Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Palaniappan, Srinivasan , Saravanan, Chandrasekaran and John, Amalraj(2005) 'Emulsion Polymerization Pathway for Preparation of Polyaniline-Sulfate Salt, using Non Ionic Surfactant', Journal of Macromolecular Science, Part A, 42: 7, 891 — 900

To link to this Article: DOI: 10.1081/MA-200063149

URL: http://dx.doi.org/10.1081/MA-200063149

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:891–900, 2005

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200063149

Emulsion Polymerization Pathway for Preparation of Polyaniline-Sulfate Salt, using Non Ionic Surfactant

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In this work, aniline was polymerized directly to the polyaniline-sulfate salt without using a protonic acid. The polyaniline-sulfate salt was prepared by emulsion polymerization, using a non ionic surfactant such as poly(ethylene glycol)–block poly(propylene glycol)-block poly(ethylene glycol). In the aniline oxidation process, to give the polyaniline salt by ammonium persulfate, the sulfate ion is generated from ammonium persulfate and doped on to the polyaniline. Ammonium persulfate acts both as an oxidizing agent, as well as the protonating agent in the aniline polymerization process, to give the polyaniline salt. This result indicates that the effect of sulfate ion, generated by ammonium persulfate during oxidation of aniline to the polyaniline salt, may be taken into consideration in the polymerization process of aniline.

Keywords polyaniline, non ionic surfactant, conductivity, FT-IR, thermogravimetric analysis

Introduction

Among the conducting polymers, polyanilines are particularly attractive based on their easy preparation, excellent electrical properties, presence of a number of intrinsic redox states, possible processability and stability. Aniline can be polymerized by chemical or electrochemical methods (1). In the chemical polymerization method, synthesis of polyaniline is commonly performed by the method of chemical oxidative polymerization of aniline using protonic acids such as hydrochloric (2), sulfuric acid (3), (inorganic acids), *p*-toluene sulfonic and 5-sulfosalicylic acid (4), (organic acids), dodecyl benzene sulfonic acid, camphor sulfonic acid (5) (functionalized protonic acid) and a polymeric acid (6), by an aqueous of emulsion polymerization technique.

In the aqueous polymerization process, aqueous protonic acid and an oxidant are generally combined with aqueous aniline. In this polymerization process, protonic acid acts as a dopant (7). In the emulsion polymerization process, a protonic acid and an oxidant are combined with a mixture of a polar liquid, typically water, and a non-polar

Received September 2004; Accepted December 2004.

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or weakly polar liquid, e.g. xylene, chloroform, toluene, decahydronaphthalene and 1,2,4-trichloro benzene, etc., along with a surfactant (8). In the emulsion polymerization process, surfactant acts as a dopant.

Smith et al. (9) reported on the polymerization of aniline in an emulsion of water and a non-polar or weakly polar organic solvent. This polymerization was carried out in the presence of a functionalized protonic acid, such as dodecylbenzenesulfonic acid, which simultaneously acted as a surfactant and protonating agent for the resulting polyaniline. Several workers (10–13) have used the emulsion polymerization pathway to improve the processability of polyaniline salts.

In this work, the polyaniline-sulfate salt was prepared using ammonium persulfate, without any protonic acid, by the emulsion and aqueous polymerization pathway. (i) The emulsion-polymerization process for the preparation of polyaniline salt was carried out using water, chloroform, non-ionic surfactant, aniline and ammonium persulfate. (ii) Aqueous polymerization was carried out using water, aniline and ammonium persulfate. Ammonium persulfate acts both as an oxidizing agent, as well as a protonating agent in the aniline polymerization process to produce the polyaniline salt.

Experimental

Materials

Aniline (reagent-grade), from E. Merck, was distilled prior to use. Reagent-grade poly(ethylene glycol)–block poly(propylene glycol)–block poly(ethylene glycol) copolymer (Fluka), ammonium persulfate, chloroform and sulfuric acid (BDH, India) were used as purchased.

Synthesis of Polyaniline-Sulfate Salt

Methods A

Emulsion Polymerization Pathway without using Acid. In the emulsion polymerization pathway, 2.3 ml of aniline was dissolved in 60 ml chloroform. Then a 40 ml aqueous solution containing 0.5 g of poly(ethylene glycol)–block poly(propylene glycol)–block poly(ethylene glycol) copolymer (amount of copolymer was varied, i.e., 0.5, 1.0, 2.0, and 3.0 g.) was added slowly while stirring, providing an emulsion. To this emulsion, 100 ml aqueous solution containing 5.71 g of ammonium persulfate was added dropwise (15–20 min. interval). The reaction mixture was kept for 4 h at ambient temperature. The reaction mixture was filtered, washed with water, and finally with acetone. The sample was dried at 100°C until constant weight was reached.

Method B

Aqueous Polymerization Pathway without using Acid. In the aqueous polymerization pathway, 2.3 ml of aniline was dissolved in 100 ml of water. To this solution, 100 ml aqueous solution containing 5.71 g of ammonium persulfate was added drop wise (15–20 min. interval). The reaction mixture was kept for 4 hrs at ambient temperature. The isolation of polyaniline powder was carried out as in method A.

Method C

Aqueous Polymerization Pathway with Sulfuric Acid. In the aqueous polymerization pathway, 5.6 ml of sulfuric acid and 2.3 ml of aniline was dissolved in 100 ml of water.

To this solution, a 100 ml aqueous solution containing 5.71 g of ammonium persulfate was added dropwise (15–20 min. interval). The reaction mixture was kept for 4 h at ambient temperature. The isolation of polyaniline powder was carried out as in Method A.

The polyaniline-sulfate samples were dedoped using 1.0 M aqueous sodium hydroxide (NaOH) solution. A known quantity of the polymer salt was treated in 1.0 M aqueous NaOH solution, stirred overnight. The product was filtered, and aqueous saturated barium chloride was added to the filtrate, followed by concentrated hydrochloric acid. A white precipitate was obtained, confirming the presence of sulfate anion. This result indicates that the polyaniline salt contains the sulfate group as a dopant ion and that this sulfate ion was generated from ammonium persulfate, which was used for oxidizing aniline to the polyaniline salt.

Characterization Techniques

Infrared Spectroscopy

Infrared spectra of the samples were recorded on a Perkin-Elmer Lamda 2 Spectrometer. The spectra of the (polyaniline-sulfate) solid samples were recorded at ambient temperature, using a KBr pellet technique.

X-ray Diffraction Spectra

Wide angle X-ray diffraction spectra for the polyaniline powder samples were obtained using a Siemens/D-5000 X-ray diffractometer, by using Cu, Kα radiation of wave length 1.54 and continuous scan speed of 0.045°/min.

Elemental Analysis

The percentage of carbon, hydrogen, nitrogen, and sulfur of the polyaniline sample were estimated using a Elementar Vario EL analyzer.

Resistance Measurement

The pellets were obtained by subjecting the polymer samples to a pressure of 950 $\mathrm{Kg/cm^2}$. Resistance measurement of the samples, in the form of compacted disk pellets, was carried out on a two probe connected to a Keithley digital multimeter (Model 2010). Conductivities were calculated based on the average of at least five pairs of consistent readings were taken at different points on the pressed pellet.

Thermal Analysis

Thermal analysis of the polymer samples was carried out using Mettler Toledo Star system in the presence of air atmosphere up to 800°C and at a heating rate of 10°C/min.

Results and Discussion

Infrared Spectra

The infrared spectrum of the polyaniline-sulfate salt, prepared by the emulsion polymerization process (Method A), is shown in Figure 1. The vibrational bands observed for the polyaniline salt are reasonably explained on the basis of the normal modes of aniline

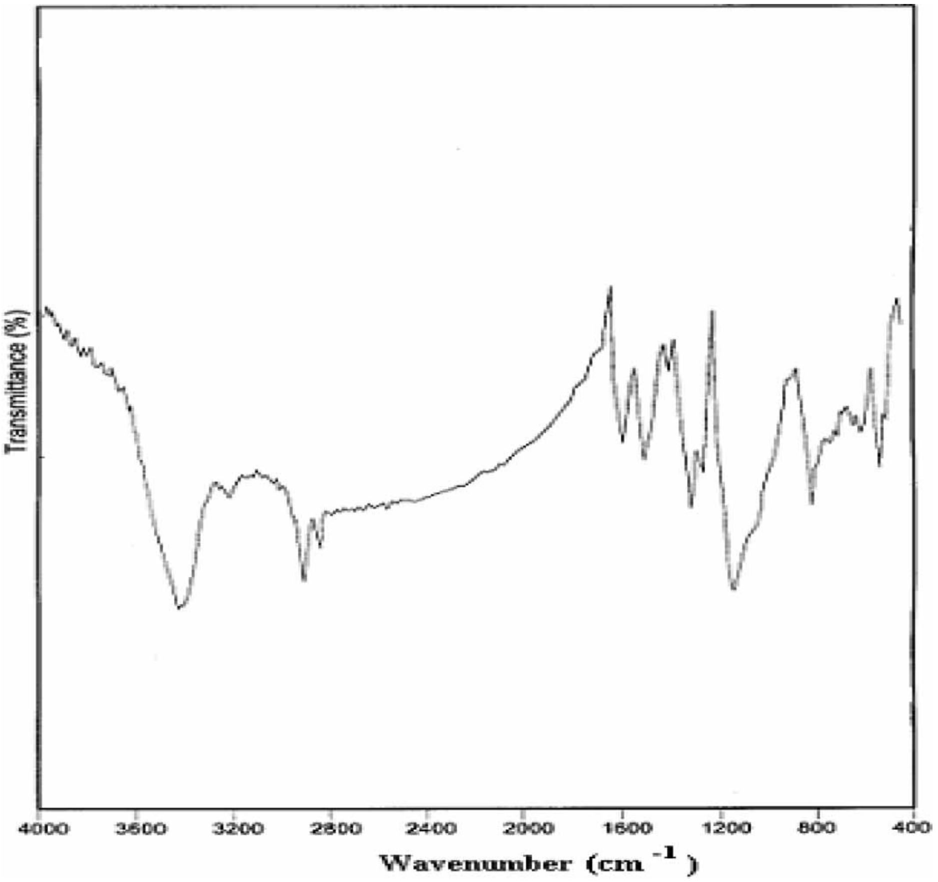


Figure 1. Infrared spectra of polyaniline–sulfate salt prepared by the emulsion polymerization pathway (Method A).

and benzene; a broad band at 3415–3460 cm^{-1} assigned to the N–H stretching vibration. The bands at 2920 and 2850 cm^{-1} are assigned to vibrations associated with the N–H part in the $C_6H_4NH_2C_6H_4$ group or sum frequency. The 1565 and 1490 cm^{-1} bands are due to the quinonoid ring (Q) and/or benzenoid ring (B). The bands at 1370 and 1300 cm^{-1} are assigned to the C–N stretching vibration in QBB, QBQ, and BBQ, along with a 1240 cm^{-1} band assigned to the C–N stretching vibration of aromatic amine. In the region of 1020–1170 cm^{-1}, the aromatic C–H in-plane-bending modes are observed. For polyaniline, a strong band characteristically appears at 1140 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm^{-1} is assigned to ring C...C bending vibration and the band at 580 cm^{-1} due to ring in plane deformation. The C–H out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. For the polyaniline salt, this mode was observed as a single band at 825 cm^{-1}, which fell in the range 800–860 cm^{-1} reported for 1,4-disubstituted benzene (14). The infrared spectrum of the polyaniline salt prepared is very close to the infrared spectrum of the polyaniline salt system reported in the literature (14, 15).

A similar infrared spectrum was observed for polyaniline-sulfate salt prepared by aqueous polymerization pathway without using acid (Method B) as well as with the use of sulfuric acid (Method C).

Thermal Analysis

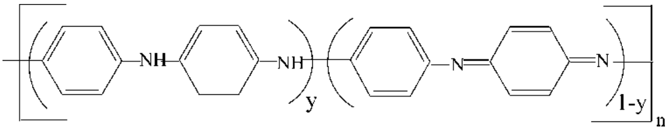
The TGA and DTA thermogram of the polyaniline-sulfate salt, prepared by the emulsion polymerization pathway (Method A), are shown in Figure 2. The DTA thermogram of polyaniline salt shows one endotherm (peak maximum at 70°C, complete at 105°C), one exotherm hump around 210°C, and another broad exotherm around 475°C. The TGA thermogram of polyaniline salt shows a typical three-step weight loss behavior. In a representative thermogram of polyaniline salt sample, the first step indicates a 5–6% weight loss at temperature up to 105°C (the DTA curve shows an endotherm at 70°C, complete at 105°C). This step can be attributed to loss of water molecule from the polymer matrix. In the second step, there is a small weight loss (3–4%), which takes place continuously from 110–250°C (the DTA curve shows a hump-shaped exotherm at 210°C). This may possibly be due to the coevolution of water and evolution of a small amount of acid present in the polymer sample. The third step starts around 250°C, resulting in total weight loss (the DTA curve shows a broad exotherm around 475°C) indicating thermal degradation of the polyaniline polymer.

X-ray Diffraction Spectra

The X-ray diffraction pattern of the polyaniline salt prepared by the emulsion polymerization pathway (Method A), is shown in Figure 3. X-ray diffraction studies revealed the polyaniline salts was partially crystalline with peaks at $2\theta = 14.5$, 20.7, 25.0 and 27.0, corresponding to the interface distances d 6.093, 4.290, 3.549 and 3.284 A, respectively. These positions are in accordance with the earlier report for polyaniline salt (16).

Conductivity and Composition

The base form of polyaniline, in principle, can be described by the following general formula:



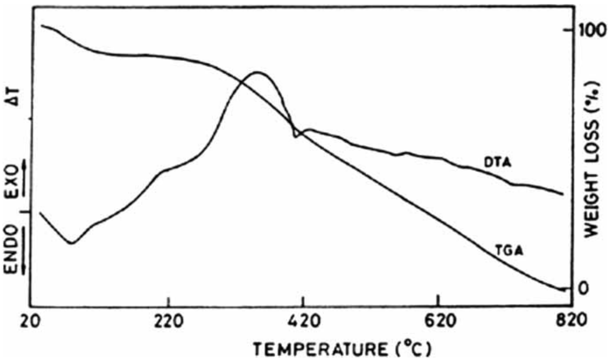


Figure 2. TGA and DTA thermograms of polyaniline-sulfate salt prepared by the emulsion polymerization pathway (Method A).

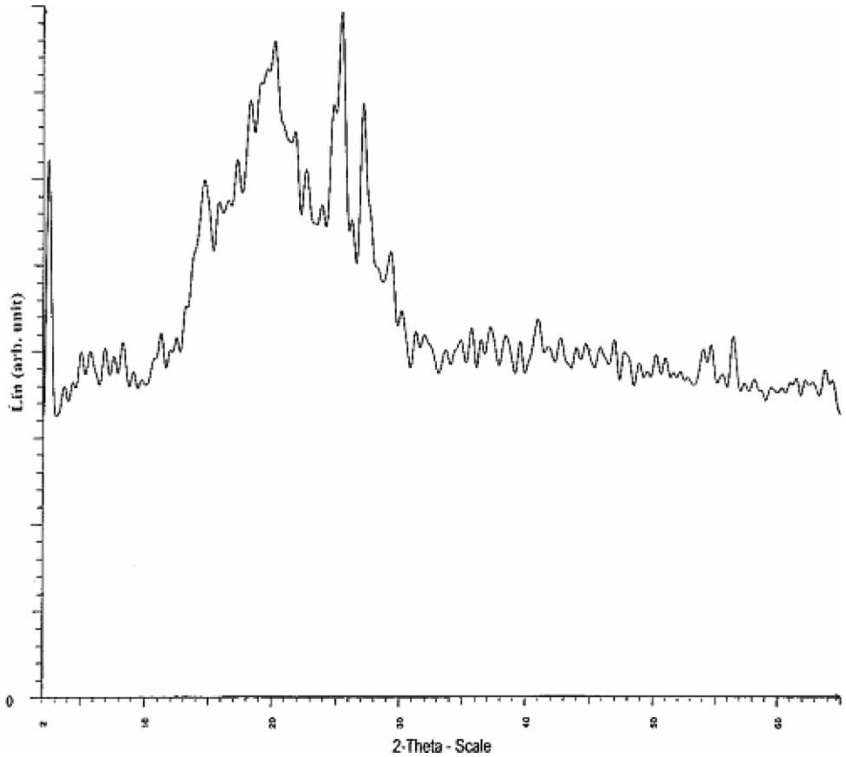
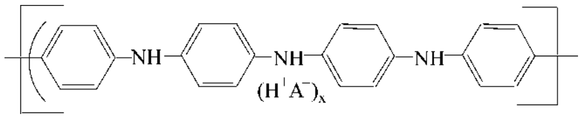
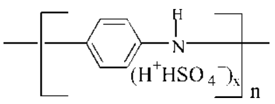


Figure 3. X-ray diffraction pattern of polyaniline-sulfate salt prepared by the emulsion polymerization pathway (Method A).

In the generalized base form, (1 − y) measures the function of oxidized units. When (1 − y) = 0, the polymer has no such oxidized groups and is commonly known as a leucoemeraldine base. The fully oxidized form, (1 − y) = 1 is referred to as a pernigraniline base. The half oxidized polymer, where the number of reduced units and oxidized units is equal, i.e., (1 − y) = 0.5, is of special importance and is termed the emeraldine oxidation state or the emeraldine base. The corresponding emeraldine salt can be represented by the following formula:



For simplicity, the following formula for polyaniline sulfate salt is taken to calculate the sulfate group (H_2SO_4) per aniline unit present in the polymer chain:



Adjusting two independent variables, namely the degree of oxidation and the degree of protonation, can control conductivity of the polyaniline salt. The degree of protonation of the polyaniline-sulfate salt was found out from elemental analysis. The percentage of carbon, hydrogen, nitrogen and sulfur of the polyaniline sample were estimated using the Elementar Vario EL analyzer with the results reported in Table 1. The percentage of carbon, hydrogen, nitrogen and sulfur were calculated theoretically by varying the sulfate group from $x = 0.01$ to 0.5 in steps of 0.01. The sulfate group per aniline unit was determined by comparing the experimental and theoretical values.

It was found that the sulfate group per unit of aniline in the polyaniline salt is 0.11 and 0.13–0.14, prepared by the aqueous polymerization and emulsion polymerization pathway (without using acid), respectively. Correspondingly, the amount of dopant (H_2SO_4) present in the polyaniline-salt is around 11% and 12.5–13.0%. However, with the use of sulfuric acid, the sulfate group per aniline unit in polyaniline salt is greater (0.30) and the amount of dopant present in the polyaniline salt is around 24.6%.

The value of conductivity, yield and density of the polyaniline-sulfate samples are reported in Table 2. The conductivity of the polyaniline-sulfate salt prepared by aqueous polymerization, without protonic acid, was found to be 4.9×10^{-5} S/cm. The conductivity of the polyaniline-sulfate salt prepared by the emulsion polymerization pathway, using non-ionic surfactant, was found to be 1.0×10^{-2} S/cm, three orders of magnitude higher than that of the salt prepared using the aqueous polymerization pathway. This can be attributed to the polymerization occurring at the interface of the water/chloroform layer and the polymer formation occurring in the chloroform solvent, followed by the polyaniline salt precipitating from the reaction mixture. This result indicates that the surfactant increases the efficiency of ammonium persulfate in oxidizing aniline to polyaniline salt. The conductivity of the polyaniline-sulfate salt prepared using sulfuric acid as the protonic acid and the aqueous polymerization technique, was found to be 4.0 S/cm, which are six orders of magnitude higher than that of the salt prepared without using sulfuric acid as the protonic acid. This result indicates that sulfuric acid greatly increased the efficiency of ammonium persulfate in oxidizing aniline to polyaniline salt.

Conductivity of the polyaniline-sulfate salts are found to be decreased as 1.0×10^{-2}, 9.2×10^{-3}, 5.2×10^{-3} and 1.1×10^{-3} S/cm with different amounts of copolymer surfactant, i.e., 0.5, 1.0, 2.0, and 3.0 g, respectively. The decrease in conductivity with surfactant may be attributed to reduced stability of the emulsion with an increase in the amount of surfactant.

The yield of polyaniline-sulfate was calculated using the polyaniline-sulfate salt formula and the result are shown in Table 2. The yield of the polyaniline-sulfate salt, prepared by the aqueous polymerization pathway without acid is 79%, and the yield prepared by the emulsion polymerization pathway, using different amounts of surfactant, were found to be very nearly the same that is 73 to 75%.

Density

Pellet density was measured from mass per unit volume of the pressed pellets. Density of the polyaniline-sulfate salts was found to be very nearly the same and it varies from 1.25 to 1.35 g/cm^3.

Conclusion

The results in this work show that it is possible to prepare polyaniline-sulfate salt by emulsion and aqueous polymerization pathways without using any protonic acids. Only

Table 1

Theoretical and experimental values of the percentage of carbon, hydrogen, nitrogen and sulfur of polyaniline-sulfate salt

	Theoretical value (%)				Experimental value (%)					
Sample	C	H	N	S	C	H	N	S	Sulfate per aniline unit	Dopant (%)
Aqueous polymerization without acid	70.7	5.1	13.7	3.5	69.1	5.5	13.8	3.4	0.11	10.6
Emulsion polymerization copolymer										
0.5 g	68.7	5.0	13.4	4.3	68.4	5.6	12.3	4.0	0.14	13.1
1.0 g	69.4	5.0	13.5	4.0	68.2	5.2	12.6	3.9	0.13	12.3
2.0 g	69.4	5.0	13.5	4.0	68.1	5.4	13.0	3.9	0.13	12.3
3.0 g	68.7	5.0	13.4	4.3	67.9	5.9	12.8	4.0	0.14	13.1
Aqueous polymerization with sulfuric acid	60.3	4.6	11.6	8.0	67.9	5.1	11.1	7.8	0.30	24.6

Table 2
Yield, conductivity, sulfate group per aniline unit and density of the polyaniline-sulfate salt

Sample	Yield (%)	Conductivity (S/cm)	Density (g/cm^3)
Aqueous polymerization	79.0	4.9×10^{-5}	1.25
Emulsion polymerization copolymer			
0.5 g	73.0	1.0×10^{-2}	1.29
1.0 g	73.0	9.2×10^{-3}	1.31
2.0 g	75.0	5.2×10^{-3}	1.34
3.0 g	75.0	1.1×10^{-3}	1.32
Aqueous polymerization with sulfuric acid	90.0	4.0	1.29

the sulfate salt of polyaniline can be prepared using the present method. Ammonium persulfate simultaneously acts as oxidizing agent as well as protonating agent in the polymerization process of aniline to polyaniline salt. The dopant i.e., sulfate group in polyaniline-sulfate salt was generated from ammonium persulfate which was used for oxidizing aniline. The surfactant increases the efficiency of oxidation of aniline and doping effect of ammonium persulfate and the efficiency is more with the use of sulfuric acid as protonic acid in the reaction.

Acknowledgment

Support of this research by the Department of Science and Technology, India (through Grant No.SR/FTP/CS-21/2001) under SERC fast track scheme and CSIR task force project (CMM-0011) is gratefully acknowledged.

References

1. Genies, E.M., Boyle, A., Lapkowski, M., and Tsintavis, C. (1990) Polyaniline: a historical survey. *Synth. Met.*, 36: 139.
2. Wang, Y. and Rubner, M.F. (1992) An investigation of the conductivity stability of acid doped polyanilines. *Synth. Met.*, 47: 255.
3. Zhang, A.Q., Cui, C.Q., and Lee, J.Y. (1995) Electrochemical degradation of polyaniline in $HClO_4$ and H_2SO_4. *Synth. Met.*, 72: 217.
4. Neoh, K.G., Pun, M.Y., Kang, E.T., and Tan, K.L. (1995) Polyaniline treated with organic acids: doping characteristics stability. *Synth. Met.*, 73: 209.
5. Long, Y., Chen, Z., Wang, N., Zhang, Z., and Wan, M. (2003) Resistivity study of polyaniline doped with protonic acid. *Physica.*, B325: 208.
6. Tsutsumi, H., Fukuzawa, S., Ishikawa, M., Morita, M., and Matsuda, Y. (1995) Preparation of polyaniline-poly(*p*-styrenesulfonic acid) composite by the post-polymerization. *Method. Synth. Met.*, 72: 231.
7. Palaniappan, S. and Narayana, B.H. (1994) Composition and spectral studies of polyaniline salts. *Polym. Adv. Tech.*, 5: 225.

8. (a) Cao, Y.; Smith, P.; Heeger, A.J. (1993) Processible forms of Electrically Conductive Polyaniline. U.S. Pat. No. 5,232,631; (b) Cao, Y.; Osterholm, J-E. (1994) Electrically conducting polyaniline: method for emulsion polymerization. U.S. Pat. No. 5,324,453.
9. Osterholm, J-E., Cao, Y., Klavetter, F., and Smith, P. (1994) Emulsion polymerization of aniline. *Polymer*, 35: 2902.
10. Li, J., Fang, K., Qiu, H., Li, S., and Mao, W. (2004) Micromorphology and electrical property of the HCl-doped and DBSA-doped polyanilines. *Synth. Met.*, 142: 107.
11. Barra, G.M.O., Leyva, M.E., Soares, B.G., and Sens, M. (2002) Solution-cast blends of polyaniline–DBSA with EVA copolymers. *Synth. Met.*, 130: 239.
12. Su, M-C. and Hong, J-L. (2001) emulsion polymerization of aniline with ionic dispersants containing ionic poly(vinylpyridinium methanesulfonate) segments. *Synth. Met.*, 123: 497.
13. Kinlen, P.J., Frushour, B.G., Ding, Y., and Menon, V. (1999) Synthesis and characterization of organically soluble polyaniline and polyaniline block copolymers. *Synth. Met.*, 101: 758.
14. Furukawa, Y., Ueda, F., Hyodo, Y., Harada, I., Nakajima, T., and Kawagoe, T. (1988) Vibrational spectra and structure of polyaniline. *Macromolecules*, 21: 1297.
15. Zeng, X.R. and Ko, T.M. (1998) Structures and properties of chemically reduced polyanilines. *Polymer*, 39: 1187.
16. Pouget, J.P., Jozefowicz, M.E., Epstein, A.J., Tang, X., and MacDiarmid, A.G. (1991) X-ray structure of polyaniline. *Macromolecules*, 24: 779.