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Dielectric properties of ZnS filled polystyrene nanoparticules

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ABSTRACT: Zinc sulfide ZnS have been synthesized in reserves cores micelles in PS synthesized by emulsion polymerization. The size and morphology of ZnS/PS particles have been characterized via XRD, TEM, IR, SEM and AFM measurement. The dielectric proprieties of ZnS/PS are synthesized membrane, obtaining a water-swelling percentage around 20% and filled with ZnS nanoparticules were studied as a function of particle coating. The complex permittivity was measured with a 7600 Meter dielectric spectroscopy analyzer at applied voltage of 1 V with frequency varying between 10Hz and up to 1 KHz at different temperatures measurements are performed in dry conditions.

KEYWORDS: Zinc Sulfide, polystyrene, nanocomposites.

1 INTRODUCTION

ZnS nanoparticles are widely studied materials due to their unique electrical, electronic, and optical properties. ZnS nanoparticles need to be dispersed homogenously in various matrices for these applications and it can be synthesized by various synthetic paths in various shapes and particle sizes [1, 2, 3, 4, 5, 11]. Two approaches have been developed to prepare organic-inorganic hybrid materials. The first route is to incorporate inorganic domains into a polymer matrix by a sol –gel technique [1, 2]. Another method is to incorporate premade inorganic colloidal nanoparticules into polymer matrix [9]. Nanoparticules and nanocomposites are used in a wide range of applications in various fields, such as medicine, textiles, optics, and electrical. Nanoparticules can be incorporated into polymeric nanocomposites. Polymeric nanocomposites consisting of inorganic nanoparticules and organic polymers represent a new class of materials. Polymer nanocomposites show great promise as electrical insulation [22]. Adding just of few weight percent of nanosized fillers can have a profound effect on material Proprieties [18].

The aim of this work is to investigate the characteristic of nanocomposites and the influence of the above mentioned surface modifications and nanoparticules content on the dielectric proprieties of the nanocomposites [21].

2 EXPERIMENTAL

2.1 MATERIALS

Styrene monomers, sodium dodcyl sulfate (SDS, Aldrich, 99%) and the initiator, potassium persulfate (KPS, Aldrich, 98%), ZnS CNCs, Zinc acetate dehydrate (Zn (OAc)$_2$. 2 H_2O) (Aldrich).

2.2 SYNTHESIES OF ZNS NANOPARTICULES

To synthesise the ZnS CNCs, Zinc acetate dehydrate [Zn (OAc)$_2$. 2 H_2O) Aldrich, AR grade]), and the thiourea [21] were dissolved in diéthylène glycol and kept for 2h under continuous magnetical agitation. At the end of the reaction, the precipitate was centrifuged, washed several times with ethanol, and then dried in vacuum for 12 h to yield a white dry ZnS powder.

2.3 SYNTHESIES OF POLYSTYRENE

Polystyrene were prepared in batch emulsion polymerization at 80°C from styrene (Aldrich, 99%), in 200 ml of H_2O the surfactant, sodium dodcyl sulfate (SDS, Aldrich, 99%) and the initiator, potassium persulfate (Kps, Aldrich, 98%). Removing SDS and conterions from the suspension using a mixture of anionic and cationic exchange technique (DOWEX Marathon MR-3, Aldrich).

2.4 SYNTHESIES OF ZNS/PS

Ten percent of the weight of ZnS was added to 20ml of ethanol. The suspension was stirred magnetically for 1h and sonicated for 1h before 2g of PS was added. The resulting mixture was magnetically stirred for 1h and sonicated for 1h, ZnS /PS nanocomposites were synthesized by an in-situ polymerization [13].

2.5 MEASUREMENTS

The X-ray diffraction patterns of the nanocomposites were measured using the $\mathrm{Cuk}_{\alpha 1}$ (1,5406Å) radiation in the range of 2θ=2-70º, with a step size of 0.02º.

The infrared spectroscopic absorption data were obtained with a Fourier Transform infrared spectrometer with an attenuated total reflectance accessory (FTIR-ATR).

Morphology of the materials was studied using Atomic forces microscope (AFM), Transmission Electron Microscopy (TEM), SEM images were obtained by means of microscope.

The dielectric constant for the nanoparticules ZnS, PS and nanocomposites ZnS/PS have been measured by using an L. C. R meter 7600.

3 RESULTATS AND DISSCUSSIONS

3.1 INFRARED ABSORPTION SPECTRA

3.1.1 INFRARED ABSORPTION SPECTRA OF ZNS

The infrared absorption spectra (FT-IR) of ZnS recorded in the region from 400-4000 cm^{-1}. Spectrum analysis of ZnS shows that despite of the successive washes of the powder with absolute ethanol, traces of solvent still exist which is confirmed by the presence of a broad and intense band at around 3340 cm^{-1} assigned to the vibrations of valence of OH group of 1.3 propandiol, the relative bands of the two vibrations of valences of the C-H groups at about 2970- 2860 cm^{-1} and the valence band located to 1073 cm^{-1} which is due to the vibrations of the valence bands of the polyol's CO group. It also distinguishes the presence of a band around 1600 cm^{-1} and 1400 cm^{-1} assigned to the valence vibrations of the acetate [10, 11], the vibration of the ZnS bond is confirmed by the presence of the band located around 662 cm-1 [12, 13].

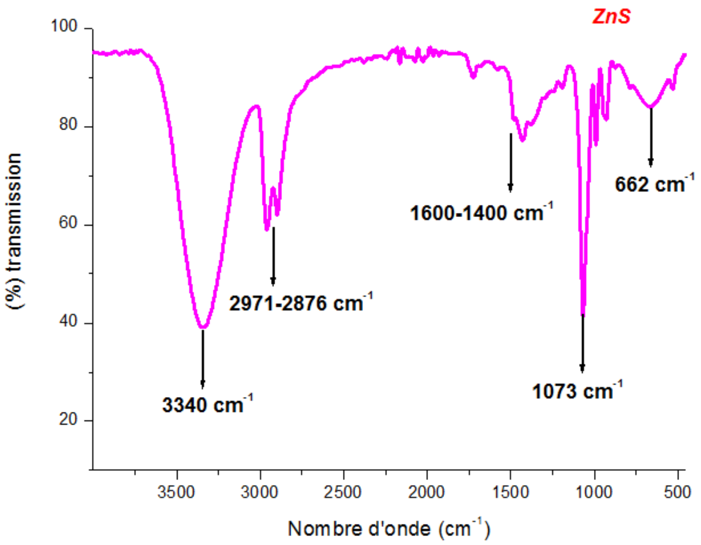


Fig.1: FTIR spectra of ZnS nanoparticles

3.1.2 INFARED ABSORPTION SPECTRA OF PS, ZNS AND PS/ZNS NANOCOMPOSITE

The Infrared absorption spectra of PS and ZnS/PS nanocomposites. The infrared of PS features bands at 3066, 3025, 2922, 2851, 1666-1945, 1491-1599, 1188-1368, 1026,698-756, and 543cm^{-1}.

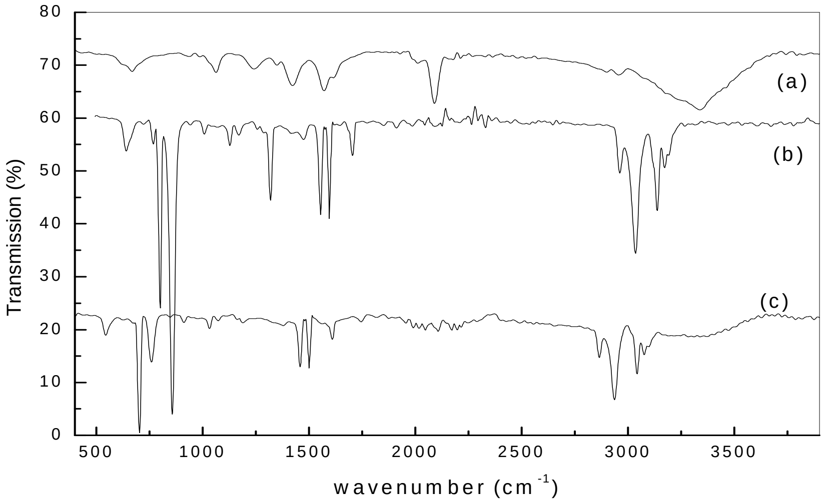


Figure.2. In situ infrared spectra of (a)PS, ZnS (b), (c) ZnS/PS nanocomposites.

3.2 X-RAY DIFFRACTION XRD

3.2.1 XRD OF ZNS

The XRD pattern of the as-synthesized revealed well-crystallized and pure ZnS particles with the cubic phase (space group F-43m, lattice constant a =5,414 Å (Figure.3). The peak broadening in the XRD pattern clearly indicates the very small nanocrystals are present in the sample. Estimated by applying the Debye-Scherer formula [4] size is about 4-5 nm.

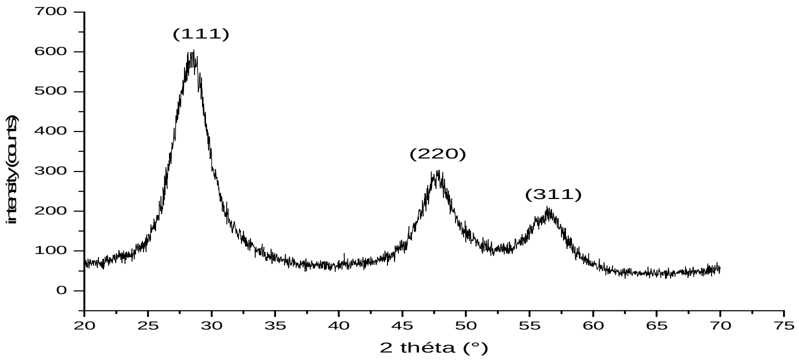


Figure. 3. X-Ray spectra of ZnS nanoparticules.

3.2.2 XRD OF ZNS/PS

X-ray the structural diffraction (XRD) measurements were also applied to analyse the characteristic of ZnS/PS nanocomposites which were prepared with 20% of ZnS. Figure. 4 show the XRD patterns of PS and ZnS/PS nanocomposites. For PS (Figure.4.a) two a broad amorphous peaks, which appeared within the range of 2 θ = (9-10) and 2 θ = (18-20) [2] can observed. For PS/ZnS nanocomposites it is clear from Figure.4.b that the crystals structures of sulfide zinc particles are not altered by the polystyrene. The final composite products have distinct coreshell morphology. As a result, XRD pattern of sulfide zinc/polystyrene composite nanospheres combines of both nanocomposites [25].

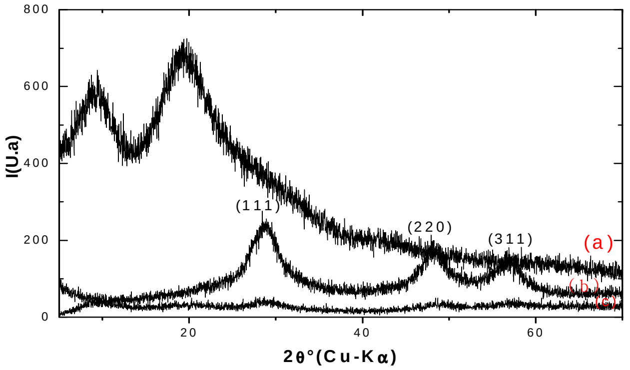
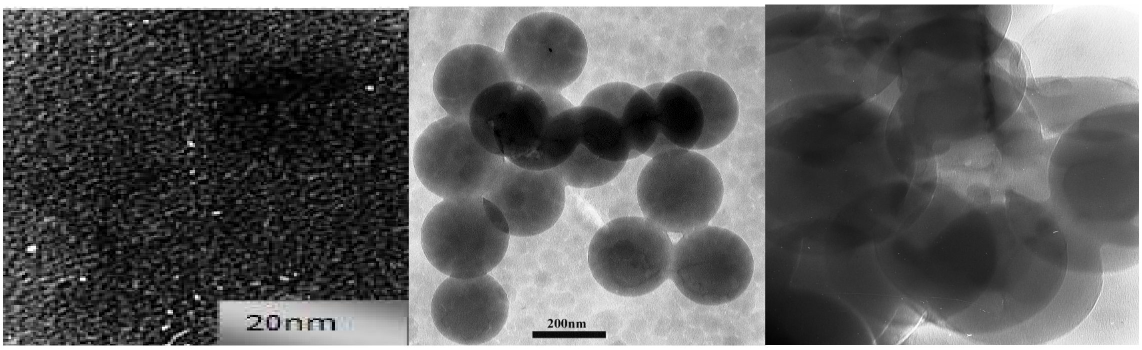


Figure. 4: X-Ray patterns of synthesized (a) PS, ZnS (b), ZnS/PS(c)

3.3 TRANSMISSION ELECTRON MICROSCOPY (TEM)

Transmission electron microscopy (TEM) provides an actual image of the ZnS/PS which permits the identification of the morphology of the nanocomposites. Thus, TEM was another method to observe evidence for the formation of the intercalated structure of the prepared nanocomposites. In Figure.5.a, presents the TEM of ZnS nanoparticules. The small nanoparticules are observed from the TEM images. The ZnS has a diameter of about 20 nm. However, Figure.5.b shows the TEM of image of PS, it has been ordered spherical. Figure.5.c reveals the typical TEM of ZnS/PS nanocomposites films with ZnS contents of 20 Wt %, it can be seen that the ZnS is uniformly dispersed in the polymeric matrix indication that the polystyrene play an important role in stabilizing and dispersing nanoparticules [12, 13, 25].

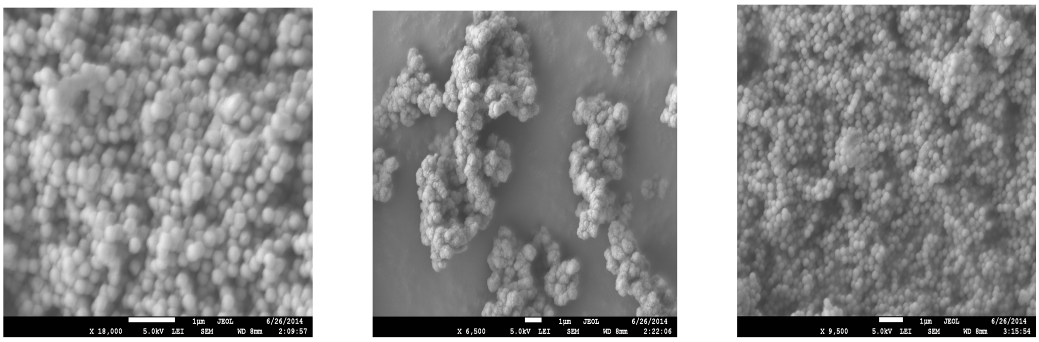


(a) (b) (c)

Figure.5. TEM particules of (a) ZnS, (b) PS, (c) ZnS/PS nanocomposites

3.4 MORPHOLOGY OF PS/ZNS COMPOSITE MICROSPHERES

The formation of Zinc sulfide/polystyrene (ZnS/PS) [6] composite microspheres can be classified as polymerization initiated by ZnS. SEM micrographs of ZnS/PS samples are shown in Figure. 6. (c) displays general images of nanocomposites microspheres, it can be clearly seen that the microspheres have ordered spherical shape and possess a good dispersion. SEM image in Figure.7.c shows the morphology of ZnS/PS microspheres under magnifications observations.



(a) (b) (c)

Fig.6. SEM images of (a)PS, (b) ZnS, (c)ZnS/PS after 1h of sonication time

3.5 ATOMIC FORCE MICROSCOPY (AFM)

The AFM images of polystyrene without and with zinc sulfide nanoparticules of 20% are shown in Figure.7, it can be seen that the polystyrene has a spherical surface (Figure. 7.a), the PS has been ordered spherical [10, 11,18]. In Figure.7.b, the spheres are assembled into closely pocked hexagonal, it can be seen that the surface of the film is very ordered; however, many small nanoparticules is around 1-4 nm. This further indicates that the ZnS nanoparticules remain their original size without aggregation at the surface of films.

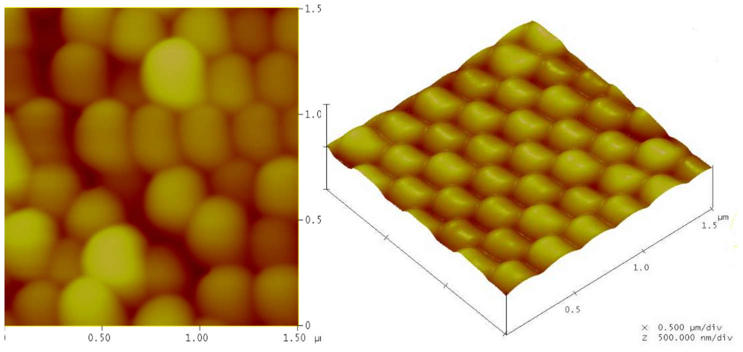


Figure.7.a. Topography AFM representing the height image (left) and the 3D image (right) of PS

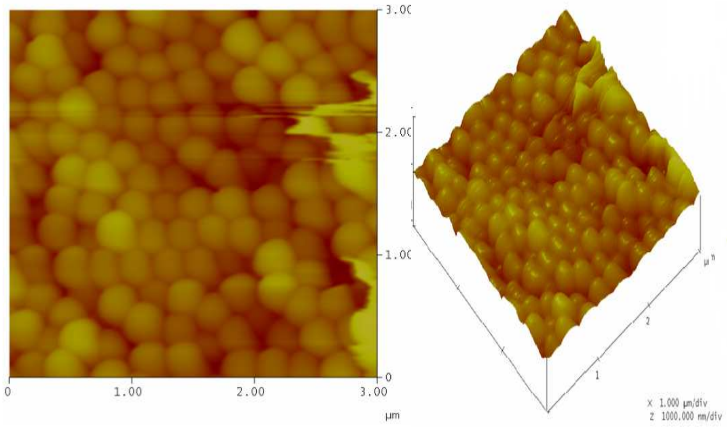
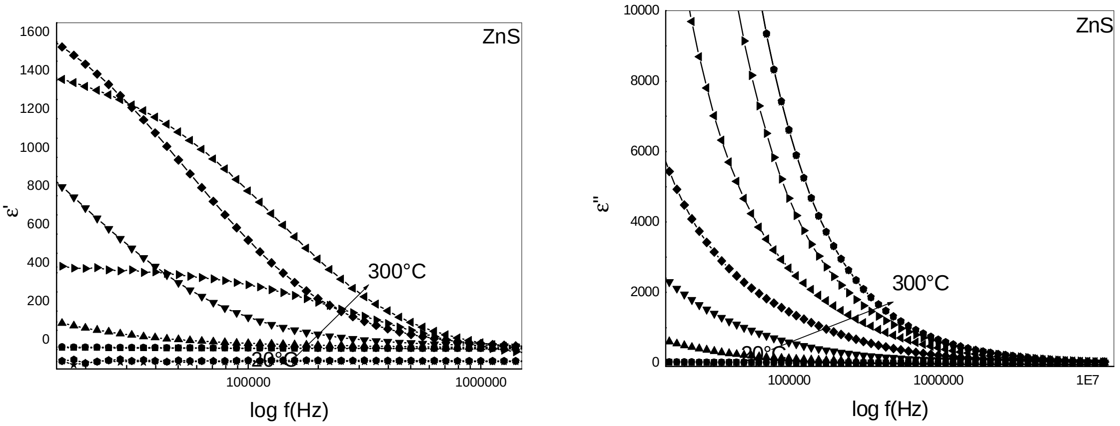


Figure.7.b. Topography AFM representing the height image (left) and the 3D image (right) of ZnS/PS.

3.6 DIELECTRIC MEASUREMENTS

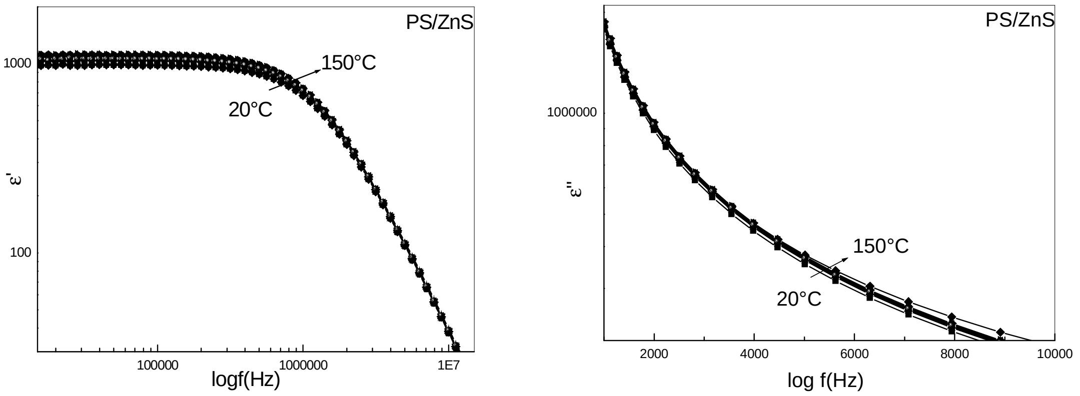
The relative dielectric permittivity ε̇ and dielectric loss ε̇' of the nanoparticules ZnS as a function of frequency of the applied ac electric is displayed respectively in Figure.8.1. The dielectric constant for the nanoparticules ZnS have been measured by using an L. C. R meter, the relative dielectric permittivity increased in low frequency and it's values were found in the range 20-200 at higher frequencies. The large value of ε̇ of ZnS nanoparticules thin film is to the fact that the nanoparticules of ZnS under of the application of electric field act as nanodipoles [21, 22, 23]. There is no dispersion at higher frequencies, the nanoparticules can not follow the rapid variations of the dielectric field and hence, they show practically no dispersion.

In Comparing dielectric constant for the nanocomposites with these for unfilled ZnS, it can be noted that the low frequency dispersion behavior changes from a Debye reponse to reponse with a less steep slope (Figure.8.2). This could be explained by nanoparticules affecting the charge transport mechanism and the net interfacial polarization. The dielectric constant seems to increase with increasing filler regardless of the surface treatment. Isotherms for dielectric constant in the frequency domain, corresponding to nanocomposites are shown in Fig. 10.2. As usual dielectric constant increase as frequency decrease reaching a plateau corresponding to the relaxed dipole [24].



(a) (b)

Fig.8.1. Relative dielectric permittivity (a) and dielectric loss (b) as a function of the frequency at temperatures between 20°C to 300°C for nanoparticules ZnS.



(a) (b)

Fig.8.2. Relative dielectric permittivity (a) and dielectric loss (b) as a function of the frequency at temperatures between 20°C to 150° for nanocomposites ZnS/PS.

4 CONCLUSIONS

An intercalate nanocomposites was formed by a free radical polymerization reaction of stay in the presence of ZnS intercalate, the high concentration of polystyrene capped ZnS nanoparticules with an average diameter of 20 nm can be seen easily immobilized into the polystyrene. The morphology (TEM, SEM, and AFM) studies suggest that the ZnS nanoparticules are uniformly dispersed in the polymer matrix. The nanocomposites exhibit excellent dielectric permittivity and dielectric loss as a function of the height frequency.

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REFERENCES

[1] Lee LH, Chen WC. Chem Mater 2001; 13:1137.
[2] Wang B, Wilkes GL. J Polym Sci Part A Polym Chem 1991; 29: 905.
[3] Srivastava, S.; Kumar, S.; Singh, V.N.; Singh, M.; Vijay, Y.K.; International Journal of Hydrogen Energy 2011, 36, 6343.
[4] Tamer A. Elbokl, Christian Detellier. J Physics and Chemistry of Solids 67 (2006) 950–955
[5] Waffa Mashael Alshabanat, Amal Al-Arrash, and Waffa Mekhamer. J. of Nanomaterials 2013, 10.1155.
[6] Mingna Xiong, Guangxin Gu, Bo You, Limin Wu, J.App. Polym. Sci. 90 (2003) 1923-1931.
[7] A. Anlovar, K. Kogej, Z. Crnjak Orel, J. XPRESS Polymer Letters Vol.5, No.7 (2011) 604–619
[8] Hou Xuemei and Ying Hao, J. Hindawi Publishing Corporation 2013; 751497.
[9] Tetsuya Yamamoto, Yoichi Kanda, Ko Higashitan. J, of Colloid and Interface Science (2006) 299, vol. 493–496.
[10] J Garnaes. J. Sci. Technol. 2011; 094001
[11] B. Mailhot, S. Morlat, J.-L. Gardette. J, Polymer 2000; 1981–1988
[12] Sy-Hann Chena, Hsu Chou Hsiungb, Wei-Bin Suc, Din Ping Tsa 81 2006; 129–132.
[13] Yong bin Zhao, Feng Wang, Qi Fu, Wenfang Shi, J. Polymer 48 2007; 2853- 2859
[14] Lee LH, Chen WC. Chem Mater. 2001; 13, 1137.
[15] Wang B, Wilkes GL. J Polym Sci Part A Polym Chem. 1991; 29:905.].
[16] Papadimitrakopoulos F, Wisniecki P, Bhagwagar DE. Chem Mater 1997; 9:2928.
[17] Kypriandou-Leodidou T, Althaus HJ, Wyser Y, Vetter D, Buchler M, Caseri W, et al. J Mater Res 1997;12:2198.
[18] Tetsuya Yamamoto, Yoichi Kanda, Ko Higashitani. Journal of Colloid and Interface Science 2006 493–496
[19] Papadiitra kopoulos F, Wisniecki P, Bhagwagar DE. Chem. Mater 1997; 9:2928.
[20] Kypriandou-Leodidou T, Althaus HJ, Wyser Y, Vetter D, Buchler M, Caseri W, et al. J Mater Res 1997; 12:2198.
[21] P.K. Ghosh, S. Jana, S. Nandy, K.K. Chattopadhyay. J. Materials Research 2007; 505–514
[22] S. Bhattacharya, S.K. Saha, D. Chakravorty, Appl. Phys. Lett. 2000; 3896.
[23] S. Bhattacharya, S.K. Saha, D. Chakravorty, Appl. Phys. Lett. 2000; 3770.
[24] J. k .Nelson. Spring-Verlage NY, 2010
[25] Chong Bi, Liqing Pan, Zhengang Guo, Yuelei Zhao, Miaofeng Huang, Xin Ju, John Q. Xiao, J. Materials Letters 64 2010; 1681–1683.