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POLYANILINE: THIN FILMS AND COLLOIDAL DISPERSIONS*

(IUPAC Technical Report)

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Abstract: Several workers from various institutions in six countries have prepared thin films and colloidal polyaniline dispersions. The films were produced in situ on glass supports during the oxidation of anilinium chloride with ammonium peroxydisulfate in water. The average thickness of the films, assessed by optical absorption, was 125 ± 9 nm, and the conductivity of films was 2.6 ± 0.7 S cm^{-1}. Films prepared in 1 mol l^{-1} HCl had a similar thickness, 109 ± 10 nm, but a higher conductivity, 18.8 ± 7.1 S cm^{-1}. Colloidal polyaniline particles stabilized with a water-soluble polymer, poly(*N*-vinylpyrrolidone) [poly(1-vinylpyrrolidin-2-one)], have been prepared by dispersion polymerization. The average particle size, 241 ± 50 nm, and polydispersity, 0.26 ± 0.12, have been determined by dynamic light scattering. The preparation of these two supramolecular polyaniline forms was found to be well reproducible.

Keywords: polyaniline; thin films; dispersions; supramolecular forms; conducting polymers; Division IV.

INTRODUCTION

Polyaniline (PANI) (Fig. 1) is one of the most important and widely studied conducting polymers [1–3]. It is easily prepared (e.g., by the oxidation of aniline with ammonium peroxydisulfate in acidic aqueous medium) and obtained as a precipitate. Such synthesis has recently been investigated within IUPAC project 1999-024-1-400, "Polyaniline: Preparation of a conducting polymer", and the results of a collaborative study of PANI preparation have been reported in [4].
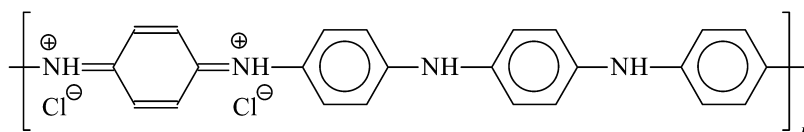

Fig. 1 Polyaniline (emeraldine) hydrochloride (one of the possible presentations).

Polyaniline protonated with inorganic acids is difficult to process because it cannot be dissolved or melted below the decomposition temperature in the conducting state. The protonation of PANI with organic acids having a bulky hydrocarbon component has been used to increase the solubility of PANI in organic solvents and the plasticity. The uses of dodecylbenzenesulfonic acid [5–7], dinonylnaphthalenesulfonic acid [8], or diesters of sulfosuccinic acid [9,10] may serve as examples. Various surfactants have also been used as a component of the reaction mixture for the same purpose [11,12]. Alternative processing strategies consist in coating of the surfaces of various substrates with a conducting PANI film and in the preparation of PANI colloids [13,14]. The latter forms, produced in situ during the polymerization of aniline, are discussed in the present study.

Practically any substrate present in the reaction mixture used for the oxidation of aniline becomes coated with a thin PANI film of submicrometre thickness. In 1912, Green and Woodhead [15] already mentioned that the "emeraldine (form of PANI) when formed on the fiber has long been known to tech-

nologists". In 1989, MacDiarmid et al. [1] noted that "PANI may also be deposited by in situ adsorption polymerization as strongly adhering films on a variety of substrates". The formation of PANI films on glass [16–20] has been investigated in detail. It has been proposed that aniline oligomers anchored at the surface [18,21] stimulate the growth of PANI chains preferentially in a perpendicular direction to the support [22,23]. Similar concepts have been suggested for electrochemically produced films [24,25]. A grass growing in a lawn can perhaps be used illustratively as a familiar macroscopic analogy.

PANI films have been grown on the flat surfaces of glass [16–20], silicon [26,27], various polymers [28,29], and noble metals [30–32]. Many other template morphologies have also been tested: carbon nanotubes [33], polymer fibers and textiles [21,34,35], membranes [36,37], polymer microspheres [38,39], natural particulate materials, like wood sawdust [19], and others have been coated with PANI. The powders of inorganic oxides, like silicon dioxide [40,41], titanium dioxide [42], copper(II) oxide [43], and ferrites [44], may serve as examples of another group of materials which have been modified on the surface with PANI. Special attention has been paid to montmorillonite and related clays [45–48]. The applications of surface-modified substrates range from sensors and electronic noses [18,49], electrodes [30,50], conducting fillers [51], electro-rheological suspensions [42,48,52], corrosion protection [45], gas-separation membranes [29], and catalysis of organic reactions [53] to electromagnetic interference shielding [34] or increasing the dielectric breakdown of polymer films [28].

When a suitable water-soluble polymer is present in the reaction mixture during the oxidation of aniline, colloidal PANI particles are obtained instead of a precipitate. The first papers on this topic date from 1987–1989 [54–56]. Progress in the preparation of conducting-polymer dispersions has recently been reviewed [13,14]. It has been observed that the dimensions of colloidal particles and the thickness of the films grown on flat surfaces are comparable [26]. It has been proposed that the formation of both forms may have a common origin [57]. As the films grow from aniline oligomers adsorbed at the surface, similar adsorption of aniline oligomer on the stabilizer chain might stimulate the nucleation of a colloidal particle.

An authority on conducting polymers has pointed out that "there are as many different types of PANI as there are people who synthesize it" [58,59]. We have therefore decided to stimulate a collaborative study testing this statement in the case that various researchers followed the same preparative protocol. Two supramolecular PANI forms, thin PANI films on glass and colloidal PANI dispersions stabilized with poly(*N*-vinylpyrrolidone) (PVP), have therefore been prepared independently in several laboratories. The films and colloids have been characterized with respect to the film thickness, film conductivity, and colloidal particle size.

Concept of film and colloidal particle formation

Before analyzing the experimental results, a short account of the potential mechanism of the formation of PANI films and colloids should be given. The oxidation of aniline in an acidic aqueous medium produces, at first, aniline oligomers. These are more hydrophobic than the original anilinium cations. They have a tendency to separate from the aqueous medium, e.g., by adsorbing themselves at available surfaces in contact with aqueous reaction mixture (Fig. 2). The adsorbed oligomers have a higher reactivity toward initiating the growth of PANI chains. This is the principle of heterogeneous catalysis, which postulates that the reactivity of adsorbed molecules may be increased because of the altered electron density distribution. It has indeed been observed experimentally that the polymerization at the surfaces precedes the polymerization in the bulk of the reaction mixture [60–62]. The first PANI chain anchored at the surface produces a nucleus of the future film. The polymerization of aniline is auto-accelerated [60]. This means that new oligomers are thus born and adsorbed close to the nucleus, and stimulate the growth of new PANI chains. The PANI chains forming a film thus proliferate along the surface and, for steric reasons, are oriented preferentially perpendicularly to the support [23].
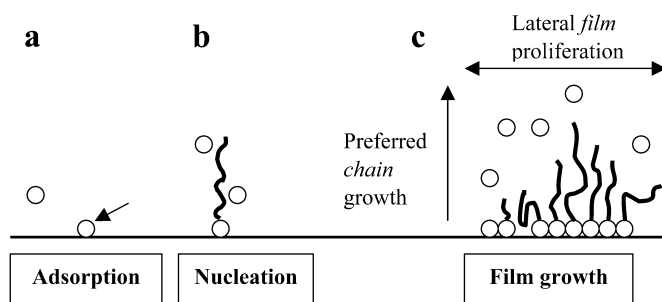
Fig. 2 The model of *film* formation: (a) aniline oligomers (open circles) are adsorbed at the available interfaces and (b) they stimulate the growth of a PANI chain (thick curve). A nucleus is produced. (c) Other PANI chains grow due to the auto-acceleration mechanism close to the nucleus. The film spreads along the surface.

A similar concept is applicable to the formation of colloidal particles (Fig. 3) [57]. These are produced by the polymerization of aniline in a medium containing the stabilizer, a suitable water-soluble polymer [13]. It has been proposed that the role of a surface is taken by the stabilizer [57]. An aniline oligomer adsorbs at the stabilizer chains and produces a PANI nucleus. By the auto-acceleration mechanism, the formation of new oligomers and polymerization proceeds in the close vicinity, and the PANI particle grows. Occasionally, other stabilizer chains become entrapped in the growing particle, producing a particle shell that prevents the particles from aggregating.
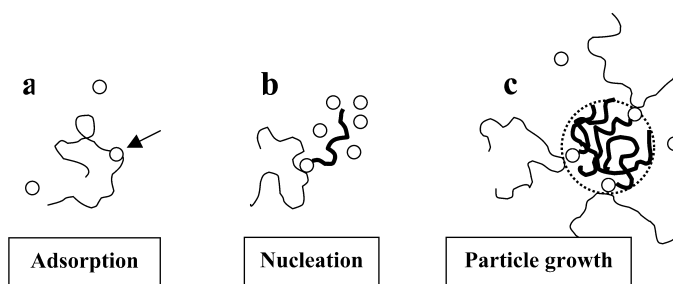

Fig. 3 The model of *colloidal particle* formation: (a) aniline oligomers (open circles) adsorb at the stabilizer chain (thin line) and (b) they stimulate the growth of a PANI chain (thick curve). A nucleus is produced. (c) Other oligomers and new PANI chains are produced close to the nucleus. The colloidal particle grows.

EXPERIMENTAL

The workers constituting the core of the task group have carried out the preparation of PANI films and colloids following the instructions given below. This study extended the preparation of PANI powders reported previously [4]. Most participants had previous experience with the preparation of PANI; some of them prepared PANI for the first time. Every worker used commonly available chemicals, except the PVP stabilizer, which was of the same origin in all cases. The films and colloids have been collected in the Institute of Macromolecular Chemistry in Prague and characterized with respect to optical spectra and colloidal particle size. The conductivity of films was determined at the Charles University in Prague.

Polyaniline films

Aniline hydrochloride (0.2 mol l^{-1}) was oxidized with ammonium peroxydisulfate (0.25 mol l^{-1}) [4] in aqueous solution to prepare PANI. Aniline hydrochloride (259 mg) and ammonium peroxydisulfate

(571 mg) were separately dissolved in water, each to 5 ml of solution. A larger volume of the reaction mixture was prepared when necessary to produce PANI films on glass supports. These were 13 mm in diameter and 1 mm thick, and were made to adhere to an adhesive tape to allow for the coating of the glass on one side only. The polymerization of aniline was started at room temperature, close to 20 °C, by mixing solutions of aniline and oxidant, and pouring the solution over the glass supports in a Petri dish. The mixture was not stirred. The polymerization was completed within 10 min. The glasses were rinsed with 0.2 mol l^{-1} HCl to remove the adhering PANI precipitate, separated from the tape, rinsed with acetone, and left to dry in air. Some film preparations have also been carried out in 1 mol l^{-1} HCl instead of water.

The optical spectra of PANI films have been recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). The thickness of the films, d_f, was estimated from the optical absorption at 400 nm, A (400 nm), by using the relation d_f/nm = 185 A (400 nm) determined earlier [63] on the basis of optical interferometry calibration. The conductivity of films was measured by a four-point van der Pauw method [63].

Polyaniline dispersions

To produce PANI colloids, aniline hydrochloride (0.2 mol l^{-1}) was oxidized with ammonium peroxydisulfate (0.25 mol l^{-1}) [4] in the presence of a stabilizer, 2 mass % poly(*N*-vinylpyrrolidone) (PVP; Fluka, type K90, M_r = 360 000). Aniline hydrochloride (259 mg) was dissolved in an aqueous solution of PVP (40 g l^{-1}), instead of water, to 5 ml of solution. The polymerization of aniline was started at room temperature close to 20 °C by adding 5 ml of aqueous solution containing 571 mg ammonium peroxydisulfate. The mixture was briefly stirred and left at rest to polymerize. The polymerization was finished in several minutes.

The colloidal dispersion was diluted 60 times with 1 mol l^{-1} HCl, and the particle diameter was determined by dynamic light scattering with an Auto-Sizer Lo-C (Malvern, UK). The apparatus also provides a parameter characterizing the polydispersity, a relative standard deviation of the particle size distribution. The optical spectra of PANI colloids have been recorded in some cases with a Lambda 20 spectrometer (Perkin Elmer, UK) after 60 times dilution with 1 mol l^{-1} HCl.

Compositional analysis of dispersion

A mixture of prepared dispersions was placed in Spectra/Por1 membrane tubing (Spectrum Medical Industries, USA) and exhaustively dialyzed against 0.2 mol l^{-1} HCl to remove ammonium sulfate resulting from the decomposition of ammonium peroxydisulfate and a potential residual monomer. The dilution accompanying this process has been determined from the change in the optical absorption. The dialyzed dispersion was then centrifuged for 15 h at 20 000 rpm using a SW 25.1 rotor in a Beckman L-55 preparative centrifuge. The colorless supernatant liquid was separated and evaporated on a Petri dish to determine the content of free stabilizer, 87 mass % of the original PVP introduced into the reaction mixture. Thus, only a fraction of the PVP has been incorporated into dispersion particles. The green sediment was redispersed in 0.2 mol l^{-1} HCl and also dried on a Petri dish to determine the concentration of dispersion particles. From the mass balance, it was found that dispersion particles contain 89.7 mass % PANI hydrochloride, the rest being PVP. Based on this analysis, the concentration of PANI in the original dispersion was found to be 2.06 mass %. Spectrophotometric determination using the calibration reported earlier [64] gave 2.16 mass %. The theoretical expectation for 100 % polymerization yield is 2.17 mass % [4]. This means that the conversion of aniline to colloidal PANI was practically complete.

RESULTS AND DISCUSSION

Polyaniline films

The fact that PANI film spreads from the various nuclei is probably responsible for the observed globular film morphology (Fig. 4). This morphology is partly a result of secondary nucleation, and the growth of a PANI film on an already existing film [22,28].
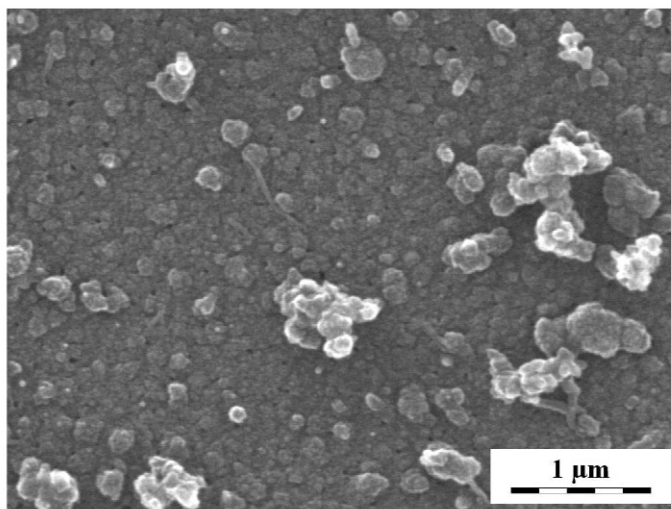

Fig. 4 A micrograph of a PANI film surface.

Optical properties

The PANI films on glass were characterized at first with respect to their optical properties (Table 1). Each project participant prepared typically 10–15 films during a single polymerization. The spectra of the films are characterized by two maxima (Fig. 5). These are located at wavelengths of 356 and 843 nm
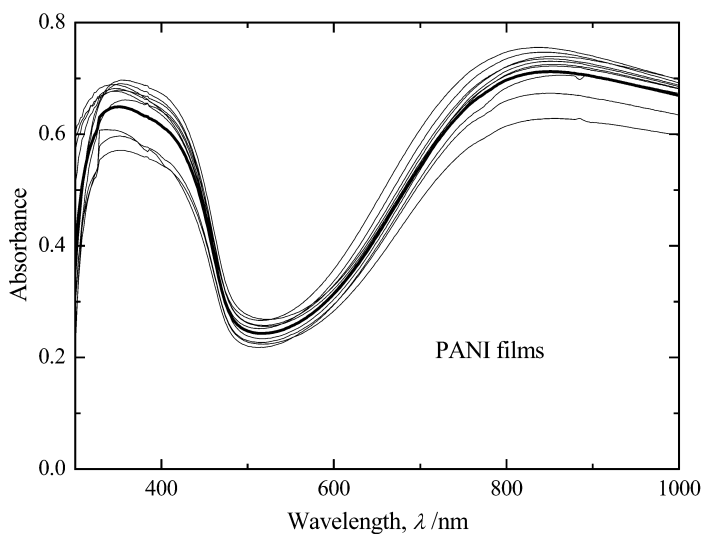

Fig. 5 Spectra of PANI films deposited on 10 glass supports in situ during a single polymerization of aniline hydrochloride in water. The averaged spectrum is shown by a thick line.

(Table 1), their absorbance ratio being A (843 nm)/A (356 nm) = 1.09. The absorbance at 400 nm, A (400 nm), served as a tool to determine the film thickness, d_f, by using the relation d_f/nm = 185 A (400 nm). The average film thickness was 125 ± 9 nm (Table 2).

Table 1 Optical properties of n polyaniline films prepared by various workers (A–D): absorbances A at two local maxima at wavelengths λ in visible region of the spectra.

Worker	n	A_1	λ_1/nm	A_2	λ_2/nm
Polymerization in water					
A	10	0.585	354	0.624	858
B	10	0.735	376	0.865	810
C	14	0.897	344	0.946	852
D	11	0.649	350	0.712	852
Average		*0.717*	*356*	*0.785*	*843*
Polymerization in 1 mol l⁻¹ HCl					
A	11	0.659	359	0.783	836
B	11	0.562	368	0.626	858
Average		*0.610*	*363*	*0.704*	*847*

Table 2 Average thickness, d_f, and conductivity, σ, and their standard deviations Δ of n polyaniline films deposited on glass[a] by various workers (A–E).

Worker	n	d_f/nm	Δd_f/nm	σ/S cm⁻¹	$\Delta\sigma$/S cm⁻¹
Polymerization in water					
A	10	104	5	2.13	0.24
B	10	131	10	1.64	0.36
C	10	150	12	2.21	0.75
D	10	114	9	3.05	1.27
E	48	–	–	3.97	0.24
Average		*125*	*9*	*2.60*	*0.67*
Polymerization in 1 mol l⁻¹ HCl					
A	13	115	14	12.6	6.9
B	13	102	6	11.9	3.3
C	14	–	–	20.9	7.3
D	15	–	–	31.5	16.1
E	10	–	–	17.1	1.8
Average		*109*	*10*	*18.8*	*7.1*

[a]Glass supports were immersed in an aqueous mixture containing 0.2 mol l⁻¹ aniline hydrochloride and 0.25 mol l⁻¹ ammonium peroxydisulfate at room temperature (~20 °C). Some polymerizations were made in 1 mol l⁻¹ HCl instead of water.

Traces of the adhering precipitate increased the optical absorption and thus also the apparent average thickness. On the other hand, scratches and other defects in the film surface resulted in an apparent decrease of the film thickness. The effect of defects on the spectra can be illustrated by Fig. 5. The standard deviation of the thickness in each series of films produced in a single polymerization was low,

below 12 %. The average film thickness, however, differed somewhat more for the individual participants (Table 2). This is probably caused by small differences in the preparation procedure, e.g., during rinsing the films after polymerization.

The similar results have been obtained for the films prepared in 1 mol l^{-1} HCl instead of water (Table 1). The absorption maxima were located at wavelengths of 363 and 847 nm (Table 1), the absorbance ratio being A (847 nm)/A (363 nm) = 1.15. The average film thickness, 109 ± 10 nm, is about the same as that of a film prepared in water considering the experimental error of the thickness determination. The absorption spectra of both types of the films are virtually identical.

Electrical properties

The conductivity of the films was determined as the next step. The average film thickness (Table 2) was used to recalculate the sheet conductivity to the conductivity of PANI film. We can conclude that the average conductivity of the films prepared in water, $\sigma = 2.6 \pm 0.7$ S cm^{-1}, is comparable with the conductivity of the PANI precipitate, $\sigma = 4.4 \pm 1.7$ S cm^{-1} [4]. The films prepared in 1 mol l^{-1} HCl had the average conductivity $\sigma = 18.8 \pm 7.1$ S cm^{-1}, within experimental error, again similar to the conductivity of the PANI precipitate isolated under the same conditions, $\sigma = 11.9 \pm 5.2$ S cm^{-1} [4]. The observation that the conductivity of PANI in the thin films and in compressed pellets is comparable has earlier been reported in the literature [63]. The standard deviation in the conductivity determination is higher than with the film thickness (26 and 38 %, cf. Table 2). The electrical properties are more sensitive to defects than the optical properties; a thin scratch need not dramatically reduce the optical absorption, but it may restrict electric contact between two parts of the film.

Polyaniline dispersions

PANI is obtained as a precipitated powder in a typical polymerization of aniline [4]. When such a polymerization is carried out in the presence of a suitable water-soluble polymer, such as PVP, the polymerization proceeds in a dispersion mode [65,66] and PANI colloids are obtained. Poly(*N*-vinylpyrrolidone) has been successfully used in the literature to stabilize PANI colloids [26,67–71].

The colloidal particles have irregular rice-grain morphology and a marked polydispersity in size (Fig. 6). Each participant has typically prepared 3 separate colloidal dispersions (Table 3). All workers involved in the experiments have succeeded in preparing a colloid. The average particle size of all 30 dispersions was 241 ± 50 nm, the polydispersity index being 0.26 ± 0.12. The preparation of the col-
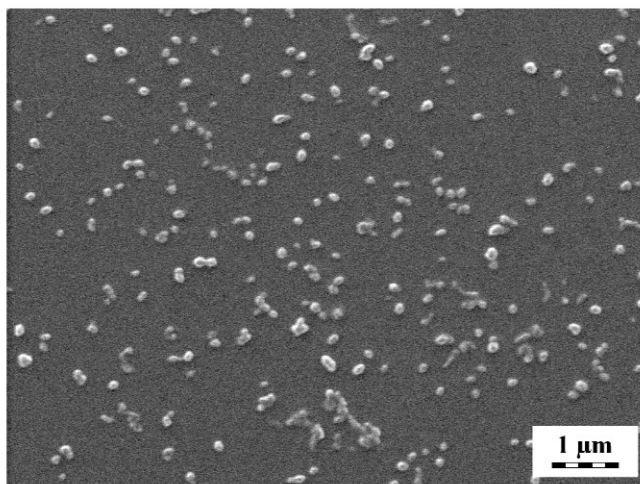

Fig. 6 A micrograph of PVP-stabilized colloidal PANI particles.

Table 3 Average particle diameter, *D*, and average polydispersity in size[a], *P*, of *n* colloidal polyaniline dispersions stabilized with PVP[b] prepared by various participants (A–I).

Worker	*n*	*D*/nm	*P*
A	3	220.6	0.231
B	5	208.4	0.195
C	3	230.0	0.126
D	3	236.6	0.221
E	3	213.0	0.353
F	1	226.0	0.360
G	5	228.6	0.290
H	4	254.5	0.190
I	3	362.0	0.530
Average		*240.5 ± 50.1*	*0.264 ± 0.116*

[a]Relative width of the particle-size distribution ranging from 0 (= monodisperse particles) to 1 (= extreme polydispersity in the size).
[b]Polymerizations have been carried out at room temperature (~20 °C) in the mixtures containing 0.2 mol l^{-1} aniline hydrochloride, 0.25 mol l^{-1} ammonium peroxydisulfate, and 2 mass % poly(*N*-vinylpyrrolidone).

loidal form of PANI can thus be regarded as well reproducible. The optical spectra of the dispersions (Fig. 7) are similar to those of the films (Fig. 5). When characterized in 1 mol l^{-1} HCl, the absorption maxima are found at 392 and 854 nm, the absorbance ratio being *A* (854 nm)/*A* (392 nm) = 1.15. They are identical for the individual dispersions, and small differences in absorbance can be attributed to small fluctuations in the dilution procedure. It should be noted that dispersions are not produced if the polymerization has been carried out in 1 mol l^{-1} HCl instead of water.
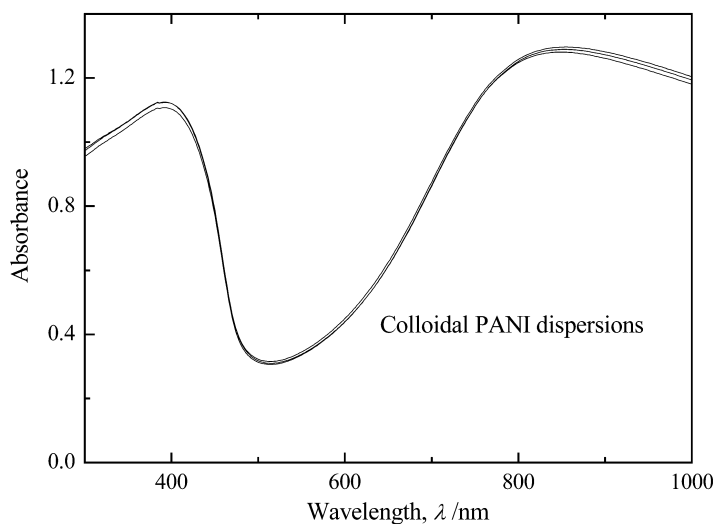

Fig. 7 Visible spectra of three colloidal PANI dispersions diluted 60 times with 1 mol l^{-1} HCl and recorded in a cell of 0.1 mm thickness.

SUMMARY AND CONCLUSIONS

Participants in several laboratories prepared two supramolecular forms of PANI, thin films and colloidal dispersions. PANI films grow during the polymerization of aniline hydrochloride on glass immersed in a reaction mixture. PANI precipitate is produced later in the surrounding aqueous phase. The formation of films on several glass supports is highly reproducible within a single polymerization, but larger differences have been observed when the polymerization was carried out independently by five workers. Altogether, 88 films prepared in water and 65 films in 1 mol l^{-1} HCl have been characterized. The average thickness of the films prepared in water was 125 ± 9 nm, about the same as that of films prepared in 1 mol l^{-1} HCl, 109 ± 10 nm, considering the experimental error of the thickness determination. The conductivity of films prepared in water, 2.6 ± 0.7 S cm^{-1}, is close to the conductivity of the PANI precipitate. The conductivity of the films improved to 18.8 ± 7.1 S cm^{-1} when the polymerization was carried out in 1 mol l^{-1} HCl instead of water. The optical properties and film thickness did not depend on the reaction medium under investigation.

When the polymerization mixture included poly(N-vinylpyrrolidone), colloidal dispersions were produced instead of a PANI precipitate. All nine participants were able to prepare the colloidal form of PANI. The average particle size in 30 prepared dispersions, 241 ± 50 nm, varied only slightly when various individuals carried out the polymerization.

ACKNOWLEDGMENTS

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