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Shear-Induced Delocalization of Polarons in Polyaniline-Zinc Salt Complexes

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SUMMARY: A zinc salt of the acid dopant has been into a doped polyaniline in order to improve the processing conditions. The complex shows viscoelastic behavior at elevated temperatures when manual shear for the sample was applied. The ratios between polyaniline, the dopant and the zinc-salt of the dopant was controlled in order to understand the optimal conditions for the shearing experiments. The initial samples are not birefringent, but the samples become birefringent and liquid crystalline after the shear. Additionally, the application of UV-spectroscopy revealed strong delocalization of the polarons after the shear process.

Introduction

A key property of most polymers, which distinguishes them from metals, is their inability to carry electricity. In fact, the insulating properties of polymers are a significant advantage for many applications of plastics. Electrical wires, for example, are protected from shorting by a coating of insulating polymer. It used to be believed that plastics and electrical conductivity were mutually exclusive. During the past 20 years, however, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current.

Electrically conducting polymers (ECP) have drawn a wide attention due to the promising applications. Due to the lightweight and the suitable processing conditions, ECP can compete with the present electronic products. For instance, ECP can be introduced to other materials to provide antistaticity and EMI-shielding. The conducting mechanism of the ECP has been interpreted by the alternating single and double bonds which offer the possibility for charge carriers hopping or tunneling through the backbones. Due to these highly conjugated backbones, ECP's are generally intractable, infusible, and insoluble.

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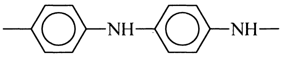
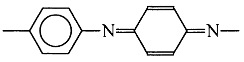
The modern era of conducting polymers began at the end of the 1970's when Heeger, MacDiarmid and Shirakawa [1] discovered that polyacetylenes could undergo an increase of conductivity by eleven orders of magnitude upon charge-transfer oxidative doping. Among many polymers known to be conductive, polyacetylene, polyaniline, polypyrrole, and polythiophene have been most studied.

The attachment of the alkyl side groups to the thiophene backbone weakened the strong interactions between the main chain molecules without a remarkable loss of the conductivity [2]. Poly(3-alkylthiophenes) are infusible when the alkyl side chains are short and the crystal packing complete due to the small disturbance of the short substituents. The melting point of P3AT's decreases with the increase of the alkyl side chains and thus poly(3-dodecylthiophenes) are melt-processable.

Polyaniline (PANI) has been the center of scientific interest due to the fact that PANI is a very stable conducting polymer. However, PANI is not a new material and its existence has been known for the past 150 years.

Early proposed structures of PANI were assumed to be a small molecule with eight aromatic rings and consisting of two basic repeat units:

(a) , benzenoid amine (oxidation number of N is -1) and

(b) , quinoid imine (oxidation number of N is 0).

Later, this structure was corrected to be a polymer with a backbone consisting of two basic repeat units as in the octamer model. The generally accepted chemical structure of synthesized polyaniline (or so-called emeraldine base) is described as a copolymer in which the backbone is combined with 50% of 1A units and 50% of 1B units [3]. The quinoid imine can be reduced into benzenoid amine by hydrazine, and the resulting polymer is called leucoemeraldine base. Leucoemeraldine base is unstable in air and is easily oxidized into half oxidized polyaniline. When all repeat units are quinoid imines, the fully oxidized polymer is called pernigraniline base. The oxidation and reduction reactions of emeraldine base into pernigraniline and leucoemeraldine are reversible and both can be executed through chemical and electrochemical methods.

The intractability of polyaniline results from the stiffness of backbone and the hydrogen bonding interaction between adjacent chains limits not only the industrial applications, but also the complete understanding of the properties of this conducting polymer. One important chemical modification has been the addition of saturated hydrocarbon alkyl or alkoxy side chains to the polymeric backbone.

The use of hydrochloric acid as the dopant has been shown to improve the crystallinity and elongation of these samples resulted in vastly improved conductivity. The HCl-doped polyaniline still remained its poor processing properties. p-toluene sulfuric acids used by Allied Signal Co. presented the first counter-ion type compounds, but still with a limited improved in solubility and processability. This may be the main reason why the state of dispersion in the polyaniline solutions is emphasized in the patents. The next improved in the technology was the use of dodecyl benzene sulfuric acid as the dopant. This result (trademark "Panipol") of the Neste/Uniax collaboration was soluble in organic solvents and was used in extrusion processes. Monsanto then developed even a better complex called Panda, which is polyaniline doped with dinonyl naphthalene sulfuric acid (DNNSA), has been reported to have solubility of 50% in toluene due to the more hydrophobic nature of the dopant. The migration of a small dopant molecule to the surface in the thermoplastic blends still remains as one of the major problems.

In this presentation, we shall discuss the influence of a metal salt of these acidic compounds on the behavior of polyaniline. We have used of a Zinc/DNNS salt as an additive for the doped polyaniline and have found that the viscoelastic behavior of such complexes is greatly improved by the presence of the Zinc salt.

Results

Although the polyaniline/DNNSA complex is said to have high solubility, the solution still shows an UV-spectrum typical for localized polarons, a heterogeneous structure. The UV-spectrum for polyaniline complex with DNNSA in solution (chloroform) is shown in Figure 1.

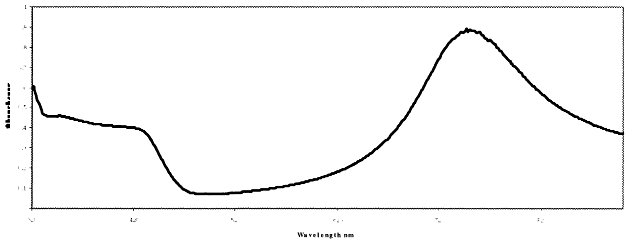


Figure 1. The UV-spectrum of Polyaniline/DNNSA in Chloroform

The addition of Zn/DNNS salt to polyaniline/DNNSA complex results in similar spectral characteristics: a sharp peak around 800nm is typical for the existence of localized polarons. When a manual shear was applied at elevated temperatures, the UV-spectrum reveals a complete delocalization of the polarons as shown in Figure 2.

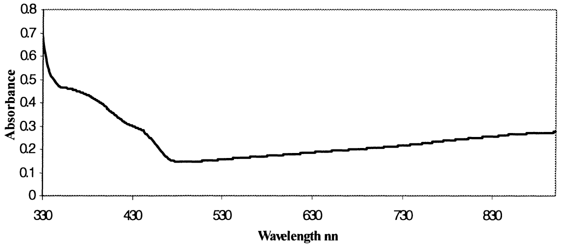


Figure 2. The UV-spectrum of Polyaniline/DNNSA/Zn-salt after shearing at elevated temperature.

The films after the shearing become strongly birefringent indicating that the delocalization of the polarons observed by the UV-spectrum is connected with the formation of liquid crystalline morphology.

References:

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