SYNTHESIS AND CHARACTERIZATIONS OF POLY(ANILINE)/Sb₂O₃ NANO COMPOSITE

A.YELIL ARASI^a, J.JULIET LATHA JEYAKUMARI^b, B.SUNDARESAN^b,
V. DHANALAKSHMI^c AND R.ANBARASAN^{*c}

^aDepartment of Physics, Kamaraj College of Engineering and Technology, Virudhunagar – 626 001, Tamilnadu, India,

^bDepartment of Physics, Ayya Nadar Janaki Ammal College, Sivakasi - 626 124, Tamilnadu, India,

^cDepartment of Polymer Technology, Kamaraj College of Engineering and Technology, Virudhunagar – 626 001, Tamilnadu, India,

(Received: October 21, 2009 - Accepted: April 19, 2011)

ABSTRACT

This paper explains the synthesis and characterizations of Poly(aniline) (PANI)/Sb₂O₃ nano composite by in-situ polymerization method. It was indicated that Sb₂O₃ itself could catalyze the oxidative polymerization of aniline through its active surface effect. This could be due to the intercalation of PANI chains into the basal spacing of Sb₂O₃. TGA counseled the thermal stability of PANI. Through FTIR study, the structure of PANI was confirmed. Comparison of polymerized aniline composite with two different initiators was done. HRTEM confirmed the nano size of Sb₂O₃. The intercalating nature of PANI chains into the basal spacing of Sb₂O₃ was also tested.

Key words: PANI; Sb₂O₃; FTIR, kinetics; TGA; HRTEM

INTRODUCTION

Poly(aniline) (PANI), an intractable green powder, is one of the important electrically conducting polymers because of its novel applications in electrochemically controlled drug release device¹, bio-mimetic applications², LPG gas sensor³ and catalyst in oxidation process⁴. Such an important polymer is made into nano composite with nano scale materials to show improved physical and chemical properties. For example, when PANI is made nano composite with Fe₃O₄ exhibited excellent magnetic properties⁵. The increase in physical and chemical properties of PANI while making nano composite is the key idea of the present investigation. To attain such an improved physical and chemical properties, PANI was made nano composite with nano meter sized metal oxides like MoO₃⁶, HTiNbO₇⁷, Al₂O₃⁸, aluminosilicate⁹, TiO₂¹⁰, BaFe₁₂O₁₉¹¹, WO₃¹², RuO₂¹³, NiFe₂O₄¹⁴, V₂O₅¹⁵ and Pr₂O₃¹⁶. The above literature simply presented the FTIR spectrum for the confirmation of PANI-nano composite structure. References from 6-16 forgot to discuss the depth applications of FTIR for PANI nano composite. By thorough literature survey we could not find any report based on PANI/Sb₂O₃ nano composite so far.

FTIR spectrometer is a useful tool in various science and engineering fields, because of its high sensitivity or detectivity towards traces amount of sample, low noise to signal ratio and this method is easy and inexpensive one. FTIR spectroscopy is used for both qualitative¹⁷⁻²¹ and quantitative²²⁻³² analysis. By thorough literature survey, we could not find any report based on the FTIR based kinetics of effect of nano-sized material on the structure-property relationship of PANI. In the present investigation, for the first time, we are reporting about the synthesis of PANI/Sb₂O₃ nano composite in the presence of two different chemical initiators and its role on the structure and properties of PANI. Study on the effect of Sb₂O₃ on the structure-property relationship of PANI is the primary aim of the present investigation. In addition, the kinetics results were verified with the FTIR spectroscopic technique.

MATERIALS AND METHODS

Materials

Aniline (ANI) monomer was purchased from M/s Merck, India. In order to remove the inhibitor present in the monomer solution, it was distilled under vacuum prior to polymerization reaction. Hydrochloric acid (HCl, Reachem, India), Potassium peroxy disulphate (PDS, Ottokemi, India) and Potassium dichromate (PDC, Reachem, India) were used without subjecting them to any purification process. Sb₂O₃ (SD fine chemicals, India) was purchased and used without further purification.

Synthesis procedure

20 mL of ANI (1M) in 1M HCl was taken in a polymer reactor and de-

aerated by purging sulphur free nitrogen gas for 30 min. The reactor was charged with 30 mL of 1M HCl to adjust the ionic strength. The polymerization was initiated by the addition of 10 mL of pre-aerated oxidizing agent such as PDS or PDC (0.10 M). The time of adding the oxidizing agent was taken as the starting time. The reaction mixture was found to turn green in color and appearance of the polymer formation was noticed. Polymerization was carried out at 45^o C for the reaction time of two hours. After two hours of polymerization time, air was blown into the reactor to arrest further polymerization reaction. PANI thus obtained was filtered through previously weighed G4 sintered crucible and dried at 80^o C for 6 h in the hot air oven. After drying, the crucible with polymer was weighed and the weight of empty crucible was deducted from that. The difference in weight gave the weight of the formed polymer. The same method was adopted for the synthesis of PANI/ Sb₂O₃ nanocomposite by adding 3% weight of Sb₂O₃ in the presence of PDS or PDC as an initiator. The rate of polymerization (R_p) was determined by gravimetric method as follows:

$$R_p = \frac{\text{Weight of polymer obtained}}{V \times t \times M} \times 1000 \quad \dots\dots\dots (1)$$

Where, V - volume of reaction mixture, t - reaction time, M - molecular weight of monomer used. The synthesis procedure given above is old one but the concept behind it is a novel one. 1)The added nano material catalyzed the polymerization reaction and altered the structure of PANI. 2)The added nano material acted as a host and accommodates the PANI chains in its interlayer space and hence confirmed the chemical interaction among them. 3)Antimony oxide in its nano size accelerates the thermal and electrical conductivity value of PANI. These three things are entirely a new one from the previous literature. These are the specific reasons for the selection of Sb₂O₃ as a nano material.

Characterizations

FTIR spectra of PANI samples in the form of pellet were recorded using Shimadzu 8400 S FTIR spectrophotometer instrument. 3mg of PANI powder was well grinded with 250 mg of KBr and made into a disc by pressing. The baseline correction was made carefully and the corrected area of the peaks was determined using FTIR software. For the quantitative determination of percentage amino and imino forms of PANI, the following areas of the peaks, which were assigned at 1490 (benzenoid form), 1590 (quinonoid form) and 720 (C-H out of plane bending vibration) cm⁻¹ were determined and the relative intensity (RI) was calculated as follows:

$$\text{Relative intensity of Benzenoid form (RI)} = A_{1490}/A_{720} \quad \dots\dots\dots (2)$$

$$\text{Relative intensity of Quinonoid form (RI)} = A_{1590}/A_{720} \quad \dots\dots\dots (3)$$

In-order to avoid error while recording FTIR spectrum, the corrected peak

area was considered and the value for the above-mentioned peak was noted. To cross check the corrected peak area values, the FTIR spectra were recorded for the same sample disc in different parts. After proper base line correction with the aid of FTIR software, again one can get the same corrected peak area values. FTIR spectrum was recorded for three times for the same sample disc, one can get the same and repeated corrected peak area values. The FTIR spectrum was recorded without predicting the lower and upper limits of peaks, because the software itself predicted exactly the lower and upper limits to nullify the errors. In such a way the errors were nullified. Further one can cross check the efficiency of FTIR software by manually predicting the lower and upper limits and the corrected peak area was determined. In this case one can get the same corrected peak area value as reported previously (without predicting the lower and upper peak limits). TGA analysis was performed under air purge at the heating rate of 10°C/min by using SDT 2960 simultaneous TGA and DSC, TA instruments. Standard Four Probe Method was adopted for the determination of conductivity value of polymer samples. HRTEM was recorded by using (TEM 3010) transmission electron microscopy (TEM) instrument, a product of JEOL. XRD of the samples were recorded with a help of Philips PW 1050/80 diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation generated 30 kV and 15 mA.

RESULTS AND DISCUSSION

FTIR spectroscopy

The structure of PANI synthesized by PDS and PDC as chemical initiators was confirmed by FTIR spectroscopy. Figure 1 showed the FTIR spectra of PDS initiated ANI polymerization in the presence of different % weight of Sb_2O_3 . A peak at 1563 cm^{-1} was due to the quinonoid structure of PANI. Another sharp peak at 1487 cm^{-1} was responsible for benzenoid structure of PANI. The peak at 720 cm^{-1} was the evidence of C-H out of plane bending vibration. In this present investigation, even though we have so many peaks due to the structure of PANI, we are interested only in the peaks corresponding to quinonoid structure, benzenoid structure and C-H out of plane bending vibration. Figure 2 showed the FTIR spectrum of PDC initiated PANI. Here also one can observe the same peaks as mentioned above. Apart from these peaks, we have one more peak around 500 cm^{-1} that confirmed the presence of metal-oxide stretching vibrations.

Figure 1. FTIR spectra of PANI [PDS-HCl- Sb_2O_3] system loaded with Sb_2O_3 at a) 1% weight, b) 2% weight, c) 3% weight, d) 4% weight, e) 5% weight

Figure 2. FTIR spectra of PANI [PDC-HCl- Sb_2O_3] system loaded with Sb_2O_3 at a) 1% weight, b) 2% weight, c) 3% weight, d) 4% weight, e) 5% weight

Effect of Time on R_p and RI of benzenoid and quinonoid forms of PANI

The time plays an important role in the R_p . The effect of time on R_p was studied by varying the reaction time between 1 and 3.5 h by keeping the other experimental conditions as constant. The R_p values were decreased as the time increased because of the presence of a bulk value in the denominator of R_p equation. The longer reaction time permits the monomer radical cations to interact with each other and resulting with the growth of polymer chain without any cross-linking. Molecular weight of the polymer is directly linking with the polymer chain length. Moreover, the polymer chain length is associated with the weight of polymer obtained. The % yield that simply explained the amount of monomer converted into polymer, but the weight of polymer accounted for the polymer chain length. That depended on the experimental condition used for the synthesis. Weight of polymer obtained by gravimetric method alone explained the approximate polymer chain length. The plots, Time Vs R_p (Figure 3a) and Time Vs R_i (Figure 3b) showed the effect of time on R_p for PDS and PDC initiators respectively. From the time variation, the optimized time was found as 2 h. We attained this conclusion by considering the % yield and electrical conductivity of the polymer samples received in each variation. Hereafter, the polymerization will be carried out at the constant time of 2 h under different experimental conditions. In comparison, the PDC initiated system showed higher R_p values because of three electron transfer reactions occurred in PDC whereas in the case of PDS two electron transfer reaction has occurred^{24,25}.

Figure 3. Effect of Time on (a,b) R_p , (c,e) $RI_{[benzenoid]}$ and (d,f) $RI_{[quinonoid]}$ (a,c,d) PANI-PDS-HCl- Sb_2O_3 , (b,e,f) PANI-PDC-HCl- Sb_2O_3 system $[ANI]=0.25\text{ M}$, $[PDS]=0.025\text{ M}$, $[PDC]=0.025\text{ M}$, Temperature = 45°C , % weight of Sb_2O_3 -3

PANI-Sb₂O₃ nano composites were synthesized under various reaction time durations with the help of an initiator PDS, while keeping the other experimental conditions like [M], [I], Temperature and (% weight of Sb₂O₃) were kept constant. The reaction time period was varied between 1 and 3.5 h. While increasing the reaction time, the RI of benzenoid form increased from 0.09031 to 0.1701. The RI of quinonoid form was also increased with increase in time. Longer reaction time permits the production of more and more free radicals and possible coupling reaction between monomer radical cations. The plots of Time Vs RI_[B/CH] (Figure 3c) and Time Vs RI_[Q/CH] (Figure 3d) were indicated by straight lines. These two plots confirmed that the RI of both benzenoid and quinonoid forms of PANI was increased while ANI was subjected to longer polymerization time. The longer reaction time permits ANI with different possible interactions leading to the formation of dimer, trimer and oligomer with different structures like pernigraniline, emeraldine etc. In comparison, the RI value of benzenoid form is greater than that of quinonoid form. This informed us that benzenoid form is dominant than the quinonoid form in PANI backbone. PANI/Sb₂O₃ nano composite was synthesized with the help of another one initiator namely, potassium dichromate (PDC) under the same experimental conditions as mentioned for PDS system. While increasing the reaction time, the RI of benzenoid form increased from 0.0818 to 0.1821. The RI of quinonoid form was also increased with the increase in reaction time. Figures 3e and f represented the plots of Time Vs RI_[B/CH] and Time Vs RI_[Q/CH] respectively. The increase in RI of PANI while increasing the reaction time indicated that during the polymerization process more and more monomer units were linked and hence length of PANI chain increased (i.e.) increase in molecular weight of PANI. The increase in RI is possible until the exhaustion of monomer units or initiator species. In the present system too, the RI value of benzenoid form is greater than that of quinonoid form. Even then PDC involved in the three electron transfer reaction it activated the formation of benzenoid form than the quinonoid form of PANI. In overall comparison the PDC system yielded higher values for both benzenoid and quinonoid forms than PDS system due to three electron transfer reaction²⁴.

Effect of [ANI] on R_p and RI of benzenoid and quinonoid forms of PANI

ANI was polymerized in the presence of nano material like Sb₂O₃ with PDS as an initiator. [ANI] was varied in the range of 0.15 to 0.35 M, while keeping the other experimental conditions as constant. If the [ANI] was increased, the R_p value also increased. This is due to the formation of more and more monomer radical cations. The polymer chain propagated through the formation of dimer, trimer, oligomer and polymer without any cross-linking. To determine the order of polymerization reaction, the log-log plot was made between log[ANI] and logR_p (Figure 4a) and the slope value was noted as 1.72 which indicated that 1.75 order of reaction with respect to [ANI], while using PDS as a chemical initiator. In a similar manner, PDC was used as an initiator and ANI was polymerized under the same experimental conditions. Here also, the log-log plot (Figure 4b) was made and the slope value was determined as 2.01. This confirmed the 2.0 order dependence with respect to [ANI] in the presence of PDC as a chemical initiator. The monomer variation optimized the 0.25 M as the suitable one for further polymerization process under different experimental conditions. This conclusion was made based on the % yield of polymer and electrical conductivity value of the same. In comparison, the PDC initiated system gave higher R_p values than the PDS system. Again this is due to the three electron transfer reaction of PDC²⁵.

Figure 4. Effect of [ANI] on (a,b)R_p, (c,e)RI_[B/CH] and (d,f)RI_[Q/CH] (a,c,d) PANI- PDS- HCl-Sb₂O₃, (b,e,f) PANI-PDC-HCl-Sb₂O₃ system [PDS] = 0.025 M, [PDC] = 0.025 M, Time = 2 h, Temperature = 45°C, % weight of Sb₂O₃ -3

The [ANI] played an important role in the preparation of polymer nano composites. The effect of various [ANI] on RI of [B/CH] and [Q/CH] were investigated. [ANI] was varied between 0.15 and 0.35 M, by keeping the other experimental conditions as constant. The RI of benzenoid form was increased from 0.0331 to 0.0612 while increasing the [ANI]. This is due to the following reasons. 1) While increasing the [ANI], the RI_[B/CH] increased up to [ANI]/[PDS]=1. Once all the free radicals were exhausted there were no more free radicals to initiate the polymerization reaction. 2) At higher concentration of monomer, the auto catalytic effect caused due to the surface effect of formed PANI led to the formation of benzenoid structure and the decrement of quinonoid structure³⁴. The log-log plot was made between [ANI] and RI_[B/CH] to determine the order of benzenoid structure formation (Figure 4c). The plot showed a straight line with the slope value of 0.964, which confirmed the 1st order reaction of benzenoid structure formation with respect to [ANI]. In such a way the effect of [ANI] on RI of quinonoid structure of PANI/Sb₂O₃ nano composite was determined. While increasing the [ANI], the RI_[B/CH] was increased from 0.3566 to 0.4452 and then it showed a decreasing trend. This can be explained as follows: 1) While increasing the [ANI], the RI_[B/CH] increased up to [ANI]/[PDS]=1. Once all the free radicals were exhausted there were no more free radicals available to initiate the polymerization reaction. Auto acceleration effect of formed polymer led to the further oxidation process. This leads to the further increase in benzenoid structure and decrease of quinonoid structure. 2) At higher concentration of monomer, the excess of ANI units interacted with PANI chains and resulted with primary oxidation (i.e.) formation of benzenoid structure. In order to find out the order of quinonoid structure formation, the log-log plot of [ANI] Vs RI_[Q/CH] (Figure 4d) was made and the slope value was determined as 0.21. This confirmed the 0.25 order of quinonoid structure formation of PANI with respect to [ANI]. In comparison the RI of benzenoid form is greater than that of quinonoid form. It means that during the [ANI] variation, the backbone of PANI is built by benzenoid form in a dominant manner. Using the PDC as another initiator, PANI/Sb₂O₃ nano composite was synthesized. The RI of the benzenoid structure was increased from 0.0915 to 0.15. In order to find the order of benzenoid structure formation, the plot of log[ANI] Vs logRI_[B/CH] (Figure 4e) was drawn. The plot showed a straight line with the slope value of 1.11. This confirmed the 1.0 order of benzenoid structure formation reaction with respect to [ANI] in the presence of PDC as a chemical initiator. Similarly, the effect of [ANI] on RI of quinonoid structure of PANI was determined. While increasing the [ANI], the RI_[Q/CH] was increased from 0.0206 to 0.026 and then decreased. The slope value was determined from the plot of log[ANI] Vs logRI_[Q/CH] as 0.45 (Figure 4f). This confirmed the 0.50 order of quinonoid structure formation reaction with respect to [ANI] for PDC system. The PDC system too exhibited that the RI of benzenoid form is greater than that of quinonoid form. In overall comparison, the RI values of benzenoid and quinonoid forms of PDC initiation system produced higher values than the PDS initiation system²⁴.

Effect of [PDS] or [PDC] on R_p and RI of benzenoid and quinonoid forms of PANI

The [PDS] was varied from 0.015 to 0.035 M by keeping the other experimental conditions as constant. It was noticed that the R_p increased with the increase in the concentration of initiator. This is due to the production of large amount of free radicals from the initiator species for the initiation of monomer³⁴. The potassium sulfate radical is the key species for the initiation of monomer. In order to find out the effect of [PDS] on R_p, the following plot was made for ANI-PDS-HCl system (i.e.) logR_p Vs log[PDS] (Figure 5a). The plot indicated a straight line with the slope value of 0.937 and which confirmed the 1st order of reaction with respect to [PDS]. It means one mole of PDS is required to initiate one mole of monomer. ANI was polymerized in the presence of PDC as a chemical initiator under identical experimental conditions. The [PDC] was varied from 0.015 to 0.035 M, keeping other experimental conditions as constant. It was observed that the R_p increased with the [PDC]. In order to find the order of reaction a plot of log[PDC] Vs logR_p (Figure 5b) was made. The slope value was determined as 1.13, which declared the 1.0 order dependence of R_p with respect to [PDC]. The increase in R_p is explained on the concept of various possible oxidation state of PDC and further propagation of aniline radical cations led to the formation of various forms and ended with PANI chain. In comparison the PDC system produced higher R_p values than the PDS system due to the various possible oxidation state of PDC.

Figure 5. Effect of $[I]$ on (a,b) R_p , (c,e) $RI_{[B/CH]}$ and (d,f) $RI_{[Q/CH]}$, (a,c,d) PANI-PDS-HCl-Sb₂O₃, (b,e,f) PANI-PDC-HCl-Sb₂O₃ system $[ANI] = 0.25$ M, Time = 2 h, Temperature = 45°C, % weight of Sb₂O₃-3

The PANI/Sb₂O₃ nano composite was synthesized by varying the $[PDS]$ between 0.015 and 0.035 M by keeping the other experimental conditions as constant. While increasing the $[PDS]$, the $RI_{[B/CH]}$ was increased. The RI values were increased up to 0.339 and then decreased, whereas the $RI_{[Q/CH]}$ values were increased linearly with $[PDS]$. This is due to the following reasons: 1) At higher $[PDS]$ all the monomer fractions were primarily oxidized and there was no more free monomer fraction to interact with free radicals. 2) Excess of free radicals led to secondary or over oxidation of ANI. 3) The excess of free radicals led to the formation of quinonoid structure³⁴. The order of reaction was determined by plotting $\log[PDS]$ Vs $\log RI_{[B/CH]}$ (Figure 5c) and $\log[PDS]$ Vs $\log RI_{[Q/CH]}$ (Figure 5d) and the slope values were determined as 1.16 and 1.18 respectively with respect to $[PDS]$. This confirmed the 1.0 order of reaction for both benzenoid and quinonoid structure formation with respect to $[PDS]$. In comparison, the RI values of quinonoid form are greater than that of benzenoid form due to the secondary or over oxidation reactions. Similarly, PANI/Sb₂O₃ nano composite was synthesized with PDC as another initiator and its concentration was varied between 0.015 and 0.035 M by keeping the other experimental conditions as constants. The $RI_{[B/CH]}$ values were increased up to 0.249 and then decreased, whereas the $RI_{[Q/CH]}$ was increased linearly with $[PDC]$. The order of reaction was determined from the universal log-log plot. The plots of $\log[PDC]$ Vs $\log RI_{[B/CH]}$ (Figure 5e) and $\log[PDC]$ Vs $\log RI_{[Q/CH]}$ (Figure 5f) were made, and the slope values were determined as 1.06 and 1.45 respectively with respect to $[PDC]$. These authenticated the 1.0 and 1.50 order of benzenoid and quinonoid structure formation reactions with respect to $[PDC]$. The increase in RI with respect to initiator concentration confirmed the lengthening of PANI chain. The general discussion in this case is at higher concentration of initiator (above $[M/I]=1$), that leads to further secondary oxidation of primarily oxidized anilinium radical cations. Because the RI values are primarily depending on the amount of each forms present in the polymer chain. This system produced higher RI values for quinonoid form than the benzenoid form. In overall comparison the PDC system yielded higher RI values for both benzenoid and quinonoid forms than the PDS system. Recently, Yelilarasi et al^{24,25} reported that the RI of PDC initiated ANI is greater than that of the RI of PDS initiated ANI.

Effect of Temperature on R_p and RI of benzenoid and quinonoid forms of PANI

The reaction temperature was varied between 10 and 70°C while keeping the other experimental conditions as constant. The R_p was found to be increased with the increase of reaction temperature. This is due to the activation of monomer radical cations from the growing polymer chains. Over oxidation or secondary oxidation led to the formation of more and more quinonoid structure. Figure 6a showed a plot of $1/T$ Vs $\log R_p$ for PDS initiator system and Figure 6b showed a plot of $1/T$ Vs $\log R_p$ for PDC initiator systems. The energy of activation (E_a) for the formation of PANI structure can be determined by the famous Arrhenius equation. The E_a was estimated from the slope of the above plots as 126.8 kJ/mol and 138.5 kJ/mol, when PDS and PDC acted as initiators respectively. Hereafter the polymerization will be carried out at 45°C under different experimental conditions. In comparison, the PDC system consumed more amount of thermal energy than the PDS system. Indeed, due to the multiple oxidation state of PDC, it produced higher % yield of PANI. This is in accordance with Yelilarasi and co-workers report²⁵.

Figure 6. Effect of Temperature on (a,b) R_p , (c,e) $RI_{[B/CH]}$ and (d,f) $RI_{[Q/CH]}$, (a,c,d) PANI-PDS-HCl-Sb₂O₃, (b,e,f) PANI-PDC-HCl-Sb₂O₃ system $[ANI]=0.25$ M, $[PDS] = 0.025$ M, $[PDC] = 0.025$ M, Time = 2 h, % weight of Sb₂O₃-3

The reaction was done in different heat atmosphere to determine the E_a and the effect of temperature was studied on the RI of PANI. While increasing the temperature from 10 to 70°C, the RI of $[B/CH]$ was increased initially and then showed a decreasing trend but $[Q/CH]$ values were increased in a linear manner. This can be ascribed to the thermal oxidation of monomer at higher temperature that led to the secondary oxidation of monomer. Hence, at higher temperatures the $RI_{[Q/CH]}$ was drastically increased. From the Arrhenius plot, the E_a was determined for both benzenoid and quinonoid structure formations. Figure 6c showed a plot of $1/T$ Vs $\log RI_{[B/CH]}$ and Figure 6d represented a plot of $1/T$ Vs $\log RI_{[Q/CH]}$ for PANI-PDS system. The slope values were determined and the E_a values were calculated as 128.4 kJ/mol and 135.9 kJ/mol for benzenoid and quinonoid structure formations respectively. This indicated that the quinonoid structure formation consumed more thermal energy than the benzenoid structure formation. Similarly, the effect of temperature was studied on the RI of PANI using PDC as an initiator. Figure 6e showed a plot of $1/T$ Vs $\log RI_{[B/CH]}$ and Figure 6f represented a plot of $1/T$ Vs $\log RI_{[Q/CH]}$. The E_a values were determined for both benzenoid and quinonoid structures. The E_a values were calculated as 142.6 kJ/mol and 148.4 kJ/mol for benzenoid and quinonoid structure formations respectively. On comparison, the PDC system consumed more amount of heat energy for the PANI formation than the PDS initiator. This is due to the various possible oxidation states of PDC. Moreover, at higher temperature the monomeric units were diffused from the polymer chain and resulted with decrease in the RI value of benzenoid form. In overall comparison even though the PDC system consumed more amount of thermal energy, due to its multiple oxidation state it produced more amount of both benzenoid and quinonoid forms, particularly quinonoid forms when compared with PDS initiator^{24,25}.

Effect of (% weight of Sb₂O₃) on R_p and RI of benzenoid and quinonoid forms of PANI

The (% weight of Sb₂O₃) was varied between 1 and 5% while keeping the other experimental conditions as constant. The R_p was estimated for different (% weight of Sb₂O₃) during the polymerization of ANI in the presence of PDS as a chemical initiator. The R_p was increased from 4.623×10^{-6} to 13.288×10^{-6} mol/lit/sec as we had increased the (% weight of Sb₂O₃). In order to find the order of polymerization reaction, plot of $\log(\% \text{ weight of Sb}_2\text{O}_3)$ Vs $\log R_p$ (Figure 7a) was drawn. The slope value of the plot was determined as 0.968 and this confirmed the first order dependence of R_p with respect to (% weight of Sb₂O₃) when PDS was used as an initiator and the slope value was 1.56 when PDC $\{\log(\% \text{ weight of Sb}_2\text{O}_3) \text{ Vs } \log R_p \text{ (Figure 7b)}\}$ acted as an initiator. The added nano sized Sb₂O₃ simply acted as a catalyst³⁴. The increase in R_p confirmed the role of nano material as a catalyst through its surface catalytic effect³⁴. In comparison, the PDC system produced higher R_p values than the PDS system. During the in-situ polymerization, exfoliation, de-lamination and intercalation reactions are possible. However, sometimes due to heavy loading of nano material, agglomeration process is a promising one. Formation of exfoliation or de-lamination or intercalation structure of Sb₂O₃ can be further confirmed by HRTEM measurements in the forth-coming sessions. Anbarasan et al³³ reported about the Clay catalyzed synthesis of Poly(α -naphthylamine), structurally similar to PANI, in which the R_p showed the first order reaction

with respect to (% weight of Clay). In the present investigation, under the identical experimental conditions, Sb_2O_3 also followed the first order reaction with respect to (% weight of Sb_2O_3). This proved the efficiency of Sb_2O_3 towards the nano composite formation through its catalytic surface effect.

Figure 7. Effect of (% weight of Sb_2O_3) on (a,b) R_p , (c,e) $RI_{[B/CH]}$ and (d,f) $RI_{[Q/CH]}$ (a,c,d) PANI- PDS- HCl- Sb_2O_3 , (b,e,f) PANI-PDC-HCl- Sb_2O_3 system [ANI]=0.25 M, [PDS] = 0.025 M, [PDC] = 0.025 M, Time = 2 h, Temperature = 45° C

The effect of various (% weight of Sb_2O_3) on the RI of [B/CH] and [Q/CH] was investigated. The (% weight of Sb_2O_3) was varied between 1 and 5%, whereas other experimental conditions were kept constant. The RI of benzenoid structure increased from 0.0613 to 0.2089 while increasing the (% weight of Sb_2O_3). In order to find out the order of benzenoid structure formation, a plot was made between $\log[\text{ANI}]$ and $\log RI_{[B/CH]}$ (Figure 7c). The plot showed a straight line with the slope value of 0.909, which confirmed the first order benzenoid structure formation reaction with respect to (% weight of Sb_2O_3). Similarly, the effect of Sb_2O_3 on the RI of quinonoid structure of PANI was determined. While increasing the (% weight of Sb_2O_3) the $RI_{[Q/CH]}$ was increased from 0.0145 to 0.0229 and the slope value was determined as 1.125 (Figure 7d). This explained the first order reaction of quinonoid structure formation with respect to (% weight of Sb_2O_3). In comparison, the RI values of quinonoid forms are greater than that of benzenoid form. This is due to the surface catalytic effect of Sb_2O_3 . Similarly, PANI/ Sb_2O_3 nano composite was synthesized by using PDC as a lone initiator. The $RI_{[B/CH]}$ was varied linearly with the (% weight of Sb_2O_3) (Figure 7e) and $RI_{[Q/CH]}$ (Figure 7f) also increased linearly, whose slope values were 1.33 and 1.48 respectively. This confirmed the 1.25 order and 1.50 order of reaction for benzenoid and quinonoid structure respectively with respect to (% weight of Sb_2O_3). In conclusion, due to the auto acceleration effect caused by the formed polymer and the surface catalytic effect caused by the nano sized Sb_2O_3 , the intensity of both the benzenoid and quinonoid forms were increased continuously. These two effects were operated simultaneously and resulted with increasing trend in the RI of both the benzenoid and quinonoid forms of PANI. This is in accordance with our recent publication³⁴. In overall comparison the PDC system produced higher R_p and RI values than the PDS system due to the multiple oxidation state of PDC²⁴.

TGA profile

The thermal stability of PANI synthesized by PDC as chemical initiator was analyzed by TGA method. TGA of PANI loaded with different (% weight of Sb_2O_3) is shown in Figure 8. The thermogram showed a three-step degradation process. The first minor weight loss step was due to the removal of physisorbed water molecules and moisture. The second minor weight loss step was associated with the removal of dopant from PANI backbone and the slight degradation of benzenoid structure of PANI. The third weight loss step was ascribed to the degradation of quinonoid form of PANI. After the degradation above 750° C, the PANI with 5% weight Sb_2O_3 showed 45.2% weight remained. This confirmed the thermal stability of PANI/ Sb_2O_3 nano composite system. The increase in thermal stability is due to the intercalation of PANI chains into the basal spacing of Sb_2O_3 and which can be further supported by HRTEM and

XRD reports in the forth coming sessions. One interesting point noted here is while increasing the (% weight of Sb_2O_3), the % weight residue remained above 750° C is also increased. The added Sb_2O_3 improved the char forming nature (flame retardant nature) of PANI. Sung et al³⁵ reported that Poly(o-ethoxy aniline)/Clay nano composite showed higher thermal stability than the pristine poly(o-ethoxy aniline). Our results are in accordance with them. Table-1 showed the TGA data of PANI-PDC- Sb_2O_3 nano composite systems.

Figure 8. TGA of PANI loaded with Sb_2O_3 at a) 1% weight, b) 2% weight, c) 3% weight, d) 4% weight, e) 5% weight

Table 1 TGA data of PANI - Sb_2O_3 nano composites.

System	% weight at				
	200° C	400° C	500° C	600° C	750° C
PANI-1% wt. Sb_2O_3	38.78	27.25	17.01	10.92	06.37
PANI-2% wt. Sb_2O_3	59.70	47.20	37.95	35.18	30.24
PANI-3% wt. Sb_2O_3	59.70	49.52	44.26	41.14	36.57
PANI-4% wt. Sb_2O_3	70.02	63.15	55.23	50.16	43.54
PANI-5% wt. Sb_2O_3	72.79	65.12	58.12	52.46	45.27

HRTEM report

Figure 9 indicated the HRTEM photograph of PANI loaded with 5% weight of Sb_2O_3 . The photograph indicated that Sb_2O_3 has layered structure with the length of 5-10 nm and part of them was exfoliated by PANI backbone (Figure 9a). The dark portion indicated that the nano sized Sb_2O_3 was coated with PANI chain. The exfoliation of nano sized Sb_2O_3 is promised one if the driving forces are sufficiently enough for the insertion of PANI chains into the interlayer space of Sb_2O_3 . The polymerization reaction was carried out at 45° C under vigorous stirring condition for 2 h in an aqueous acidic medium by an in-situ method. These forces were sufficiently enough to insert the PANI chains in the basal spacing of Sb_2O_3 and resulted with intercalation and exfoliation structure of Sb_2O_3 . Under the given experimental conditions used for the synthesis of PANI- Sb_2O_3 nano composite, the HRTEM confirmed that part of the layered structure of Sb_2O_3 was exfoliated. Figure 9b indicated the uniform distribution of nano sized Sb_2O_3 on PANI backbone. Figure 9c showed the topography of agglomerated coconut fiber like morphology of Sb_2O_3 due to heavy loading. The agglomerated nano particles exhibited the size of <100 nm (Figure 9d). The agglomeration of Sb_2O_3 occurred in two different ways in the present investigation. As mentioned earlier, coconut fiber like agglomeration was noticed for Sb_2O_3 and the second one is the bundle like agglomeration (Figure 9e). This is also due to the heavy loading of

Sb₂O₃ on the PANI backbone. Figure 9f revealed the SAED pattern of Sb₂O₃ and indicated that the polymer nano composite exhibited a semi-crystalline structure. This can be further supported with XRD results in the forth coming session. The agglomerated form of nano sized Sb₂O₃ is presented in Figure 9e. In the present investigation, we would like to insist that the nano sized Sb₂O₃ could catalyze the chemical polymerization of ANI in the presence of PDS, a chemical initiator, and boosted the physical and chemical properties of the resultant PANI-Sb₂O₃ nano composite system. The catalytic activity of Sb₂O₃ was confirmed through measuring the R_p . This is due to availability of more surface area on Sb₂O₃ structure. Further, the added nano sized Sb₂O₃ altered the structure of PANI which can be confirmed through the FTIR-RI kinetics. Moreover, the thermal stability and electrical conductivity values were accelerated by the addition of nano sized Sb₂O₃. Hence, the further structural investigation of Sb₂O₃ is not required for the present investigation. The primary aim of the present investigation is to study the effect of nano sized Sb₂O₃ on the structure - property relationship of PANI.

Figure 9. HRTEM of PANI loaded with 5% weight of Sb₂O₃

Conductivity

The d.c. conductivity of PANI synthesized with two different initiators was mentioned here. When PDS concentration was 0.025 M, the conductivity value of PANI was 3.0×10^{-3} S/cm whereas at the same concentration of PDC, the electrical conductivity value was 3.4×10^{-3} S/cm. A slight increase in electrical conductivity of PANI – PDS - Sb₂O₃ system proved that Sb₂O₃ was not only acted as a nano initiator but also acted as a dopant during the chemical polymerization of ANI. The electrical conductivity value was slightly increased while using 5% weight of Sb₂O₃ (5.481×10^{-2} S/cm) as a nano initiator (i.e.) one order of magnitude conductivity was increased. This proved that the added nano material not only increased the thermal stability and R_p but also increased the conductivity, by acting as a host. This is in accordance with our earlier publication³⁶.

XRD report

Figure 10a indicates the XRD of pristine Sb₂O₃. The pattern showed six crystalline peaks. A sharp crystalline peak at the 2 theta value of 27.2° is corresponding to the inter layer space of Sb₂O₃. Tigau et al³⁷ reported that the crystalline peaks at 27.71° and 46.26° are responsible for the poly crystalline cubic structure of Sb₂O₃. Figure 10b represents the XRD of PANI-Sb₂O₃ nano composite system. The spectrum showed one broad peak around 22° , which confirmed the semi-crystalline nature of the PANI-Sb₂O₃ nano composite system. A small hump at 23.3° is due to the 222 crystalline peak of Sb₂O₃. Appearance of this peak with slight shifting towards lower 2 theta confirmed the intercalation of PANI chains into the basal spacing of Sb₂O₃. Thus the XRD results supported the TGA and HRTEM reports.

Figure 10. XRD of a)Pristine Sb₂O₃, b)PANI loaded with 5% weight of Sb₂O₃

CONCLUSIONS

From the above kinetic study the following important points are summarized here as conclusions. 1)PANI/Sb₂O₃ nano composite was synthesized successfully by an in-situ polymerization method. 2)While increasing the (% weight of Sb₂O₃), the RI values of both benzenoid and quinonoid structures were increased linearly. 3)Quinonoid structure formation consumed more amount of heat energy than the benzenoid structure formation. 4)The initial degradation as well as the PANI backbone degradation temperatures was increased for the PANI/Sb₂O₃ nano composite systems. 5)HRTEM confirmed the dispersion of Sb₂O₃ platelets of 5-10 nm on the PANI matrix. 6)The d.c. conductivity value of PANI/Sb₂O₃ nano composite was increased with the increase of (% weight of Sb₂O₃) which confirmed the catalytic effect as well as host nature of Sb₂O₃ for PANI chains. The added nano sized Sb₂O₃ not only acted as a host, dopant but also acted as a nano catalyst/initiator. XRD results confirmed the intercalation of PANI chains into the basal spacing of Sb₂O₃.

REFERENCES

- 1.- R.C. Barthus, L.M. Lira and S.I.C. de Torresi, *J. Braz. Chem. Soc.* **19** 630 (2008).
- 2.- M. Qu, G. Zhao, X. Cao and J. Zhang, *Langmuir* **24** 4185 (2008).
- 3.- S.S. Joshi, T.P. Gujar and C.D. Lokhande, *Sensors Actuators B* **132** 349 (2008).
- 4.- P.R. Likhari, M. Roy, S. Roy, and B. Sreedhar, *Adv. Synth. Catal.* **350** 1968 (2008).
- 5.- S. Xiong, Q. Wang and Y. Chen, *J. Appl. Polym. Sci.* **111** 963 (2009).
- 6.- T. Itoh, I. Matsubara, W. Shin, and M. Nishibori, *Mater. Chem. Phys.* **110** 115 (2008).
- 7.- J. Ma, X. Zhang, C. Yan and H. Inoue, *J. Mater. Sci.* **43** 5534 (2008).
- 8.- C. Basavaraja, T.K. Vishnuvardhan and D.S. Huh, *Eur. Polym. J.* **44** 1556 (2008).
- 9.- L. Zhang and P. Liu, *Nanoscale Res. Lett.* **3** 299 (2008).
- 10.- X. Zhang, G. Yan, H. Ding and Y. Shan, *Mater. Chem. Phys.* **102** 249 (2007).
- 11.- Y. Li, H. Zhang, Y. Liu, Q. Wen and J. Li, *Nanotechnology*. **19** 105605 (2008).
- 12.- A.Z. Sadek, W. Wlodarski, K. Shin and K.K. Zadek, *Synth. Met.* **158** 29 (2008).
- 13.- C.R.K. Rao and M. Vijayan, *Synth. Met.* **158** 516 (2008).
- 14.- J. Jiang, *J. Macromol. Sci. Part B: Phys.* **47** 242 (2008).
- 15.- J. Dexmer, C.M. Leroy and R. Bockov, *Chem. Mater.* **20** 5541 (2008).
- 16.- Z. Mo, P. Zhang and H. Chen, *Mat. Res. Bull.* **43** 1664 (2008).
- 17.- S. Chakraborty, S. Bandyopadhyay and A.S. Dueri, *Polym. Test.* **26** 38 (2007).
- 18.- F. Svegl and B. Orel, *Mat. Tech.* **37** 29 (2003).
- 19.- J. Copikova, A. Synytsya and M. Novethna, *Czech J. Food Sci.* **19** 51 (2001).

- 20.- J.S. Wang, J.S. Shi and J.G. Wu, J.G.; *World J. Gastro.* **9** 1897 (2003).
- 21.- I. Xueref and F. Domine *Atmos. Chem. Phys.* **3** 1779 (2003).
- 22.- S.M. Matkovic, G.M. Valle and L.E. Briand, *Latin Am. Appl. Res.* **35** 189 (2005).
- 23.- R. Anbarasan, S. Kanchana and V. Dhanalakshmi, *J. Appl. Polym. Sci.* **115** 315 (2010).
- 24.- A. Yelilarasi, J. Juliat Latha Jeyakumari, B. Sundaresan, V. Dhanalakshmi, R. Anbarasan, *Spectrochim. Acta Part A.* **74** 1229 (2009).
- 25.- A. Yelilarasi, J. Juliat Latha Jeyakumari, B. Sundaresan, V. Dhanalakshmi, R. Anbarasan, *Polym. Polym. Compos.* **17** 397 (2009).
- 26.- A. Omrani, L.C. Simon and Ghaemy, *Int. J. Chem. Kinet.* **40** 663 (2008).
- 27.- M. Saule, S. Navarre, O. Babot and B. Maillard, *Macromolecules* **36** 7469 (2003).
- 28.- M. Saule, S. Navarre, O. Babot and B. Maillard, *Macromolecules* **38** 77 (2005).
- 29.- S. Navarre and B. Maillard, *J. Polym. Sci. Part A Polym. Chem.* **38** 2957 (2000).
- 30.- R. Anbarasan, O. Babot, M. Dequiel and B. Maillard, *J. Appl. Polym. Sci.* **97** 761 (2005).
- 31.- R. Anbarasan, O. Babot, M. Dequiel and B. Maillard, *J. Appl. Polym. Sci.* **97** 766 (2005).
- 32.- K. Duraimurugan, S. Rathika and R. Anbarasan, *Chi. J. Polym. Sci.* **26** 393 (2008).
- 33.- R. Anbarasan, R. Anandhakrishnan and G. Vivek, *Polym. Compos.* **29** 949 (2008).
- 34.- S. Rathika, I. Baskaran and R. Anbarasan, *J. Mater. Sci.* **44** 3542 (2009).
- 35.- J. H. Sung and H.J. Choy, *Korea Aust. Rheol. J.* **16** 193 (2004).
- 36.- R. Anbarasan and S. Sivakumaravel, *Intern. J. Polymeric Mater.* **55** 803 (2006).
- 37.- N. Tagau, *Rom. J. Phys.* **51** 641 (2006).