JOURNAL OF Materials CHEMISTRY

Synthesis and characterization of electrically conducting polyaniline in water–oil microemulsion

Feng Yan and Gi Xue*

Department of Polymer Science, The Institute of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: xuegi@nju.edu.cn

Received 28th June 1999, Accepted 9th September 1999

Nanoscopic polyaniline particles were successfully synthesized in a stable water–oil microemulsion. FT-IR spectra showed that sodium dodecylbenzenesulfonate (SDBA) acted both as surfactant and dopant in the acidic reaction media. Wide-angle X-ray diffraction, UV–visible spectra and thermal analysis suggested that the crystallinity of PANI synthesized in the microemulsion system was increased dramatically while the chain-transfer reactions of co-surfactants decreased the π-conjugation length along the polymer chain.

Introduction

During the past two decades, a wide variety of electrically conducting polymers have been extensively studied due to their exclusive physical properties. Of all these polymers, polyanilines are unique because of their good environmental stability and controllable electrical and optical properties. Usually, conducting polyaniline (PANI) can be easily synthesized from monomeric aniline by either chemical oxidative polymerization or electropolymerization.[1–3] Considerable interest has been focused on the chemical oxidative polymerization of aniline and other polymeric heterocyclic compounds.[4–9] The chemical polymerization of aniline is very important since it is the more feasible route for the production of polymers on a large scale. As a starting material for PANI, monomeric aniline is often dissolved in acidic aqueous media to which an oxidative agent such as ammonium persulfate is added, and then the green-black polyaniline salt is obtained.

Recently, the preparation of nanostructured conducting materials has become an important branch of materials research. These materials are expected to exhibit unusual chemical and physical properties and to have applications in the biomedical field, microelectronics and information industry areas.[10,11] Several research groups[12–14] have reported the synthesis of nanoscopic conducting polymer colloids in the presence of a soluble polymeric 'steric stabiliser' such as poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) which adsorbs or even grafts to the polymer latex particles. Namely, in the polymerization system the polymeric surfactant acted not only as steric stabilizer but also as a co-monomer. However, sometimes the polymerization still resulted in macroscopic precipitation and, in certain cases, in a low yield of colloidal particles. Thus, it is not easy to get the pure polymers with these methods and the nanoscopic microspheres obtained are often copolymers or composites.

It has been well known that microemulsion polymerization is effective in producing polymer particles in the size range of 5–100 nm and much interest has been attracted during the past two decades.[15–17] A microemulsion is an organized micro-heterogeneous system which provides a large interfacial area and is generally less viscous. Usually, a typical microemulsion system contains water, oil and surfactant, and often with a co-surfactant to stabilize the system. According to the previous works it has been widely accepted that a microemulsion is a molecularly ordered system, and in this system the orientation behavior of the surfactants can be detected.[18,19] During the past two decades, many studies have been done on non-conducting polymers in the microemulsion system; however, relatively little work has been done on conducting polymers.[20,21]

In accord with the early work, we report here a method of preparation of PANI in a microemulsion system, in which the polymerization of aniline proceeds in a molecularly ordered system and pure nanoscopic conducting polymer is expected to be prepared. Usually, polyaniline can be synthesized in various concentrations of HCl solutions.[6,22,23] Since a high concentration of acid has a detrimental effect on the microemulsion and often causes a macroscopic precipitation of the system, here we synthesized the polyaniline in a 0.1 M HCl–oil microemulsion system. In this system, ammonium persulfate was used as an oxidizing agent, and sodium dodecylbenzenesulfonate (SDBA) and butanol were used as the surfactant and the co-surfactant respectively. For comparison, conventional emulsion and homogeneous solution polymerizations were also carried out.

Experimental

Synthesis of polyaniline

A typical microemulsion system was prepared as follows. As an oxidant, 1.2 g (0.0053 mol) ammonium persulfate was dissolved in 20 ml 0.1 M HCl solution, then 12 g SDBA, 3 ml butanol and 40 ml hexane were introduced into the prepared solution. The mixture was stirred with a magnetic stirrer and the system became transparent suddenly, thus, a clear and transparent microemulsion system was obtained. On stirring, 0.33 ml (0.0035 mol) aniline monomer was added into the microemulsion system, and the molar ratio of oxidant to aniline monomer was kept at 1.5 in the polymerization system. Without any more stirring the polymerization was carried out for 24 h at room temperature. During the polymerization no evident precipitation was observed and the polymerization system changed from colorless to brown–yellow and then to green–black very slowly. The viscosity of the system was found to be higher with increasing polymerization time. The polymerization was terminated by pouring the mixture into a great deal of acetone whereupon the polyaniline precipitated. The green-black PANI powder was filtered and washed with 0.1 M HCl and acetone until the washing solution became clear and SDBA was removed thoroughly. Then the powder was dried in dynamic vacuum for 48 h at room temperature before characterization.

In a similar manner, a conventional emulsion system polymerization was taken on with 10 wt% SDBA in a 0.1 M

This Journal is © The Royal Society of Chemistry 1999

HCl–oil system with the same ratio of oxidant to monomer. The polymerization was kept for 24 h at room temperature with vigorous stirring. The precipitated polymer was rinsed with 0.1 M HCl and acetone thoroughly and dried in dynamic vacuum for 48 h at room temperature.

For comparison, homogeneous solution polymerizations of aniline with the same molar ratio of oxidant to monomer were also carried out in 0.1 M and 1 M HCl. The polymerization mixtures were stirred for 24 h at room temperature. The polymer powder was also filtered and rinsed with the corresponding HCl solution respectively, and the PANI powder was dried in dynamic vacuum for 48 h at room temperature.

The obtained PANI emeraldine salt was converted to the base form by treatment with 1 M aqueous NH_4OH, and then washing with distilled water and acetone and drying in dynamic vacuum for 48 h at room temperature.

Characterization

Electrical conductivities of PANIs were measured by a conventional four-probe method under laboratory conditions. The polymer powder was compacted into a disk pellet 12.7 mm in diameter under a pressure of 4700 kg cm^{-2}. All the pellets were about 0.3 mm in thickness and with almost the same density of 0.48 g cm^{-3} .

Wide-angle X-ray diffractograms were run on a Rigaku D/MAX-RC 12 kW X-ray diffractometer using Ni-filtered Cu Kα radiation at a scan speed of 4° min^{-1}.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS66V spectrometer under vacuum. The spectra were collected from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution over 100 scans.

UV–visible spectra of dilute solutions of PANI in 1-methyl-2-pyrrolidone (NMP) were recorded on a UV-3100 PC Shimadzu spectrophotometer in the wavelength 300–800 nm under the control of a computer.

TGA–DTA analysis of the polymers was carried out on a TA Instruments 2100 Thermal Analyzer with a heat rate of 20 °C min^{-1} and a dynamic dry air flow of 100 cm^3 min^{-1}.

The particle sizes of the polymer latexes were determined by transmission electron microscopy (TEM). The samples were prepared by placing a drop of diluted latex on a carbon coated copper grid and placing in the cold stage of a Phillips 300 Transmission Electron Microscope.

Results and discussion

The elemental compositions of the chemically prepared polymers are shown in Table 1. It can be seen that the chlorine content of PANI which was prepared in 1.0 M HCl is slightly higher than that in 0.1 M HCl aqueous media indicating a relatively higher protonated state. This higher doping level may be due to the relatively high concentration of acid media used in the reaction systems. It also can be found that the doping levels were almost the same among three PANIs prepared in 0.1 M HCl acidic media.

The structures of polyanilines prepared in microemulsion and solution were studied by FT-IR spectroscopy. The resulting spectra have been plotted in transmittance mode as shown in Fig. 1 and Fig. 2. It can be seen that characteristic peaks of PANIs are observed from 1800 cm^{-1} to 500 cm^{-1}. Between the spectra of polymers obtained from different reaction systems, no pronounced differences are observed indicating that the main components of each specimen have the

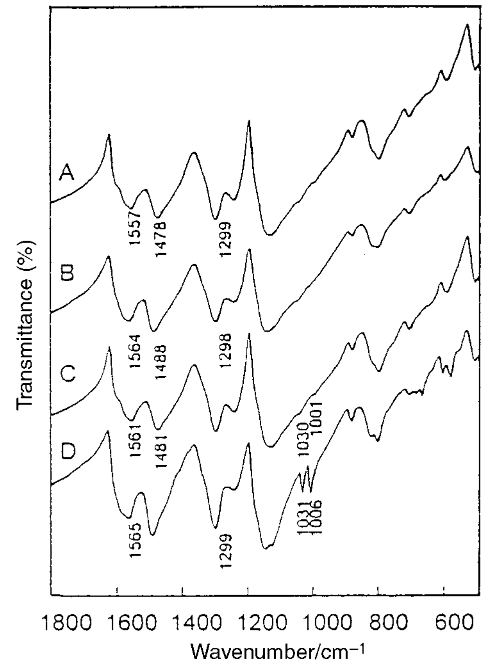

Fig. 1 FT-IR spectra of polyanilines obtained from (A) 1 M HCl solution; (B) 0.1 M HCl solution; (C) conventional emulsion system; (D) microemulsion system.

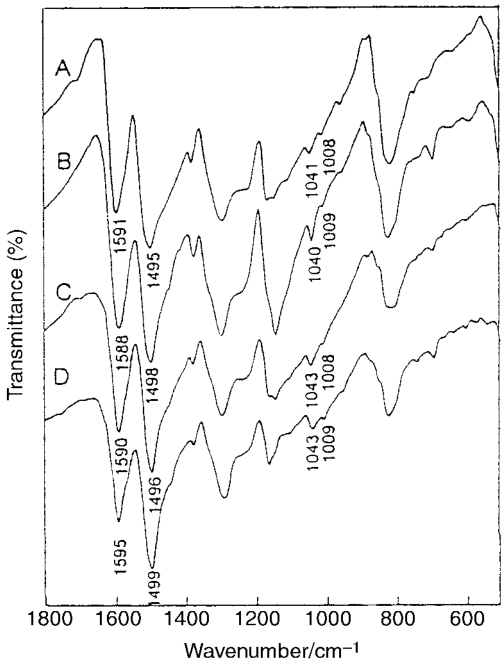

Fig. 2 FT-IR spectra of polyaniline-bases obtained from (A) 1 M HCl solution; (B) 0.1 M HCl solution; (C) conventional emulsion system; (D) microemulsion system.

Table 1 Elemental compositions and conductivity of polyanilines obtained from different polymerization systems

Polymerization system	Concentration of HCl/M	Elemental compositions (atomic ratios)	Conductivity/S cm^{-1}
Solution	1.0	$C_{6.12}H_{8.04}N_1Cl_{0.36}O_{0.83}S_{0.01}$	6.72
	0.1	$C_{5.97}H_{7.92}N_1Cl_{0.23}O_{0.72}S_{0.00}$	1.46
Emulsion	0.1	$C_{6.03}H_{8.11}N_1Cl_{0.23}O_{0.93}S_{0.04}$	2.08
Microemulsion	0.1	$C_{6.28}H_{8.03}N_1Cl_{0.22}O_{1.28}S_{0.07}$	1.50

same chemical structures. The spectra of both PANI-salts and PANI-bases are all in good agreement with the previously reported results.[4,6,24] In Fig. 1A the quinoid (N=Q=N) and benzenoid (N–B–N) stretching vibration modes occurred at about 1557 and 1476 cm^{-1} respectively. However, in spectra 1B,1C and 1D (PANIs synthesized in 0.1 M HCl media), two stretching bands shifted to higher frequencies. The band shifts may be due to the relatively lower protonated state, and the extent of shift depends on the concentration of dopant in the polymer and increases with a reduction in the level of protonation.[25] Moreover, for spectra 1B, 1C and 1D no obvious differences between them can be observed due to the same doping levels in the three samples. On closer inspection of the spectra of the PANI powders obtained from the emulsion and microemulsion systems, one can find that two new absorption peaks near 1031 cm^{-1} and 1006 cm^{-1}, assigned to the stretching vibration of SO_3, appeared in spectra 1C and 1D. However, once the polymers are de-doped with NH_4OH, the stretching bands at 1031 cm^{-1} and 1006 cm^{-1} disappear as shown in Fig. 2, indicating that PANIs synthesized in emulsion and microemulsion systems are also partially protonated with ionic dodecylbenzenesulfonate. Namely, SDBA may also act as a secondary dopant in acidic aqueous media. This result agrees well with the elemental compositions of PANIs shown in Table 1, and in Table 1 it can be seen that only trace amounts of the secondary dopant counter-ion are found in the PANIs.

Wide-angle X-ray diffraction analysis of PANI synthesized in the three reaction systems are presented in Fig. 3, and the XRD pattern of SDBA is also shown for comparison. It can be seen that the PANI prepared in 0.1 M HCl solution exhibits two broad bands at 19° and 26° indicating a low level of crystalline phase in the polymer (Fig. 3C). However, in Fig. 3B the peak at 26° becomes sharper and stronger. It has been demonstrated that the ratio of half-width to height (HW/H) of X-ray diffraction peak reflects the order of the polymer backbone (the smaller the value of HW/H the higher the order),[26,27] indicating that PANI which was prepared in an emulsion is in a higher crystalline state. It is worth noting that in Fig. 3A, not only the peak at 26° but also the peak at 19° became sharper and stronger, and a new shoulder peak at about 28° also developed, implying that the molecular chains of polyaniline prepared in the microemulsion are in a much more ordered state, and the crystallinity of the polymer is increased significantly.

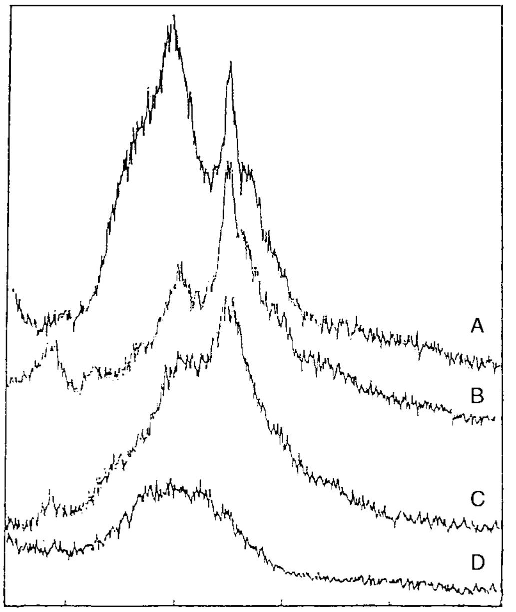

Fig. 3 X-Ray scattering patterns of polyanilines particles prepared from (A) microemulsion system; (B) conventional emulsion system; (C) 0.1 M HCl solution; (D) pure surfactant SDBA.

Both the dopant and orientation behavior are major factors which affect the morphology of conducting polymers. In the doped polymer, the dopant species can act as a 'plasticizer' which promotes the movement of polymer chains and often increases the crystallinity of polymers.[28a] In this work, PANIs prepared in emulsion and microemulsion systems show higher crystallinity. According to the published literature,[29,30] the secondary dopant counter-ion dodecylbenzenesulfonate could not increase the crystallinity of PANIs, and here the influences of secondary dopant on the morphology of PANIs can be excluded. Based on the reported works,[18,19] it can be assumed here that the highest crystallinity of PANI obtained by microemulsion polymerization may be due to the orientation behavior of the surfactants in the polymerization system. In the microemulsion system, the aniline monomer is present in microdroplets and the molecular chains of monomer and oligomer are molecularly oriented by the surfactants in the interface layer of the oil and water phases. Following this alignment, the radicals of PANI oligomers couple to form a conducting polymer which results in PANI with an ordered arrangement of macromolecule chains.[18,19] Since the concentration of surfactants in a conventional emulsion is relatively low in comparison to that in a microemulsion system, the orienting effect of the surfactant in emulsion polymerization is not as significant as in the former system. In the homogeneous solution system, molecular chains of aniline monomer are randomly aligned which results in an amorphous polymer.

The conductivities of PANIs are shown in Table 1. It can be clearly seen that the PANI prepared in 1 M HCl has the highest conductivity value due to its heavy doping level. PANI synthesized in 0.1 M HCl emulsion has a relatively higher conductivity than that obtained from 0.1 M HCl solution. It has been reported that the macroscopic conductivity of the polymer depends on both charge transport along the polymer chain (intrachain transport) and charge hopping from polymer chain to polymer chain (interchain transport), so the ordered arrangement of the polymer chains favors higher conductivity.[31–33] According to MacDiarmid's previous works, the higher crystallinity of PANI is often accompanied by a higher conductivity.[33–35] Since the doping levels were almost the same among three samples prepared in 0.1 M HCl, the relatively higher conductivity of PANI synthesized in emulsion system comes from the better ordered chain conformation in polymer. However, it is noteworthy that polyaniline which was synthesized in a microemulsion system has the highest crystallinity but does not show the highest conductivity, and according to the discussions above, it seems that maybe the charge transport along the polymer chains has been retarded, which decreases the conductive ability of the polymer.

Fig. 4 shows the UV–visible spectra of very dilute PANI-bases in NMP. It can be clearly seen that all spectra show two major absorption peaks at about 328 nm and 634 nm. As reported earlier, the former peak could be assigned to the π–π^* transition of the benzenoid rings which relates to the extent of conjugation between adjacent phenyl rings in the polymer chain, while the latter peak at 634 nm was assigned to the exciton absorption of the quinoid rings which is attributed to the intrachain or interchain charge transport.[36] As we can see here, the UV–visible spectra of PANI-bases prepared in emulsion and solution systems are nearly the same. The locations of π–π^* transition and exciton absorption are almost unchanged. However, hyposochromic shifts of the two absorption peaks are exhibited in curve D, implying a decrease in the extent of π-conjugation and an increase in the bandgap in the polymer chain. UV–visible spectra confirmed that the charge transport along the polymer chain has been retarded. Based on the reported works,[37] the reason for this result can be explained as follows. In the microemulsion system, as a co-

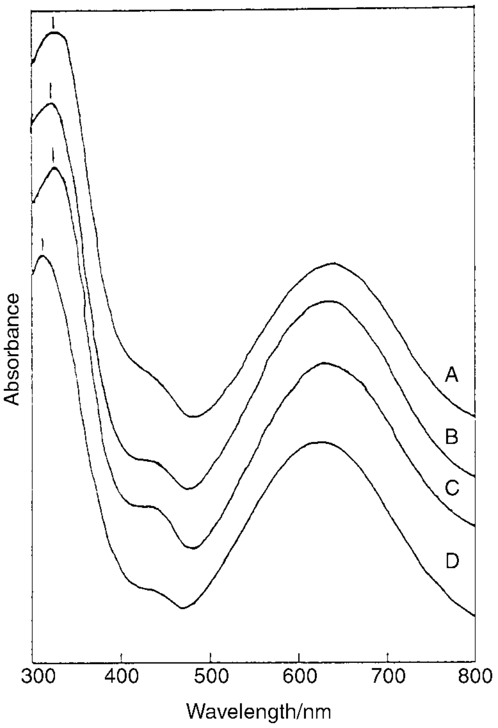

Fig. 4 UV–Visible absorption spectra of polyaniline-bases prepared from (A) 1 M HCl solution; (B) 0.1 M HCl solution; (C) conventional emulsion system; (D) microemulsion system.

surfactant butanol mainly acts as a destabilizer for the latex by desorbing the surfactant from the surface of polymer monomer particles, but it may also act as a potential chain-transfer agent. Here, it is the chain-transfer reactions of co-surfactants that retard the growth of the polymer chain and decrease the extent of conjugation length along the polymer backbone. Thus, although polymer chains are much more ordered in microemulsion polymerization systems, the conductivity of PANI is still not increased.

Some more supporting evidence on the structure of PANIs is obtained by thermal analysis (TGA–DTA). The TGA–DTA patterns of PANIs in air are shown in Fig. 5. The thermal stability of the PANI prepared from 0.1 M HCl solution is shown in Fig. 5C. It can be seen that the first small fractions of weight loss from room temperature to *ca.* 120 °C are mainly attributed to the expulsion of absorbed water and the free acid trapped in the polymer matrix (since it is difficult to remove the moisture in the samples completely by drying). The second step for weight loss from 120 °C to 320 °C is due to the loss of acid dopant. Then a very significant weight loss begins to occur at about 353 °C due to thermal oxidative decomposition of polymer chains.[38] A larger mass loss of PANI synthesized in emulsion begins at about 356 °C (Fig. 5B), and the higher decomposition temperature indicates a better thermal stability. Fig. 5A shows the thermogram of PANI synthesized in a microemulsion. It can be clearly seen that a very significant thermal degradation begins to occur at about 351 °C, and this lower decomposition temperature may again be due to shorter conjugation chain segments in PANI polymer units.[39] The sharp exothermic peak in Fig. 5A may be due to some morphological change, possibly crystallization of the polymer which also implies a much more ordered arrangement of the polymer chains of PANI synthesized by microemulsion polymerization.[39,40]

Synthesis of polyaniline in water–oil microemulsion results in the formation of very fine PANI particles. Normally, it is difficult to control the shape of chemically polymerized PANI particles, and the particle is most often 'rice-grain' fibrillar or 'needle-shaped' rather than globular.[13,28b] It has been reported

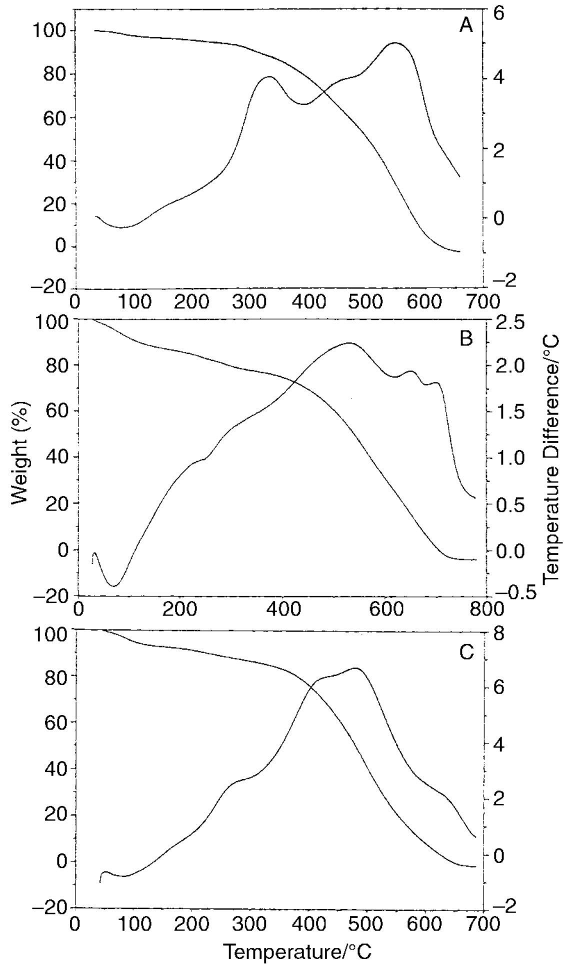

Fig. 5 TGA–DTA thermograms of polyanilines synthesized from (A) microemulsion; (B) conventional emulsion system; (C) 0.1 M HCl solution.

that the key to producing individual spherical particles must be very efficient steric stabilization during the early stages of polymerization process.[13] In this work, the obtained microemulsion polymerization system is quite stable and without any evident precipitation can even be kept for several months. As seen from the TEM micrographs (Fig. 6) the size of spherical PANI particles is in the range about 30–60 nm.

Conclusion

In summary, pure nanoscopic conducting polyanilines were successfully synthesized in the water–oil microemulsion. During the polymerization, the reaction system was quite

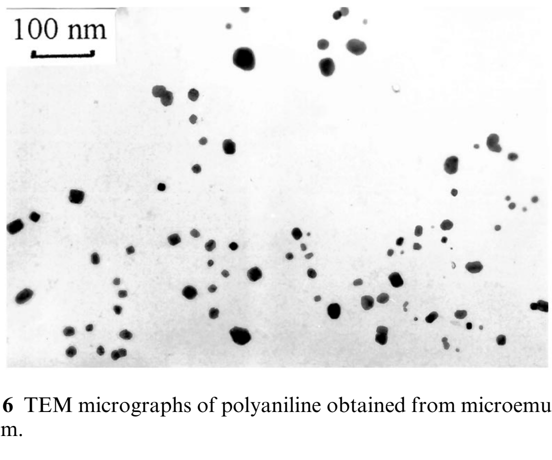

Fig. 6 TEM micrographs of polyaniline obtained from microemulsion system.

stable without any evident precipitation. Characterization of the polymers by a number of techniques mentioned above showed that in the microemulsion polymerization system SDBA acted both as surfactant and dopant. It was also found that polyaniline powder obtained from microemulsion had a higher crystallinity, and it was assumed to be due to the orientation behavior of the organized molecularly ordered microemulsion system. However, the conductivity of the PANI synthesized in the microemulsion was not greatly increased, mainly due to the chain-transfer reactions of co-surfactants used in the microemulsion which decreased the extent of π-conjugation along the polymer chain. Now the improvement of the electric conductivity of PANI and further investigations on the preparation of PANI in ternary microemulsion systems (without cosurfactant) are in progress in our laboratory.

References

1 E. M. Genies, P. Hany and C. Santier, *Synth. Met.*, 1989, **28**, 647.
2 N. S. Sariciftci and H. Kuzmany, *J. Chem. Phys.*, 1990, **92**, 4530.
3 A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, 1980, **111**, 111.
4 M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, 1988, **160**, 151.
5 S. Wang, F. Wang and X. Ge, *Synth. Met.*, 1986, **78**, 1.
6 S. A. Chen and H. T. Lee, *Macromolecules*, 1993, **26**, 3254.
7 K. Shannon and J. Fernandez, *J. Chem. Soc., Chem. Commun.*, 1994, 643.
8 H. S. O. Chan, S. C. Ng, W. S. Sim, K. L. Tan and B. T. G. Tan, *Macromolecules*, 1992, **25**, 6029.
9 S. Jin and G. Xue, *Macromolecules*, 1997, **30**, 5753.
10 K. Ishizu, H. Tanaka and R. Saito, *Polymer*, 1996, **37**, 863.
11 R. H. Ottewill and J. N. Shaw, *J. Electroanal. Chem.*, 1972, **37**, 133.
12 S. P. Armes and B. Vincent, *J. Chem. Soc., Chem. Commun.*, 1987, 288; S. P. Armes and M. Aldissi, *J. Chem. Soc., Chem. Commun.*, 1989, 88; N. Cawdery, T. M. Obey and B. Vincent, *J. Chem. Soc., Chem. Commun.*, 1988, 1198.
13 B. Vincent and J. Waterson, *J. Chem. Soc., Chem. Commun.*, 1990, 683.
14 N. Gospodinova, P. Mokreva, T. Tsanov and L. Terlemezyan, *Polymer*, 1997, **38**, 43.
15 J. Barton, *Prog. Polym. Sci.*, 1996, **21**, 399.
16 M. Antonietti, S. Lohmman and C. Vanniel, *Macromolecules*, 1989, **25**, 1515.
17 M. Dreja, W. Pyckhout-Hintzen and B. Tieke, *Macromolecules*, 1998, **31**, 272.
18 F. Yan, C. Zheng, X. Zhai and D. Zhao, *J. Appl. Polym. Sci.*, 1998, **67**, 747.
19 S. Roy and S. Devi, *J. Appl. Polym. Sci.*, 1996, **67**, 1509.
20 H. S. O. Chan, L. Ming, C. H. Chew and L. Ma, *J. Mater. Chem.*, 1993, **3**, 1109.
21 D. Ichinohe, T. Arai and H. Kise, *Synth. Met.*, 1997, **84**, 75.
22 M. T. Nguyen and A. F. Diaz, *Macromolecules*, 1995, **28**, 3411.
23 G. E. Asturias, A. G. MacDiarmid, R. P. McCall and A. J. Epstein, *Synth. Met.*, 1989, **29**, 157.
24 R. Singh, V. Arora, R. P. Tandon and S. Chandre, *Polymer*, 1997, **38**, 4897.
25 I. Kulszewicz-Bajer, J. Sobczak, M. Hasik and J. Pretula, *Polymer*, 1996, **37**, 25.
26 L. F. Warren, J. A. Walker, D. P. Anderson, C. G. Rhodes and L. J. Buckley, *J. Electroanal. Chem.*, 1989, **136**, 2286.
27 Y. Wei, G. W. Jang, K. F. Hsueh, E. M. Scherr, A. G. MacDiarmid and A. J. Epstein, *Polymer*, 1992, **33**, 314.
28 (*a*) F. Wang, J. Tang, W. L. Zhang and Z. Mo, *Mol. Cryst. Liq. Cryst.*, 1988, **160**, 175; (*b*) J.-E. Österholm, Y. Cao, F. Klavetter and P. Smith, *Polymer*, 1994, **35**, 2902.
29 J. M. Ko, S. Kim and I. J. Chung, *Synth. Met.*, 1995, **69**, 139.
30 L. T. Cai, S. B. Yao and S. M. Zhou, *Synth. Met.*, 1997, **88**, 209.
31 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1996, **78**, 1.
32 D. S. Pearson, P. A. Pincus and G. W. Heffner, *Macromolecules*, 1993, **26**, 1570.
33 W. Zheng, M. Angelopoulos, A. J. Epstein and A. G. MacDiarmid, *Macromolecules*, 1997, **30**, 7634.
34 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1995, **69**, 179.
35 M. E. Jozefowicz, R. Laversanne, H. H. S. Javadi, A. J. Epstein, J. P. Pouget, X. Tang and A. G. MacDiarmid, *Phys. Rev. B*, 1989, **39**, 12958.
36 W. B. Euler, *Solid State Commun.*, 1986, **57**, 857; S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, *Phys. Rev. Lett.*, 1987, **59**, 1464.
37 L. M. Gan, C. H. Chew, I. Lye, L. Ma and G. Li, *Polymer*, 1993, **34**, 3860.
38 X. Zeng and T. Ko, *Polymer*, 1998, **39**, 1187.
39 B. C. Roy, M. D. Gupta and J. K. Ray, *Macromolecules*, 1995, **28**, 1727.
40 S. Wang, F. Wang and X. Ge, *Synth. Met.*, 1986, **16**, 99.

Paper 9/05146E