CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorption isotherm

The adsorption isotherm of CTAB on nonporous silica (Aerosil® OX50) is shown in Figure 4.1. The CTAB adsorption isotherm illustrates regions II, III and IV of the standard adsorption isotherm(Rosen,1989). Plateau adsorption is approximately 130 μmol CTAB per gram silica.

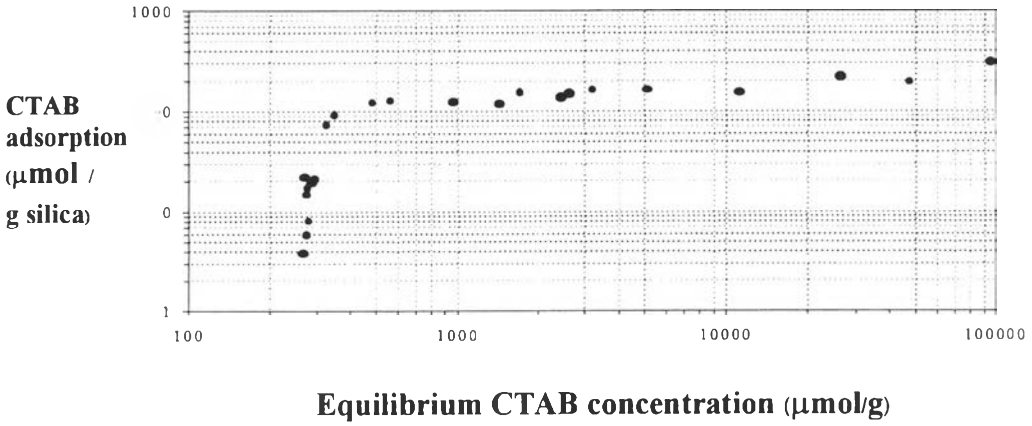

Figure 4.1 CTAB adsorption isotherm on nonporous silica.

4.2 Adsolubilization isotherm

The increase in equilibrium styrene concentration with increasing bulk styrene concentration is nearly is nearly linear. As the amount adsorbed surfactant was increased, the amount of adsolubilized styrene also increased, as shown in Figure 4.2.

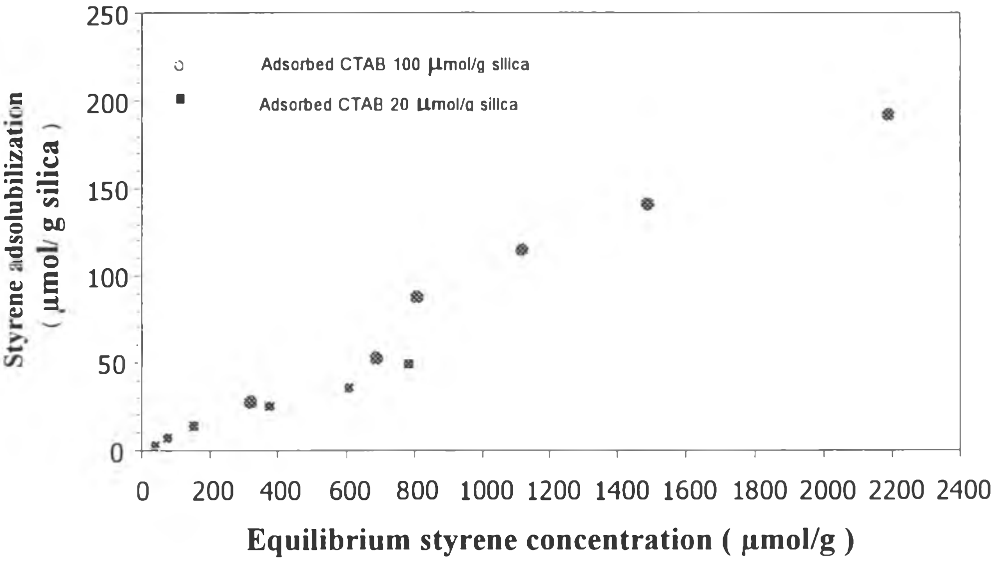

Figure 4.2 Adsolubilization isotherm of styrene in CTAB admicelles at 20 and 100 μmol/g of adsorbed surfactant.

4.3 Polymer characterization

4.3.1 Fourier Transform Infrared Spectroscopy Result (FITR)

The presence of polystyrene on the modified silica surface was confirmed by FTIR. The spectrum of unmodified silica, CTAB, modified silica and extracted material are shown in Figures 4.3, 4.4, 4.5 and 4.6, respectively.

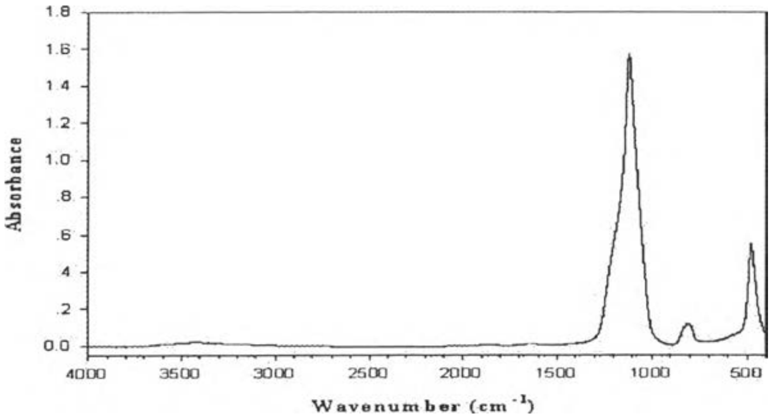

Figure 4.3 FTIR spectrum of unmodified silica.

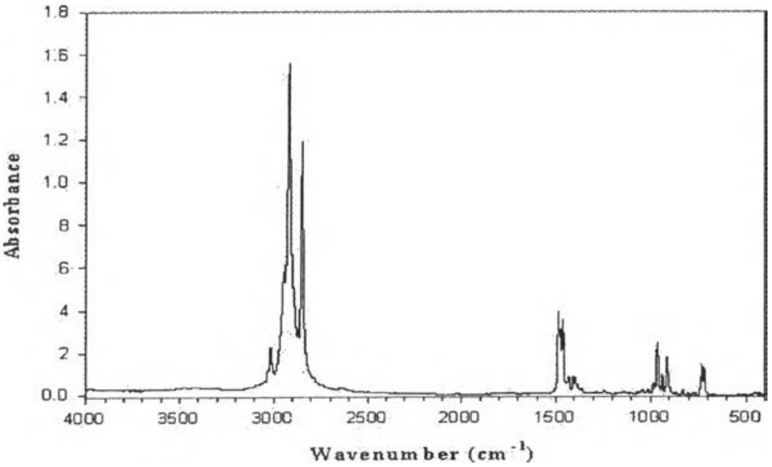

Figure 4.4 FTIR spectrum of CTAB.

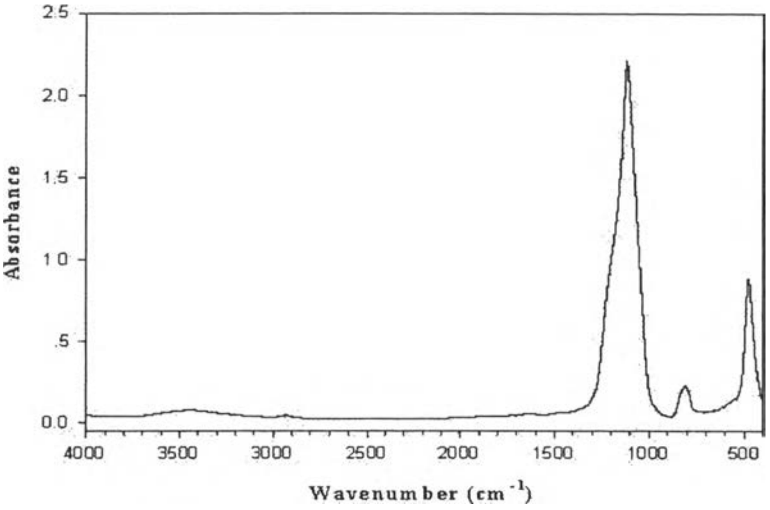

Figure 4.5 FTIR spectrum of modified silica.

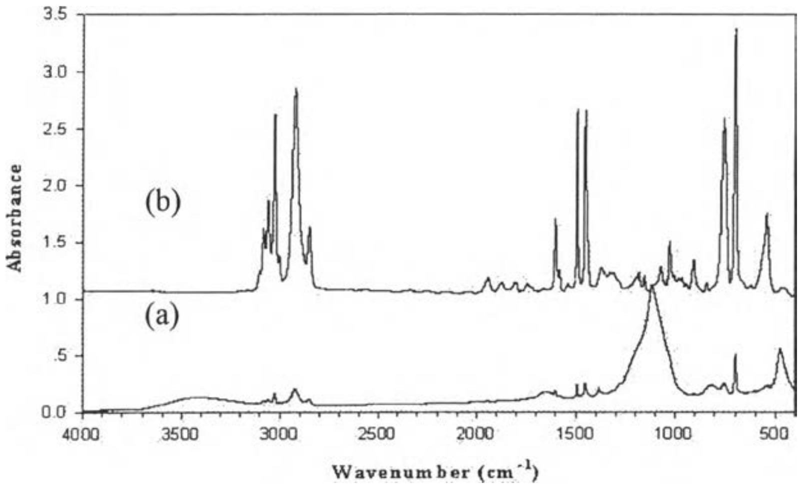

Figure 4.6 FTIR spectrum of (a) extracted material and (b) polystyrene standard.

The spectrum of modified silica (Fig 4.5) shows small absorbance peak of methylene C-H stretching in the range of 2926-2856 cm^{-1}, confirming the presence of polystyrene on silica particle. However, all of the characteristic polystyrene peaks are not clearly represented because of the interference from silica in those absorption bands. Figure 4.6 shows a comparison of FTIR spectra of extracted material and a polystyrene standard. The result shows that all peaks observed from extracted material were consistent with the characteristic polystyrene peaks, that is: aromatic C-H stretching at 3100-3000 cm^{-1}, aromatic C=C stretching at 1602 cm^{-1}, 1493 cm^{-1}, 1454 cm^{-1} and out of plane aromatic C-H bending at 699 cm^{-1}.

4.3.2 Thermogravimetric Analysis Result (TGA)

TGA was used to study the thermal stability of extracted polystyrene and to quantify the amount of polystyrene formed. Figure 4.7, 4.8, 4.9 and 4.10 show thermograms of unmodified silica, CTAB, modified silica and extracted material (under N_2 atmosphere), respectively.

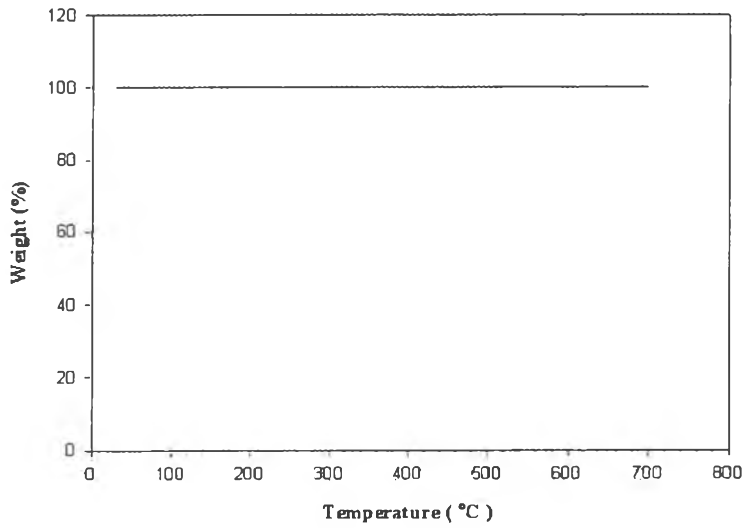

Figure 4.7 Thermogram of unmodified silica.

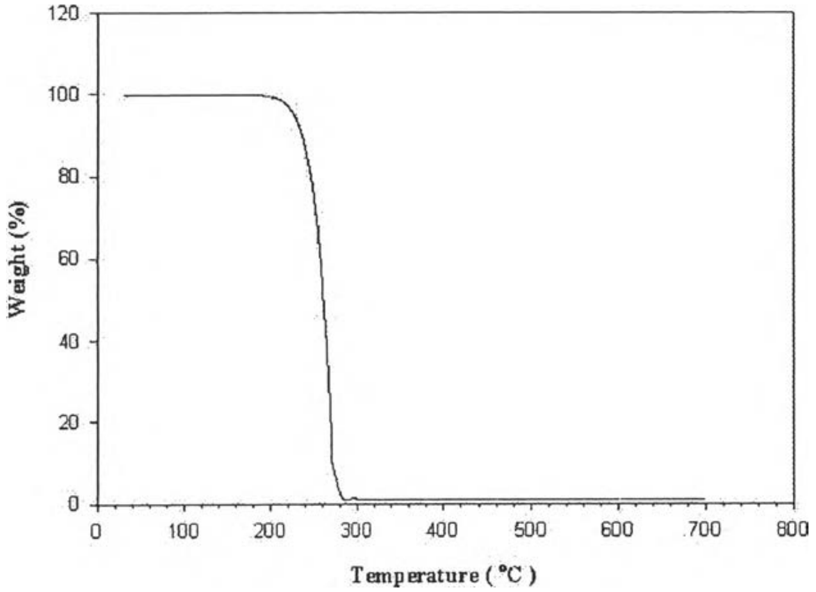

Figure 4.8 Thermogram of CTAB.

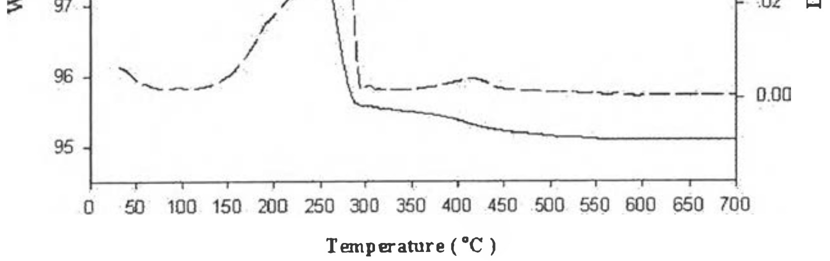

Figure 4.9 Thermogram of modified silica.

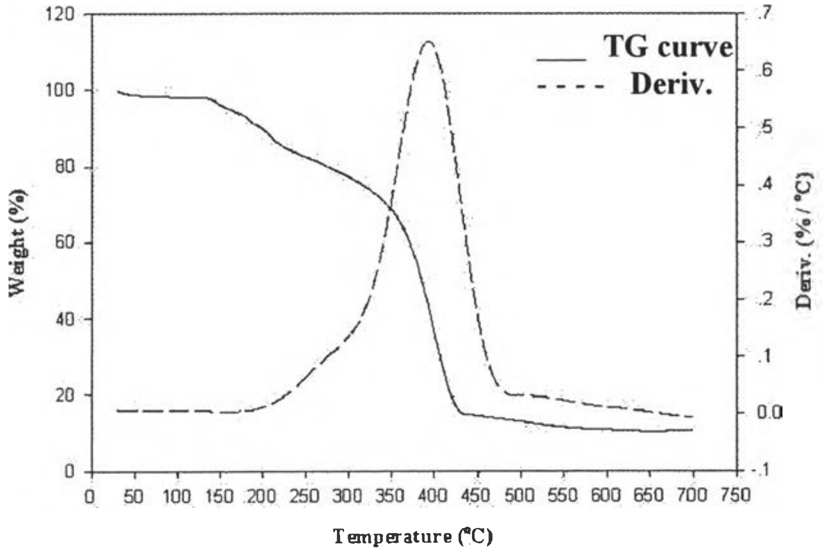

Figure 4.10 Thermogram of extracted material.

The unmodified silica shows no weight loss in the temperature range of 30-700 °C. Figure 4.8 shows that the degradation of CTAB occurs between 200-300 °C. The thermogram of modified silica shows a 2-step degradation, step 1 from 150-300 °C and step 2 from 350-470 °C. The first step appears to be the degradation of CTAB and the second step due to the degradation of polystyrene on the silica. This is supported by the data in Figure 4.10 which show that the extracted polystyrene degrades in the range 300-470 °C. The degradation below 300 °C may be from the loss of low molecular weight polystyrene or radical end chains.

Table 4.1 shows the amount of polystyrene formed by admicellar polymerization at two hours reaction time. The results suggest that when the concentration of the initiator decreased, the amount of formed polystyrene slightly decreased. At constant initiator concentration, the amount of polystyrene formed on silica particles clearly increased as the amount of styrene feed increased.

Table 4.1 % weight of polystyrene formed on silica particle obtained from TGA result

Adsorbed CTAB (μmol/g)	AIBN : Styrene Ratio	Weight of PS (%, w/w silica) at CTAB: adsolubilized styrene ratio of 2:1	% yield of PS formed	Weight of PS (%, w/w silica) at CTAB: adsolubilized styrene ratio of 1:2	% yield of PS formed
20	1:1	-	-	0.42/0.60	70.0
	1:5	-	-	0.36/0.60	60.0
	1:7	-	-	0.25/0.60	41.7
	1:10	-	-	0.26/0.60	43.3
	1:15	-	-	0.24/0.60	40.0
	1:20	-	-	0.21/0.60	35.0
	1:25	-	-	0.23/0.60	38.3
	1:50	-	-	0.10/0.60	16.7
100	1:1	0.54/0.66	81.8	2.27/2.50	90.8
	1:5	0.45/0.66	68.2	1.55/2.50	62.0
	1:7	0.42/0.66	63.6	0.31/2.50	19.0
	1:10	0.21/0.66	31.8	0.34/2.50	13.6
	1:15	0.23/0.66	34.8	0.35/2.50	14.0
	1:20	0.18/0.66	27.3	0.25/2.50	10.0
	1:25	0.17/0.66	25.8	0.21/2.50	8.4
	1:50	0.11/0.66	16.7	0.15/2.50	6.0

4.3.3 Gel Permeation Chromatography Result (GPC)

Extracted material was characterized by GPC to study the effects of initiator, surfactant, and styrene feed concentrations on the molecular weight of the formed polymer.

Tables 4.2 and 4.3 show the number average molecular weight (Mn), weight average molecular weight (Mw), and molecular weight distribution (MWD) of material extracted from the admicellar polymerization modified silicas. These modified silicas were formed at two CTAB concentrations (20 and 100 μmol/g) and at different initiator and monomer loadings.

The GPC curve of extracted materials showed two peaks of different retention times which indicated two different molecular weight ranges of polymer. The two peaks observed were Mw's in the ranges of 134,000 to 5000 gmol^{-1} and 1200-230 gmol^{-1} . The second peak is consistent with the molecular weight of CTAB and that of low molecular weight polymer. Since, during the extraction process, we expect to get both polystyrene and surfactant, we expect to see both in the GPC results.

Figure 4.11 and 4.12 show the molecular weight of polystyrene formed by a two-hour admicellar polymerization at an adsorbed CTAB to adsolubilized styrene ratio of 1:2 and at CTAB adsorption levels at 20 and 100 μmol/g, respectively.

Figure 4.13 shows the molecular weight of polystyrene formed by a two-hour admicellar polymerization at an adsorbed CTAB to adsolubilized styrene ratio of 2:1 and CTAB adsorption at 100 μmol/g.

From Figures 4.11 to 4.13, the effect of initiator, surfactant and styrene loading can be seen. The results show that as the initiator concentration decreased, the molecular weight of the polystyrene tended to increase, as would be expected. More initiator means the formation of more active chains, which would lower the molecular weight of each chain. However, at AIBN to styrene ratios lower than 1:15, the molecular weight of the formed polymer started to decrease. We believe this is because there is a competition within the admicelle between the reaction kinetics and diffusion into the admicelle from the bulk and diffusion within the admicelle for styrene monomers. Thus, initiation occurs within the admicelle and begins to consume monomer. As it is consumed, additional monomer diffuses in from the bulk and the surrounding admicelle. It appears that with the given reaction kinetics, when the initiator to monomer ratio is below 1:15, then the polymer chains terminate faster than monomer can diffuse in, causing a drop in the molecular weight. From this, we suggest that, for the given admicellar polymerization reaction, the ratio of the initiator to styrene should not be less than 1:15 if the goal is to obtain high molecular weight polymer.

When we compare Figures 4.11 and 4.12, we see that at the higher level of CTAB adsorption, the molecular weight of the formed polymer is higher than at the low level of CTAB adsorption. We propose that this is because the admicelle is "patchy" on the surface, that is, composed of scattered aggregates which are not continuous. Thus, some polymerizations will occur in small aggregates that do contain sufficient monomer to form high molecular weight polymer. The patchy admicelle will have more exposure to water surrounding it and this should increase the rate of termination. Thus, to obtain high molecular weight polymer, a high level of CTAB adsorption is preferable.

Comparing all three figures, one can see that increased monomer loading causes the expected increase in molecular weight. High monomer loading levels cause the CTAB bilayer to swell and the density of styrene per CTAB molecule increases. The monomer has more mobility to react more within the swollen bilayer as well as having a high concentration. Thus, in the competition between diffusion and termination, high molecular weight polymer can form in most cases.

However from the Figures 4.11, 4.12, and 4.13, the results suggest that when surfactant loading and monomer loading increase, the molecular weight of polymer formed also increased.

Table 4.2 Mw, Mn, and MWD of extracted materials formed at $CTAB_{adsorp}$: $Styrene_{adsol}$ = 1 : 2 for two hours reaction time

Ratio of AIBN:Styrene	High CTAB adsorption (100 μmol/g)						Low CTAB adsorption (20 μmol/g)					
	First peak			Second peak			First peak			Second peak		
	Mn	Mw	MWD	Mn	Mw	MWD	Mn	Mw	MWD	Mn	Mw	MWD
1:1	2852	7172	2.51	251	264	1.06	N/A	N/A	N/A	-	-	-
1:5	11000	22000	2.00	-	-	-	226	306	1.35	-	-	-
1:7	17157	54532	3.17	201	269	1.33	239	321	1.34	-	-	-
1:10	N/A	N/A	N/A	N/A	N/A	N/A	232	316	1.36	-	-	-
1:15	49903	134118	2.68	230	264	1.14	468	516	1.10	-	-	-
1:20	N/A	N/A	N/A	N/A	N/A	N/A	445	501	1.12	-	-	-
1:25	22325	47035	2.10	853	1294	1.51	256	341	1.33	-	-	-
1:50	1904	2487	1.30	249	297	1.19	N/A	N/A	N/A	-	-	-

$CTAB_{adsorp}$ = Adsorption of CTAB bilayer (μmol/g) , $Styrene_{adsol}$ = Adsolubilization of styrene (μmol/g)

N/A = the amount of extracted material is not enough for characterization.

Table 4.3 Mw, Mn, and MWD of extracted materials formed at $\mathrm{CTAB}_{\mathrm{adsorp}}$: $\mathrm{Styrene}_{\mathrm{adsol}}$ = 2 : 1 for two hours reaction time

Ratio of AIBN:Styrene	High CTAB adsorption (100 μmol/g)						Low CTAB adsorption (20 μmol/g)					
	First peak			Second peak			First peak			Second peak		
	Mn	Mw	MWD	Mn	Mw	MWD	Mn	Mw	MWD	Mn	Mw	MWD
1:1	1537	2499	1.62	209	235	1.12	238	330	1.38	-	-	-
1:5	N/A	N/A	N/A	N/A	N/A	N/A	274	371	1.36	-	-	-
1:7	232	296	1.27	-	-	-	516	580	1.13	-	-	-
1:10	209	260	1.24	-	-	-	N/A	N/A	N/A	-	-	-
1:15	207	239	1.15	-	-	-	N/A	N/A	N/A	-	-	-
1:20	208	247	1.16	-	-	-	405	502	1.28	-	-	-
1:25	N/A	N/A	N/A	-	-	-	-	-	-	-	-	-
1:50	-	-	-	-	-	-	-	-	-	-	-	-

$\mathrm{CTAB}_{\mathrm{adsorp}}$ = Adsorption of CTAB bilayer (μmol/g) , $\mathrm{Styrene}_{\mathrm{adsol}}$ = Adsolubilization of styrene (μmol/g)

N/A = the amount of extracted material is not enough for characterization.

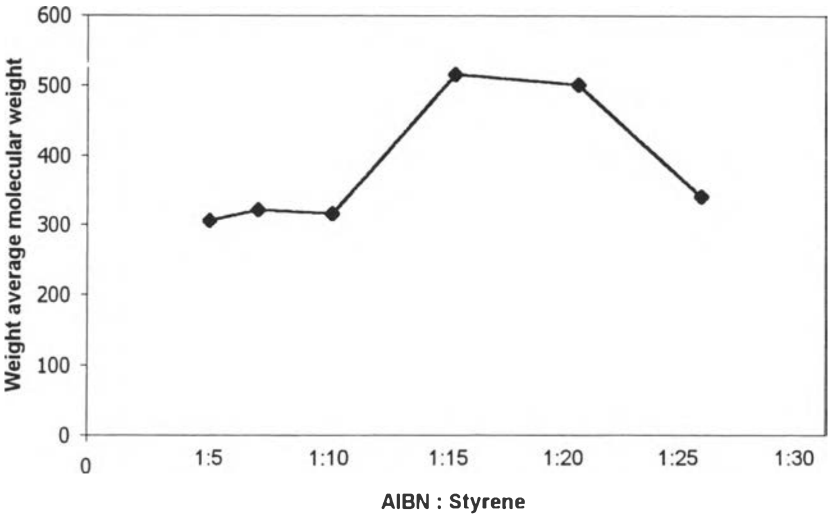

Figure 4.11 Molecular weight of extracted material formed at adsorbed CTAB of 20 µmol/g and the ratio of CTAB adsorbed to styrene adsolubilized at 1 : 2.

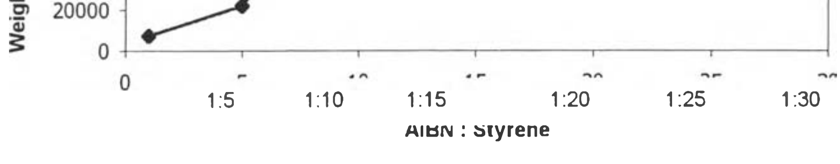

Figure 4.12 Molecular weight of extracted material formed at adsorbed CTAB of 100 µmol/g and the ratio of CTAB adsorbed to styrene adsolubilized at 1 : 2.

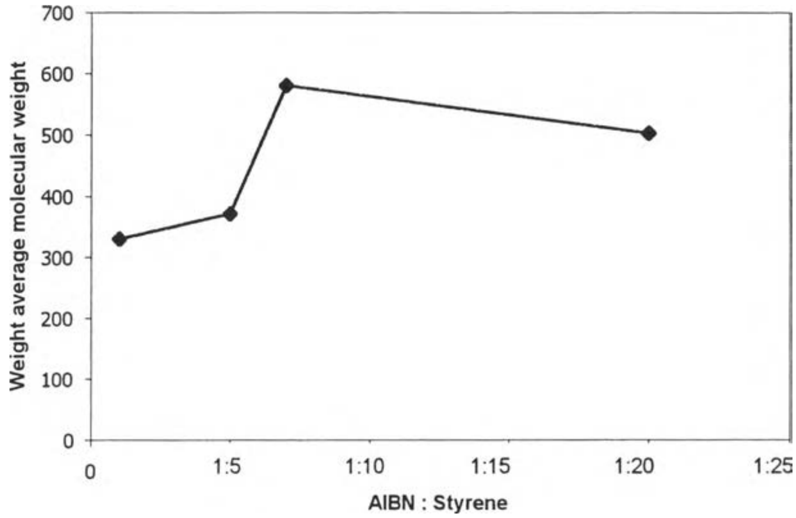

Figure 4.13 Molecular weight of extracted material formed at adsorbed CTAB of 100 μmol/g and the ratio of CTAB adsorbed to styrene adsolubilized at 2 : 1.

4.3.4 Atomic Force Microscopy Result (AFM)

Modified silicas and extracted material were characterized by AFM to determine the effect of initiator and monomer loading. The results show two types of images, topographic image and phase image.

Figure 4.14 shows the atomic force microscopy image of unmodified silica. The micrograph shows only the aggregated silica particles with no distinguishing features in the phase image, indicating that the whole surface is similar in hardness. The darker regions in the phase image represent the edge of the silica particles. At constant tapping force, or constant tapping oscillating amplitude, the tip must travel further to reach the "valleys" between the primary particles. In order to maintain the constant force or constant distance between tip and surface, the tapping frequency is thus delayed, which shows up as a phase shift, appearing as darker regions, much the same as polymer films.

Figure 4.15 shows the Atomic force micrograph of silica modified with an adsorbed CTAB to adsolubilized styrene ratio of 1:2, two hours reaction time, with an initiator to styrene ratio of 1:1. The micrograph shows that the silica particle is 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.

Figure 4.16 shows the atomic force micrograph of silica modified by an adsorbed CTAB to adsolubilized styrene ratio of 2:1 (100 μmol/g:50μmol/g), two hours reaction time, and an initiator to styrene ratio of 1:1. Uneven patches of polystyrene can be seen coating the "valleys" between silica particles.

Figure 4.17 shows the atomic force micrograph of silica modified by an adsorbed CTAB to adsolubilized styrene ratio of 1:2 (100 μmol/g:200μmol/g), two hours reaction time, and an initiator to styrene ratio of 1:50. Uneven patches of polystyrene on the silica surface are not easily seen in the topographic image but clearly shown in the phase image as darker areas.

The effects of styrene loading on the morphology of the formed polystyrene film were investigated at the high CTAB level (100 μmol/g). Comparing Figures 4.15 and 4.16, one can see that, as the amount of styrene increased, more of the surface was covered by polymer, as is clearly shown by the darker areas in the phase image.

The effects of initiator concentration were also studied. Comparing Figures 4.15 and 4.17, one can see that, as the initiator concentration increased, the area coverd by polystyrene films on the silica particle also increased.

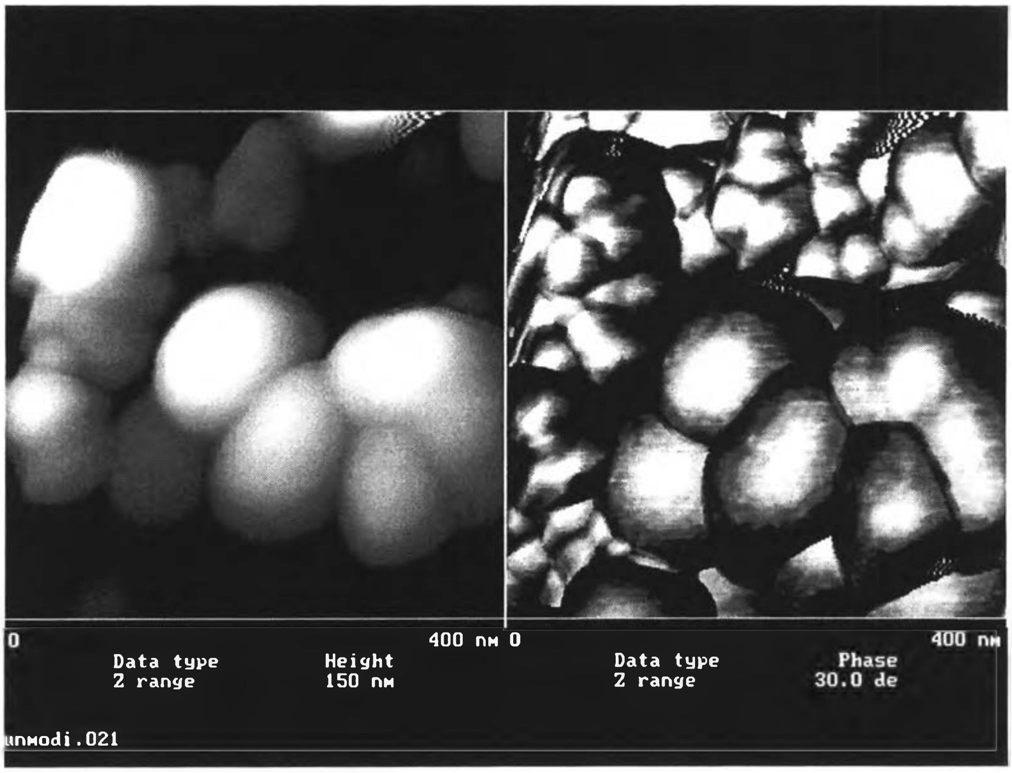

Figure 4.14 Atomic force micrograph of unmodified silica.

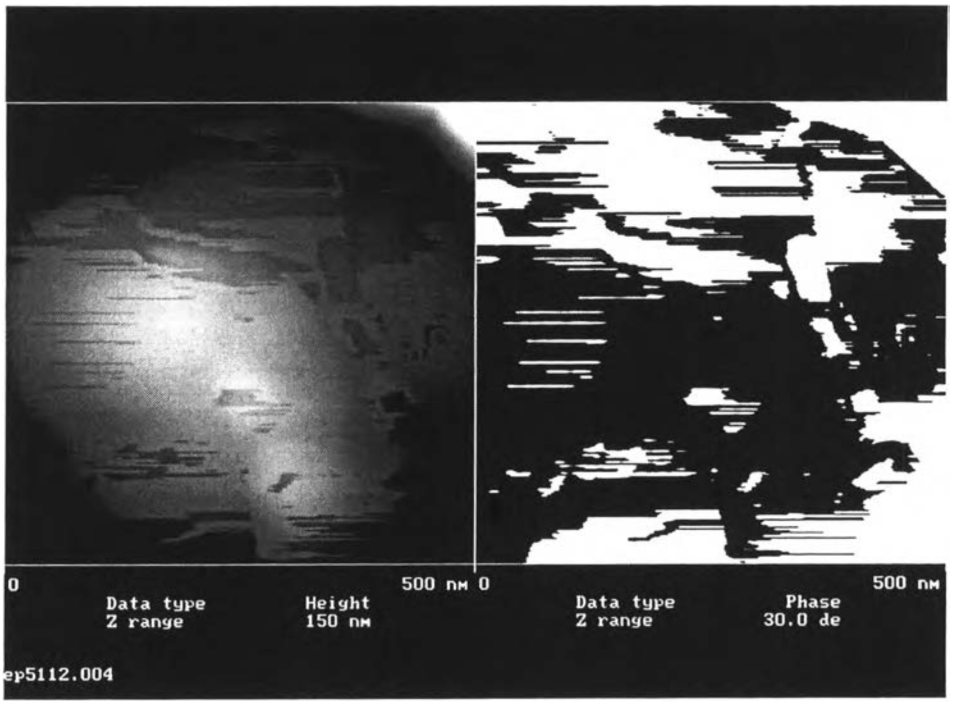

Figure 4.15 Atomic force micrograph of silica modified at an adsorbed CTAB to adsolubilized styrene ratio of 1:2 (100 μmol/g : styrene 200 μmol/g), two hours reaction time, and an initiator to styrene ratio of 1:1. The surface is covered by the polystyrene film.

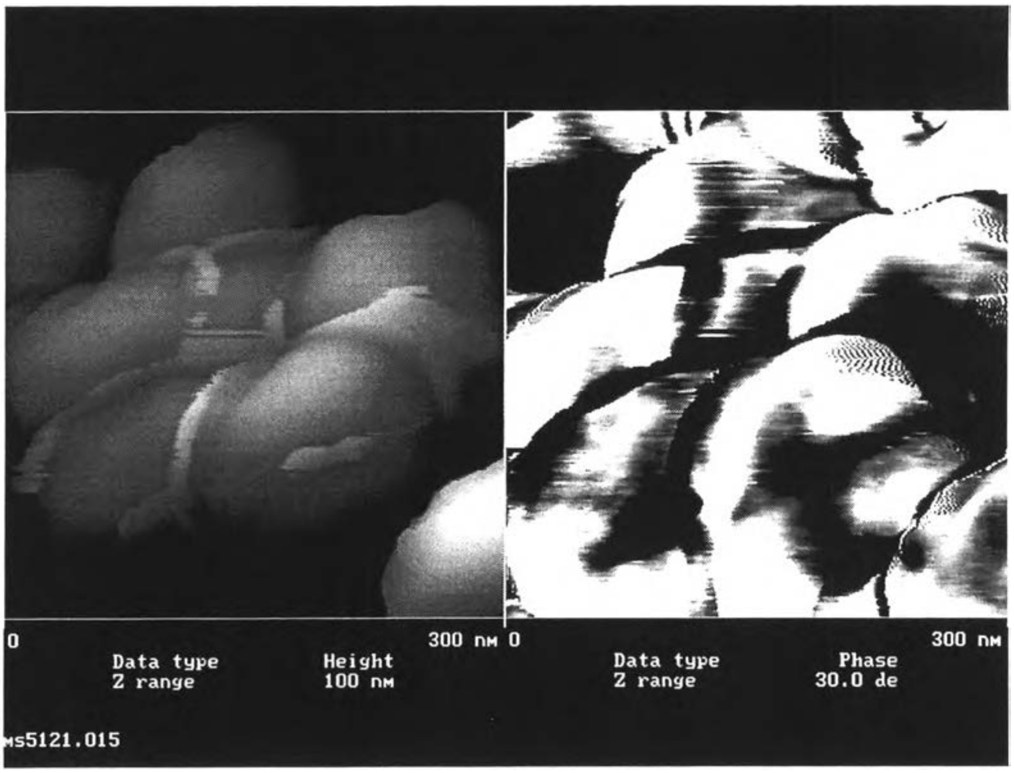

Figure 4.16 Atomic force micrograph of silica modified by an adsorbed CTAB to adsolubilized styrene ratio of 2:1 (100 μmol/g : 50 μmol/g), two hours reaction time and an initiator to styrene ratio of 1:1. Polystyrene film is evident in the "valleys" between the silica particles.

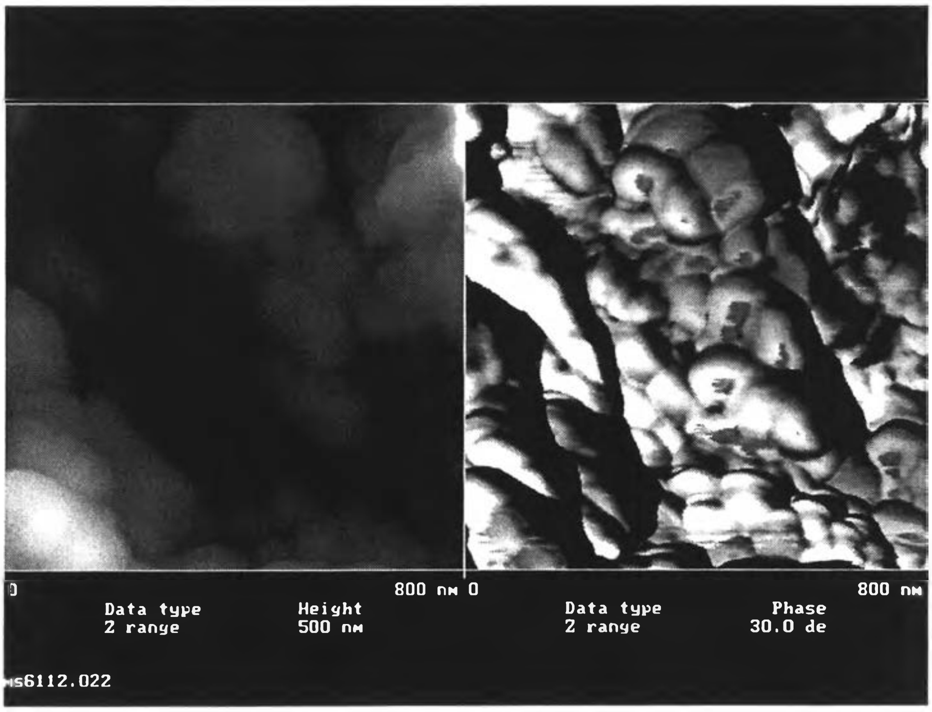

Figure 4.17 Atomic force micrograph of silica modified by an adsorbed CTAB to adsolubilized styrene ratio of 1:1 (100 μmol/g:100 μmol/g), two hours reaction time and an initiator to styrene ratio of 1:50. Uneven patches of polystyrene coated on silica particle.