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POLYANILINE. PREPARATION OF A CONDUCTING POLYMER

(IUPAC Technical Report)

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Polyaniline. Preparation of a conducting polymer

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Abstract: Eight persons from five institutions in different countries carried out polymerizations of aniline following the same preparation protocol. In a "standard" procedure, aniline hydrochloride was oxidized with ammonium peroxydisulfate in aqueous medium at ambient temperature. The yield of polyaniline was higher than 90 % in all cases. The electrical conductivity of polyaniline hydrochloride thus prepared was 4.4 ± 1.7 S cm^{-1} (average of 59 samples), measured at room temperature. A product with defined electrical properties could be obtained in various laboratories by following the same synthetic procedure. The influence of reduced reaction temperature and increased acidity of the polymerization medium on polyaniline conductivity were also addressed. The conductivity changes occurring during the storage of polyaniline were monitored. The density of polyaniline hydrochloride was 1.329 g cm^{-3}. The average conductivity of corresponding polyaniline bases was 1.4×10^{-8} S cm^{-1}, the density being 1.245 g cm^{-3}. Additional changes in the conductivity take place during storage. Aging is more pronounced in powders than in compressed samples. As far as aging effects are concerned, their assessment is relative. The observed reduction in the conductivity by ~10 % after more than one-year storage is large but, compared with the low conductivity of corresponding polyaniline (PANI) base, such a change is negligible. For most applications, an acceptable level of conductivity may be maintained throughout the expected lifetime.

INTRODUCTION

Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties [1–4]. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 10^0 S cm^{-1}, many orders of magnitude higher than that of common polymers ($<10^{-9}$ S cm^{-1}) but lower than that of typical metals ($>10^4$ S cm^{-1}). Protonated PANI, (e.g., PANI hydrochloride) converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide [2] (Fig. 1).
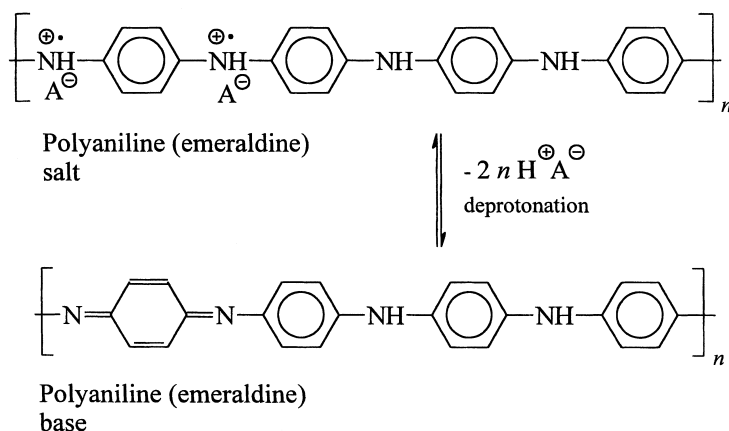
Fig. 1 Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. A$^-$ is an arbitrary anion, e.g., chloride.

The changes in physicochemical properties of PANI occurring in the response to various external stimuli are used in various applications [5–6], e.g., in organic electrodes, sensors, and actuators [7–9]. Other uses are based on the combination of electrical properties typical of semiconductors with materials parameters characteristic of polymers, like the development of "plastic" microelectronics [6,10], electrochromic devices [11], tailor-made composite systems [12,13], and "smart" fabrics [14]. The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance.

Project description

The present project has been inspired by an occasionally expressed opinion that "there are as many polyanilines as the number of people who prepare them" and attempting to check whether and to what extent this hypothesis is true. Polyaniline was therefore prepared at various laboratories by experimentalists of various levels of experience who were following the same written instructions. Some prepared PANI for the first time in their lives while others had extensive prior experience in this preparation. The electrical conductivity was taken as the basic criterion for the assessment of the products.

The polymerization of aniline was designed to be as simple as possible. The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulfate (Fig. 2) at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. The goal of this study was to prepare PANI with a defined conductivity, not necessarily the highest possible.

The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI; the resulting PANI, protonated with various acids, differs in solubility, conductivity, and stability [3]. For the present study, we have selected hydrochloric acid in equimolar proportion to aniline, i.e., aniline hydrochloride was used as a monomer. The handling of solid aniline salt is preferred to liquid aniline from the point of view of toxic hazards. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt was preferred to the potassium counterpart because of its better solubility in water. The concentration of aniline hydrochloride was set to 0.2 M. Various oxidant/monomer ratios have been used in the literature [15]. To minimize the presence of residual aniline and to obtain the best yield of PANI, the stoichiometric peroxydisulfate/aniline ratio 1.25 is recommended [15] (Fig. 2). The polymerization is completed within 10 min at room temperature and within 1 h at 0–2 °C [16]. The oxidation of aniline is exothermic so the temperature of the reaction mixture can be used to monitor the progress of reaction [16–18]. Temperature profile is well reproducible. Figure 3 shows a typical course of polymerization recorded at the Institute of Macromolecular

$$4\,n \left\langle\bigcirc\right\rangle\!\!-\!NH_2.HCl \quad + \quad 5\,n\,(NH_4)_2S_2O_8 \quad \longrightarrow$$

$$\left[-NH-\left\langle\bigcirc\right\rangle\!\!-\!\!\overset{\oplus\,\bullet}{\underset{Cl^\ominus}{NH}}\!\!-\!\left\langle\bigcirc\right\rangle\!\!-\!NH-\left\langle\bigcirc\right\rangle\!\!-\!\!\overset{\oplus\,\bullet}{\underset{Cl^\ominus}{NH}}\!\!-\!\left\langle\bigcirc\right\rangle\!\!-\right]_n$$

$$+\,2\,n\,HCl \quad +\,5\,n\,H_2SO_4 \;+\,5\,n\,(NH_4)_2SO_4$$
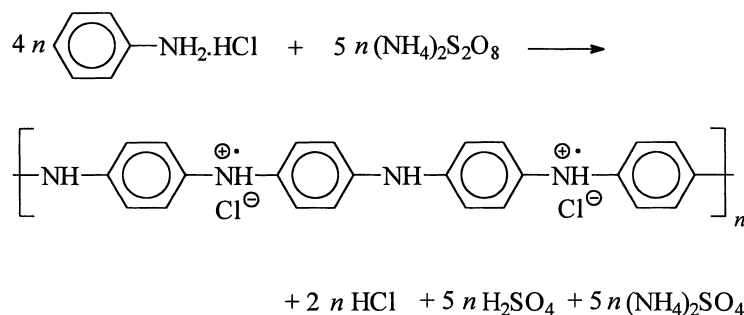
Fig. 2 Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields polyaniline (emeraldine) hydrochloride.
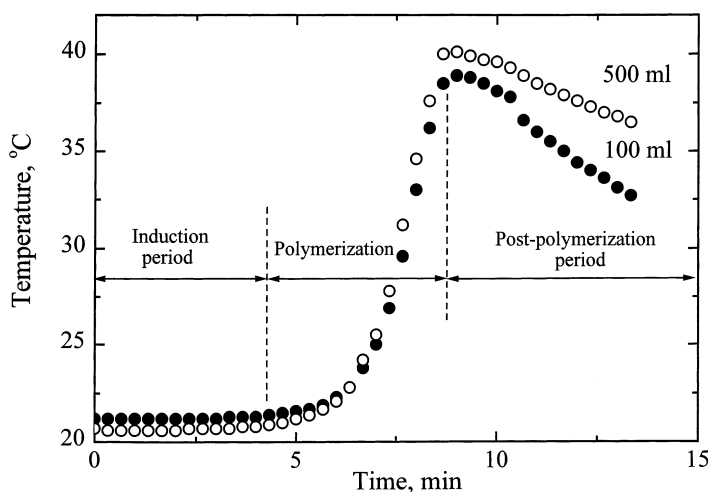
Fig. 3 Temperature profile in the polymerization of aniline. 0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate in 100 ml or 500 ml of aqueous medium. The oxidation was started at room temperature.

Chemistry in Prague. After an induction period, polymerization commences and the temperature of the reaction mixture increases; it passes through a maximum after the reaction is finished, and the medium cools down (Fig. 3). Polymerizations using aniline concentrations over 1 M, especially when carried out in large volumes (over 0.5 L), can result in the overheating of the system, followed by an explosion [19]. Such reaction conditions should be avoided.

EXPERIMENTAL PART

"Standard" preparation of polyaniline

Project participants followed the same instructions to oxidize 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in aqueous medium. Aniline hydrochloride (purum; 2.59 g, 20 mmol) was dissolved in distilled water in a volumetric flask to 50 mL of solution. Ammonium peroxydisulfate (purum; 5.71 g, 25 mmol) was dissolved in water also to 50 mL of solution. Both solutions were kept for 1 h at room temperature (~18–24 °C), then mixed in a beaker, briefly stirred, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with three 100-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in vacuo at 60 °C. Polyanilines prepared under these reaction and processing conditions are further referred to as "standard" samples. Additional polymerizations were carried out in an ice bath at 0–2 °C. The acidity of the reaction mixture was increased by replacing 10 mL of water with 10 mL of 10 M HCl in several experiments.

Characterization of polyaniline

Conductivity of all samples was measured at room temperature by a four-probe method on pellets compressed at 700 MPa, 13 mm in diameter and 1–1.5 mm thick, using a Keithley 237 high-voltage current source and Keithley 2010 low-noise multimeter [12]. The Archimedes method was used to determine the polymer density by weighing the pellets in air and in decane at 20 °C with a Sartorius Research R160P balance.

RESULTS AND DISCUSSION

Preparation conditions

Polyaniline of higher molar mass is produced at lower reaction temperatures [19–21], but the electrical properties of the polymer are not greatly influenced by molar mass. We have selected ambient temperature for the present study while being aware of the ambiguous definition of such conditions. As temperature increases during the reaction, this increase being dependent on the surface-to-volume ratio of the experimental set-up (Fig. 3), the precise control of temperature was not attempted. The effect of reaction temperature on the conductivity of PANI was assessed and is discussed. Polymerization in the presence of excess 1 M HCl, i.e., at higher acidity, proceeds faster than in its absence and yields a product of enhanced conductivity. A still higher concentration of HCl above 2 M concentration leads to the reduction of conductivity [22]. The rate of aniline oxidation depends on the presence of various impurities and additives that may promote the progress of oxidation [16,23]. Distilled water was used; the potential presence of iron(III) ions in tap water may accelerate the aniline oxidation. Washing the PANI precipitate with 0.2 M HCl removes residual monomer, oxidant, and its decomposition products. The treatment with hydrochloric acid solution provides a more uniform protonation of PANI with chloride counterions, although some of the sulfate or hydrogensulfate anions from the decomposition of peroxydisulfate also participate as counterions. A final washing with acetone removes low-molecular-weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitate during drying, and the product is obtained as a fine powder. The greenish PANI (emeraldine) hydrochloride was stored in polyethylene containers.

Conductivity of polyaniline

Synthesis of polyaniline in various laboratories

Standard polymerizations of aniline have been made by eight individuals from five institutions in five different countries (Table 1). The project participants followed written instructions given in the Experimental Part. The PANI powders were collected from all participants at the Institute of

Table 1 Conductivity of polyaniline hydrochloride prepared according to the same "standard" recipe[a] at different institutions (A–E) and by various persons (1,2).

Institution –person	Number of samples	Conductivity[b] ($S\ cm^{-1}$)	Standard deviation ($S\ cm^{-1}$)
A–1	5	5.10	1.16
A–2	4	3.82	0.25
A	**9**	**4.53**	**1.08**
B–1	35	4.50	1.56
B–2	3	6.98	0.59
B	**38**	**4.70**	**1.64**
C–1	2	2.37	1.01
C–2	1	2.07	0
C	**3**	**2.27**	**0.35**
D	**6**	**2.08**	**0.37**
E	**3**	**6.41**	**0.66**

[a]0.2 M aniline hydrochloride, 0.25 M ammonium peroxydisulfate, room temperature (~20 °C), 100 ml reaction volume. Cf. Experimental Part.
[b]The average conductivity of all samples prepared by an experimentalist. A similar average of samples prepared within an institution is given in bold.

Macromolecular Chemistry in Prague, compressed into pellets, and subjected to the determination of conductivity at Charles University Prague within three weeks of preparation.

The average conductivity of 59 samples prepared by all participating laboratories (Table 1) was 4.37 S cm^{-1} (standard deviation 40 %). This is comparable with the average obtained by a single person who prepared 35 samples of average conductivity 4.50 S cm^{-1} (standard deviation 39 %). This means that it was not significant whether experiments were made by one person or by more individuals. Virtually the same results were achieved by experimentalists highly experienced in the preparation of PANI and by those who prepared PANI for the first time. The results slightly differed within each institution, even if the same batch of chemicals was used for the preparation, but a low number of samples does not allow one to make statistically significant conclusions.

Effect of reaction conditions

A series of polymerizations was made at altered conditions (Table 2), and the results are summarized in Table 3. The reduction of starting reaction temperature to 0–2 °C nearly doubled the conductivity of the resulting PANI to a value of 7.58 S cm^{-1} (standard deviation 35 %) (Table 3). Higher acidity of the reaction medium also led to the increase in the conductivity to 11.9 S cm^{-1} (standard deviation 43 %) (Table 3). Both trends are in accordance with data reported in the literature [19,21]. The reduction of temperature in the acidic media had, however, no marked effect on PANI conductivity (Table 3). The standard deviation of about 40 % is accepted as being typical for the products of aniline polymerizations made under simple experimental conditions.

Polymerization carried out in a five-fold reaction volume yielded product of relatively low conductivity (Table 2), but still within the experimental error associated with the standard polymerization (Table 3). This decrease in conductivity could be explained, e.g., by the elevation of reaction temperature. The lower surface-to-volume ratio in 500 mL batches and the consequent reduced heat loss lead to a slightly increased temperature at the end of reaction and to a slower cooling during the post-polymerization period compared with the standard polymerization (Fig. 3) but the differences in temperature profile are small. The reduced conductivity of the product is more likely to be attributed to less efficient washing of the larger quantities of PANI processed after polymerization.

Table 2 Effect of reaction conditions on the conductivity of PANI hydrochloride.

Institution –person	Number of samples	Conductivity (S cm^{-1})	Standard deviation (S cm^{-1})
Polymerization at ~0 °C (instead of room temperature)			
A–1	3	6.58	0.71
B–2	3	8.40	0.38
D	3	4.33	1.77
E	3	11.0	0.31
Polymerization in the presence of excess 1 M HCl			
A–1	7	8.98	2.63
A–2	3	9.04	6.08
B–2	3	17.0	2.52
E	3	16.5	5.17
Polymerization in 500 ml reaction volume (instead of 100 ml)			
A–1	3	3.29	0.19

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate.

Table 3 Average conductivity of PANI hydrochlorides and PANI bases at 20 °C and the polymerization yield (numbers of prepared samples are given in parentheses).

Reaction conditions[a]	Conductivity (S cm^{-1})		Yield (%)
	PANI hydrochloride	PANI base	
~20 °C	4.37 ± 1.74 (59)	$(6.0 ± 1.8) \times 10^{-11}$ (4)	97.9 ± 3.4 (12)
~0 °C	7.58 ± 2.63 (12)	$(8.3 ± 0.3) \times 10^{-8}$ (4)	102.1 ± 2.5 (10)
+ 1 M HCl, ~20 °C	11.90 ± 5.17 (16)	$(3.9 ± 1.4) \times 10^{-9}$ (4)	90.7 ± 0.8 (9)
+ 1 M HCl, ~0 °C	9.83 ± 0.51 (4)	$(2.5 ± 1.9) \times 10^{-8}$ (4)	95.0 ± 1.8 (4)

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at given temperature and in the presence of excess HCl when specified.

Polyaniline base

The conductivity of PANI bases is many orders of magnitude lower compared to that of PANI "salts" (Table 3) and ranks them among nonconducting materials. The average conductivity of 16 samples was 1.4×10^{-8} S cm^{-1}. Moreover, there are variations in the conductivity of PANI bases, depending on the method of preparation. The lowest conductivities of the order of 10^{-11} S cm^{-1} have been obtained by the deprotonation of standard PANI hydrochlorides. Systematic research on the preparation of PANI bases is required, and it would be premature to draw any conclusion on the basis of the present results.

Processing and characterization effects

Pelletization

There are additional factors influencing the conductivity of PANI to be briefly mentioned. Several pellets were prepared from a given sample of the PANI hydrochloride powder, and their conductivity was determined. The first sample had average conductivity of 2.58 ± 0.06 S cm^{-1} on 21 measured pellets, i.e., a standard deviation 2.5 %. The second sample had an average conductivity of 12.65 ± 0.54 S cm^{-1} when measuring 11 pellets, i.e., relative standard deviation 4.3 %. This means that differences less than ±5 % in the conductivity can be assigned to the pelletization effect.

Temperature of conductivity measurement

The temperature coefficient of resistivity is ca. –0.004 Ω cm K^{-1} at 20–30 °C range. If the room temperature randomly fluctuated ±5 °C, the measured values of conductivity, e.g., 1.5 S cm^{-1}, would have a standard deviation of ±3.5 % because of this effect alone.

Storage of samples

Suspensions: In repeated polymerizations, portions of the PANI suspensions from 40 standard polymerizations, produced over a period of three months, were successively collected and stored in a single vessel and only then isolated, washed, and dried. The conductivity of the PANI thus obtained was 5.23 ± 0.40 S cm^{-1} (5 pellets), indicating that prolonged storage in acidic aqueous medium did not have any pronounced effect on the electrical properties of PANI.
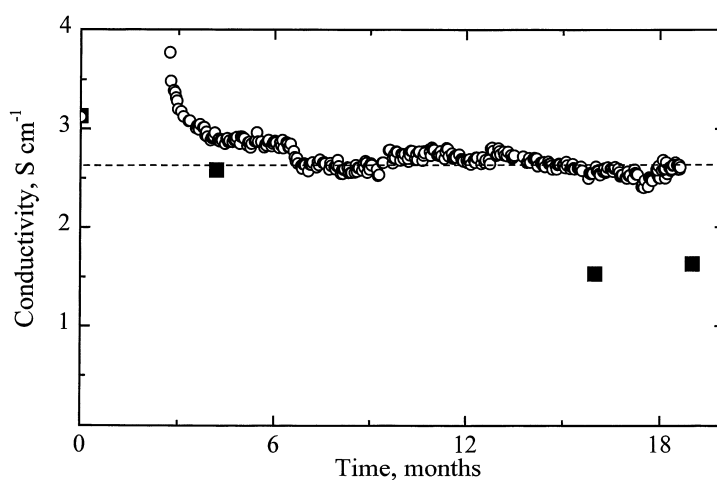
Powders: In another experiment, pellets were compressed after some time from the dry PANI powders stored in polyethylene containers. A general decrease in the conductivity is observed (Table 4). After 16 months of storage, the conductivity of a standard PANI has dropped to 48 % of the original conductivity and for a more conducting sample prepared in excess HCl to 70 % of the original level. An increase in the conductivity of the latter sample after 4 months was noted (Table 4), but cannot be unambiguously explained. We can speculate that, e.g., an uptake of moisture during the storage of the well-dried sample could be responsible for such a change.

Pellets: It may be anticipated that the aging would be reduced if the PANI were stored as compressed pellets. Monitoring the conductivity of a set of compressed pellets showed an initial increase in

Table 4 Changes of conductivity during the storage of PANI hydrochloride powder.

Storage time	Conductivity[a] (S cm^{-1})	
	Standard PANI	PANI prepared in excess 1 M HCl
3 days	3.20 ± 0.04	9.94 ± 0.27
4 months	2.59 ± 0.06	12.70 ± 0.34
16 months	1.53 ± 0.03	6.91 ± 0.14
19 months	1.63 ± 0.02	6.87 ± 0.41

[a]Samples prepared by the polymerization at room temperature. Powder was compressed to pellets after specified storage time. Conductivity measurement on 5 pellets.

Fig. 4 Conductivity aging of PANI hydrochloride as a pellet (open circles) and as a powder occasionally compressed into a set of pellets (full squares).

conductivity followed by a steady decline and, after about 7 months, the conductivity leveled off (Fig. 4). When a corresponding powder was compressed into pellets at various time intervals, these always had a lower conductivity than the pellets prepared after PANI preparation. This again confirms the hypothesis that the aging is less pronounced in compressed PANI samples.

Even after a long-term storage, the conductivity remains more than 10^8-times higher than the conductivity of PANI base (Table 3) and, in this sense, the conductivity change during storage may be considered as being negligible. For many applications, it is important that electric parameters are maintained at an operative level during their lifetime, and such demands need not be difficult to meet.

Other properties of polyaniline

Polymerization yield

Based on the stoichiometry of the oxidation reaction (Fig. 2), the polymerization of 1.0 g aniline hydrochloride yields theoretically 0.840 g of PANI hydrochloride. The apparent yield of PANI hydrochloride under the standard polymerization conditions approaches 100 % within the experimental error (Table 3). The elemental analysis indicates (Table 5) that more bulky counterions, like sulfate

Table 5 Elemental composition of PANI.

Reaction conditions[a]	% C	% H	% N	% Cl	% S
Polyaniline hydrochloride					
Standard	59.7	4.9	10.6	11.1	1.0
+ 1 M HCl	59.6	4.8	10.6	12.1	0.5
Expected [b]	*66.2*	*4.6*	*12.9*	*16.3*	*–*
Polyaniline base (obtained after deprotonation of polyaniline hydrochloride)					
Standard	75.0	5.0	13.9	0.6	0.3
+ 1 M HCl	74.0	4.8	13.6	2.3	0.3
Expected [b]	*79.5*	*5.0*	*15.5*	*–*	*–*

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at room temperature and in the presence of excess HCl as specified.
[b]Based on formulae shown in Fig. 1.

or hydrogensulfate anions, may participate in the protonation of PANI along with the chloride anions. This would lead to an apparent increase in the yield. The yield is higher when the polymerizations are carried out at reduced temperature. Increased acidity of the reaction medium leads, on the other hand, to its reduction.

Elemental composition
The differences in elemental composition of PANI prepared under standard conditions and in an excess of 1 M HCl are small (Table 5). The results of elemental analysis clearly indicate the presence of oxygen in PANI (12.5 % in hydrochloride and 5.1 % in the base). This may be due to bound water molecules or, more likely, to partial oxidation of the PANI chains. The structure depicted in Fig. 1 is thus idealized. The presence of sulfur in hydrochlorides is partly due to the residual sulfate counterions produced by the reduction of peroxydisulfate during polymerization (Fig. 2).

Hydrochloric acid is removed from the aniline hydrochloride after deprotonation with ammonium hydroxide (Fig. 1). The relative participation of carbon and nitrogen in PANI base is thus increased, at the expense of the lower content of chlorine. We can see that some chlorine remains in PANI base even after deprotonation, indicating a partial benzene-ring substitution with chlorine [24]. The content of covalently bound chlorine is higher when the oxidation of aniline hydrochloride takes place in excess HCl (Table 5). Partial sulfonation of benzene rings is responsible for the presence of sulfur in the PANI base (Table 5).

Density
The average value of PANI hydrochloride density found on all 94 pellets prepared from various samples was 1.329 ± 0.027 g cm^{-3} at 20 °C. The method of preparation had no significant effect on the density of PANI (Table 6). The density determined on 27 and 19 pellets compressed from two single PANI

Table 6 Density of polyaniline hydrochloride and PANI base at 20 °C (number of prepared samples is given in parentheses).

Reaction conditions[a]	Density (g cm^{-3})	
	PANI hydrochloride	PANI base
~20 °C	1.333 ± 0.016 (54)	1.244 ± 0.008 (4)
~0 °C	1.323 ± 0.046 (24)	1.242 ± 0.007 (4)
+ 1 M HCl, ~20 °C	1.326 ± 0.014 (13)	1.250 ± 0.002 (4)
+ 1 M HCl, ~0 °C	1.322 ± 0.007 (3)	1.243 ± 0.007 (4)

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at given temperature and in the presence of excess HCl as specified.

powders yielded the standard deviation of 0.008 g cm^{-3} (0.6 %) in both cases. Polyaniline sulfate has a density of 1.43 g cm^{-3} [25]. An inconclusively higher density of samples prepared in the absence of excess HCl may thus be assigned to partial protonation with sulfate counterions. The average density of 16 PANI bases was 1.245 ± 0.006 g cm^{-3}.

CONCLUSIONS

Each participant in the project succeeded in preparing conducting polyaniline, regardless of the level of previous experience. A standard deviation of 40 % in the conductivity of polyaniline was typical for a set of polymerizations. Differences less than 5 % can be attributed to the pelletization effect. Considering the variability of reaction conditions, sample processing, and uncertainties introduced in electrical measurements, a single value of conductivity cannot be assigned to the PANI samples produced by the method adopted here. A statement that products of a "standard" polymerization have the conductivity of the order of 10^0 S cm^{-1}, occasionally exceeding a value of 10 S cm^{-1}, best reflects reality. Any quantitative data should be supplemented by additional information: PANI prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate at room temperature within a few days after preparation has a conductivity of 4.4 ± 1.7 S cm^{-1} (average of 59 samples), measured at room temperature.

ACKNOWLEDGEMENT

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