CHAPTER IV
RESULTS AND DISCUSSION

4.1 Time for Equilibrium Adsorption

DBSA adsorbs readily on polyester at 30°C and pH 4 (Figure 4.1). The initial DBSA concentration used was 5 mM, which is well above its CMC of around 1.2 mM. The adsorption was found to increase rapidly until about 10 h after which it started to slow down and became constant at 13.0 μmol/g of polyester after 15 h. Therefore, in subsequent experiments, the adsorption step was carried out for 15 h to ensure the establishment of the equilibrium.
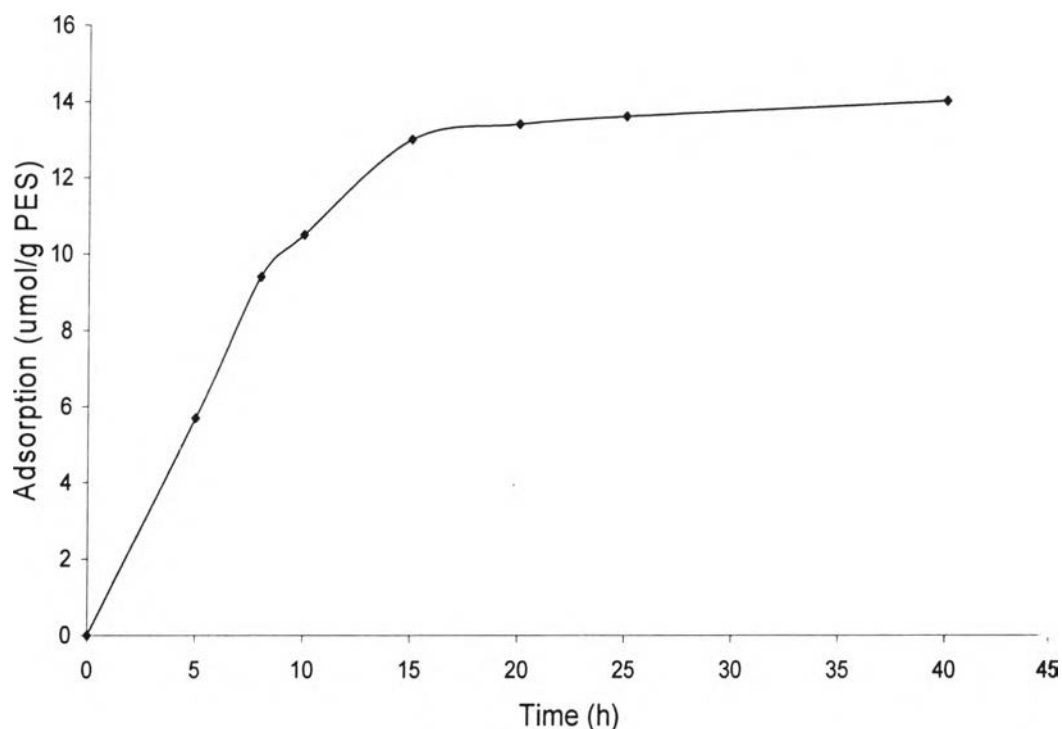

Figure 4.1 Rate of adsorption of DBSA on polyester fabric (Temp = 30°C, [DBSA] = 5 mM, pH = 4).

4.2 The Effect of Electrolyte on the Adsorption of DBSA on Polyester Fabric

The amount of DBSA adsorption changes in the presence of different concentrations of NaCl (Figure 4.2). The results show that the adsorption of DBSA on polyester fabric increased with increase in NaCl concentration. The amount of DBSA adsorption on polyester fabric was found to increase from around 11.0 μmol/g of polyester with no salt to around 18.0 μmol/g of polyester with 0.15 M NaCl. From this experiment, the 0.15 M NaCl was chosen for subsequent experiment.
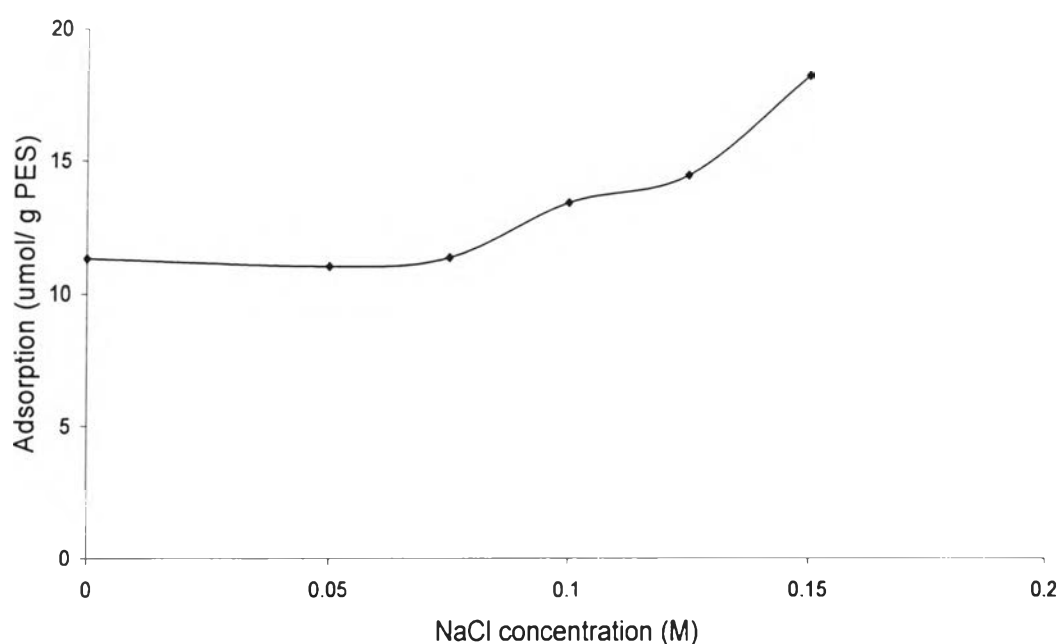

Figure 4.2 Effect of electrolyte on the amount of DBSA adsorption on polyester fabric (Temp. $=30^{\circ}$C, time$=15$ h, [DBSA] $= 5$ mM, pH $= 4$).

4.3 Surfactant Adsorption Isotherm

The adsorption isotherms of DBSA on polyester fabric at pH 4 with no salt and 0.15 M NaCl are presented in Figure 4.3. It can be seen that the adsorption of DBSA on polyester fabric conforms to S-shaped adsorption isotherm for an ionic surfactant on neutral substrate. The amount of DBSA adsorbed on polyester fabric was found to initially increase sharply with an increase in DBSA concentration. As

the DBSA concentration increased further, the slope started to decline, leading eventually to a constant value.
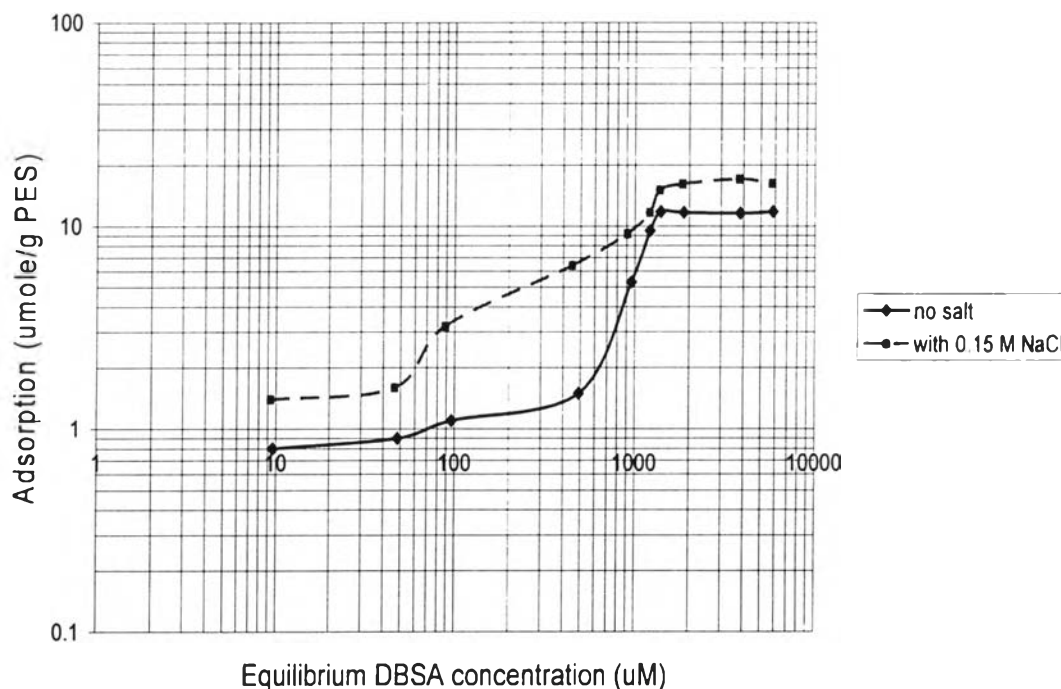

Figure 4.3 Adsorption isotherms of DBSA on polyester (Temp. = 30°C, time = 15 h, pH = 4).

Table 4.1 summarizes the CMCs of the various systems and the amount of DBSA adsorbed on polyester fabric at the CMC. Increasing the amount of salt led to a decrease in the CMC, as expected, due to reduction in the repulsion of the head groups on the surfactants. The results clearly show that the presence of salt has an effect on both the CMC and the equilibrium adsorption of the surfactant. |In admicellar polymerization process, the concentration of surfactant in the system should be just below or near its CMC to ensure significant coverage while avoiding the emulsion polymerization. From the adsorption isotherm, a concentration of 1.5 mM DBSA, which is near the CMC, was chosen for the polymerization reaction.

Table 4.1 The CMC of DBSA solution in the presence of polyester fabric at different conditions

Conditions		CMC	Adsorbed DBSA
pH	[NaCl] (M)	(μM)	(μmol/g of PES)
4	0	1390	11.7
4	0.15	1370	15.1

4.4 Area occupied by DBSA Molecules on the Polyester Fabric Surface

The surface area of polyester fabric as determined from BET with nitrogen was found to be 2.5 m^2/g. Thus, knowing the accessible surface area of polyester fabric, the surface area occupied by a DBSA molecule on the polyester fabric can be calculated. Assuming that the area occupied by a DBSA molecule was found to be 50 A^2 so the amount of adsorbed DBSA on polyester fabric was 16.6 μmol/g for a bilayer and 8.3 μmol/g for a monolayer. From the above results, the maximum amount of DBSA adsorption on polyester fabric was around 15.1 μmol/g at an equilibrium DBSA concentration of 1370 μM, which is in good agreement with the calculated amount of adsorbed DBSA bilayer on polyester. At this point, it seems reasonable to assume that the polyester fabric is near saturation.

4.5 Admicellar Polymerization

In this experiment, the initial concentration of DBSA was fixed at 1.5 mM and the DBSA:MMA molar ratio was varied in the range of 1:2, 1:5, 1:8, to 1:10. Initiator: monomer molar ratio was varied in the range of 1:5, 1:10, to 1:20. PMMA ultrathin films were coated on polyester fabric using the admicellar polymerization process. This was confirmed by FTIR and SEM. The IR spectrum of the extracted PMMA film on polyester fabric is represented in Figure 4.4. The results are presented in absorbance arbitrary units. It can be seen that the extracted PMMA

from the admicellar-treated sample shows a very intense characteristic peak at 1730 cm^{-1}, which corresponds to the C=O bond of the pendant group (-COOCH$_3$) of PMMA. An absorption band in the range of 1500-700 cm^{-1} comes from the C-O stretching vibration (1270-990 cm^{-1}), C-H bending vibration (1450-1350 cm^{-1}) and CH$_2$ rocking vibration (810 and 750 cm^{-1}). Additionally, when compared with a PMMA standard, there is a match on the finger print region. Thus, the FTIR spectra indicated that PMMA films had been coated on the fabric surface.
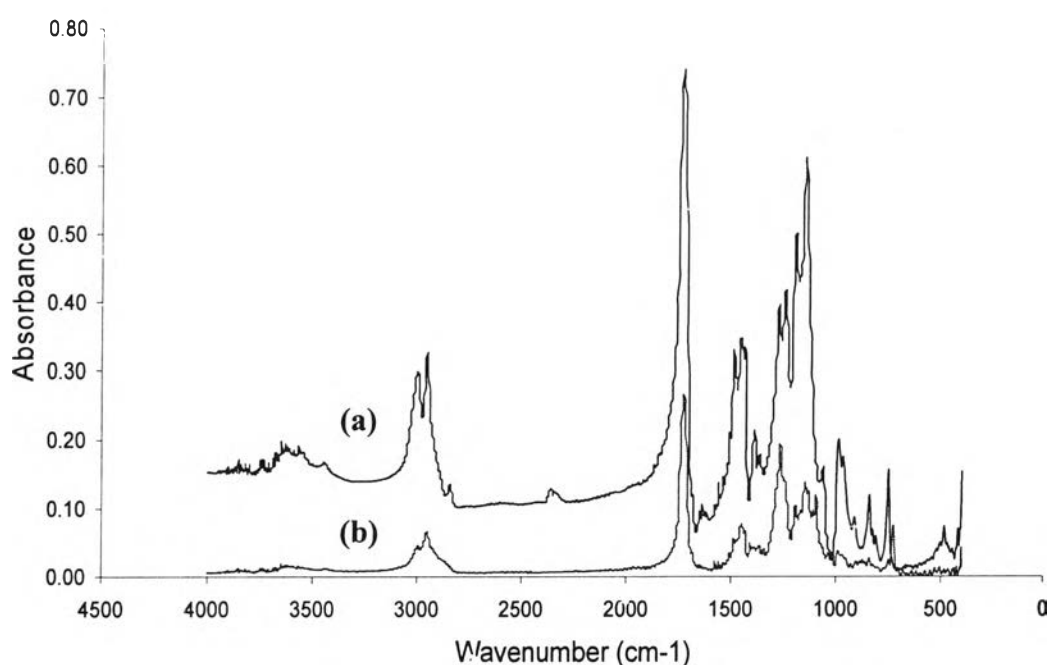
Figure 4.4 FTIR spectrum of extracted PMMA: (a) standard PMMA and (b) extracted PMMA on polyester fabric.

Representative SEM images of untreated and coated polyester fabric are presented in Figure 4.5. Figure 4.5 (b) shows the presence of PMMA on the polyester fabric surface. The SEM images showed that the PMMA films were rough and covered most of the surface on each filament of the fabric. The pictures also show that the coating occurred only on the fiber surface and not in the space between the fibers. These observations were in agreement with the FTIR results and confirmed that PMMA films had been coated on the polyester fabric by admicellar

polymerization. However, it appears that the film did not uniformly cover the fiber surface, since some areas appears not to have been involved in the polymerization. This observation may explain the decrease with time in the contact angle with water.
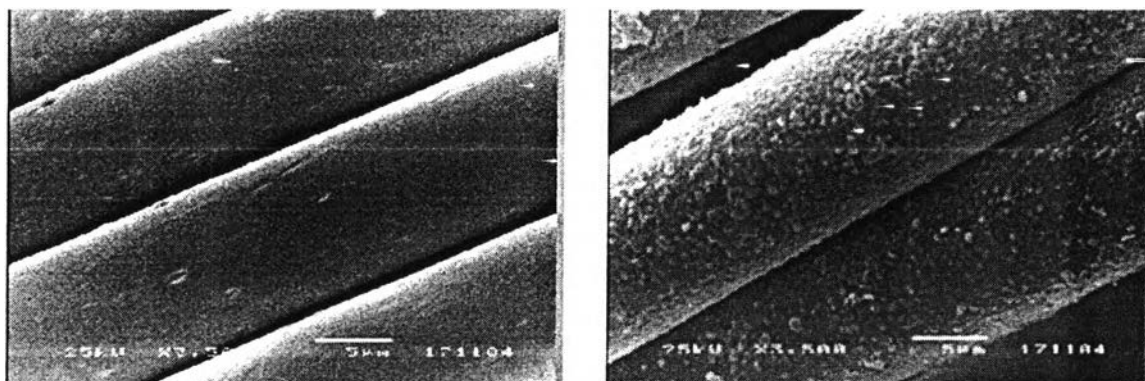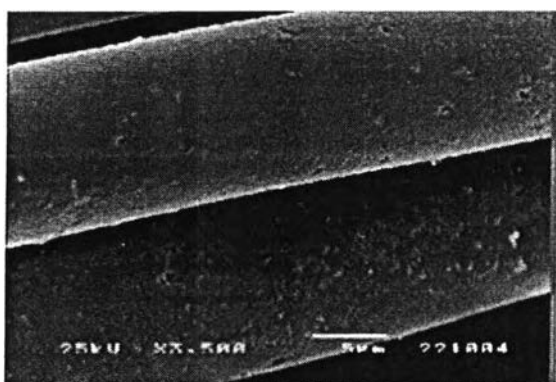

Figure 4.5 SEM micrographs of (a) untreated polyester fabric and (b) PMMA-coated polyester fabric (×3,500).

4.6 Effects of the Amount of Monomer and Initiator

4.6.1 Effect of DBSA:MMA Ratio

As observed in Figure 4.6, 4.7 and 4.8, the amount of PMMA deposited on the fiber surface increased when increasing the monomer concentration. For ratio of 1:2, the coating was very thin, whereas for ratios of 1:5, 1:8 to 1:10, the amount of the thickness not the coatings increased as the amount of monomer increased. Matarredona et al. (13) proved that the increase in the thickness of the coated films could be related to a higher concentration of monomer in the admicelle during the polymerization reaction. As the polymerization reaction proceeds, more monomer can partition into the admicelle and react to form additional polymer leading to an increase in the film thickness. However, excess monomer resulted in unsolubilized monomer that formed drops in solution that could be deposited on the surface producing a non-uniform film. Also, at high monomer ratios, solution polymerization can take place in solution and not on the fabric surface. Therefore, a 1:8 DBSA:MMA ratio was chosen for admicellar polymerization before hydrolysis. Contact angle with water on fabric surfaces was measured at varying condition.

Before the polymer was coated onto the polyester fabric surface, the average contact angles using deionized water was around 110°, indicating that the uncoated polyester fabric was moderately hydrophobic in nature. As the amount of monomer increased, the contact angles with water increased corresponding to the improvement of the hydrophobic character after admicellar polymerization, with contact angles that exceed 110° in almost conditions.
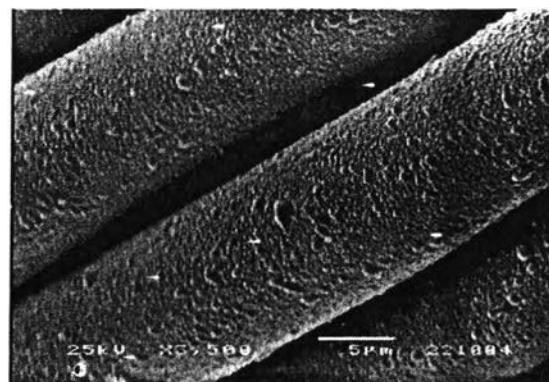

DBSA:MMA molar ratio = 1:2   DBSA:MMA molar ratio = 1:5
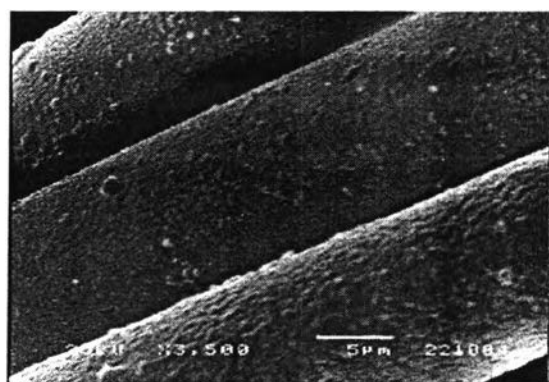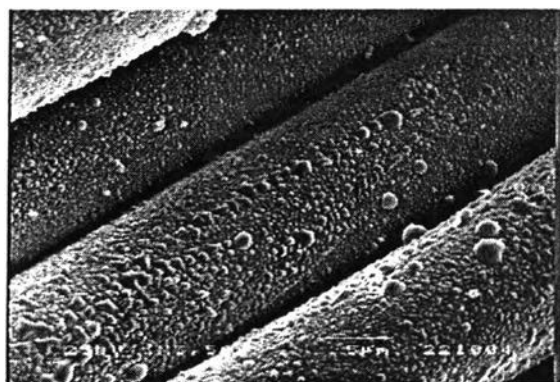
DBSA:MMA molar ratio = 1:8   DBSA:MMA molar ratio = 1:10
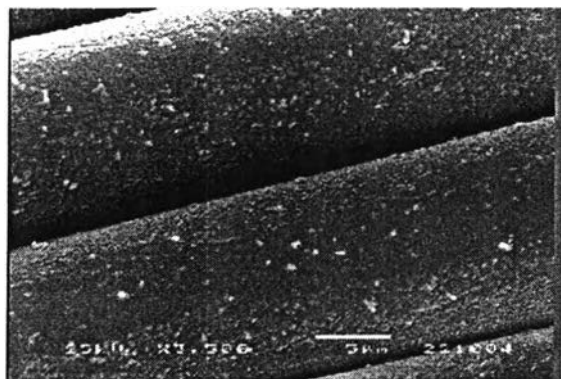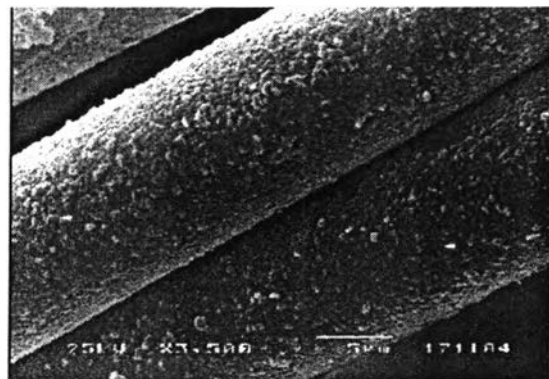
Figure 4.6 SEM micrographs of treated polyester fabric using different monomer concentrations with 1.5 mM DBSA, 0.15 M NaCl, and AIBN:MMA ratio 1:5.

DBSA:MMA molar ratio = 1:2
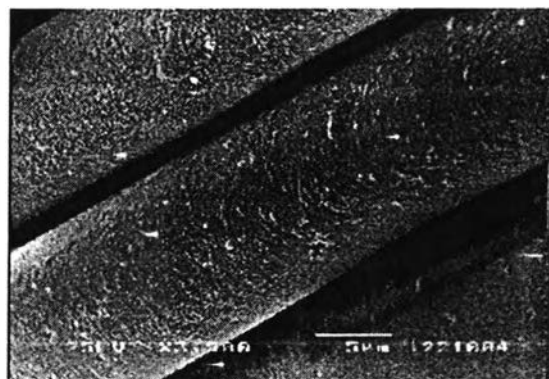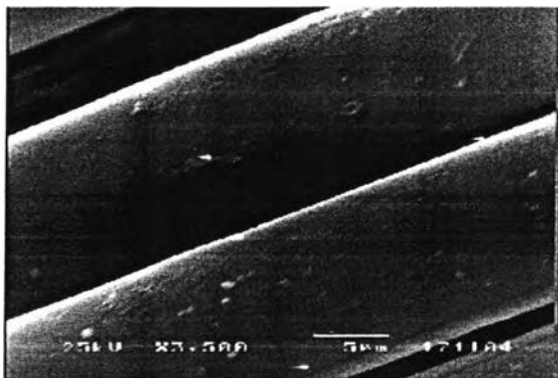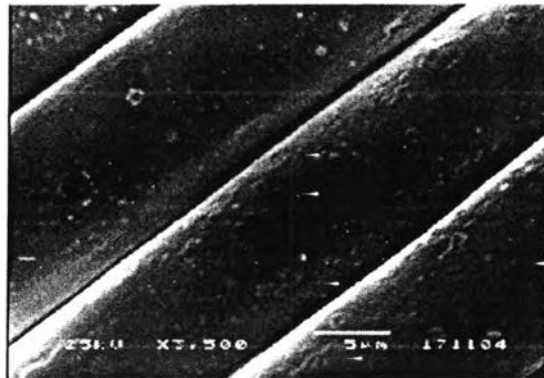
DBSA:MMA molar ratio = 1:5

DBSA:MMA molar ratio = 1:8
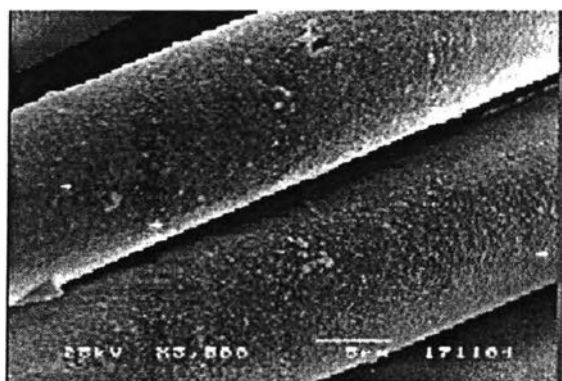
DBSA:MMA molar ratio = 1:10

Figure 4.7 SEM micrographs of treated polyester fabric using different monomer concentrations with 1.5 mM DBSA, 0.15 M NaCl, and AIBN:MMA ratio 1:10.

DBSA:MMA molar ratio = 1:2   DBSA:MMA molar ratio = 1:5

DBSA:MMA molar ratio = 1:8   DBSA:MMA molar ratio = 1:10

Figure 4.8 SEM micrographs of treated polyester fabric using different monomer concentrations with 1.5 mM DBSA, 0.15 M NaCl, and AIBN:MMA ratio 1:20.
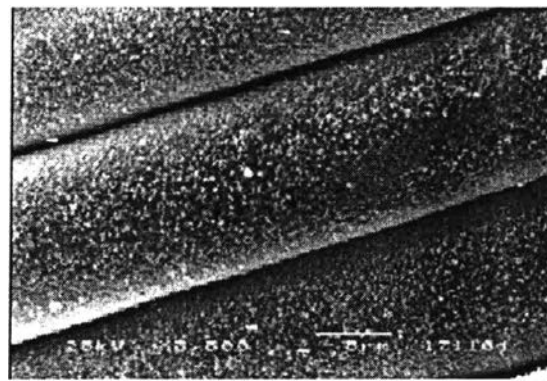
4.6.2 The Effect of AIBN:MMA Ratio

The initiator:monomer ratio was varied from 1:5, and 1:10, to 1:20. As observed in Figure 4.9, the highest initiator:monomer ratio resulted in the roughest films. However, when this ratio was reduced, the surface presented less roughness. Apparently, higher concentrations of initiator led to lower molecular weights in polymer with shorter chains forming a patchwise morphology on the fabric surface. On the other hand, the lowest AIBN:monomer ratio led to higher molecular weights in polymer with longer and more entangled chains, which can be almost coated, on the fiber surface with less roughness. In case of the untreated fabric, the water

droplet was found to disappear within a few seconds, with water spreading over a wide area. In case of the PMMA-coated fabric, the droplet remained spherical and stayed for a longer time. As the amount of initiator increased, the time the water droplet remained on the fabric surface increased and the water contact angle increased due to the increase in hydrophobic character of the fabric. In case of polyacrylate, such as PMMA, it has been suggested that strong interactions between the COO- groups and water molecules lower the diffusion of water to the polymer by the creation of hydrogen bonds between two polar groups and a water molecules.
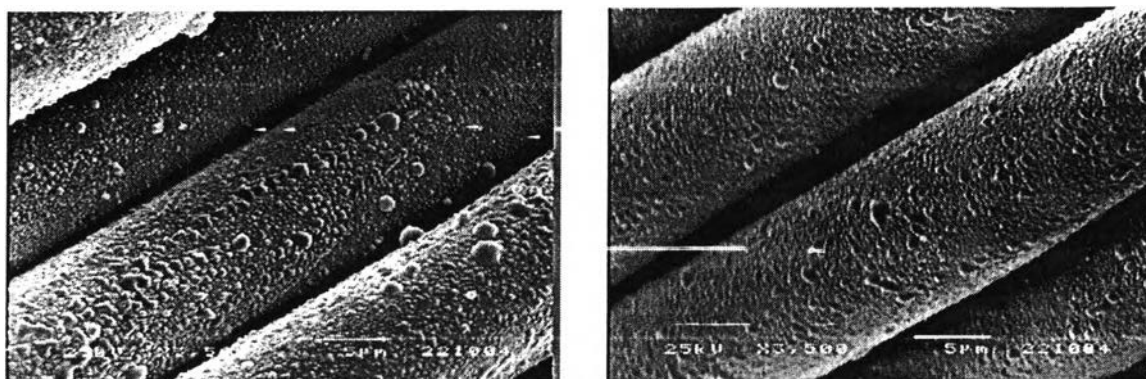
AIBN:MMA molar ratio = 1:5
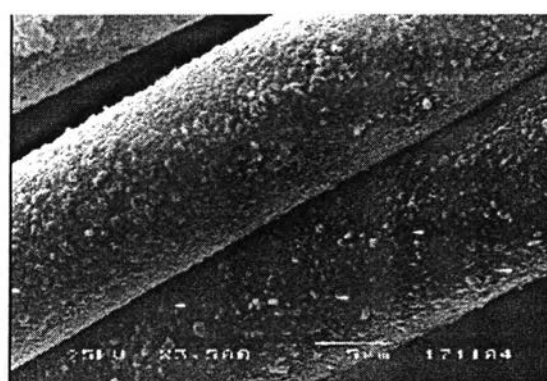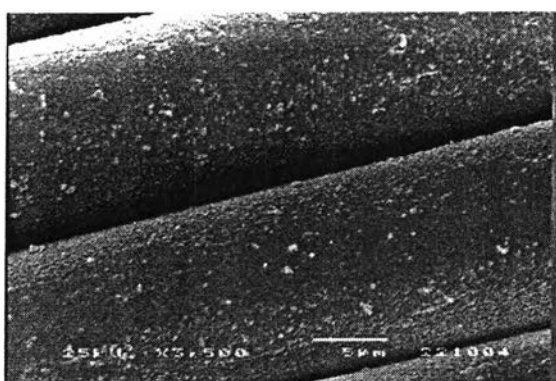
AIBN:MMA molar ratio = 1:10
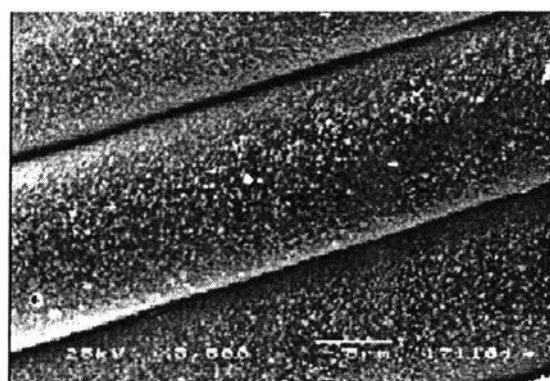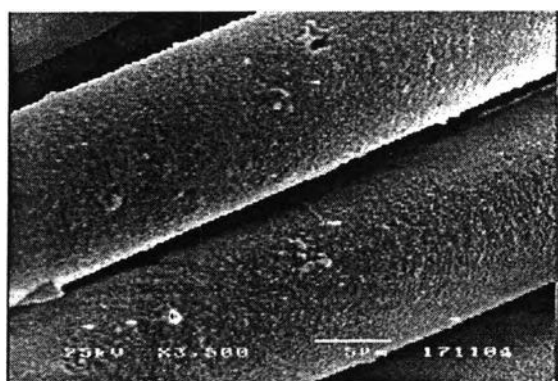
AIBN:MMA molar ratio = 1:20

(a)   (b)

Figure 4.9 SEM micrographs of treated polyester fabric using different AIBN:
MMA ratio with 1.5 mM DBSA, 0.15M NaCl, and DBSA:MMA ratio (a) 1:8
(b) 1:10.

4.7 Contact Angles Measurements

Contact angle measurements were measured at varying condition. Table 2 shows average contact angles obtained from PMMA coated samples. As the amounts of monomer increased, the contact angles of water increased corresponding to the improvement of the hydrophobicity of the treated fabric. The treated polyester fabric exhibited more hydrophobic character after admicellar polymerization, with contact angles that exceed $110°$ in almost conditions.

Table 4.2 Average contact angle of polyester fabric polymerized with methyl methacrylate at different conditions

AIBN:MMA molar ratio	Average contact angle (θ)deg			
	DBSA:MMA molar ratio			
	1:2	1:5	1:8	1:20
1:2	113.9±3.5	113.0±3.4	114.8±2.5	114.6±1.4
1:10	107.2±4.3	114.1±5.4	117.3±1.2	119.5±2.3
1:20	*	*	116.7±0.1	116.4±0.8

* The water droplets disappear immediately after dropping to the fabric surface

4.8 Hydrolysis of PMMA-coated Polyester Fabric

In this experiment, PMMA ultrathin films were hydrolyzed by hydrochloric acid, sulfuric acid, nitric acid, and p-toluenesulfonic acid. The hydrolysis time was varied from 1, 2, and 5 h. The hydrolysis temperature was varied from 30-80°C. The hydrolysis of PMMA film resulted in the formation of carboxylic acid groups on the fabric surface. The water contact angle of untreated polyester and PMMA-coated fabric is $110°$ and $117.3°$, respectively. Figure 4.10, 4.11 and 4.12 show that the water contact angle of hydrolyzed PMMA-coated fabric slightly decreased with hydrolysis time. As the hydrolysis temperature increased, the water contact angle

decreased due to the improvement of hydrophilicity of the polyester fabric which corresponded to the increase in the polar carboxylic acid groups on the fabric surface during the hydrolysis procedure. Table 4.3, 4.4 and 4.5 indicate that the moisture regain of the polyester increased from 0.55% to 0.87%. It is known that polyester fabric are hydrophobic in nature and has moisture regain around 0.4% at a standard condition (temperature = 25°C, % relative humidity = 65%). The moisture regain value of PMMA-coated fabric was around 0.57%. Hydrolysis of PMMA films increases hydrophilicity of the polyester which is responsible for the formation of the polar groups on the fabric surface. However, moisture regains and the water contact angle of the treated polyester fabric did not appear to be markedly affected by the hydrolysis. This may be due to the fact that admicellar polymerization technique produced a thin film with thickness below 1 nm so it did not affect the bulk properties such as moisture regain of the polyester fabric that much.
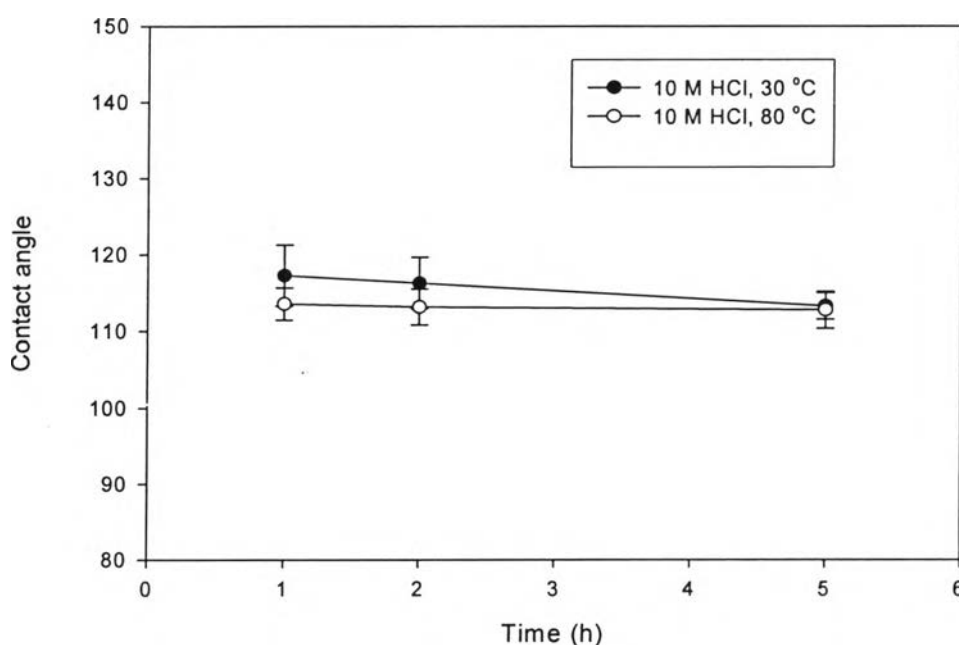

Figure 4.10 Water contact angle of treated polyester fabric as a function of hydrolysis time and temperature after hydrolysis by 10 M HCl.
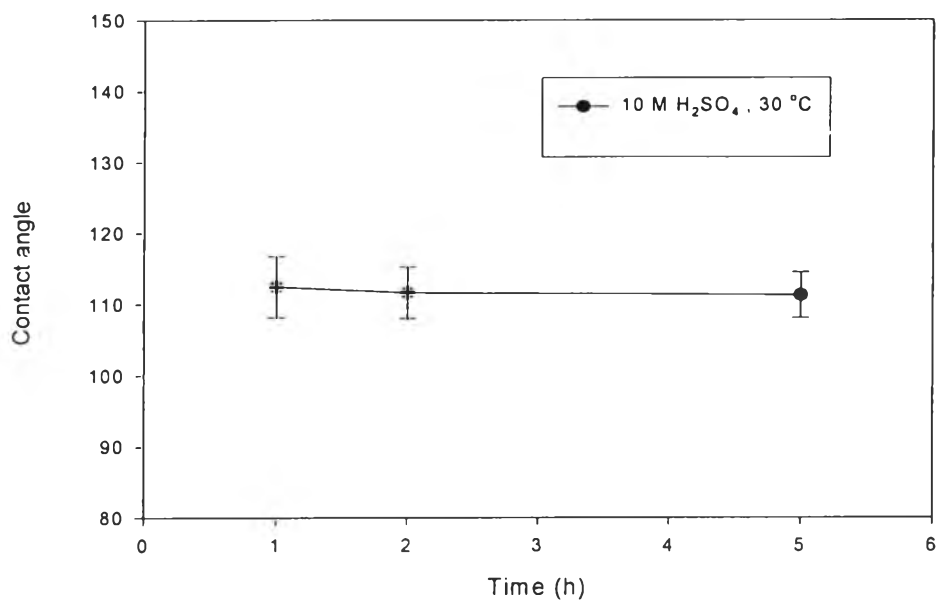
Figure 4.11 Water contact angle of treated polyester fabric as a function of hydrolysis time and temperature after hydrolysis by 10 M H_2SO_4.
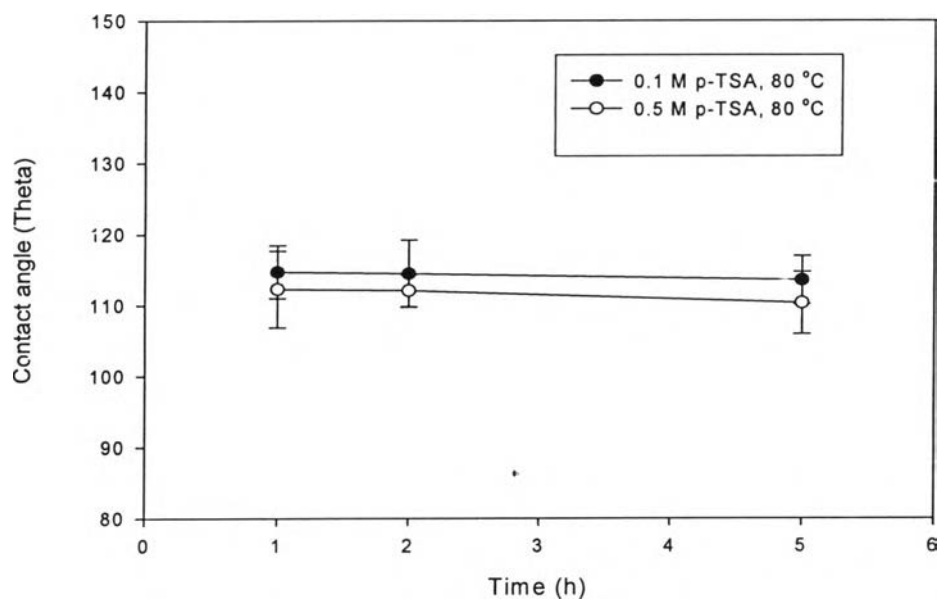

Figure 4.12 Water contact angle of treated polyester fabric as a function of hydrolysis time and temperature after hydrolysis by 0.1 and 0.5 M p-TSA.

Table 4.3 Average moisture regain value of hydrolyzed PMMA-coated fabric at temperature = 22°C, Relative humididty = 65 % after hydrolysis by 10 M HCl

Temperature (°C)	Average Moisture Regain (%)		
	1-h	2-h	5-h
30	0.63	0.64	0.60
80	0.62	0.66	0.70

Table 4.4 Average moisture regain value of hydrolyzed PMMA-coated fabric at temperature = 22°C, Relative humididty = 65 % after hydrolysis by 10 M H_2SO_4

Temperature (°C)	Average Moisture Regain (%)		
	1-h	2-h	5-h
30	0.63	0.59	0.62
80	0.70	0.72	0.87

Table 4.5 Average moisture regain value of hydrolyzed PMMA-coated fabric at temperature = 22°C, Relative humididty = 65 % after hydrolysis by p-TSA

[p-Toluenesulfonic acid] (M)	Average Moisture Regain (%)		
	1-h	2-h	5-h
0.1	0.57	0.58	0.50
0.5	0.58	0.60	0.61