Synthesis and Characterization of Polyaniline Films Using Fenton Reagent

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ABSTRACT: The chemical oxidation of aniline to form polyaniline (PANI) films and powder samples was made using Fenton reagent as an oxidizing agent in aqueous sulfuric acid medium. The PANI films were monitored by using the quartz crystal microbalance and the electronic absorption techniques. The optimum concentration was determined and the results were justified by measuring the UV–vis absorption spectra for the *in situ* PANI films. The conductivity for the PANI films and powder samples, prepared in different conditions, was measured. Also, the IR spectra, X-ray and the thermogravimetric analysis for the PANI powder formed in the bulk were measured and compared with the polymer prepared using ammonium peroxydisulfate. A preliminary investigation to the dielectric properties of the polymer powder was measured and discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3410–3419, 2008

Key words: Fenton reagent H_2O_2–Fe^{2+} system; polyaniline; film; conductivity

INTRODUCTION

Polyaniline (PANI) is prepared by the chemical oxidation of aniline using different oxidizing agents such as ammonium peroxydisulfate (APS), $K_2Cr_2O_7$, KIO_3, and H_2O_2. It has been concluded that the redox potential of the oxidants was not a determining factor in the chemical polymerization of aniline.[1] However, it is generally prepared by the oxidative polymerization of aniline by APS in $1M$ HCl. The obtained PANI is often neither soluble nor fusible, and, thus, its applications are limited. APS is a strong oxidant, and the polymerization of aniline is an exothermal reaction, so the reaction heat is difficult to control, leading to a wide molecular weight distribution. Post-treatments become complicated because the inorganic by-product (ammonium sulfate) exists in the product.[2]

H_2O_2 is an important oxidant, which is used widely in industry. Its reduction product is only H_2O, thus greatly simplifying the post-treatment. Another advantage is the possibility of recycling the reaction medium, because it does not contain any harmful components to aniline polymerization. Therefore, the H_2O_2 approach is easy to industrialize. But when H_2O_2 was used alone as an oxidant, the reaction rate was found to be extremely low. To increase the PANI yield, the reaction activity of H_2O_2 must be improved.[2] Samuelson and coworkers[3] reported the enzyme-catalyzed polymerization of aniline in the presence of H_2O_2. Also, Moon et al.[4] have used H_2O_2 in combination with Fe^{2+} to afford PANI powder in high yields. The polymer obtained has a high solubility in organic solvents. On the other hand it shows similar chemical, physical, and spectral properties as previously prepared PANI using APS.[4] Similarly, Sun et al.[2,5] have studied the aniline polymerization in the bulk using H_2O_2 as an oxidizing agent and $FeCl_2$ as catalyst. They have mentioned that if the polymerization of aniline is carried out by using only H_2O_2 as an oxidant, little PANI is obtained, even after 24 h and hence they have added the catalyst. The polymerization conditions were achieved to give polymerization powder yield of 60%. The polymer formed shows a conductivity of 10 S/cm and a solubility of 50% in THF, 95% in DMF and DMSO, and 100% in NMP. The reaction medium may be reused for further polymerization without special treatment. Therefore, this approach may lower the cost of PANI and makes it suitable for industrialization.[2] Inoue et al. reported the oxidation of aniline using H_2O_2 in the presence of Fe^{2+} to prepare PANI powder; its conductivity was 10^{-6}–10^{-9} S/cm.[6] Such low conductivity was attributed to the deprotonation of PANI, because PANI was treated using a boiling aqueous solution of ammonium hydroxide before measurement of conductivity.

The above reports imply that the addition of Fe^{2+} into the system speeds up the decomposition of H_2O_2 and formation of the radical ions which

accelerate the polymerization rate of aniline[7] according to the following equation:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH^\bullet$$

It has been mentioned[2,5] that the polymerization of aniline in the H_2O_2–Fe^{2+} system may follow a different mechanism from that of APS system.

Based on the above literatures, no work was done to study the formation of thin PANI films using H_2O_2 which has an importance in the technological applications. Therefore, the present work was devoted to study the chemical oxidation of aniline to form PANI films using Fenton reagent as an oxidizing agent in aqueous sulfuric acid medium. The PANI films were monitored by using the quartz crystal microbalance (QCM) technique. A wide variety of synthesis parameters were studied such as the concentrations of aniline, H_2O_2 and sulfuric on the film formation and its conductivity. In addition, these parameters were studied on the PANI powder formation in the bulk solution. The deposited *in situ* PANI films onto glass supports during polymerization were also studied and investigated using electronic absorption spectroscopy. Finally, the IR spectra, the X-ray diffraction and the thermogravimetric analysis were measured for the polymer powder and compared with the powder obtained using APS as oxidant. A preliminary measurement of the dielectric properties of the polymer powder was made and discussed.

EXPERIMENTAL

Chemicals

Aniline (ADWIC, Egypt) was distilled twice under atmospheric pressure. H_2O_2 (ADWIC, Egypt), ferrous sulfate ($FeSO_4.7H_2O$) (Qualikems, India) and sulfuric acid were used without further purification. Freshly distilled water was used to prepare all aqueous solutions.

Solution preparations

A series of solutions were made in which the molar ratio (*r*) of H_2O_2/aniline was kept constant at 1 whereas the concentration of aniline and H_2O_2 was changed from 0.05*M* up to 0.5*M* in 0.3*M* sulfuric acid solution.

The second series of solutions were made in which the concentration of H_2O_2 was varied from 0.025*M* up to 0.5*M* whereas the aniline concentration was kept constant at 0.1*M*, and hence *r* of H_2O_2/aniline was varied from 0.25 up to 5. Both the aniline and H_2O_2 solutions were prepared in 0.3*M* sulfuric acid solution.

The third series of solutions were made where the concentration of aniline was varied from 0.025*M* up to 0.5*M* and the H_2O_2 concentration was kept constant at 0.1*M* and hence *r* of H_2O_2/aniline was varied from 4 up to 0.2. Both the aniline and H_2O_2 solutions were prepared in 0.3*M* sulfuric acid solution.

The fourth series of solutions were made in which the concentration of sulfuric acid was changed from 0.15*M* up to 0.5*M* whereas the concentration of H_2O_2 and aniline were kept constant at 0.1 and 0.2*M*, respectively. In all series, the ferrous sulfate concentration was kept constant at 0.001*M*.

QCM measurements

A 5 MHz-cut quartz crystal was used. The resonance frequency of the crystal was determined by using the crystal as the frequency determining element of an electronic oscillator, the measurements being taken using a GW frequency counter, Model GFC-8055G. Details of the apparatus design and the procedures were described in earlier studies.[8–10] The mass per unit area of PANI film, m' (g/cm^2), grown onto the gold electrode of QCM was determined from the change in its resonance frequency. The relation between the frequency change Δf (Hz) and m' is well-established from the work of Sauerbrey[11] and is given by

$$\Delta f = -(2f_o^2/\sqrt{\rho_Q\mu_Q})m' \tag{1}$$

where, f_o (Hz) is the natural frequency of the quartz crystal (unloaded resonator frequency), ρ_Q is the quartz density has the value (2.649 g/cm^3), and μ_Q is the shear modulus has the value (2.947 10^{10} dyn/cm^2).

The solutions of the reactants were added to the polypropylene bottle which serves as the reaction vessel. As the polymerization proceeds, the polymer is formed in the bulk as powder simultaneously with *in situ* film deposition onto the gold electrode of the QCM.

When QCM is used in an aqueous solution eq. (1) cannot be simply adopted due to the effects of interfacial liquid properties such as viscosity, density, and conductivity. It is however known that eq. (1) can be used for the solution system under specific conditions where the influence of the viscoelasticity of the polymer is negligible.[12] In our experiments, a linear relationship was observed between the change in mass and frequency shift of QCM both in air and in aqueous solution. Thus, the Sauerbrey equation can be applied to the aqueous solution system under study. Also we are dealing with dilute reactant solutions, the variation of viscosity and liquid density was assumed to be negligible during the experiment,

and hence the change in frequency due to this effect can be considered constant.[12]

In situ PANI films and powder preparation

In situ PANI films were deposited onto rectangular glass supports during the polymerization of aniline. These supports were stuck onto an adhesive tape and introduced into the reaction vessel before the polymerization starts. Once the reactants are introduced into the vessel, the film grows simultaneously onto the gold electrode of the QCM and the glass supports. After the polymerization process, the glass supports were removed from the reaction mixture and rinsed with $0.1M$ sulfuric and finally dried. These supports coated with PANI films were used to measure the UV–vis absorption spectra and the conductivity of the films.

The PANI powder precipitated in the bulk of the solution was collected from the reaction medium—after the polymerization process was terminated—by filtration then washing it with $0.1M$ sulfuric solution, and acetone.

UV–vis absorption spectra measurements

The UV–vis absorption spectra for the PANI films deposited onto glass supports were measured using Shimadzu UV-2101 DC Spectrophotometer. Uncoated glass supports were used as a reference.

Conductivity measurements for PANI powder and films

The conductivity of the PANI films was measured using the four-probe technique. A Simpson 260 VOM multimeter and a Keithley 617 Programmable Electrometer were used. The contacts in the sample holder were made of gold. The thickness of the films was estimated with four samples from the optical absorption,[13] whereas the conductivity of copolymer powders was measured in the form of compressed disk pellets of thickness 2–3 mm and surface area of $1.3 \ cm^2$ using two-point probe technique.

IR measurements

The IR spectra of the PANI powder were measured as KBr pellets using Perkin–Elmer 1430 Ratio Recording Infrared Spectrophotometer.

X-ray analysis

Wide-angle X-ray diffractograms of the PANI powder were recorded using PW 1729 X-ray generator, PW 1840 diffractometer, PW 1840 diffractometer control and PM 8203A one line recorder with mono-chromatized CuKα ($\lambda = 0.1541$ nm) radiation operated at 40 kV and 30 mA in a reflection mode.

Thermogravimetric analysis

The thermogravimetric analysis for the PANI powder were carried out using a Shimadzu TGA-50H thermogravimetric analyzer at a flow rate of 20 mL/min and a heating rate of $10°C$/min under nitrogen atmosphere.

Dielectric measurements

The dielectric properties of PANI powder were measured. PANI powder was placed in Teflon cell which evacuated to 10^{-2} torr to prevent humidity. Dielectric constant (ε'), loss (ε'') and modulus (M' and M'') were measured as a function of frequency at different temperatures using SR 510 Stanford look-in amplifier in two-probe circuit.

RESULTS AND DISCUSSION

Effect of the initial aniline and H_2O_2 concentrations

The change of m' of the film during the time course of polymerization for different solutions of molar ratio (r) of H_2O_2/aniline equals one at different concentrations of aniline and H_2O_2 in $0.3M$ sulfuric acid is shown in Figure 1(a). The concentrations of aniline and H_2O_2 were changed from $0.05M$ up to $0.5M$. *In situ* doping occurs due to the presence of sulfuric acid. The polymer films were also deposited onto glass supports that were immersed in the polymerization media. The UV–vis absorption spectra of the films were measured and shown in Figure 1(b). The PANI powders precipitated in the bulk solution were collected from the reaction media after 24 h.

The effect of H_2O_2 and aniline concentrations on m' of the PANI films after 100 min of polymerization and on the weight of the PANI powders formed in the bulk after 24 h are shown in Figure 1(c,d), respectively. It is clear that m' of the film and the weight of the powder increase as the concentrations of aniline and H_2O_2 increase up to $0.25M$ and then decrease at higher concentrations. It is worth noting that the PANI prepared at concentrations $>0.25M$, the films and powder have a greenish brown color, whereas at higher concentrations, the PANI changed completely to brown color. This is attributed to the formation of pernigraniline phase of PANI[13] as indicated from the spectra shown in Figure 1(b). The spectra show that at concentrations of aniline and $H_2O_2 \leq 0.2M$, the presence of a shoulder at 435 nm that can be assigned to the localized polarons characteristic of the protonated PANI, together with the
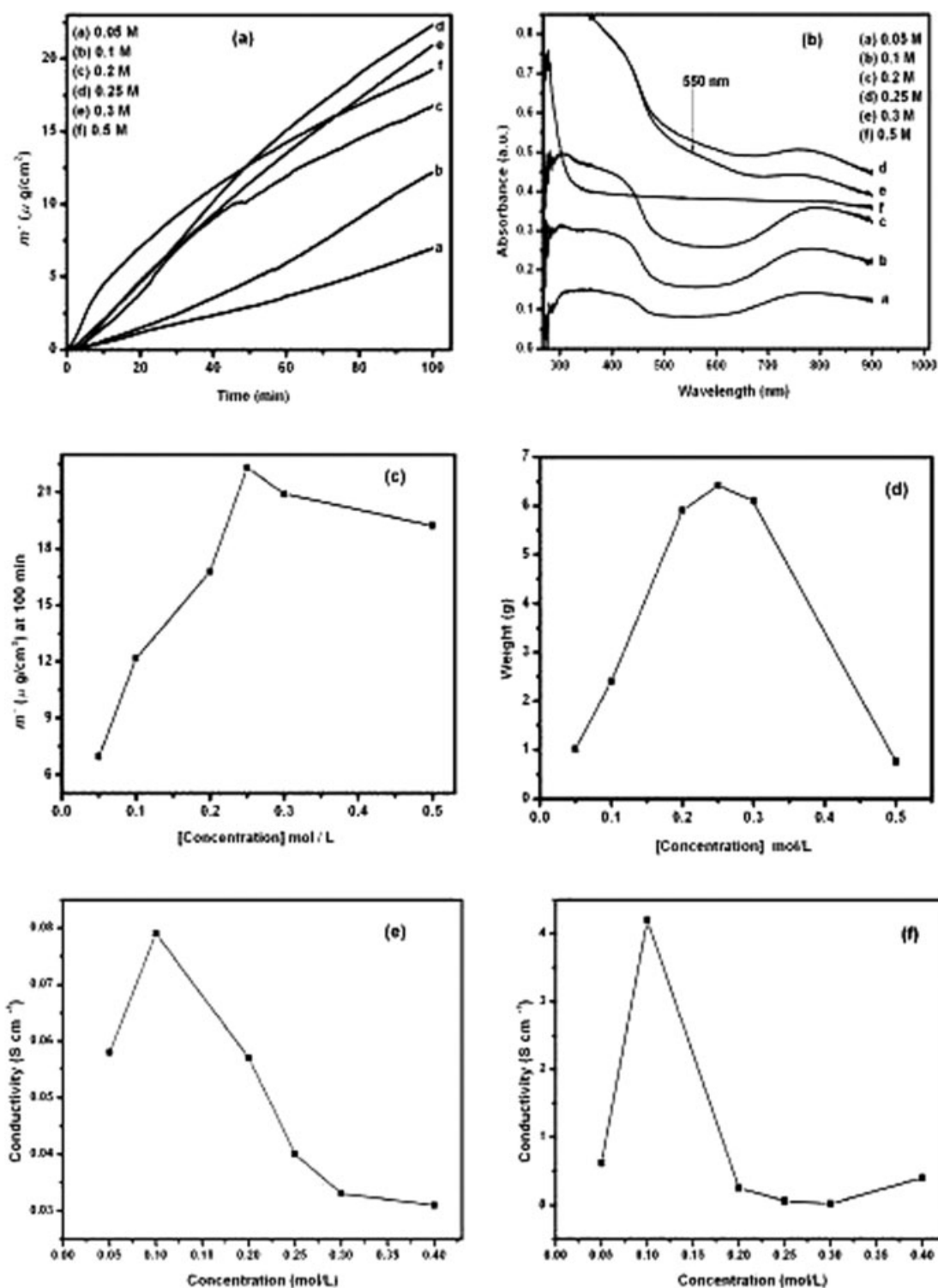
Figure 1 (a) m' during the time course of polymerization, (b) UV–vis absorption spectra of PANI films, (c) m' obtained at 100 min of polymerization, (d) the weight of polymer powder after 24 h, (e) the conductivity of the PANI films, and (f) the conductivity of powder. This is for different solutions of $r = 1$ at different concentrations of aniline and H_2O_2 in 0.3M sulfuric acid.

band at 786 nm representing the conducting emeraldine salt phase of PANI.[15–17] The absorption at 786 nm is blue shifted at higher concentrations of both aniline and H_2O_2. This blue shift is a symbol of decreasing the emeralidine salt and the formation of

pernigraniline phase. The formation of the latter form is assigned by the absorption at ~ 550 nm.[14]

The conductivity of PANI depends on various factors like: (i) oxidizing agents, (ii) oxidant/aniline molar ratio, (iii) concentration of protonic acid, (iv)
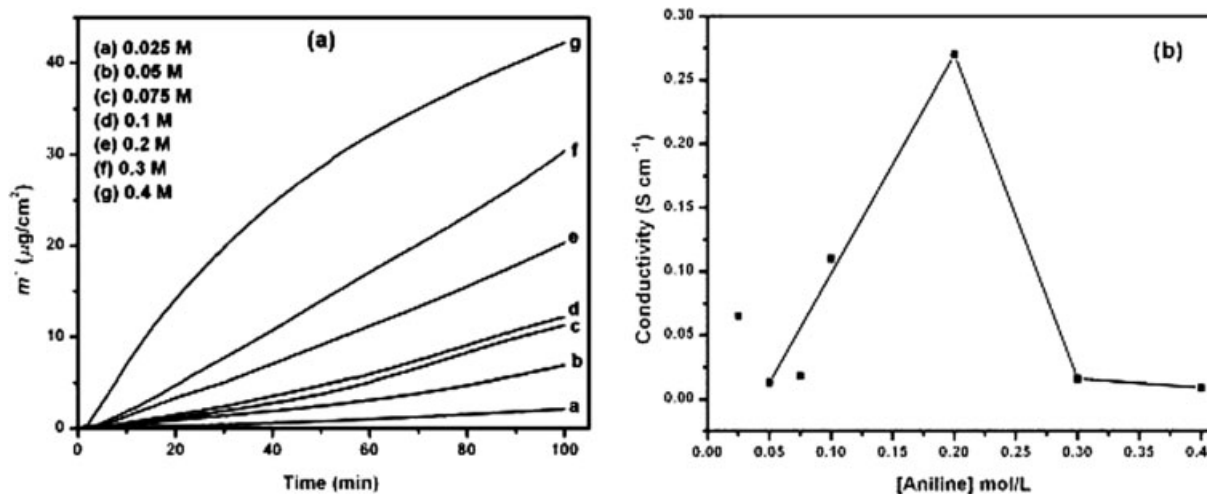
Figure 2   (a) m' against the polymerization time and (b) the conductivity of the films against aniline concentrations.

protonic acid, (v) reaction temperature, and (vi) the time of the polymerization.[18] To explore the effect of the initial molar concentration of aniline and H_2O_2, the conductivity was measured for the PANI films and powders. The variation of the film conductivity is too small and therefore five to eight samples at each concentration were measured and the average value was calculated. However, the variation in the powder samples is more significant and the measurements were carried only for one polymer disk at each concentration. Figure 1(e,f) shows the relation between the conductivity and concentration. The film conductivity increases from 0.058 ± 0.02 to 0.079 ± 0.03 S/cm on increasing the concentration from 0.05 to $0.1M$ then decreases at higher concentrations. The same behavior was observed in the conductivity of the polymer powders which increases from 0.62×10^{-5} to 4.2×10^{-5} S/cm. It is observed also that the film conductivity values are higher than that of the bulk. This can be attributed to the difference in the polymerization time. The films were removed from the polymerization medium after 100 min; whereas the powder samples were filtered after 24 h which may contain products arose from the over oxidation process that occur at high polymerization time.[7]

Effect of aniline concentration

A series of experiments were carried out in which the concentration of H_2O_2 and ferrous sulfate were kept constant at $0.1M$ and $0.001M$, respectively, and the concentration of aniline was varied from 0.025 up to $0.5M$. The concentration of sulfuric acid medium was $0.3M$. Figure 2(a) shows the relationship between m' of the PANI films obtained at different concentrations of aniline against the polymerization

time. It is clear that as the concentration of aniline increases, m' increases. However, the relation between the weights of PANI powder with aniline concentrations shows an optimum condition at $\sim 0.3M$ of aniline and then slightly decreases (the figure not shown). This behavior was interpreted by the formation of PANI oligomers and pernigraniline form of brown color on using concentrations higher than $0.3M$ as observed during the washing processes. These species escape during filtration.

The conductivity was measured for the polymer films prepared using different concentrations of aniline. Figure 2(b) shows that the film conductivity increases on increasing the aniline concentration up to $0.2M$ then decreases at higher concentrations. This is consistent with Sari et al.'s[19] results. They have mentioned that when sulfuric concentration was kept constant, the conductivity of PANI powder decreases with increasing aniline concentration. If aniline concentration is higher than that of sulfuric, there are not enough dopant anions in the medium to provide electroneutrality with radical cations and the number of dopant polymer segments decreases, and consequently the conductivity decreases. This conclusion was justified by Sun et al.[2] who have reported that higher aniline concentration is not suitable, as it leads to more side reactions and thus to more irregularity in PANI molecular chains.

The effect of H_2O_2 concentration

The effect of H_2O_2 on m' was studied using solutions in which the concentrations of aniline was kept constant at $0.1M$. The concentrations of H_2O_2 were varied from 0.025 up to $0.25M$. The aqueous $0.3M$ sulfuric media were used in all solutions. Figure 3(a) shows the relationship between m' after 100 min of
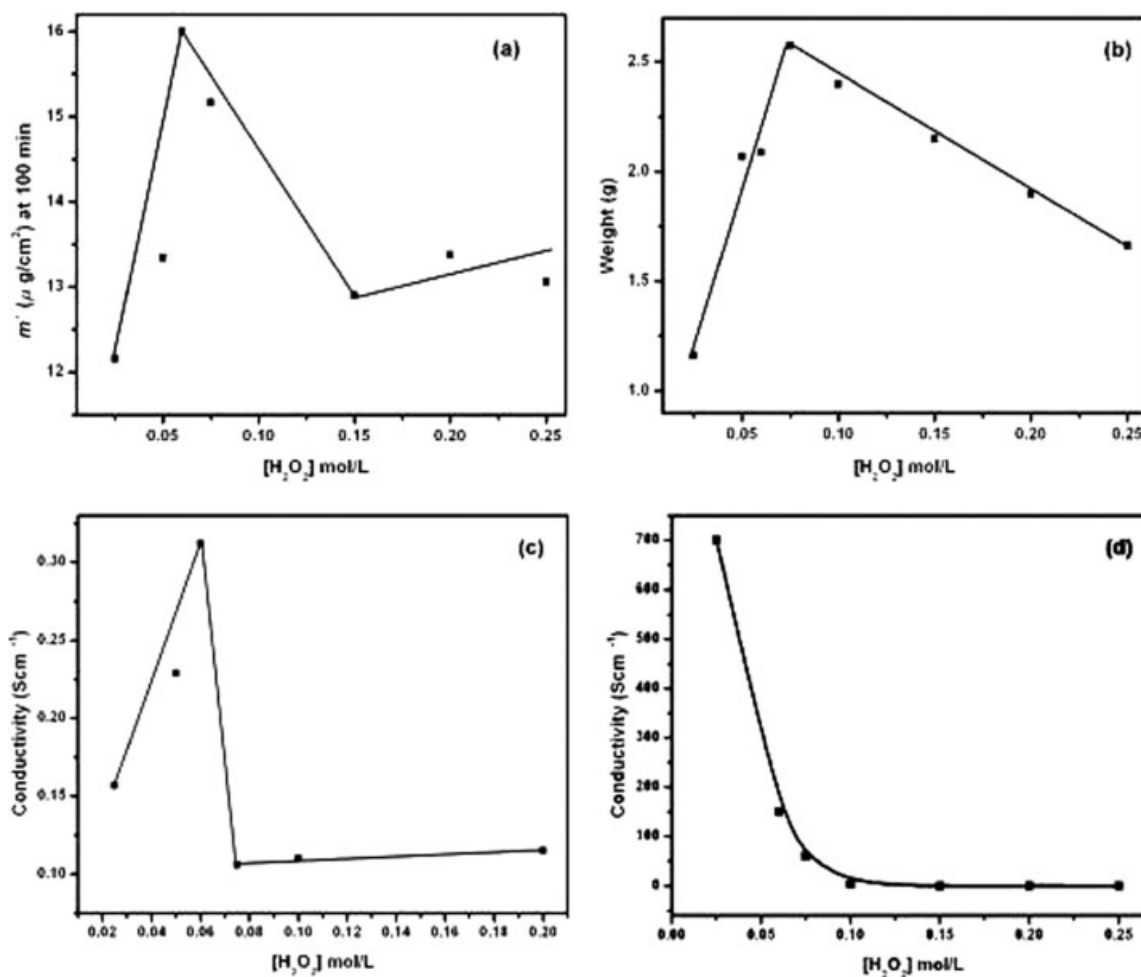
Figure 3 (a) m' obtained at 100 min of polymerization, (b) the weight of polymer powder after 24 h, (c) the conductivity of the PANI films, and (d) the conductivity of the powder at different H_2O_2 concentrations.

polymerization time and H_2O_2 concentrations. It can be shown that m' increases with increasing the concentration of H_2O_2 up to $0.06M$ then decreases at higher concentrations. A similar trend was obtained when the weight of the PANI powders relation with the concentration of H_2O_2 was considered. An optimum yield was obtained at the concentration of H_2O_2 equals $0.075M$ as shown in Figure 3(b). These conclusions are justified by measuring the UV–vis spectra of PANI films at different H_2O_2 concentrations (the figure not shown). The spectra show the presence of two absorptions at 420 and 770 nm, which are characteristic of the protonated PANI.[20] There is an optimum condition at $0.075M$ when the maxima absorptions at 770 nm were plotted against the concentration of H_2O_2. This is consistent with data obtained previously from the relation between m' of the film and the weight of the powder and the concentration of H_2O_2.

The effect of H_2O_2 concentration on the conductivity of the PANI films and powder are shown in Figure

3(c,d), respectively. The film conductivity increases as the concentration of H_2O_2 increases till $0.06M$ then decreases at higher concentrations, while the powder conductivity decreases as the concentration of H_2O_2 increases. The high concentrations of H_2O_2 bring about high concentration of free radicals and thus degradation to the polymer chains and hence the conductivity decreases. Also, when high concentrations of H_2O_2 are used, the possibility of hydrolysis and crosslinking of PANI molecular chains would be formed, leading to less conductivity. Similar behavior was observed by Sun et al.[2] during the synthesis of PANI powder using H_2O_2–$FeCl_2$.

The effect of sulfuric concentration

The effect of sulfuric acid on m' and the conductivity of the films was studied. A series of experiments were carried out in which r of H_2O_2/aniline was kept constant at $0.5M$ and the concentration of aniline at $0.2M$. The concentration of sulfuric was var-
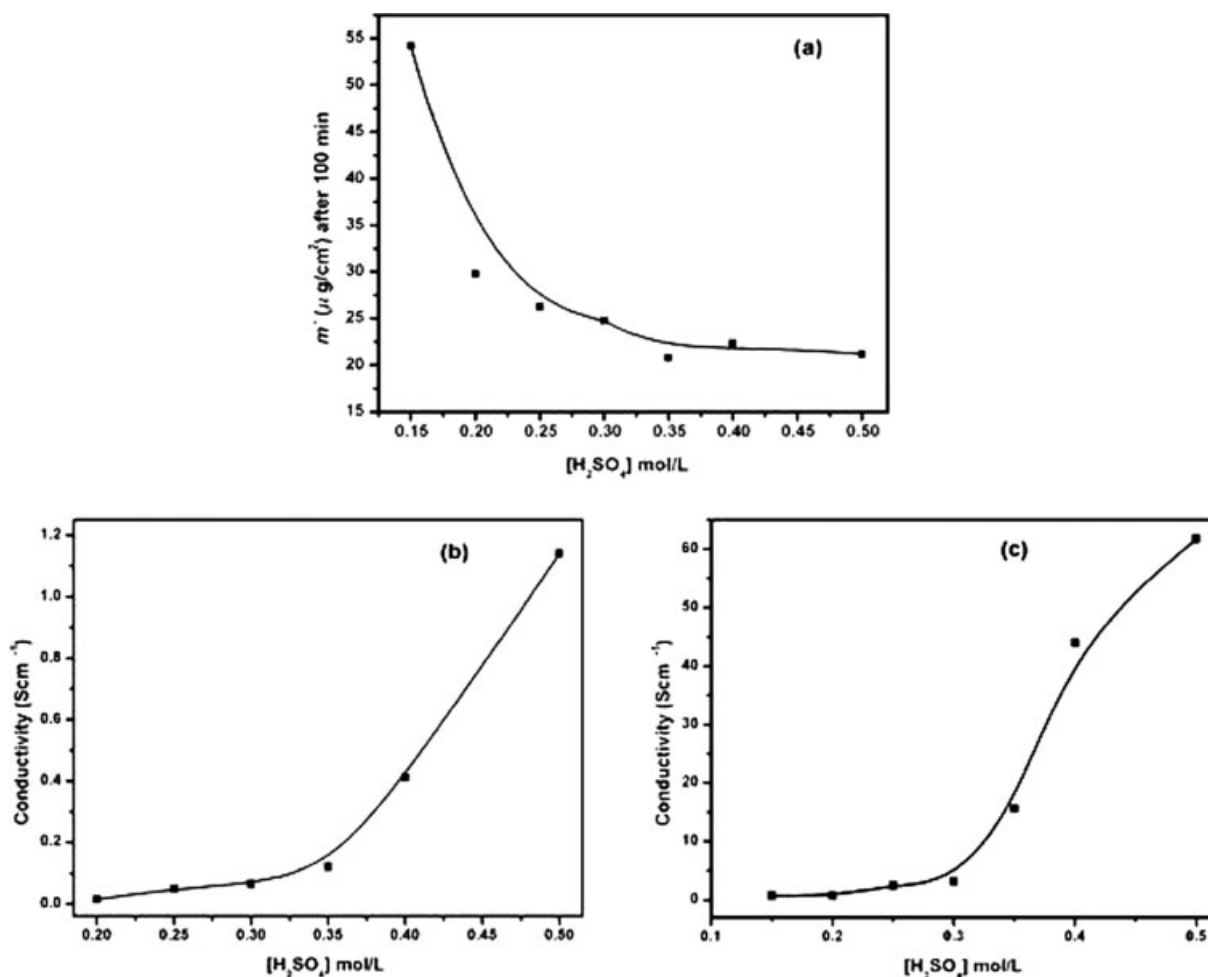
Figure 4 (a) m' at different polymerization time, (b) the conductivity of the polymer films, and (c) the conductivity of the powder at different H_2SO_4 concentrations.

ied from 0.15 up to 0.5M. m' of the PANI films was measured after 100 min of polymerization and plotted against the acid concentrations as shown in Figure 4(a). It can be shown that as the concentration of sulfuric increases, m' decreases. This can be interpreted on the basis that stronger protonation produced at high acid concentration makes the oxidation of aniline more difficult.[7] It is also noted that at concentration $\leq 0.2M$, the films show mixed color from brown and green; whereas at concentration larger than 0.2M, the film shows a green color. This behavior of color change was justified from the UV–vis spectra of PANI films deposited using different sulfuric acid concentrations.

The conductivity was measured for the polymer films and powders and plotted against the acid concentration; Figure 4(b,c). At 0.15M sulfuric, the film conductivity is too low to be measured. The conductivity of PANI films and powders shows approximately constant variation with the acid concentration up to 0.35 and 0.3M, respectively, and then increases as the acid concentration increases. This behavior can be explained on the basis that the protonation of

aniline increases with increasing the acid concentration. It is worth noting that Sun et al.[2] have reported that the conductivity and the yield of PANI powder
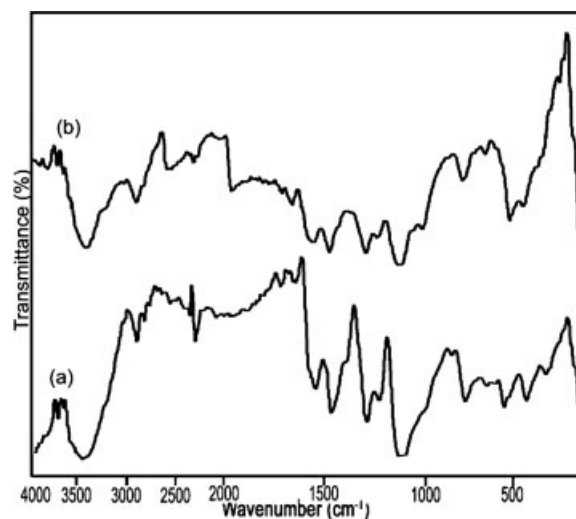

Figure 5 (a) IR spectra of PANI using APS, and (b) using Fenton reagent.
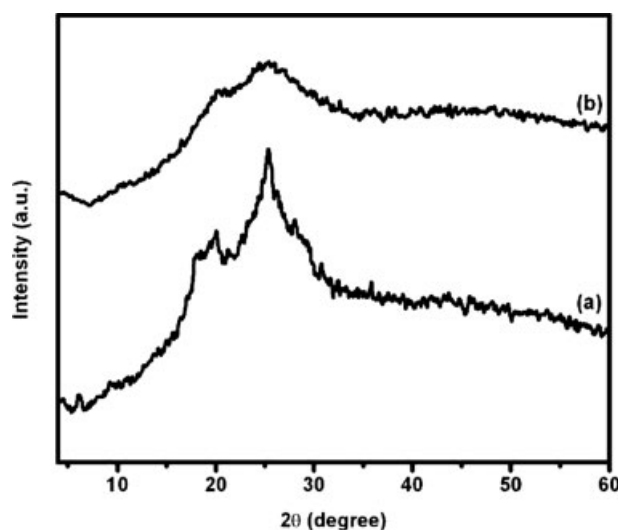
Figure 6 (a) X-ray diffractograms of PANI using APS, and (b) using Fenton reagent.

using H_2O_2–$FeCl_2$ in aqueous HCl media increases up to 2M.

IR spectra analysis

Figure 5 shows the IR spectra of two PANI powder samples; using APS (a) and Fenton reagent prepared at 0.2M aniline and 0.1M H_2O_2 in 0.35M sulfuric acid (b).

In case of using APS, the broad band at 3470 cm^{-1} is attributed to the characteristic-free N—H stretching vibration which indicates the presence of secondary amino groups (—NH—). The weak band at 2918 cm^{-1} arises from the aromatic C—H stretching vibration. The spectra exhibit main bands at 1482 cm^{-1} and 1562 cm^{-1} corresponding to the benzenoid and quinoid ring stretching frequency, respectively.[21,22] The absorption band at 1302 cm^{-1} is related to C—N stretching vibration of secondary aromatic amine.[23] The band characteristic of the conducting protonated form is observed at 1241 cm^{-1}. It has been interpreted as C—N$^{\bullet+}$ stretching vibration in the polaron structure. The prominent 1122 cm^{-1} band is assigned to a vibration mode of the —NH$^{\bullet+}$ = structure, which is formed during protonation.[24,25] The broad nature of this peak is owing to the high degree of electron delocalization[26] which was expected because of the greater degree of oxidation. The C—H out of plane bending vibration band of 1,4-disubstituted benzene ring appears at 808 cm^{-1}.[27]

The IR spectra of the PANI generated from Fenton reagent are identical with that obtained in case of using APS and are consistent with the reported ones in the literature except for some marginal differences.[22,23] Hence, the use of Fenton reagent was not found to affect the chemical structure of PANI.

X-ray diffraction analysis

X-ray diffraction patterns of two PANI samples were measured; the first was prepared using APS as an oxidant, whereas the second was prepared using Fenton reagent prepared by using 0.2M aniline and 0.1M H_2O_2 in 0.3M sulfuric and shown in Figure 6(a,b), respectively. Figure 6(a) reveals that PANI has some degree of crystallinity. Two diffraction peaks appear in the spectrum region of sample (a); the first centered at $2\theta = 25°$ and is more prominent than the other existed at $2\theta = 19°$. However, in case of using Fenton reagent, the peak at 25° becomes broad whereas the other peak tends to disappear; hence the crystallinity is less and an amorphous region is the main body.[25]

Thermogravimetric analysis

Figure 7 shows the thermograms of two PANI samples; the first is obtained using APS (a) and the other is obtained with Fenton reagent (b) taken between the room temperature and 750°C.

There are three stages of weight losses. The first weight loss before 120°C is attributed to the loss water molecules from the sample. The amounts of weight loss are 8.6% and 4.1% for samples (a) and (b), respectively. The second stage observed within the temperature range of 120–300°C is related to the removal of dopant molecules from the polymer structure.[28] The amounts of weight loss are 8 and 12.1% for samples (a) and (b), respectively. The weight loss observed between 300 and 700°C corresponds to the degradation of the polymer chain.[29] It is clear from the figure that sample (b) is less thermally stable than sample (a) as the former is com-
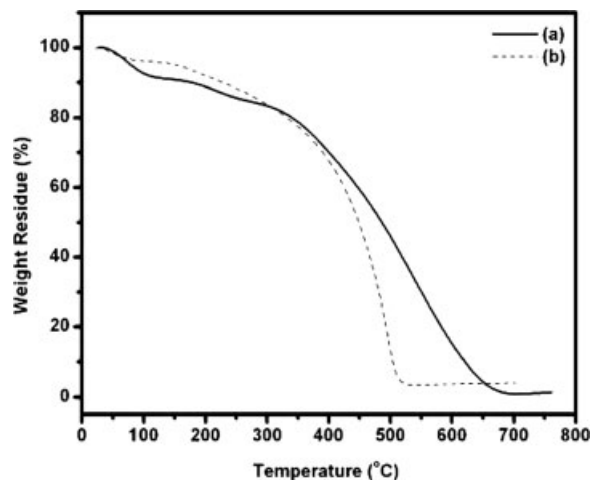

Figure 7 (a) TGA curves of PANI using APS, and (b) using Fenton reagent.
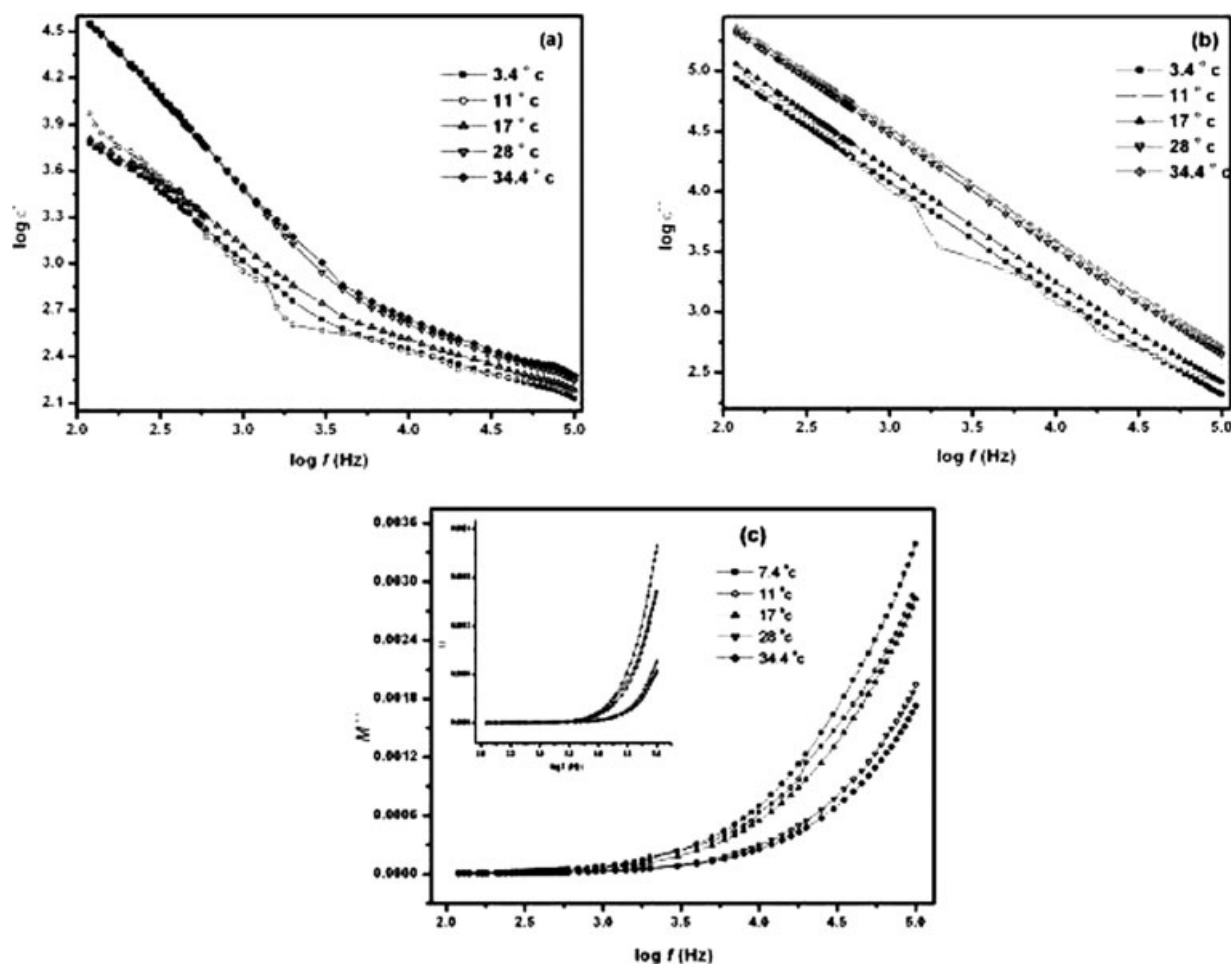
Figure 8   The dependence of (a) dielectric constant, (b) dielectric loss, and (c) M'' and M' (the inset curve) on frequency at different temperatures for PANI sample prepared at $r = 1$ and the concentration of aniline = 0.2M (double logarithmic scale).

pletely degradated at 520°C whereas the latter is degradated at 670°C.

Dielectric measurements

Figure 8(a,b) shows the frequency dependence of the dielectric constant (ε') and the dielectric loss (ε'') at different temperatures of polymer sample prepared at $r = 1$ and the concentration of aniline equals 0.2M in 0.3M sulfuric. The values of (ε') are high at low frequencies and at high temperature. The dependence at high frequency is relatively small.[30] However, (ε'') shows an inversely linear relation dependence on the frequency changes. Such high values of (ε') and (ε'') may be due to the interfacial effects within the bulk of the sample and the electrode effects. When an electric field was applied to the sample, the long-range drift of ions and barrier layer formation on the electrode surface results in large values of (ε') and (ε'').[31,32] At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction

of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the values of (ε') and (ε'').[33,34]

The electric modulus M' and M'' representations of dielectric process give us some idea of relaxation of dipoles that exists in different energy environments, independent of the strong effect of dc conductivity, which often mask the actual dielectric relaxation processes. The real and imaginary parts of the electric modulus (M' and M'') can be calculated from (ε') and (ε'') as follows[35]

$$M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \qquad M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2}$$

M' and M'' were plotted against the frequency at different temperature for PANI samples as shown in Figure 8(c). The almost zero values of M' at low frequency indicate the removal of electrode polarization.[36] M' and M'' values increase as the frequency increases but decrease as temperature increases.

CONCLUSIONS

The use of H_2O_2, as simple and industrially favorable chemical reagent, in combination with Fe^{2+} as catalyst affords PANI film formation. The optimum conditions for the film formation were determined and compared with the corresponding of the PANI powder formation in the bulk. The results were justified by measuring the UV–vis absorption spectra for the deposited *in situ* PANI films.

A comparison between the PANI prepared using APS and Fenton reagent was made. It is concluded that the chemical structures are the same; however, the PANI obtained using Fenton reagent is less crystalline and thermal stability than the PANI prepared using APS.

The optimum conductivity of the formed films was determined. It is concluded that the film conductivity values are higher than that of the polymer powder. This was attributed to the difference in the polymerization time of both samples. It is also concluded that the conductivity of PANI prepared using Fenton reagent is different from those of PANI synthesized normally. The dielectric properties [(ε'), (ε''), M' and M''] were determined for PANI powder at different frequencies and temperatures. It is concluded that the large value of (ε') at low frequency originates mainly from electrode polarization. A further study for the dielectric properties for the polymer at different reaction conditions is currently under investigation.

References

1. Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. Synth Met 1988, 24, 193.
2. Sun, Z.; Geng, Y.; LI, J.; Wang, X.; Jing, X.; Wang, F. J Appl Polym Sci 1999, 72, 1077.
3. Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. J Am Chem Soc 1999, 121, 71.
4. Moon, D. K.; Osakada, K.; Maruyama, T.; Yamamoto, T. Makromol Chem 1992, 193, 1723.
5. Sun, Z.; Geng, Y.; Li, J.; Jing, X. B.; Wang, F. S. Synth Met 1997, 84, 99.
6. Inoue, H.; Kida, Y.; Imoto, E. Bull Chem Soc Jpn 1966, 39, 551.
7. Zhu, H.; Mu, S. Synth Met 2001, 123, 293.
8. Ayad, M. M.; Rehab, A. F.; El-Hallag, I. S.; Am, W. A. Eur Polym Mater 2007, 43, 2540.
9. Ayad, M. M.; Salahuddin, N.; Sheneshin, M. A. Synth Met 2004, 142, 103.
10. Ayad, M. M.; Salahuddin, N.; Sheneshin, M. A. Synth Met 2003, 132, 185.
11. Sauerbrey, G. Z Phys 1959, 155, 206.
12. Kanazawa, K. K.; Gordon, J. G. J Anal Chem II 1985, 57, 1770.
13. Ayad, M. M.; Shenashin, M. A. Eur Polym Mater 2003, 39, 1319.
14. Chakraborty, M.; Mandal, B. M.; Mukherjee, D. C. Polym Int 2005, 54, 1158.
15. Stejskal, J.; Kratochvil, P.; Radhakrishnan, N. Synth Met 1993, 61, 225.
16. Anitha, G.; Subramanian, E. J Sens Actuators B 2003, 92, 49.
17. Goncalves, D.; dosSantos, D. S.; Mattoso, L. H. C.; Karasz, F. E.; Akcelrud, L.; Faria, R. M. Synth Met 1997, 90, 5.
18. Cao, Y.; Andretta, A.; Hegger, A. J.; Smith, P. Polym J 1989, 30, 2305.
19. Sari, B.; Talu, M.; Yildirim, F. Russ J. Electrochem 2002, 38, 707.
20. Kulkarni, M. V.; Viswanath, A. K.; Marimuthu, R.; Seth, T. J Polym Eng Sci 2004, 44, 1676.
21. Trchová, M.; Šedenková, I.; Stejskal, J. Synth Met 2005, 154, 1.
22. Šedenková, I.; Trchová, M.; Blinova, N. V.; Stejskal, J. Thin Solid Films 2006, 515, 1640.
23. Bhat, N. V.; Seshadri, D. T.; Phadke, R. S. Synth Met 2002, 130, 185.
24. Quillard, S.; Louarn, G.; Buisson, J. P.; Boyer, M.; Lapkowski, M.; Pron, A. Synth Met 1997, 84, 805.
25. Prokeš, J.; Trchová, M.; Hlavatá, D.; Stejskal, J. Polym Degrad Stab 2002, 78, 393.
26. Hu, H.; Cadenas, J. L.; Saniger, J. M.; Nair, P. K. Polym Int 1998, 45, 262.
27. Tang, J.; Jing, X.; Wang, B.; Wang, F. Synth Met 1988, 24, 231.
28. Palaniappan, S.; Narayana, B. H. J Polym Sci A 1994, 32, 2431.
29. Chan, H. S. O.; Oh, P. K.; Khor, E.; Tan, M. M. Synth Met 1989, 31, 95.
30. Soares, B. G.; Leyva, M. E.; Barra, G. M. O.; Khastgir, D.; Eur Polym Mater 2006, l42, 676.
31. Macedo, P. B.; Moynihan, C. T.; Bose, R. Phys Chem Glasses 1972, 13, 171.
32. Sengwa, R. J.; Sankhla, S. Colloid Polym Sci 2007, 48, 2737.
33. Campbell, J. A.; Goodwin, A. A.; Simon, G. P. Polym J 2001, 42, 4731.
34. Tsonos, C.; Apekis, L.; Viras, K.; Stepanenko, L.; Karabanova, L.; Sergeeva, L. M. Solid State Ionics 2001, 143, 229.
35. Smyth, C. P. Dielectric Behavior and Structure; McGraw-Hill Book Company: New York, 1955, p 191.
36. Dutta, P.; Biswas, S.; De, S. K. Mater Res Bull 2002, 37, 193.