

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

The Kinetics of DBSA-Doped Polyaniline Film Formation in a Constant Magnetic Field (0.6 T)

Ma Li^a; Yan Jun^a; Gan Meng-Yu^a; Qiu Wei^a; Luo Lai-Zheng^a; Lu Wei^a

^a College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China

To cite this Article Li, Ma, Jun, Yan, Meng-Yu, Gan, Wei, Qiu, Lai-Zheng, Luo and Wei, Lu(2008) 'The Kinetics of DBSA-Doped Polyaniline Film Formation in a Constant Magnetic Field (0.6 T)', *International Journal of Polymer Analysis and Characterization*, 13: 4, 269 – 279

To link to this Article: DOI: 10.1080/10236660802140992

URL: <http://dx.doi.org/10.1080/10236660802140992>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Kinetics of DBSA-Doped Polyaniline Film Formation in a Constant Magnetic Field (0.6 T)

Ma Li, Yan Jun, Gan Meng-Yu, Qiu Wei, Luo Lai-Zheng,
and Lu Wei

College of Chemistry and Chemical Engineering, Chongqing University,
Chongqing, China

Abstract: Polyaniline (PANI) doped with dodecylbenzene sulfonic acid (DBSA) was synthesized by emulsion polymerization using ammonium persulfate (APS) as oxidant in the presence of a constant magnetic field (0.6 T). The kinetics of the PANI film formation was investigated by the quartz crystal microbalance (QCM) technique. The reaction exhibited first order with respect to aniline and half-order to APS and DBSA. The effects of temperature and different magnetic field intensity on the film growth rate were investigated. The activation energy calculated from the temperature dependence of the growth rate was 40.4 KJ/mol. It was observed from the plot of the PANI film growth rate versus the magnetic field intensity that the growth rate increased with the increasing magnetic intensity. The UV-visible spectra of the PANI polymerization was measured and compared to the polymerization process of the PANI using the QCM technique. The result showed that the absorption intensity of the PANI polymerized in the presence of a magnetic field was greater than that of the PANI polymerized in the absence of a magnetic field at the same time.

Keywords: Activation energy; Conjugated polymers; Emulsion polymerization; Kinetics; Polyamines

Received 3 March 2008; accepted 10 April 2008.

Correspondence: Ma Li, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, China. E-mail: mlsys607@126.com

INTRODUCTION

As one of the most interesting conducting polymers, polyaniline (PANI) has been extensively researched due to its environmental stability, ease in preparation, antistatic or anticorrosion purposes,^[1] exciting electrochemical and physical properties, and use as microelectronics^[2] and sensors and actuators.^[3]

Processing of PANI high polymers into useful objects and devices, however, has been problematic. Melt processing is not possible. In addition, major difficulties have been encountered in attempts to dissolve the high molecular weight polymer. Numerous studies^[4-6] were done to improve the processibility of PANI. Recently, it has been reported that PANI in emeraldine salt form doped with protonic acid without the redoping process could be synthesized by the emulsion polymerization method directly in the presence of functionalized protonic acid, oxidant, water, and nonpolar solvent such as toluene.^[5] Synthesis of PANI soluble in organic solvents utilizing the emulsion polymerization method has also been reported by Kinlen et al.^[6]

Magnetic fields are known to affect chemical reactions containing radicals (pairs)^[7,8] and to induce orientation of most organic molecules and biological macromolecules.^[9] The alignment can change the properties of a polymer significantly, increasing its electrical conductivity in one direction.^[10]

The quartz crystal microbalance (QCM) technique has a wide range of applications in biochemistry, analytical science, and other fields.^[11-14] Ayad et al.^[15-17] have applied the QCM technique to monitor the chemical method of aniline oxidation and to study PANI film formation.

However, a few concerns have been raised on its emulsion polymerization in the presence of a magnetic field, especially on its kinetics. Thus, it is our purpose to discuss the kinetics of emulsion polymerization of polyaniline in a magnetic field.

EXPERIMENTAL SECTION

Polyaniline was synthesized by emulsion in the presence of a constant magnetic field (0.6 T), where dodecylbenzoyl sulfonic acid (DBSA) was used as dopant and emulsifier.^[18] Different concentrations of ammonium persulfate (APS) and aniline were prepared for each experiment. A QCM technique was used to monitor the film formation of the PANI.

A 10 MHz cut quartz crystal was used and the measurement was taken by using a handheld testing instrument, Model AGA2003, manufactured by Chongqing University, China. The mass per unit area of the PANI, Δm ($\mu\text{g}/\text{cm}^2$), deposited on the gold electrode on the crystal

surface, was determined from the change in its resonance frequency. The relation between the frequency changes Δf (Hz) and Δm was already established from the work of Sauerbrey and Ayad^[19–20] and is given by:

$$\Delta f = -2 \times 10^6 \left(\frac{f_0^2}{\sqrt{\rho_Q \mu_Q}} \right) \cdot \Delta m$$

where f_0 (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g/cm^3), and μ_Q is the shear modulus ($2.947 \times 10^8 \text{ N/cm}^2$).

An emulsion for each experiment was made in which, for example, aniline and DBSA were mixed and fully emulsified, and then an APS solution was added and shook strongly for the uniform mixing. After that, $200 \mu\text{L}$ of the mixture were added into the QCM detection cell immediately. The temperature of the system was kept constant at $20^\circ \pm 1^\circ\text{C}$. Once the polymerization starts, the PANI deposits on the gold electrode surface. The reaction system was kept unstirred. The frequency change with time for each emulsion was measured and then Δm was calculated at different time intervals of polymerization. The effect of the magnetic field on the film growth rate was investigated with different magnetic intensities (0.2–0.8 T). The absorption spectra of the real-time detection of aniline polymerization taking place in the sample cell were recorded with a Shimadzu UV-2450 spectrophotometer.

RESULTS AND DISCUSSION

Different kinds of emulsion were prepared in which the concentrations of APS and DBSA were kept constant (0.028 M, 0.01 M, respectively) and the concentration of aniline was varied. The molar ratio between aniline and APS was varied from 0.8:1 to 2.0:1. It was worth nothing that the time required to carry out each experiment for different emulsions was approximately 1 h.

Figure 1 shows the plots of Δm against time of polymerization for different ratios between aniline and APS. It can be seen that Δm increased with increasing concentration of aniline and reached a maximum value after approximately 20 min.

To study the kinetics of PANI film deposition in emulsion in the presence of a magnetic field, the growth rate ($\Delta m/s$) was calculated from the slope of the mass-time relation in Figure 1. This slope represented the growth rate (R) at a given concentration of APS, DBSA, and aniline. Since the APS and DBSA concentrations were kept constant and only the concentration of aniline was varied, the double logarithmic plot of R versus [Aniline] was calculated and is shown in Figure 2. A straight line

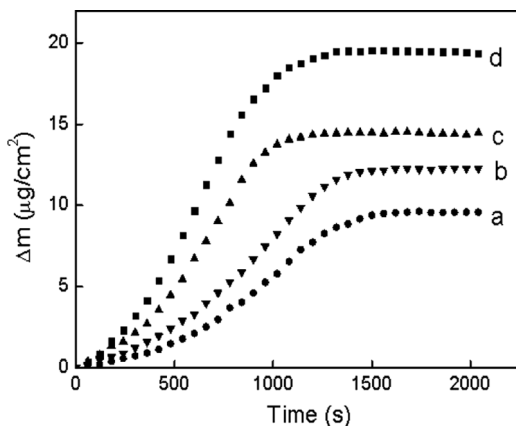


Figure 1. Relationship between Δm ($\mu\text{g}/\text{cm}^2$) of the PANI deposited and time at different molar ratios of [Aniline]/[APS]: (a) 0.8, (b) 1.2, (c) 1.6, and (d) 2.0.

was obtained with slope equal to 0.98, which is nearly equal to 1. That indicated the PANI formation was first order with respect to An.

Then, the concentrations of aniline (0.035 M) and DBSA (0.01 M) were kept constant while the concentration of APS was varied. Figure 3 shows the plots of Δm against time for different ratios of [APS]/[Aniline] (0.08 to 2.0). The double logarithmic plot of R versus [APS] is in Figure 4. A straight line could also be obtained with slope equal to

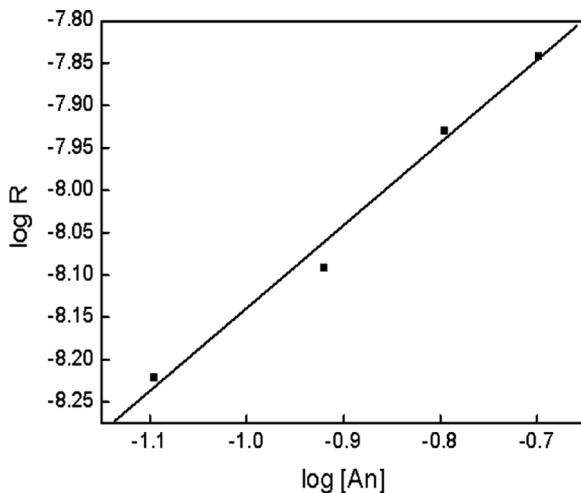


Figure 2. Logarithmic plot of the growth rate (R) vs. \log [Aniline].

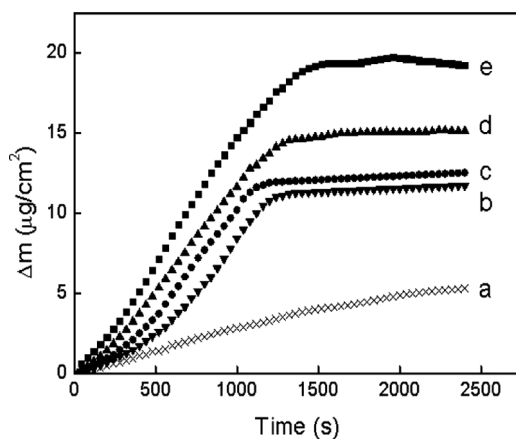


Figure 3. Relationship between Δm ($\mu\text{g}/\text{cm}^2$) of the PANI deposited and time at different molar ratios of $[\text{APS}]/[\text{Aniline}]$: (a) 0.08, (b) 0.8, (c) 1.2, (d) 1.6, and (e) 2.0.

0.49, which almost equals 0.5. That indicated the PANI film formation was half-order with respect to APS.

Similarly, the concentrations of aniline (0.035 M) and APS (0.028 M) were kept constant while the concentration of DBSA was varied. The mass-time relationship of PANI deposition is shown in Figure 5. It was shown that the mass of PANI deposited on the gold electrode increased

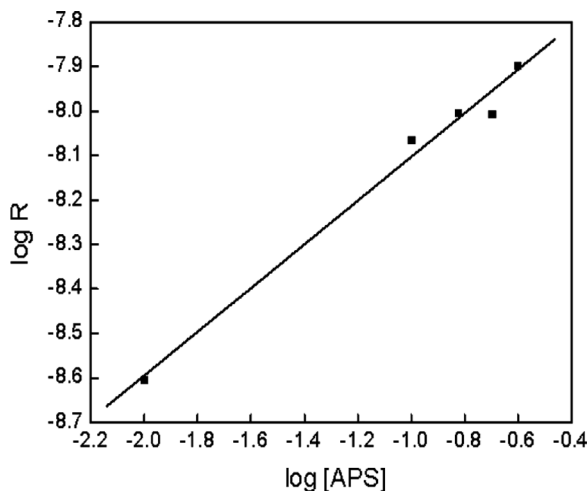


Figure 4. Logarithmic plot of the growth rate (R) vs. $\log [\text{APS}]$.

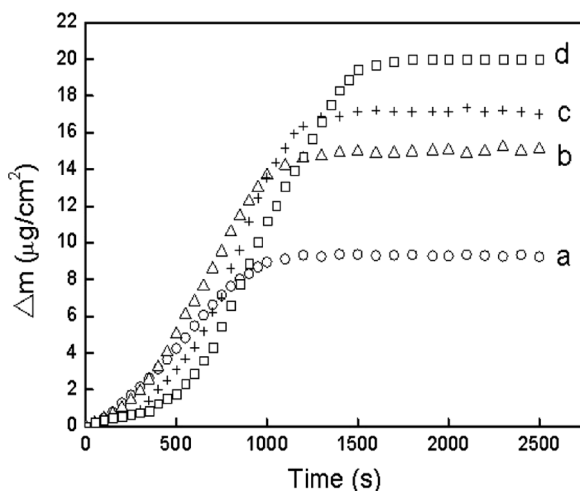


Figure 5. Relationship between Δm ($\mu\text{g}/\text{cm}^2$) of the PANI deposited and time at different concentrations of DBSA: (a) 0.01 M; (b) 0.014 M; (c) 0.018 M; (d) 0.0228 M.

with increasing concentration of DBSA, which is in agreement with the results of classical emulsion polymerization. The growth rate was calculated from the slope of the mass-time relation in Figure 5. The double logarithmic plot of R versus $[\text{DBSA}]$ is shown in Figure 6. A straight line was obtained with slope equal to 0.51, which is nearly equal

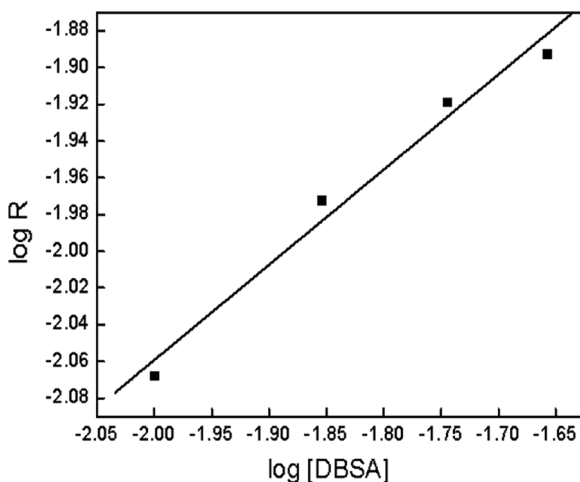


Figure 6. Logarithmic plot of the growth rate (R) vs. $\log [\text{DBSA}]$.

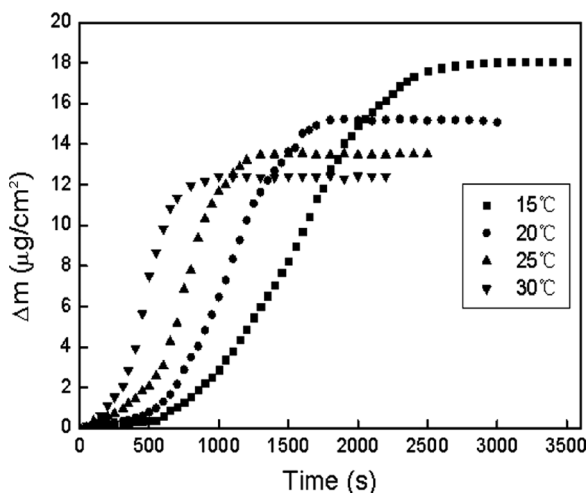


Figure 7. Relationship between Δm ($\mu\text{g}/\text{cm}^2$) of the PANI deposition and time at different temperatures.

to 0.5. That indicated the PANI film formation was half-order with respect to DBSA. Consequently, the overall kinetic order of the PANI polymerization was second order.

The effect of temperature on the growth rate of PANI film formation is shown in Figure 7, for which the concentration of aniline, APS, and DBSA were 0.035 M, 0.028 M, and 0.01 M, respectively. As can be seen in Figure 7, the growth rate increased as the temperature increased. Also, increasing temperature brought about a decrease in the length of the induction period in the temperature range $15^\circ \sim 30^\circ\text{C}$. That might be due to fact that the free radicals could not take part in the side reactions at lower temperatures. The growth rates at different temperatures were determined and plotted according to the Arrhenius equation (Figure 8). The activation energy here was 40.4 KJ/mol, which was in correspondence with the value (44.3 ± 2.1 KJ/mol) reported by Jozefowicz et al.^[21] Since the polymerization was an exothermic progress, it could therefore be expected that increasing temperature would decrease the yield.

Figure 9 shows the mass-time relation of the PANI polymerized in different magnetic intensities for which the concentrations of aniline, APS, and DBSA were 0.035 M, 0.028 M, and 0.01 M, respectively. Figure 10 shows the variation of the PANI growth rate with different magnetic field intensities according to Figure 8. It was shown that the rate of the PANI deposited on the gold electrode increased with increasing intensity of magnetic field. According to Chiriac and Simionescu,^[22]

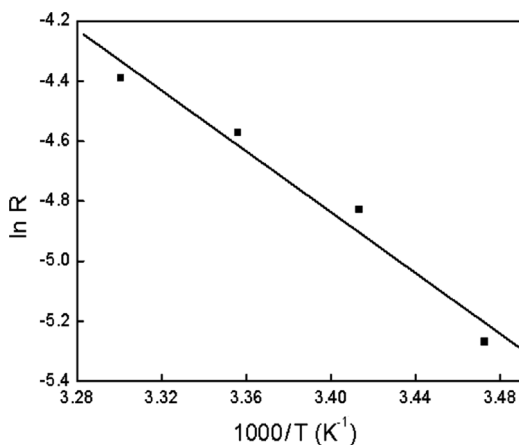


Figure 8. Temperature dependence of the growth rate (R).

owing to the presence of the magnetic field, changes occurred from the singlet to the triplet state in the spin multiplicity of the initiator radicals and the concentration of transient free radicals, which initiate polymerization, and the radical life increased. As a result, the initiation efficiency and the rate of polymerization were enhanced due to the decrease of the “cage” effect and the reduction of radical recombination.

Figure 11 shows the UV-visible spectra of PANI during polymerization in the presence and absence of a magnetic field (0.6 T). The spectra were measured at the same reaction time. By comparing spectrum (a) with spectrum (b) in Figure 11, it was found that the absorption

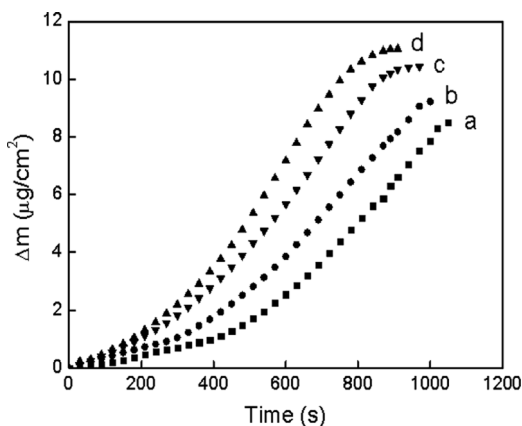


Figure 9. Relationship between Δm ($\mu\text{g}/\text{cm}^2$) of the PANI deposited and time in different intensities of magnetic field: (a) 0.2 T, (b) 0.4 T, (c) 0.6 T, and (d) 0.8 T.

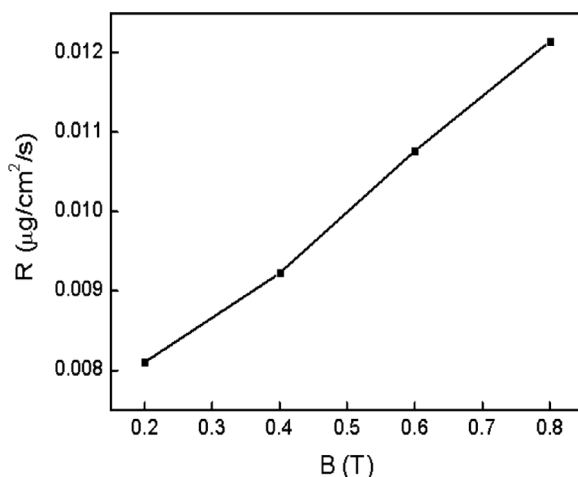


Figure 10. Variation of the PANI growth rate (R) with magnetic field intensity.

intensity of the PANI polymerized in a magnetic field was greater than that of the PANI polymerized in the absence of a magnetic field at the same time. This may indicate that the reaction rate of the PANI polymerized in the presence of a magnetic field was higher than that of the PANI

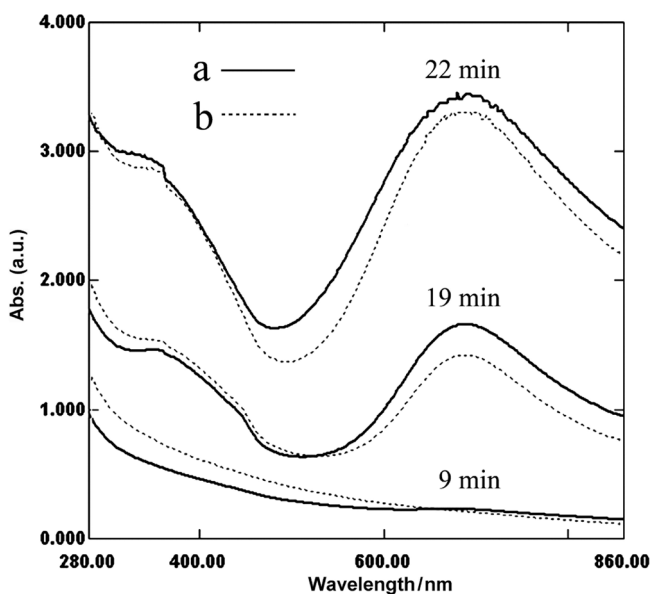


Figure 11. Absorption spectra during the polymerization of aniline: (a) with a magnetic field (0.6 T); (b) without magnetic field.

polymerized in the absence of a magnetic field, which is in agreement with the results obtained by using the QCM technique.

Furthermore, it was found that the trends of the PANI film formation were similar to the detection of the QCM technique. The only difference that existed was the sensitivity on the detection. The sensitivity of the QCM technique to any formation of polymers might be superior to the traditional UV-visible absorption detection. Therefore, the QCM technique can provide a more suitable technique for monitoring the induction periods than absorption spectroscopy.

CONCLUSION

The QCM technique was used to study the kinetics of DBSA-doped PANI film formation by emulsion polymerization using APS as oxidant. The PANI film formation exhibited first order with respect to aniline and half-order to APS and DBSA. The overall kinetic order of the PANI polymerization was second order. Polymerization carried out in different magnetic field intensities was investigated. The result indicated that the reaction rate increased with increasing intensity due to the application of magnetic field increasing the concentration of transient free radicals, which initiate polymerization. The activation energy calculated from the temperature dependence of the growth rate was 40.4 KJ/mol. The UV-visible spectra for PANI film formation were measured. The result showed that the trends of the film growth of PANI with time were similar. The detection of polymerization by using the QCM technique was more sensitive than the detection of UV-visible spectra under the same conditions.

REFERENCES

- [1] Abdiryim, T., X. G. Zhang, and R. Jamal. (2005). Comparative studies of solid-state synthesized polyaniline doped with inorganic acids. *Mater. Chem. Phys.* **90**, 367–372.
- [2] Paul, E. W., A. J. Ricco, and M. S. Wrighton. (1985). Resistance of polyaniline films as a function of electrochemical potential and the fabrication of polyaniline-based microelectronic devices. *J. Phys. Chem.* **89**, 1441–1447.
- [3] Gao, J. B., J. M. Sansinena, and H. L. Wang. (2003). Chemical vapor driven polyaniline sensor/actuators. *Synth. Met.* **135**, 809–810.
- [4] Dan, A., and P. K. Sengupta. (2007). Preparation and characterization of soluble polyaniline. *J. Appl. Polym. Sci.* **106**, 2675–2682.
- [5] Osterholm, J. E., Y. Cao, F. Klavetter, and P. Smith. (1993). Emulsion polymerization of aniline. *Synth. Met.* **55**, 1034–1039.

- [6] Kinlen, P. J., J. Liu, Y. Ding, C. R. Graham, and E. E. Remsen. (1998). Emulsion polymerization process for organically soluble and electrically conducting polyaniline. *Macromolecules* **31**, 1735–1744.
- [7] Turro, N. J., M. F. Chow, C. J. Chung, G. C. Weed, and B. Kraeutler. (1980). Magnetic field and magnetic isotope effects on cage reactions in micellar solutions. *J. Am. Chem. Soc.* **102**, 4843–4845.
- [8] Rintoul, I., and C. Wandrey. (2007). Magnetic field effects on the free radical solution polymerization of acrylamide. *Polymer* **48**, 1903–1914.
- [9] Torbet, J., Y. F. Nicolau, and D. Djurado. (1999). Orientation of CSA-protonated polyaniline chains in solution in m-cresol and in films induced by a high magnetic field. *Synth. Met.* **101**, 825–826.
- [10] Stupp, I. (1986). Pulling polymers into line. *Sci. News* **129**, 297–311.
- [11] Bunde, R. L., E. J. Jarvi, and J. J. Roseentreter. (1998). Piezoelectric quartz crystal biosensors. *Talanta* **46**, 1223–1236.
- [12] Okahata, Y., K. Nikura, Y. Sugiura, M. Sawada, and T. Morii. (1998). Kinetic studies of sequence-specific binding of GCN4-bZIP peptides to DNA strands immobilized on a 27-MHz quartz-crystal microbalance. *Biochemistry* **37**, 5666–5672.
- [13] Carmon, K. D., R. E. Baltus, and L. A. Luck. (2004). A piezoelectric quartz crystal biosensor: The use of two single cysteine mutants of the periplasmic *Escherichia coli* glucose/galactose receptor as target proteins for the detection of glucose. *Biochemistry* **43**, 14249–14256.
- [14] Toshima, N., H. Yan, M. Kajita, Y. Honda, and N. Ohno. (2000). Novel synthesis of polyaniline using iron(III) catalyst and ozone. *Chem. Lett.* **29**, 1428–1429.
- [15] Ayad, M. M., N. Salahuddin, and M. A. Shenashin. (2003). Optimum reaction conditions for in situ polyaniline films. *Synth. Met.* **132**, 185–190.
- [16] Ayad, M. M., and M. A. Shenashin. (2004). Polyaniline film deposition from the oxidative polymerization of aniline using $K_2Cr_2O_7$. *Eur. Polym. J.* **40**, 197–202.
- [17] Ayad, M. M., and M. A. Shenashin. (2004). Effect of acids on in situ polyaniline film formation. *Polym. Int.* **53**, 1180–1184.
- [18] Moreira, V. X., F. G. Garcia, and B. G. Soares. (2006). Conductive epoxy/amine system containing polyaniline doped with dodecylbenzenesulfonic acid. *J. Appl. Polym. Sci.* **100**, 4059–4065.
- [19] Sauerbrey, G. (1959). Use of a quartz vibrator for weighing thin layers on a microbalance. *Physik Z.* **155**, 206.
- [20] Ayad, M. M., A. H. Gemaey, N. Salahddin, and M. A. Shenashin. (2003). The kinetics and spectral studies of the in situ polyaniline film formation. *J. Colloid Interface Sci.* **263**, 196–201.
- [21] Jozefowicz, M., L. T. Yu, G. Belorgey, and R. Buvet. (1967). Conductivity and chemical properties of oligomeric polyaniline. *J. Polym. Sci. Polym. Symp.* **16**, 2934–2941.
- [22] Chiriac, A. P., and C. I. Simionescu. (2000). Magnetic field polymerization. *Prog. Polym. Sci.* **25**, 219–258.