CHAPTER IV

RESULTS AND DISCUSSION

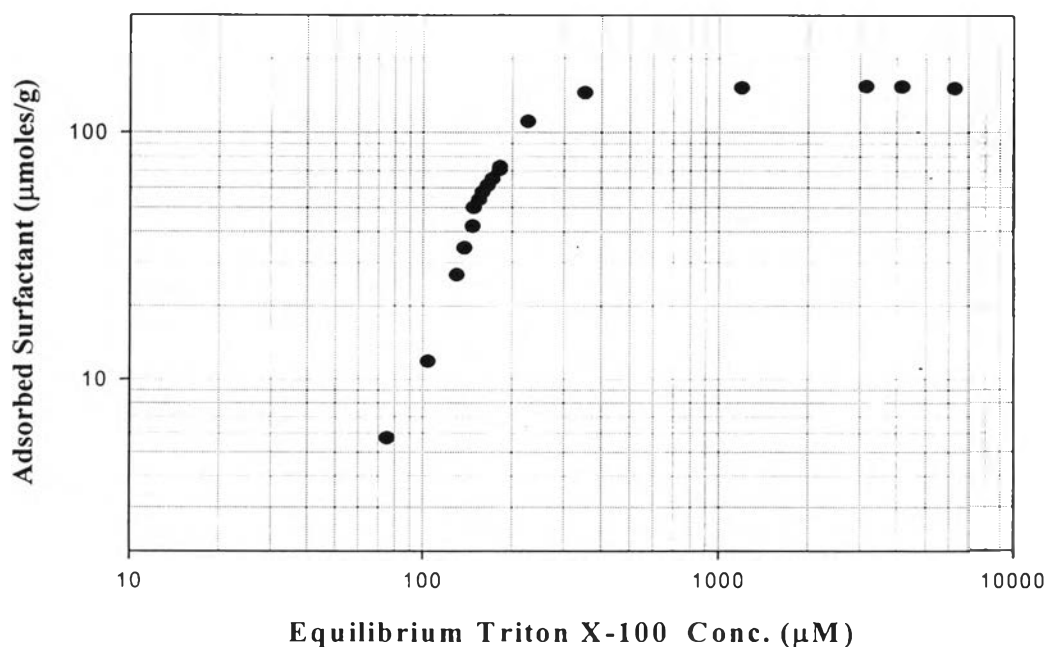## 4.1 Adsorption Isotherm of Triton X-100 on Aeroxil®OX 50

Figure 4.1 Adsorption isotherms of Triton X-100 surfactant on silica.

The adsorption isotherm of Triton X-100 on nonporous silica (Aerosil®OX50) is shown in Figure 4.1. The Triton X-100 adsorption isotherm shows the traditional sigmodial shape. The adsorption of Triton X-100 molecule on silica surface take place through hydrogen bonding between the large size of hydrophilic group and silanol group of silica. The plateau region shows the maximum adsorption of Triton X-100 approximately 150 μmol of Triton X-100 per gram of silica.

4.2 Adsolubilization of Styrene by Triton X-100 Surfactant

In the absence of surfactant, there was negligible styrene adsorption on silica (Tan and O'Haver, 2004). Whereas in the presence of surfactant the amount of adsolubilized styrene increased slowly with increasing equilibrium styrene concentration in the bulk phase. With the surfactant concentration below the CMC the isotherm was studied at two different levels of surfactant concentration which are 100 and 50 μmoles/g of silica. Figure 4.2 showed that the amount of styrene adsolubilized at high surfactant loading (100 μmoles/g of silica) was higher than at low surfactant loading only at high equilibrium styrene concentrations. However, it was difficult to say exactly what the "maximum" styrene adsolubilization was. Because the curves became nearly vertical at high styrene concentration.
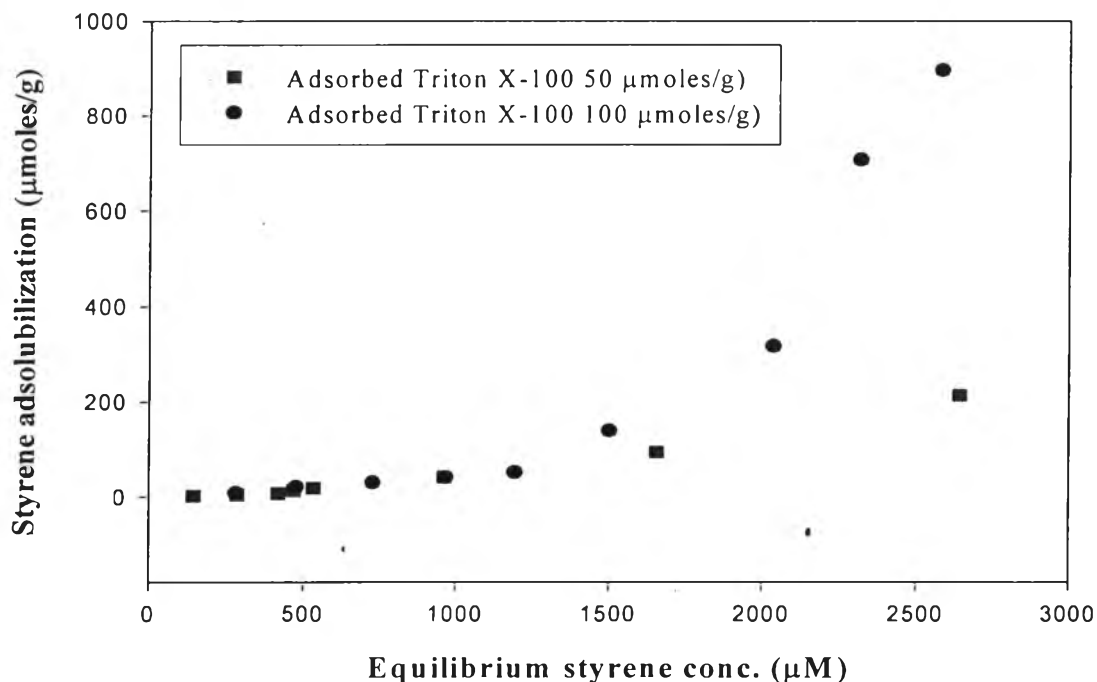

Figure 4.2 Styrene Adsolubilization isotherm in Triton X-100 surfactant.

4.3 Fourier Transform Infrared Spectroscopy Result

In order to confirm the formation of a polymeric film on the substrate, spectra of extracted material was compared to the standard polystyrene. Figure 4.3 shows the comparison between FTIR spectra of extracted material and polystyrene standard. The extracted material was extracted from modified silica conducted in the condition of Triton X-100 100 µmol/g: styrene 400 µmol/g (1:4). The results showed that the spectra of the extracted materials were fully consistent with the spectra of the polystyrene standard. In particular, they clearly showed important peaks representing the benzene ring which are aromatic C-H stretching at 3100-3000 cm^{-1}, aromatic C=C stretching at 1600 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1}, and C-H deformation (out-of-plane) at 700 cm^{-1}.
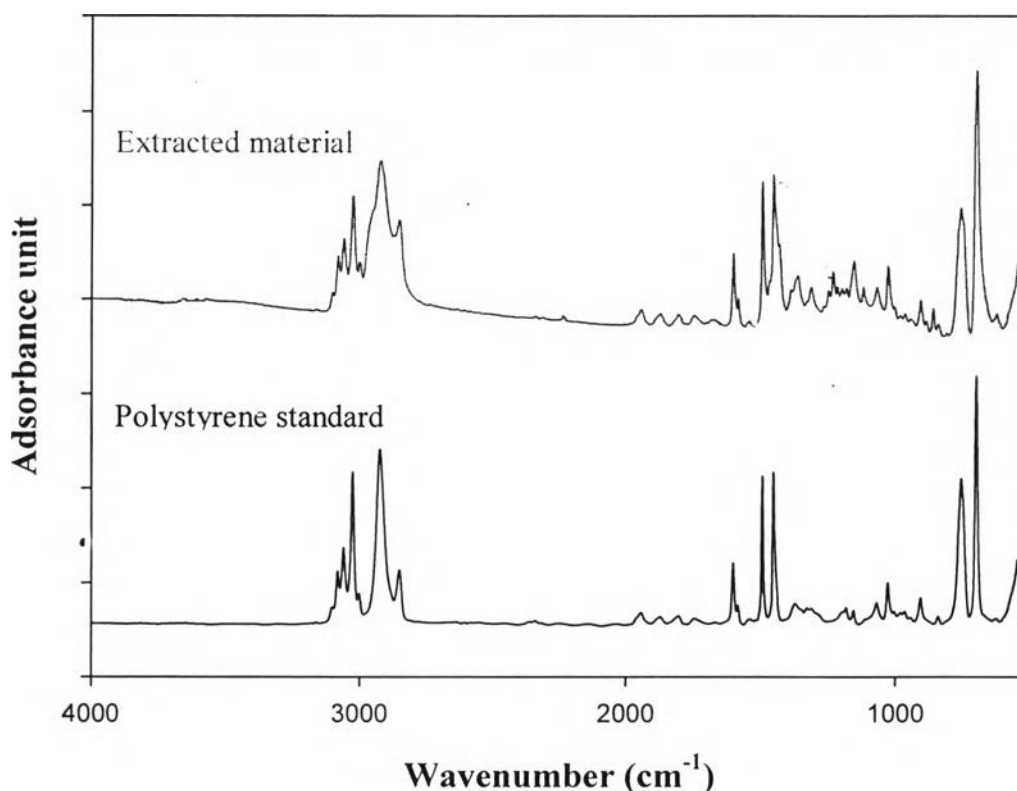
Figure 4.3 FTIR spectra of polystyrene standard and extracted material.

However, the peaks of polystyrene were not clearly represented on spectrum of the modified silica because polystyrene peaks coincide with some of the high intensity silica adsorption bands and the amount of polystyrene coated on silica particles was very low when compared to the amount of silica. So it is difficult to see the characteristic spectrum of polystyrene. Therefore, after modified silica was passed through the polymer extraction process, the extracted material was characterized. Figure 4.4 shows the spectra of polystyrene standard, Triton X-100, modified silica and unmodified silica.
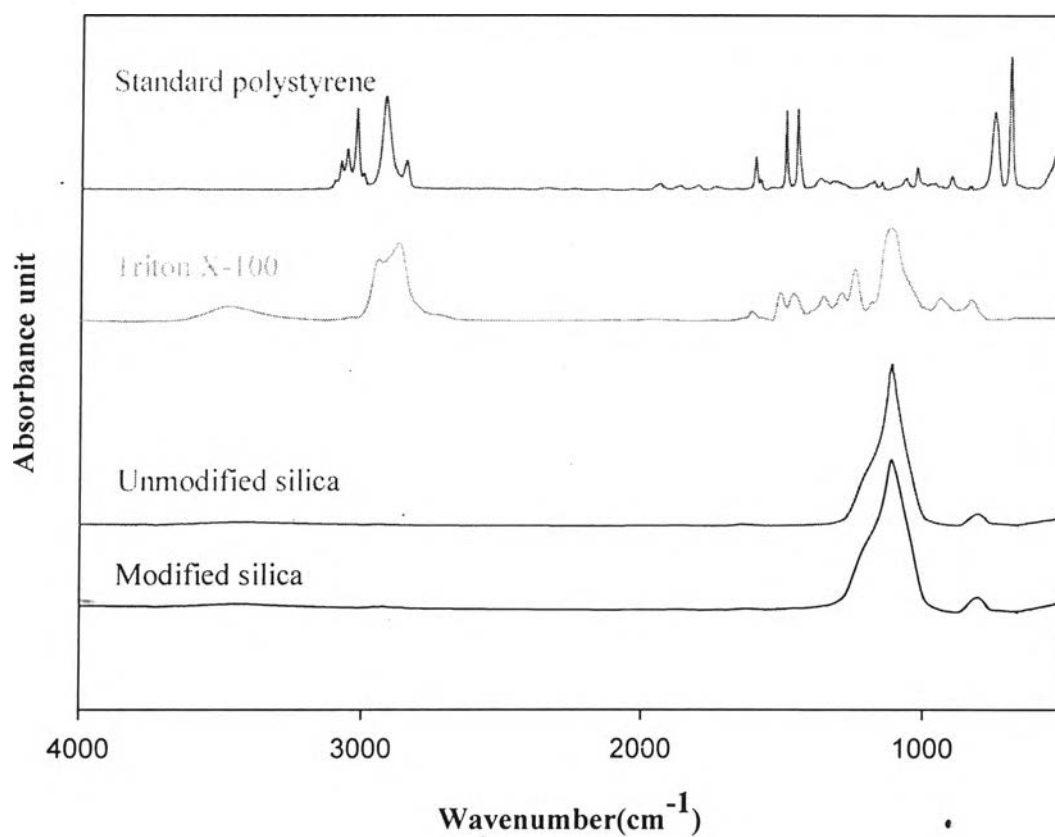

Figure 4.4 FTIR spectra of polystyrene standard, Triton X-100, Unmodified silica and modified silica.

4.4 Thermogravimetric Analysis Result

Thermogravimetric analysis was able to verify the existence of polystyrene formed on silica surface. In this work thermal stability of Triton X-100 surfactant, modified silica, extracted silica, standard polystyrene and extracted polystyrenes were studied. The results were plotted into two y-axis which are weight loss (%) and deriv.wt. (%/°C) and the degradation temperature.
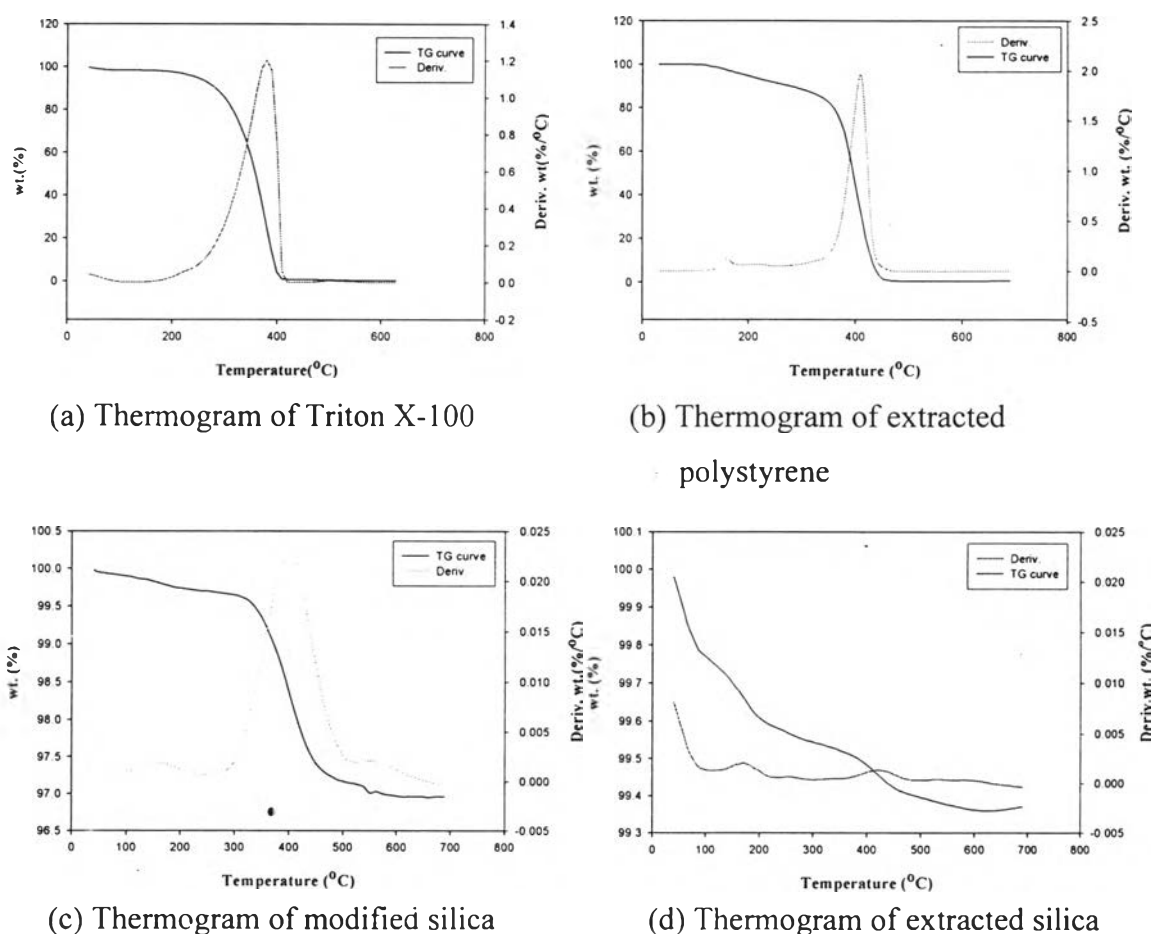

(a) Thermogram of Triton X-100

(b) Thermogram of extracted polystyrene

(c) Thermogram of modified silica

(d) Thermogram of extracted silica

Figure 4.5 (a) Thermogram of Triton X-100, (b) thermogram of extracted polystyrene, (c) thermogram of modified silica, and (d) thermogram of extracted silica.

Thermograms showed that Triton X-100 degrades in the range 200°C to 400°C while the extracted polymer degraded in the range between 300°C to 470°C. Modified silica displayed two steps of weight loss between temperature ranges of 300 °C to 600 °C. The first step degradation in the temperature of 300–450°C should be Triton X-100 and some low molecular weight polystyrene while the second loss, between 450 to 550 °C, was due to the decomposition of relatively high molecular weight polystyrene. The weight loss between 100-200°C is most likely water loss. When comparing the thermograms of modified silica before and after extraction, an absence of weight loss between 450-550 °C confirmed that both polymer and surfactant were removed from the silica particles.

Since the decomposition temperature of Triton X-100 is close to that of styrene it is difficult to measure the exact quantity of formed polystyrene from percent weight loss of TGA results.

4.5 Gel Permeation Chromatography Result

The effect of surfactant and monomer loading on the number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$), and molecular weight distribution (MWD) of the obtained polystyrene were studied by Gel permeation chromatography (GPC). These polystyrene were extracted from nonporous silica substrate which were modified by two different Triton X-100 concentrations (50 and 100 µmol/g of silica) and various monomer loading. Table 4.1 and 4.2 show $\overline{M_n}$, $\overline{M_w}$, MWD of extracted polystyrene in Triton X-100 50 and 100 µmol/g of silica respectively.

The results show that the GPC curve of extracted material are different when one compares the high and low surfactant concentrations. At low surfactant conditions (50 µmol/g of silica), the GPC curve showed only one peak which represents the low molecular weight polystyrene.

At the high surfactant condition the GPC curve showed two peaks representing high and low molecular weight polymer.

Table 4.1 $\overline{M_w}$, $\overline{M_n}$, and MWD of extracted materials produced in Triton X-100 at 50 µmol/g adsorption

Triton X-100$_{adsorp}$: Styrene$_{adsol}$ (µmol/g) (µmol/g)	First peak			Second peak		
	$\overline{M_n}$	$\overline{M_w}$	MWD	$\overline{M_n}$	$\overline{M_w}$	MWD
25:50, (2:1)	-	-	-	657	890	1.354
50:50, (1:1)	-	-	-	719	992	1.380
50:100, (1:2)	-	-	-	684	954	1.400
50:150, (1:3)	-	-	-	702	959	1.367
50:200, (1:4)	-	-	-	782	1080	1.382
50:250, (1:5)	-	-	-	794	1075	1.354
50:300, (1:6)	16053	33092	2.061	862	1210	1.404

Table 4.2 $\overline{M_w}$, $\overline{M_n}$, and MWD of extracted materials produced in Triton X-100 at 100 µmol/g adsorption

Triton X-100$_{adsorp}$: Styrene$_{adsol}$ (µmol/g) (µmol/g)	First peak			Second peak		
	$\overline{M_n}$	$\overline{M_w}$	MWD	$\overline{M_n}$	$\overline{M_w}$	MWD
100:50, (2:1)	-	-	-	774	1018	1.368
100:100, (1:1)	-	-	-	963	1180	1.225
100:200, (1:2)	11533	21147	1.834	852	1051	1.233
100:300, (1:3)	13137	32230	2.453	816	900	1.103
100:400, (1:4)	13102	42121	3.215	697	728	1.044
100:500, (1:5)	14186	42813	3.018	833	877	1.053
100:600, (1:6)	19234	45258	2.353	780	1055	1.352

Triton X-100$_{adsorp}$ = Adsorption of Triton X-100,(µmol/g) ;

Styrene$_{adsol}$ = Adsolubilization of styrene,(µmol/g)

The low molecular weight extracted polystyrene is in the range of 900-1200 g/mol while the high molecular weight polystyrene is in the range of 21000-46000 g/mol. The effect of styrene loading on the molecular weight of polystyrene in Triton X-100 concentration 50 and 100 μmol/g of silica is shown in Figures 4.6 and 4.7 respectively.

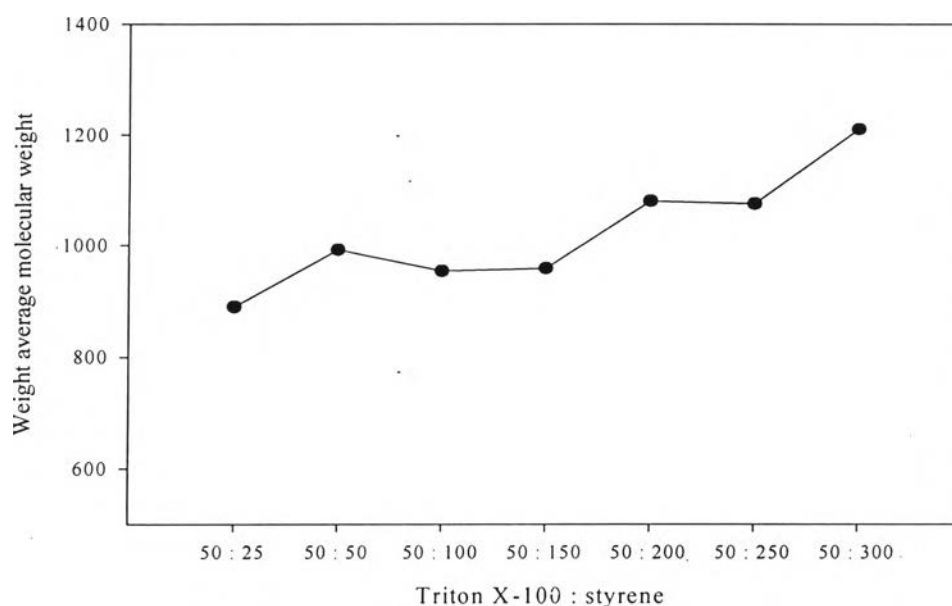**Figure 4.6** Weight average molecular weight ($\overline{M_w}$) of extracted polystyrene formed at the level of 50 μmol/g adsorbed Triton X-100 on silica.

Figures 4.6 and 4.7 show that at high levels of Triton X-100 adsorption, the molecular weight of the formed polymer is higher than at the low level of Triton X-100 adsorption. This is consistent with the idea that the admicelle will consist of larger aggregates of molecules at high adsorption levels. Thus, polymerization occurring in small aggregates will not contain sufficient monomer to form high molecular weight polymer. Also, at low levels of surfactant loading, the patchy admicelle will have more exposure to the surrounding water which should increase water penetration into the admicelle and thus the rate of termination.

Moreover, due to the large size of hydrophilic group of non-ionic surfactant, the surfactant will lie prone on the silica substrate at low surfactant concentration making it more difficult for the monomer to solubilize in the hydrophobic region.

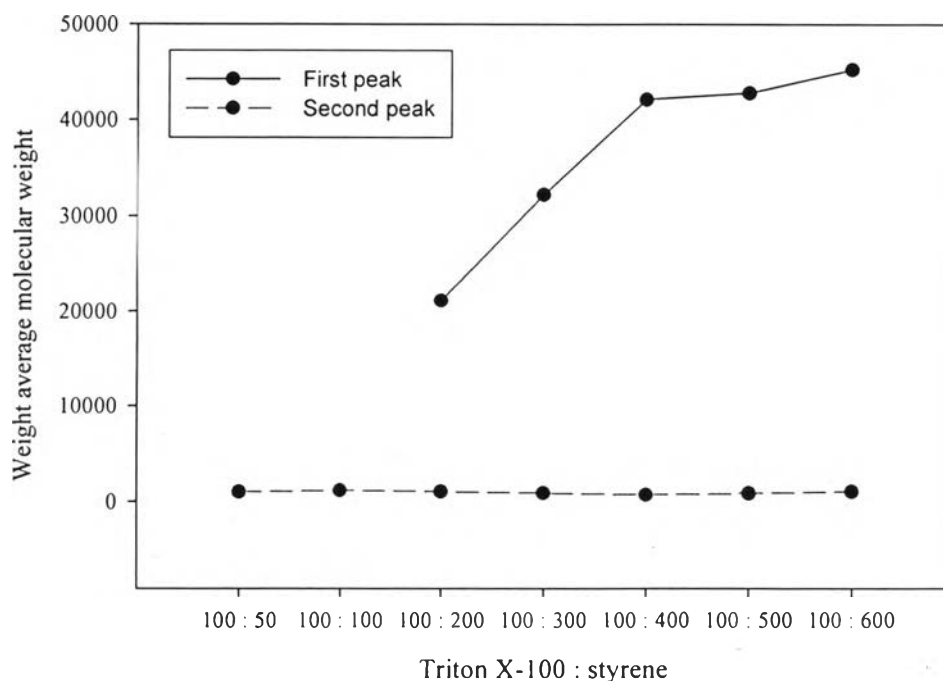Therefore, to obtain high molecular weight polymer, a high level of Triton X-100 adsorption is preferable.

Figure 4.7 Weight average molecular weight ($\overline{M_w}$) of extracted polystyrene formed at the level of 100 μmol/g adsorbed Triton X-100 on silica.

In the same way, high levels of monomer loading causes an increase in molecular weight. As the density of styrene in the admicelle increases, it increases the likelihood of polymer diffusing into active chains before termination. The monomers will have greater mobility and are in closer proximity to react more in the bilayer. At low levels of monomer loading, the styrene monomer are spread out in the admicelle and the chances for two styrene monomers to collide are reduced making the formation of higher molecular weight polymer unlikely.

Thus, in the competition between diffusion and termination, high monomer loading and high surfactant loading allow for the formation of high molecular weight polymer.

4.6 Atomic Force Microscopy Result

Unmodified and modified silicas were studied by AFM in order to determine the distribution and characteristics of the polymer film formed. Film thickness was measured using topographic images while confirmation of the presence of polymer can be obtained through a combination of both topographic and phase images. The topographic image of tapping mode image was interpreted by changing the oscillating amplitude of the tip during a tip tapped on the sample surface. The phase image can be used to interpret the hardness of sample surface. "Soft" samples will be seen as darker contrast regions while hard regions will appear brighter in contrast.

Figure 4.8 shows the atomic force microscopy image of unmodified silica. The micrograph shows the aggregated silica particles with a surface that is uniformly similar in hardness. The darker regions at the edges of the primary silica particles in the phase images represent the edge of the silica particles. The delay in the phase image is caused by the tip having to travel longer distances to reach down into the valleys between the primary particles. In order to maintain the constant force or constant distance between tip and surface, the tapping frequency will be delayed, which shows as a lower phase shift, thus appearing as darker regions in the phase image, much the same as polymer film.
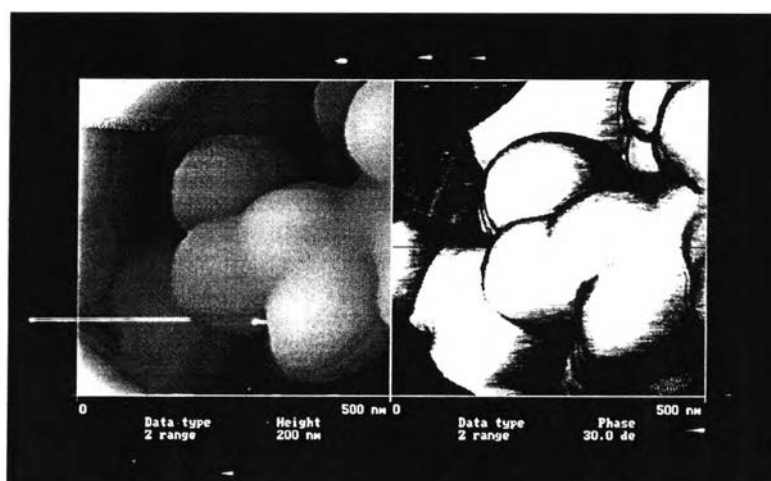
Figure 4.8 Atomic force micrograph of unmodified silica.

Figure 4.9 and 4.10 show the atomic force microscopy of silica modified by a system including 100 μmol/g adsorbed Triton X-100 and 600 and 500 μmol/g adsolubilized styrene, a ratio of adsorbed surfactant to adsolubilized monomer of 1:6 and 1:5 respectively. The silica particles are nearly encapsulated with polystyrene polymer which can be distinguished by the lighter regions in the topographic image and the darker regions in the phase image. The average thickness of the polystyrene film is approximately 7.5 nm.
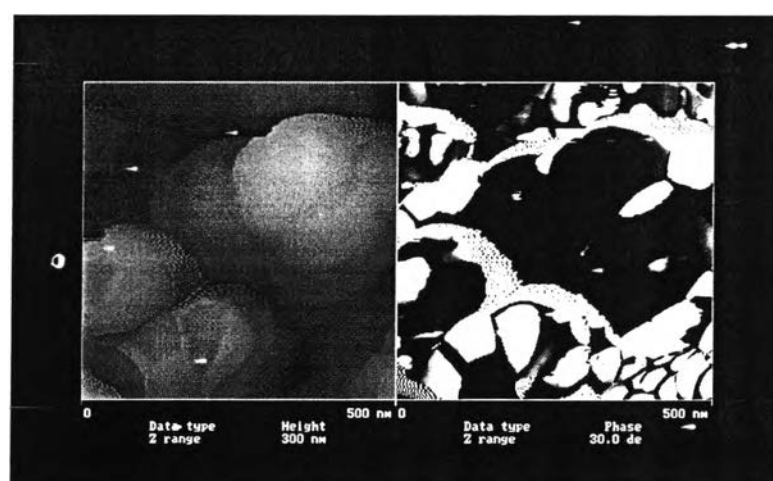
Figure 4.9 Atomic force micrograph of silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 600 μmol/g. (1:6).
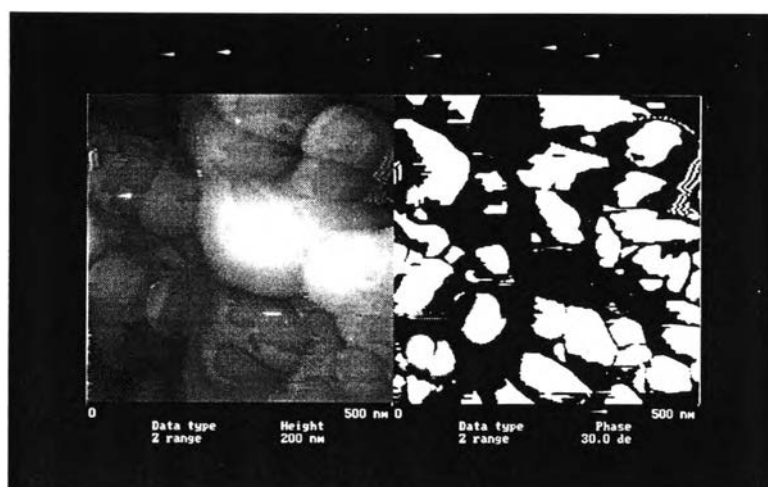
Figure 4.10 Atomic force micrograph of silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 500 μmol/g (1:5).
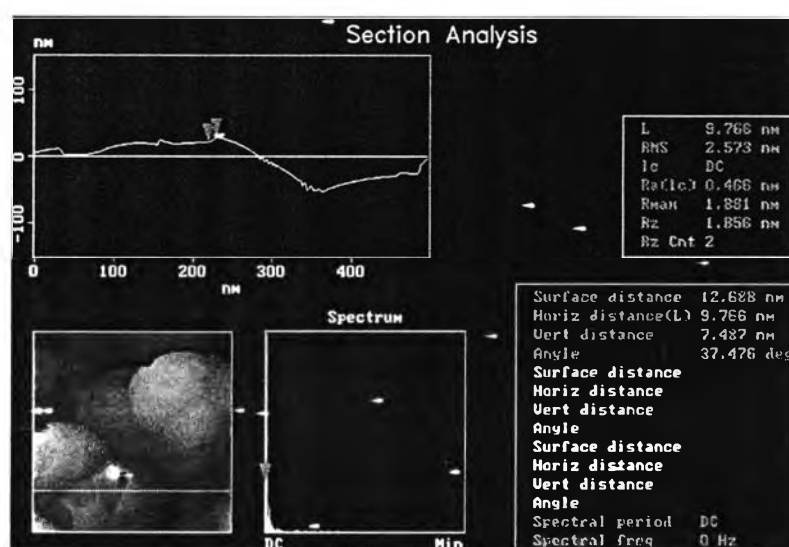

Figure 4.11 Thickness of polystyrene film measured on silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 600 μmol/g. (1:6).

Figure 4.12 shows the AFM image of silica modified by a system consisting of 100 μmol/g adsorbed Triton X-100 and 400 μmol/g adsolubilized styrene, a surfactant to monomer ratio of 1:4. The micrograph shows a non-continuous film that is concentrated in the "valleys" of the silica but also extends as patches onto the surface, as can be seen by the darker areas in the phase image.

However, the average thickness of film is approximately 6 nm, which is not much difference the first system or by that modified at a ratio of 1:6 (100 μmol/g adsorbed Triton X-100 to 600 μmol/g adsolubilized styrene).

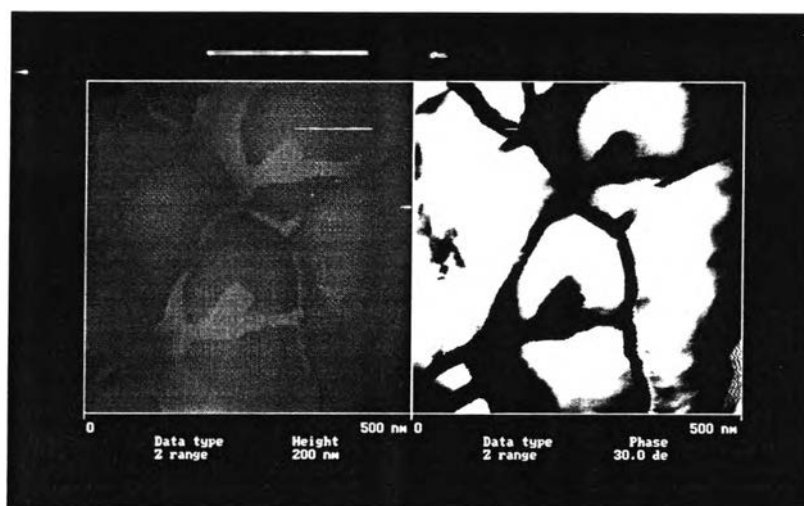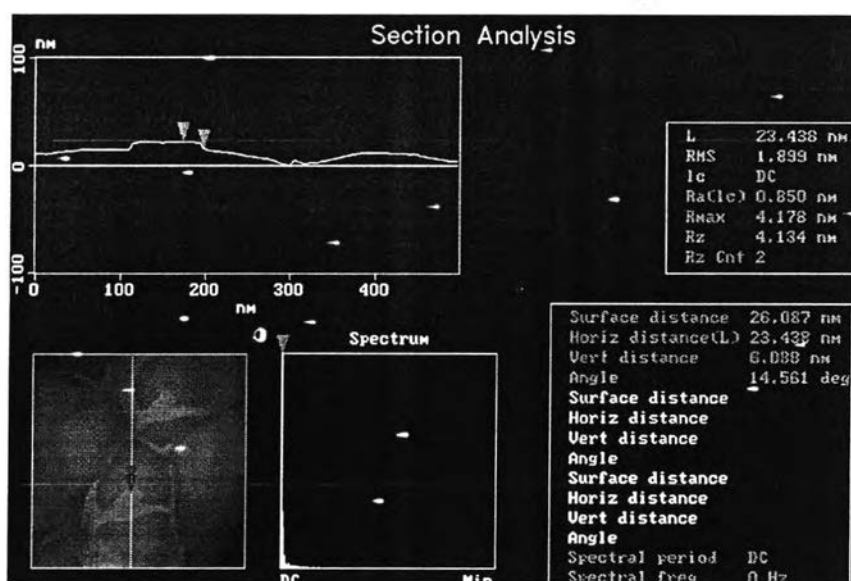**Figure 4.12** Atomic force micrograph of silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 400 μmol/g (1:4).

Figure 4.13 Thickness of polystyrene film measured on silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 400 μmol/g. (1:4).

Figure 4.14 shows the AFM image of silica modified by 100 µmol/g adsorbed Triton X-100 and 200 µmol/g adsolubilized styrene (1:2 ratio). The micrograph shows a thin polystyrene film. This film is concentrated in valleys of the silica and extends somewhat onto the surface. However, the average thickness of film is approximately 3 nm which is thinner than silica modified by and adsorbed Triton X-100 100 µmol/g to adsolubilized styrene 400, 500, and 600 µmol/g of silica.
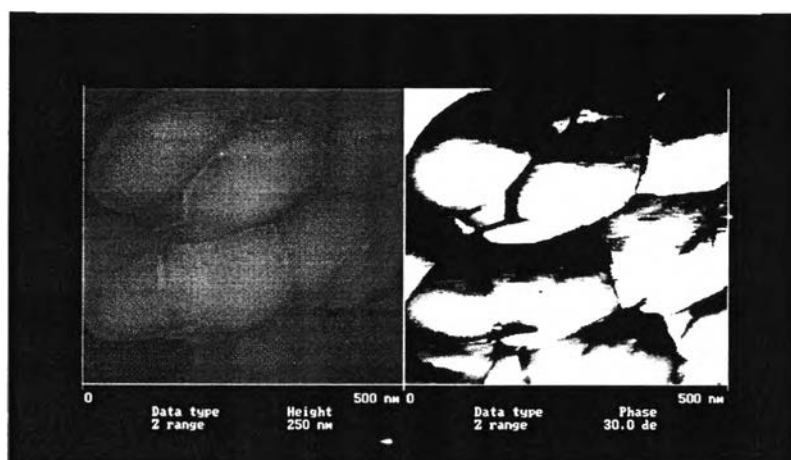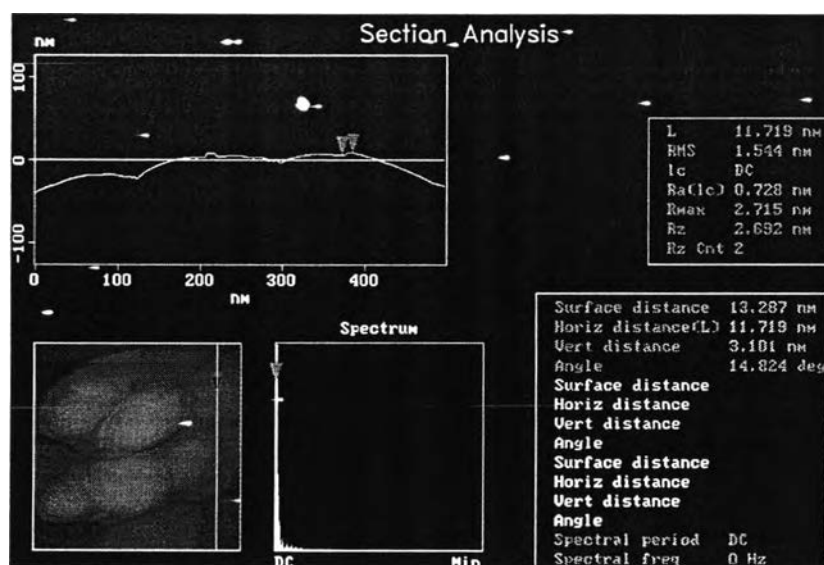

Figure 4.14 Atomic force micrograph of silica modified by an adsorbed Triton X-100 100 µmol/g to adsolubilized styrene 200 µmol/g (1:2).

Figure 4.15 Thickness of polystyrene film measured on silica modified by an adsorbed Triton X-100 100 µmol/g to adsolubilized styrene 200 µmol/g. (1:2).

When the ratio of adsorbed Triton to adsolubilized styrene is reduced to 2:1, 100 μmol/g Triton, 50 μmol/g adsolubilized styrene, the polystyrene film is observed only in the "valleys" between the primary silica particles.(Figure 4.16)
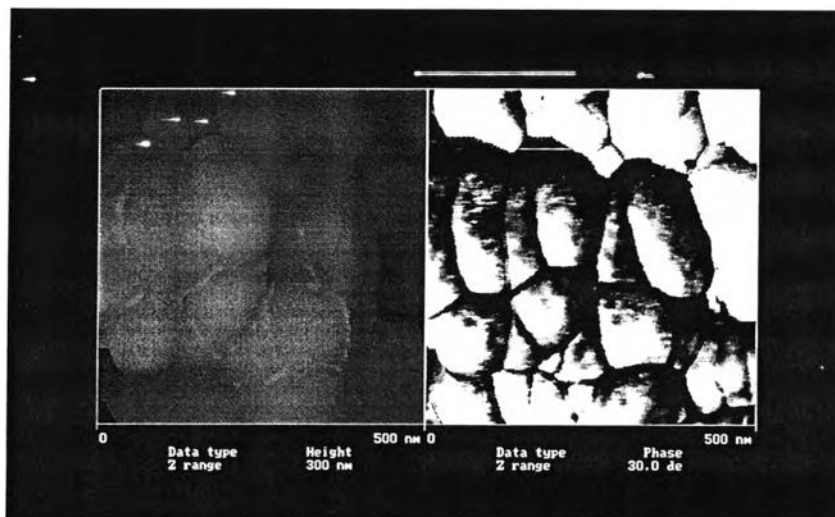

Figure 4.16 Atomic force micrograph of silica modified by an adsorbed Triton X-100 100 μmol/g to adsolubilized styrene 50 μmol/g (2:1).
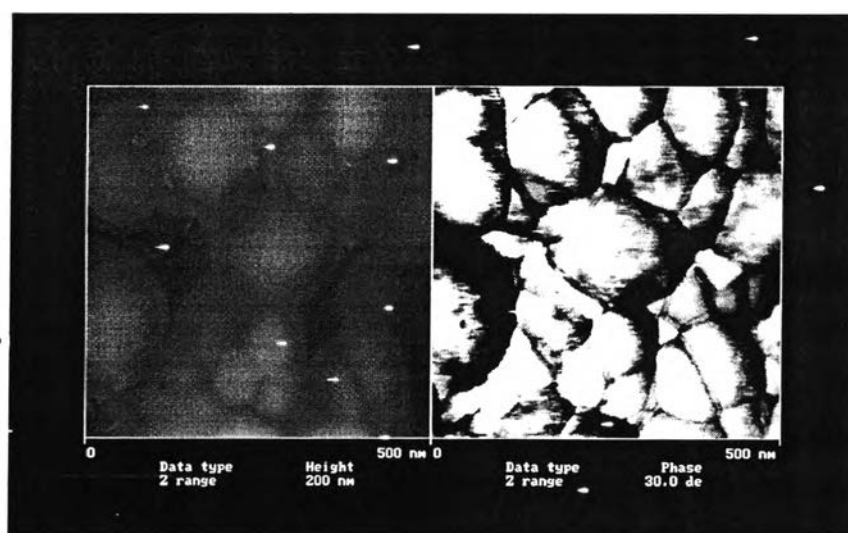

Figure 4.17 Atomic force micrograph of silica modified by an adsorbed Triton X-100 50 μmol/g to adsolubilized styrene 25 μmol/g (2:1).

When you compare Figure 4.16 to the Figure 4.17, which is a system with 50 μmol/g Triton X-100 and 25 μmol/g adsolubilized styrene (2:1, low Triton). The image shows that the polystyrene film is barely observed, even in the valleys between silica particles.

Thus, higher surfactant and higher monomer loading causes a thicker, and more extensive, polymer film, as would be expected. The average thickness of polystyrene is in the range of 3-8 nm.

AFM images were also used to confirm the efficiency of the extraction process. Figure 4.18 is typical of a silica which has had the polymer extracted by THF. As can be seen, no polymer patches are observed and the silica looks like the unmodified silicas.
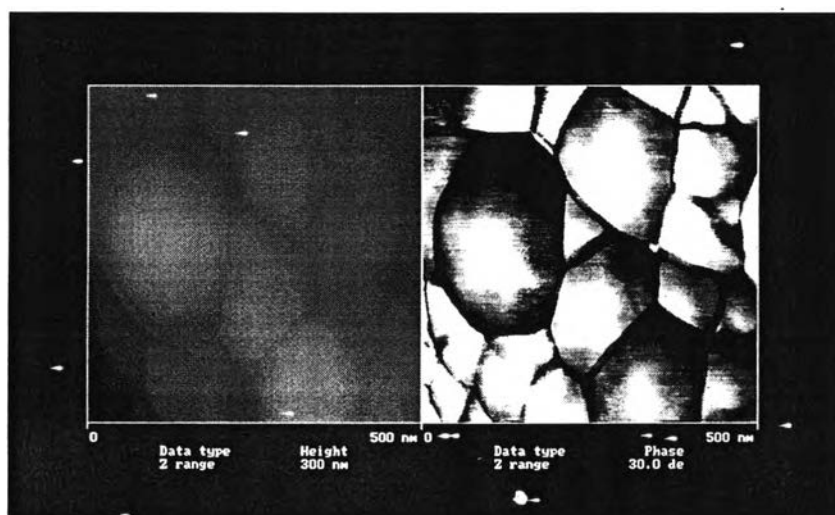

Figure 4.18 The extracted silica.