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Soluble n-Doped Polyaniline: Synthesis and Characterization

Mu-Yi Hua,[†] Gue-Wuu Hwang,[‡] Yuan-Hsinn Chuang, and Show-An Chen*

Chemical Engineering Department, National Tsing-Hua University, Hsinchu 30013, Taiwan, R.O.C.

Rung-Ywan Tsai

Opto-Electronic and System Laboratories, Industrial Technology Research Institute,
Chutung, Taiwan 31015, R.O.C.

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ABSTRACT: We report a novel soluble n-doped polyaniline in dimethyl sulfoxide (DMSO), which is obtained by doping the emeraldine base type polyaniline with the strong reductant, KH or NaH. At room temperature, it shows a broad strong new optical absorption peak above 1100 nm, indicating the formation of a new energy band within the energy gap, and has a conductivity of $10^{-1}-10^{-2}$ S/cm, a spin density of 3.4×10^{20} (for KH-doping) and 4.3×10^{19} spins/g (for NaH-doping), which are close to those of self-acid-doped polyanilines, and a magnetic susceptibility of $(4.6-7.2) \times 10^{-3}$ emu/mol of ring, which is 2 orders of magnitude higher than that of acid-doped polyaniline. When exposed to air, the conductivity decreases rapidly by 6−7 orders of magnitude within 90 s due to undoping by moisture. An n-doping mechanism is proposed, from which the n-doping can also be considered as a direct doping on the oxidized form of polyaniline (pernigraniline) by the alkali metals K and Na.

Introduction

Conducting polymers such as polyacetylene, poly(*p*-phenylene), poly(phenylenevinylene), and poly(2,5-pyridine) can be doped chemically or electrochemically through an oxidation (p-type) or a reduction (n-type) of their thin films or powders.[1−6] These p- and n-doped polymers are in general insoluble in common solvents. The polyaniline (PAn) is the conjugated conducting polymer that can be doped either by protonation with a protonic acid or by charge transfer with an oxidation agent.[7−10] Both doping methods yield p-doped PAn with an increase of conductivity from 10^{-9} up to about 1 S/cm. However, no report on n-doped PAn appears in the literature. In this paper, the first soluble n-doped PAn in dimethyl sulfoxide (DMSO) is obtained by doping the PAn with the strong reductant, KH or NaH. The characterizations by various spectroscopies and conductivity and magnetic property measurements are studied.

Experimental Section

1. Synthesis and Preparation of Samples. 1.1. Purification of Hydrides (KH, NaH, LiH, and CaH$_2$). About 10 g of hydride was mixed with 40 mL of dried *n*-hexane and then filtered immediately with glass-fiber filter paper. The pretreated hydride was further washed with dried *n*-hexane several times and then dried under vacuum at room temperature.

1.2. Preparation of PAn and PAn/DMSO Solution. The emeraldine base form PAn was synthesized by a chemical oxidation method similar to that of MacDiarmid and coworkers.[7] The PAn so obtained has an oxidation level of about 0.5 as determined from its N(ls) core level spectrum obtained using X-ray photoelectron spectroscopy (XPS). The dried PAn (0.5 g, 2.75 mmol of amine form repeat unit) was dissolved in 50 mL of dried DMSO. The solution was filtered with a filter of 0.45 μm pore size to remove undissolved PAn, and a deep-blue PAn/DMSO solution was obtained. The concentration of this solution, which was deterined by vacum-drying at 80 °C and weighting, is 0.102 mmol of PAn/mL of DMSO. The purified hydride was added into the 20 mL PAn/DMSO solution (the mole ratio of hydride to amine unit ($-C_6H_5-NH-$) are 10/1, 1/1, and 0.25/1, respectively) at about 25 °C in a drybox. The mixture was shook slightly to yield a homogeneous solution and then filtered with a 0.45 μm filter. The n-doped PAn/DMSO solution so obtained was stored in an hydride system.

1.3. Preparation of K$^+$−Dimsyl and Na$^+$−Dimsyl. 20.4 mol of hydride (818 mg of KH or 490 mg of NaH) was added into 20 mL of dimethyl sulfoxide (DMSO). After mixing by slightly shaking and holding for 2 h, the light-yellow liquid was filtered by a 0.25 μm filter. The obtained solution contains 16.8 mmol of K$^+$ or 15.6 mmol of Na$^+$ in 20 mL of DMSO as determined by an inductively coupled plasma spectrometer (simultaneous ICP-AES allied analytical system JARREL-ASH, model ICAP 9000).

2. Characterization. Electronic spectra of hydride-doped PAn in DMSO were measured at room temperature using an UV−vis−near-IR spectrophotometer (Perkin-Elmer Lambda 19) in the wavelength range 300−2000 nm. The DMSO solution sample was prepared by injecting it into a quartz cell with the dimension 1 cm × 4 cm × 1.5 mm, and the cell was immediately sealed with wax.

Electron spin resonance (ESR) measurements starting from 50 K and ending at 350 K were performed using an IBM Bruker 200 D 10/12 ESR spectrometer interfaced with an IBM computer for data acquisition and analysis. The DMSO solution sample was prepared by injecting it into an ESR tube of o.d. 3 mm and height 25 cm, and the tube was sealed immediately with an acetylene/oxygen flame. 1,1′-Diphenyl-2-picrylhydrazyl (DPPH) was used as the calibration standard.

The static magnetic susceptibility (χ_g) and magnetization (M) of the solutions were measured using a MPMS superconducting quantum interference device (SQUID) magnetometer (from Quantum Design). The solution for measurement was injected into a quartz tube of o.d. 3 mm and height 10 cm, and the tube was sealed immediately with an acetylene/oxygen flame.

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* Corresponding author: e-mail sachen@che.nthu.edu.tw.

[†] Present address: Chemical and Material Engineering Department, Chang Gung University, Kwei-San, Tao-Yuan, Taiwan 33302, R.O.C.

[‡] Present address: Union Chemical Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan 310, R.O.C.

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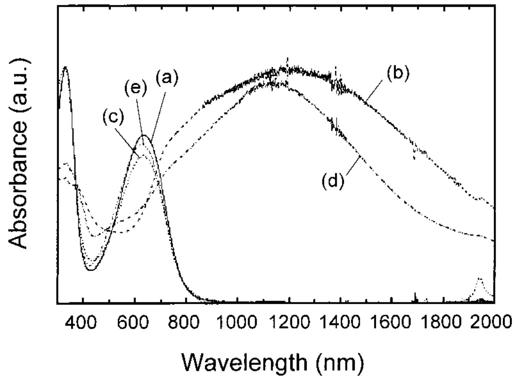


Figure 1. UV−vis−near IR spectra at room temperature of the (a) PAn, (b) NaH-doped and (c) water-undoped PAn, (d) KH-doped, and (e) water-undoped PAn in DMSO; (f) PAPSAH aqueous solution. In the hydride-doped solutions, the mole ratio of the hydride added to amine unit is 10.

The four-probe[11] method was used to measure the conductivity at room temperature under vacuum. The film samples of KH- and NaH-doped PAn were prepared by coating their DMSO solutions on glass plates in a drybox, drying under dynamic vacuum at room temperature for removing DMSO, and then transferring the entire assemblies to the sample cells for conductivity measurements.

Results and Discussion

1. Electronic Spectroscopy. Figure 1 shows the electronic spectra of PAn and NaH- and KH-doped PAn in DMSO. For PAn (Figure 1, curve a), the strong absorption maxima at 328 nm (3.79 eV) and 635 nm (1.96 eV) originated from the $\pi-\pi^*$ transition of the benzenoid rings[12] and the exciton transition of the quinoid rings.[13] After doping with the hydride KH and NaH (the mole ratio to amine unit of PAn is 10), the color of the solutions changes from blue to blue-greenish and then to deep yellow-greenish. For NaH-doped PAn (Figure 1, curve b), the intensities of absorption peaks at 328 and 635 nm decrease, and a broad new absorption peak at 1136 (1.09 eV) and a shoulder at about 700 nm (1.84 eV) appear. For the case with KH (Figure 1, curve d), similarly, the intensities of absorption peaks at 328 and 635 nm decrease also, and a broad new absorption peak at 1196 nm (1.04 eV) and a shoulder at about 700 nm appear. The generation of the strong broad absorption peak at lower energy after the reaction with either NaH or KH indicated an occurrence of doping. As LiH and CaH_2 were used as dopants, no change in the color of their solutions and UV−vis−near-IR spectra were observed, indicating that no doping reaction occurred.

The absorption spectra of the NaH-doped and KH-doped PAn in DMSO are different from those of the self-doped PAn in water, poly(aniline-*co*-*N*-propanesulfonic acid aniline) (PAPSAH)[14] or sulfonic acid ring-substituted polyaniline (SPAN) aqueous solution,[15] and protonated PAn in the nonaqueous solvents, fluorinated alcohols.[16,17] For the PAPSAH aqueous solution (Figure 1, curve f), it exhibits a $\pi-\pi^*$ transition of the benzenoid rings[12] at 310 nm and polaron band transitions[18] at about 410 and 856 nm. Similar transitions at about 400 and 800 nm have also been observed for the nonaqueous case. In addition, a very weak shoulder at 590 nm still appears, which might be contributed from the residual quinoid rings. For the hydride-doped PAn's, they exhibit an absorption peak at 328 nm, an absorption shoulder at about 700 nm, and a broad absorption peak at above 1100 nm. The presence of the absorption shoulder indicates that some of the quinoid units do not participate in the delocalization of the unpaired electrons along the chains after the doping. Thus, the electronic structure of the hydride-doped PAn in DMSO is different from that of the p-doped PAn in water. As in the case of p-doping, the absorption peak at about 328 nm due to the $\pi-\pi^*$ transition of the benzenoid rings still exists in the n-doped PAn. The new broad absorption peak at above 1100 nm of the KH-doped PAn is broader than that of NaH-doped PAn, indicating that the unpaired electrons in the former are more delocalized than those in the latter. Furthermore, the broad absorption bands at above 1100 nm of the hydride-doped PAn's are broader than that of PAPSAH at 856 nm, indicating that the unpaired electrons in the hydride-doped PAn's in DMSO are more delocalized than those in the PAPSAH in its aqueous solution. When the hydride-doped PAn's are treated with water, it is undoped to give the neutral PAn (Figure 1, curves c and e). Note that the hydride-doped PAn's after undoping with water have lower intensity at about 635 nm (characteristic peak of quinoid rings) relative to that at 328 nm (characteristic peak of benzenoid rings) than the pristine PAn, indicating that the undoping with water causes an reduce of oxidation level.

To provide another evidence of n-doping, we tried to mix the hydride-doped PAn with KBr powder and to prepare a compressed pellet in a drybox for IR analysis. However, the NaH- and KH-doped PAn's are too sensitive to moisture, which leads to an undoping by the moisture during the transfer of samples and makes the measurement difficult. Similarly, X-ray photoelectron spectroscopy measurement was also found to be difficult to carry out. It is also very difficult to purify the n-doped PAn from the hydride salts, and thus we cannot determine the doping level of the n-doped PAn.

2. Electron Spin Resonance (ESR). To verify the formation of the new energy band accompanying a formation of free spins after the doping with hydrides, the ESR measurements on the PAn/DMSO solutions during doping with NaH and KH (the mole ratio of hydride to amine unit is 10) at room temperature were carried out, and the characteristic values, spin density (*Ns*) and peak-to-peak line width (ΔH_{pp}), are 4.3×10^{19} spin/g and 1.8 G for NaH doping ($g = 2.003\ 50$) and 3.4×10^{20} spin/g and 1.2 G for KH doping ($g = 2.003\ 32$), respectively. These values remain almost unchanged with time at room temperature and are comparable to that of the HCl-doped PAn powder ($Ns = 2.2 \times 10^{20}$ spin/g, $\Delta H_{pp} = 0.3$ G),[14a] the self-acid doped PAn, PAPSAH ($Ns = 7.5 \times 10^{19}$ spin/g, $\Delta H_{pp} = 10.8$ G),[14] and sulfonic acid ring-substituted polyaniline (SPAN) ($Ns = 9.1 \times 10^{19}$ spin/g, $\Delta H_{pp} = 2.88$ G)[15] in water. To ensure that the *Ns* is contributed from the n-doping, ESR measurements were also carried out for the neutral PAn in DMSO and hydrides in DMSO at the same relative compositions as for the hydride-doped PAn in DMSO reported above. For the neutral PAn/DMSO solution, the *Ns* value and peak-to-peak line width (ΔH_{pp}) are 2.1×10^{18} spin/g and 6.9 G, which are contributed from the defect and/or the trace amount of radical cation nitrogen on the neutral PAn chain as was observed by XPS,[15,19] and for the NaH/DMSO and KH/DMSO solutions, no ESR signal was observed. These two tests indicate that more than 97% of the free spins are generated from the hydride doping. Comparing the doping with KH and

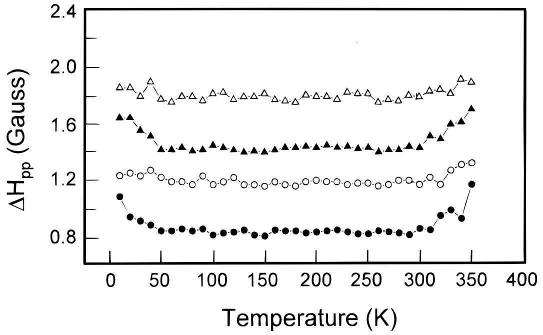


Figure 2. Temperature dependence of the ΔH_{pp} of the ESR signal for NaH- and KH-doped PAn solutions: (a) NaH-doped PAn and (b) KH-doped PAn, applying additional magnetic field of 5000 G before cooling; (c) NaH-doped PAn; and (d) KH-doped PAn. In these hydride-doped PAn solutions, the mole ratio of the hydride added to amine unit is 10.

Table 1. Conductivities of NaH- and KH-Doped PAn at Room Temperature

dopant	PAn/dopant (mole ratio)[a]	σ (S/cm)
NaH	1/10	8×10^{-2}
	1/1	1.8×10^{-2}
	1/0.25	6×10^{-4}
KH	1/10	4×10^{-1}
	1/1	3.2×10^{-2}
	1/0.25	6.8×10^{-4}

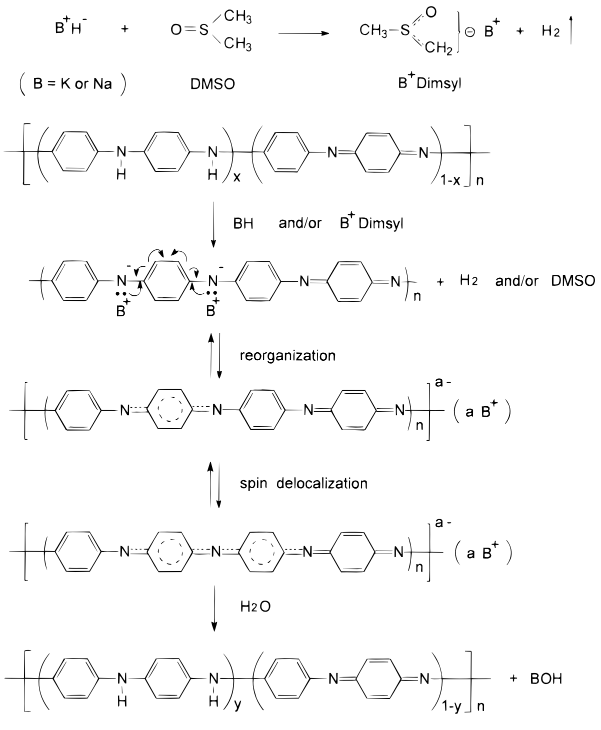
[a] Based on the content of the amine unit: $-C_6H_5-NH-$.

NaH after equilibration, the lower ΔH_{pp} (1.2 G) and the higher absorption intensity ratio (1.86) of the new peak at above 1100 nm to the $\pi-\pi^*$ transition at 328 nm of the KH-doped PAn than those of the NaH-doped PAn (1.8 G, 1.58) indicates that the charge-pinning effect by the counterions K^+ on the free spins is lower than that by Na^+ due to the larger ion size of the former.

The temperature dependences of the ΔH_{pp} of the ESR signals for NaH- and KH-doped PAn solutions are shown in Figure 2. The ΔH_{pp} remains essentially constant from 50 to 290 K but increases slightly above the melting point (290 K) of DMSO due to increased thermal agitation of the polymer chains. The hydride-doped PAn solutions were applied by the magnetic field before and during cooling so that the polymer chains in the solution were aligned. The values of ΔH_{pp} in the entire temperature range are found to decrease by 22% and 33% for NaH and KH systems, respectively. These results indicate that the polymer chains do respond to the applied magnetic field by alignment of the chains such that the free spins can delocalize more freely along the backbones.

3. Magnetic Properties. At room temperature, the χ_g values of the KH(10)- and NaH(10)-doped PAn solutions are 7.20×10^{-3} and 4.56×10^{-3} emu/mol (1-ring) at 1500 G, respectively, which are 2 orders of magnitude higher than those of HCl-doped PAn powder,[20] AsF_5-doped polythiophene[21] and BF_4^--doped polypyrrole[22] at 300 K (magnetic field unspecified), and $FeCl_4^-$-doped poly(3-hexylthiophene)[23] at 250 K and 500 G. Such high values of magnetic susceptibility are probably originated from the presence of negative charges on the main chain, allowing the unpaired electrons responding to the magnetic field more easily.

4. Electrical Properties. The conductivities at 25 °C of the solid films of the NaH- and KH-doped PAn prepared at various dopant concentrations are shown in Table 1. The conductivity is found to increase with doping level and reaches 8×10^{-2} and 4×10^{-1} S/cm at the hydride to amine unit mole ratio of 10 for NaH and KH, respectively. The conductivities of NaH- and KH-doped PAn are very sensitive to moisture. As a stream of nitrogen bubbling through water passes through the conductivity measurement cell, the conductivities of both films decrease rapidly by a factor of 10^6 within 1 min, resulting from an undoping with water to yield aqueous NaOH as reflected in the color changing of a pH paper attaching to the film surface.



Where, y > x

Figure 3. n-Doping mechanism of emeraldine base type polyaniline doped with KH (or NaH) in DMSO and its undoping mechanism with the addition of H_2O at room temperature.

5. n-Doping Mechanism. On the basis of the analysis above, the n-doping mechanism is proposed as shown in Figure 3. Since KH and NaH are strong reductants, the proton (H^+) on DMSO can also be captured by KH (or NaH) to form K^+dimsyl (or Na^+dimsyl)[24] and to release hydrogen gas as observed in our experiment. In addition, both dimsyl salts can take the proton (H^+) away from PAn to form the original DMSO and to make PAn main chain carrying negative charges with Na^+ (or K^+) as counterions. The unpaired electrons are formed through a reorganization of the π-electrons in benzenoid rings attached to the two neighboring nitrogen atoms carrying negative charges, which then delocalize along the chain to yield semiquinoid units. When the n-doped PAn reacts with water, K^+ (or Na^+) combines with OH^- to form KOH (or NaOH), and H^+ is added to the PAn main chain to give the neutral PAn. Therefore, a new energy band is generated within the energy gap due to the n-doping, which disappears by undoping with water. The undoping with water causes a reduce of oxidation level as revealed in the section of electronic spectroscopy above. Although the n-doping was proceeded by abstraction of amine hydrogen atom in the emeraldine base PAn via reaction with hydride, it can also be considered as a n-doping of the oxidized form PAn (pernigraniline) directly by the alkali metals, K and Na, as can be seen from the proposed structure after the n-doping. These n-doped PAn's have very poor stability in air due to rapid undoping by moisture; thus, their practical usefulness is very limited. However, the present work reports the preparation and characterization of the first n-doped PAn, which would provide valuable information on electronic structures of conjugated polymers.

Conclusion

The novel n-doped PAn, which are soluble in dimethyl sulfoxide (DMSO), can be obtained by reaction of the emeraldine base type polyaniline with the strong reductants, KH or NaH. It is the first n-doped PAn found so far. At room temperature, it has a conductivity of $10^{-1}-10^{-2}$ S/cm and a spin density of 3.4×10^{20} (KH) and 4.3×10^{19} spin/g (NaH) comparable to that of the self-acid-doped polyaniline and magnetic susceptibility $(4.6-7.2) \times 10^{-3}$ emu/mol of ring, which is 2 orders of magnitude higher than those of acid-doped PAn. It can be undoped by adding deionized water into the solution. When exposed to air, the conductivity decreases rapidly by 6 orders of magnitude within 1 min due to undoping by moisture.

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