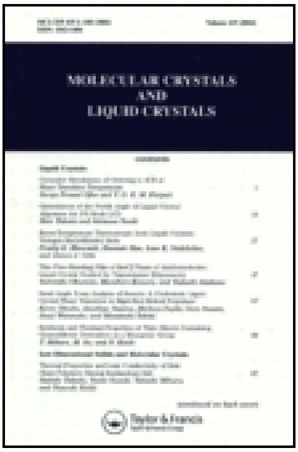

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In-situ Attainment of Paramagnetic Behaviour of Poly(Amino-Acetanalide) during Synthesis

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Polyaniline and its derivatives have gained significant interest because of their unique electronic property, simple synthesis process and their environmental stability. We report on the cerium (IV) ammonium nitrate mediated synthesis of poly (amino-acetanilide), PAA, using an interfacial polymerization technique in which PAA serves as a guest of the cerium (III) ion, a paramagnetic species produced during the synthesis condition. The cerium (III) ionic species bonded with the chain nitrogen of the PAA and the supramolecular system show the paramagnetic behavior throughout the experimental temperature range 400-1.9 K.

Keywords Cerium ammonium nitrate (CAN); composite; optical characterization; paramagnetism; SEM

Introduction

Among the known conducting polymers, polyaniline is unique due to its doping adjustable electrical conductivity and metal-like transport property at both room temperature and low temperatures [1]. The electrical conductivity of the polyaniline can be varied over the full range from insulator to metal by doping. Through doping, the chemical potential (Fermi level) can be moved into the region of energy of the high density of electronic states either by a redox reaction or by an acid-base reaction. Doped polyaniline and its derivatives are good conductors due to the fact that doping introduces charge carriers into the electronic structure. The attraction of an electron in one repeat unit to the nuclei in the neighboring unit leads to carrier delocalization along the polymer chain and to charge carrier mobility, which extends into three dimensions through inter-chain electron transfer [2]. Paramagnetic behaviour in highly protonic acid doped polyaniline has also been reported at low temperatures

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[3]. An Electron Paramagnetic Resonance (EPR) study of the camphor-sulphonic acid doped conducting polyaniline showed temperature independent Pauli susceptibility within the temperature of 300 to 50K. The Curie contribution to the electronic paramagnetic susceptibility of the heavily doped polyaniline arises from a disordered metallic state close to the metal-insulator transition. This has been observed only below 50K [3]. Paramagnetism in polyaniline has been reported by introducing paramagnetic metal nanoparticles into the polyaniline matrix [4,5].

In this study, we report on an *in situ* synthesis technique for the preparation of a paramagnetic poly-(amino-acetanilide) (PAA)-cerium (III) supramolecular composite material by applying an '*in situ* polymerization and composite formation' (IPCF) technique [6] using cerium (IV) ammonium nitrate (CAN) as an oxidizing agent for polymerizing *para*-amino-acetanilide. CAN is most extensively used in synthetic organic chemistry as an oxidant (reduction potential value of $+1.61$V vs. Normal Hydrogen Electrode (NHE)) [7]. During the polymerization process, each step is associated with a release of an electron and that electron reduces the Ce^{4+} ion to form a Ce^{3+} ion. The Ce^{3+} ion binds with the chain nitrogen of the polyaniline, which causes the emergence of paramagnetism in polyaniline.

Experimental

Materials

Cerium ammonium nitrate and *para*-amino acetanilide were purchased from Sigma-Aldrich and BDH respectively. Ultra-pure water (specific resistivity $>17\text{M}\Omega$ cm) was used to prepare the solution of cerium ammonium nitrate (10^{-2} mol dm^{-3}). Toluene was purchased from Merck.

Characterization Techniques

Scanning electron microscopy (SEM) studies were undertaken in a FEI FEG Nova 600 Nanolab at 5 kV. For UV-vis spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range 300-800 nm using a Varian, CARY, 1E, digital spectrophotometer. Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser as the excitation source. Light dispersion was undertaken via the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. Power at the sample was kept very low (0.73 mW), while the laser beam diameter at the sample was $\sim$1 μm. X-ray photoelectron spectra (XPS) were collected in an Ultra High Vacuum (UHV) chamber attached to a Physical Electronics 560 ESCA/SAM instrument. Magnetic measurements were performed under controlled temperatures using a Magnetic Properties Measurement System (MPMS) (Quantum Design, USA).

Synthesis of Ce^{3+} Doped Poly (Amino-Acetanilide)

In a typical experiment, 0.104 g of *para*-amino-acetanilide was placed in a conical flask. 10 mL of toluene was slowly added to it under a mild stirring condition. Cerium ammonium nitrate, CAN, (10 ml) with a concentration of 10^{-2} mol dm^{-3} was added dropwise to the conical flask. A dark brown colour developed at the bottom of the conical flask during the addition of the CAN solution to the toluene suspended amino acetanilide. After all the CAN was added, the dark brown precipitation was kept under static conditions for another 10 min. The whole process was carried out at room temperature ($\sim$25°C). Subsequently,

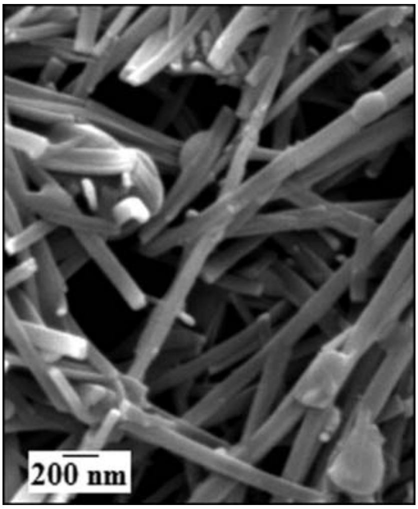

Figure 1. SEM images of the cerium (III) ion doped poly-(amino-acetanilide).

the colloidal precipitation was taken from the bottom of the flask and pipetted onto lacey, carbon-coated, copper transmission electron microscope (TEM) grids for SEM analysis. The rest of the solution was filtered and washed with distilled water several times. A small portion of the solid mass was used for UV-vis and Raman analysis. For the magnetic property study, the solid mass was dried and measured under controlled temperatures using a MPMS system.

Results and Discussion

Figures 1 and 2 show a typical SEM image and the schematic diagram of the poly (amino-acetanilide) respectively. The image reveals that the product consists of regular straight

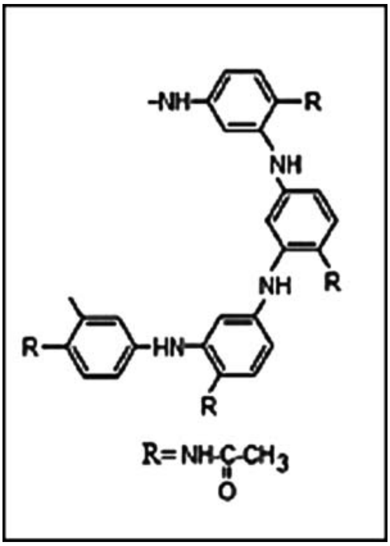

Figure 2. Schematic diagram of poly-(amino-acetanilide) [PAA].

nanofibers a few microns in length and 100-150 nm in diameter. The fibers were almost identical in morphology and very straight, suggesting a high level of rigidity. In the Raman spectrum, the bands within the range of 1100 and 1700 cm^{-1} are sensitive to the PAA oxidation state. The spectrum reveals C—C deformation bands of the benzenoid ring at 1605 cm^{-1}, which is the characteristic for semiquinone rings [8,9]. Further the 1504 cm^{-1} band corresponds to the N–H bending deformation band of Ce^{3+} functionalized amine. Two bands at 1325 and 1370 cm^{-1} correspond to $C{-}N^{\bullet +}$ stretching modes created as a result of the incorporation of Ce^{3+} ions with the chain nitrogen. A strong band at 1467 cm^{-1} corresponds to the C=N stretching mode of the quinoid units. The broad band at 1230 cm^{-1} corresponds to the C—N stretching mode of single bonds, the benzenoid units. The position of the benzene C—H bending deformation band at 1171 cm^{-1} is characteristic of reduced and semiquinone structures. The Raman spectrum indicates the presence of both benzenoid and quinoid structures present in the polymer chain. For the acetamide functional group ($CH_3{-}CO{-}NH{-}$) the symmetric CH_3 stretching mode appeared at 2925 cm^{-1} and for $CH_3{-}CO{-}$ functional group the asymmetric CH_3 stretching mode appeared at 3040 cm^{-1} (inset Fig. 3) [10].

The electronic absorption spectra of the polyaniline base, the polyaniline salt and their respective derivatives have been well documented in the literature [11,12]. The polyaniline (PANI) salt shows three absorption peaks at 310–360, 400–440, and above 700 nm. The absorption peak at 310–360 nm is due to the π-π^* transition of the benzenoid rings. The peak at 400–440 nm is due to the polaron–bipolaron transition, whereas the broad absorption band appearing above 700 nm is due to the benzenoid-to-quinoid excitonic transition. In this study, the UV–vis spectrum of PAA (Fig. 4), which was synthesized with toluene as a solvent and using CAN as an oxidant, showed two absorption bands with peak positions at 310 and 450 nm corresponding to the aforementioned transitions. In this case, we did not find any prominent absorption band for the excitonic transition, which probably overlapped with the strong absorption due to the polaron–bipolaron transition.

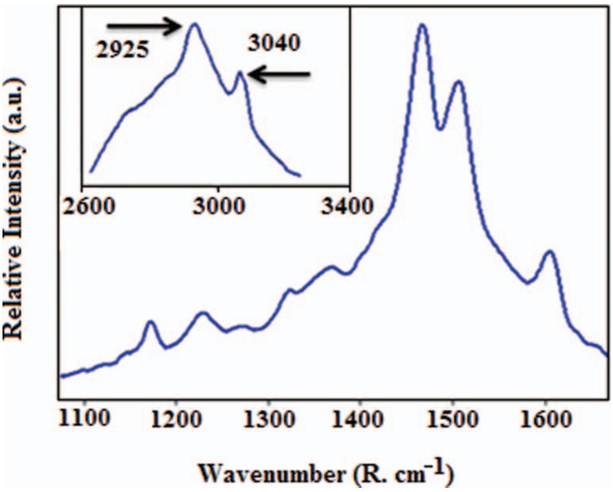

Figure 3. Raman spectrum of the cerium doped poly-(amino-acetanilide) within the range from 1100 to 1700 cm^{-1}. The spectrum indicates the presence of both the benzenoid and the quinoid structures in the poly-(amino-acetanilide). The inset spectrum indicates the presence of acetanilide group in the polymer.

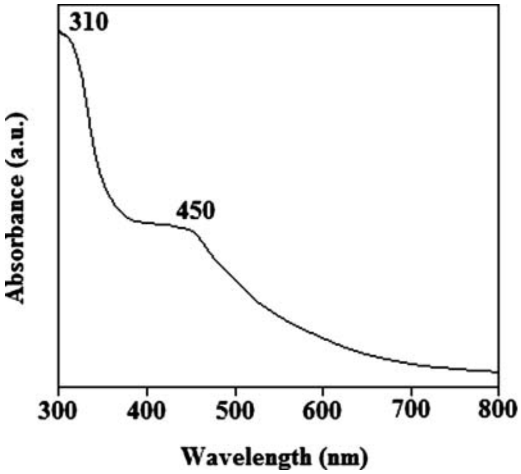

Figure 4. UV-vis spectrum of the Ce^{3+} doped poly (amino-acetanilide).

Figure 5 shows the temperature dependence of reverse magnetic susceptibility, $(M/B)^{-1}$, of Ce-PAA measured in a small field of 300 Oe. The temperature evolution is that of a paramagnetic material. There are no co-operative ordering effects down to the lowest measured temperature (2 K). At intermediate temperatures, the $(M/B)^{-1}$ values proceed linear in temperature. In an effort to characterize the magnetic species giving rise to this behaviour, we provide a qualitative measure of the Curie-Weiss law, in terms of the permeability of free space μ_0, Avogadro's number N_A, the Bohr magneton μ_B, and Boltzmann's constant k_B.

$$\chi(T) = \frac{C}{T - \theta_p}, \quad C = \frac{\mu_0 N_A \mu_B^2}{3k_B}\mu_e^2 \tag{1}$$

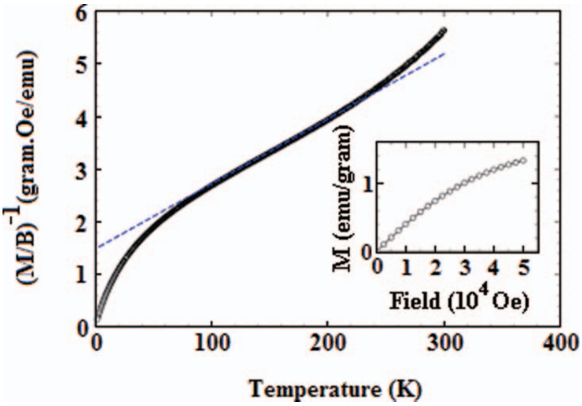

Figure 5. Temperature dependence of reverse magnetic susceptibility, $(M/B)^{-1}$, of Ce (III)-poly (amino-acetanilide), measured at 300 Oe. The inset figure is the magnetization at 2 K as function of applied field. The curvature is due to the coupling of the applied field with the magnetic species in the sample.

The free parameters are the Weiss temperature θ_p and μ_e, the effective moment of the magnetic species giving rise to paramagnetic behaviour. Here, this role would be assumed by cerium, which could in general take on either the magnetic Ce^{3+} ionic form, or the non-magnetic Ce^{4+} state. For purposes of illustration, since the precise molar mass of cerium is not known, the susceptibility data at intermediate temperatures are fitted well according to the Curie-Weiss law with a $\theta_p = -120$ K, and $\mu_e = 2.27$. Although a Weiss temperature that is negatively signed points towards an antiferromagnetic kind of interaction, caution has to be exercised in the present situation in view of the lack of an accurate cerium ion concentration level. The obtained effective moment value, on the other hand, is close to but somewhat less than that of the full $J = 5/2$ magnetic multiplet value (J the total angular momentum) which amounts to 2.54 for the free-ion situation of Ce^{3+}. Furthermore, we present the magnetization at the base temperature of 2 K (inset, Fig. 4) as a function of the applied field. A weak curvature is observed, which arises from coupling of the applied field with the magnetic species in the sample and hence a small decrease in magnetic susceptibility at elevated fields. The magnetization is clearly in evidence of a substance containing a magnetic species, i.e. Ce^{3+}, in the paramagnetic state in this sample.

Conclusions

The results demonstrate that two diamagnetic reactant species form a single supramolecular paramagnetic product due to the *in situ* formation of the paramagnetic Ce^{3+} species at the reaction condition. We believe that this material holds promise for magnetic applications by tuning magnetism (nature and strength of exchange interaction between the magnetic species) through suitable concentration levels of the ionic dopant. The advantages of CAN are its low toxicity, ease of handling, experimental simplicity and solubility in a number of solvents. During the polymerization process each step is associated with a release of an electron and that electron reduces the Ce^{+4} ion to form a Ce^{+3} ion. The Ce^{+3} ion binds with the chain nitrogen of the polyaniline which causes the emergence of paramagnetism in polyaniline. The resultant paramagnetic organic macromolecule complex compound could be useful in the application of flexible magnetic materials and we believe this work will show the way towards further research for synthesizing organic magnetic materials.

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