



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Model of *in situ* Polyaniline Film Coating on Mylar: Influence of Aniline Polymerization Parameters

¹Theofilus A. Tockary, ¹W. Endang Asijati and ^{1,2}Yanti S. Soebianto

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Indonesia, Depok Campus, Depok 16424, Indonesia

²Center for Research and Development of Isotope and Radiation Technology, Indonesian National Nuclear Energy Agency (PATIR-BATAN), Pasar Jumat, Jakarta 12070, Indonesia

Abstract: A comprehensive model of *in situ* polyaniline film coating on mylar under the influence of aniline polymerization parameters is proposed. This is achieved by studying hydrochloric acid concentration, ammonium peroxydisulfate to aniline molar ratio and initial mixture temperature influence on both polymerization and the resulting polyaniline films. Polymerization was investigated mainly using solution calorimetry, while polyaniline films were characterized by UV-vis spectrophotometry. Hydrochloric acid concentration affects polyaniline film coating by controlling induction period duration for growing site formation and polymerization period duration for polyaniline chain propagation. Ammonium peroxydisulfate to aniline molar ratio affects coating by controlling growing site formation and polyaniline chain propagation intensity. Temperature affects coating by controlling overall polymerization duration. Reaction intensity and periods duration controlled by level of these parameters dictate growing sites adsorption onto mylar and polyaniline film growth. The model shows that polyaniline film coating is optimized towards bulk polymerization stoichiometric condition and is expected to qualitatively predict how a film property changes when a certain parameter is altered.

Key words: Polyaniline, mylar, *in situ* adsorption, solution calorimetry, UV-vis spectrophotometry

INTRODUCTION

Polyaniline, a well known conducting polymer (Fedorova and Stejskal, 2002; Trehová *et al.*, 2005; Šedinková *et al.*, 2006), has been attracting considerable attention since MacDiarmid and his colleagues reinvestigated this material (Vilènik *et al.*, 1998). Polyaniline can exist in a variety of forms that differ in chemical and physical properties (Stejskal and Gilbert, 2002) (Fig. 1). The wide range of electrochemical and optical properties associated with this variety of forms, coupled with good stability and simple synthesis, makes polyaniline potentially attractive for application as electronic material and chemical sensor (Vilènik *et al.*, 1998).

Many researches direct polyaniline for application as optical sensor. Among preceding experiments on this topic was for the simple case of polyaniline film pH sensor as demonstrated by Grummt *et al.* (1997), Pringsheim *et al.* (1997) and Jin *et al.* (2000). Several challenges still exist. Concerning specific use as pH sensor for example, deprotonation and reprotonation

hysteresis (Jin *et al.*, 2000) restrict each polyaniline film application to a single use. In spite of this, polyaniline film optical sensors may still have advantages in area of applications where other conventional measuring devices fail to cover. For example, the above mentioned optical pH sensor may be suitable for the direct measurement of blood pH (Jin *et al.*, 2000).

Polyaniline film coating on substrate is very closely related to polyaniline application as optical sensor. In 1989, MacDiarmid and Epstein had already reported that polyaniline may be deposited as strongly adhering films on a variety of substrates by immersion of substrate into an aqueous acidic solution of aniline containing an oxidant, i.e., by *in situ* adsorption polymerization of aniline (Stejskal *et al.*, 1999). Interestingly, although reagents concentration in this solution can be directly determined from stoichiometric calculation of aniline polymerization reaction, researchers often choose other conditions in order to achieve favourable film properties to meet particular purposes. The basis for this practice has not been thoroughly addressed. Furthermore, polyaniline film coating process is seldom discussed in

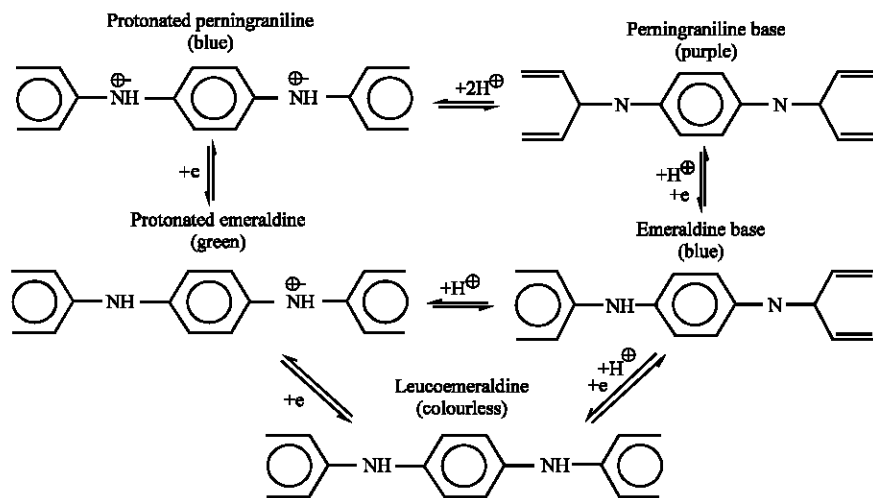


Fig. 1: Scheme of polyaniline structures (from Trchová *et al.*, 2005)

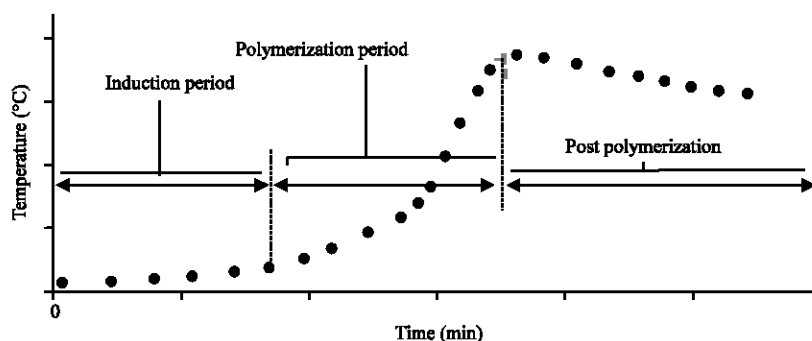


Fig. 2: Typical aniline polymerization temperature profile (from Stejskal and Gilbert, 2002)

relation to bulk aniline polymerization mechanism. This study aims to propose a comprehensive model of *in situ* polyaniline film coating on mylar under the influence of aniline polymerization parameters (concentration of hydrochloric acid (HCl), molar ratio of ammonium peroxydisulfate to aniline (APS/aniline) and initial mixture temperature) by correlating polymerization parameters with *in situ* polyaniline film coating on mylar. The model for film coating adopted in this study is that of Stejskal and Sapurina (2005), where polyaniline growing sites were initially adsorbed onto substrate and later followed by film growth (Riede *et al.*, 2000).

Throughout the study, polyaniline films were studied using UV-vis spectrophotometry, while a simplified approach using solution calorimetry was established for the macroscopic study of aniline polymerization. The approach is based on the division of aniline polymerization temperature profile into 3 periods by Stejskal and Gilbert (2002) (Fig. 2). The chemical reactions

confined within a certain polymerization period are assumed to be the same in any polymerization condition. The duration of each of the three periods and the intensity of chemical reaction confined within each of this polymerization period however, may be affected by polymerization parameters. From the temperature profiles, this change in duration of the three periods is expected to be observable from the temporal division, while chemical intensity from the maximum temperature of the polymerization process.

MATERIALS AND METHODS

Analytical grade aniline, hydrochloric acid (HCl) and ammonium peroxydisulfate (APS) were obtained from Merck. HCl and APS were used as obtained, while aniline was always added with zinc powder and then distilled prior to use. Yashica Overhead Projector transparencies were used to represent the bi-axially oriented polyethylene terephthalate (mylar) substrate.

Polyaniline film coating on mylar was carried out by *in situ* absorption polymerization by immersing mylar substrate into aniline polymerization mixture for 30 min. Aniline polymerization was conducted almost according to IUPAC technical report by Stejskal and Gilbert (2002) which mixes aniline hydrochloride salt with APS in aqueous medium, but in this study the salt was substituted by the separate use of aniline and HCl. The standard condition in this study was determined to be at the initial mixture temperature of 27°C, with aniline, HCl and APS concentration stoichiometrically set at 0.2, 0.2 and 0.25 M, respectively. Aniline polymerization was also carried out in other conditions in order to study the influence of polymerization parameters. Apart from this standard condition, HCl concentration were studied at 0.0, 0.5 and 1.0 M, APS to aniline molar ratio (APS/aniline) were studied at 0.625 and 1.875, while initial mixture temperature were set at low temperature (7.5°C) by placing reactants into ice bath for 10 min prior to polymerization.

Aniline polymerization was characterized by solution calorimetry using a laboratory mercury thermometer. A reference temperature profile was obtained from the standard aniline polymerization condition determined above. When regarded as necessary, additional aniline polymerization characterization was carried out using *in situ* mode UV-vis spectrophotometry. In this study, *in situ* mode UV-vis spectrophotometry was conducted only to aniline polymerization at low temperature and aniline polymerization without HCl. Intermediary and final polyaniline films were characterized using double beam Hitachi UV-vis spectrophotometer. Thickness (df in nm) was determined using an equation by Stejskal *et al.* (1999):

$$A_{400} = (5.4 \pm 0.2) \times 10^{-3} \text{ df}; A_{400} \text{ is the absorbance at } 400 \text{ nm}$$

Due to different polymerization conditions from Stejskal *et al.* (1999), the calculated thickness of polyaniline films were treated only as qualitative data, allowing only relative comparison of thickness of one polyaniline film to another.

$$\text{df} \sim A_{400}$$

RESULTS AND DISCUSSION

Effects of polymerization parameters on temperature profiles: In order to understand the chemical reaction confined within a certain polymerization period of the temperature profile, a paper by Gospodinova and Terlemezyan (1998) was consulted. The first

period, known as the induction period, is a period of p-aminodiphenylamine (PADPA) formation and N-phenyl-1,4-benzoquinonediimine (PBQ) accumulation (Fig. 3). PADPA was suggested to be the growing site for aniline polymerization, the formation of which is only possible during the induction period. The second period, known as the polymerization period, is a period of polyaniline chain propagation (Fig. 3). This period is characterized by higher gradient due to the exothermic nature of polyaniline oxidation occurring very dominantly. The third and last period, known as the post polymerization period, is a period of polyaniline chain termination by excess aniline monomer (Fig. 3).

HCl concentration effect on temperature profiles: The temperature profiles at various HCl concentration (Fig. 4A) shows that HCl concentration level can change duration of induction and polymerization period of aniline polymerization. Both induction period and polymerization period was observed to be longer at low HCl concentration. Gospodinova and Terlemezyan (1998) had explained that in induction period, aniline salt deprotonates to aniline before being oxidized into dimer, while in polymerization period, polyaniline must usually protonates before propagation. Based on this and the temperature profiles, it is concluded that at high HCl concentration, growing site formation is slow and can happen only briefly, because chain propagation quickly takes over and then proceeds at a very fast rate. At low HCl concentration, growing site formation proceeds rapidly, but chain propagation reaction does not immediately take over. *In situ* UV-vis measurement similar to Gospodinova and Terlemezyan (1998) was conducted at HCl 0.0 M (Fig. 5A) to ensure that this argument was valid. It is revealed that N-phenyl-1,4-benzoquinonediimine (PBQ) (420 nm) is the accumulated species in this extended induction period and the result agrees with previous finding (Gospodinova and Terlemezyan, 1998).

In this study, except at HCl 0.0 M, HCl concentration was observed to have no significant effect on the maximum temperature of aniline polymerization. Presumably, although chain propagation proceeds at a faster rate at higher HCl concentration, the extent of polyaniline chain oxidation reaction is only slightly altered when APS/aniline is fixed.

APS/aniline effect on temperature profiles: By contrary to HCl concentration, APS/aniline (Fig. 4B) does not significantly change the duration of aniline polymerization periods. However, it was observed that APS/aniline alters the maximum of the temperature profile. Higher maximum

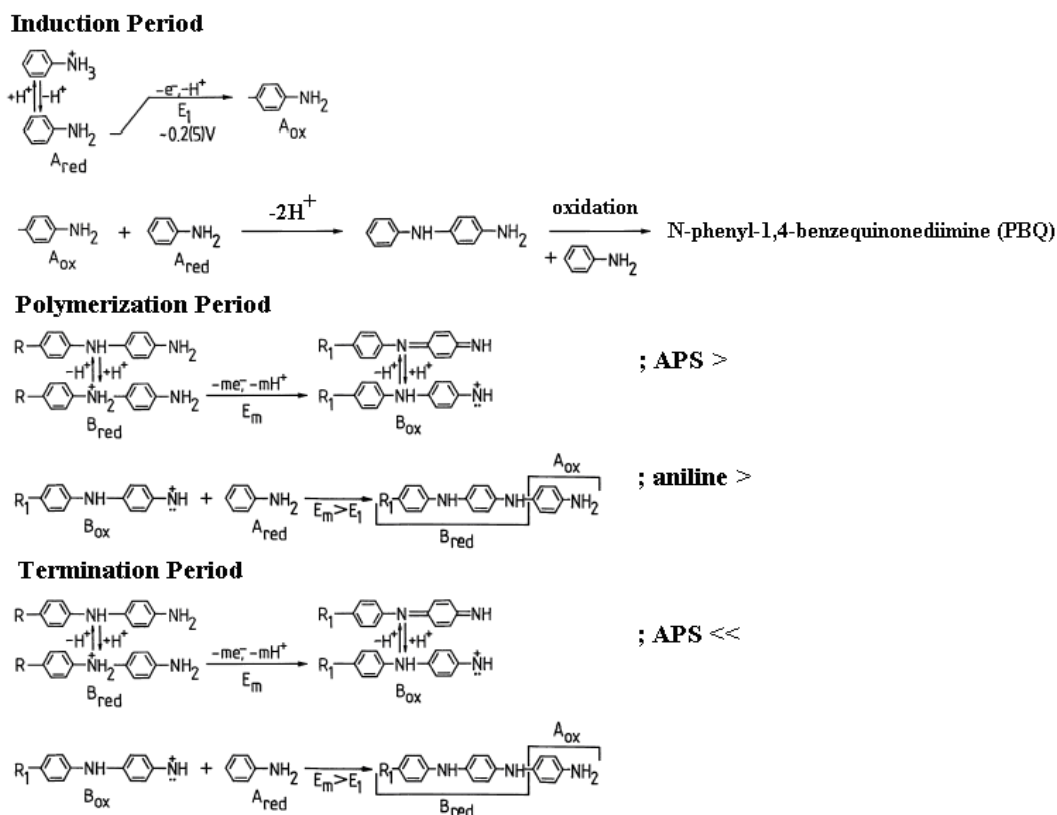


Fig. 3: Aniline polymerization mechanism according to Gospodinova and Terlemezyan (1998)

was achieved at higher level of APS/aniline. This suggests that while APS/aniline intensifies chemical reaction confined within a period of aniline polymerization, it is incapable of speeding up/slowing down the duration of aniline polymerization periods.

Lowered temperature effect on aniline polymerization temperature profiles: Temperature profile at low initial mixture temperature reveals that low temperature slows down all three aniline polymerization periods (Fig. 4C). Temperature decrease was observed at the transition from induction to polymerization period, indicating a possible endothermic reaction which may be due to considerable extent of imine bonds hydrolysis reaction (Gospodinova and Terlemezyan, 1998). Under this condition, polyaniline highly saturated with imine bonds may already be accumulated near the end of induction period. *In situ* UV-vis spectrophotometry (Fig. 5B) shows pernigraniline characteristic peak at 560 nm (Gospodinova and Terlemezyan, 1998) have longer lifetime than usually observed. This may reveal the difference between the effect of HCl concentration and lowered temperature on induction period of aniline polymerization. Although both cause longer induction period, at lowered temperature,

pernigraniline, instead of only PBQ, may be predominantly accumulated.

Effects of polymerization variables on polyaniline film on mylar: Aniline polymerization parameters influence on *in situ* polyaniline film coating was studied by UV-vis spectrophotometry at corresponding time to the previous temperature profile recording. It was difficult to wash off excessive polyaniline from the films and this affected their UV-vis spectrum for thickness calculation. Since reproducibility was very poor, only sets of films with reoccurring similar thickness were selected as representative of each batch.

HCl concentration effect on polyaniline film on mylar: By observing each polyaniline film UV-vis spectrum at the 5th min (Fig. 6A), HCl is concluded to speed up polyaniline film coating on mylar. This is consistent with the explanation on the effect of HCl on aniline polymerization process. Interestingly, the final polyaniline films UV-vis spectrum in Fig. 6B are non-uniform in shape. There are several possible explanation for this. First, these may be caused by differing concentration level of the HCl anchored in polyaniline. Secondly, polyaniline at high HCl

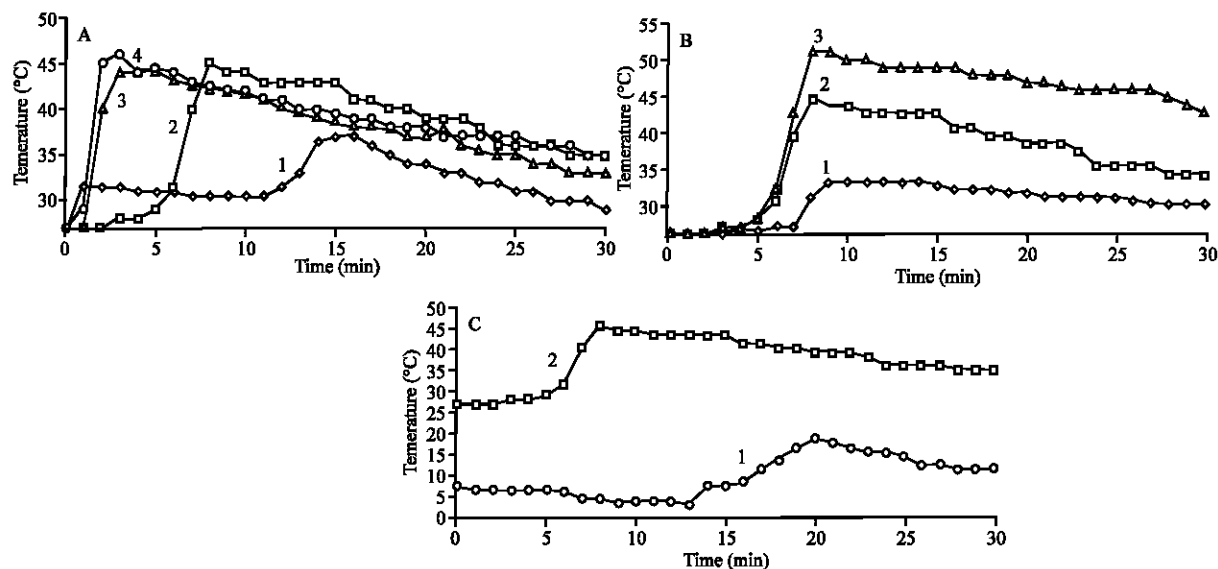


Fig. 4: Aniline polymerization temperature profile at (A) various HCl concentrations (27°C, APS/aniline molar ratio 1.25), legends: (1) HCl 0.0 M, (2) HCl 0.2 M, (3) HCl 0.5 M and (4) HCl 1.0 M, (B) various APS/aniline molar ratios (27°C, HCl 0.2 M), legends: (1) APS/aniline 0.625, (2) APS/aniline 1.25, (3) APS/aniline 1.875 and (C) various temperature (HCl 0.2 M, APS/aniline molar ratio 1.25), legends: (1) 7.5°C and (2) 27°C

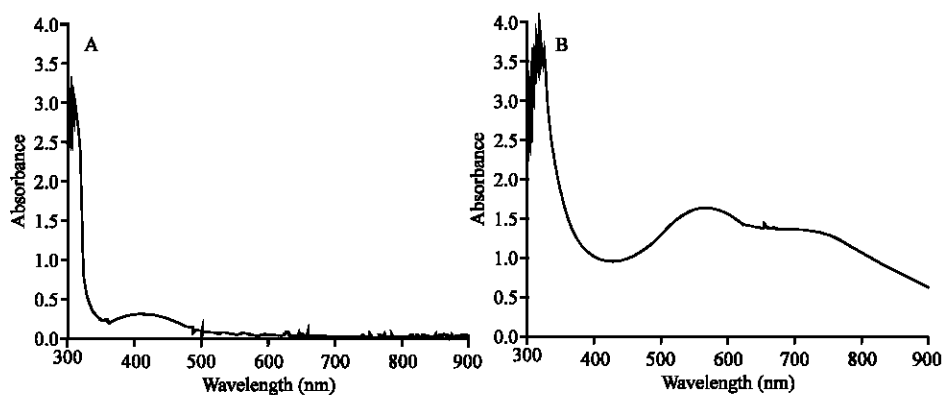


Fig. 5: *In situ* aniline polymerization spectrum at (A) HCl 0.0 M (t = 2 min) and (B) low temperature (t = 4 min)

concentration maybe susceptible to hydrolysis due to high proton concentration (Ayad *et al.*, 2004). Regardless of what the reason might be, the relative thickness of these final polyaniline films are obvious. Polyaniline film is thickest at HCl 0.2 M and then followed by 0.5 M and 1.0 M in decreasing order. In this study, UV-vis spectrum at HCl 0.0 M was not obtained because polyaniline film failed to form on substrate. From these results, it is concluded that HCl is necessary for polyaniline film coating, but the concentration should not be excessive.

APS/aniline effect on polyaniline film on mylar: By observing the UV-vis spectrum at the fifth minute for low

and standard APS/aniline (Fig. 7A), APS/aniline has no profound effect in speeding up/slowing down polyaniline adsorption on substrate. This is consistent with the effect of APS/aniline on aniline polymerization. However, for high APS/aniline, the polyaniline film UV-vis spectrum at the fifth minute have a significantly higher value compared to the previous two. This seems to show that high APS/aniline speeds up induction period. We believe that this is not conclusive because this set of UV-vis spectrum, recorded at the fifth minute of aniline polymerization, was very near to the start of polymerization period. This unfortunate choice of late measurement was imposed by experimental limitation

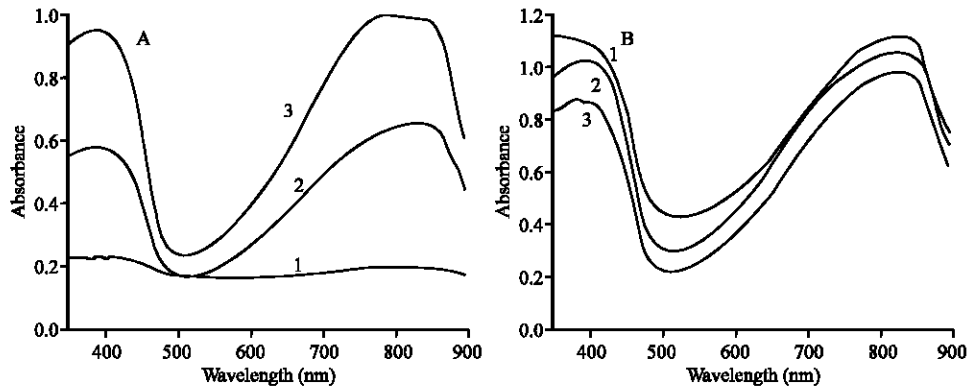


Fig. 6: Polyaniline film spectrum at various HCl concentrations (A) $t = 5$ minutes and (B) $t = 30$ minutes (27°C , APS/aniline molar ratio 1.25). Legends: (1) HCl 0.2 M, (2) HCl 0.5 M and (3) HCl 1.0 M

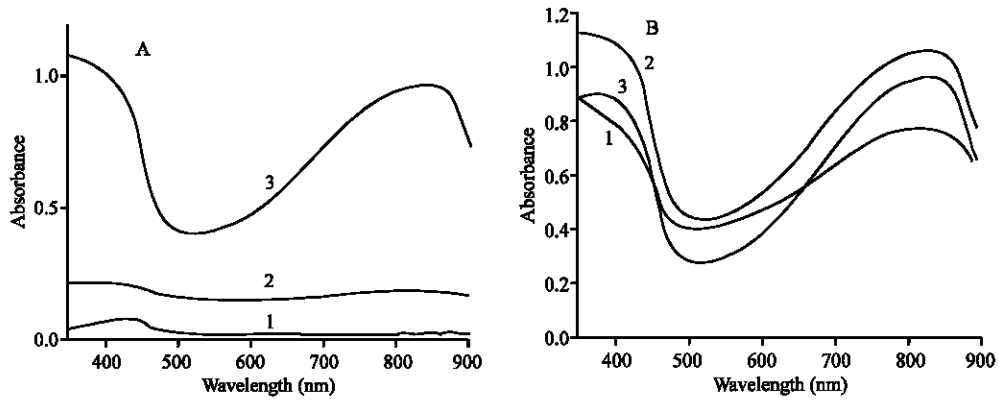


Fig. 7: Polyaniline film spectrum at various APS/aniline molar ratios (A) $t = 5$ min and (B) $t = 30$ min (27°C , HCl 0.2 M). Legends: (1) APS/aniline 0.625, (2) APS/aniline 1.25 and (3) APS/aniline 1.875

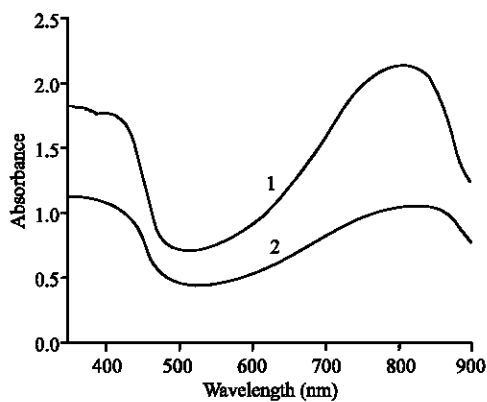


Fig. 8: Polyaniline film UV-vis spectrum at various temperature (HCl 0.2 M, APS/aniline molar ratio 1.25, $t = 30$ min). Legends: (1) 7.5°C and (2) 27°C

where polyaniline films obtained at earlier time than the fifth minute could hardly be characterized. Therefore, we hold on to the above conclusion and suggest that the

high APS/aniline does not speed up the start of polymerization process. The final polyaniline film UV-vis spectrum obtained at various levels of APS/aniline (Fig. 7B) are again non-uniform in shape, which may be due to the three polyaniline film being in three different oxidation levels. However as the measurement for thickness was at 400 nm near the isosbestic point of polyaniline oxidation (Albuquerque *et al.*, 2004) at 390 nm, it is obvious that polyaniline film thickness is optimum at APS/aniline molar ratio of 1.25.

Low temperature effect on polyaniline film on mylar:

Polyaniline film UV-vis spectrum obtained from aniline polymerization at low temperature and standard aniline polymerization (Fig. 8) showed polyaniline film to be thicker at low temperature aniline polymerization. This is similar to the conclusion of Stejskal *et al.* (1999).

Model of *in situ* polyaniline film coating on mylar:

Hereby, we propose a comprehensive model of *in situ* polyaniline film coating on mylar under the influence of

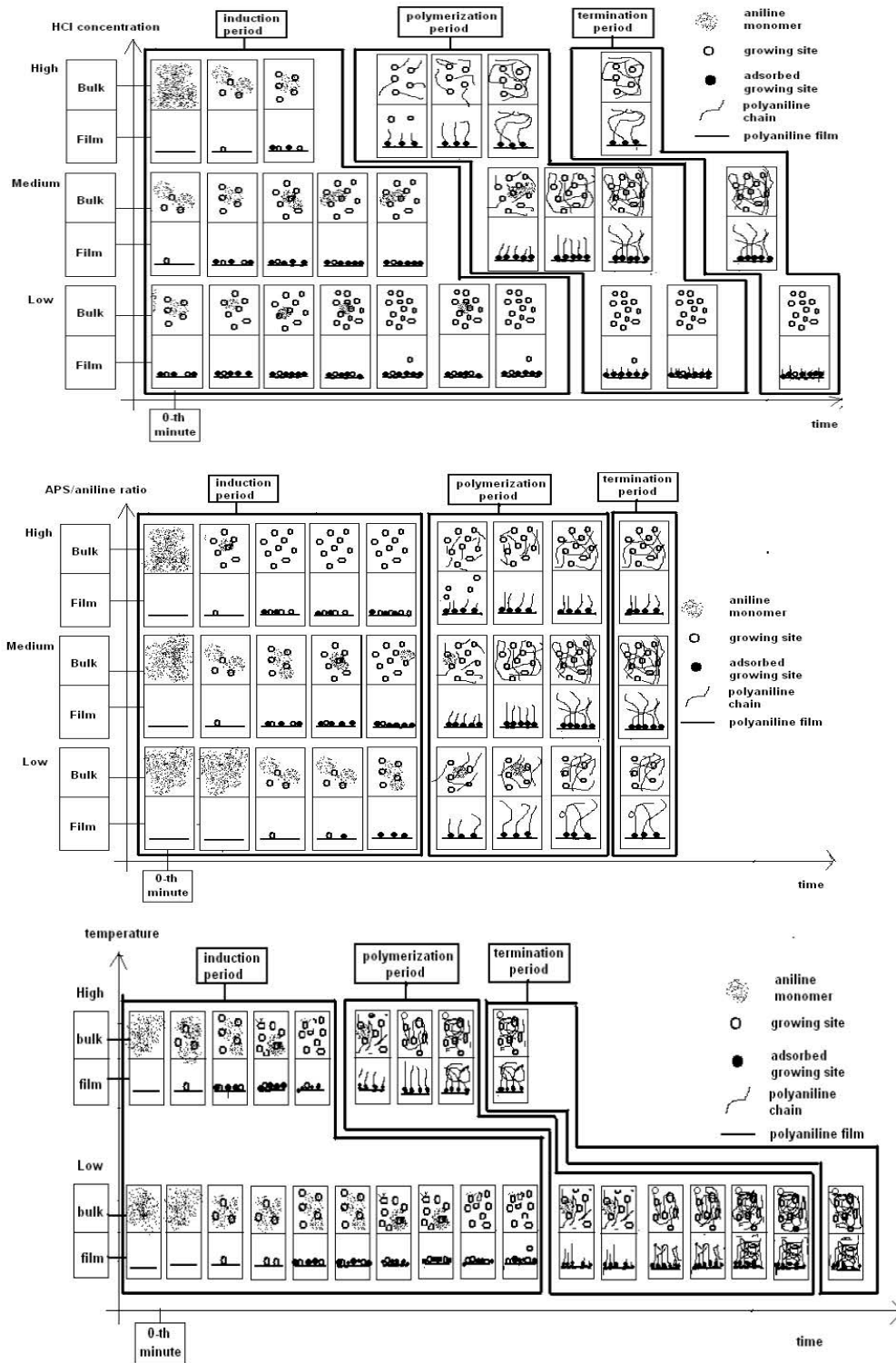


Fig. 9: Proposed model of polyaniline film coating on mylar at (A) various HCl concentrations, (B) various S/aniline molar ratios and (C) various temperature

aniline polymerization parameters (HCl concentration, APS/aniline and initial mixture temperature) by correlating observed temperature profiles with corresponding *in situ* UV-vis spectrum of polyaniline films. The model is partly based on previous proposal by Stejskal and Sapurina (2005) where polyaniline growing sites were initially adsorbed onto substrate and later followed by film growth.

As previously indicated from the temperature profile at various HCl concentrations, at high HCl concentration, growing sites formation is slow and brief. Since these growing sites may be the only species capable of being adsorbed on mylar, then a shorter duration of growing sites formation corresponds to a smaller number and more weakly adsorbed polyaniline chains. However, excess aniline monomer is abundant in this condition and polyaniline chain will be able to propagate rapidly resulting long polyaniline chains. On the other hand, at low HCl concentration, growing sites formation is faster and occurs at a much longer duration. The formation of more growing sites consume more aniline monomer and will then leave a smaller concentration for polyaniline chain propagation. This condition is also obviously not favourable for polyaniline film coating since resulting polyaniline chains will be short. Polyaniline film coating will only be optimum at medium HCl concentration, where the formation of growing sites is extensive while still maintaining adequate concentration of excess aniline monomer (Fig. 9A). This may explain why polyaniline film is thickest at medium HCl concentration.

To explain the influence of APS/aniline molar ratio, we suggest that at high APS/aniline, aniline oxidation into growing sites intensifies in induction period, consuming a large amount of aniline and then subsequently leaving small concentration of excess aniline in polymerization period (Fig. 9B). This shortage of excess aniline and the excessive number of growing sites cause resulting polyaniline chains to be short and have weak adhesive property on mylar (Fig. 9B). At low APS/aniline, growing sites formation in induction period is less intense and consumes a smaller number of aniline monomers. This leaves a large concentration of excess aniline for polyaniline propagation resulting in long polyaniline chains. However, film thickness is also not highest at low APS/aniline because smaller number of growing sites anchors on mylar. Following similar explanation for HCl concentration, polyaniline film coating is thickest at medium APS/aniline (Fig. 9B).

As observed from the temperature profiles, aniline polymerization proceeds slower at low temperature. Presumably, at low temperature, the growing sites have more time to adsorb on mylar which resulted the thicker polyaniline film (Fig. 9C).

CONCLUSION

By very simple methods, we have proposed a comprehensive model of *in situ* polyaniline film coating on mylar under the influence of aniline polymerization parameters. HCl concentration is concluded to affect polyaniline film quality by controlling the duration of induction period for growing sites formation and of polymerization period for polyaniline chain propagation on substrate. APS/aniline molar ratio affects polyaniline film quality by controlling intensity of growing sites formation in induction period and of polyaniline chain propagation in polymerization period. Temperature affects polyaniline film quality by controlling overall polymerization duration. Reaction intensity and periods duration specified by level of these parameters dictate growing sites adsorption onto mylar and polyaniline film growth. The proposed model shows that polyaniline film coating is optimized towards bulk polymerization stoichiometric condition and is expected to qualitatively predict how film property changes when a certain parameter is altered. However, the model is not yet complete because globular polyaniline deposits (Stejskal *et al.*, 1999) on mylar under the influence of aniline polymerization is not yet considered in this study.

ACKNOWLEDGMENT

The authors thank Indonesian Directorate General of Higher Education (No.APHB/2006/00011/024, No.276V/DRPM-UI/NL.4/2007) for financial support.

REFERENCES

- Albuquerque, J.E. de, L.H.C. Mattoso, R.M. Faria, J.G. Masters and A.G. MacDiarmid, 2004. Study of the interconversion of polyaniline oxidation states by optical absorption spectroscopy. *Synth. Met.*, 146: 1-10.
- Ayad, M.M., N. Salahudin and M.A. Shenashin, 2004. The optimum condition for *in situ* polyaniline film formation. *Synth. Met.*, 142: 101-106.
- Fedorova, S. and J. Stejskal, 2002. Surface and precipitation polymerization of aniline. *Langmuir*, 18: 5630-5632.
- Gospodinova, N. and L. Terlemezyan, 1998. Conducting polymers prepared by oxidative polymerization: Polyaniline. *Prog. Polym. Sci.*, 23: 1443-1484.
- Grummt, U.W., A. Pron, M. Zagorska and S. Lefrant, 1997. Polyaniline based optical pH sensor. *Anal. Chim. Acta*, 357: 253-259.

- Jin, Z., Y. Su and Y. Duan, 2000. An improved optical pH sensor based on polyaniline. *Sens. Actuators, B* 71: 118-122.
- Pringsheim, E., E. Terpetschnig and O.S. Wolfbeis, 1997. Optical sensing of pH using thin films of substituted polyanilines. *Anal. Chim. Acta*, 357: 247-252.
- Riede, A., M. Helmstedt, V. Riede, J. Zemek and J. Stejskal, 2000. *In situ* polymerized polyaniline films 2. Dispersion polymerization of aniline in the presence of colloidal silica. *Langmuir*, 16: 6240-6244.
- Šedinková, I., M. Trchová, N.V. Blinova and J. Stejskal, 2006. *In situ* polymerized polyaniline films. Preparation in solutions of hydrochloric, sulfuric, or phosphoric acid. *Thin Solid Films*, 515: 1640-1646.
- Stejskal, J., I. Sapurina, J. Prokis and J. Zemek, 1999. *In situ* polymerized polyaniline films. *Synth. Met.*, 105: 195-202.
- Stejskal, J. and R.G. Gilbert, 2002. Polyaniline: Preparation of a conducting polymer. *Pure Applied Chem.*, 74 (5): 857-867.
- Stejskal, J. and I. Sapurina, 2005. Polyaniline: Thin films and colloidal dispersions. *Pure Applied Chem.*, 77 (5): 815-826.
- Trchová, M., I. Šedinková and J. Stejskal, 2005. *In situ* polymerized polyaniline films 6. FTIR spectroscopic study of polyaniline polymerization. *Synth. Met.*, 154: 1-4.
- Vilènik, M., M. Zigon, M. Župan and A. Šebenik, 1998. Influence of polymerization parameters on the molecular weight of polyaniline. *Acta Chim. Slov.*, 45: 173-183.