Macromolecules **2003,** *36,* 3967−3973

Synthesis of Polyaniline Particles via Inverse and Direct Miniemulsion

Emmanuelle Marie, Regina Rothe, Markus Antonietti, and Katharina Landfester*

Max Planck Institute of Colloids and Interfaces, Forschungscampus Golm,
D-14424 Potsdam, Germany

Received October 21, 2002; Revised Manuscript Received March 27, 2003

ABSTRACT: Polyaniline (PANI) latex particles have been synthesized using both inverse and direct miniemulsion polymerization techniques. It is shown that inverse miniemulsions of anilinium hydrochloride can be oxidized by simple H_2O_2, thus resulting under optimized conditions in highly crystalline PANI particles dispersed in hydrocarbons with high volume fraction. The resulting structure is identified as emeraldine, which however crystallizes in a new crystal morphology. Oxidation of aniline miniemulsions in water with diverse oxidants from the continuous phase also leads to highly crystalline PANI, which however has a low colloidal stability. Additional employment of a costabilizer in this case leads to stable aqueous PANI dispersions with for water-based systems otherwise unreached local structural order.

Introduction

Intrinsically conducting polymers are useful for a large number of applications: conducting paints and glues, electromagnetic shielding, antistatic formulations, sensors and actuators, electronic devices, and corrosion protection are a few examples.[1,2] Among other conducting polymers such as polypyrrole, polythiophene, and polyacetylene, polyaniline (PANI) has emerged as one of the most promising polymers because of its good environmental stability and controllable electrical properties.[3] Indeed, depending on the oxidation state and protonation level, this polymer is either totally insulating or exhibits high conductivity. Actually, only the intermediate oxidation state, the protonated emeraldine form, is conducting (see Figure 1). The fully reduced leucoemeraldine and the fully oxidized pernigraniline are insulating materials. Protonation induces an insulator-to-conductor transition.

Usually, conducting polyaniline can be synthesized from monomeric aniline by either oxidative polymerization or electropolymerization. However, the chemical oxidation of aniline is the more feasible route for the production of polymers on a large scale. In this case, aniline is usually dissolved in acidic aqueous media in which an oxidative agent such as ammonium persulfate is added, and the green-black polyaniline salt precipitates. The polymer thus obtained is insoluble in common solvents and exhibits a poor processability. It is therefore an actual topic to bring PANI in form which is easily processable and applicable. A first approach is to modify the polyaniline backbone: the use of substituted aniline monomer[4−6] leads to soluble polymers, unfortunately often accompanied by a conductivity decrease. Moreover, a polymer bearing amino functions can act as precursor and allows the synthesis of soluble copolymers.[7] A second approach is the so-called counterion-induced processability: by using an organic acid instead of an inorganic one, the polymer thus obtained becomes soluble in common solvent such as DMF or DMSO for example. The acid used is often camphorsulfonic acid[8,9] or dodecylbenzenesulfonic acid (DBSA).[10−14] Indeed, DBSA acts simultaneously as organic dopant and as surfactant. DBSA and aniline form a complex, which can be dispersed in water in the form of needles. When potassium persulfate (KPS) is added, the needles turn to particles stabilized by DBSA as the polymerization proceeds.

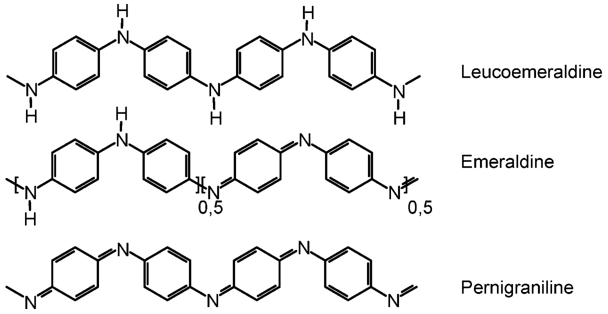


Figure 1. Oxidation states of polyaniline.

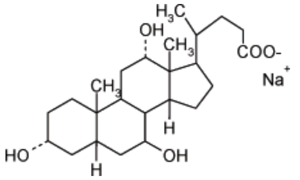
DBSA was also used in the heterophase polymerization of aniline.[15,16] The DBSA−aniline complex is dissolved in xylene, and an aqueous solution of KPS is dispersed in this continuous organic phase. However, only the oxidation agent is dispersed; the aniline and the polymer formed are dissolved in the continuous phase. In a similar way, an aqueous solution of ammonium persulfate (APS) was dispersed in hexane using DBSA as surfactant to form a microemulsion.[17] Aniline was then added, and the polymerization was carried out at room temperature without stirring. It has to be noted again that also in this example only the oxidation agent is dispersed; the aniline and the polymer formed are dissolved in the continuous phase.

Stable colloidal dispersions of PANI particles are prepared via dispersion polymerization.[18−22] Aniline monomer is dissolved in acid aqueous solution, and a strong oxidizing agent, mainly KPS or APS, is added. Sodium dodecyl sulfate (SDS),[23−25] poly(vinyl alcohol),[20] poly(vinylpyrrolidone),[20,22,26] poly(ethylene oxide),[18] poly(2-vinylpyridine-*co*-(*p*-aminostyrene)),[19] and even silica particles[27] were used to stabilize the formed polyaniline particles. However, the morphology control is rather poor, and particles with rice-grain or fiber morphology are often obtained. These particles can be encapsulated in a film-forming polymer such as polycarbonate[28] or dispersed in a polymer solution to form a blend, which can then be cast into films.[29,30]

Only a few attempts of emulsion polymerization of aniline were made.[31] A solution of aniline in 3 M aqueous HCl was dispersed in petroleum ether to form a microemulsion. A second microemulsion with an aqueous APS solution as dispersed phase is added. The droplets react instantaneously; the polymer obtained is

10.1021/ma0257550 CCC: $25.00

Table 1. Surfactants Used for Direct and Inverse Miniemulsions of Aniline

surfactant	description	mol wt (g mol^{-1})
SDS	$CH_3(CH_2)_{11}OSO_3Na$	288
Lutensol AT50	$(C_{16}H_{33})(EO)_{50}$	2425
CTMA-Cl	$CH_3(CH_2)_{15}N(CH_3)_3Cl$	320
sodium salt of cholic acid		409
SE3030	poly[styrene-*b*-ethylene oxide]	M_w (Sty block) = 3000 M_w (EO block) = 3000
DBSA	$CH_3(CH_2)_{11}(C_6H_4)OSO_3H$	327
PVA	poly(vinyl alcohol) (hydrolysis grade 87−89%)	85 000−146 000
PVP K30	poly(vinylpyrrolidone)	40 000
PVP K90	poly(vinylpyrrolidone)	360 000
P(B/E-*b*-EO)	poly[(ethylene-*co*-butylene)-*b*-(ethylene oxide)], 49 wt % EO	M_w (E−B block) = 3700 M_w (EO block) = 3600
PEG-Acrylat	$CH{=}CH_2CO(CH_2CH_2O)_nH$	375

highly crystalline as compared to conventional methods. However, the solid content is rather low, and the amount of surfactant required is impracticably high (1.75 g of the surfactant Empilan NP5 was necessary to stabilize 1 g of 5% aqueous aniline solution, i.e., 0.05 g of aniline).

In this paper, the possibilities of a miniemulsion polymerization approach to synthesize polyaniline particles are explored. The miniemulsion polymerization is known to be a powerful technique to produce a whole variety of new polymer latexes.[32,33] The particles are preformed as droplets with a size of 50−500 nm already from the beginning of the reaction by applying high shear or stress to a system containing the phase to be dispersed, the continuous phase, a surfactant, and a compound which is highly insoluble in the continuous phase, the so-called osmotic agent which is a hydrophobe for direct systems or a lipophobe for inverse systems.[32,34] The surfactant stabilizes the droplets against collisions; mass exchange (Ostwald ripening) between the droplets is suppressed by the use of the osmotic agent. Each droplet behaves like a nanoreactor, and the polymer particles produced have ideally the same size as the monomer droplets.[35] For the formulation of direct miniemulsions, a wide variation of ionic and nonionic surfactants could be used resulting in differently charged and stable polymer dispersions.[33,36] As stabilizers for inverse miniemulsion, block copolymers are favorably applied. It was proved that miniemulsion is a powerful technique to disperse a wide range of materials with noticeably smaller amount of surfactants than required in the case of microemulsion. Furthermore, the miniemulsion process can be applied in a much broader range than only radical polymerization.[37−40] Also, metallic nanoparticles were successfully synthesized in inverse miniemulsion.[41] This makes miniemulsion inherently very attractive to produce polyaniline particles.

In this paper, polyaniline particles are synthesized both in inverse and in direct miniemulsions. The synthesis conditions are optimized in both cases with respect to oxidation agent and stabilizers. In the inverse case anilinium chloride was dispersed in Isopar or cyclohexane using the block copolymer poly[(butylene-*co*-ethylene)-*b*-(ethylene oxide)] (P(B/E-*b*-EO)) as stabilizer and a solution of potassium peroxodisulfate (KPS) in hydrogen peroxide (H_2O_2) as oxidation agent. In direct miniemulsion, aniline was directly dispersed in water using SDS as surfactant and ammonium peroxodisulfate (APS) as oxidation agent. In this case, an additional polymeric stabilizer is required to keep the stabilization throughout the polymerization. The obtained polymers are analyzed by means of UV and IR spectroscopy and X-ray scattering and compared with a polyaniline synthesized in tetrahydrofuran.

Experimental Part

Chemicals. Aniline was purchased from Aldrich and distilled under vacuum prior to use. Potassium peroxodisulfate (KPS, from Fluka), ammonium peroxodisulfate (APS, from Aldrich), hydrogen peroxide (30%, from Fluka), dodecyl benzenesulfonic acid (DBSA, from Fluka), cetyltrimethylammonium chloride (CTMA-Cl, 25% aqueous solution from Aldrich), and sodium dodecyl sulfate (SDS, from Fluka) were used as received. Lutensol AT50 is a commercial product of BASF AG. Poly(ethylene glycol) acrylate (PEG-acrylate), poly(vinyl alcohol), and the different poly(vinylpyrrolidone)s were supplied by Aldrich and used as received. SE 3030 (Goldschmidt) is a block copolymer consisting of a polystyrene block (3000 g mol^{-1}) and a poly(ethylene oxide) block (3000 g mol^{-1}). The block copolymer emulsifier poly[(butylene-*co*-ethylene)-*b*-(ethylene oxide)] P(B/E-*b*-EO) consisting of a poly(butylene-*co*-ethylene) block (M_w = 3700 g mol^{-1}) and a poly(ethylene oxide) block (M_w = 3600 g mol^{-1}) was synthesized starting from Kraton liquid (Shell), which was dissolved in toluene by adding ethylene oxide under the typical conditions of anionic polymerization. Isopar M (isoparaffinic hydrocarbon) was given by Exxon Chemical. The characteristics of the used surfactants are listed in Table 1.

Synthesis of Polyaniline Particles. *Reference Product.* 0.5 g of aniline is dissolved in 10 mL of THF. Under vigorous stirring, 0.7 g of concentrated HCl followed by an aqueous solution of 0.738 g of KPS in 15 mL water is added. The mixture turns dark green in a few minutes. The dispersion is kept at room temperature under vigorous stirring for one night. The polymer is then precipitated in methanol and dried at 70 °C under normal pressure.

Inverse Miniemulsions. A mixture of 3 g of aniline and 3.9 g of concentrated aqueous HCl is dispersed in a solution of 500 mg of P(B/E-*b*-EO) in 24 g of cyclohexane by ultrasonicating the mixture for 180 s at 90% amplitude (Branson sonifier W450 Digital) at 0 °C. A second miniemulsion is prepared by dispersing a solution consisting of 640 mg of KPS and 6 g of a 30% aqueous solution of hydrogen peroxide in 24 g of cyclohexane using 500 mg of P(B/E-*b*-EO) as surfactant. After stirring the emulsion at room temperature for 1 h, the miniemulsion is obtained by ultrasonicating the mixture for 120 s at 90% amplitude (Branson sonifier W450 Digital) at 0

°C. Different amounts of this miniemulsion are then added to the first miniemulsion containing aniline as described in detail in the tables. Upon stirring, the mixed miniemulsion turns dark green within a few hours. The dispersion is kept under vigorous stirring at room temperature for one night.

Direct Miniemulsions. A mixture of 3 g of aniline and 125 mg of ethylbenzene as hydrophobe is added to 12 g of water containing 125 mg of SDS. After stirring for 1 h at room temperature, a miniemulsification was obtained by ultrasonicating for 120 s at 90% amplitude (Branson sonifier W450 Digital) at 0 °C. After emulsification, an aqueous solution of additional stabilizing agent as indicated in detail in the tables is added. 7.35 g of APS (one equivalent to aniline) is dissolved in 10 g of water to obtain a saturated aqueous solution. This solution is then added to the miniemulsion at room temperature. The miniemulsion turns brown and then dark green within a few hours as the polymerization proceeds.

Analytical Methods. The particles sizes were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°.

Electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400 mesh carbon-coated copper grid and left to dry. No further contrasting was applied.

Atomic force microscopy (AFM) was performed with a NanoScope IIIa microscope (Digital Instruments, Santa Barbara, CA) operating in tapping mode. The instrument was equipped with a 10 × 10 μm E-Scanner and commercial silicon tips (model TSEP, the force constant was 50 N m^{-1}, the resonance frequency was 300 kHz, and the tip radius was smaller than 20 nm). The samples were prepared by allowing droplets of diluted aqueous dispersions to dry on freshly cleaved muscovite mica surfaces at room temperature.

Infrared (IR) spectroscopy was performed on a Biorad FTS 600 spectrometer in the absorbance setup. The samples were measured as pure products with an ATR accessory.

The UV spectra were measured with an Uvikon 931 spectrophotometer from Kontron Instruments in 1 cm quartz cells. The dispersions were diluted 100 times or more in cyclohexane to achieve a suitable absorbance. All spectra were recorded between 190 and 700 nm in differential mode, using cyclohexane as reference.

The wide-angle diffractograms were measured with a wide-angle goniometer (Enraf-Nonius PS-120, Cu Kα) with a line detector. The samples were measured in reflection mode.

For the IR and the WAXS measurements, after drying the dispersion, the samples were washed three times with water and three times with cyclohexane in order to remove possible soluble fractions.

Results and Discussion

Inverse Miniemulsions. The possibilities offered by the inverse miniemulsion process for the synthesis of polyaniline particles are discussed first. For that purpose, two miniemulsions, one with the anilinium chloride and the other with the oxidizing agent, were formed. For the first miniemulsion, a concentrated solution of anilinium salt in water is prepared by simply mixing aniline and concentrated HCl in a 1:1.3 weight ratio in order to protonate the aniline. This solution crystallizes at room temperature but melts at 40 °C and can therefore be miniemulsified in 24 g of Isopar M or cyclohexane using P(B/E-*b*-EO) as stabilizer. Upon mixing the stabilizer solution and the anilinium salt, a kind of complex seems to form, and the salt precipitates together with the stabilizer forming a highly viscous phase, which is then miniemulsified. This miniemulsion has an aniline content of 10%, which is noticeably higher than in the previous microemulsion case where the aniline content was limited to only 1%.

The oxidizing agent is miniemulsified to form a second miniemulsion. Since most of the oxidation agents, e.g. KPS, have a quite limited water solubility, an impracticably large amount of the inverse miniemulsion containing the rather low concentrated aqueous solution would be necessary for polymerization. The use of simple hydrogen peroxide as an oxidation agent, however, allows direct dispersion in Isopar M or cyclohexane using P(B/E-*b*-EO) as surfactant to get a miniemulsion with a reasonable oxidation capacity and a dispersed to continuous phase ratio of 15%. A small amount of KPS is dissolved in H_2O_2 as a saturated solution to promote the oxidation reaction.

Table 2. Polyaniline Particles Synthesized in Inverse Miniemulsions; Variation of the Stabilizer P(B/E-*b*-EO) to Aniline Ratio in the Aniline Miniemulsion[a]

latex	KLE/aniline (wt %)	av particle size (nm)
EM 334	8	139 and 588[b]
EM 335	16	99 and 489[b]
EM 336	23	189 and 380[b]
EM 337	33	154 and 441[b]

[a] The H_2O_2 miniemulsion is kept constant with a dispersed phase content of 15%. An equimolar ratio of aniline and H_2O_2 after mixing of the miniemulsions is ensured. [b] Bimodal size distribution.

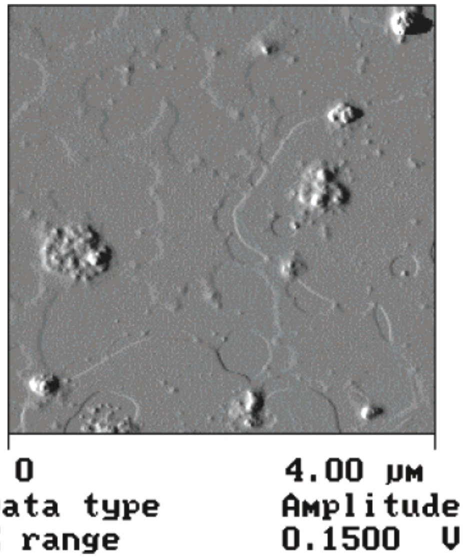


Figure 2. Typical AFM picture of polyaniline prepared from inverse miniemulsions, taken in the amplitude picture.

The two prepared miniemulsions are then mixed, at first in an equimolar aniline to H_2O_2 ratio. Within a few hours the dispersion turns dark green to black, indicating that the polymerization occurs. This means that mass exchange takes place between the droplets of aniline and the droplets of hydrogen peroxide, contrary to the usual behavior of stable miniemulsions where droplets stay separated and further ultrasonication is required when the droplets have to react with each other.[42] Obviously, in the case of mixing droplets containing highly concentrated aniline and H_2O_2 solutions, the chemical potentials of the droplets are able to balance this difference via exchange processes.

To optimize the stabilizer concentration, the P(B/E-*b*-EO)/aniline ratio was varied. These experiments are listed in Table 2.

Apparently, the particle size does not depend on the surfactant concentration, as usually expected. The AFM pictures (see Figure 2), however, show that the bimodality and sizes as measured by light scattering are rather due to aggregates composed of smaller particles with a

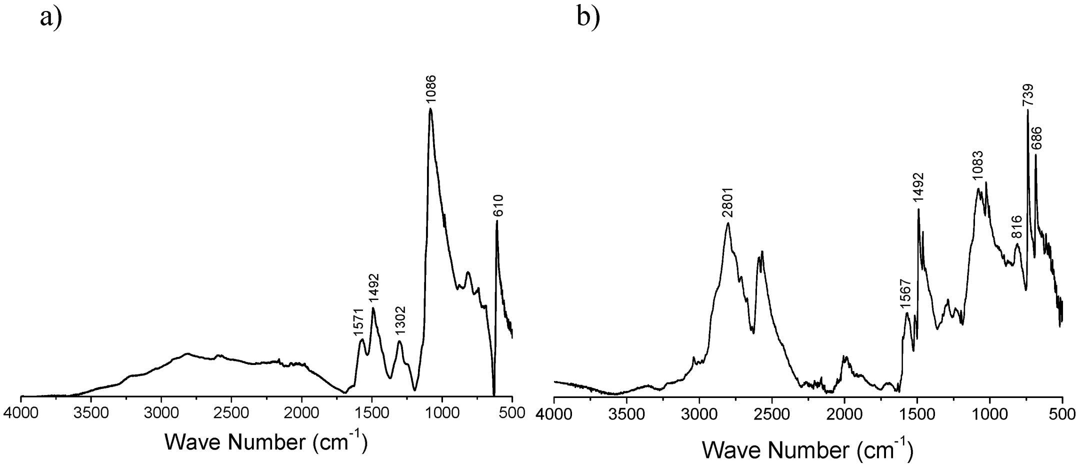


Figure 3. IR spectra of polyaniline synthesized: (a) as reference polymer in THF; (b) in indirect miniemulsion.

diameter of around 90 nm. Partial aggregation is an expression of the very strong particle—particle interaction due to the very high polarizabilities of conducting polymers and had—more or less pronounced—to be expected. Nevertheless, the dispersions, although bimodal, show long-term colloidal stability and practically no coagulum.

For all further experiments, the surfactant/aniline ratio was fixed at 16 wt %. This amount of surfactant is typical for an inverse miniemulsion and much smaller than the quantity required for a corresponding microemulsion polymerization.[43]

The polymer was isolated by means of centrifugation and washed several times with cyclohexane until the supernatant was clear. The products were first analyzed by IR spectroscopy and were compared with the reference polymer synthesized in THF as described in the Experimental Part (see Figure 3).

The IR spectra of the two products are rather different. The spectrum of the product obtained via dispersion polymerization is consistent with the emeraldine form of polyaniline. The bands at 1567 and 1492 cm^{-1} correspond to the stretching of the N=Q=N and N—B—N unit in the polymer chain, respectively, where Q represents the quinoide structure and B the benzene ring. The band at 816 cm^{-1} corresponds to the deformation of the CH out of the plane. The band at 1083 cm^{-1} and the long tail above 2000 cm^{-1} are associated with high electrical conductivity and a high degree of electron delocalization as reported in the literature.[3,44,45] In the spectrum of the polymer synthesized in inverse miniemulsion, additional peaks appear. These peaks are sharp and correspond probably to oligomers of aniline as shown earlier by Kang et al.[3]

One possibility for the formation of oligomers is the incomplete exchange between the droplets during the miniemulsification. To maximize reactant exchange between the droplets of aniline and the droplets of H_2O_2, the miniemulsions were sonicated after mixing.[42] However, it was found that this process only increases the rate of polymerization, the dispersion turning black during sonication instead of hours when the two miniemulsions are simply mixed. However, the IR spectra of the polymers obtained were almost identical.

Although the mechanism of oxidative polymerization of aniline is still under debate, it was shown by other authors that the amount of oxidation agent has a great influence on the molecular weight of the polymers.[1] At the beginning, only the totally oxidized form of aniline, the pernigraniline form, is present. When the chain adds a new monomer, it is reduced and reoxidized through the medium. When the oxidation agent is consumed, the polymer chain can add monomer units until its oxidation stage achieves the one of the emeraldine form. At this point, the oxidation potential of the chain becomes too low and the polymerization stops. From this mechanistic observation, it would be necessary to add higher amounts of H_2O_2 to avoid the formation of oligomers. The amount of oxidation agent was thus varied between 25% and 600% compared to the amount of aniline.

The colloidal stability, but also the particles size and the particle size distribution, was not influenced by the amount of H_2O_2. The dispersions were first analyzed by UV spectroscopy. The absorbance of the dispersion increases with the ratio of H_2O_2/aniline, indicating that more polymer is formed when the amount of H_2O_2 increases. At the same time the IR spectra change and show the same characteristics as the spectrum of the reference product (see Figure 4).

Up to an amount of H_2O_2 of 300%, the peaks characteristic in the IR spectra for polyaniline change drastically. The sharp peaks of the oligomers disappear, and the spectrum resembles the one of the reference sample (Figure 3a). Further increase to 600% does not lead to further changes of the spectra. Therefore, the “optimal” 300% polymer was analyzed by means of X-ray diffraction (see Figure 5).

The polymer exhibits an unusually high degree of crystallinity for a polyaniline synthesized in dispersion. This high crystallinity is usually the sign of a high conductivity.[46,47] However, diffractograms, although nicely narrow peaked, are quite different from those reported in the literature for polyaniline[48,49] and the reference sample synthesized in THF (see Figure 5). It has to be noted that any soluble parts, e.g., the anilinium salt (soluble in water) and the surfactant (soluble in cylcohexane), were carefully removed from the samples. This was verified by the comparison of reference spectra of these substances. We can only speculate about the reason for this technologically presumably very important difference of the polyaniline spectrum. It is nearby to assume that it is the confinement of the crystallization process within the 90 nm large compartments (as determined by light scattering) which will change crystal morphology and sometimes even crystal structure. A similar influence of nanocompartmental-

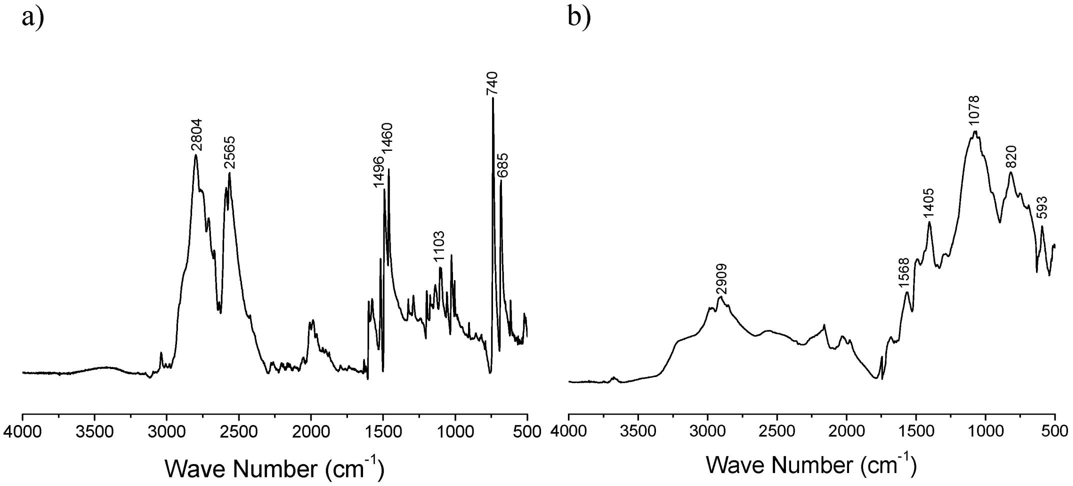


Figure 4. IR spectra of polyaniline synthesized in indirect miniemulsion: (a) low amounts of H_2O_2 (25% compared to aniline); (b) high amounts of H_2O_2 (600% compared to aniline).

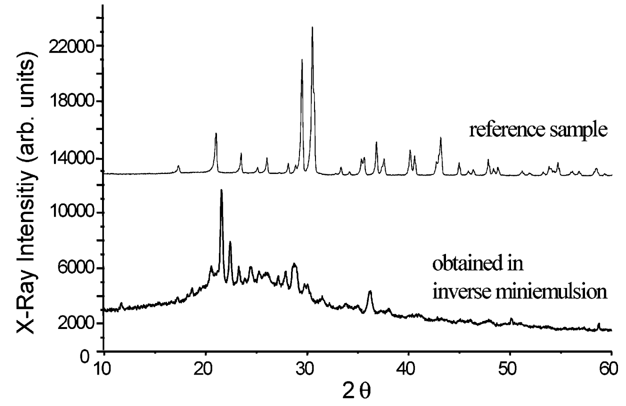


Figure 5. X-ray diffractogram of polyaniline synthesized in indirect miniemulsion compared to reference sample.

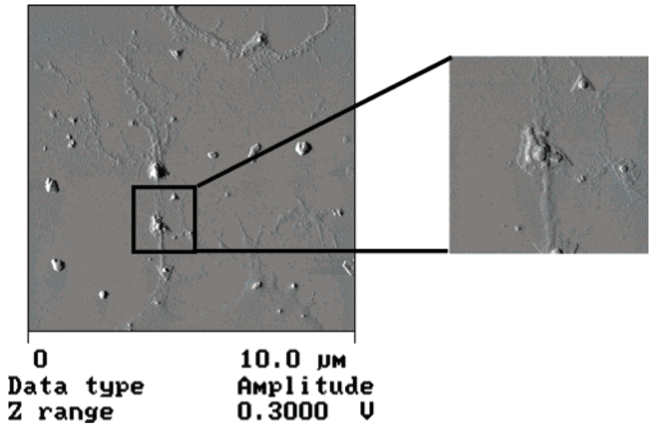


Figure 6. Typical AFM picture of direct polyaniline dispersion (PA/SDS/PVP/3).

ization on crystal structure and morphology has been described for polyacrylonitrile,[50] water,[51] and diverse *n*-alkanes.[52]

Direct Miniemulsions. In the second set of experiments, aniline was dispersed in water using SDS, Lutensol AT50, CTMA-Cl, cholic acid, the PS/PEO block copolymer (SE3030), and a poly(ethylene oxide) polymer bearing an acrylate group. This acrylate group was thought to react with the growing polyaniline chains, thereby grafting the surfactant onto the particle. In all cases the miniemulsification process was successful, and stable miniemulsions containing aniline droplets could be obtained.

For a successful polymerization, it is also known that the presence of an acid is necessary as only the protonated growing polymer chain can add a new monomer unit.[1] However, it was proved through UV spectroscopy that polyaniline is already protonated at pH 8 in the presence of SDS (as driven by the energy gain of surfactant complexation); without SDS a pH 4 is required for protonation.[25] Therefore, no addition of acid is needed.

However, addition of KPS and reaction destabilized all dispersions, and the systems separated within a few minutes. Different other oxidation agents (e.g., $FeCl_3$ and $KClO_4$) were also tested, without any success. If aniline was dispersed using 1 equiv of dodecylbenzenesulfonic acid (DBSA), polymerization occurs without phase separation. However, the particles obtained are rather big, in the micrometer range. Furthermore, the solid content is low because the amount of water needed to get a fluid dispersion is higher (up to 30 g of water for 1.5 g of aniline) than in the case of SDS.

From all those variations, it can only be concluded that the surfactants, which were suitable to stabilize aniline in water, are ineffective to stabilize the polyaniline particles. Three possible reasons can be identified: (i) The ionic strength of the dispersion increases and leads to instability. (ii) The formed polymer is highly positively charged and compensates the negatively charged surfactants. (iii) The polarizability of the polymerized particles is very high, which results in a very high Hamaker constant and van der Waals attraction. This makes classical nonionic surfactants ineffective.

For all those reasons, addition of a second, strong steric stabilizer (e.g., PVA or PVP) after the formation of the miniemulsion using SDS, CTMA-Cl, Lutensol AT50, SE3030, sodium salt of cholic acid, or PEG-acrylate was expected to improve the dispersion stability. The different experiments in this direction are listed in Table 3.

The best results were obtained for the poly(vinyl alcohol) with a molecular weight of around 100 000 g mol^{-1} and poly(vinylpyrrolidone)s. A small amount of 0.2 g (6.7 wt % related to aniline) is already sufficient in order to obtain stable dispersions. In all cases, small polyaniline particles which aggregate to larger entities were obtained, as depicted in the AFM pictures (see

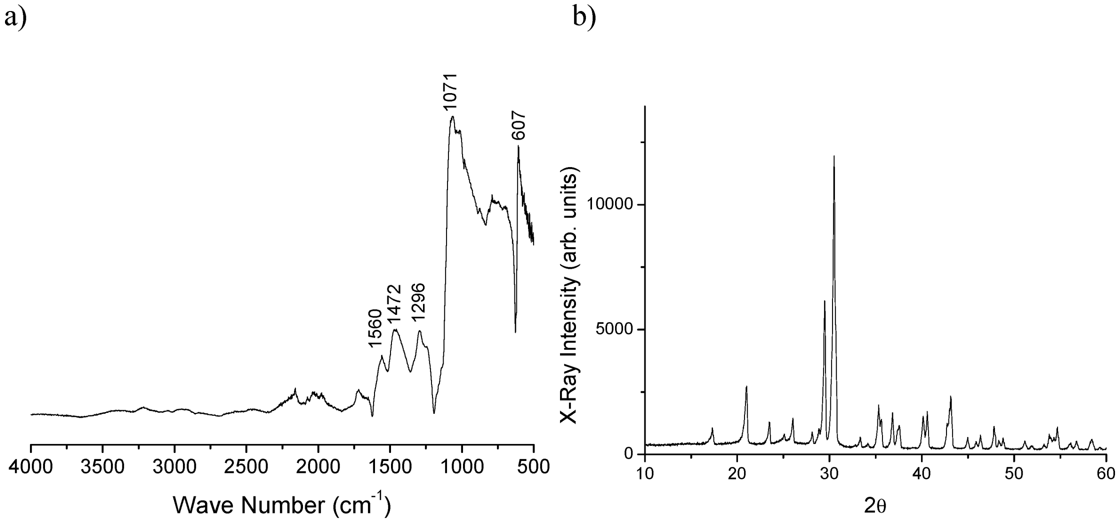


Figure 7. Analysis of polyaniline particles synthesized in direct miniemulsion: (a) IR spectrum; (b) X-ray diffractogram of the purified and dried sample.

Table 3. Polyaniline Particles Synthesized in Direct Miniemulsion; Type and Amount of Surfactant I (Added Prior to Miniemulsification) and the Additional Surfactant II (Added after Miniemulsification) Used for 3 g of Aniline

sample	surfactant I	amount [g]	surfactant II	amount [g]	particles size [nm]
PA/SDS/PVP/0.2	SDS	0.125	PVP K30	0.2	1930
PA/SDS/PVP/3	SDS	0.125	PVP K30	3.0	121 and 792
PA/CTMACl/PVP	CTMA-Cl	0.125	PVP K30	0.2	1370
PA/LUT/PVP	Lutensol AT50	0.2	PVP K30	0.2	1130
PA/PEG-A/PVP	PEG-acrylate	0.2	PVP K30	0.2	1570
PA/CS/PVP	cholic acid, Na salt	0.15	PVP K30	0.2	1760
PA/SE3030/PVP/0.2	SE3030	0.4	PVP K30	0.2	900
PA/SE3030/PVP/1.5	SE3030	0.4	PVP K30	1.5	790
PA/SDS/PVP2	SDS	0.125	PVP K90	3.0	270 and 900
PA/SDS/PVA	SDS	0.125	PVA	3.0	382
PA/LUT/PVA	Lutensol AT50	0.2	PVA	0.2	1140
PA/LUT/PVP/0.5	Lutensol AT50	0.2	PVP K30	0.5	1610
PA/LUT/PVP/1.5	Lutensol AT50	0.2	PVP K30	1.5	950
PA/LUT/PVP/3	Lutensol AT50	0.2	PVP K30	3.0	600
PA/SDS/LUT/PVP	SDS/Lutensol AT50	0.125/0.2	PVP K30	0.2	860
PA/CTMACl/LUT/PVP	CTMA-Cl/ Lutensol AT50	0.125/0.2	PVP K30	0.2	1080

Figure 6). With increasing amount of polymer the aggregate size decreased and could be as small as 400 nm.

As in the case of the inverse systems, partial aggregation is a sign for the very strong particle–particle attraction in conducting polymer dispersions.

The polymer was isolated by means of centrifugation and washed several times with water until the supernatant was clear. The products were analyzed by IR spectroscopy and X-ray and were compared (Figure 7 and also Figures 3 and 5) with the polymer synthesized in THF as described in the Experimental Part. The two polyaniline samples exhibit very similar IR spectra and X-ray diffractograms although very different reaction processes were used.

The discussion of the infrared spectrum essentially follows the discussion given above. This indicates, as reported before,[25] that SDS is able to protonate the polyaniline and acts simultaneously as a surfactant and as an efficient dopant.

Looking at the WAXS diffractograms, it is seen that the samples exhibit an unusual high degree of crystallinity for polyaniline synthesized in dispersion. The X-ray diffractogram exactly corresponds to the one of the reference polymer, indicating that the same polymer with a high structural order is obtained, a sign for a inherently high conductivity.[46,47] Diffractograms found the literature for polyaniline made by precipitation and dispersion polymerization usually reveal a much more ill-defined structure.[48,49] This underlines that miniemulsion polymerization is indeed mechanistically more close to solvent or the bulk polymerization, i.e., that the polyaniline is indeed synthesized in very small "nanoreactor" droplets.

Conclusions

Polyaniline (PANI) latex particles have been synthesized using both inverse and direct miniemulsion polymerization techniques. In the case of inverse miniemulsion, anilinium hydrochloride was dispersed and could be oxidized by simple H_2O_2, thus resulting under optimized conditions in highly crystalline PANI particles dispersed in hydrocarbons with high volume fraction. The resulting structure is identified as emeraldine, which however crystallizes in a new crystal morphology. Aniline itself can be used for the formulation of direct miniemulsion using typical surfactants, such as the ionic surfactants SDS, CTMA-Cl, the nonionic surfactant Lutensol AT50, and the block copolymeric surfactant SE3030. Oxidation of aniline miniemulsions in water with diverse oxidants from the continuous phase also leads to highly crystalline PANI, which however has a low colloidal stability. Additional employment of a costabilizer like PVA or PVP in this case leads to stable aqueous PANI dispersions with for water-based systems otherwise unreached local structural order.

Acknowledgment. We thank Anne Heilig for the AFM measurements. Support by Deutsche Forschungsgemeinschaft (DFG) and the Max Planck Society is gratefully acknowledged.

References and Notes

(1) Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998**, *23*, 1443−1484.
(2) Chen, S. A.; Chuang, K. R.; Chao, C. I.; Lee, H. T. *Synth. Met.* **1996**, *82*, 207−210.
(3) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277−324.
(4) Prevost, V.; Petit, A.; Pla, F. *Synth. Met.* **1999**, *104*, 79−87.
(5) Nguyen, M. T.; Kasai, P.; Miller, J. L.; Diaz, A. F. *Macromolecules* **1994**, *27*, 3625.
(6) Mav, I.; Zigon, M. *Polym. Bull. (Berlin)* **2000**, *45*, 61−68.
(7) Kinlen, P. J.; Frushour, B. G.; Ding, Y.; Menon, V. *Synth. Met.* **1999**, *101*, 758−761.
(8) Jang, W. H.; Kim, B. J.; Choi, H. J.; Jhon, M. S. *Colloid Polym. Sci.* **2001**, *279*, 823−827.
(9) Luzny, W.; Samuelsen, E. J.; Djurado, D.; Nicolau, Y. F. *Synth. Met.* **1997**, *90*, 19−23.
(10) Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, A. *Synth. Met.* **1999**, *106*, 59−66.
(11) Kababya, S.; Appel, M.; Haba, Y.; Titelman, G. I.; Schmidt, A. *Macromolecules* **1999**, *32*, 5357−5364.
(12) Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, A. *Synth. Met.* **2000**, *110*, 189−193.
(13) Su, S. J.; Kuramato, N. *Synth. Met.* **2000**, *108*, 121−126.
(14) Yin, W.; Ruckenstein, E. *Synth. Met.* **2000**, *108*, 39−46.
(15) Osterholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. *Synth. Met.* **1993**, *55*−*57*, 1034−1039.
(16) Osterholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. *Polymer* **1994**, *35*, 2902−2906.
(17) Yan, F.; Xue, G. *J. Mater. Chem.* **1999**, *9*, 3035−3039.
(18) Vincent, B.; Waterson, J. *J. Chem. Soc., Chem. Commun.* **1990**, 683−684.
(19) Armes, S. P.; Aldissi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 88−89.
(20) Stejskal, J.; Kratochvil, P.; Helmstedt, M. *Langmuir* **1996**, *12*, 3389−3392.
(21) Stejskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polym. Int.* **1993**, *32*, 401−405.
(22) Gospodinova, N.; Terlemezyan, L.; Mokreva, P.; Stejskal, J.; Kratochvil, P. *Eur. Polym. J.* **1993**, *29*, 1305−1309.
(23) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Langmuir* **2000**, *16*, 5841−5845.
(24) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Synth. Met.* **2001**, *122*, 297−304.
(25) Kuramato, N.; Genies, E. M. *Synth. Met.* **1995**, *68*, 191−194.
(26) Stejskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polymer* **1992**, *33*, 4857−4858.
(27) Stejskal, J.; Kratochvil, P.; Armes, S. P.; Lascelles, S. F.; Riede, A.; Helmstedt, M.; Prokes, J.; Krivka, I. *Macromolecules* **1996**, *29*, 6814−6819.
(28) Jeon, B. H.; Kim, S.; Choi, M. H.; Chung, I. J. *Synth. Met.* **1999**, *104*, 95−100.
(29) Lee, W. J.; Kim, Y. J.; Kaang, S. *Synth. Met.* **2000**, *113*, 237−247.
(30) Roichman, Y.; Titelman, G. I.; Silverstein, M. S.; Siegmann, A.; Narkis, M. *Synth. Met.* **1999**, *98*, 201−209.
(31) Gan, L. M.; Chew, C. H.; Chan, H. S. O.; Ma, L. *Polym. Bull. (Berlin)* **1993**, *31*, 351−358.
(32) Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* **1999**, *32*, 5222−5228.
(33) Landfester, K. *Macromol. Rapid Commun.* **2001**, *22*, 896−936.
(34) Landfester, K.; Willert, M.; Antonietti, M. *Macromolecules* **2000**, *33*, 2370−2376.
(35) Landfester, K.; Bechthold, N.; Förster, S.; Antonietti, M. *Macromol. Rapid Commun.* **1999**, *20*, 81−84.
(36) Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* **1999**, *32*, 2679−2683.
(37) Barrere, M.; Maitre, C.; Dourges, M. A.; Hemery, P. *Macromolecules* **2001**, *34*, 7276−7280.
(38) Maitre, C.; Ganachaud, F.; Ferreira, O.; Lutz, J. F.; Paintoux, Y.; Hemery, P. *Macromolecules* **2000**, *33*, 7730−7736.
(39) Landfester, K.; Tiarks, F.; Hentze, H.-P.; Antonietti, M. *Macromol. Chem. Phys.* **2000**, *201*, 1−5.
(40) Tiarks, F.; Landfester, K.; Antonietti, M. *J. Polym. Sci., Polym. Chem. Ed.* **2001**, *39*, 2520−2524.
(41) Willert, M.; Rothe, R.; Landfester, K.; Antonietti, M. *Chem. Mater.* **2001**, *13*, 4681−4685.
(42) Landfester, K. *Adv. Mater.* **2001**, *10*, 765−768.
(43) Candau, F. *Macromol. Symp.* **1995**, *92*, 169−178.
(44) Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth. Met.* **1986**, *16*, 305.
(45) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.
(46) Zheng, W.; Angelopoulos, M.; Epstein, A. J.; MacDiarmid, A. G. *Macromolecules* **1997**, *30*, 7634−7637.
(47) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 85−92.
(48) Winokur, M. J.; Mattes, B. R. *Macromolecules* **1998**, *31*, 8183−8191.
(49) Luzny, W.; Banka, E. *Macromolecules* **2000**, *33*, 425−429.
(50) Landfester, K.; Antonietti, M. *Macromol. Rapid Commun.* **2000**, *21*, 820−824.
(51) Montenegro, R.; Antonietti, M.; Mastai, Y.; Landfester, K. *J. Chem. Phys.*, in press.
(52) Montenegro, R.; Landfester, K. *Langmuir*, in press.

MA0257550