

**CHAPTER IV**  
**ADMICELLAR POLYMERIZATION OF POLYSTYRENE ON**  
**NATURAL RUBBER PARTICLES**

**ABSTRACT:**

A thin film of polystyrene (PS) was deposited onto natural rubber (NR) particles by admicellar polymerization (AP). The AP process involves polymerization of an adsolubilized monomer in the hydrophobic regions of surfactant bilayers adsorbed on the substrate surface. The point of zero charges (PZC) of NR, the equilibration time for surfactant (hexadecyltrimethylammonium bromide, CTAB) adsorption, the adsorption isotherm of CTAB on NR particles and the adsolubilization of styrene monomer into the surfactant aggregates were examined to find a suitable pH, time for surfactant adsorption, CTAB concentration and styrene concentration for admicellar polymerization. Moreover, the effects of salt on CTAB adsorption and monomer adsolubilization were studied. PS coated onto characterized by FTIR and TGA. FTIR of the products showed the characteristic peaks of PS and NR. Degradation temperature of the products from TGA also confirmed the presence of PS and NR.

**KEYWORDS:**

Polystyrene; natural rubber; admicellar polymerization

## INTRODUCTION

Thin-film coatings on solid substrates have been a popular research topic because they have many applications in composite materials [1-2], microelectronics [3], and electronic devices [4-5]. They can provide many beneficial physical and chemical properties, such as improvement in adhesion between polymer matrix and reinforcing filler in composite materials, increase in composite strength, reduction of cure time, increase in tear strength, improvement of elongation at break and improvement in processability.[6-11]. One method used to produce a thin-film coating on solid substrates is called admicellar polymerization or the thin film via surfactant template (TFST).

Admicellar polymerization has been shown to be effective for depositing ultra-thin polymer films onto charged surfaces in aqueous solution. The method is based on the formation of surfactant bilayers as reaction templates on surfaces where polymerization takes place. AP can be described as a four step process. The first step involves the adsorption of a surfactant bilayer, an admicelle, on the substrate in aqueous solution. Second, the monomer to be polymerized is added and solubilized by the admicelles, forming a region of high monomer density at the water/substrate interface. Third, the monomer is polymerized inside the admicelles, forming an ultra-thin film. Finally, the substrate is rinsed to wash away excess surfactant. The advantage of such a process is the ability to deposit ultra-thin layers of polymer into very small spaces normally difficult to reach by conventional coating process [12].

Many types of polymer-substrate systems have been produced successfully by AP. PS, which can be used in many applications, including home construction, refrigerator components and electronic devices, has often been formed in application of AP. However, limitations of polystyrene in its properties, such as brittleness and low strength, must be improved in order to achieve satisfactory applications. Wu *et al.* studied the formation of ultra-thin polystyrene films on alumina by using admicellar polymerization and sodium dodecylsulfate (SDS) as a surfactant template. From a study of the adsorption isotherm of SDS, their findings also revealed that the presence of styrene enhanced SDS adsorption [13]. Essumi *et al.* employed admicellar polymerization to prepare polystyrene coated on alumina surface by using

sodium 10-undecenoate as a surfactant. They found that the films prepared were nanometer-thick films [14].

In this study, the effect of styrene and salt concentration on adsorption isotherm was investigated in order to employ admicellar polymerization to prepare polystyrene coated on natural rubber. This effort brought the improvement in mechanical properties of polystyrene, which is brittle, by natural rubber. Due to its well-established structure, high interaction, and stability in several surfactants, NR latex was chosen as the substrate for polystyrene coating.

## **EXPERIMENTAL**

### **Materials**

The Rubber Research Institute of Thailand provided natural rubber (60% dry rubber content). Hexadecyltrimethylammonium bromide (CTAB, 98%) and styrene monomer (99%) were purchased from Fluka. Aldrich supplied 2,2' Azo-bis(2-methylpropionamide) (V50, 97%), a water insoluble initiator. Sodium bromide (99.5%) was obtained from Unilab. Solvents tetrahydrofuran (THF/99.8%) and absolute anhydrous ethanol (99.9%) came from LAB-SCAN and J.T. Baker, respectively. All materials except NR were used without further purification.

### **Purification of the NR Latex**

NR latex particles were purified by centrifugation (at 20°C, 8,000 rpm, 20 min) and were redispersed in distilled water twice to remove any dissolved impurities and to reduce the particle size distribution. The resulting particles were considered to be clean. After washing, the particles were resuspended in distilled water at pH8 adjusted with NaOH.

### **Particle Size Measurement**

The average particle size, the standard size distribution and the specific surface area of NR latex after purification was measured by the principle of beam obscuration using a particle size analyzer, lens 45mm (Malvern Instruments Ltd., Mastersizer X

Ver. 2.15). Specific surface area was calculated from the particle diameter with the assumption of spherical particles of constant volume.

### **Electrophoretic Mobility Measurement**

Because solution pH affects the charge of particles and because surface charge of latex particles influences surfactant adsorption, electrophoretic mobility was used to determine the surface charge of the latex particles at various solution pHs. The pH of the natural rubber solution was adjusted by 0.01 and 0.1 M standard solution of hydrochloric solution (HCl) and sodium hydroxide (NaOH). The electrophoretic mobility of the latex particles was then observed at room temperature with Zeta Meter 3.0+.

### **Surfactant Adsorption Isotherm**

Solutions of various initial CTAB concentrations were prepared in water pH 8. Each solution was added to a 6 dram test tube vial with a screw cap containing 1 mL of 1 % NR solution (0.01 g DRC—not defined). Tubes were agitated in a shaking bath at 30 °C for a period of 15 h to ensure equilibration. NR particles were separated from the mixture by filtering the mixture through a nylon membrane. Concentrations of filtrates or equilibrium CTAB concentration were determined by surface tension measurement. The linear region of a Gibbs plot (i.e., the relationship between surface tension and CTAB concentration) was used as the calibration curve. CTAB solutions were diluted into the linear region for measurement and the concentration back-calculated.

### **Styrene Adsolubilization Measurement**

Hexadecyltrimethylammonium bromide solution of concentration 2,100  $\mu\text{M}$  was prepared in water pH 8. Then, 10 mL was pipetted into a 6 dram test tube vial with a screw cap containing 1 mL of 1 % NR solution and 9 mL of water. The mixture was agitated in a shaking bath at 30°C for an equilibration period of 15h to form surfactant bilayer. Pure styrene monomer was pipetted into each tube. These mixtures consist of 0.01g rubber particles, 1,000  $\mu\text{M}$  CTAB and styrene monomer at

various concentrations in a total volume of 21 mL. Tubes were agitated in a shaking bath at 30 °C again for 2 h for adsolubilization of styrene into surfactant bilayer. The NR particles were separated from the mixture by filtering the mixture through a nylon membrane. The concentrations of styrene monomer in the filtrates or equilibrium styrene concentrations were determined using UV-visible spectroscopy at wavelength 247 nm. The difference between the initial styrene concentration and equilibrium styrene concentration times the volume yielded the amount of adsolubilized styrene.

### **Polymerization of Polystyrene onto Latex Particle**

Admicellar polymerization of styrene on natural rubber was carried out at various styrene concentrations. The conditions of polymerization of styrene on NR particles were: CTAB concentration 1,000  $\mu\text{M}$ , 2:1 styrene:V50 molar ratio, and 1g dry natural rubber content. The polymerization experiment followed the same procedure as in monomer adsolubilization experiment with initial styrene monomer at various concentrations as shown in Table 4.1. The mixture was continuously agitated in the shaking bath for 2 hrs for monomer adsolubilization. The initiator V50 was added into the system with the amounts as shown in Table 4.1 for starting polymerization reaction. Polymerization reaction was performed at 70°C in the shaking bath for 2 h. At the end of the polymerization time, the reaction was stopped by immersing the vials in the ice bath for 10 min. NR particles were washed with water to remove excess surfactant by filtering through a dialysis tube (Cellulose membrane) and NR particles were separated from the mixture by centrifuging at 3000 rpm. Finally, the products were dried in a vacuum oven at 70°C for 16 h.

### **Testing and Characterization**

#### *FTIR Spectra*

FTIR was used to study the chemical composition of the product with 32 scans at a resolution of 4  $\text{cm}^{-1}$ . Samples were scanned over the frequency range 4000-400  $\text{cm}^{-1}$  using a deuterated triglycinesulfate (DTGS) as a detector with a specific directivity,  $D^*$ , of  $1 \times 10^9 \text{cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$ . Because FTIR has very high sensitivity, the products were compressed by compression molding before characterization to form a very thin

film of sample and to get sharp peaks in the FTIR spectra. The condition of compression molding (Wabash model V50H-18-CX) was preheating at 150 °C for 3 minutes and compressing at 150 °C, with a force 10 tons for 3 min, then cooling the sample to 40°C under pressure.

#### *Thermogravimetric Analysis*

To study the thermal property of the product, TG-DGA (Perkin Elmer, Model Pyris Diamond TG-DTA) was used to observe thermal stability and degradation temperatures of the product. Samples were put into the Pt pan and heated from 30-600°C at a heating rate of 10°C/minute under nitrogen atmosphere with 100 mL/min flow rate.

## **RESULTS AND DISCUSSION**

### **Particles Size Determination**

From the histogram in Figure 4.1, it shows that particle diameter of NR covered a wide range. The diameter of NR ranged from 0.28-1.5  $\mu\text{M}$ , confirming that the particle size of NR was naturally polydisperse. The mean diameter of NR was 0.86  $\mu\text{m}$  by volume average. This result compares well to values from the literatures [6,15]. The specific surface area of NR was equal to 8.4721  $\text{m}^2/\text{g}$ . Particle size of NR was measured in each experiment after purification.

### **Electrophoretic Mobility Result**

The electrophoretic mobility (EM) of NR particles in water at various pH was measured by Zeta Meter<sup>3+</sup>. The plot between the EM and pH helped determine the point of zero charge (PZC), an important parameter affecting surfactant adsorption. From Figure 4.2, at pH equal to 3.3, the EM was equal to zero. When the pH is lower than the isoelectric point of 3.3, the EM has positive values; when the pH is higher than 3.3, the EM has negative values. The rate of change of EM was rapid at pH between 2.4 and 4. At pH higher than 4, the EM changed slowly and indicated that ionization of acidic groups was nearly complete. This amphoteric character

confirms the presence of protein on the NR particles. However, the isoelectric point from this experiment did not fall in the normal range of protein (4.0-6.0) [15] due to the presence of fatty acid on NR particles.

The point of zero charge found for NR particles at pH 3.3 is comparable to values previously reported in the literatures [6,15]. This experiment indicates that a suitable pH must be higher than 3.3 to achieve the adsorption of the cationic surfactant CTAB. A pH of 8 was chosen for remaining experiments to get highly negatively-charged surface favorable to adsorption.

### **Surfactant Adsorption Isotherm**

From Figure 4.3, the adsorption isotherm (L-shape) of CTAB surfactant onto the NR particle surfaces shows the characteristic of surfactant adsorbed on non-highly charged surface. The critical micelle concentration (CMC) is about 890  $\mu\text{M}$  equilibrium concentration or at 1,100  $\mu\text{M}$  of final concentration which is acceptable when comparing to the reference, i.e. critical micelle concentration (CMC) of CTAB = 920  $\mu\text{M}$  [16]. The effect of salt (NaBr) on the CTAB adsorption isotherm was studied, too. The result shows that the adsorption of CTAB on NR increased with NaBr concentration. The CMC was reduced from 888  $\mu\text{M}$  to 692  $\mu\text{M}$  when the NaBr concentration equaled to 1 mM. As in the literatures [8,17,18], the reasonable explanation of this effect can be attributed to 2 factors. The first is reduction of headgroup repulsion in the adsorbed CTAB. The second is increased repulsion between the hydrocarbon tail of CTAB and water. As a result, good packing of CTAB on NR surface occurs giving a higher amount of CTAB adsorbed on NR particles. The CMC point of no\_salt system was about 890  $\mu\text{M}$  which gave CTAB adsorption 69.01  $\mu\text{M}/\text{m}^2$  ( 5.34  $\mu\text{mol}/\text{g}$ ). In the part of particle size measurement, the specific surface area of NR was 8.4721  $\text{m}^2/\text{g}$ . If it is assumed that CTAB formed a perfect bilayer and completely cover NR surface, the head of a CTAB molecule will cover 5.27  $\text{nm}^2$  on NR surface. The head group of CTAB was 0.5  $\text{nm}^2$ . (Thakulsukanant, 1997) It is possible that there was electric repulsion between adjacent CTAB head groups or CTAB did not completely cover NR surface. The concentration of CTAB selected for admicellar polymerization was 1,000  $\mu\text{M}$  to give

an equilibrium CTAB concentration lower than the CMC and to avoid micelle formation in the supernatant while providing a high amount of CTAB bilayer formation on NR surface.

### **Adsolubilization of Styrene**

Figure 4.4 shows the styrene adsolubilization. The result obtained indicated that the higher amount of initial styrene concentration, which resulted in higher amount of equilibrium concentration styrene in the supernatant, gave correspondingly higher amounts of styrene adsolubilization at both 0 and 1mM NaBr concentrations. This experiment can also explain the effect of NaBr on the styrene adsolubilized at the interface. From the effect of NaBr on the CTAB adsorption on NR, the salt improved the amount, orientation and packing of CTAB. The better packing of CTAB formed a stronger hydrophobic region in the admicelle resulting in better styrene adsolubilization.

### **Characterization of PS coated on NR**

#### *FTIR*

Figures 4.5a and 4.5b show FTIR spectra of standard PS, NR and polystyrene coated on NR particles at different initial concentrations of styrene monomer. The spectra encompass results for polymerizations carried out at different concentrations of NaBr, 0 M and 1 mM, respectively. Composite material of PS and NR was obtained because the spectra show both characteristics of PS and NR when compared to standard PS and pure NR. FTIR spectra of the product were similar to FTIR spectrum of pure NR but they also showed distinct peaks for PS. The important peaks of PS include aromatic C-H stretching at 3100-3000  $\text{cm}^{-1}$ , aromatic C=C stretching at 1600  $\text{cm}^{-1}$ , 1495  $\text{cm}^{-1}$ , 1454  $\text{cm}^{-1}$  and out-of-plane aromatic C-H bending at 700  $\text{cm}^{-1}$ , some of which are masked by NR. Figure 4.6c is the plot of FTIR intensity at 700  $\text{cm}^{-1}$  and initial styrene concentration. From Figure 4.6c, it shows that the intensity of characteristic peaks of PS in the product increased proportionally with the concentration of styrene monomer used. Intensities of FTIR spectra at initial styrene monomer 100 mM did not differ much. This may be due to



saturation or limitation of monomer adsorbed into the surfactant aggregates. The presence of NaBr also resulted in a greater amount of PS in the composite. Peaks of PS in the admicellar polymerized samples became obvious at concentrations of 50 mM and 20 mM for the sample without salt and with salt respectively. This is attributed to the more adsorption and better packing of CTAB on substrate surface in the presence of salt resulting in higher amount of styrene adsorbed at the interface and thus more PS was produced.

#### *TGA*

Figure 4.6a and 4.6b show the TGA results of PS coated on NR particles at various initial styrene concentration compared with standard PS and pure NR under conditions of different salt concentrations of 0 M and 1 mM, respectively. From the thermograms, one can determine the degradation temperature and weight loss of samples (%) with increasing temperature. Products formed at low initial styrene concentration (10, 20, 30, 40 and 50 mM) did not exhibit any significant difference from NR, but at high initial styrene concentration (100 mM), the degradation rate slightly increased. It could be concluded that the degradation rate of the product increased when the initial styrene concentration increased.

#### **CONCLUSIONS**

In this research, admicellar polymerization of PS on NR particles was studied and conditions suitable for admicellar polymerization determined. Acceptable pH range for polymerization was ascertained from EM measurement and the isoelectric point of NR which was equal to 3.3. A pH higher than 3.3 and a cationic surfactant were chosen because at pH lower than the isoelectric point, the stabilizer for NR particles hydrolyzes resulting in the coagulation of NR. The pH 8 was chosen to form a relatively highly negatively charged surface of NR since the surfactant used in this experiment was CTAB. Equilibration experiments indicated that 15 h was sufficient for surfactant adsorption. [CTAB adsorptions on NR 890 and 692  $\mu\text{M}$  for equilibrium CTAB concentration with 0 M and 1 mM of NaBr, respectively. To avoid micelle formation, the initial concentration of CTAB for admicellar

polymerization was 1000  $\mu\text{M}$  which gave an equilibrium CTAB concentration lower than CMC. Moreover, the adsorption isotherm experiment showed that addition of NaBr resulted in greater adsorption of CTAB. It was found that the higher the initial styrene concentration, which gave higher equilibrium styrene concentration, the higher the styrene adsolubilization. The effect of NaBr on styrene adsolubilization showed the same trend as the adsorption isotherm. The products from admicellar polymerization were characterized by FTIR and TGA. FTIR spectra showed the combination of characteristic peaks of NR and PS. The intensities of the PS peak increased with the % weight of PS. The TGA results did not show the significant character of PS at low % weight of PS but at high % weight of PS, it showed a slight change in the degradation rate.

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## REFERENCES

1. Liu, Y.C., and Tsai, C.J., *Chemistry Materials*, **15**, 320-326, (2003).
2. Bhat, N.V., Geetha, P., Pawde, S., and Nallathambi, R., *Journal of Applied Polymer Science*, **58**, 2251-2257 (1995)
3. Chen, J.H., Huang, Z.P., Wang, D.Z., Yang, S.X., Li, W.Z., Wen, J.G., and Ren, Z.F., *Synthetic Metals*, **125**, 289-294 (2002)
4. Cooper, G.P., and Vincent, B., *Journal of Physics D: Applied Physics*, **22**, 1580-1585 (1989)
5. Makhlouki, M., Morsi, M. Bonnet, A., Conan, A., Pron, A., and Lefrant, S., *Journal of Applied Polymer Science*, **44(3)**, 443-446 (1992)
6. Bunsomsit, K., Magaraphan, R., O'Rear, E.A., and Grady, B.P., *Colloid and Polymer Science*, **280**, 509-516 (2002)
7. Kitiyanan, B. O'Haver, J.H. Harwell, J.H., and Osuwan, S., *Langmuir*, **12(9)**, 2162-2168 (1996)
8. Pongprayoon, T., Yanumet, N. and O'Rear, E.A., *Journal of Colloid and Interface Science*, **59**, 1427-1435 (1996)
9. Sakhalkar, S.S., and Hirt, D.E., *Langmuir*, **11(9)**, 3369-3373 (1995)
10. O'Haver, J.H., Harwell, J.H., Evans, L.R., and Waddel, W.H., *Journal of Applied Polymer Science*, **59**, 1427-1435(1996)
11. Arayawongkul, S., *M.S.Thesis, The Petroleum and Petrochemical College, Chulalongkorn* (2002)
12. Funkhouser, G.P., Arevalo, M.P., Glatzhofer, D.T., and O'Rear, E.A., *Langmuir*, **11(5)**, 1143-1147 (1995)
13. Esuni, K., Watanabe, N., and Meguro, K., *Langmuir*, **7(8)**, 1175-1178 (1991)
14. Wu, J., Harwell, J.H., and O'Rear, E.A., *Langmuir*, **3(4)**, 531-537 (1987)
15. Thakulsukanant, C., Lobban, L.L., Osuwan, S., and Waritswat, A. *Langmuir*, **13**, 4595-4599 (1997)
16. Tangboriboonrat, P., Suchiva, K., and Riess, P., *Polymer*, **36(4)**, 781-785 (1995)
17. Rosen, M.J. (1989). *Surfactants and Interfacial Phenomena*. 2<sup>nd</sup> ed. New York: Wiley.
18. Zhao, J., and Brown, W., *Langmuir*, **11(8)**, 2944-2950 (1995)
19. Zhao, J., and Brown, W., *Langmuir*, **12(5)**, 1141-1148 (1996)

**Table 4.1** Feed concentrations of styrene monomer and V50 used in the experiments.

Monomer(styrene) ( $\mu\text{M}$ )	Initiator(V50) ( $\mu\text{M}$ )
10	5
20	10
30	15
40	20
50	25
100	50

**Table 4.2** The final contents of PS (as calculated) that correlated to the initial styrene concentration for polymerization.

Monomer(styrene) ( $\mu\text{M}$ )	%weight of polystyrene
10	2.124
20	4.167
30	6.121
40	7.995
50	9.804
100	17.947

Result Statistics			
Distribution Type: Volume	Concentration = 0.0019 %Vol	Density = 1.000 g / cub. cm	Specific S.A. = 8.4721 sq. m / g
Mean Diameters:	D (v, 0.1) = 0.47 $\mu$ m	D (v, 0.5) = 0.75 $\mu$ m	D (v, 0.9) = 1.17 $\mu$ m
D [4, 3] = 0.86 $\mu$ m	D [3, 2] = 0.71 $\mu$ m	Span = 9.323E-01	Uniformity = 3.825E-01

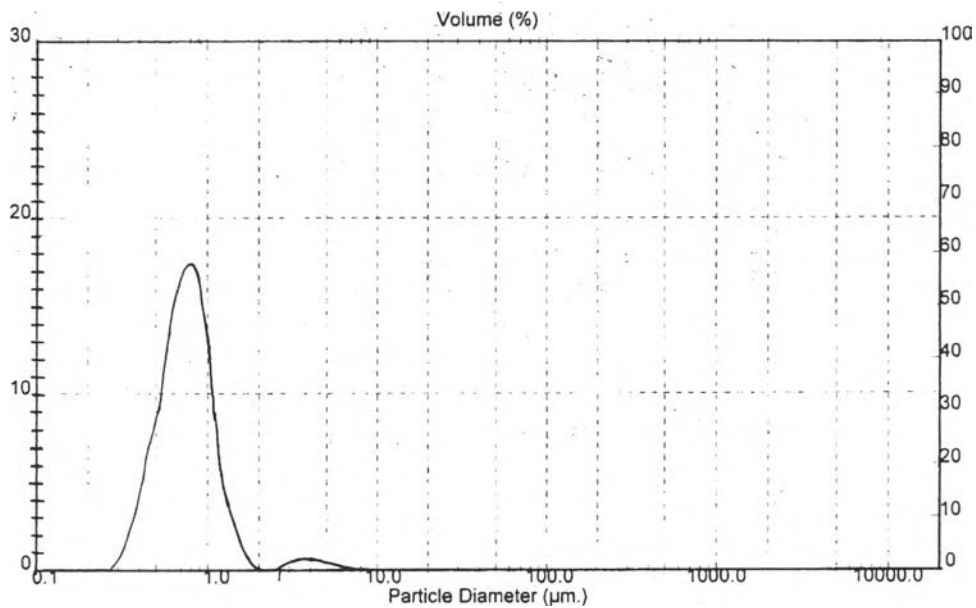


Figure 4.1 The relationship of particle diameter of NR and volume.

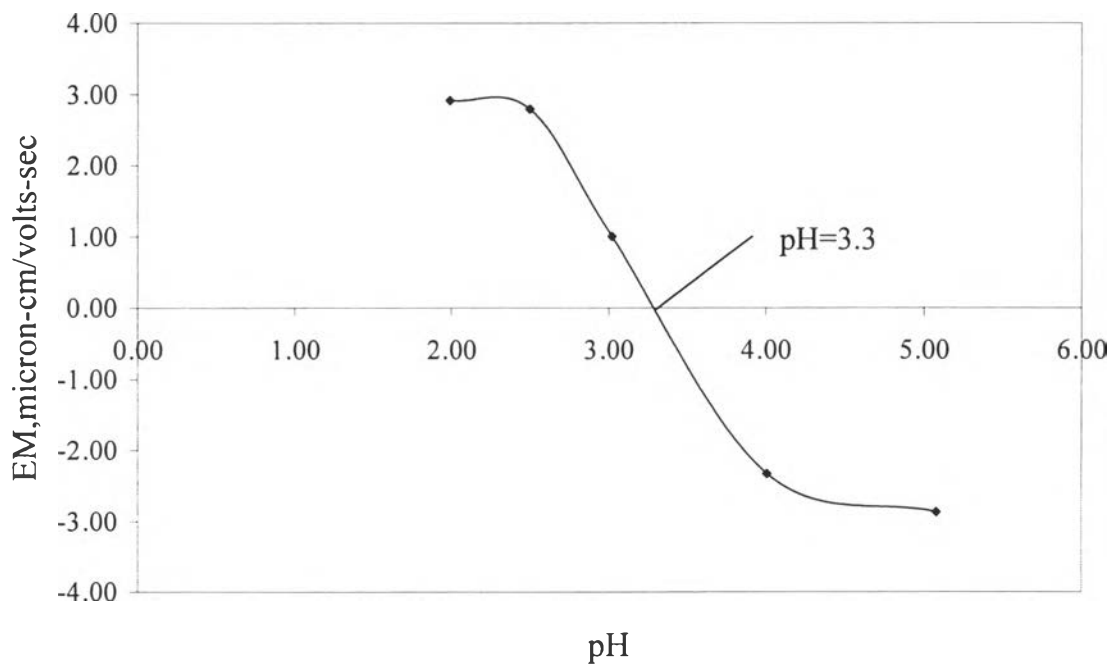


Figure 4.2 The electrophoretic mobility of NR particles in water at various pH.

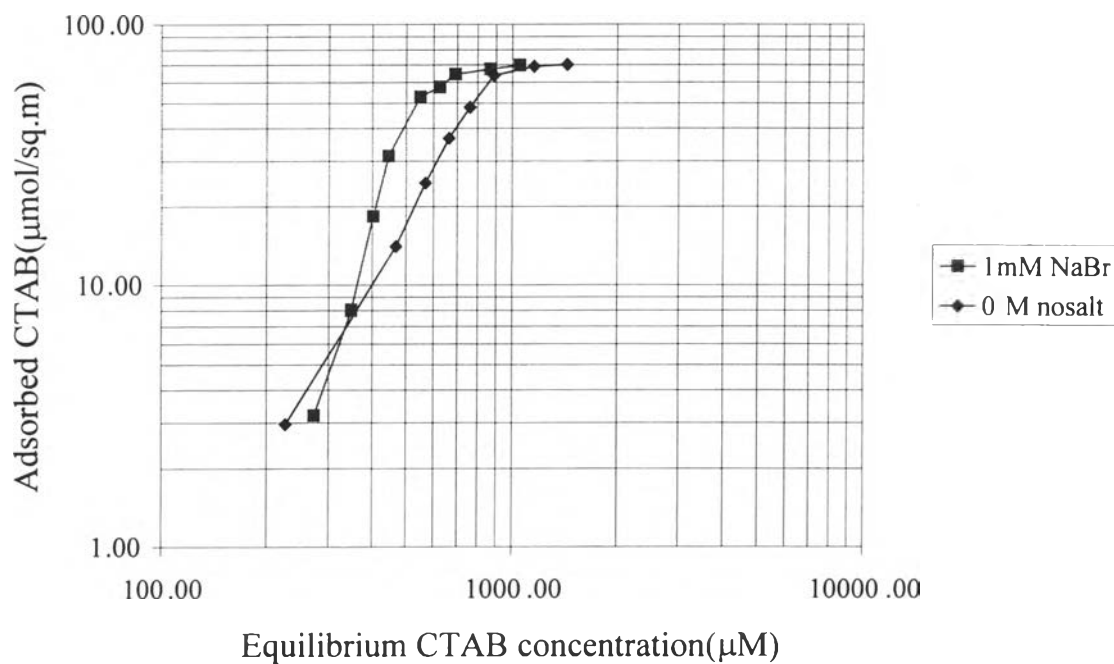


Figure 4.3 Adsorption isotherm of CTAB on NR.

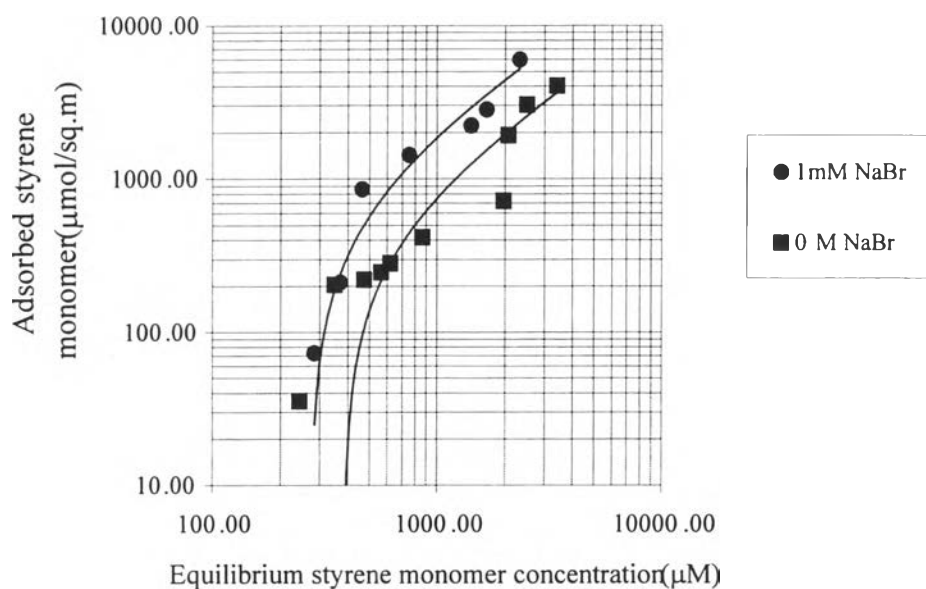
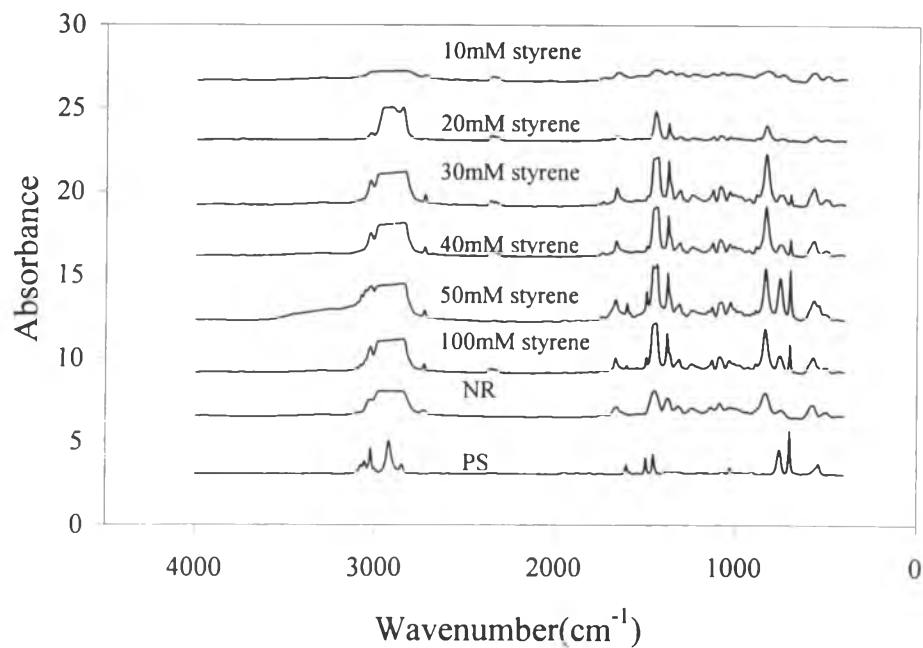
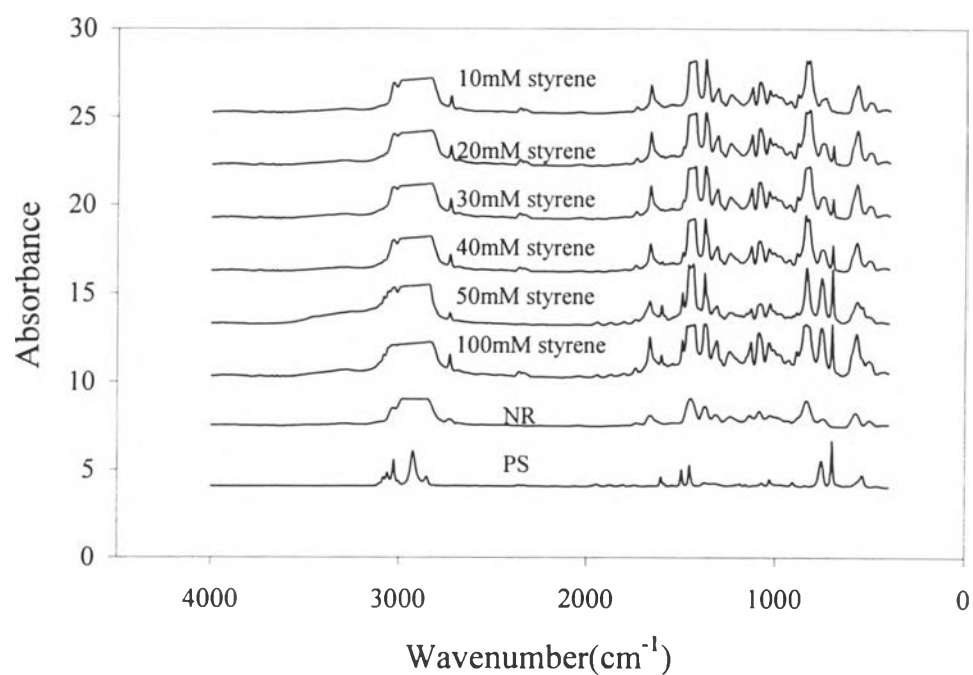


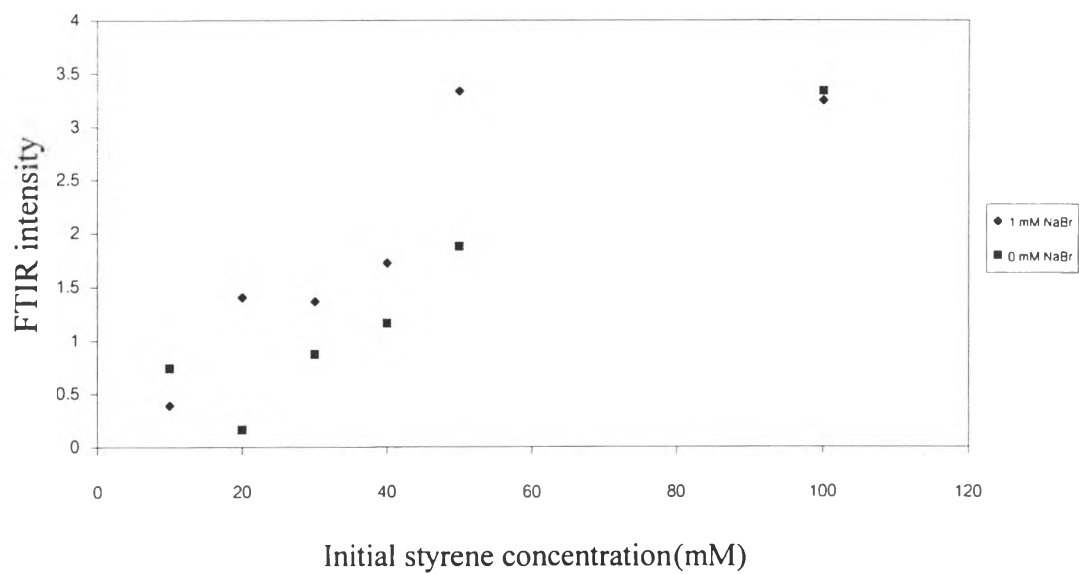
Figure 4.4 Adsolubilized isotherm of styrene monomer in CTAB aggregates.



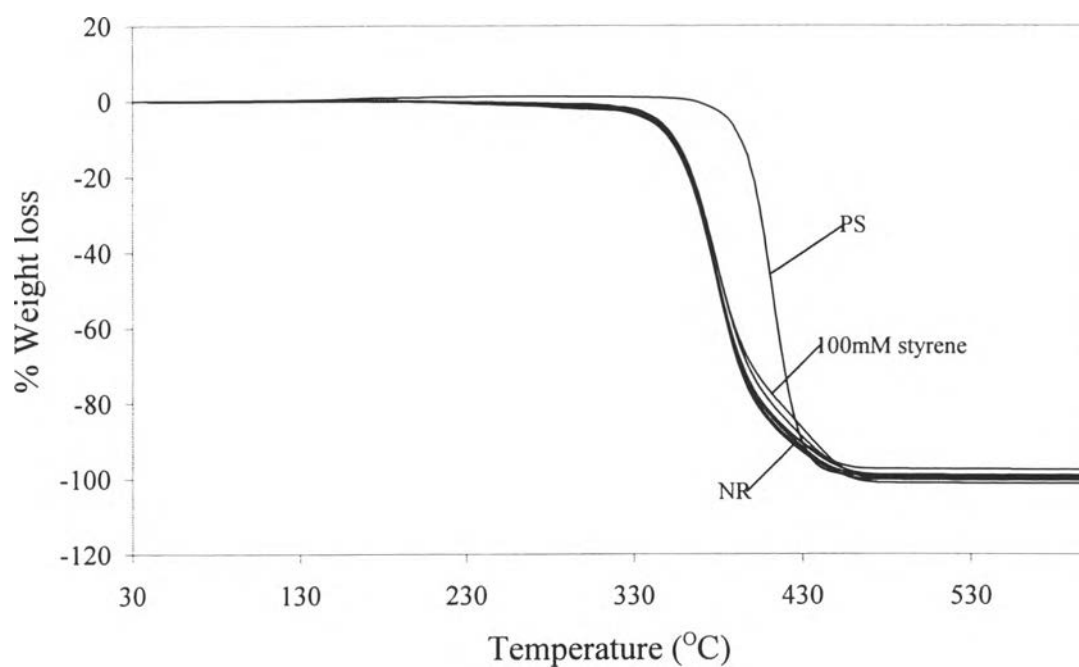
**Figure 4.5a** FT-IR spectra of PS, NR, and PS coated on NR at various %weight of PS.



**Figure 4.5b** FT-IR spectra of PS, NR, and PS coated on NR at various %weight of PS and polymerization in 1mM NaBr.

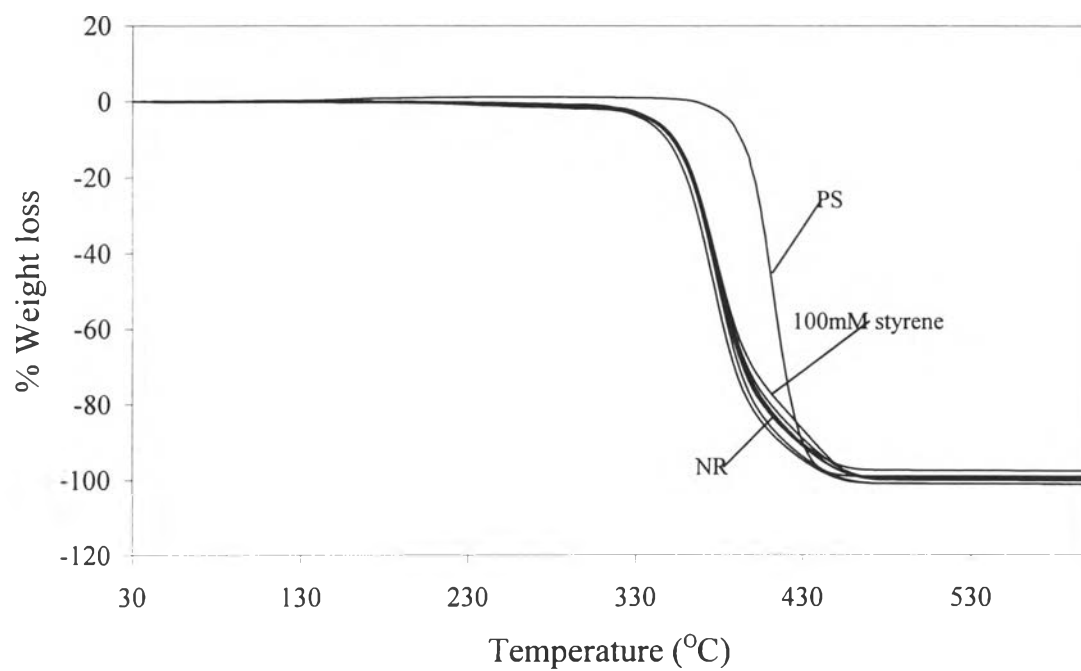


**Figure 4.5c** The relationship between FTIR intensity at  $700\text{ cm}^{-1}$  and initial styrene concentration.



**Figure 4.6a** TGA curves of pure PS, pure NR and PS coated on NR at various % weight of PS.





**Figure 4.6b** TGA curves of pure PS, pure NR and PS coated on NR at various % weight of PS and polymerization in 1mM NaBr.