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Highly Conducting and Solution-Processable Polyaniline Obtained via Protonation with a New Sulfonic Acid Containing Plasticizing Functional Groups

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ABSTRACT: New solution processing systems were studied with the goal to obtain highly conductive polyaniline films with good mechanical properties and its conducting blends with poly(methyl methacrylate). A new dopant, namely, 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(2-ethylhexyl) ester (DEHEPSA), was studied as a protonating agent. It was found that the use of this dopant together with dichloroacetic acid (DCAA) or difluorochloroacetic acid (DFCAA) as solvents leads to films showing conductivities of 180 and 100 S/cm, respectively. Films cast from DCAA are metallic in character down to 220 K. Since the protonation agent used exhibits doping as well as plasticizing properties, the resulting polyaniline films, in addition to high conductivity, show excellent flexibility and much lower glass-transition temperature, T_g, (280 K) as compared to polyaniline doped with other protonating agents. Moreover, the same processing system can be used for the fabrication of polyaniline−poly(methyl methacrylate) blends with low percolation threshold (much below 1 wt % of PANI). Upon casting, the overwhelming majority of the solvent can be efficiently removed from the polymer matrix, whereas the remaining residual solvent is strongly bound to the polymer matrix. For this reason, the resulting blends do not show the disadvantages of the blends cast from *m*-cresol which release the residual solvent upon aging.

Introduction

Polyaniline belongs to one of the most intensively studied polymers in the past decade. This scientific interest is stimulated mainly by its extremely interesting electronic and electrochemical properties. Unfortunately, polyaniline is very difficult to process, especially in its protonated, i.e., conducting, state. Research efforts led however to the discovery of several solvents, which can be used in the solution processing of conducting polyaniline. For example, if polyaniline base is added to acetic acid or formic acid, it undergoes protonation with simultaneous dissolution.[1] However, the films cast from these solutions show low conductivities (0.1−0.5 S/cm) and very poor mechanical properties. In addition, they are not resistant against deprotonation. Much higher conductivity is obtained for the films cast from a three-component mixture: polyaniline (PANI), camphor sulfonic acid (CSA) as the dopant, and *m*-cresol (MC) as the solvent. Nonoriented films of PANI(CSA)$_{0.5}$ show a conductivity exceeding 300 S/cm. In addition, this conductivity is metallic in character down to 220 K. Unfortunately, films processed from *m*-cresol exhibit very poor mechanical properties and have the tendency to slowly release the solvent, whose large quantities (up to 15 wt %) remain in the polymer film after casting.[2,3] Films of polyaniline exhibiting metallic type conductivity can also be prepared from polyaniline/camphorsulfonic acid/hexafluoro2-propanol three-component system.[4] However, the use of fluorinated alcohols at the industrial scale does not seem possible due to their toxicity and high cost. Very recently, a new processing system leading to “metallic” polyaniline has been developed. It consists of polyaniline, 2-acryloamido-2-methyl-1-propanesulfonic acid as the dopant, and dichloroacetic acid as the solvent.[5]

Both crystallinity and conductivity of the solution-processed polyaniline films strongly depend on specific interactions between all three components of the system used for the casting. For example, for PANI/CSA/MC, a concept of “secondary doping” has been introduced.[6,7] This concept was further developed by Ikkala et al.[8,9] who showed that due to molecular matching and H-bonding interactions a molecular complex is formed involving all three components of the processing system. The formation of this complex facilitates the ordering of the polymer upon the removal of the solvent, and the resulting PANI(CSA)$_{0.5}$ films show enhanced crystallinity as compared to other types of polyaniline.

In view of the rather poor mechanical properties of highly conducting PANI, we were tempted to develop a new polyaniline processing system which would lead to films of high conductivity and good mechanical properties. In particular, we decided to synthesize a new PANI protonating agent which would combine doping and plasticizing properties. Protonation of such a dopant should result in a significant improvement of doped polyaniline flexibility by lowering its glass-transition temperature (T_g). It should be noted here that doping-induced plasticizing of polyaniline is not new.[10,11] Dodecylbenzenesulfonic acid when used in excess is an efficient plasticizing agent,[2] dialkyl phosphates plasticize polyaniline even at 0.3 dopant to PANI mer ratio,[10] where PANI mer involves one ring and one nitrogen. Camphorsulfonic acid-doped PANI films cast from *m*-cresol are also plasticized by the dopant and residual solvent. This is not surprising since camphor was

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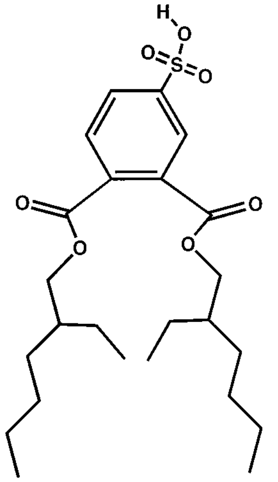
Chart 1



employed decades ago to plasticize cellulose derivatives. However, none of the mentioned above plasticizing/doping agents led to solution-processed PANI of good mechanical properties.

Phthalic acid esters belong to the most efficient plasticizers for a large variety of polymers. One can therefore postulate that the functionalization of the most popular plasticizer di-2-ethylhexyl phthalate with a $-SO_3H$ group should produce a molecule with doping and plasticizing properties. In this paper, we describe the synthesis of this dopant (see Chart 1), 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(2-ethylhexyl) ester (abbreviated as DEHEPSA, the di(2-ethylhexyl) ester of phthalosulfonic acid), and discuss the properties of polyaniline doped with this protonating agent. In the last part of the paper, we describe the fabrication of PANI(DEHEPSA)$_{0.5}$-based blends with poly(methyl methacrylate).

Experimental Section

1. Synthesis of 1,2-Benzenedicarboxylic Acid, 4-Sulfo, 1,2-Di(2-ethylhexyl) Ester (DEHEPSA) (Chart 1). 4-Sulfophthalic acid (6.3 g, 25.6 mmol) in a form of 50 wt % water solution was mixed with 10 g (76.8 mmol) of 2-ethyl-1-hexanol at room temperature, under nitrogen flow. The temperature of the reaction mixture was then raised to 110−120 °C. At this temperature, the reaction was carried out for 2−3 h with constant evaporation of water, which was a side product. The reaction mixture was then poured into 1 M HCl aqueous solution. After 5−10 min, it separated into two layers. The organic layer was recovered, washed three times with 1 M HCl aqueous solution, and finally extracted with ether. The crude product was then dried over $MgSO_4$. The volatile contaminants were removed by rotary evaporation. The product was identified by elemental analysis, IR, ^{1}H NMR, and mass spectroscopy. The slight excess in oxygen and hydrogen content observed in elemental analysis is due to the hygroscopic nature of the synthesized acid. The yield calculated with respect to the reagent taken in deficit (the acid) is essentially 100%. Anal. Calcd for $C_{24}H_{38}SO_7$: C, 61.28; H, 8.09; S, 6.80; O, 23.83. Found: C, 61.28; H, 8.71; S, 6.35; O, 24.36. ^{1}H NMR ($CDCl_3$, ppm): 0.91 (12 H), 1.31 (16H), 1.68 (2H), 4.25 (4H), 7.74 (d, 1H), 7.99 (d, 1H), 8.17 (s, 1H), 9.40(s,1H). IR (KBr, cm^{-1}): 3403 (m), 3060 (w), 2946 (s), 2938 (s), 2873 (m), 2967 (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). MS (FAB mode), Micromass (Trio-2): *m*/*z* 471.2 (MH$^+$).

2. Synthesis of Polyaniline Base. Polyaniline was synthesized using a modification of the method described by Beadle et al.[12] The reaction was carried out at − 27 °C. First, the solution of aniline was prepared in HCl-acidified water/alcohol containing LiCl. The exact composition of the solution was as follows: 10 mL (0.1097 mol) of aniline, 85 mL of 3 M HCl, 95 mL of ethanol, and 16 g of LiCl. This solution was mixed with precooled oxidizing solution: 6.25 g (0.0274 mol) of ammonium persulfate, 60 mL of 2 M HCl, and 8 g of LiCl.

The reaction was carried out with constant monitoring of the temperature and the potential. After approximately 2 h, a reducing solution consisting of 3.64 g (0.0183 mol) of $FeCl_2$, 5 g of LiCl, and 50 mL of 2 M HCl was added in order to better control the oxidation state of polyaniline. After an additional 1 h, the reaction was terminated by the separation of the precipitated polymer on a Buchner funnel. The precipitate was then repeatedly washed with distilled water and then methanol and finally dried to constant mass.

The obtained emeraldine hydrochloride was then transformed to the free base state by treatment with 2 L of 0.3 M NH_3 (aq) for 48 h. Emeraldine base was then rinsed with 5−6 L of distilled water and then 2 L of methanol and dried to constant mass. In the next step, the low-molecular-weight fractions were removed by consecutive extractions with methanol and chloroform in a Soxhlet apparatus. The resulting polyaniline in the form of emeraldine base showed inherent viscosity of 2.25 dL/g for 0.1 wt % solution in 96 wt % sulfuric acid.

3. Protonation of Polyaniline. Protonation of polyaniline base with DEHEPSA was carried out at room temperature using four solvents, namely, *m*-cresol, hexafluoro-2-propanol (HFIP), dichloroacetic acid (DCAA), and difluorochloroacetic acid (DFCAA).

In all cases, the DEHEPSA molecule to PANI(mer) ratio was 0.5. The concentrations of the solutions used for the protonation were ca. 0.8 wt % with respect to the polyaniline base. In these conditions, the dissolution of the protonated polymer is essentially complete. However, it should be noted that some precautions must be taken if DCAA is used as the solvent. In this case, the solutions of the concentrations exceeding 3 wt % undergo some gelation. The protonation reaction lasted typically 5 days, which was sufficient to fully dissolve the polymer. Freshly prepared solutions were then filtered through a 0.45 μm microfilter.

4. Casting of Films of PANI(DEHEPSA)$_{0.5}$. Films of PANI(DEHEPSA)$_{0.5}$ were cast in nitrogen flow in a specially designed apparatus which enabled precise control of the casting temperature and atmosphere. In the cases of MC and DCAA, the casting temperature was 40 °C. Films from DFCAA were cast at 26 °C. Typical casting time was 48 h. All free-standing films prepared by casting were additionally pumped in a vacuum of 10^{-5} Torr at 50 °C overnight in order to completely remove the solvent.

5. Preparation of Blends of PANI(DEHEPSA)$_{0.5}$ with Poly(methyl methacrylate). Blends of PANI(DEHEPSA)$_{0.5}$ with poly(methyl methacrylate) (PMMA) were cast from DCAA solvent at 40 °C under nitrogen flow. Prior to casting, the solution of PMMA and the plasticizer, dibutylphthalate (DBP), was mixed with DCAA solution containing an appropriate amount of PANI(DEHEPSA)$_{0.5}$. The concentration of the matrix polymer solution was 6 wt % with respect to PMMA, and the DBP/PMMA weight ratio was 0.35. The mixture was carefully homogenized by vigorous stirring for 24 h at room temperature. Films were cast on glass substrates.

6. Characterization Techniques. Both the solutions and the cast films were characterized by UV−vis−NIR spectroscopy.

The spectra were registered on Lambda 900 Perkin-Elmer spectrometer.

The cast films were additionally subjected to elemental analysis, conductivity measurements, and thermomechanical investigations.

Room temperature conductivity was measured in air using a four-points technique with pressure contacts. The temperature dependence of conductivity was measured on pumped samples using the same method. However in this case, to ensure good electrical contacts, four gold lines were evaporated through a mask to which 25 μm golden wires were attached by pressing. The temperature of the sample during the

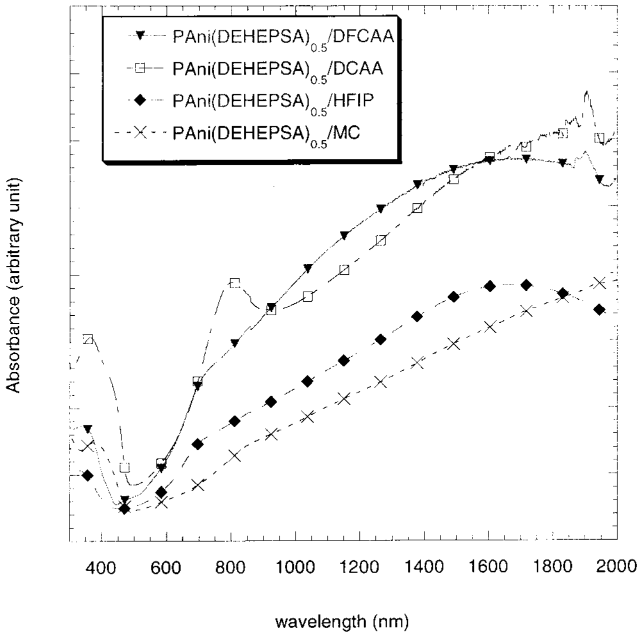


Figure 1. Solution spectra of PANI(DEHEPSA)$_{0.5}$ in four solvents studied.

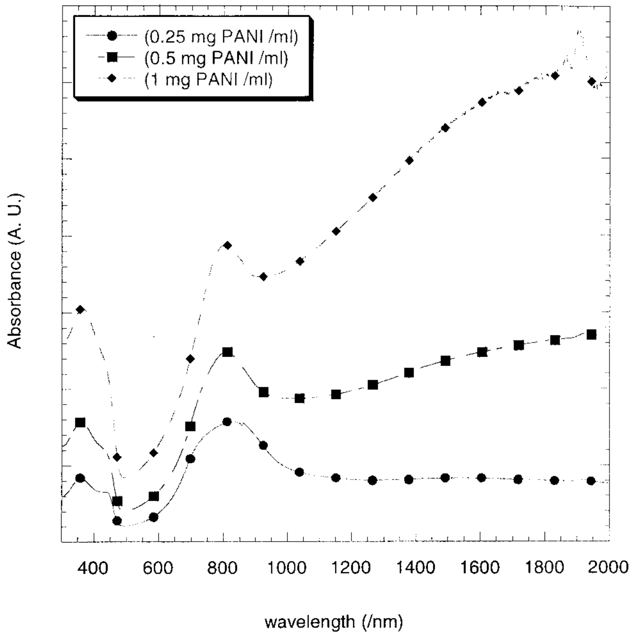


Figure 2. Effect of concentration on the solution spectra of PANI(DEHEPSA)$_{0.5}$ in dichloroacetic acid (DCAA).

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 impedance of 2×10^{14} Ω. The probe was placed into a continuous-flow helium cryostat allowing the conductivity measurements in the temperature range 4–320 K.

Dynamical mechanical tests were carried out in a temperature range of 130–600 K using a Rheometrics RSA2 spectrometer in the tensile mode. For thermomechanical investigations, the samples were cut as thin rectangular strips with typical dimensions of $20 \times 6 \times 0.1$ mm^3. The tests were performed in linear viscoelasticity region (maximum strain ϵ was 5. 10^{-4}), using isochronal mode at 1 Hz with temperature varying in 3 K increments. The spectrometer measures the complex tensile modulus E^*, i.e., both the storage E' and the loss E'' components. The results are displayed through E' and tan δ ($=E''/E'$).

Results and Discussion

UV–vis–NIR spectroscopy is a very sensitive tool for the studies of polyaniline protonation and more precisely for the elucidation of the interactions between the solvent, the doping anion, and the polymer chain. To date, most spectroscopic studies were devoted to the PANI/camphorsulfonic acid (CSA)/*m*-cresol system.[13] In this case, strong broadening of the near-infrared absorption in the solution spectra was observed. MacDiarmid et al.[14] interpreted this increasing absorption tail as a spectroscopic manifestation of the charge carriers (polarons) delocalization. Using the concepts of supramolecular chemistry, Ikkala et al.[8,9] have demonstrated that in this particular system a molecular complex was formed between the polymer, the CSA originating anion, and *m*-cresol. According to these authors, the formation of this complex favors polaron delocalization along the polymer chain which in turn gives rise to the broadening of the absorption band in the near-infrared part of the spectrum. More recently, other solvent/dopant couples were found which give rise to more or less broadened NIR bands.[4]

In Figure 1, spectra of PANI(DEHEPSA)$_{0.5}$ in four different solvents are collected. The spectrum registered in *m*-cresol is essentially indistinguishable from that of PANI(CSA)$_{0.5}$ in the same solvent.[14] Strong delocalization of polarons is also observed for PANI(DEHEPSA)$_{0.5}$ in DCAA. In this case, a small peak with a maximum at ca. 780 nm attributed to localized polarons is superimposed on a monotonically increasing absorption characteristic of charge delocalization. The spectra recorded in DFCAA and HFIP strongly resemble the spectrum of PANI(CSA)$_{0.5}$ recorded in HFIP.[4] In both cases, a very broad NIR absorption with a clear maximum around 1700 nm is observed. From this quick inspection, it is clear that DCAA is a very promising solvent for solution processing of highly conducting polyaniline films. The spectra of PANI(DEHEPSA)$_{0.5}$ recorded in this solvent are almost as good as those recorded in *m*-cresol, and the solvent is much easier to work with and much easier to remove completely from the film (vide infra).

Processing of PANI(DEHEPSA)$_{0.5}$ from DCAA should however be treated with caution because transport properties of the resulting film depend on the initial concentration of the processing solution. In Figure 2, UV–vis–NIR spectra of PANI(DEHEPSA)$_{0.5}$ solutions in DCAA are shown for three different concentrations. It is clear that the shape of the spectra is concentration-dependent. Upon dilution, the contribution of the peak associated with localized polarons increases. For the concentration of 0.25 mg/mL of PANI solution in DCAA, the spectrum of PANI(DEHEPSA)$_{0.5}$ is indistinguishable from that of PANI(CSA)$_{0.5}$ in inert solvents such as chloroform. Three observed transitions at 360, 440, and ca. 800 nm are associated with localized polarons,[14] the NIR tail due to delocalized charge is virtually nonexistent.

The spectra of solid films of PANI(DEHEPSA)$_{0.5}$ prepared by casting from DCAA and DFCAA solutions are shown in Figure 3. The small contribution due to localized polarons, clearly observed in the DCAA solution spectrum, disappears almost totally upon removal of the solvent (compare Figures 2 and 3). Thus, spectral features of thin solid films cast from DCAA indicate that PANI(DEHEPSA)$_{0.5}$ may exhibit high electrical conductivity, possibly of metallic character. In the spectrum

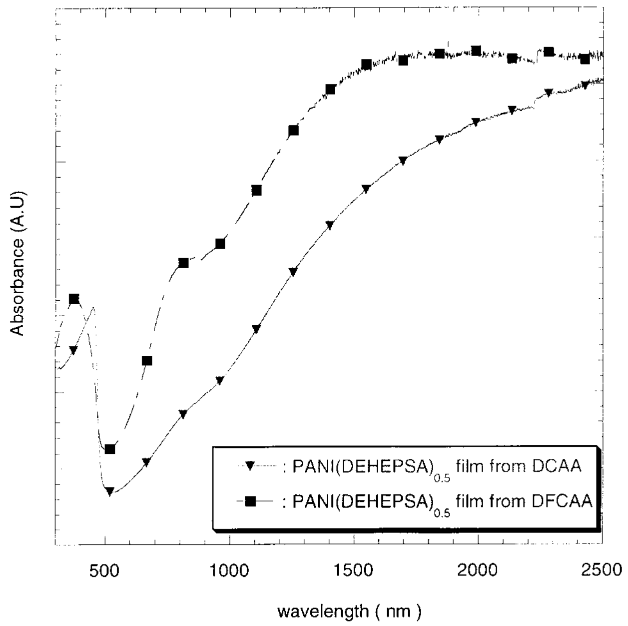


Figure 3. Solid-state spectra of PANI(DEHEPSA)$_{0.5}$ thin films prepared by casting from 1 mg of PANI/mL DCAA solution and 1 mg of PANI/mL DFCAA solution.

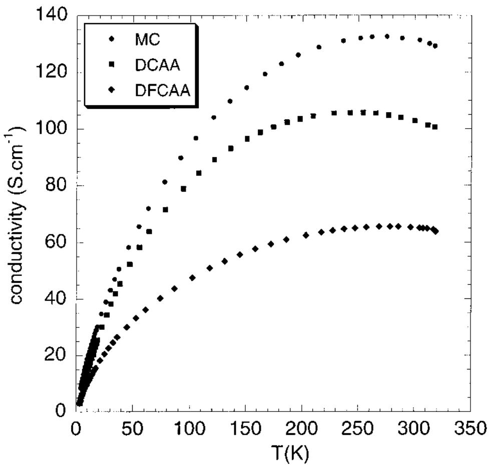


Figure 4. Linear plot of the conductivity vs temperature for PANI(DEHEPSA)$_{0.5}$ films cast from MC, DCAA, and DFCAA.

of PANI(DEHEPSA)$_{0.5}$ film cast from DFCAA, the band attributed to localized polarons is more pronounced.

Room temperature conductivities of free-standing PANI(DEHEPSA)$_{0.5}$ films cast from MC and DCAA are very high, in the range of 230 and 180 S/cm for MC- and DCAA-processed films, respectively. The films cast from DFCAA show lower conductivity, in the range of 100 S/cm. It is clear that DCAA is a very good solvent for preparing highly conducting films of PANI(DEHEPSA)$_{0.5}$. In Figure 4, temperature dependence of direct current conductivity is presented for PANI(DEHEPSA)$_{0.5}$ films cast from DCAA, DFCAA, and MC. Correct determination of σ versus T characteristics requires careful removal of water from the sample. It is known that water strongly influences electronic conductivity of doped polyaniline.[15] For this reason, samples must be pumped prior to the measurements for an extended period of time until no further drop in the conductivity is observed. As a result, room temperature conductivities reported in Figure 4 are lower than those measured in air. Films cast from DCAA and MC are metallic in character over a limited temperature range, down to 220 and 280 K, respectively. In the former case, the zone of metallic type conductivity is comparable to that reported for the best PANI(CSA)$_{0.5}$ samples cast from MC.[16,17]

DCAA solvent used for PANI(DEHEPSA)$_{0.5}$ is quite acidic (pK_a = 1.48). One can therefore expect that DCAA can participate in the doping of PANI together with DEHEPSA. To verify this hypothesis, we have carried out elemental analysis of doped PANI films. As already stated, the PANI base used for doping with DEHEPSA in DCAA was washed with chloroform in a Soxhlet apparatus. Such a procedure improves the molecular weight of the polymer. However, it introduces a small amount of chlorine of unclear chemical nature which is virtually impossible to remove. To determine the extent of PANI doping with DCAA solvent, one must take into account the correction for chlorine originating from Soxhlet-washed PANI base. This correction was calculated as follows: First, the content of chlorine in PANI base was determined analytically as 2.41 wt %. Then, the increase of PANI mass after doping was determined gravimetrically. It turned out that the initial mass of PANI base used in the doping reaction constituted 30.1 wt % of the mass of the doped sample. This means that in the doped sample the percentage of chlorine originating from PANI base must be equal to $2.41 \times 0.301 = 0.72$ wt %. Since elemental analysis for doped PANI gives 1.96 wt % of chlorine, the content of chlorine originating from DCAA solvent must be equal to $1.96 - 0.72 = 1.24$ wt %. Using this assumption, one can propose the following formula for PANI doped with DEHEPSA in DCAA solution: PANI(DEHEPSA)$_x$(H$_2$O)$_y$-(DCAA)$_z$. The best agreement between the calculated and analytically determined data is obtained for $x = y = 0.45$, $z = 0.06$ (see Table 1). The above formula indicates that each DEHEPSA molecule entering to the polymer matrix is solvated with one molecule of water. This is not unexpected when the high hydrophilicity of $-$SO$_3$H group which can serve as a “drying agent” in the solution used for doping is taken into account. The results of elemental analysis also indicate that ca. 12% of sites available for protonation are protonated with the solvent and not by DEHEPSA. This however constitutes only 2.3 wt % of the total mass of the sample, which is much less than in the case of PANI(CSA)$_{0.5}$ cast from MC where up to 15 wt % of the solvent may remain in the film after casting. Despite very similar volatility of dichloroacetic acid and *m*-cresol (194 and 203 °C, respectively) residual DCAA cannot be pumped off because, being a much stronger acid than MC, it is strongly bound to the polymer matrix via protonation. On the contrary, MC in the presence of a stronger acid does not protonate PANI but forms a weak complex (via hydrogen bond) with the counterion. As a result, it is being constantly released from the doped PANI matrix upon pumping or aging.[8,9]

We confirmed the hypothesis of partial protonation with DCAA and hydration with water by an additional elemental analysis that was carried out for PANI which was not washed with chloroform. In this case, the content of residual chlorine is much lower (0.98 wt %). Moreover, we carefully dried PANI, the dopant, and the solvent with the goal of fitting elemental analysis without the necessity of taking into account the hydration of the dopant. Using the same procedure as described above for the calculation of chlorine originating from the solvent, we got a very good agreement

Table 1. Elemental Analysis of PANI Protonated with DEHEPSA in DCAA

	% Cl					
	originat. from PANI base	originat. from DCAA solvent	%C	%H	%N	%S
found (sample 1[a])	0.72	1.24	63.58	6.92	4.43	4.41
calcd for PANI(DEHEPSA)$_{0.45}$(H$_2$O)$_{0.45}$(DCAA)$_{0.06}$		1.34	63.68	7.09	4.39	4.51
found (sample 2[b])	0.29	0.93	65.28	7.12	4.44	4.70
calcd for PANI(DEHEPSA)$_{0.46}$(DCAA)$_{0.04}$		0.91	65.66	7.05	4.47	4.67

[a] PANI base used in the doping experiments was washed with chloroform in a Soxhlet apparatus. [b] PANI base used in the doping experiments was not washed with chloroform.

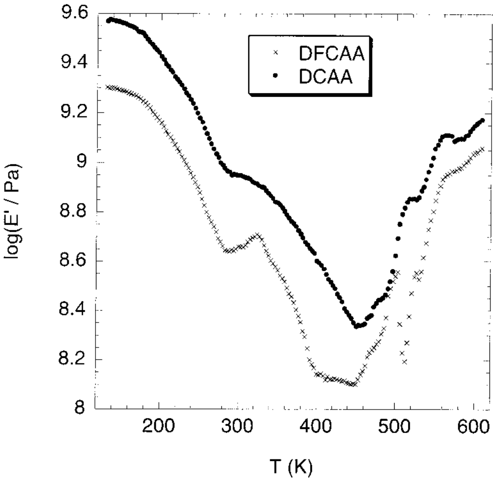


Figure 5. Logarithm of the storage tensile modulus E' vs temperature at 1 Hz for PANI(DEHEPSA)$_{0.5}$ cast from DCAA and DFCAA.

between the calculated and analytically determined values for the following formula: PANI(DEHEPSA)$_{0.46}$(DCAA)$_{0.04}$, which does not need to take into account the presence of water (see Table 1).

Taking into account that PANI(DEHEPSA)$_{0.5}$ films are very flexible at room temperature, one should expect a rather low T_g for the system studied. We have therefore carried out thermomechanical analysis for the samples prepared, which is a convenient method for the determination of T_g. We have extended these studies to temperatures above 300 K with the goal of verifying thermal stability of DEHEPSA-doped PANI and more precisely of determining the onset of the cross-linking which frequently occurs in conducting polymers at elevated temperatures. This cross-linking process causes an irreversible increase in the Young modulus and an irreversible drop in polymer conductivity.

Figures 5 and 6 show the plot of the storage tensile modulus (E') and loss angle tangent (tan δ) as a function of temperature registered at 1 Hz for PANI(DEHEPSA)$_{0.5}$ films cast from DCAA and DFCAA. At low temperatures, the storage tensile modulus (E') is high and is typical of a glassy polymer. As the temperature increases above 180 K, E' decreases rapidly. This phenomenon is ascribed to the glass−rubber transition. The modulus drop corresponds to an energy dissipation displayed in a relaxation process where tan δ passes through a maximum (Figure 6). This relaxation process involves cooperative motions of long amorphous chain sequences. T_g calculated from the maximum of the first peak in the tan $\delta = f(T)$ relationship in both cases studied is 280 K, which is much lower than that typically observed for protonated polyaniline. For example Abell et al.[18] on the basis of DSC and DMA analysis determined T_g in PANI(CSA)$_{0.5}$ cast from MC as being in the range of 403−423 K. The significantly lower T_g value observed in our case can be rationalized by a plasticizing effect of the dopant. Above 330 K, a new relaxation process starts which gives rise to a new maximum in the tan $\delta = f(T)$ plot at 435 K. The origin of this relaxation is not clear at the present time. Above 460 K, a quick increase of E' is observed which can be correlated with a strong maximum in the tan $\delta = f(T)$ curve. As already stated, the increase of the real part of the modulus can be attributed to cross-linking effects, influencing in an irreversible way the conductivity of the polymer as shown by aging studies.[19]

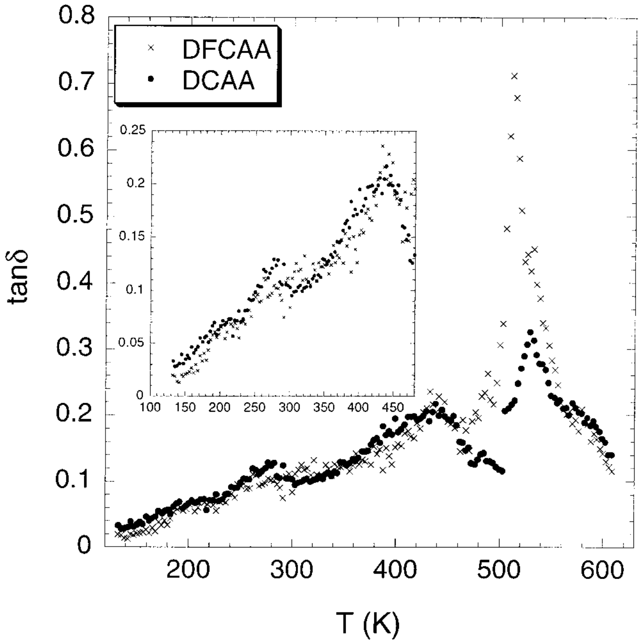


Figure 6. Loss angle tangent (tan δ) vs temperature at 1 Hz for PANI(DEHEPSA)$_{0.5}$ cast from either DCAA or DFCAA. The inset shows the temperature zone 100−480 K in detail.

Taking into account excellent electrical transport and mechanical properties of PANI(DEHEPSA)$_{0.5}$ cast from DCAA, we have selected this solvent as the processing medium in the preparation of PANI-based blends with poly(methyl methacrylate). Similarly as DEHEPSA-protonated polyaniline, the matrix polymer can be readily dissolved in DCAA which makes possible solution processing of the blends.

It is known from our previous work[20] that the addition of a plasticizer to the matrix polymer efficiently lowers the percolation threshold in the solution-cast polyaniline-based blends. It would seem therefore highly probable that the blend consisting of DEHEPSA-protonated and -plasticized polyaniline and dibutyl phthalate-plasticized PMMA should exhibit a very low per-

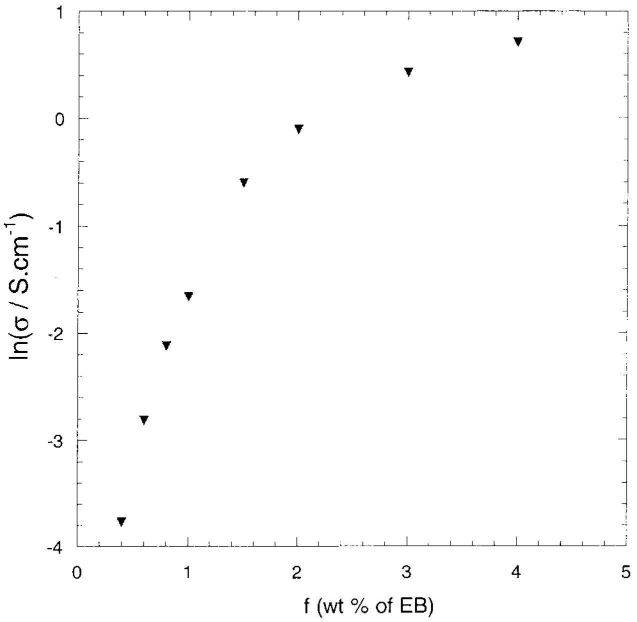


Figure 7. Conductivity vs PANI content in PANI(DEHEPSA)$_{0.5}$–DBPh-plasticized PMMA blends prepared by casting from DCAA. DBPh/PMMA weight ratio = 0.35.

colation threshold. In Figure 7, the conductivity of such blend is plotted versus the content of the conductive phase (polyaniline). For comparative reasons, it is convenient to express the content of the conductive phase as weight percent of polyaniline base (EB) used for the preparation of a given blend because it allows for a comparison of the blends of polyaniline protonated with protonating agent of different molecular weights. The observed conductivity changes are characteristic of percolating systems. To determine the percolation threshold (f_p), we have fitted the data presented in Figure 7 to the scaling law of the percolation theory:[21]

$$\sigma(f) = c(f - f_p)^t$$

where c is a constant, t is the critical exponent, f is the volume fraction of the conductive phase, and f_p is the volume fraction at the percolation threshold.

In our calculations, we have used mass fraction instead of the volume fraction. This change is of minimal significance because the densities of all components of the blend are very close. The best fit of the data is shown in Figure 8. Although the best fit we get for f_p is 0.21 wt %, almost equally good correlation coefficients for the linear regression are obtained for $0.19 < f_p < 0.23$. Thus, for this series of samples, the determined percolation threshold is therefore equal to 0.21(0.02). However, a complete error analysis requires multiple samples from different preparations. Such studies are in progress. Presently, we can state that f_p is much lower than 1%, an unusually low value. Systems exhibiting percolating conducting networks at such small conducting phase content are rare.[22,23,24] The calculated critical exponent is equal to 1.6, a smaller value than that predicted by percolation theory ($t = 2.0$). However, for polyaniline-based blends, such low values are frequently found for critical exponents.[23] It should be stressed here that casting from DCAA is much more convenient than casting from MC, the obtained films show better mechanical properties, and finally, they do not release residual solvent upon aging.

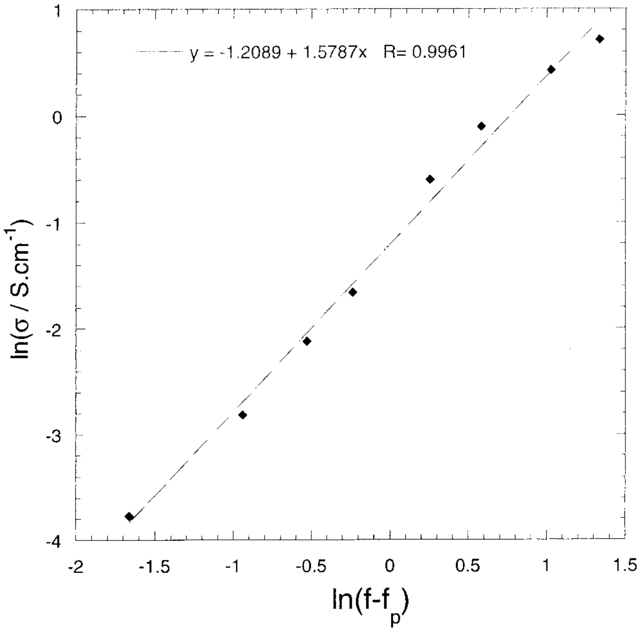


Figure 8. Fit of data presented in Figure 7 to the scaling law of percolation.

Conclusions

To summarize, to prepare highly conducting polyaniline films with good mechanical properties and to improve the processing of polyaniline-based conducting blends, we have developed a new processing system consisting of a polyaniline base, a protonating agent which combines doping and plasticizing properties, and an acetic acid halo derivative as the solvent. The dopant of choice is 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2-di(2-ethylhexyl) ester, whereas the solvent of choice can be either dichloroacetic or difluorochloroacetic acid. Polyaniline films obtained from this three-component system show very good conductivity and a low glass-transition temperature ($T_g = 280$ K) which results in excellent flexibility of PANI films at room temperature. This new processing system can also serve for the fabrication of conducting polyaniline–poly(methyl methacrylate) blends with low percolation threshold which do not show the disadvantages of *m*-cresol cast blends.

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