

# Effect of Plasticizing Dopants on Spectroscopic Properties, Supramolecular Structure, and Electrical Transport in Metallic Polyaniline

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Several 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(alkyl), or di(alkoxy) esters were synthesized and tested as plasticizing dopants which lead to solution processible (via counterion) polyaniline with improved mechanical properties and metallic-type conductivity. As evidenced by wide-angle X-ray diffraction and small-angle X-ray scattering studies, PANI doped with the above dopants shows in the solid state a layered type of structural organization with the chain–dopant–chain distance clearly correlated with the length of the alkyl substituent in the dopant. The addition of an external plasticizer of the type of dioctyl phthalate or tritolyl phosphate to PANI doped with the above diesters improves both the molecular ordering and the metallic behavior of the material. The largest range of metallic type of conductivity was found for di-butoxyethyl ester doped-PANI. Solution processibility of PANI can also be improved by the application of a new procedure called “mixed-doping” which involves Brønsted acid doping followed by Lewis acid one.

## Introduction

Preparation of processible conductive polymers exhibiting metallic-type conductivity and good mechanical properties constitutes a great challenge for materials chemists. Doped poly(acetylene)—the first organic polymer exhibiting metallic-type conductivity—is neither fusible nor soluble and for this reason virtually impossible to be processed.<sup>1</sup> Other intractable polymers such as, for example, doped poly(pyrrole)<sup>2</sup> or poly(*p*-phenylene vinylene)<sup>3</sup> in some cases also show features of metallic behavior. Solution processible conductive polymers can be prepared by grafting appropriate functional groups to such stiff backbone polymers as poly(3-alkylthiophene)s.<sup>4</sup> Processible in the undoped, i.e., insulating state, they require postprocessing doping. From this point of view polyaniline, another widely studied conductive polymer, behaves differently. Grafting of solubilizing functional groups, to the phenylene ring and/or to the nitrogen atom, has a negative effect on the conductivity of doped polyaniline, and for this reason

the above-described methods cannot be used in this case. However, polyaniline can be processed in the doped (conductive) state provided that appropriately functionalized dopants are used in the doping process. This method sometimes called “counterion-induced processibility” was used with success in the preparation of polyaniline with features of metallic-type conductivity. For example PANI(CSA)<sub>0.5</sub> (where PANI denotes polyaniline repeat unit involving one ring and one nitrogen atom and CSA denotes DL-camphor-10-sulfonic acid) processed from *m*-cresol<sup>5,6</sup> or 1,1,1,3,3,3-hexafluoro-2-propanol<sup>7</sup> is metallic down to 230 and 200 K, respectively. Metallic polyaniline can also be obtained by casting films of PANI doped with 2-acryloamido-2-methyl-1-propanesulfonic acid from 2,2'-dichloroacetic acid (DCAA).<sup>8</sup>

In our recent paper<sup>9</sup> we focused on developing new processing systems leading to metallic PANI with good mechanical properties and in particular good flexibility. Our approach consisted of the synthesis of a “tailor-made” dopant which combines plasticizing properties with PANI doping capability, namely, 1,2-benzenedicarboxylic acid, 4-sulfo-1,2-di(2-ethylhexyl) ester (abbreviated as DEHEPSA). In the present paper we extend this research by presenting a systematic study of metallic PANI prepared by protonation of PANI base with two families of protonating-plasticizing agents: 1,2-benzene-

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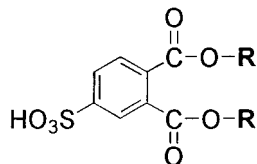
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dicarboxylic acid, 4-sulfo, 1,2-di(alkyl) esters, and 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(alkoxy) esters. In particular we investigate the influence of internal plasticizers (dopants) and external plasticizers on supramolecular structure, mechanical, and transport properties of metallic PANI. We also propose a new method of conductive PANI processing which consists of mixed-doping, i.e., Brønsted acid doping followed by Lewis acid complexation.

### Experimental Section

**Synthesis of Plasticizing Dopants.** The general formula of the dopants synthesized in this research can be expressed as follows:



where R = *n*-pentyl, *n*-octyl, *n*-decyl, *n*-dodecyl, 2-ethylhexyl, -butoxyethyl, and -butoxyethoxyethyl. In the subsequent text the following abbreviations will be used: DPEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(*n*-pentyl) ester, DOEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(*n*-octyl) ester, DDeEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(*n*-decyl) ester, DDoEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(*n*-dodecyl) ester, DEHEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-bis(2-ethylhexyl) ester, DBEEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-bis(butoxyethyl) ester, and DBEEEPSA for 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-bis(butoxyethoxyethyl) ester.

A typical synthetic procedure can be briefly described as follows. 1,2-benzenedicarboxylic, 4-sulfonic acid (6.3 g, 25.6 mmol) in a form of 50 wt % water solution was mixed with 76.8 mmol of the appropriate alcohol (1-pentanol, 1-octanol, 1-decanol, 1-dodecanol, 2-ethyl-1-hexanol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, respectively). The esterification reaction was carried out for 4 h at 110 °C with constant nitrogen flow which assured effective removal of water formed in the course of the reaction as a side product. In the case of shorter chain diesters (DPEPSA and DBEEPSA) no special purification procedures were needed. Since the yield calculated with respect to the reagent taken in deficit (the acid) is essentially 100%, the excess of the alcohol could be in both cases removed by pumping off the reaction product in a vacuum line. Total removal of unreacted alcohol, as evidenced by its absence in <sup>1</sup>H NMR and mass spectra, required ca. 4 h of dynamic pumping with heating at 50 °C. In the cases of DOEPSA, DDeEPSA, and DDoEPSA a different purification procedure had to be applied due to the low volatility of alcohols used in the reaction. In a typical purification procedure 100 mL of 1 M HCl was added to the reaction mixture. After a few minutes the mixture separated into two layers. The organic phase was recovered, and the crude product was extracted with ether. It was then dried over MgSO<sub>4</sub> and finally pumped in a vacuum line at 50 °C for 3 h in order to remove the volatile contaminants. DBEEEPSA was purified by washing three times with 100 mL of 1 M HCl followed by drying and pumping as described above. In the elemental analysis of the reaction products a slight excess of oxygen and hydrogen content is observed which is due to the hygroscopic nature of the synthesized compounds. The presence of water in the synthesized compounds was also evidenced by <sup>1</sup>H NMR spectroscopy.

The chemical nature of the products was identified by elemental analysis, <sup>1</sup>H NMR, FTIR, and mass spectroscopies. <sup>1</sup>H NMR spectra were recorded on a Bruker AC 200 MHz spectrometer, whereas the FTIR and mass spectra were measured on a FTIR Perkin-Elmer Paragon 500 spectrometer and Finnigan Mat LCG spectrometer, respectively.

**DPEPSA.** Anal. Calcd for C<sub>18</sub>H<sub>26</sub>O<sub>7</sub>S: C, 55.95; H, 6.78; S, 8.30. Found: C, 55.22; H, 6.90; S, 7.93. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.90 (6H), 1.35 (8H), 1.73 (4H), 4.32 (4H) 7.75 (1H), 7.95 (1H), 8.15 (1H). IR (KBr, cm<sup>-1</sup>): 3420 (m), 3080 (w), 2959 (s), 2933 (m), 2863 (m) 1729(s), 1600 (w), 1568 (w), 1467 (m), 1377 (m), 1274 (s), 1185 (m), 1129 (s), 1070 (m), 1034 (m), 959 (m), 915 (w), 771 (m), 671 (m), 637 (m). MS (FAB mode): *m/z* 385.3 (MH)<sup>-</sup>.

**DOEPSA.** Anal. Calcd for C<sub>24</sub>H<sub>38</sub>O<sub>7</sub>S: C, 61.25; H, 8.14; S, 6.81. Found: C, 62.17; H, 8.89; S, 5.70. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.83 (6H), 1.24 (20H), 1.68 (4H), 4.24 (4H) 7.67 (1H), 7.93 (1H), 8.11 (1H). IR (KBr cm<sup>-1</sup>): 3404 (w), 3083 (w), 2956 (s), 2928 (m), 2857 (m) 1730(s), 1598 (w), 1570 (w), 1467 (m), 1379 (m), 1276 (s), 1183 (m), 1129 (s), 1070 (m), 1035 (m), 949 (m), 771 (m), 670 (m), 635 (m). MS (FAB mode): *m/z* 469.3 (MH)<sup>-</sup>.

**DDeEPSA.** Anal. Calcd for C<sub>28</sub>H<sub>46</sub>O<sub>7</sub>S: C, 63.85; H, 8.80; S, 6.09. Found: C, 65.96; H, 9.85; S, 5.26. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.78 (6H), 1.17 (28H), 1.65 (4H), 4.23 (4H), 7.76 (3H). IR (KBr cm<sup>-1</sup>): 3429 (m), 3083 (w), 2954 (m), 2925 (s), 2854 (s) 1731(s), 1599 (w), 1569 (w), 1464 (m), 1373 (m), 1274 (s), 1185 (m), 1124 (s), 1068 (m), 1032 (m), 963 (m), 932 (w), 771 (m), 667 (w), 623 (m). MS (FAB mode): *m/z* 525.4 (MH)<sup>-</sup>.

**DDoEPSA.** Anal. Calcd for C<sub>32</sub>H<sub>54</sub>O<sub>7</sub>S: C, 65.94; H, 9.34; S, 5.50. Found: C, 66.45; H, 9.79; S, 4.79. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.86 (6H), 1.23 (36H), 1.69 (4H), 4.30 (4H), 7.82 (3H). IR (KBr cm<sup>-1</sup>): 3410 (m), 3083 (w), 2952 (m), 2925 (s), 2854 (s) 1732(s), 1598 (w), 1570 (w), 1467 (m), 1376 (m), 1275 (s), 1185 (m), 1128 (s), 1069 (m), 1034 (m), 951 (m), 923 (w), 772 (m), 720 (w), 669 (w), 635 (m). MS (FAB mode): *m/z* 581.4 (MH)<sup>-</sup>.

**DEHEPSA.** Anal. Calcd for C<sub>24</sub>H<sub>38</sub>SO<sub>7</sub>: C, 61.25; H, 8.14; S, 6.08; O, 23.83. Found: C, 61.28; H, 8.71; S, 6.35. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.91 (12 H), 1.31 (16H), 1.68 (2H), 4.25 (4H), 7.74 (1H), 7.99 (1H), 8.17 (1H). IR (KBr, cm<sup>-1</sup>): 3403 (m), 3060 (w), 2946 (s), 2938 (s), 2873 (m), 1727 (s), 1619 (w), 1571 (w), 1462 (m) 1381 (m), 1271 (s), 1125 (s) 1068 (m), 1034 (s), 771 (m), 670 (m), 637 (m).

**DBEEEPSA.** Anal. Calcd for C<sub>24</sub>H<sub>38</sub>O<sub>11</sub>S: C, 53.92; H, 7.16; S, 6.00. Found: C, 52.64; H, 7.10; S, 5.72. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.85 (6H), 1.30 (4H), 1.49 (4H), 3.64 (16H), 4.47 (4H), 7.77 (1H), 7.99 (1H), 8.26 (1H). IR (KBr, cm<sup>-1</sup>): 3421 (S), 3070 (w), 2950 (m), 2931 (s), 2871 (m), 1731 (s), 1599 (w), 1569 (w), 1465 (m) 1372 (m), 1272 (s), 1180 (w), 1126 (s) 1067 (m), 1035 (s), 959 (w), 849 (w) 773 (m), 697 (w), 670 (m), 638 (m). MS (FAB mode): *m/z* 533.3 (MH)<sup>-</sup>.

**DBEEPSA.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.87 (6H), 1.24 (8H), 3.54 (4H), 3.73(4H), 4.56 (4H) 7.65 (1H), 7.89 (1H), 8.06 (1H). IR (KBr, cm<sup>-1</sup>): 3438 (S), 3081 (w), 2959 (m), 2933 (m), 2872 (m), 1730 (s), 1599 (w), 1569 (w), 1455 (m) 1373 (m), 1276 (s), 1185 (m), 1124 (s) 1068 (m), 1033 (s), 928 (m), 850 (w) 767 (m), 697 (w), 667 (m). MS (FAB mode): *m/z* 445.2 (MH)<sup>-</sup>.

**Synthesis of Polyaniline.** Polyaniline was synthesized at -27 °C in HCl/LiCl water/ethanol solution using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the oxidizing agent. The obtained polyaniline hydrochloride salt was then converted to the base form by treatment with an excess of 0.3 M NH<sub>3</sub>(aq) solution. The inherent viscosity of the obtained polymer was measured at 25 °C in 0.1 wt % solution in 96 wt % H<sub>2</sub>SO<sub>4</sub> using an automatic Ubbelohde viscosimeter. The obtained value was 2.25 dL·g<sup>-1</sup>. The detailed polymerization procedure can be found elsewhere.<sup>9</sup>

**Casting of Free-Standing Films of Doped-PANI.** In the subsequent text diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid used for (PANI) protonation (doping) will be called "internal plasticizers", whereas dioctyl phthalate (DOP) or tritolyl phosphate (TTP) used as supporting plasticizers will be termed "external plasticizers". Free-standing films of protonated (doped) PANI were cast from 0.5 wt % solution with respect to the PANI base in 2,2'-dichloroacetic acid (abbreviated as DCAA). The ratio of dopant molecule to PANI repeat unit was 0.5 in all cases studied. Three types of solutions were prepared: without the external plasticizer, with 10 wt % of the external plasticizer with respect to the mass of PANI base and with 30 wt % of the external plasticizer with respect to the mass of PANI base. The solutions were magnetically

**Table 1. Elemental Analysis of PANI Protonated with Diesters of 1,2-Benzenedicarboxylic, 4-Sulfonic Acid in DCAA**

	%C	%H	%N	%S	%Cl
Dopant DPEPSA					
found	58.63	5.81	4.33	5.36	3.90
calcd for PANI(DPEPSA) <sub>0.5</sub> (DCAA) <sub>0.15</sub>	58.66	5.88	4.47	5.12	3.90
Dopant DOEPSA					
found	62.90	6.79	4.48	4.43	3.16
calcd for PANI(DOEPSA) <sub>0.45</sub> (DCAA) <sub>0.12</sub> (H <sub>2</sub> O) <sub>0.30</sub>	63.00	6.96	4.31	4.44	3.11
Dopant DDeEPSA					
found	64.89	7.50	4.15	3.65	2.65
calcd for PANI(DDeEPSA) <sub>0.45</sub> (DCAA) <sub>0.10</sub> (H <sub>2</sub> O) <sub>0.35</sub>	64.88	7.44	4.35	3.98	2.70
Dopant DDoEPSA					
found	66.15	8.14	3.28	3.90	2.67
calcd for PANI(DDoEPSA) <sub>0.47</sub> (DCAA) <sub>0.12</sub> (H <sub>2</sub> O) <sub>0.30</sub>	66.04	8.00	3.61	3.89	2.61
Dopant DBEEEPSA					
found	56.23	5.95	3.63	4.44	2.70
calcd for PANI(DBEEEPSA) <sub>0.50</sub> (DCAA) <sub>0.13</sub> (H <sub>2</sub> O) <sub>0.50</sub>	56.92	6.48	3.64	4.16	2.81

stirred typically for 3–4 weeks until no evolution in their UV–vis–NIR spectrum was observed. Films were cast either on polypropylene or alumina covered aluminum substrate at 45 °C under argon flow. They were then pumped until constant mass in a vacuum line. Typical film thickness was ca. 20–30  $\mu\text{m}$ .

Films of mixed-doped-PANI were also prepared. Mixed-doping of PANI consists of two steps. First PANI base is doped with a Brönsted acid, and the resulting product is then additionally complexed with a Lewis acid. Following our previous experience we have selected DEHEPSA as the Brönsted acid dopant and FeCl<sub>3</sub> as the Lewis acid dopant.<sup>10</sup> A typical doping procedure can be described as follows: A 300 mg (0.64 mmol) amount of DEHEPSA was dissolved in 20 mL of nitromethane (abbreviated as NM). Then 100 mg of the PANI base was added to the doping solution. DEHEPSA was taken with ca. 20% of excess with respect to the optimum protonation level corresponding to PANI(DEHEPSA)<sub>0.5</sub>. A powder of DEHEPSA doped-PANI was then repeatedly washed with pure nitromethane in order to remove the excess of the dopant and finally dried in a vacuum line until constant mass was reached. The analytically determined doping level was PANI-(DEHEPSA)<sub>0.42</sub>, i.e., slightly lower than expected. This could be associated with the fact that protonation of PANI base with DEHEPSA in nitromethane is a solid-state reaction during which PANI powder remains insoluble. Taking into account that the dopant molecules are rather bulky, one can expect some limitation in the doping due to diffusion of the dopant in the solid state. Before Lewis acid complexation PANI-(DEHEPSA)<sub>0.42</sub> was additionally washed, in a drybox, with small portions of rigorously dried nitromethane with the goal of complete removal of water from the system. Even minute amounts of water interfere with Lewis acid doping and complicate the interpretation of Mössbauer spectra of mixed-doped-PANI due to the formation of several hydrated species.<sup>10</sup> In the next step 210 mg of PANI(DEHEPSA)<sub>0.42</sub> was mixed with 51 mg of FeCl<sub>3</sub> in 60 mL of CH<sub>3</sub>NO<sub>2</sub>. Complexation with FeCl<sub>3</sub> renders PANI(DEHEPSA)<sub>0.42</sub> soluble in nitromethane, which is manifested by a green coloration of the solution. The solution was stirred typically for 5–7 days and then filtered. Free-standing films were cast at room temperature on a polypropylene surface in a drybox. Elemental analysis of the films gave the formula PANI(DEHEPSA)<sub>0.42</sub>(FeCl<sub>3</sub>)<sub>0.42</sub>(NM)<sub>0.12</sub>.

**Characterization Techniques.** The obtained films were subjected to the following characterization techniques: elemental analysis, temperature dependence of conductivity, mechanical tests (stress–strain relationship), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD) investigations.

The temperature dependence of conductivity was determined by a four-probe technique. To ensure good electrical contacts, four gold lines were evaporated through a mask to

which 25  $\mu\text{m}$  golden wires were attached by pressing. The temperature of the sample during the measurement was checked with a rhodium–iron resistance thermometer which was placed in the proximity of the sample. The current was applied by a Keithley model 220 current source, and the voltage was measured independently by two Keithley model 6512 electrometers with an input resistance of  $2 \times 10^{14}$  ohms. The probe was placed into a continuous flow helium cryostat and pumped for 14 h before the measurement.

Mechanical tests were carried out at room temperature on an Instron apparatus using rectangular samples (6 mm  $\times$  20 mm) and applying a draw rate of 0.5 mm/min.

WAXD studies were carried out in reflection geometry (Bragg–Brentano) using Cu K $\alpha$ 1 radiation (1.5406 Å). The scan step was 0.06° (in  $2\theta$ ) with the counting time of 15 s/step. The diffractometer was equipped with a 800 channel multidetector with a step of 0.02°. SAXS studies were performed at ESRF Grenoble on Beam Line D2AM using a monochromatic beam of 15 keV energy (wavelength of 1.2 Å). The 2D detector was located 2.2 m from the sample position. The separation between two channels was 4.5  $\mu\text{m}$ .

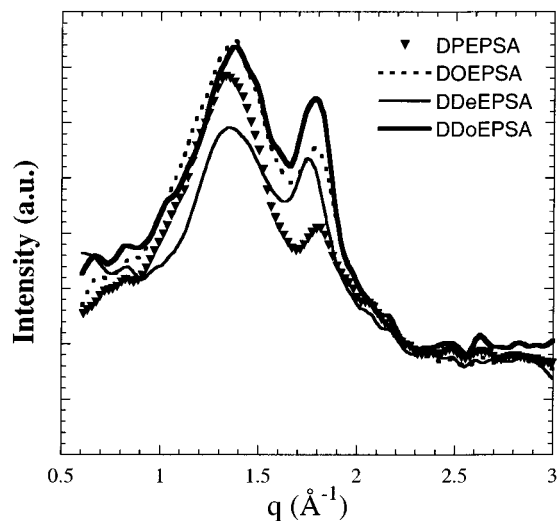
Mössbauer spectra mixed (Brönsted and Lewis acid) poly-aniline were measured at 77 K. The samples were loaded in a drybox into a tight polyamide container prior to the experiment and immediately transferred to the cryostat of the spectrometer. Typical thickness of the absorber was 5 mg/cm<sup>2</sup> of natural iron. Co(Rh) was used as a Mössbauer source. An  $\alpha$ -Fe absorber operating at room temperature was used for the velocity calibration. The spectra were recorded in a constant acceleration mode and analyzed in a least-squares procedure.

## Results and Discussion

Elemental analyses of PANI doped with diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid show the presence of significant amounts of chlorine which is indicative of the participation of the solvent (DCAA) in the doping process. This is not unexpected taking into account that DCAA is acidic and shows  $\text{p}K_{\text{a}} = 1.48$ . One must however stress here that PANI base prepared by subzero temperature synthesis in HCl/LiCl aqueous medium always contains a small amount of chlorine which cannot be removed by deprotonation. In our case this content, determined analytically, was 1.71%. Thus, the determination of the extent of PANI protonation by the solvent requires a correction for the residual content of Cl in the PANI base used in the doping experiments. The results of elemental analysis are collected in Table 1. It is clear that DCAA is a co-dopant. In fact ca. 20% of protonated sites are occupied by DCAA instead of the diester. Extended pumping does not lead to a decrease in the content of DCAA in the film which again indi-

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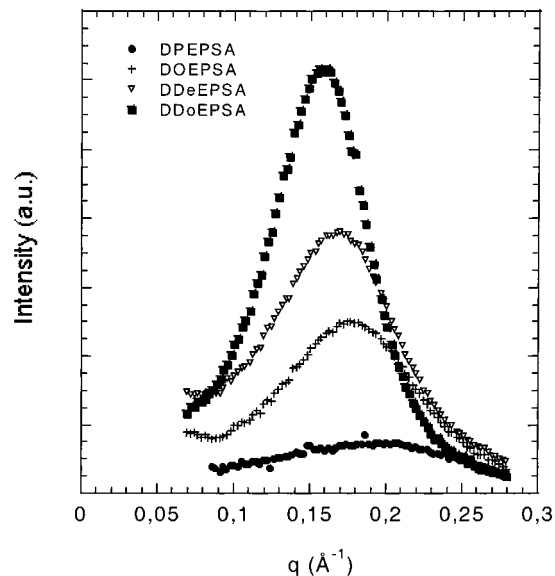


**Figure 1.** WAXD patterns for PANI doped with *n*-alkyl diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid.

cates that the solvent molecules are strongly bound to the polymer matrix via protonation. Elemental analysis shows additionally that some of the dopant molecules entering the polymer matrix are solvated with a molecule of water. In fact, only in one case (DPEPSA) the analytical data could be fitted without the assumption of partial hydration. In all other cases, even extended pumping did not result in a complete removal of water. The highest hydration level was found for PANI doped with DBEEEPSA which can be rationalized by the presence of ether type oxygen in the dopant. Thus, the general formula of diesters of phthalosulfonic acid (DEPSA)-doped-PANI studied in this research can be expressed as follows: PANI (DEPSA)<sub>*x*</sub> (DCAA)<sub>*y*</sub>(H<sub>2</sub>O)<sub>*z*</sub>. It should be noted here that in all cases but DDeEPSA the protonation level, expressed as the sum of *x* + *y*, exceeds the expected value of 0.5 and is usually in the vicinity of 0.6. Again one is tempted to rationalize it by co-protonation with the solvent molecules.

Physical properties of polymers in the solid state are governed by their supramolecular structure, which in turn strongly depends on the conditions of their processing. In particular, in the case of solution processing of PANI several interactions between the host polymer, the dopant, and the solvent must be considered, which can either induce or inhibit supramolecular ordering.<sup>11,12</sup> Moreover the addition of an external plasticizer to the polymer plasticized internally by doping may also influence the supramolecular structure of PANI processed from solution. For this reason we have undertaken structural studies of the films prepared in the course of this research using WAXD and SAXS.

WAXD and SAXS diffractograms recorded for PANI doped with plasticizing dopants are presented in Figures 1 and 2, respectively. They are distinctly different from those measured for PANI base and PANI doped with simple inorganic acids.<sup>13</sup> WAXD patterns of PANI doped with diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid



**Figure 2.** SAXS profiles for PANI doped with *n*-alkyl diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid.

**Table 2. Dopant Dimensions from CS Chem 3D Pro Calculations and *d* Spacings from SAXS and WAXD Studies in PANI Doped with Diesters of 1,2-Benzenedicarboxylic, 4-Sulfonic Acid**

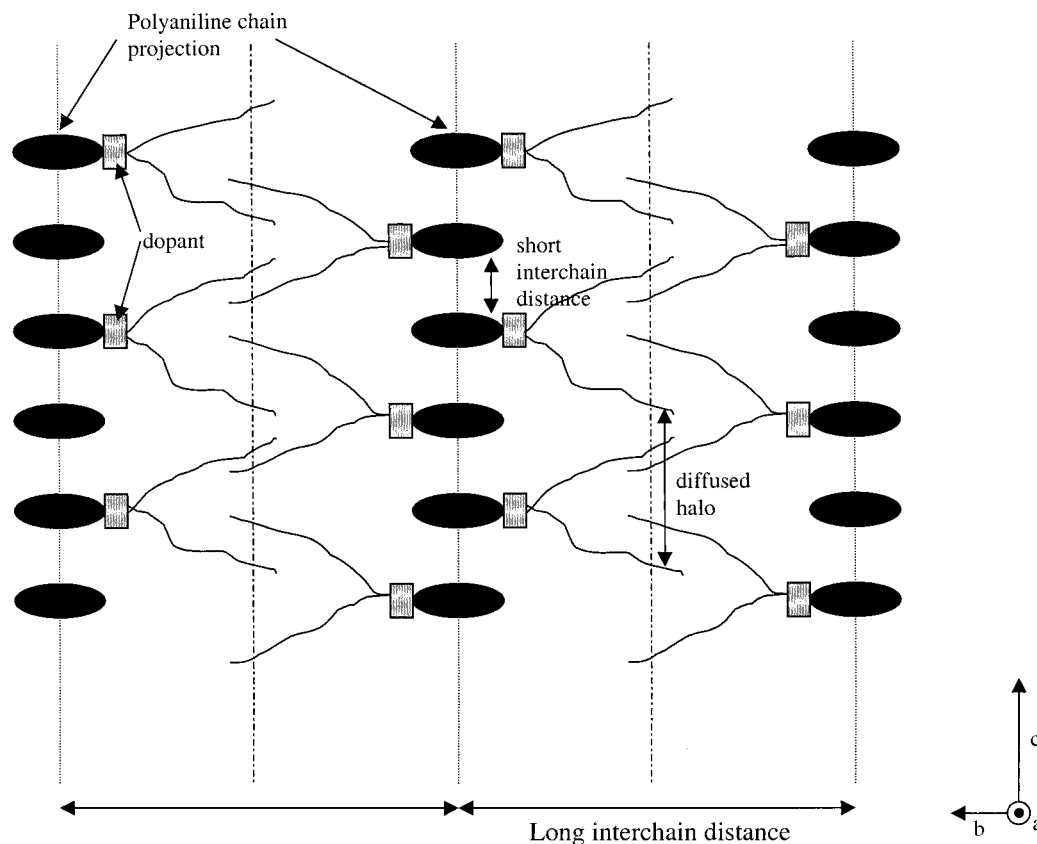
dopant	dopant length from Chem 3D, Å	SAXS, Å	WAXD, Å
DPEPSA	14.4	32.1	4.65 3.48
DOEPSA	17.9	35.6	4.56 3.49
DDeEPSA	20.1	37.4	4.59 3.53
DDoEPSA	22.3	39.9	4.48 3.53

containing *n*-alkyl substituents (DPEPSA, DOEPSA, DDeEPSA, and DDoEPSA) can be described as consisting of one sharp reflection at small *q* values ( $q = 0.15 - 0.25 \text{ \AA}^{-1}$ ) not presented in Figure 1, one broad reflection peaked at  $q = 1.35 \text{ \AA}^{-1}$  and a narrower one at  $q = 1.78 \text{ \AA}^{-1}$ . For peaks at  $q = 0.15 - 0.25 \text{ \AA}^{-1}$  we are close to the instrument limits. In this case an abrupt cut due to the beam stop may lead to incorrect determination of the peak features (its maximum and halfwidth). For this reason we have undertaken SAXS experiments which allow for a precise determination of the position of the reflection at small *q*. It is clear that the position of the reflection in the small-angle region is strongly dependent on the size of the alkyl substituent in the dopant, being shifted toward lower *q* with increasing alkyl chain length. To the contrary the positions of two peaks at  $q = 1.35$  and  $1.78 \text{ \AA}^{-1}$ , corresponding to  $d = 4.6$  and  $3.5 \text{ \AA}$ , respectively, are independent of the size of the dopant (compare Figures 1 and 2). The positions of the small-angle reflection, for all alkyl substituted dopants studied, are collected in Table 2. In the simplest interpretation one is tempted to attribute this reflection to the chain-dopant-chain repeat distance in which the alkyl groups of the dopant act as a spacer. *d* spacings corresponding to the two remaining reflections are characteristic of the van der Waals distances between stacks of phenylene rings ( $d = 3.5 \text{ \AA}$ ) and between aliphatic chains ( $d = 4.5 \text{ \AA}$ ). This simple picture leads us to a layered structure in which stacks of polymer

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**Figure 3.** Suggested layered stacking mode for structural organization for PANI doped with *n*-alkyl diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid.

chains are separated by dopant anions. Figure 3 shows idealized structure of this type with PANI(dopant)<sub>0.5</sub> stoichiometry. In reality the extent of this layered ordering differs strongly depending on the size of the alkyl substituent in the doping ester. The SAXS peak registered for PANI(DPEPSA)<sub>0.5</sub> is very broad and rather poorly defined. One may even expect that this peak is not due to layered ordering but due to simple correlation hole effects. We strongly believe however that the observed SAXS reflections, registered for all esters with *n*-alkyl substituents studied, can be attributed to the periodic order of the type described above because of the following reasons. First, the position of the peak can be clearly correlated with the size of the dopant. Moreover with increasing length of the substituent the peak becomes more intensive and narrower, indicating increasing ordering (see Figure 2). Second, for a given dopant, it is possible to increase this order by changing the processing conditions, for example by the addition of an external plasticizer (vide infra). It is therefore highly improbable that the same effects would be observed if the SAXS reflection originated from simple correlation hole effects. The next question to be answered is whether the alkyl spacers are interdigitated (see structure presented in Figure 3). Using the CS Chem 3D pro package (Version 3.5.1, Cambridge Soft) one can calculate the size of an individual dopant molecule. The values obtained for the dopants studied are collected in Table 2. If no interdigitation is assumed, the interlayer distance must be equal to twice the length of the dopant + the minimum distance between the ends of the alkyl spacer + twice the length of the ionic bond

between the dopant anion and the protonated PANI chain. This of course exceeds the interlayer distance determined on the basis of the small-angle reflection, especially in the case of dopants with longer substituents (DDeEPSA and DDoEPSA). Thus, some interdigitation must be postulated as shown schematically in the structure presented in Figure 3.

The layered and in some cases lamellar type of structural organization is frequently observed in stiff-chain conducting polymers doped with surfactant type anions containing long flexible chains. It was postulated for poly(pyrrole) doped with *n*-alkyl sulfates<sup>14</sup> and for PANI doped with dodecylbenzenesulfonic acid.<sup>15,16</sup> They were also reported for different types of polymers containing basic sites in the chain backbone and protonated with acids containing alkyl type surfactant groups.<sup>17–19</sup> The main difference that distinguishes the diffractograms recorded in this research from those observed for PANI doped with dodecylbenzenesulfonic acid<sup>15,16</sup> is the presence of a relatively sharp reflection with  $d = 3.5 \text{ \AA}$ , which is nonexistent in the latter system. This observation can be taken as an indication

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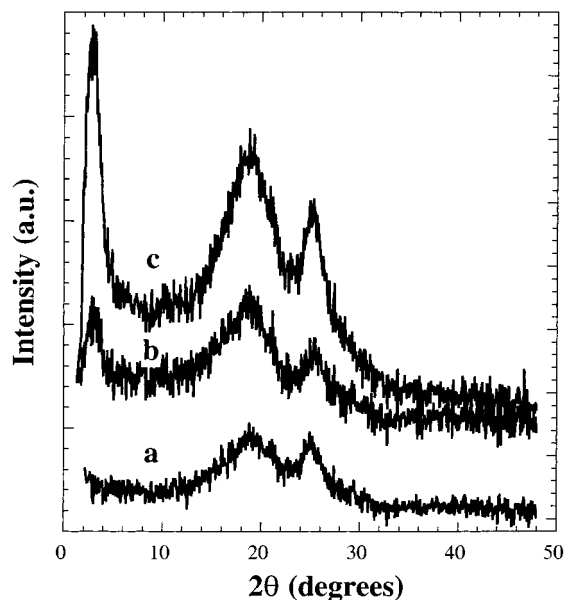
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**Figure 4.** Effect of external plasticizer on WAXD patterns of DPEPSA-doped-PANI: (a) film without the external plasticizer; (b) film containing 30 wt % of dioctyl phthalate (DOP) with respect to PANI base; (c) film containing 30 wt % of tritoyl phosphate (TTP) with respect to PANI base.

of a much more regular stacking of PANI chains in our newly developed materials as compared to other doped-PANI-based systems.

PANI doped with the esters containing alkoxy substituents exhibited similar diffraction patterns; however, the samples were less crystalline.

We have also studied the influence of an external plasticizer on supramolecular structure of polyaniline doped with diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid, in view of our recent finding that its addition to the processing medium improves electrical transport properties of the solution processed films. As it has already been mentioned, two types of plasticizers were tested, namely, dioctyl phthalate (DOP) and tritoyl phosphate (TTP). In Figure 4 WAXD patterns of DPEPSA doped-PANI with and without the external plasticizer are shown. Surprisingly the addition of either DOP or TTP leads to a better crystalline order in doped-PANI films. This effect is especially pronounced for TTP (compare Figure 4a,c). The amount of the plasticizer added in both cases studied was 30 wt % with respect to PANI base. This corresponds to ca. 1 molecule of the plasticizer per 13.5–14 PANI repeat units. However even the addition of a very small amount of the plasticizer corresponding to one TTP (or DOP) molecule per 40–42 PANI repeat units has a measurable effect on the supramolecular structure and transport properties of doped-PANI (vide infra).

We must discuss the distribution of the external plasticizer in the polymer matrix. It is evident that the addition of the external plasticizer improves the crystalline order and the degree of crystallinity in PANI doped with diesters of 4-sulfophthalic acid. However, it does not enter the crystalline part of the polymer because the diffraction patterns of the films of externally plasticized PANI and those of PANI without the external plasticizer consist of the same set of Bragg reflections. Thus, it must remain in the amorphous regions. This,

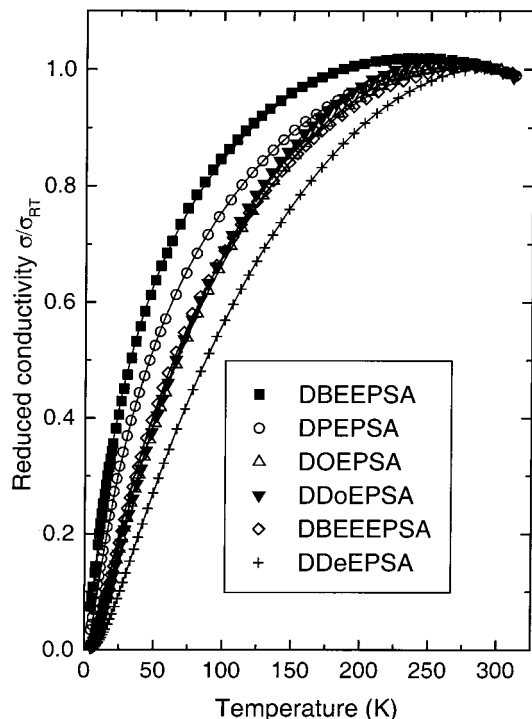
**Table 3. Room Temperature Conductivities<sup>a</sup> and Fit Parameters of Equation 1 for PANI Doped with Diesters of 1,2-Benzenedicarboxylic, 4-Sulfonic Acid**

dopant	$\sigma_{RT}$ , S·cm <sup>-1</sup>	$T_0$ , K	$\rho_0 \times 10^3$ , Ω·cm	$\rho_1 \times 10^2$ , Ω·cm
DPEPSA	138	81.4	8.87	3.80
DOEPSA	100	174.1	6.99	5.70
DDeEPSA	59	289.5	11.26	11.12
DDoEPSA	79	181.2	9.78	9.81
DBEEPSA	172	49.6	7.48	3.60
DBEEEPSA	97	151.8	11.07	7.13

<sup>a</sup> Measured at ambient atmosphere.

in turn, is manifested by changes in the shape and the relative intensity of the diffuse background of X-ray profiles of the films containing DOP or TTP. There is no evidence for phase separation between doped-PANI and the plasticizer in the amorphous zones of the polymer. For example, TTP plasticizer is a crystalline solid which gives a set of distinct sharp Bragg reflections. No such peaks are detected in PANI doped with DPEPSA and plasticized with TTP. Thus, we may conclude that the plasticizer is molecularly dispersed in the amorphous part of doped-PANI, and if any molecular aggregates exist, they are too small and too diluted to be detected by our measurements. The role of the external plasticizer in inducing a higher degree of crystallinity of doped-PANI can be described as follows. Although the plasticizer does not penetrate the crystalline regions, it induces higher flexibility of the system which, in turn, facilitates the creation of zones of crystalline order in the last stages of film casting. This effect of the external plasticizer is not astonishing since crystallization induced by solvents or other admixtures is known for nearly 40 years.

Room temperature conductivity and its temperature dependence were measured for both types of samples studied, i.e., without and with the external plasticizer. The results are collected in Table 3. It is clear that room temperature conductivity is strongly dependent on the length of the *n*-alkyl substituent in the dopant decreasing from pentyl to decyl, then increasing again for R= dodecyl group. In all series of experiments identical sequence of conductivities was found independently of the substrate used for casting. In Figure 5 the temperature dependence of the conductivity is presented for all samples studied. We have chosen to plot  $\sigma/\sigma_{RT}$  rather than the absolute value of the conductivity because this presentation allows for a better comparison of metallic behavior of PANI doped with different esters since all curves start from the same point. The relationship between the degree of crystalline order and the conductivity is not simple. First, as stated above, the crystalline order increases with the length of the *n*-alkyl substituent in the dopant, whereas the room temperature conductivity decreases (Table 3). Second, DBEEPSA-doped-PANI which is less crystalline than PANI doped with esters containing *n*-alkyl substituents is the most conductive and most metallic in character of all samples studied (Figure 5). In the analysis of the electrical transport properties of doped-PANI a heterogeneous model is generally adopted, which implies the coexistence of ordered regions of metallic conductivity with disordered regions exhibiting hopping-type conductivity.<sup>20</sup> In such a model charge carriers are supposed to travel successively across both types of regions in order

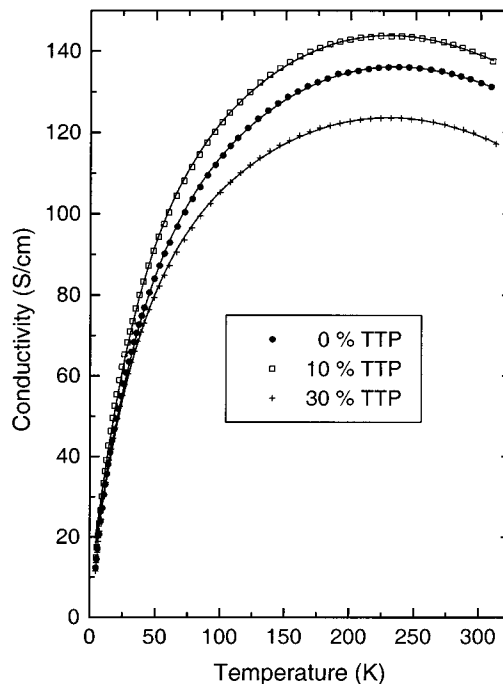


**Figure 5.** Temperature dependence of reduced conductivity  $\sigma/\sigma_{RT}$  for PANI doped with diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid.

to be displaced over macroscopic distances in the sample. The conductivity can thus be described by the following formula:

$$\sigma^{-1} = \rho_0 \exp(T_0/T)^\alpha + \rho_1 \exp(-\hbar\omega_0/kT) \quad (1)$$

where the first term accounts for the contribution to the resistivity originating from the hopping process in less ordered regions, whereas the second one is related to the metallic regions.  $\rho_0$  and  $\rho_1$  are constants which embrace both the intrinsic electrical properties of the system as well as geometrical (morphological) aspects of the two types of coexisting regions. In our calculations we tried to limit the number of free adjustable parameters. In particular, the energy of the phonons which are responsible for the scattering of electrons was fixed ( $\hbar\omega_0 = 0.08$  eV), and the value of  $\alpha$  was fixed as 0.5, taking into account our previous studies on CSA-doped-PANI.<sup>21</sup> With these two parameters fixed, we got a very good agreement between the calculated and experimental data (Figure 5). The fit parameters are collected in Table 3. From the inspection of the data it can be immediately noticed that  $T_0$  is the most sensitive of all parameters of eq 1 and can be correlated with the conductivity of the sample. It increases almost 6 times when going from the most to the least conductive sample. Since  $T_0$  is associated with the hopping conductivity term, it can be postulated that the differences in the conductivity values observed for the samples studied are mainly governed by the variation of the conductivity of the disordered area. This observation



**Figure 6.** Effect of external plasticizer, tritolyl phosphate (TTP), on electrical conductivity of DPEPSA doped-PANI.

underlines the importance of the processing conditions. If disorder in the hopping conductivity areas is further reduced, samples of much more pronounced metallic behavior can be fabricated. Similarly the  $\rho_1$  parameter reflecting the metallic contribution can be correlated with the conductivity of the sample.

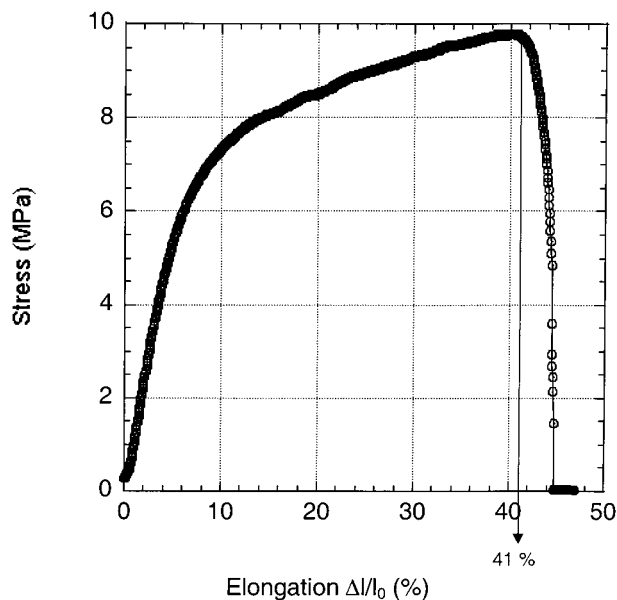
The influence of the addition of the external plasticizer on the electrical transport properties of diester doped-PANI is clearly illustrated for DPEPSA as the dopant and TTP as the external plasticizer. Qualitatively the same behavior is observed for other dopants and other external plasticizers tested (DOP). The addition of small amounts of the external plasticizer leads to an increase in the conductivity of doped-PANI (Figure 6). Further increase in the external plasticizer content leads to a ca. 10% drop in the conductivity, but this drop is only apparent because it can be correlated with the 10% decrease in the content of the electrically active component of the sample, i.e., PANI chains which constitute the pathway for charge carriers. For 30 wt % of TTP (with respect to PANI base) the content of PANI in the sample decreases from 30 to 27 wt %, i.e., by 10% of the mass of PANI base. The addition of TTP results in lowering of  $T_0$  by 15% when going from the sample with 0% TTP to the one with 30% TTP, whereas the  $\rho_1$  parameter remains essentially unchanged. It is therefore clear that the addition of an external plasticizer leads to a better crystalline order in the sample, which in turn improves its metallic character.

Two excellent properties of our newly developed conducting PANI films should be underlined. They exhibit mechanical properties typical of plastics. Even without the addition of the external plasticizer, they can be bent several times without damage and show elongation at break up to 45%, which is 1 order of magnitude higher than in the case of CSA-doped-PANI cast from *m*-cresol. A typical stress-strain curve is presented in Figure 7. It should be noted here that PANI(CSA)<sub>0.5</sub>

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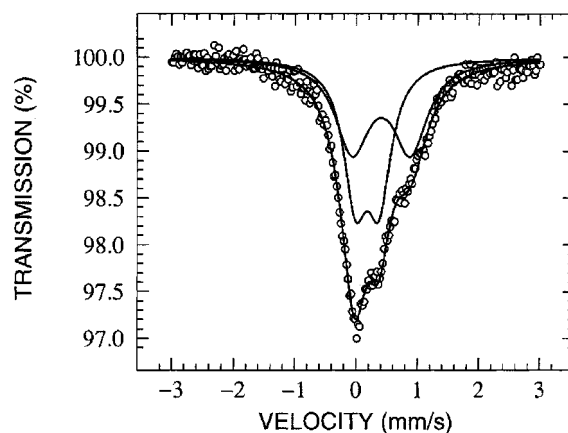




**Figure 7.** Stress-strain curve for DBEEPSA doped-PANI (drawing rate, 0.5 mm/min).

tested in the same experimental conditions shows 20 times lower elongation at break. The films are also thermally stable. PANI(DEHEPSA)<sub>0.5</sub> of the initial room temperature conductivity of  $92 \text{ S}\cdot\text{cm}^{-1}$ , after 27 days of heating at  $135 \text{ }^\circ\text{C}$  in air, still showed a relatively high room temperature conductivity of  $6.7 \text{ S}\cdot\text{cm}^{-1}$ .

Our search for new systems improving solution processibility of polyaniline have recently led us to the discovery of a new class of PANI dopants, namely, Lewis acids.<sup>10,22</sup> Complexation of PANI base with Lewis acids such as  $\text{AlCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{SnCl}_4$ , and  $\text{FeCl}_3$ , etc., renders PANI soluble in nitromethane or acetonitrile, i.e., solvents, which dissolve neither the PANI base nor its protonated form. Improved solubility of Lewis acid doped-PANI is due to the fact that this type of doping occurs at essentially 100% of PANI basic sites, eliminating in this manner the possibility of interchain hydrogen bonding formation which, in turn, constitutes the major obstacle in PANI solubilization.<sup>23</sup> However, one disadvantage of the Lewis acid doping must be pointed out. It leads to films which are less conductive than films of Brönsted acid doped-PANI, showing the conductivity of the order  $10^{-2}$ – $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ . For this reason we have applied mixed (Brönsted acid followed by Lewis acid) doping. The reasoning behind the use of the mixed-doping can briefly be presented as follows. Brönsted acid doping is limited to ca. 50% of available basic sites; thus, it cannot eliminate completely the hydrogen bonding formation in PANI. This can be however achieved by additional complexation with a Lewis acid. In protonated PANI two types of bases coexist: anions introduced into the polymer matrix via protonation which are weaker bases and nonprotonated nitrogens which are stronger bases. Lewis acid should react only with the latter ones if added stoichiometrically with respect to nonprotonated sites. Mixed-doping should combine some advantages of both Brönsted and Lewis acid dopings.



**Figure 8.** Mössbauer effect spectrum of PANI(DEHEPSA)<sub>0.42</sub>(FeCl<sub>3</sub>)<sub>0.42</sub>(NM)<sub>0.12</sub> registered at 78 K.

For mixed-doping we have used DEHEPSA as the Brönsted acid and  $\text{FeCl}_3$  as the Lewis acid. The addition of  $\text{FeCl}_3$  to a suspension of DEHEPSA-doped-PANI powder in nitromethane results in a quick dissolution of the polymer. The obtained solution has film forming properties, and free-standing films can be obtained by casting in dry  $\text{N}_2$  atmosphere. The composition of the cast film, determined analytically, was PANI-(DEHEPSA)<sub>0.42</sub>(FeCl<sub>3</sub>)<sub>0.42</sub>(NM)<sub>0.12</sub>, where NM denotes nitromethane. The degree of solvation of  $\text{FeCl}_3$  dopant molecules by nitromethane in mixed-doped-PANI is significantly lower than in the case of Lewis acid doping of PANI base where ca. 2/3 of dopant molecules were solvated.<sup>10</sup>

Mixed-doped-PANI of the composition of PANI-(DEHEPSA)<sub>0.42</sub>(FeCl<sub>3</sub>)<sub>0.42</sub>(NM)<sub>0.12</sub> gives clear  $^{57}\text{Fe}$  Mössbauer effect spectra whose intensity is strongly temperature-dependent as in the case of purely Lewis acid doped samples (Figure 8). The spectrum can be deconvoluted into two doublets of roughly identical intensity with Mössbauer parameters characteristic of Fe(III) with high degree of covalency, as predicted. The Mössbauer parameters registered at 78 K are as follows: (internal doublet) isomer shift (IS) = 0.29 mm/s vs  $\alpha$ -Fe, quadrupole splitting (QS) = 39 mm/s (53% of intensity); (external doublet) IS = 0.53 mm/s vs  $\alpha$ -Fe, QS = 95 mm/s (47% of intensity). No traces of the reduced form of iron (Fe(II)) unequivocally shows that the doping with  $\text{FeCl}_3$  is purely acid-base in nature and does not involve redox side reactions. However, the coexistence of two nonequivalent doublets can be taken as evidence of two nonequivalent complexation sites for Lewis acid dopant in PANI chains, possibly due to syn- and anti-chain conformation as postulated by Kulszewicz-Bajer and Suwalski.<sup>24</sup> Films of mixed-doped-PANI, cast from solution, show the conductivity of  $8 \text{ S}\cdot\text{cm}^{-1}$  at room temperature.

One may expect that doping of solid PANI base with DEHEPSA in nitromethane may lead to inhomogeneous dopant distribution due to diffusion limits in the solid-state reaction. However, the fact that  $\text{FeCl}_3$  complexation of PANI(DEHEPSA)<sub>0.42</sub> leads to a complete solubilization of the sample, without the presence of an insoluble fraction, seems to indicate that the complex-

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ation with  $\text{FeCl}_3$  must be homogeneous. This of course is possible only under the condition that the Brønsted acid doping (DEHEPSA doping), which is carried out prior to the Lewis acid ( $\text{FeCl}_3$ ) doping, is also homogeneous. Otherwise, upon complexation with  $\text{FeCl}_3$ , an insoluble fraction should exist and the soluble fraction should show lower content of DEHEPSA, with respect to PANI repeat unit, which is not the case.

### Conclusions

To summarize, we have demonstrated that solution processible polyaniline of metallic-type conductivity can be prepared by its doping (protonation) with plasticizing dopants, namely, diesters of 1,2-benzenedicarboxylic, 4-sulfonic acid containing either alkyl or alkoxy substituents (so-called internal plasticizers). The resulting

films exhibit a layered supramolecular structure whose degree of ordering depends on the size of the substituent in the ester used for doping. The addition of an external plasticizer together with the internal one improves both the processibility and the metallic behavior of PANI. Application of a sequence of dopings (Brønsted acid doping followed by the Lewis acid one) also improves solution processibility of PANI.

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