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Structural Properties of Polyaniline Blended with PNIPAM

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Abstract Polyaniline (PANi) composite particles were synthesized by chemical oxidation polymerization of aniline in presence of poly-n-isopropyl acryl amide (PNIPAM). The PANi particles formed in the reaction medium deposited onto non-conducting PNIPAM template to produce PANi-coated composite particles. The formation of composite was confirmed by FT-IR spectroscopy, and UV-VIS spectroscopy, and their morphological structures were examined by scanning electron microscopy (SEM). From the experimental results, it was determined that PANi was successfully coated onto non-conducting PNIPAM.

1. Introduction

Polyaniline is an important electrically conducting materials and has been studied extensively due to its high conductivity, good redox reversibility, swift change in film color with potential, high stability in air. However, polyaniline is infusible and insoluble or partly soluble in common organic solvents (DMSO, alcohol, toluene, MEK, chloroform, etc.) due to its chain stiffness. Emeraldine salt (half oxidized PANi, y=0.5) is the most conductive form of PANi, which can be obtained by protonation of emeraldine base and oxidation of leucoemeraldine base. Besides the emeraldine, leucoemeraldine (fully reduced PANI, y=0), and pernigraniline (fully oxidizes form, y=1); nigraniline (75% oxidized form, y=0.75) has also been reported. Many attempts have been receiving in such way this intractable polymer processed with insulating polymer to make blends [1]. The dispersion polymerization (by steric stabilization mechanism) is mostly used chemical polymerization among the variety of chemical and electrochemical techniques viz. emulsion polymerization [2], steric stabilization, consolvation of components, graft polymerization, etc [3]. Elyashevich *et al.* [4] have used the dispersion of polyaniline to coat polyethylene (PE) sheet for making conducting film. Polyaniline (PANi) exists in a variety of protonaion and oxidation forms as shown in Figure 1.

Doping and oxidation levels are the most important factors affecting the electrical properties of polyaniline. Among the various forms, emeraldine salt is the most important form, which is produced by the oxidative polymerization of aniline in aqueous acids. The fundamental process of doping is a charge transfer reaction between dopant and organic polymer chain. Charges produced by acid doping on polymer chain can move along polymer backbone, and they are regarded as charge carriers in conducting polymers. These quasi-particles are classified into polarons, bipolarons and solitons according to their charge and spin as shown in Figure 2. Emeraldine salt (green color) converts to emeraldine base (blue color) in alkaline medium, called dedoping..

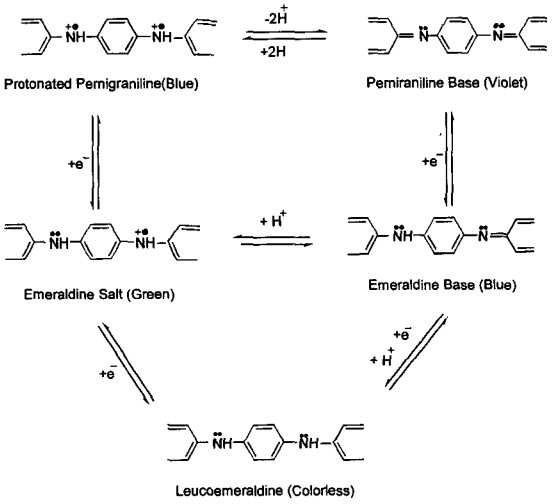

Figure 1. Different forms of Polyaniline

Blending of different polymeric materials is often performed to produce new compositions with desir-

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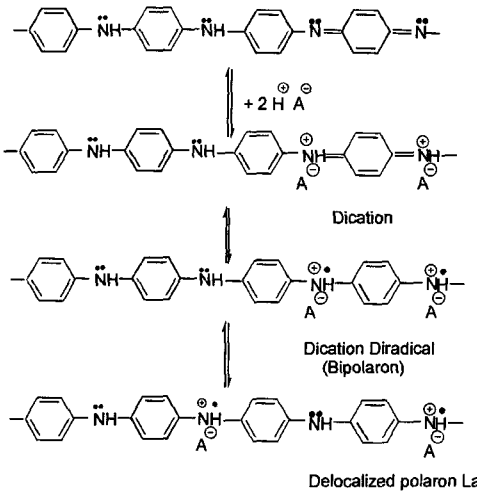


Figure 2. Protonation of polyaniline (EB) and formation of conductive chain

able properties, which are lacking in individual components of the blend. By proper selection of insulating polymer, polyaniline blends have been made that possess excellent mechanical, optical, and electrical properties. Polyaniline dispersions have been prepared by using surfactants such as sodium dodecyl sulphate (SDS), dodecyl benzene sulfonic acid (DBSA), etc at various pHs with ammonium peroxodisulfate (APS) as an oxidant. Recently Gospodinova *et al.* [5] have reported that they prepared PANi/PVA composites as nano-particles (5-30 nm) in DBSA micellar solution. Kawaguchi *et al.* [6] found PNIPAM adsorbed at air/water interface can form a two-dimensional film, which leads to a decrease of the surface tension so that PNIPAM can be used as a surfactant.

In the present work, we have focused on the chemical synthesis of PNIPAM using azo-initiator, VA-044 [2,2'-azobis{2-(2'-imidazolin-2-yl)propane}dihydro-chloride], which can decompose at higher temperature (half life at 44°C is 10 hrs) with liberation of molecular nitrogen and free-radicals as shown in Figure 3. The PNIPAM thus prepared was used as supporting polymer (template) for conductive polyaniline composite.

2. Experimental

2.1 Materials

Aniline (guaranteed reagent) was purchased from

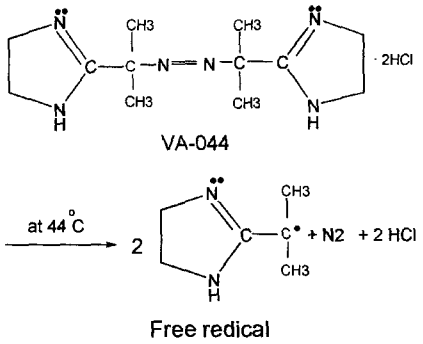
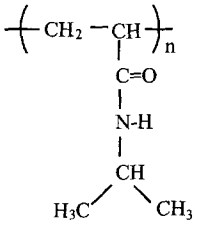


Figure 3. Structure and decomposition of VA-044

Junsei Chemical Co. Ltd, Japan, VA-044 [2,2'-azobis{2-(2-imidazolin-2-yl)propane}dihydrochloride] was purchased from Wako Pure Chemical Industries Ltd., Japan, ammonium peroxodisulphate (APS, 98.5%), *n*-isopropyl acryl amide(NIAM), *N,N'*-methylenebis (acrylamide) (BIS), and sodium dodecyl sulfate (SDS) were purchased from Aldrich Chemical Company. These reagents were used without further purification.

2.2 Synthesis of PNIPAM

1.13 gm of NIPAM was dissolved in 50 ml hot distilled water followed by 0.75 BIS and 0.100 gm VA-044 initiator. The mixture was stirred for one hour at 30°C, resulting white precipitate was filtered, washed with methanol and distilled water several times and dried in dry oven at 30°C for 5 hrs. Chemical structure of synthesized PNIPAM is following.



2.3 Synthesis of PANi/PNIPAM

Plyaniline emeraldine salt/poly(isopropyl acrylamide) (PANi/PNPIAM) composite was prepared by room temperature oxidative polymerization of aniline (0.93 gm) using ammonium peroxodisulfate (0.28 gm in 20 ml distilled water) in 50 ml 1M HCl in the presence of 0.5 gm of PNIPAM. After 6 hrs of oxidative polymerization, the solution was precipitated

with methanol. The precipitate was filtered and washed with methanol and distilled water several times to remove the unreacted materials until the colorless filtrate was obtained. Then the PANi/ PNIPAM blend was dried in dry vacuum oven at 50°C for 4 days.

3. Results and Discussion

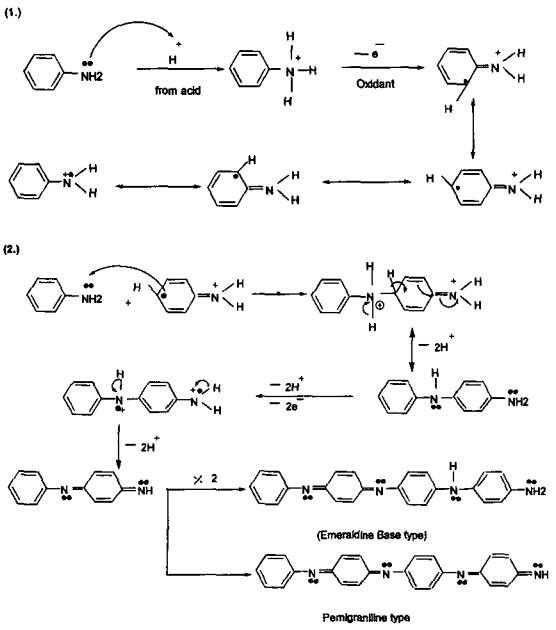
3.1 Mechanism of Polymerization

The possible mechanisms of polymerization are shown in Scheme I and II. The key of our investigation is thus obtained free radical attacks on anilinium ion and hence polymerization proceeds. It is believed that the free radical may serve two important other functions: firstly, it may prevent the formation of high molecular weight polyaniline by impeding the one or often two end of polymerization of polymer chain, secondly, the hydrogen atom of N-atom forms H-bond with O-atom of solvent which causes well dispersion.

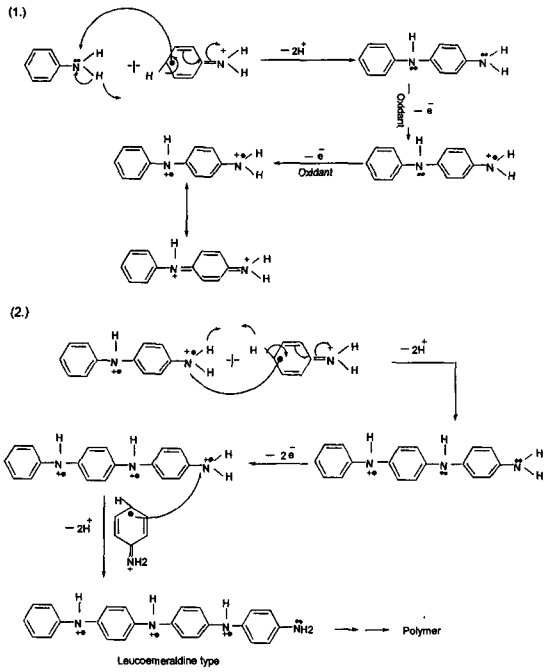
.3.2. FT-IR spectra of NIPAM and PNIPAM

The FT-IR spectra of NIPAM and PANIPAM are shown in Figure 4. The FT-IR spectrum of NIPAM is shown only for comparison with the spectrum of PNIPAM.

The peaks at 3436, 2975, and 1651 cm^{-1} can be attributed to stretching of the hydrogen-bonded N-H group, stretching vibration of C-H in the CH_3 group,



Scheme I



Scheme II

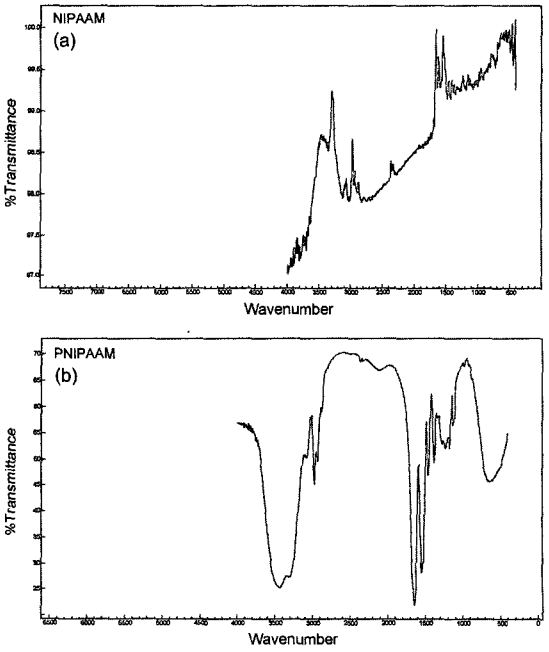


Figure 4. FT-IR Spectra of (a) NIPAM, (b) PNIPAM

and very strong and distinctive absorption of C=O group respectively, clearly indicate successful polymerization as PNIPAM. These data are consistent with the literature [7].

3.3 UV-VIS spectroscopy of PANi/DBSA and PANi/PNIPAM composite

Aniline polymerization in aqueous acid medium is in higher extent of 80~85% but in presence of steric stabilizers and blends polymerization is lowered to some extent. The UV-VIS absorption spectra of synthesized polyaniline for different polymerization condition are presented in Figure 5. They exhibit three absorption peaks: (i) absorption peak at 351 nm corresponding to the $\pi \rightarrow \pi^*$ transition, (ii) absorption peaks at about 426 and 775 nm, which can be assigned to the polaron band transitions. These three peaks constitute a typical emeraldine salt spectrum. The peak 775 nm shifted to 570 nm by dedoping with 2 M NaOH shown pattern (b) in Figure 5. This peak can be attributed as donor-acceptor interaction between quinoid fragments in PANi and the counter anion. As shown pattern (c) in Figure 5, broadening of the polaron/bipolaron transition band over the region of 391 nm for PANi/PNIPAM composite is a consequence of structural modifications [9]. Such a blue shift is explained as a result of interaction between the components through H-bonding.

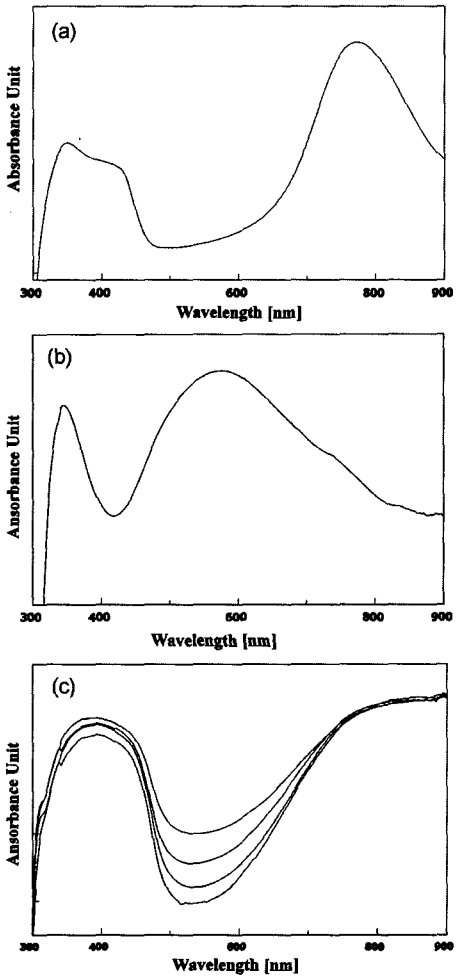


Figure 5. UV-VIS spectra of (a) in-situ polymerization PANi-EM salt in presence of PVP as steric stabilizer and DBSA as dopant, during 1 hr oxidation, (b) dedoped EM-base by 2 M NaOH during 6 hrs, and (c) PANi/PNIPAM with oxidation for 2, 3, 5, 6 hrs from bottom to top

3.4 FT-IR Spectroscopy

Representative IR spectra of PANi/PNIPAM are shown in Figure 6. The broad band around 3432-3295 cm^{-1} is characteristic of NH_2 and H-bonded NH stretching and peak at 2970 cm^{-1} is characteristic peak of C-H stretching. The peak at 1540 cm^{-1} is assigned to C=N- of quinoid ring, and the strong peak at 1292 cm^{-1} is characteristic of B-C-N stretching mode. A broad band at 1123 cm^{-1} is assigned to B-NH-B [8]. The mutual PANi/PNIPAM structural modifications lead to significant shift of >C=O peak to 1640 cm^{-1} for PANi/PNIPAM composite.

3.5 Scanning Electron Microscopy

The SEM pictures of PANi/PNIPAM powder are shown in Figure 7. The particle size covers a broad range in micro-level. The lower size particles seem to

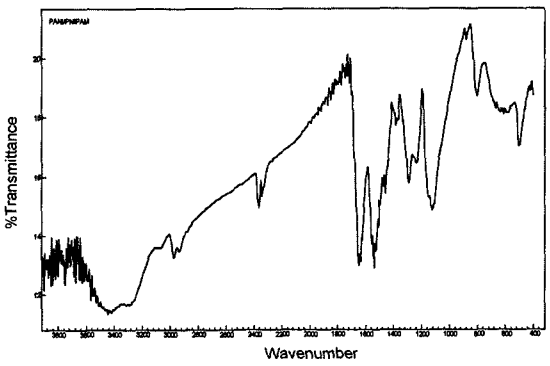
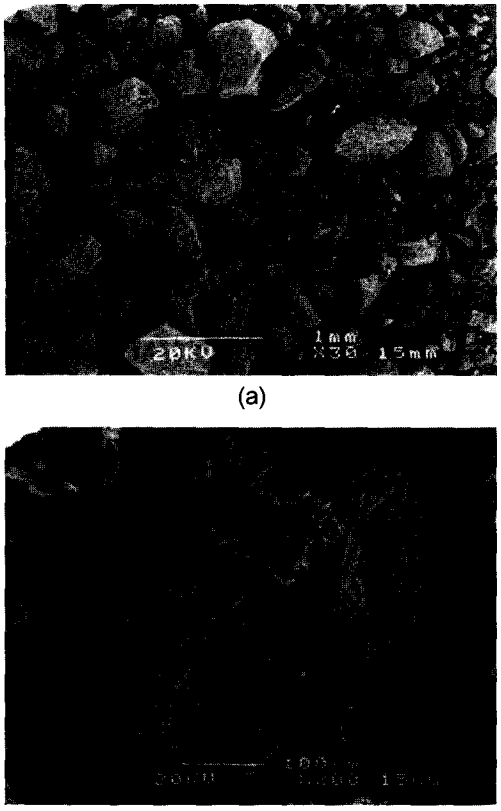


Figure 6. FT-IR spectra of PANi/PNIPAM composite



(a)

(b)

Figure 7. SEM images of PANi/PNIPAM composite

contribute more to the formation of conducting network.

4. Conclusions

From the results of UV-VIS spectra it can be concluded that PNIPAM is poor dispersing agent. Probably due to higher steric hindrance the polymerization is slow and poor than in DBSA micellar solution. Blue shift of normal polaron/bipolaron band to 391 nm is explained as a result of interaction between the components through H-bonding. FT-IR spectroscopy reveals that the formation of PANi/PNIPAM composite and formation of H-bond between amine group of PANi and >C=O group of PNIPAM due to which the standard peak of >C=O group shifted to lower wave number.

Acknowledgements

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