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Flexible Polyaniline of Metallic Type Conductivity Obtained via Protonation of Emeraldine Base with 2-Ethylhexyl Diester of 5-Sulfo-*i*-Phthalic Acid

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Polyaniline doped with 2-ethylhexyl diester of 5-sulfo-*i*-phthalic acid shows electrical conductivity exceeding 120 $S.cm^{-1}$ at room temperature which in addition is metallic in character down to 190 K. Due to plasticizing properties of the protonating dopant the polymer exhibits excellent mechanical properties.

Keywords Polyaniline; Esters of 5-sulfo-*i*-phthalic acid, Conductivity

INTRODUCTION

Diesters of sulfophthalic acids constitute a new class of dopants which improve mechanical properties of doped polyaniline (PANI). In our recent paper [1] we have demonstrated that diesters of 4-sulfophthalic acid not only induce solution processibility of polyaniline but also improve its flexibility due to plasticizing effects. Free standing films of doped polymer are stretchable and show metallic type conductivity down to 200 K [2]. Diesters of 5-sulfo-*i*-phthalic acid, if used as dopants, also improve the flexibility of doped polyaniline. However in this case it is more difficult to achieve metallic-type conductivity. None of the diesters of 5-sulfo-*i*-phthalic studied in Reference [3] rendered polyaniline metallic.

In this paper we demonstrate that polyaniline doped with diesters of 5-sulfo-*i*-phthalic acid may also exhibit metallic-type conductivity provided that appropriate processing conditions are established. In the preparation of free standing films of doped polyaniline we have changed three parameters as compared to those used in the research described previously [3]:

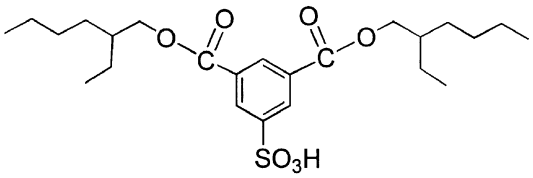
i) we have used polyaniline base of higher molecular weight

ii) we have selected 2-ethylhexyl ester of 5-*i*-phthalic acid as the dopant i.e. the dopant not studied in [3]

iii) we have carried out the casting of the film from 2,2'-dichloroacetic acid (DCAA) in inert atmosphere and at lower temperature.

EXPERIMENTAL

5-sulfo-*i*-phthalic acid (SIPA) was prepared by sulfonation of *i*-phthalic acid according to the method described in [4]. 2-ethylhexyl diester of 5-sulfo-*i*-phthalic acid (DEHESIP) of the formula depicted below:



was prepared from SIPA and the corresponding alcohol as described in [5]. The product was characterized by elemental analysis and ^{1}H NMR: *Elemental analysis:* Calculated for $C_{24}H_{38}O_7S$: C, 61.41; H, 8.48; S, 6.16. Found: C, 61.25; H, 8.14; S, 6.81. *^{1}H NMR ($CDCl_3$, ppm)*: 0.93 (12H), 1.35 (16H), 1.75 (2H), 4.30 (4H), 8.80 (3H), 12.05 (1H).

Polyaniline in the oxidation state of emeraldine was prepared at -27°C using the procedure described in [6]. The inherent viscosity of the polymer in its base form measured at 25°C in 0.1 wt% solution in 96% sulfuric acid was 2.2 dl.g^{-1}.

Polyaniline (PANI) was protonated with DEHESIP in DCAA. The concentration of the solution was 0.5 wt% with respect to PANI base and the ratio of PANI mer to DEHESIP molecule was 0.5 . Thus in the subsequent text the formula of the doped polymer is abbreviated as PANI(DEHESIP)$_{0.5}$. It is additionally assumed that PANI mer consists of the unit containing one aromatic ring and one nitrogen. Free standing films of the thickness of *ca.* 30 μm were cast from the above solution at the temperature of 45°C in the constant flow of dry argon.

RESULTS AND DISCUSSION

Spectroscopic properties of protonated PANI in solution depend strongly on specific interactions between the polymer, the solvent and the dopant [7][8]. UV-Vis-NIR spectroscopy can be diagnostic of charge carriers delocalization which constitutes the "*conditio sine qua non*" for the conductivity of solid polymer samples. This charge delocalization is manifested by a monotonically increasing absorption tail in the NIR part of the spectrum. In the spectrum of PANI(DEHESIP)$_{0.5}$ solution in DCAA (Figure 1) two contributions can be distinguished. A relatively narrow absorption peak in the vicinity of 800 nm characteristic of localized charge carriers (in the case of PANI-polarons) is superimposed on the NIR absorption tail originating from the delocalized polarons.

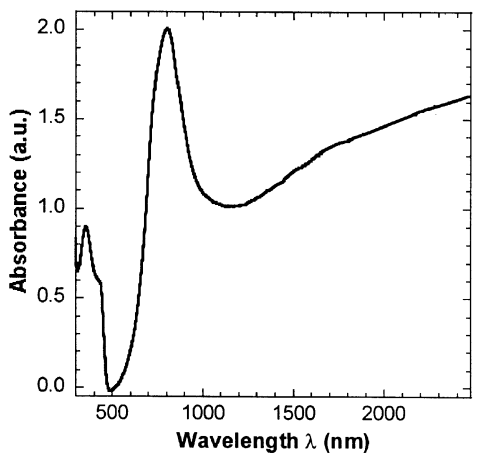


FIGURE 1 Absorption spectrum of PANI(DEHESIP)$_{0.5}$ in DCAA solution.

The removal of DCAA solvent improves the delocalization of charge carriers since in the solid state spectrum of PANI(DEHESIP)$_{0.5}$ spectroscopic contribution originating from delocalized polarons decreased significantly.

From spectroscopic studies one can therefore expect that PANI(DEHESIP)$_{0.5}$ cast from DCAA may exhibit metallic-type conductivity. This is indeed the case. In Figure 2 temperature dependence of conductivity is presented for PANI(DEHESIP)$_{0.5}$.

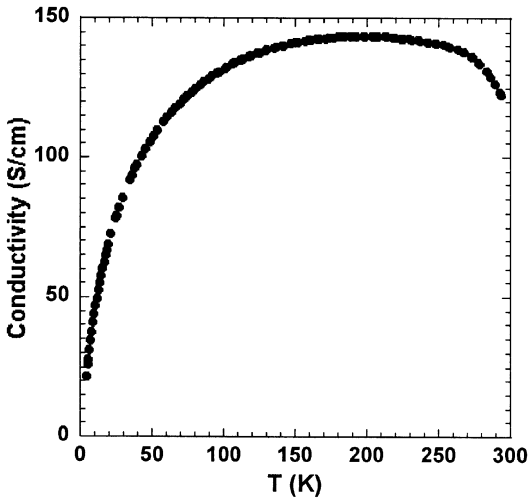


FIGURE 2 Linear plot of the conductivity vs. temperature for the film of PANI(DEHESIP)$_{0.5}$ cast from DCAA

The conductivity shows a clear maximum in the vicinity of 190 K, being metallic in character above this temperature i.e. showing negative temperature coefficient of the conductivity. This type of behavior is

usually interpreted in terms of heterogeneous nature of protonated PANI [9]. In the doped polymer which is partially crystalline well ordered regions with metallic type conductivity coexist with less ordered (amorphous) regions of hopping-type conductivity. The total resistance of the sample embraces therefore the contributions from the resistance of "metallic" zones and the zones of hopping conductivity. Different temperature dependence of both contributions gives rise to the observed conductivity maximum. It should be noted here that electrical conductivity of PANI(DEHESIP)$_{0.5}$ films is very sensitive to the temperature and atmosphere of casting. It is significantly lower if the casting is carried out in air and at temperatures exceeding 50 °C. Moreover it shows no features of metallic behavior. The molecular weight of PANI base used for the preparation of conducting films also influences both the RT conductivity value as well as its temperature characteristics. For PANI of inherent viscosity of 1.4 dl.g^{-1}, i.e. lower than used in this research, no metallic-like behavior was detected at any temperature zone.

Preliminary investigations of thermal properties of PANI(DEHESIP)$_{0.5}$ have been carried out by thermogravimetry (TG) and differential thermal analysis (DTA). In the temperature range of 25–125 °C the sample looses *ca.* 5 wt% of its initial mass. A broad endothermic effect is registered in the DTA curve for the same temperature range. This mass loss is associated with the removal of water molecules since in the protonation process of PANI the DEHESIP molecules enter the polymer matrix being hydrated. In the temperature range of 225 - 270 °C an additional mass loss,

corresponding to additional 20 wt% of the initial mass, is registered. Evidently above 225 °C PANI(DEHESIP)$_{0.5}$ starts to decompose.

Free standing films of PANI(DEHESIP)$_{0.5}$ are very flexible and can be bent several times without damage. Detailed studies of their mechanical properties by thermomechanical analysis (TMA) are in progress.

CONCLUSIONS

We have demonstrated that electrical properties of polyaniline protonated with diesters of 5-sulfo-*i*-phthalic acid are strongly sensitive to the molecular weight of the emeraldine base used for the protonation and the processing conditions. In particular films of polyaniline doped with diester containing 2-ethylhexyl substituents and cast from 2,2'-dichloroacetic acid combine metallic conductivity down to 190 K with high flexibility induced by plasticizing properties of the protonating agent.

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