



CHAPTER IV RESULTS AND DISCUSSION

4.1 Adsorption Isotherm of CTAB on Aerosil®OX50

Figure 4.1 shows the adsorption isotherm of CTAB on nonporous silica (Aerosil®OX50). The CTAB adsorption isotherm illustrates three regions II, III and IV of the standard isotherm. The plateau region shows the maximum amount of CTAB on silica is ~ 130 μmol of CTAB per gram of silica.

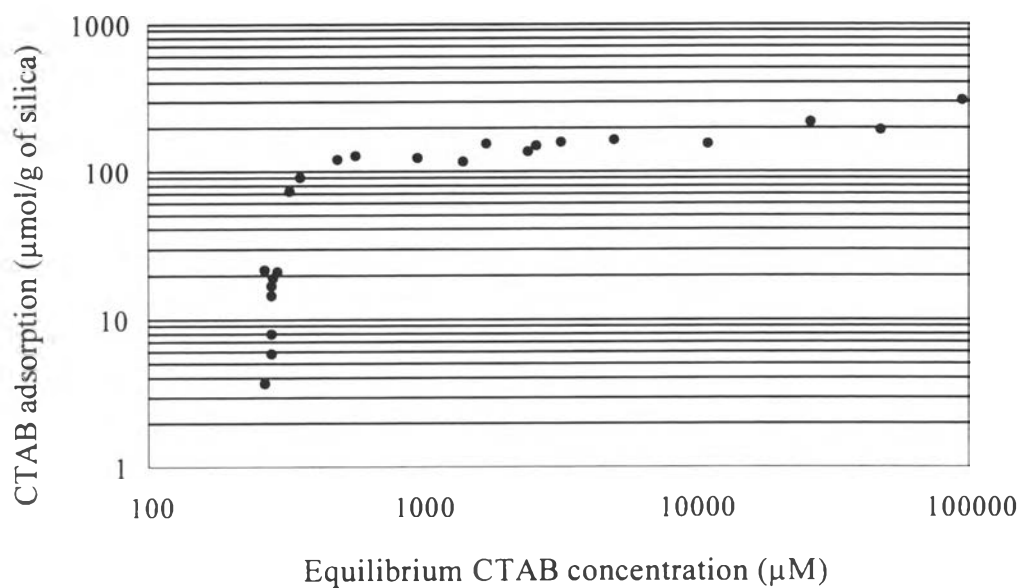


Figure 4.1. CTAB adsorption isotherm on Aerosil®OX50 showing a maximum adsorption of CTAB ~ 130 $\mu\text{mol/g}$ of silica

4.2 Adsolubilization Measurement

Styrene adsolubilization increased with increasing styrene equilibrium concentration. The maximum measured adsolubilization was ~ 190 $\mu\text{mol/g}$ of silica (Figure 4.2).

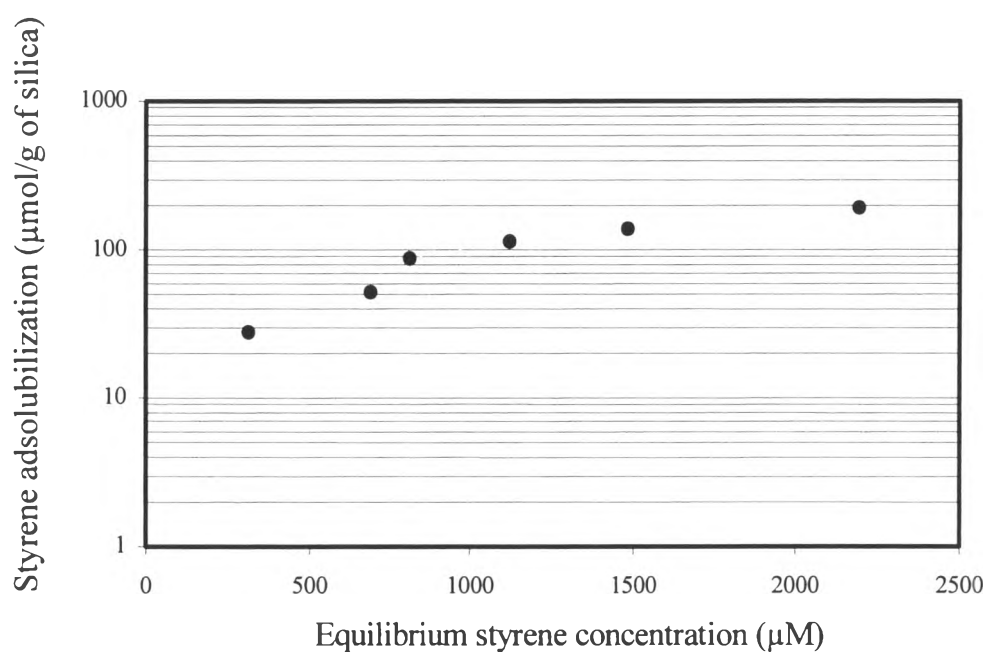


Figure 4.2 Adsolubilization isotherm of styrene into 100 $\mu\text{mol/g}$ of CTAB on silica.

4.3 Thermal Gravimetric Analysis (TGA)

Thermograms show that CTAB degrades in the 200 °C to 300 °C (Figure 4.3) range while the standard and extracted polymer degrade in the range between 300 °C to 500 °C (Figure 4.5). Silica doesn't show any weight loss in this temperature range. Modified silica displayed two steps of weight loss between temperature ranges of 200 °C to 500 °C. The first step degradation in the temperature of 200 – 300 °C should be CTAB and some low molecular weight polystyrene while the second loss, between 300 to 500 °C, is due to the decomposition of relatively high molecular weight polystyrene. The extracted silica showed less significant weight loss between 300 and 500 °C compare to modified silica one, as we expected (Figure 4.4). This indicated that most of the polystyrene was extracted from the modified silica.

The quantity of formed polystyrene can be studied from percent weight loss of TGA results. All the mass losses were evaluated on the second degradation step at temperatures >300 °C. TGA analysis of the results for modified silica, extracted silica and extracted polystyrene confirm that polystyrene was successfully formed on the silica surface together with CTAB surfactant using both water soluble (VA-044) and insoluble (AIBN) initiator via AP.

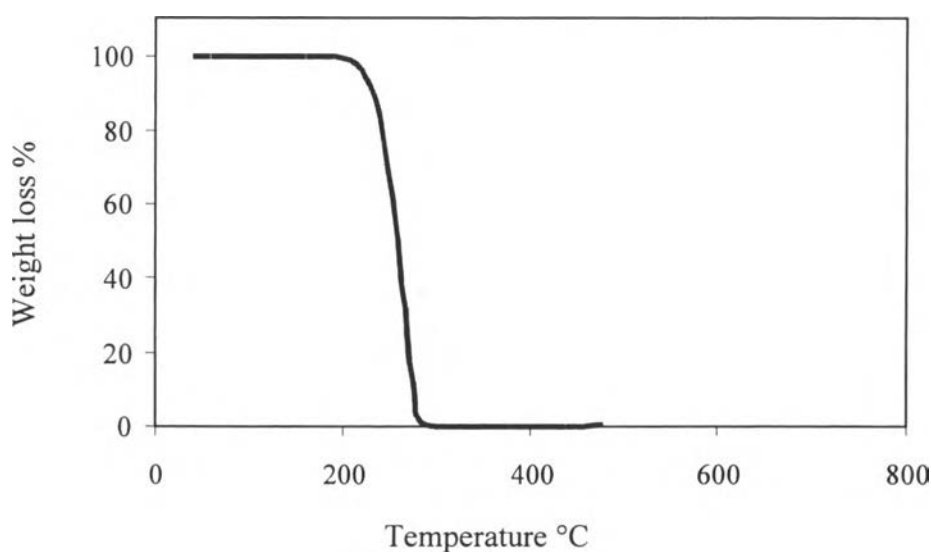


Figure 4.3 Thermal analysis of CTAB.

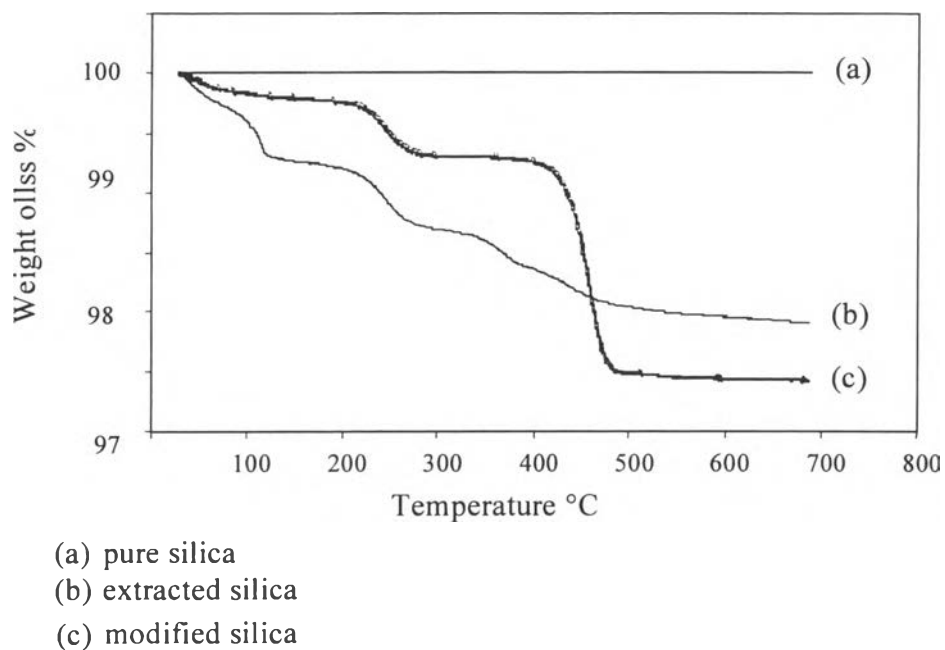


Figure 4.4 Thermal analysis of pure silica, modified and extracted silica of CTAB:styrene (1:2) and styrene:VA-044 (1:25).

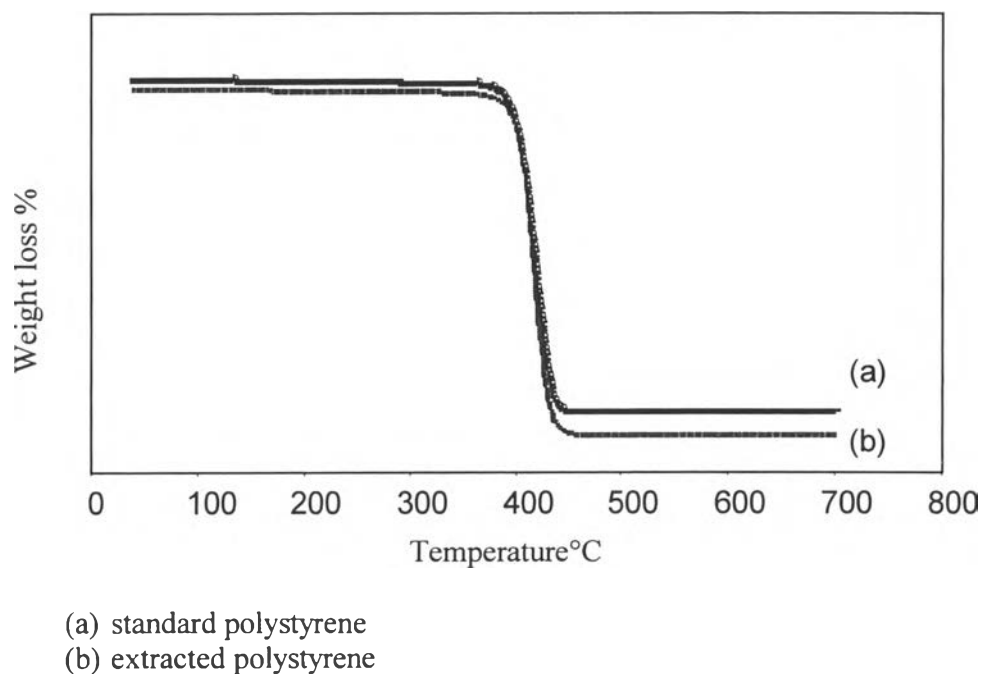


Figure 4.5 Thermal analysis of standard and extracted polystyrene of CTAB:styrene (1:2) and styrene :VA-044 (1:25).

4.3.1 Effect of Reaction Time

TGA results for AP reactions for 1,2,4, and 6 hours showed that relatively high amounts of polystyrene could be formed on silica by 2 hrs (Table 401)

4.3.2 Effect of Monomer Loading

In addition, at the same reaction time, the amount of polystyrene formed on silica was clearly increased when the ratio of styrene loading increased (Table 4.1)

4.3.3 Effect of Initiator Loading

4.3.3.1 *AIBN*

The mass loss of polystyrene formed via AP using AIBN at two hours reaction time showed that when the initiator concentration decreased the amount of styrene formed on silica particle also decreased and at the same initiator concentration, the amount of polymer formed increased with increased in amount of monomer loading as expected (Table 4.2).

4.3.3.2 *VA-044*

The thermal analysis results of polystyrene formed via VA-044 at two hours reaction time showed an unexpected result. That is, when the initiator concentration decreased, the amount of styrene formed on silica particle gradually increased, which is different from using AIBN and at the same initiator concentration, the amount of polymer formed increased with increases in the amount of monomer feed as we expected (Table 4.3).

4.3.4 RAFT in AP

TGA thermograms show degradations in several ranges. Mass loss in the 200 – 300 °C range indicates the loss of CTAB together with some low molecular weight polystyrene. Mass loss in the 300 to 500 °C range indicates the loss of relatively high molecular weight polystyrene on both modified and extracted silicas (Fig: 4.6 and 4.7). The amount lost is approximately the same (Table 4.4) as there was no collection polystyrene on extraction process. The second loss does confirm the formation of relatively high MW polystyrene on the silica surface by RAFT polymerization via admicellar polymerization.

Table 4.1 % weight loss of polystyrene formed on Aerosil OX50 under various reaction time and monomer loading.

| CTAB _{adsorp} : Styrene _{adsol} μmol/g : μmol/g | Reaction time (h) | Weight of polystyrene (% w/w of modified silica) |
|--|----------------------|---|
| 2:1 | 1 | 0.28 |
| | 2 | 0.39 |
| | 4 | 0.29 |
| | 6 | 0.71 |
| 1:1 | 1 | 0.35 |
| | 2 | 0.87 |
| | 4 | 0.97 |
| | 6 | 1.14 |
| 1:2 | 1 | 1.57 |
| | 2 | 1.88 |
| | 4 | 1.79 |
| | 6 | 1.94 |

Table 4.2 % weight loss of polystyrene formed on silica using AIBN via AP.

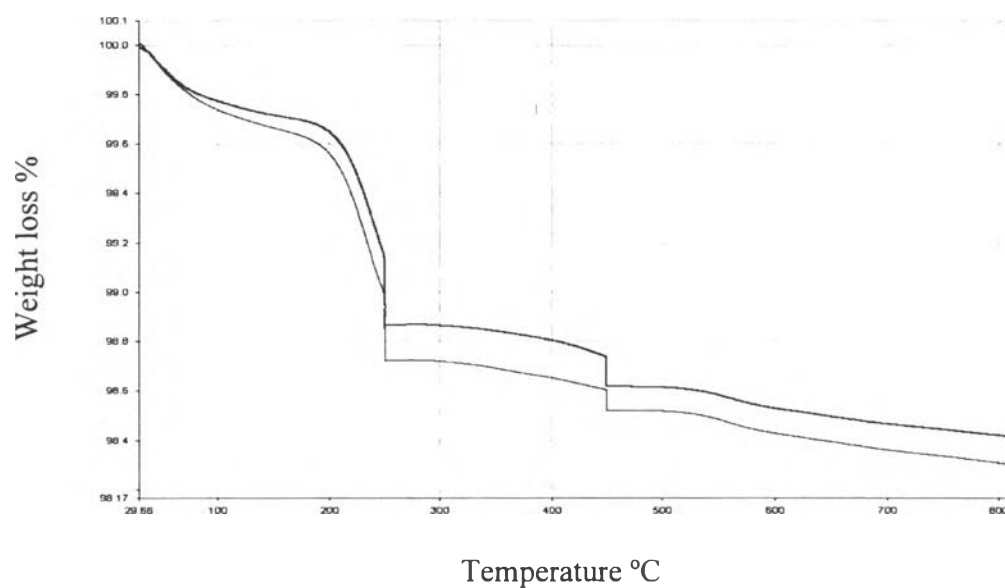
| Adsorbed CTAB ($\mu\text{mol/g}$) | AIBN:Styrene | Weight of polystyrene (% w/w of modified silica) | |
|--|--------------|---|------|
| | | CTAB _{adsorp} : Styrene _{adsol} | |
| | | 2:1 | 1:2 |
| 100 | 1:1 | 0.54 | 2.27 |
| | 1:5 | 0.45 | 1.55 |
| | 1:7 | 0.42 | 0.31 |
| | 1:10 | 0.21 | 0.34 |
| | 1:15 | 0.23 | 0.35 |
| | 1:20 | 0.18 | 0.25 |
| | 1:25 | 0.17 | 0.21 |
| | 1:50 | 0.11 | 0.15 |

Table 4.3 % weight loss of polystyrene formed on silica using VA-044 via AP.

| Adsorbed CTAB ($\mu\text{mol/g}$) | VA-044:Styrene | Weight of polystyrene (% w/w of modified silica) | |
|--|----------------|---|-------|
| | | CTAB _{adsorp} : Styrene _{adsol} | |
| | | 2:1 | 1:2 |
| 100 | 1:1 | 0.139 | 0.886 |
| | 1:5 | 0.783 | 0.533 |
| | 1:7 | 0.816 | 0.643 |
| | 1:10 | 0.265 | 0.653 |
| | 1:15 | 0.982 | 0.665 |
| | 1:20 | 0.984 | 1.062 |
| | 1:25 | 0.825 | 1.821 |
| | 1:50 | 1.013 | 1.050 |

Table 4.4 % weight loss of polystyrene formed on silica by RAFT via AP.

| Adsorbed CTAB ($\mu\text{mol/g}$) | Type of initiator | CDB : Initiator | Weight of polystyrene (% w/w of modified silica) | |
|--|-------------------|-----------------|---|------------------|
| | | | Modified silica | Extracted silica |
| 100 | AIBN | 0.04:1 | 0.44 | 0.39 |
| | | 3:1 | 0.25 | 0.25 |
| | | 5:1 | 0.25 | 0.25 |
| | VA-044 | 0.02:1 | 0.24 | 0.2 |



- (a) modified silica
(b) extracted silica

Figure 4.6 Thermal analysis of modified and extracted silica of CTAB:styrene (1:1) and CDB :VA-044 (0.02:1).

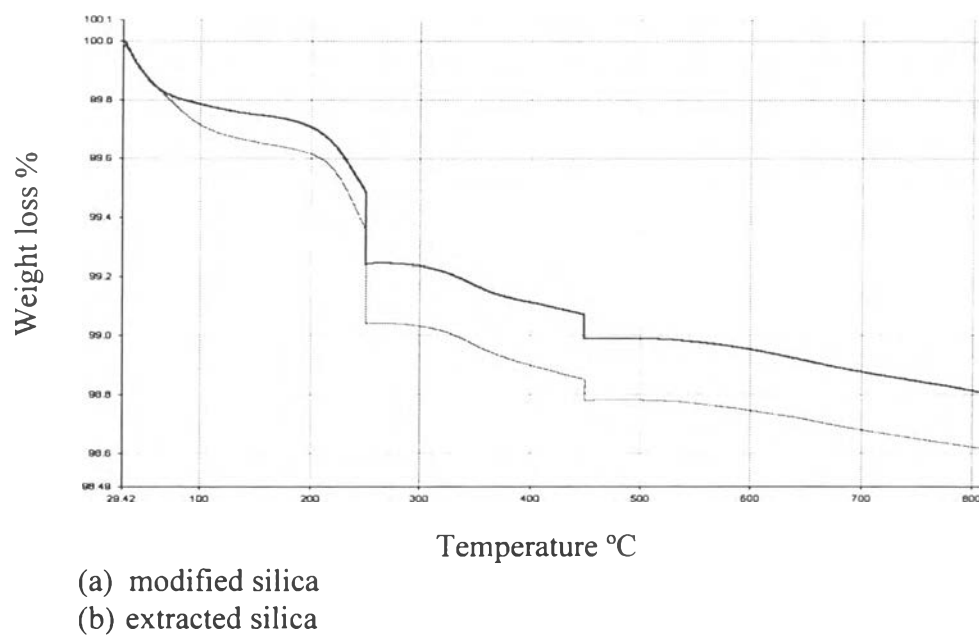


Figure 4.7 Thermal analysis of modified and extracted silica of CTAB:styrene (1:1) and CDB :AIBN (5:1).

4.4 Fourier Transform Infrared Spectroscopy Results (FTIR)

4.4.1 Admicellar Polymerization

CTAB, VA-044, silica, modified silica, standard polystyrene and extracted material were studied by FTIR to confirm the presence of polystyrene on silica after modification. The spectrum of modified silica does not show the polystyrene peaks significantly except very small absorbency peaks of methylene C-H stretching in the range of $2800\text{-}3050\text{ cm}^{-1}$ (Figure 4.9) compare to that of pure silica (Figure 4.8). That is because of high intensity of silica absorption bands and the amount of polystyrene formed on silica particle is very low. Therefore the extracted material from modified silica has to be characterized.

The presence of polystyrene on the modified silica was confirmed by FTIR analysis of the extracted polymer. The results showed that the spectra of the extracted materials are fully consistent with the spectra of the polystyrene standard. In particular, they clearly showed that important peaks representing the benzene ring (aromatic C-H stretching at $3100\text{-}3000\text{ cm}^{-1}$, aromatic C=C stretching at 1600 cm^{-1} , 1495 cm^{-1} , 1454 cm^{-1} , and out of plane aromatic C-H bending at 700 cm^{-1}) (Figures 4.10, 11, 12).

Results of spectrum of modified/pure silica and extracted materials which obtained from FTIR could support the modification of nonporous silica via admicellar polymerization in ambient polymerization conditions.

4.4.2 RAFT in AP

The amount of extracted polymer formed on silica surface was insufficient for characterization for both the CDB/ AIBN and CDB/VA-044 systems.

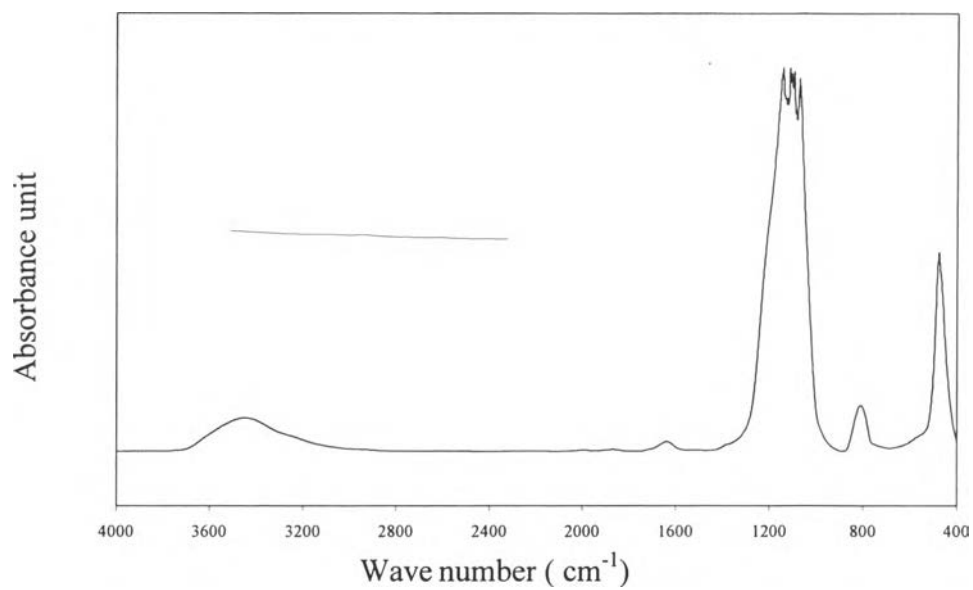


Figure 4.8 FTIR spectrum of pure silica.

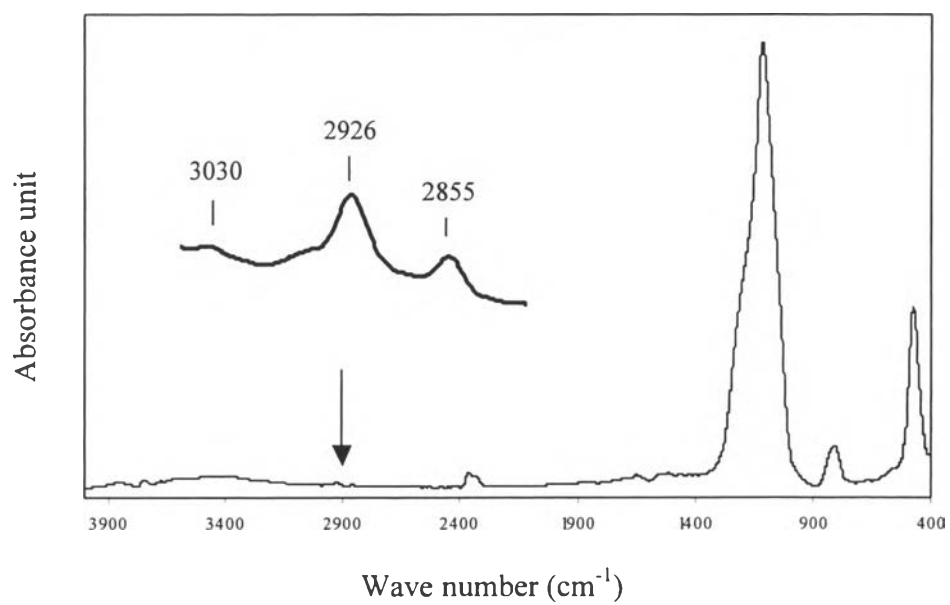
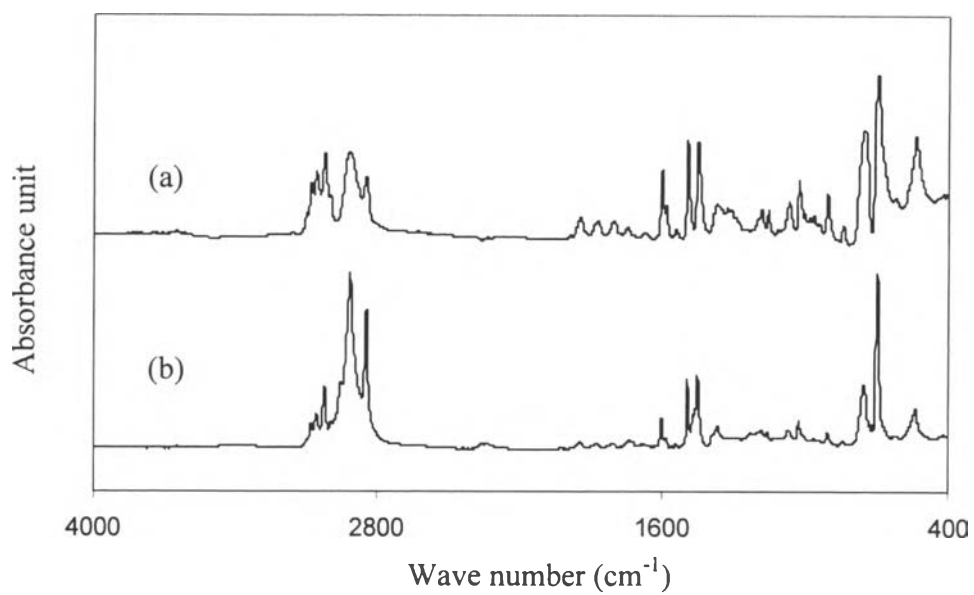


Figure 4.9 FTIR spectrum of modified silica.



(a) standard polystyrene

(b) extracted polystyrene of VA-044:styrene (1:5) and CTAB:styrene(2:1)

Figure 4.10 FTIR spectrum of polystyrene standard.

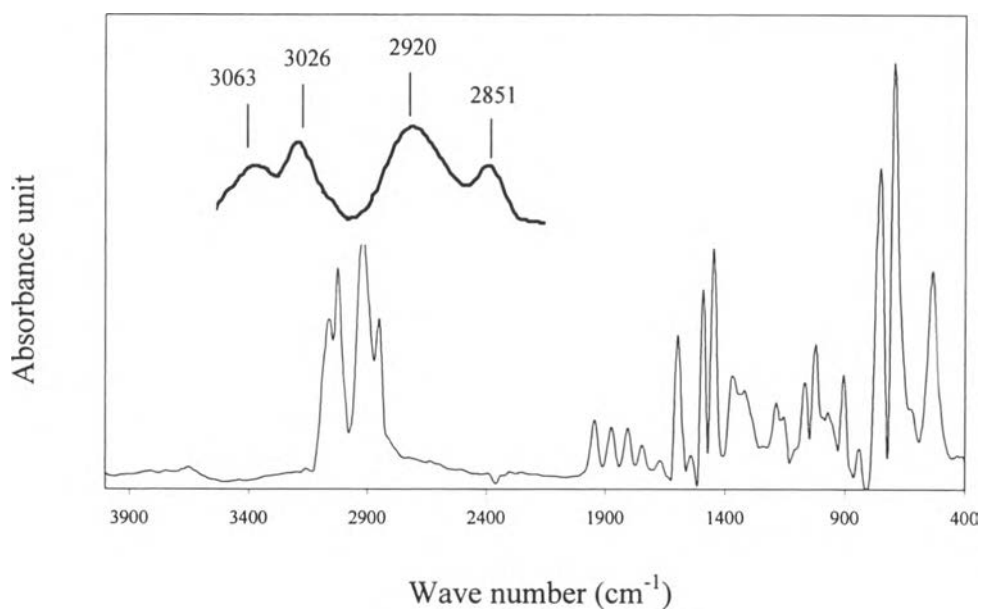
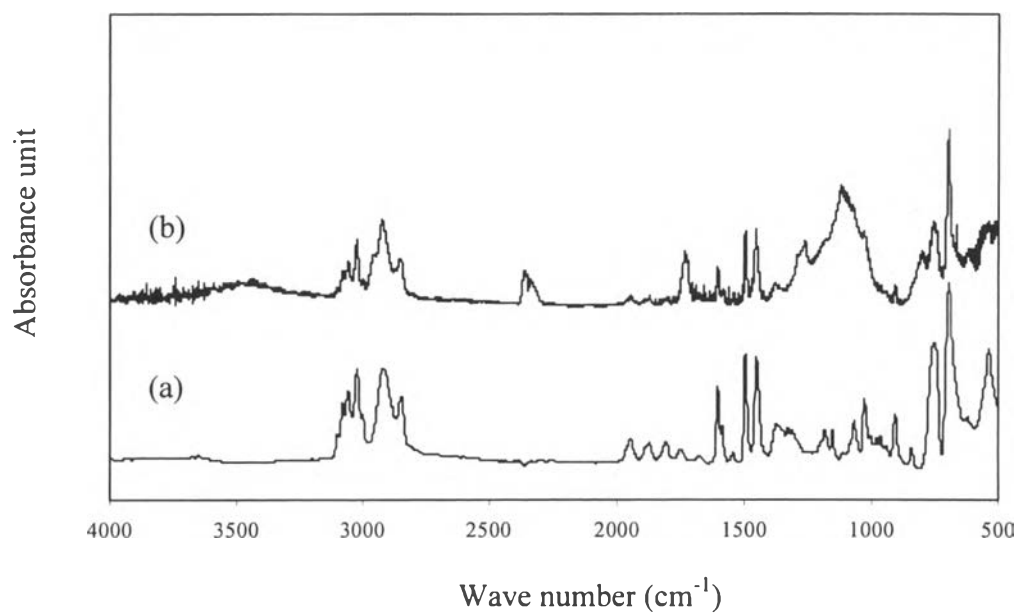


Figure 4.11 Spectrum of standard and extracted polystyrene of styrene: va-044 (1:7) at CTAB:styrene (2:1).



- (a) Standard polystyrene
- (b) Extracted polystyrene

Figure 4.12 Spectrum of standard and extracted polystyrene using AIBN at CTAB:styrene (1:2)

4.5 Gel Permeable Chromatography Results (GPC)

The number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (MWD) of all the extracted materials for every various initiator to monomer ratios from both CTAB: styrene at 1:2 and 2:1 had been investigated by GPC. The GPC data for all extracted polystyrene demonstrated two or three peaks; the first peak represents the high molecular weight polymer formed, the second peak the relatively lower molecular weight polymer and the third peak is consistent with the presence of CTAB, which we expect to be trapped in the polymer during extraction process. Polymer formed using AIBN and VA-044 showed only two peaks with the lower M_w peak using AIBN centered around ≈ 200 and that of VA-044 at ≈ 900 .

4.5.1 Effect of Reaction Time

At one hour reaction time with monomer to CTAB ratios of 1:1 and 2:1 formed low M_w polymer while the 1:2 ratio samples formed relatively high M_w (Table 4.4). This may be due to the high amount of styrene in CTAB bilayer which converted into polymer very quickly and reasonable M_w polymer is achieved in a shorter time. Moreover, when the reaction time exceeded two hours, the M_w of polymer is fairly constant, showing some raise in some samples and decline in others. A number of samples will need to be done to see if the observed trends are statistically meaningful. However, it is clear that a reaction time of not less than two hours is needed to achieve complete polymerization. The initiator to styrene ratio is constant at 1:5 for this study (Figure 4.13).

4.5.2 Effect of Styrene Loading in Reaction Time

At the same sample preparation condition, the Mw of polystyrene formed on silica for every reaction time increased with increasing styrene loading (except the 6 h reaction time). For 6 h reaction time Mw of polystyrene remained constant at CTAB to styrene 1:1 and 1:2, that could be due to the difficulties of mixing the large amount of styrene into the system. However the Mw increased with increasing monomer loading (Figure 4.14).

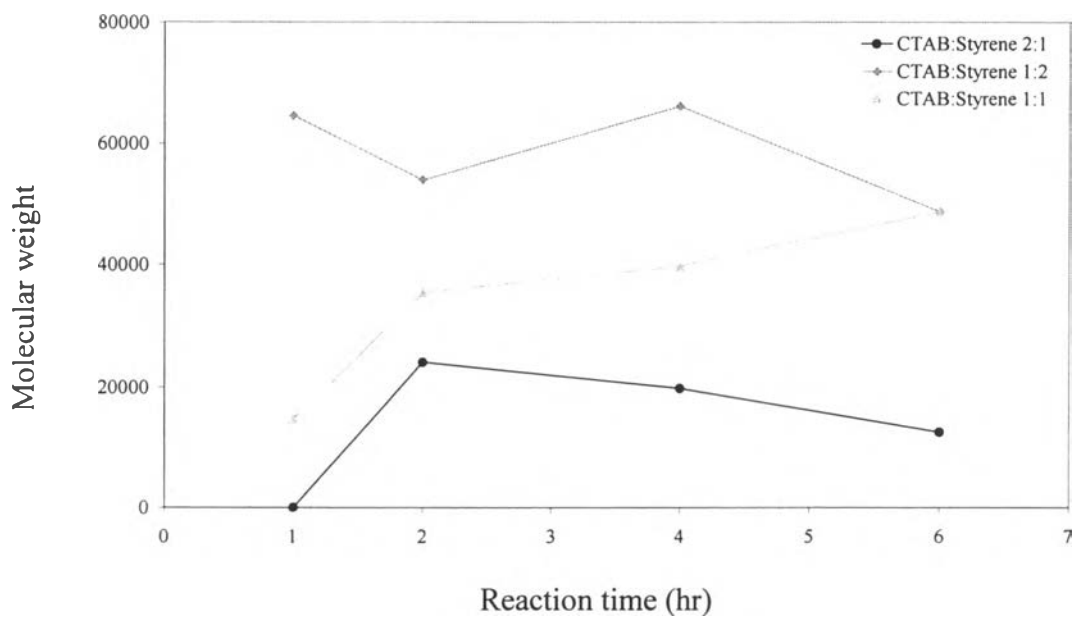


Figure 4.13 Effect of reaction time on molecular weight.

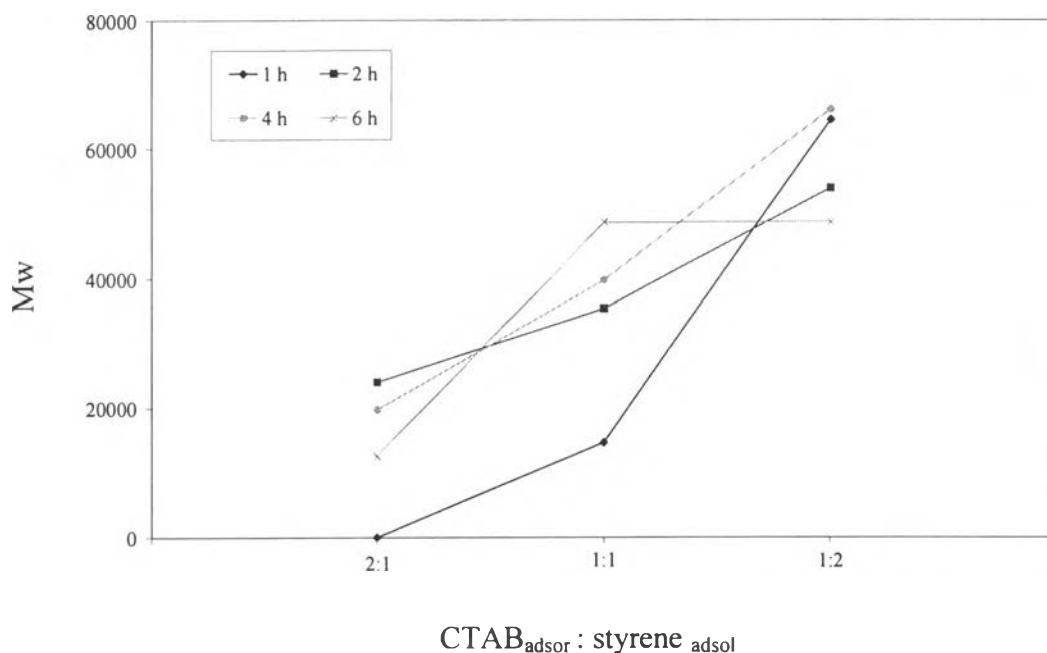


Figure 4.14 Effect of monomer loading on Mw in different reaction time.

4.5.3 Effect of Initiator

4.5.3.1 *AIBN*

Results for a CTAB to styrene ratio of 1:2 demonstrated that the Mw tended to increase as initiator concentration decreased as one would find in emulsion polymerization. But at AIBN to styrene ratios lower than 1:15 for a CTAB to styrene ratio of 1:2 and at all initiator to monomer ratios for a CTAB to styrene ratio of 2:1, the Mw decreased with decreasing initiator feed concentration (Tables 4.5 and 4.6). The difference here may be explained in the following way. At high styrene concentrations, styrene forms pools within the admicelle and thus polymerization proceeds as it would with emulsion polymerization where there are drops of monomer within micelles. At the lower styrene loadings, however, the styrene is more evenly dispersed within the admicelle with no pools. Thus, when polymerization is initiated, there is a competition between the kinetics of new monomer molecules diffusing from the bulk or from somewhere else in the bilayer to the radical

and the termination step. Thus, termination may occur before diffusion brings more monomer, and the MW decreases. It would mean that it is quite possible that all of the radicals terminate before all of the monomer has reacted. For AIBN, an AIBN to styrene ratio of 1:15 should be used if the goal is to obtain relatively high molecular weight (Figure 4.15).

4.5.3.2. VA-044

Parallel to conventional polymerization, the Mw of extracted polystyrene increased with decreasing initiator concentration at both CTAB to styrene ratios (Tables 4.7, 4.8). However, the higher monomer loading did not produce the highest molecular weight, as we expected (see Tables 4.7 and 4.8). This could be because VA-044 is a very effective initiator and is present in sufficient excess in the water phase that many radicals are formed and then combine before forming high molecular weight polymer. VA-044 showed the ability to form high molecular weight polymer at all monomer ratios. The results could suggest that VA-044 to styrene of 1:7 should give the highest Mw (Figure 4.16).

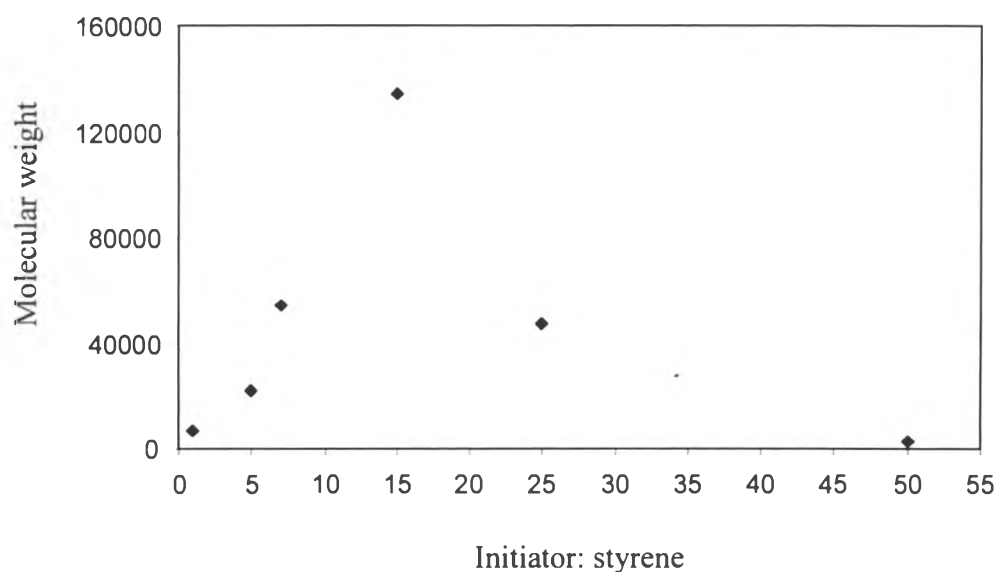


Figure 4.15 Mw of polystyrene formed using AIBN at CTAB:styrene (1:2).

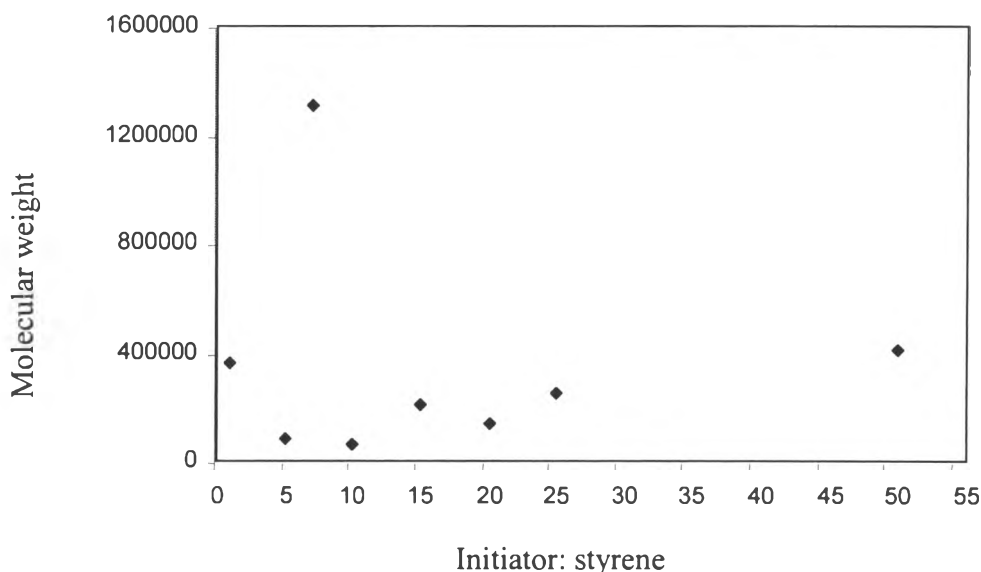


Figure 4.16 Mw of polystyrene formed using VA-044 at CTAB:styrene(2:1).

4.5.4 A Comparison of Results: AIBN Vs. VA-044

The extractable polymer formed using the water-soluble initiator (VA-044) had much higher molecular weight than the extractable polymer formed using AIBN, and there was more of it at every ratio of initiator to styrene for both feed monomer levels (Table 4.9). That difference might depend on the characteristic of each initiator. In this aqueous system, VA-044 could be more effective as it is in contact with the admicelle at all water-admicelle interfaces. AIBN, being water insoluble, should reside primarily within the admicelle. Thus, upon initiation, the AIBN should already be intimately in contact with styrene while the VA-044 diffuses into the admicelle. AIBN, as shown previously, yields lower molecular weight polymer than VA-044 for the same conditions. The presence of AIBN in the admicelle causes many small chains to form which terminate before monomer from the bulk or surrounding regions can diffuse in (figure 4.17).

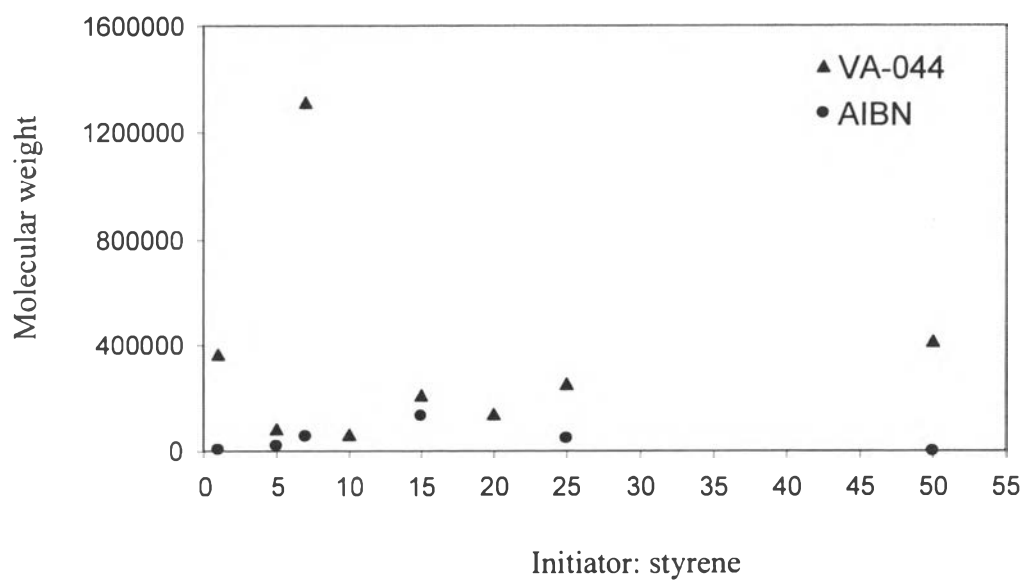


Figure 4.17 Mw of polystyrene formed using both AIBN and VA-044.

4.5.5 RAFT via AP

The amount of extracted polymer was insufficient for characterization that might be because of the low formation of polystyrene on silica or the poor extraction of THF solvent to high molecular weight polymer.

Table 4.5 Mn, Mw and MWD of polystyrene formed under various reaction time.

| CTAB _{adsorp} : Styrene _{adsol} μmol/g : μmol/g | Reaction time (h) | First peak | | | Second peak | | | Third peak | | |
|--|----------------------|------------|-------|------|-------------|-----|------|------------|-----|------|
| | | Mn | Mw | MWD | Mn | Mw | MWD | Mn | Mw | MWD |
| 100:100 (1:1) | 1 | 9419 | 14695 | 1.56 | 350 | 526 | 1.50 | - | - | - |
| | 2 | 9956 | 35397 | 3.56 | 720 | 835 | 1.16 | 282 | 298 | 1.06 |
| | 4 | 9784 | 39726 | 4.06 | 691 | 783 | 1.13 | 277 | 296 | 1.07 |
| | 6 | 10300 | 48666 | 4.72 | 736 | 820 | 1.11 | 282 | 296 | 1.05 |
| 100:50 (2:1) | 1 | - | - | - | 675 | 776 | 1.15 | 291 | 304 | 1.05 |
| | 2 | 6532 | 24020 | 3.78 | 468 | 691 | 1.48 | - | - | - |
| | 4 | 6397 | 19749 | 3.09 | 424 | 588 | 1.39 | - | - | - |
| | 6 | 6350 | 12530 | 1.94 | 761 | 912 | 1.2 | 278 | 301 | 1.09 |
| 100:200 (1:2) | 1 | 10963 | 64526 | 5.89 | 638 | 725 | 1.06 | 285 | 299 | 1.05 |
| | 2 | 12515 | 53916 | 4.31 | 641 | 694 | 1.08 | 282 | 298 | 1.06 |
| | 4 | 10943 | 66149 | 6.04 | 682 | 737 | 1.08 | 292 | 306 | 1.05 |
| | 6 | 9639 | 48728 | 5.06 | 736 | 807 | 1.10 | 291 | 306 | 1.05 |

Table 4.6 Mn, Mw and MWD of extracted polymers formed at CTAB:styrene (1:2) using AIBN.

| AIBN:Styrene | First peak | | | Second peak | | |
|--------------|----------------|----------------|------|----------------|----------------|------|
| | M _n | M _w | MWD | M _n | M _w | MWD |
| 1:1 | 2852 | 7172 | 2.51 | 251 | 264 | 1.06 |
| 1:5 | 11000 | 22000 | 2.00 | - | - | - |
| 1:7 | 17157 | 54532 | 3.17 | 201 | 269 | 1.33 |
| 1:10 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1:15 | 49903 | 134118 | 2.68 | 230 | 264 | 1.14 |
| 1:20 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1:25 | 22325 | 47035 | 2.10 | 853 | 1294 | 1.51 |
| 1:50 | 1904 | 2487 | 1.30 | 249 | 297 | 1.19 |

Table 4.7 Mn, Mw and MWD of extracted polymers formed at CTAB:styrene (2:1) using AIBN.

| AIBN:Styrene | First peak | | | Second peak | | |
|--------------|----------------|----------------|------|----------------|----------------|------|
| | M _n | M _w | MWD | M _n | M _w | MWD |
| 1:1 | 1537 | 2499 | 1.62 | 209 | 235 | 1.12 |
| 1:5 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1:7 | 232 | 296 | 1.27 | - | - | - |
| 1:10 | 209 | 260 | 1.24 | - | - | - |
| 1:15 | 207 | 239 | 1.15 | - | - | - |
| 1:20 | 208 | 247 | 2.16 | | | |
| 1:25 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1:50 | N/A | N/A | N/A | N/A | N/A | N/A |

Table 4.8 Mn, Mw and MWD of extracted polymers formed at CTAB:styrene (1:2) using VA-044.

| Styrene: VA-044 | First peak | | | Second peak | | |
|-----------------|------------|--------|--------|-------------|------|--------|
| | Mn | Mw | MWD | Mn | Mw | MWD |
| 1:1 | 17368 | 38508 | 2.2171 | 1770 | 2311 | 1.3056 |
| 1:5 | 13335 | 44465 | 3.3343 | 1537 | 2024 | 1.3171 |
| 1:7 | 70762 | 205208 | 2.8999 | 1416 | 2766 | 1.9528 |
| 1:10 | 16045 | 38279 | 2.3856 | 1550 | 2042 | 1.3175 |
| 1:15 | 41169 | 99741 | 2.4227 | 2353 | 3760 | 1.5979 |
| 1:20 | 57662 | 114509 | 1.9858 | 1738 | 4424 | 2.5450 |
| 1:25 | N/A | N/A | N/A | N/A | N/A | N/A |
| 1:50 | N/A | N/A | N/A | N/A | N/A | N/A |

Table 4.9 Mn, Mw and MWD of extracted polymers formed at CTAB:styrene (2:1) using VA-044.

| Styrene: VA-044 | First peak | | | Second peak | | | Third peak | | |
|-----------------|----------------|----------------|---------|----------------|----------------|---------|----------------|----------------|----------|
| | M _n | M _w | MWD | M _n | M _w | MWD | M _n | M _w | MWD |
| 1:1 | 100332 | 362097 | 3.60898 | - | - | - | - | - | - |
| 1:5 | 28379 | 81620 | 2.87604 | - | - | - | - | - | - |
| 1:7 | 1036329 | 1310813 | 1.26486 | 34093 | 108258 | 3.17541 | 753 | 974 | 1.293304 |
| 1:10 | 18107 | 62763 | 3.46621 | 743 | 909 | 1.22329 | - | - | - |
| 1:15 | 48197 | 209674 | 4.35041 | - | - | - | - | - | - |
| 1:20 | 6793 | 137345 | 20.2172 | - | - | - | - | - | - |
| 1:25 | 118441 | 251391 | 2.12250 | 2803 | 11709 | 3.95301 | - | - | - |
| 1:50 | 56445 | 409136 | 7.24840 | - | - | - | - | - | - |

Table 4.10 Mw of polystyrene formed using both AIBN and VA-044.

| Initiator : Styrene | CTAB _{adsorp} : Styrene _{adsol} (1:2) | | CTAB _{adsorp} : Styrene _{adsol} (2:1) | |
|---------------------|--|--------|--|---------|
| | AIBN | VA-044 | AIBN | VA-044 |
| 1:1 | 7172 | 38508 | 2499 | 362097 |
| 1:5 | 22000 | 44465 | N/A | 81620 |
| 1:7 | 54532 | 205208 | 296 | 1310813 |
| 1:10 | N/A | 38279 | 260 | 62763 |
| 1:15 | 134118 | 99741 | 239 | 209674 |
| 1:20 | N/A | 114509 | 247 | 137345 |
| 1:25 | 47035 | N/A | N/A | 251391 |
| 1:50 | 2487 | N/A | N/A | 409136 |

4.6 Atomic Force Microscopy

All unmodified, modified and extracted silicas were studied by AFM in order to (1) determine the presence and characteristics of the formed polymer film, and (2) determine the efficiency of the extraction process in removing the formed polymer. Film thickness was measured using topographic images while confirmation of the presence of polymer can be obtained from phase images. The distribution can be then studied from amplitude images which gave the best resolution of the surfaces.(Figure 4.18).

Figure 4.19 is of unmodified silica. No polymer patches can be seen and the black regions at the edges of the primary silica particles in the phase images are due to a delay in the phase caused by the tip having to travel longer distances to reach down into the pores. Thus, in these images, black regions don't necessarily indicate the presence of softer polymer.

AFM images of modified silicas confirmed the formation of polystyrene on the surface with film thicknesses ranging from 2-14nm. (Figures 23 and 24)

4.6.1 Effect of Monomer Loading

For both initiator systems, higher monomer loadings yielded thicker polymer films on the silica surface, as expected (Figures 4.23 and 4.24).

4.6.1.1 *AIBN*

Samples modified using AIBN formed films that ranged in thickness from 2-7 nm at low monomer loadings to 4-9 nm thick at high monomer loadings (Fig 4.23).

4.6.1.2 *VA-044*

Samples modified using VA-044 formed films that ranged in thickness from 2-4 nm at low monomer loadings to 4-15 nm thick at high monomer loadings (Fig 4.24).

4.6.2 AIBN vs VA-044

The polystyrene film did not, in any sample, completely cover the silica surface. However, films composed of higher molecular weight polymer seemed to form thinner films that covered a greater percentage of the surface.

The samples modified using VA-044 seemed to cover more of the silica surface than those modified using AIBN (figure 4.22). Typical images may be seen in Figures 4.20 and 4.21. However, for extracted silicas, samples modified using AIBN show nearly complete extraction of polymer while those modified using VA-044 show that the extraction process was definitely not complete. (figures 4.25 and 26). This is consistent with the more efficient extraction of lower molecular weight polymer by the THF. This could also be caused by due to some difference in the nature of the polystyrene films, that is, that the adhesion of the VA-044 initiated film may be higher than that of the AIBN initiated film, but this will need more work to prove.

The thicknesses of the polystyrene films after extraction on the VA-044 samples had decreased. This could be due to the removal of some lower molecular weight polymer, or a rearranging of the existing polymer film, or both. (figures 4.24 and 4.25).

An interesting observation is that no polystyrene films may be detected in a small percentage of “modified” silica particles. Thus, the modification does not appear to be “homogeneous” across particles.

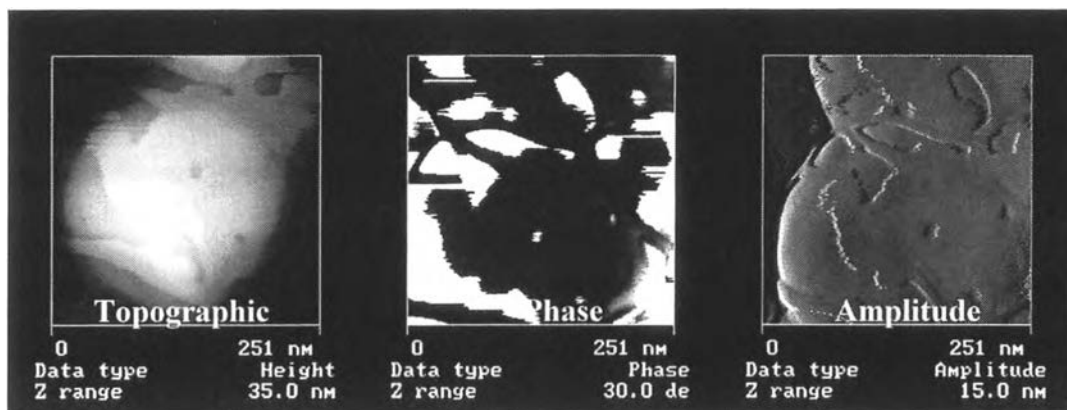


Figure 4.18 AFM topographic, phase amplitude images of modified silica at CTAB:styrene (2:1) and styrene:VA-044 (1:7) showing the presence of polymer on much of the surface.

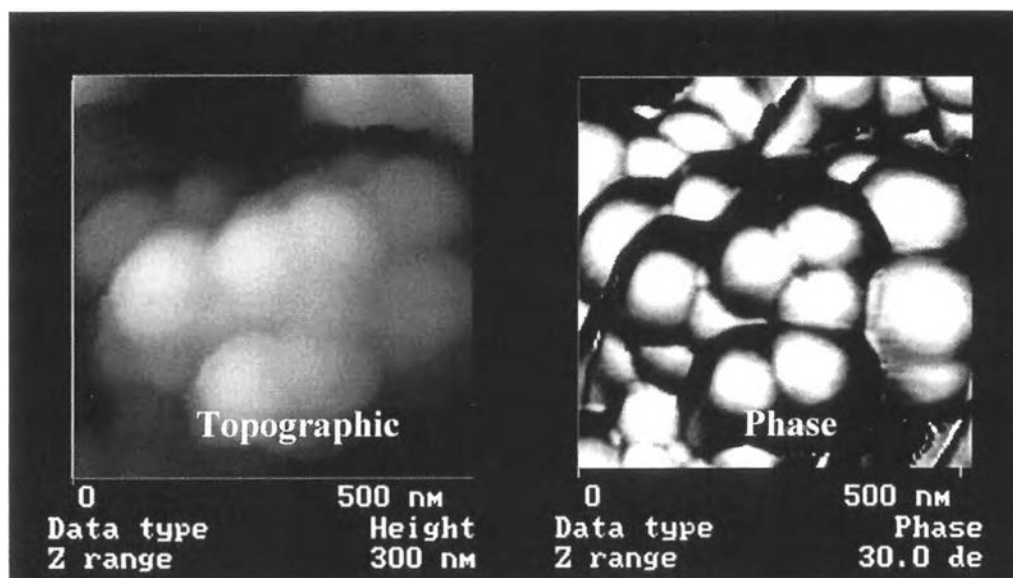


Figure 4.19 AFM topographic and phase images of unmodified silica showing only primary silica particles.

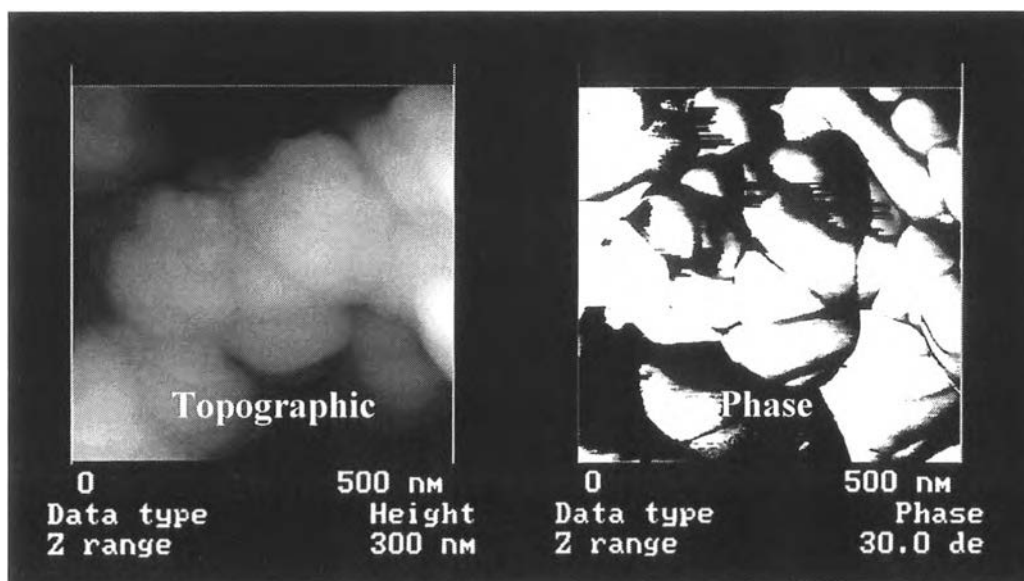


Figure 4.20 AFM topographic and phase images of modified silica at CTAB:styrene (1:2) and styrene:AIBN (1:5) showing the presence of polymer on some parts of the surface.

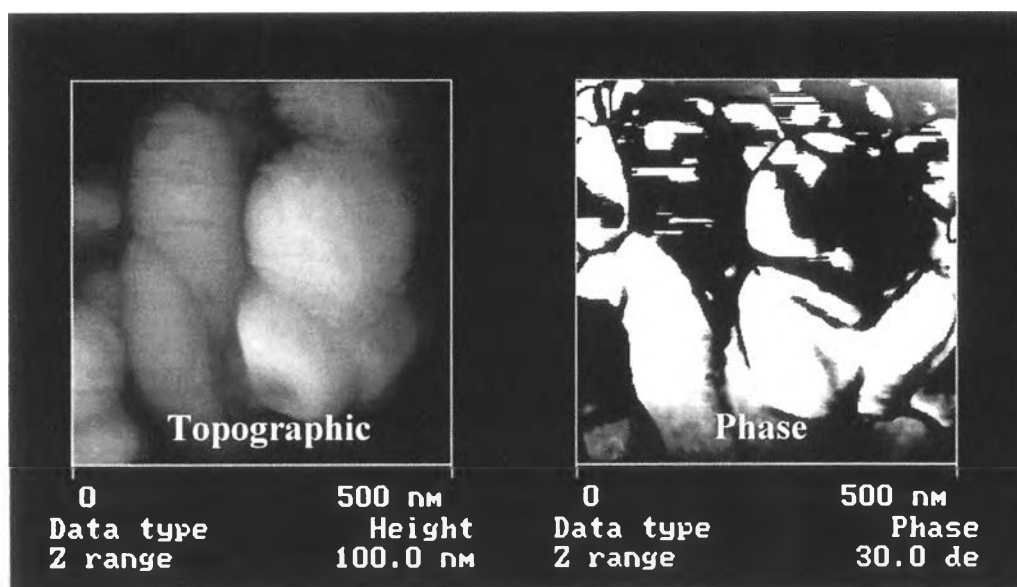


Figure 4.21 AFM topographic and amplitude images of modified silica at CTAB:styrene (1:2) and styrene:VA-044 (1:7) showing the presence of polymer on the surface.



Figure 4.22 AFM topographic images of unmodified (middle) and modified silica using AIBN (right) and VA-044 (left) at CTAB:styrene (1:2) showing the difference surface of the presence and absence of polystyrene formed on silica surface.

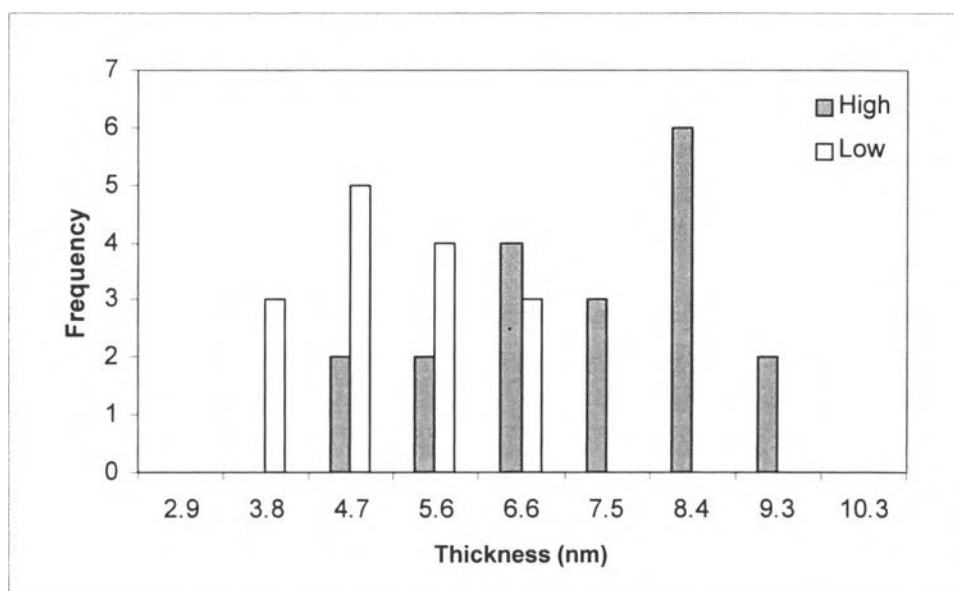


Figure 4.23 Polystyrene film thickness at high and low monomer loadings using AIBN initiator showing the increasing of film thickness with increasing monomer loading.

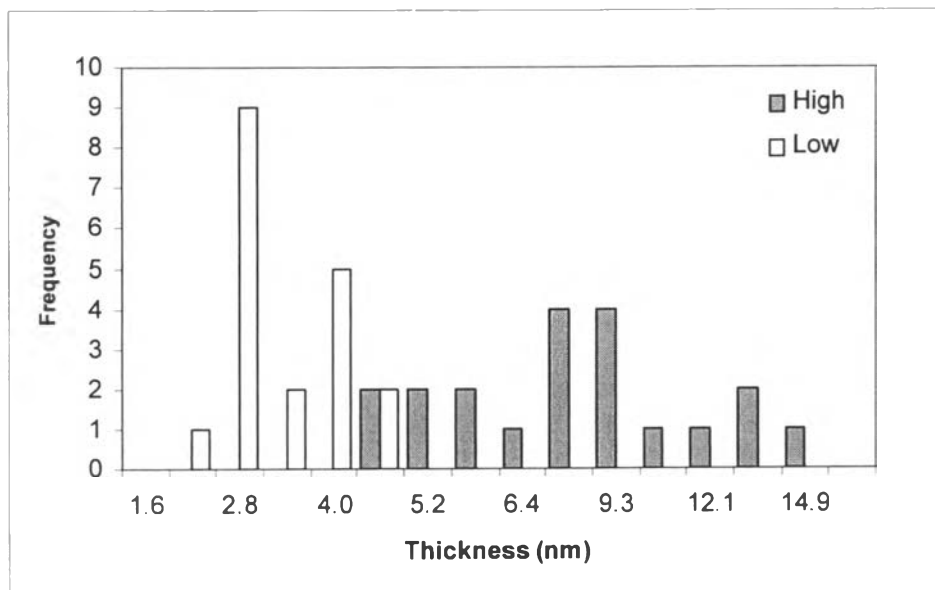


Figure 4.24 Polystyrene film thickness at high and low monomer loadings using VA-044 initiator showing the increasing of film thickness with increasing monomer loading.

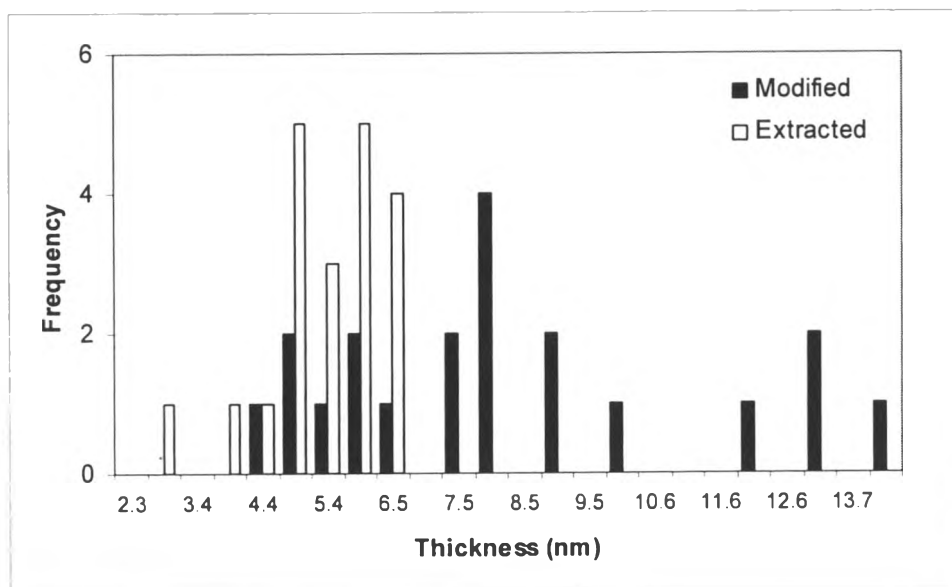


Figure 4.25 Polystyrene film thicknesses on modified and extracted silicas {CTAB:styrene (1:2) and styrene:VA-044 (1:1)} showing decreasing of polystyrene film thickness on extracted silica surface.

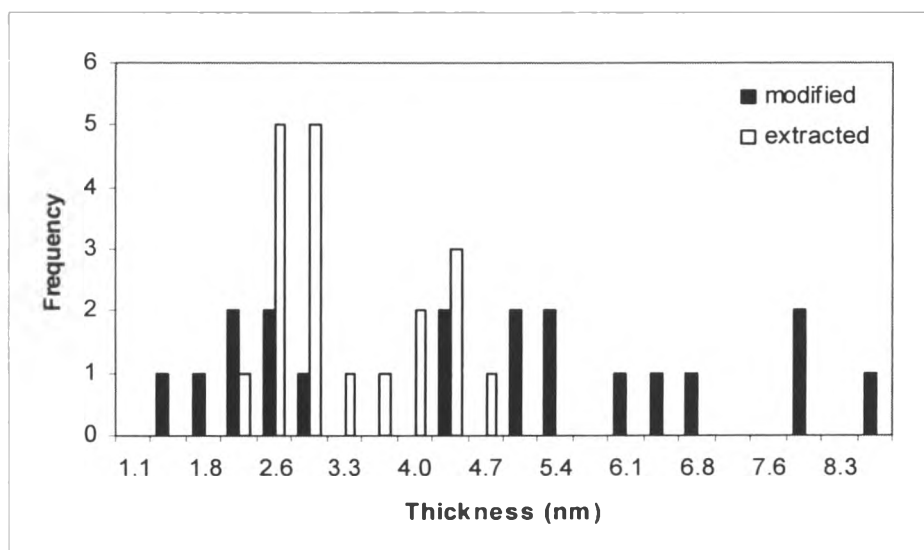


Figure 4.26 Polystyrene film thicknesses on modified and extracted silica surfaces { CTAB:styrene (2:1) and styrene:VA-044 (1:7)} showing decreasing of polystyrene film thickness on extracted silica surface.

4.6.5 RAFT via AP

Images showed extensive surface coverage of the polymer film on the surface on both modified and modified-and-extracted silicas (figures 27 and 28). This demonstrates the failure of the extraction process for these silicas and makes analysis of the formed polymer impossible. The thickness of the formed polystyrene film was not different for modified and modified-and-extracted silicas (Fig: 4.29), indicating little or no removal of polymer and / or rearrangement of the film during the process.

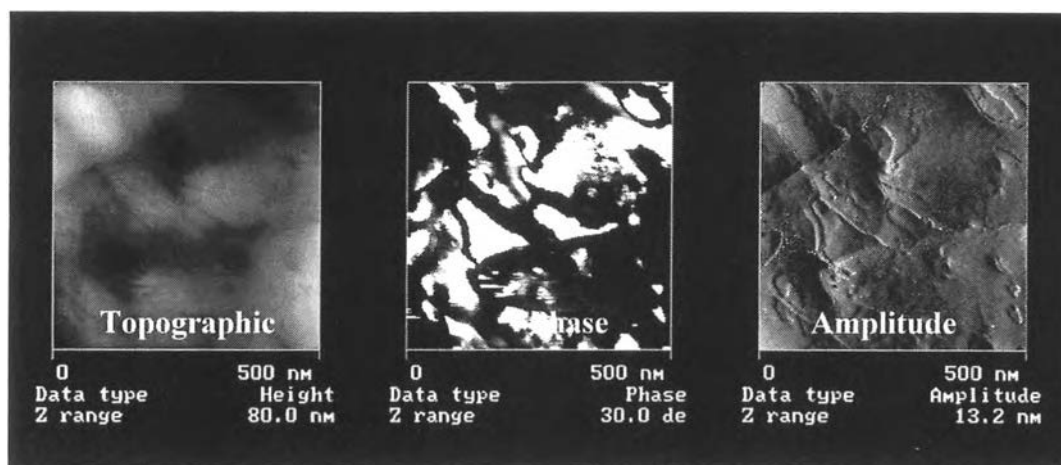


Figure 4.27 AFM topographic, phase and amplitude images of modified silica at CTAB:styrene (1:1) and CDB:AIBN (0.04:1) showing the presence of polymer on much of the surface.

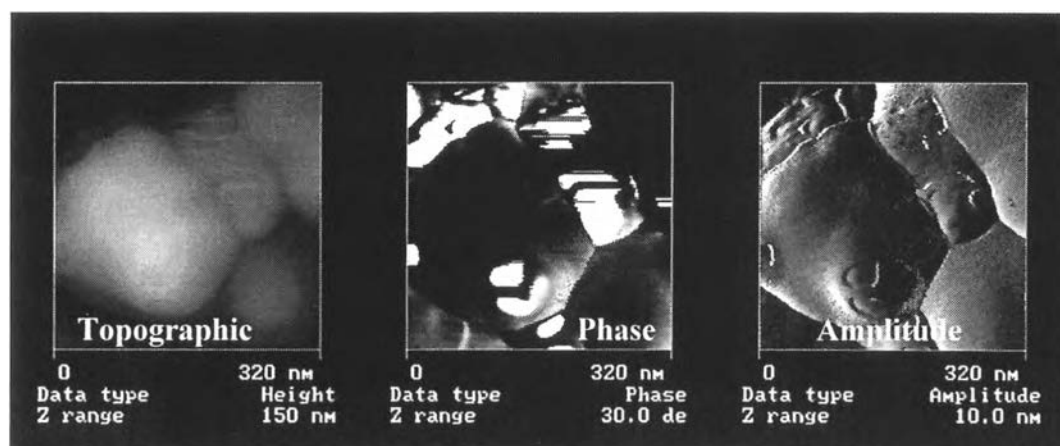


Figure 4.28 AFM topographic, phase and amplitude images of extracted silica at CTAB:styrene (1:1) and CDB:AIBN (0.04:1) showing the presence of polymer on much of the surface.

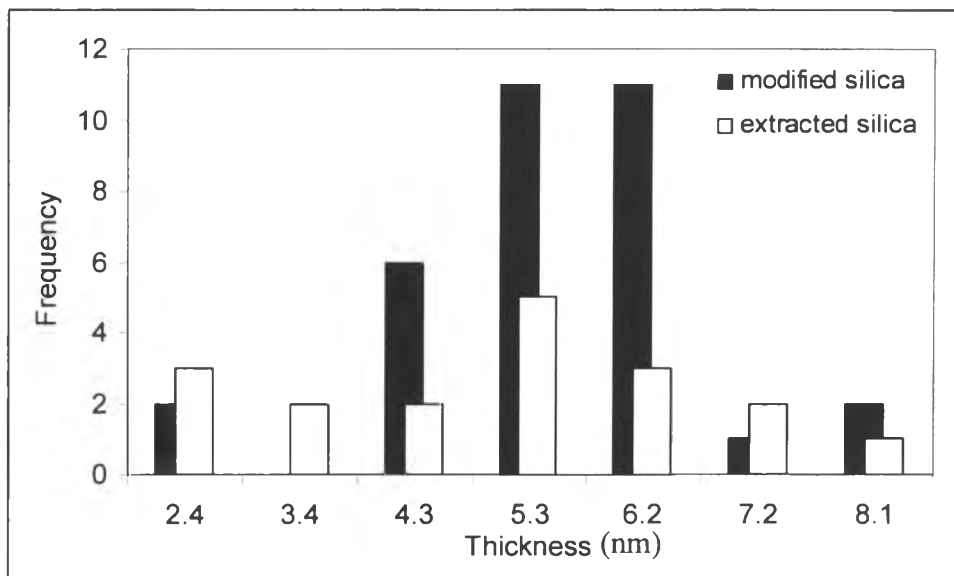


Figure 4.29 Polystyrene film thicknesses on modified and extracted silica surfaces {CTAB:styrene (1:1) and CDB:AIBN (5:1)} showing the equality of polystyrene film thickness on both silica surface.