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 are 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 PANIPAM.

1. INTRODUCTION

Polyaniline is an important electrically conducting material 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. 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] 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[Fig.1].

Blending of different polymeric materials is often performed to produce new compositions with desirable properties, which are lacking in individual components of the blend. By proper selection of insulatingpolymer, 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), dodecylbenzene sulfonic acid(DBSA) etc at various pHs with APS as oxidant. Kawaguchi *et al.*[5] found PNIPAM adsorbed at air/water interface can form a two-dimensionalfilm, 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}dihyd rochloride], which decomposes at higher temperature(half life at 44℃ is 10hrs) with liberation of molecular nitrogen and free-radicals as shown in Fig. 2. The PNIPAM thus prepared was used as supporting polymer(template) for conductive polyaniline composite.

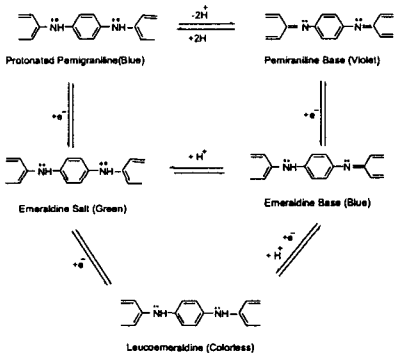


Fig. 1. Different forms of polyaniline.

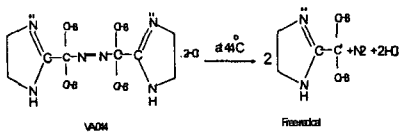
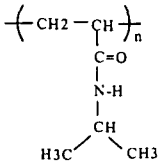


Fig. 2. Structure and decomposition of VA-044.

2. EXPERIMENTAL

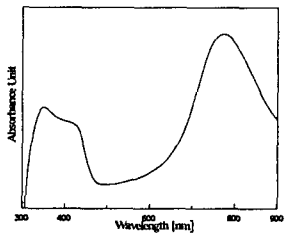
Aniline(Junsei, Japan), VA-044 [2,2'-azobis{2-(2-imidazolin-2-yl)propane}dihydrochlori de](Wako, Japan), ammonium peroxodisulphate(APS, 98.5%), N-isopropyl acryl amide (NIAM), N,N'-methylene bis(acrylamide)(BIS), sodium dodecyl sulfate(SDS) were used as received. 1.13gm of NIPAM was dissolved in 50ml hot distilled water followed by 0.75 BIS and 0.100gm VA-044 initiator. The mixture was stirred for one hour at 30℃, resulting white precipitate was filtered, washed with methanol and distilled water several times and dried in dry oven at 30℃ for 5hrs.



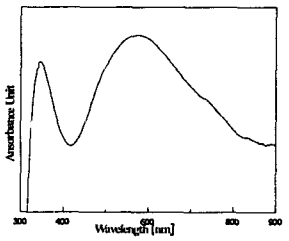
Plyaniline emeraldine Salt/Poly(Isopropylacrylamide) (PANi/PNPIAM) composite was prepared by oxidative polymerization of aniline(0.93gm) at room temperature using ammonium peroxodisulfate as an oxidant(APS, 0.28gm in 20ml distilled water) in 50ml 1M HCl in the presence of 0.5gm of PNIPAM. After 6hrs 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℃ for 4 days.

3. RESULTS AND DISCUSSION

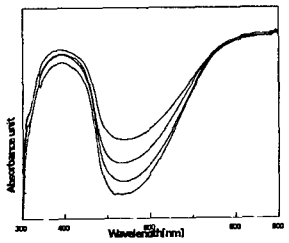
Aniline polymerization in aqueous acid medium is in higher extent of 80-85% but in presence of steric stabilizers and blends polymerization is lowered to some extent. The UV-VIS absorption spectra of synthesized polyaniline for different polymerization condition are presented in Fig. 3. They exhibit three absorption peaks:(i) absorption peak at 351nm corresponding to the $\pi \rightarrow \pi^*$ transition, (ii) absorption peaks at about 426 and 775nm, which can be assigned to the polaron band transitions. These three peaks constitute a typical emeraldine salt spectrum. The peak 775nm shifted to 570nm by dedoping with 2M NaOH(Fig.3(b)). This peak can be attributed as donor-acceptor interaction between quinoid fragments in PANi and the counter anion. As shown in Fig. 3(c), broadening of the polaron/bipolaron transition band over the region of 391nm for PANi/PNIPAM composite is a consequence of structural modifications[6]. Such a blue shift is explained as a result of interaction between the components through H-bonding.



(a)



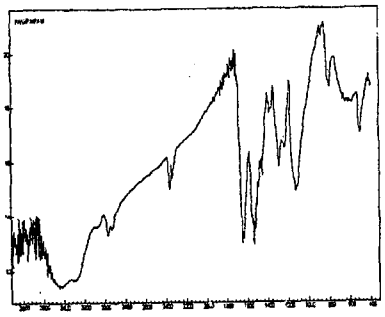
(b)



(c)

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

Representative IR spectrum of PANi/PNIPAM is shown in Fig. 4. The broad band around 3432-3295cm-1 is characteristic of NH_2 and H-bonded NH stretching and peak at 2970 is characteristic peak of C-H stretching. The peak at 1540 cm^{-1} is assigned to C=N- of quinoid ring. 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[7]. The mutual PANi/PNIPAM structural modifications lead to significant shift of >C=O peak to 1640 cm^{-1} for PANi/PNIPAM composite.



wavenumber

Fig. 4. FT-IR spectrum ofPANi/PNIPAM composite.

4. CONCLUSIONS

From the results of UV-VIS spectra it can be concluded that PAIPAM 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 391nm 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.

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