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Solid-State Protonation and Electrical Conductivity of Polyaniline

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ABSTRACT: Polyaniline base was protonated by blending with camphorsulfonic and picric acids in the solid state. The electrical conductivity of the equimolar mixture was more than 10^7 times higher compared with the conductivity of components used for blending. The electrical conductivity still increased several times after heating of mixtures to 85 °C. The protonation is reflected by the changes in the infrared spectra. The dependences of the electrical conductivity on the composition of blends differ for the partly protonated polyaniline and mixtures of protonated polyaniline with an excess acid.

Introduction

The protonation of polyaniline[1,2] (PANI) with organic acids can be used for the preparation of electrically conducting polymers with improved processibility.[3,4] Sulfonic acids have often been employed for the preparation of soluble products: Polyaniline dodecylbenzenesulfonate was reported to be soluble in toluene,[3,4] PANI protonated with *p*-phenolsulfonic acid in dimethyl sulfoxide,[5] etc. Protonations of polyaniline base with cresolsulfonic acid,[6] *p*-toluenesulfonic acid,[7,8] methanesulfonic acid,[9−11] and other sulfonic acids[4] were used to produce electrically conducting polymers partly soluble in various solvents. Polyaniline protonated with camphorsulfonic acid (CSA) has a good solubility in *m*-cresol.[3,4,11−13]

Electrical conductivity of films cast from solutions of polyaniline camphorsulfonate (PANI−CSA) in *m*-cresol,[4,12,14−16] $\sigma \sim 10^2$ S cm^{-1}, is about 2 orders of magnitude higher than that of polyaniline protonated with mineral acids,[6,8,14,17,18] $\sigma \sim 10^{-1}-10^1$ S cm^{-1}, and other organic acids.[4] This observation raised an interest in understanding the conduction mechanism of these materials.[19,20] Also optical properties[21] and morphology[22] of PANI−CSA have been recently investigated. Camphorsulfonic acid has therefore been selected for the present study of PANI protonation.

We have recently observed that, besides sulfonic acids, picric acid (PA; 2,4,6-trinitrophenol) also protonates polyaniline base and yields an electrically conducting polymer. Picric acid is often used for the identification of amines in organic chemistry; picrates are compounds of defined melting points. 2,4,6-Trinitrophenol is an example of an acid which contains neither a sulfonic nor a carboxyl group. In this case, the proton is easily released from the hydroxy group due to the reduced electron density on the oxygen atom. The

mesomeric effect of the aromatic system containing three nitro groups (attracting electrons) is thus responsible for the acidity, which is comparable with that of mineral acids. Polyaniline picrate (PANI−PA) is soluble in dimethyl sulfoxide. Protonation of the PANI base with CSA and PA are compared in this paper.

Levon *et al.*[23] as well as other authors[24−26] have reported that protonation of polyaniline base with liquid dodecylbenzenesulfonic acid (DBSA) can be made by blending both components in the absence of auxiliary solvent and by subsequent heating to 80−150 °C. The acid was found to protonate polyaniline in stoichiometric ratio.[23] Also Cao *et al.*[4] have observed the conductivities as high as 20 S cm^{-1} for equimolar blends of polyaniline base with various sulfonic acids prepared in the solid state and then treated for 1 min at 165 °C. Solid-state protonation has often been used in the case of the PANI base and CSA,[3,4,12,27,28] however, this fact has not been stressed, because the blends were further treated with solvents. Matveeva[29] has recently discussed the reaction of polyaniline base with hydroquinone and concluded that there is no substantial difference between the "dry" solid-state blending and "wet" protonation in the presence of solvent.

Although the theory of the reactivity in solid-state chemistry has still to be formulated, chemical reactions in solids are of substantial practical interest.[30] With polymers, the interchain transesterification during solid-state processing of aromatic copolyesters[31] may serve as an example. Dry blending of polyaniline with organic acids allows one to set the proportion between the polyaniline base and an organic acid[12] and, consequently, to control the degree of protonation. This procedure seems to be an alternative to a protonation of polyaniline base by its treatment with dilute mineral acids of varying acidity.[17,32−38]

Emeraldine base is converted in the presence of acids, e.g., CSA or PA, into the protonated emeraldine form of polyaniline (Figure 1).[39,40] The proton from the acid becomes attached to the imine nitrogen of the base and the positive charge on polyaniline chain is balanced by

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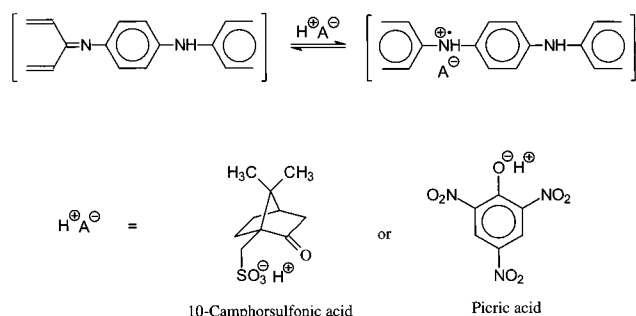
Figure 1. Scheme of the protonation of PANI base with acids.

Table 1. Electrical Conductivity, σ, Molar Mass, M, and Density, d, of Components at 20 °C

	σ, S cm^{-1}	M, g mol^{-1}	d,[a] g cm^{-3}
camphorsulfonic acid	1.3×10^{-8}	232.30	1.35
picric acid	5.0×10^{-15}	229.10	1.76
polyaniline base	4.3×10^{-9}	181.22[c]	1.19
polyaniline camphorsulfonate	0.047[b]	413.52[c]	1.24
polyaniline picrate	0.12[b]	410.32[c]	1.46
polyaniline sulfate[d]	8.9	230.26[c]	1.43

[a] Density of PANI (± 0.01 g cm^{-3}) calculated from mass and dimensions of pellets. [b] Conductivity of equimolar mixture of PANI base with an organic acid (after heating at 85 °C for 1 h). Average value from three samples. [c] Molar mass of the constitutional repeating unit of PANI.[39] [d] As prepared, before conversion to the base.

the anion of acid. The protonated quinonediimine structure converts into the benzenoid one by injection of an electron from nitrogen into the neighboring ring.[41] The remaining unpaired electron on the nitrogen is responsible for the electrical conductivity of the protonated PANI, while both reaction components, polyaniline base and organic acid, are virtually nonconducting (Table 1). The solid-state protonation of the PANI base with organic acids, CSA and PA, and the resulting changes in the electrical conductivity are reported in this paper.

Experimental Section

Polyaniline. Polyaniline was prepared by chemical oxidation of aniline with ammonium peroxodisulfate. Aniline (37.3 g, 0.4 mol) was dissolved in 284 mL of water, and 280 mL of 5 M sulfuric acid (=1.4 mol) was added. The mixture was stirred at room temperature until the precipitated aniline sulfate dissolved. The polymerization was started by addition of 400 mL of aqueous 1 M ammonium peroxodisulfate (91.2 g, 0.4 mol) solution at room temperature. The concentrations of components thus were as follows: 0.4 M aniline, 0.4 M ammonium peroxodisulfate, and 1.4 M sulfuric acid. The next day the mixture was diluted with water, and the precipitate was separated by filtration, treated with an excess of 1 M ammonium hydroxide, and washed with acetone. The resulting polyaniline (emeraldine) base was dried at 60 °C *in vacuo.*

Acids. (±)-Camphor-10-sulfonic acid (Fluka, Switzerland; purum, water content 3.4 wt %) was dried for 1 week over phosphorus pentoxide *in vacuo.* The moisture content was then <0.1 wt %. Picric acid[42] (2,4,6-trinitrophenol; Fluka, Switzerland; puriss., delivered as a suspension in water) was dried in the air; the picric acid used for blending contained 4.0 wt % of water, and the composition of blends was corrected for its content.

Solid-State Protonation of Polyaniline Base. The polyaniline base and organic acid were mechanically blended with a pestle in an agate mortar for 15 min. The basic characteristics of components are given in Table 1. From the weight fraction of organic acid in blends, w_A, its molar fraction (in mixture with constitutional repeating units[39] of the PANI

base) was calculated as $x_A = w_A M_B/[w_A(M_B - M_A) + M_A]$, where M are molar masses of components (subscript A refers to acid and B to PANI base).

There are two cases, which should be discussed separately. When acid is in molar deficit, $x_A < 0.5$ (case I), it is consumed in the protonation of the polyaniline base. Assuming the quantitative reaction between the components, the molar fraction of protonated units, x_P, increases with increasing fraction of acid introduced to the system until $x_A = 0.5$ when the protonation becomes complete, $x_P = 1$. When an excess acid is introduced above equimolar concentration of components, $x_A > 0.5$ (case II), the degree of protonation does not further change, and the acid acts as a mere diluent of protonated polyaniline. The molar fraction of protonated polyaniline units in the system, x_P, is thus going to decrease again as the acid content grows.

Case I: Polyaniline Units in Molar Excess and Acid in Deficit, $x_A \leq 0.5$. Let n be the total number of moles of both components. The mixture thus contains $n_A = x_A n$ moles of acid and $n_B = (1 - x_A)n$ moles of polyaniline base units. If the components react quantitatively, all acid becomes consumed in protonation of the PANI base units and the system is thus composed of unprotonated and protonated PANI constitutional units. Total number of moles present after the protonation is equal to the number of moles of the original base units, n_B. Of these, n_A moles of units are protonated by reaction with an acid. Molar fraction of the protonated units (=degree of protonation) is thus $x_P = n_A/n_B = x_A/(1 - x_A)$ for $x_A \leq 0.5$.

Case II: Acid in Molar Excess, $x_A \geq 0.5$. In contrast to the previous case, all polyaniline base, $(1-x_A)n$ moles, becomes protonated. The mixture is thus composed of the protonated PANI and excess acid. The total number of moles in the system is given by the number of moles of an acid, $x_A n$, which is either free or exists as a part of the PANI protonated units. Molar fraction of protonated PANI is then $x_P = (1 - x_A)/x_A$ for $x_A \geq 0.5$.

Electrical Conductivity. About 250 mg of the blend was pressed into a pellet (13 mm diameter) with a manual hydraulic press at 700 MPa. The pellets were heated for 1 h to 85 °C, unless specified otherwise. The four-probe measurement based on the van der Pauw theorem[43] was used for the samples with an electrical conductivity of $\sigma > 10^{-3}$ S cm^{-1}. A digital multimeter Solartron-Schlumberger 7841, Keithley 220 current source, and Keithley 705 scanner with Keithley 7052 matrix scanner card were used in the experimental setup. The contacts in the sample holder were made from silver–palladium alloy. Gold electrodes were deposited on less conducting pellets, $\sigma < 10^{-3}$ S cm^{-1}, and the conductivity was calculated from the volume resistivity and geometry of samples. The Keithley 6517 electrometer connected by triaxial cable with a metal box enclosing the sample holder was used in this case.

Infrared Spectra. Polyaniline samples were dispersed in potassium bromide and compressed into pellets. Fourier transform infrared (IR) spectra were recorded with a fully computerized Nicolet Impact 400 instrument (200 scans per spectrum at 2 cm^{-1} resolution). The spectra were corrected for humidity and carbon dioxide in the optical path.

Results and Discussion

Solid-State Blending and Heat Treatment. When powdered polyaniline base is mechanically blended with a solid organic acid, an electrically conducting product is obtained. While the electrical conductivity of the PANI base is of the order of 10^{-9} S cm^{-1} (Table 1), the equimolar mixture of the base with an organic acid (56 wt % of CSA or PA, as both acids have nearly the same molar mass, cf. Table 1) has a conductivity of 10^{-2} S cm^{-1}, i.e., 7 orders of magnitude higher. When the blends were heated to 85 °C, the conductivity measured again at 25 °C increased 1.4 times for blends with CSA and 8.9 times for mixtures with PA (Figure 2). The PANI–CSA displayed during heating a well-
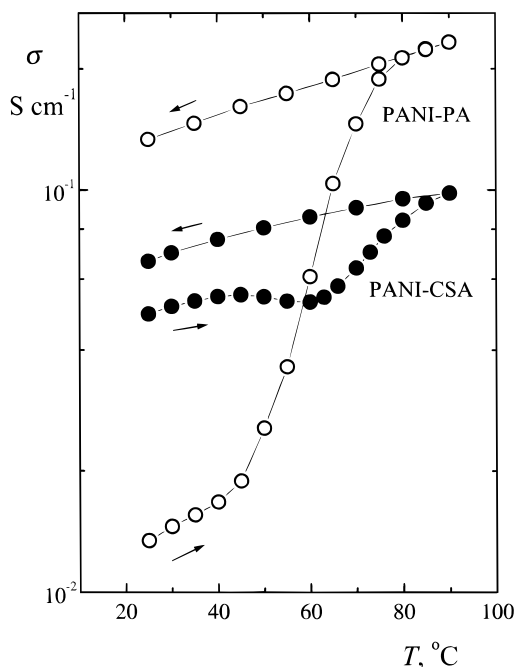
Figure 2. Electrical conductivity, σ, of equimolar blends of the PANI base with camphorsulfonic acid (●) and picric acid (○) during heating and subsequent cooling. Heating/cooling rate: 20 °C/h.

Figure 3. FTIR spectra of PANI sulfate, the corresponding PANI base, and the PANI base reprotonated in the solid state with an equimolar amount of CSA. The spectra were vertically shifted for clarity.

reproducible local minimum of the conductivity at 55–60 °C (Figure 2), similar to that observed with PANI protonated with DBSA[24,26] and possibly associated with changes in morphology of blends. The temperature to which samples were exposed in this experiment was lower than the melting point of organic acids (mp 195 °C for CSA and 122 °C for PA). The heat evolution was observed at 80–90 °C in the first heating of the samples by differential scanning calorimetry (at >150 °C for PANI protonated with DBSA[26]), while this effect was absent during the repeated run.

During the mechanical blending, protonated PANI is produced at the interfaces between particles of the polyaniline base and crystals of the organic acid. In the resulting material, the continuous conducting phase formed by these interfaces is filled with insulating areas of unreacted components (PANI base and/or organic acid). After heating, the enhanced diffusion of components enables them to react further, until one of the components becomes consumed (or both components, at their equimolar ratio) and the conductivity becomes higher. The decrease in the conductivity observed during cooling (Figure 2) is due to the positive temperature coefficient of PANI conductivity.[11,37,44–46]

The heating of equimolar mixtures to 85 °C for 1 h was found to provide the products with the highest electrical conductivity. Neither prolonged exposure to 85 °C nor the treatment at 100 °C has further improved the conductivity. Heating at 120–140 °C for 1 h produced samples with lower conductivities compared with those treated at 85 °C.

The electrical conductivities of the samples are little dependent on the methods of their preparation. Blending of components for 5 min was found to be sufficient to obtain an electrically conducting product, and blending for another 10 min improved the conductivity only marginally. Nevertheless, all samples were carefully homogenized for 15 min to achieve a good uniformity of products. The same electrical conductivity was found
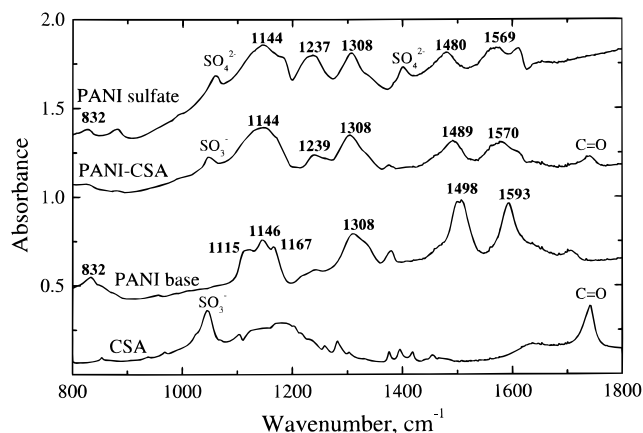
when the blends were first heated and then pressed into pellets or if the pellets were prepared and only later exposed to elevated temperature. Both the prolonged mechanical blending and the application of pressure are connected with the evolution of heat. Consequently, they may produce a similar effect like the exposure of the sample to the elevated temperature and thus somewhat increase the electrical conductivity.

Infrared Spectra. Although the fact that electrically conducting products are obtained after blending of the PANI base with organic acids is the most conclusive proof of the protonation, the supporting evidence can be found in the IR spectra. The IR absorption spectrum of PANI sulfate (Figure 3), obtained after polymerization, is in a good agreement with previously reported results.[8,47–49] (The absorption bands at 1056 and 1400 cm^{-1} are attributed to the sulfate anion). The 1593 and 1498 cm^{-1} modes in the PANI base (consistent with quinone and benzene ring deformations) show a red shift to 1569 and 1480 cm^{-1} in the PANI sulfate. In the spectrum of PANI base, the 1308 cm^{-1} band is assigned to the C–N stretch of secondary aromatic amine and 832 cm^{-1} band to an aromatic C–H out-of-plane bending vibration. In the region 1010–1170 cm^{-1} aromatic C–H in-plain bending modes are usually observed. The band characteristic of the conducting protonated form is observed at 1237 cm^{-1} in the spectrum of PANI sulfate. It has been interpreted as originating from a bipolaron structure, related to the C–N stretching vibration.[8] The band at about 1610 cm^{-1} is believed to be influenced by the deformation vibration of residual water molecules in PANI or in the KBr matrix.

The most prominent change of the spectrum of the PANI base after solid-state protonation with an equimolar amount of CSA is the red shift of peaks at 1593 and 1498 cm^{-1} to 1570 and 1489 cm^{-1} (Figure 3) and the increase in absorption at 1239 cm^{-1} corresponding to the bipolaron structure. The spectum of PANI–CSA exhibits all characteristic peaks observed in PANI sulfate, thus confirming the ability of CSA to protonate the PANI base (Figure 3; the bands at 1048 and 1740 cm^{-1} in PANI–CSA belong to the sulfonic group and carbonyl vibration in CSA).

After protonation of the PANI base with picric acid at equimolar proportion, the 1593 and 1498 cm^{-1} bonds are similarly red-shifted to 1558 and 1483 cm^{-1} (Figure 4) and the increase of the 1241 cm^{-1} band, characteristic
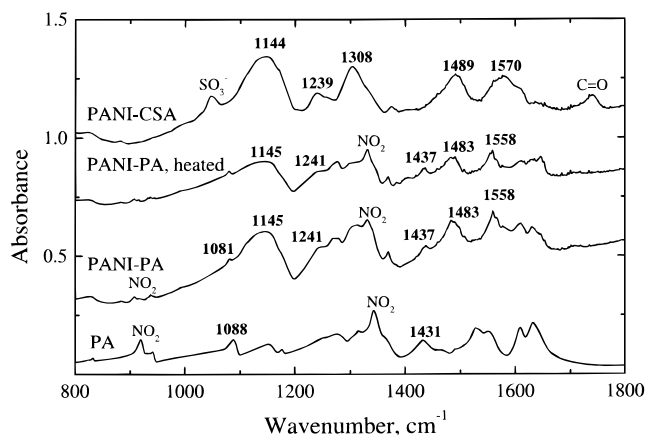
Figure 4. FTIR spectra of the PANI base protonated in the solid state at equimolar proportion with picric acid (as prepared and after heat treatment) and the comparison to the protonation of PANI with CSA.
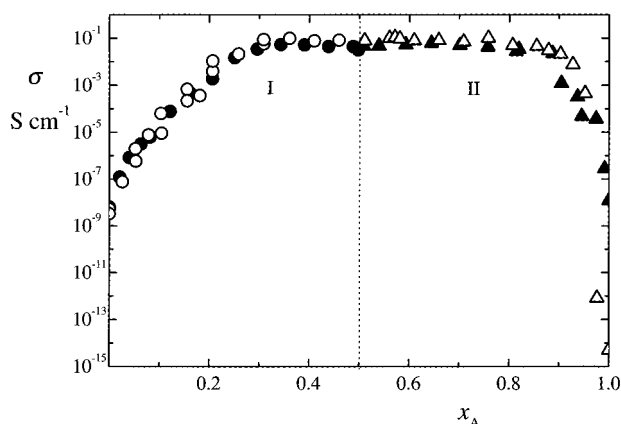

Figure 6. Electrical conductivity, σ, of PANI base blended in the solid state with (a) camphorsulfonic acid (full symbols) and (b) picric acid (open symbols), in dependence on calculated molar fraction of protonated PANI, x_P, for acid in deficit (case I, $x_A < 0.5$, circles) and acid in excess (case II, $x_A > 0.5$, triangles).

an excess acid (case II, $x_A > 0.5$) is more clearly seen when the electrical conductivity is plotted against the calculated molar fraction of protonated units in the system, x_P (Figure 6). In the former case, the conductivity increases as the protonation proceeds, without any indication of the percolation threshold. In the latter, the existence of the percolation threshold can be traced to the range of high acid content (i.e., at a few mole % of protonated polyaniline (Figure 5)). Such a low percolation limit has been reported for the blends of PANI with crystalline substances, like ammonium sulfate,[45] where the electrically conducting phase is forced into the space between insulating crystals. Analogous behavior thus may be anticipated for the protonated PANI embedded into the matrix of a crystalline nonconducting organic acid (Table 1). The nonuniform distribution of the conducting component results in a much lower percolation limit compared with 16−17 vol % Scher−Zallen criterion[50] predicted for the uniformly distributed system of spherical particles.

Conclusions

Polyaniline base can be protonated with organic acids by blending of both components in the solid state. The electrical conductivity increased by 7 orders of magnitude after blending of acid and base at equimolar proportion and still increased after their heating at 85 °C for 1 h. Besides sulfonic acids, e.g., camphorsulfonic acid, picric acid (2,4,6-trinitrophenol) can also be employed for the solid-state protonation of polyaniline. The structural changes induced by the protonation are reflected in infrared spectra. The extent of protonation can be changed, and thus the electrical conductivity controlled, by varying the composition of blends.

Figure 5. Electrical conductivity, σ, of the PANI base blended in the solid state with camphorsulfonic acid (full symbols) and picric acid (open symbols) in dependence on molar fraction of acid, x_A, for acid in deficit (case I, $x_A < 0.5$, circles) and acid in excess (case II, $x_A > 0.5$, triangles).

of the protonated form of PANI, is observed. (The bands belonging to PA, especially vibrations of nitro groups, are also present in the spectrum of PANI−PA.) The heating of the blends (1 h at 85 °C) has no discernible effect on the spectrum of PANI−CSA, and also the changes of the PANI−PA spectrum are marginal (Figure 4). The red shift of absorption peaks of nitro groups of PA after its protonation reaction with the PANI base should be noted (Figure 4). It indicates a more intimate interaction between the PANI base and PA, possibly based on the charge-transfer complex of both components. After reaction of the PANI base with acids, an increased absorption above 2000 cm^{-1}, characteristic of protonated PANI,[49] has been observed.

Electrical Conductivity. The dependence of the electrical conductivity on the composition of blends is similar for protonation both with CSA and PA (Figure 5) despite of diverse chemical nature of these acids. Even though the chemical reaction between the polyaniline base and an organic acid proceeds in the solid state, smooth dependences of conductivity on composition of mixtures are obtained. The maximum electrical conductivity is observed, as expected, in the vicinity of an equimolar composition of mixtures ($x_A = 0.5$).

The difference between the gradual protonation of polyaniline base with increasing acid content (case I, $x_A < 0.5$) and the dilution of the protonated form with
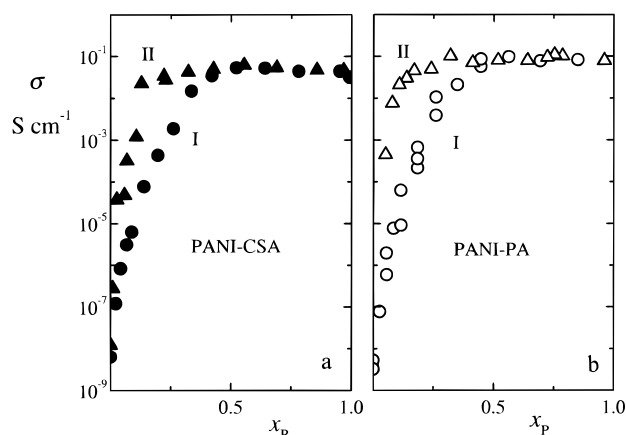
References and Notes

(1) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.

(2) Trivedi, D. C. In *Hanbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, England, 1997, Vol. 2; pp 505−572.

(3) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *55−57*, 3514.

(4) Cao, Y.; Qiu, J.; Smith, P. *Synth. Met.* **1995**, *69*, 187.

(5) Goh, S. H.; Chan, H. S. O.; Ong, C. H. *Polymer* **1996**, *37*, 2675.

(6) Tang, H.; Kitani, A.; Yamashita, T.; Ota, Y.; Shiotani, M. *Chem. Lett.* **1996**, 7, 525.

(7) Li, S.; Cao, Y.; Xue, Z. *Synth. Met.* **1987**, *40*, 87.

(8) Palaniappan, S.; Narayana, B. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2431.

(9) Chang, T.C.; Shen, W. Y.; Ho, S. Y. *Microporous Mater.* **1995**, *4*, 335.

(10) Adams, P.N.; Laughlin, P. J.; Monkman, A. P. *Synth. Met.* **1996**, *76*, 157.

(11) Sanjai, B.; Raghunathan, A.; Natarajan, T. S.; Rangarajan, G. *Phys. Rev. B* **1997**, *55*, 10734.

(12) Holland, E. R.; Pomfret, S. J.; Adams, P. N.; Monkman, A. P. *J. Phys. Condens. Matter* **1996**, *8*, 2991.

(13) Monkman, A. P.; Rebourt, E., Petr, A. *Synth. Met.* **1997**, *84*, 761.

(14) Reghu, M.; Cao, Y.; Moses, D.; Heeger, A. J. *Phys. Rev. B* **1993**, *47*, 1758.

(15) Heeger, A. J. *Trends Polym. Sci.* **1995**, *3*, 39.

(16) Adams, P. N.; Laughlin, P. J.; Monkman, A. P.; Kenwright, A. M. *Polymer* **1996**, *37*, 3411.

(17) Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1987**, *36*, 3475.

(18) Pavesi, L.; Tedoldi, F. *Polym. Adv. Technol.* **1996**, *8*, 30.

(19) Joo, J.; Priogodin, V. N.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1994**, *50*, 12226.

(20) Kohlman, R. S.; Zibold, A.; Tanner, D. B.; Ihas, G. G.; Ishiguro, T.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. Lett.* **1997**, *78*, 3915.

(21) Bernard, M.-C.; Hugot-Le Goff, A.; Bich, V. T.; Zeng, W. *Synth. Met.* **1996**, *81*, 215.

(22) Kugler, T.; Rasmusson, J. R.; Österholm, J.-E.; Monkman, A. P.; Salaneck, W. R. *Synth. Met.* **1996**, *76*, 181.

(23) Levon, K.; Ho, K.-H.; Zheng, W.-Y.; Laakso, J.; Kärnä, T.; Taka, T.; Österholm, J.-E. *Polymer* **1995**, *36*, 2733.

(24) Ahlskog, M.; Isotalo, H.; Ikkala, O.; Laakso, J.; Stubb, H.; Österholm, J.-E. *Synth. Met.* **1995**, *69*, 213.

(25) Ikkala, O. T.; Lindholm, T. M.; Ruohonen, H.; Seläntaus, M.; Väkiparta, K. *Synth. Met.* **1995**, *69*, 135.

(26) Ikkala, O. T.; Laakso, J.; Väkiparta, K.; Virtanen, E.; Ruohonen, H.; Järvinen, H.; Taka, T.; Passiniemi, P.; Cao, Y.; Andreatta, A.; Smith, P.; Heeger, A. J. *Synth. Met.* **1995**, *69*, 97.

(27) Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Macromolecules* **1994**, *27*, 7212.

(28) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. G. *Polymer* **1996**, *37*, 359.

(29) Matveeva, E. S. *Synth. Met.* **1996**, *83*, 89.

(30) Boldyrev, V. V., Ed. *Reactivity of Solids: Past, Present and Future*; Blackwell; Oxford, England, 1996.

(31) Frich, D.; Goranov, K.; Schneggenburger, L.; Economy, J. *Macromolecules* **1996**, *29*, 7734.

(32) Gow, C. J.; Zukoski, C. F., IV. *J. Colloid. Interface Sci.* **1990**, *136*, 175.

(33) Xie, H.-Q.; Guan, J.-G. *Angew. Makromol. Chem.* **1996**, *235*, 21.

(34) Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1989**, *39*, 3570.

(35) Chartier, P.; Mattes, B.; Reiss, H. *J. Phys. Chem.* **1992**, *96*, 3556.

(36) Pingsheng, H.; Xiaohua, Q.; Chune, L. *Synth. Met.* **1993**, *55−57*, 5008.

(37) Campos, M.; Bello, B., Jr. *J. Phys. D: Appl. Phys.* **1997**, *30*, 1531.

(38) Wang, Z. H.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1992**, *45*, 4190.

(39) The definition of the constitutional repeating unit of the PANI chain is somewhat ambiguous. From the formal point of view, the constitutional repeating unit is defined as the smallest constitutional unit whose repetition describes a polymer (Metanomski, W. V. *Compendium of Macromolecular Nomenclature,* Blackwell, Oxford, England, 1991; p 15); i.e., a segment composed of two aniline molecules (Figure 1) may be appropriate. This definition seems to be useful when describing chemical and macromolecular properties of polyaniline. The unit composed of four aniline molecules, which is frequently used in the literature, seems to reflect well the electrical properties of polyaniline.

(40) Stejskal, J.; Kratochvíl, P.; Jenkins. A. D. *Polymer* **1996**, *37*, 367.

(41) Stafström, S.; Brédas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.

(42) Picric acid is an explosive chemical. Mechanical preparation of its blends with polyaniline base and subsequent heating of the material to temperature up to 140 °C has never caused any difficulties.

(43) Van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, 1.

(44) Quadrat, O.; Stejskal, J.; Klason, C.; Kubát, J.; McQueen, D. H. *J. Phys. Condens. Matter* **1995**, *7*, 3287.

(45) Prokeš, J.; Křivka I.; Stejskal, J. *Polym. Int.* **1997**, *43*, 117.

(46) Gosh, M.; Barman, A.; De, S. K.; Chatterjee, S. *Solid State Commun.* **1997**, *103*, 629.

(47) McCall, R. P.; Roe, M. G.; Ginder, J. M.; Kusumoto, T.; Epstein, A. J.; Asturias, G. E.; Scherr, E. M.; MacDiarmid, A. G. *Synth. Met.* **1989**, *29*, E433.

(48) Quillard, S.; Louarn, G.; Buisson, J. P.; Boyer, M.; Lapkowski, M.; Pron, A.; Lefrant, S. *Synth. Met.* **1997**, *84*, 805.

(49) Sariciftci, N. S.; Kuzmany, H.; Neugebauer, H.; Neckel, A. *J. Chem. Phys.* **1990**, *92*, 4530.

(50) Scher, H.; Zallen, R. *J. Chem. Phys.* **1970,** *53*, 3759.