerization of aniline in pure 1.0 M HCl solution and in the presence of 2.0 M LiCl. A difference of approximately 190 mC at maximum time (corresponding to an increase of 52%) was determined in the potentiostatic curve by the addition of 2.0 M LiCl, which indicates a higher rate of film growth. *Figure 2* shows that the cyclic voltammograms of these PANI films, with different molecular weights, are very similar to those reported in the literature[4] and do not present the middle degradation peaks. These voltammograms also show two other important features of their electrochemical behaviour. The first one is the shift in potential of the anodic and cathodic peaks, to more positive values with increasing M_w, which agrees with that observed by Aguirre *et al.*[17], using different alkali-metal ions. The second feature is that the number of coulombs obtained from the cyclic voltammogram for the 2.0 M LiCl film is also greater (50%) than that for the film prepared in the solution without LiCl, which is qualitatively consistent with the molecular-weight increase previously discussed.

The influence on the molecular weight of the type of alkali-metal ion present in the electrolyte is shown in *Table 6*. An increase to approximately 85 000 g mol^{-1} was observed for various other salts, compared to the former electrolyte solution. It is interesting to observe that a further increase of 26% in M_w was obtained when the ionic strength of the solution containing Ca^{2+} was increased.

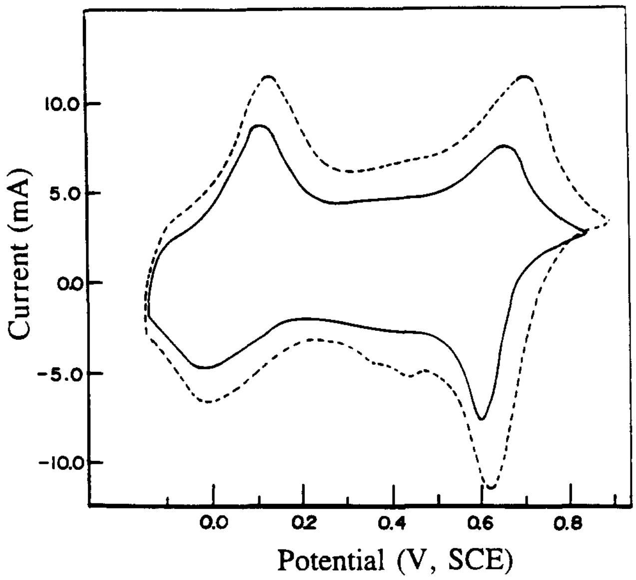

Figure 2 Cyclic voltammogram of polyailine electrochemically synthesized in 1.0 M HCl in (——) absence of salt and (- - -) presence of 2.0 M LiCl

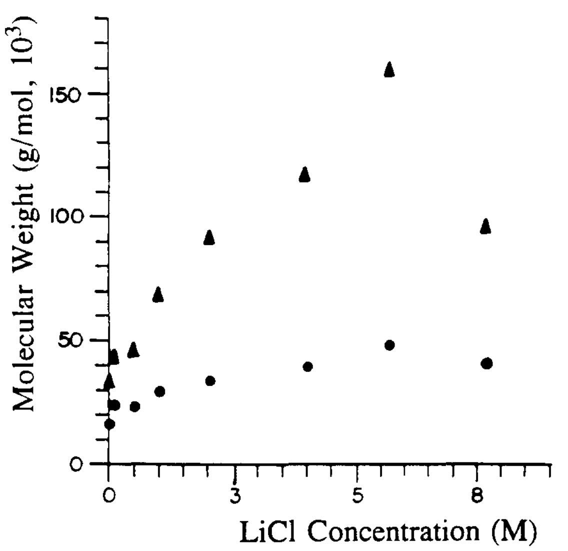

Figure 3 Molecular weights M_w (▲) and M_n (●) of polyaniline as functions of the LiCl concentration used in the electropolymerization of 0.5 M aniline with 1.0 M HCl at 0.7 V and 25°C

Table 6 Molecular weight of PANI (g mol^{-1}) as a function of salt type: polymerized in 1.0 M HCl with 0.5 M aniline; at 0.7 V; $t = 5$ min; $T = 25$°C

Salt added	M_w	M_n	M_w/M_n
2 M LiCl	90 600	34 500	2.6
2 M $LiNO_3$	86 600	32 200	2.7
2 M KCl	86 400	37 400	2.3
2 M $CaCl_2$	83 400	31 100	2.7
3 M $CaCl_2$	105 900	39 800	2.7

Under constant polymerization conditions, the molecular weights of the resulting polyaniline films were greatly affected by the concentration of LiCl in the electrolyte, as shown in *Figure 3*. An increase in M_w from 34 000 g mol^{-1} to 160 000 g mol^{-1} is observed by changing the LiCl concentration from 0 M to ~6 M. Similar tendencies were also observed with the salt $CaCl_2$ (*Table 6*).

A possible explanation is based on the mechanism proposed for the salt effect on M_w of chemically synthesized polyaniline[15]. In the usual electrochemical polymerization the amine structure is oxidized to a diimine structure and a radical cation is formed at an N-position as proposed previously by Mohilner *et al.*[18]. The dimer formed by the coupling reaction is promptly oxidized and these radical coupling reactions are repeated among radical cations. During these coupling reactions, insoluble oligomers are formed and deposited on the electrode surface, thus forming a polyaniline film. This mechanism is in agreement with the steps proposed recently for the initial stage of electropolymerization of aniline in acidic aqueous solution[19].

It is well known that the rate of reaction between positively charged ions is increased by the presence of dissolved neutral salts[20]. Hence, it is to be expected that the rate of reaction of radical cations with positively charged oligomers or positively charged growing polymer chains will be increased in the presence of dissolved salts. However, regardless of the above effect, it is expected that the rate of reaction with the polymer will be greater than the rate of reaction with oligomer, since the higher the molecular weight, the greater will be the (positive) charge delocalization, thus facilitating preferential reaction of the radical cation with the growing positively charged polymer chain.

CONCLUSIONS

The present study has demonstrated the possibility of producing high-molecular-weight polyanilines via electropolymerization. Although M_w does not change significantly for a wide range of electropolymerization conditions, high-molecular-weight polyanilines can be obtained by controllably adding neutral salts to the electrolyte medium. The M_w achieved here (up to 160 000 g mol^{-1}) is higher than those reported in the literature for electrochemically synthesized polyaniline and it is as high as those obtained via classical chemical methods. The salt effect on the molecular weight of polyaniline was also observed for other salts studied with a similar increase in M_w. The salt effect on the molecular weight of polyaniline can be explained by charge screening effects.

ACKNOWLEDGEMENTS

This work was supported in part by the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico CNPq–Brazil. We are also grateful for the support of the Office of Naval Research (ONR Grant No. NPPP14-92-J-1369) and the NSF-MRL program, under Grant No. DMR-91-20668.

REFERENCES

1 Osawa, S., Ito, M., Iwase, S., Yajima, H., Endo, R. and Tanaka, K. *Polymer* 1992, **33**, 914
2 Watanabe, A., Mori, K., Iwasaki, Y. and Nakamura, Y. *J. Chem. Soc., Chem. Commun.* 1987, 3
3 Yoshikawa, K., Yoshioka, K., Kitani, A. and Sasaki, K. *J. Electroanal. Chem. Short Commun.* 1989, **270**, 421
4 Wei, Y., Jang, G. W., Hariharan, R., Chan, C. C. and Hsueh, K. F. *Polym. Prepr.* 1990, **30**, 911

5 Watanabe, A., Mori, K., Iwasaki, Y., Murakami, S. and Nakamura, Y. *J. Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 4431
6 Genies, E. M. and Noel, P. *Synth. Met.* 1992, **46**, 285
7 Tang, X., Sun, Y. and Wei, Y. *Makromol. Chem., Rapid Commun.* 1988, **9**, 829
8 Wei, Y., Hsueh, K. F., Tang, X. and Sun, Y. *Polym. Prepr.* 1989, **30**, 226
9 Wei, Y., Hsueh, K. F., Nagy, S., Ray, A., MacDiarmid, A. G., Dykins, J., Epstein, A. J. and Wnek, G. E. *Mater. Res. Soc. Symp. Proc.* 1990, **173**, 341
10 Dao, L. H., Leclerc, M., Guay, J. and Chevalier, J. W. *Synth. Met.* 1989, **29**, E377
11 Tang, X. PhD Thesis, University of Pennsylvania, 1991
12 MacDiarmid, A. G. and Epstein, A. J. *Mater. Res. Soc. Symp. Proc.* 1992, **247**, 565
13 Abe, M., Ohtani, A., Umemoto, Y., Akizuki, S., Ezoe, M., Higuchi, H., Nakamoto, K., Okuno, A. and Noda, Y. *J. Chem. Soc., Chem. Commun.* 1989, 1736
14 MacDiarmid, A. G., Manohar, S. K. and Mattoso, L. H. C. US Pat. Appl. 07/789095, 1992
15 Mattoso, L. H. C., MacDiarmid, A. G. and Epstein, A. J. *Synth. Met.* in press
16 Mattoso, L. H. C., Faria, R. M., Bulhões, L. O. S. and MacDiarmid, A. G. *J. Polym. Sc., Polym. Chem. Edn* in press
17 Aguirre, M. J., Retamal, B. A., Ureta-Zañartu, M. S., Zagal, J. H., Córdova, R., Schrebler, R. and Biaggio, S. R. *J. Electroanal. Chem.* 1992, **328**, 349
18 Mohilner, D. M., Adans, R. N. and Argersinger, W. J. *J. Am. Chem. Soc.* 1962, **84**, 3618
19 Yang, H. and Bard, A. J. *J. Electroanal. Chem.* 1992, **339**, 423
20 Atkins, P. W. in 'Physical Chemistry', 4th Edn, Oxford University Press, Oxford, 1990, p. 858