CHAPTER 4

Results and Discussion

4.1 Characteristic of Oil-in-Water Microemulsion Containing AIBN Initiator

Oil-in-water microemulsion containing AIBN initiator were successfully prepared by vigorously mixing AIBN containing benzene solution, 2-propanol surfactant, and water at the stirring speed of 1400 rpm. The appropriate amounts of each composition used to produce transparent solution were obtained from ternary-phase diagram (Figure 2.2). Two types of oil-in-water microemulsion systems, CTAB-water-benene/propanol and SDS-water-benzene/propanol, were prepared in this experiment. Light scattering microscopy was employed to determine particle size distribution of microemulsion droplets. The results are presented in both z-averaged particle size and graphical distribution of particle size of microemulsion illustrated in appendix. The averaged sizes of microemulsion droplets calculated by Stokes-Einstein equation have diameter about 161 to 167 nm. However, there are some of microemulsion with smaller than 100°A in diameter. It was presumable that those microemulsion with a diameter less than 100°A would play a large part in bringing water insoluble AIBN into the interior of cellulose fiber.

4.2 The Study of In-situ Polymerization of Methacrylic Acid inside Cellulose Using Oil-in- Water Microemulsion

4.2.1 The Effect of Immersing Time

Cotton fabric was immersed in oil-in-water microemulsion (CTAB-water-benzene/ propanol/ water) containing AIBN initiator for determined times ranging from 30 to 240 minutes to allow cotton fiber absorbing microemulsion droplets at liquor ratio of 20:1. After that, treated fabrics were transferred to a 500 ml beaker containing methacrylic acid solution at liquor ratio of 40:1. Polymerization was carried out at 80°C for 3 hours. Then modified fabrics were boiled in hot ethanol to remove surface homopolymer. The percent add-on of in-situ polymethacrylic acid on the cotton fabric was measured and presented in Table 4.1.

Table 4.1 The dependence of % add-on of in-situ polymethacrylic acid on cotton fabric on times immersion

Immersing time (min)	% add-on
30	0.77
60	1.31
90	2.32
120	4.35
180	4.61
240	4.46

*The raw data were presented in appendix 2

The results showed that % add-on (after ethanol extraction) increased with an increase in times of immersion and then leveled off at immersion times of 180 min. It can be seen that in-situ polymethacrylic acid formed within cellulose structure is closely related to times of immersion. This suggests that longer immersion times allowed microemulsion droplet to diffuse into the interior of cellulose fiber, increasing the concentration of AIBN initiator.

4.2.2 The Effects of an Increase in Concentration of Methacrylic Acid and Times of Polymerization on % Add-on

The immersion time of 120 min was chosen in this section. Polymerization of methacrylic acid with various concentrations and different times of polymerization in the presence of oil-in-water microemulsion treated fabrics were carried out at 80°C without purging with nitrogen gas. The results of % add-on obtained are given in Table 4.2 and graphically illustrated in Fig. 4.1.

Table 4.2 Effects of increased concentrations of methacrylic acid and time of polymerization on % add-on

Sample	Conc. of methacrylic acid (%w/w)	Time of polymerization (hr)	Wt. of fabric before polymerization (g)	Wt. of fabric after polymerization (g)	%add-on
1	0.5	1	4.3840	4.3894	0.12
2	0.5	2	4.3875	4.3994	0.27
3	0.5	3	4.1951	4.2313	0.86
4	0.5	4	4.5439	4.5947	1.11
5	1	1	4.6139	4.6159	0.04
6	1	2	4.4326	4.4343	0.03
7	1	3	4.2851	4.3209	0.83
8	1	4	4.3437	4.3931	1.13
9	2	1	4.5290	4.5390	0.22
10	2	2	4.4981	4.5207	0.50
11	2	3	4.3866	4.5015	2.61
12	2	4	4.1878	4.3156	3.05
13	3	1	4.2306	4.2504	0.46
14	3	2	4.5475	4.5717	0.53
15	3	3	4.4354	4.5924	3.53
16	3	4	4.2244	4.3966	4.07
17	4	1	4.5526	4.5851	0.71
18	4	2	4.5979	4.6351	0.80
19	4	3	4.2209	4.4520	5.47
20	4	4	4.4070	4.6630	5.80
21	5	1	4.5367	4.5744	0.83
22	5	2	4.4546	4.5072	1.18
23	5	3	4.3085	4.5474	5.54
24	5	4	4.4122	4.6758	5.97

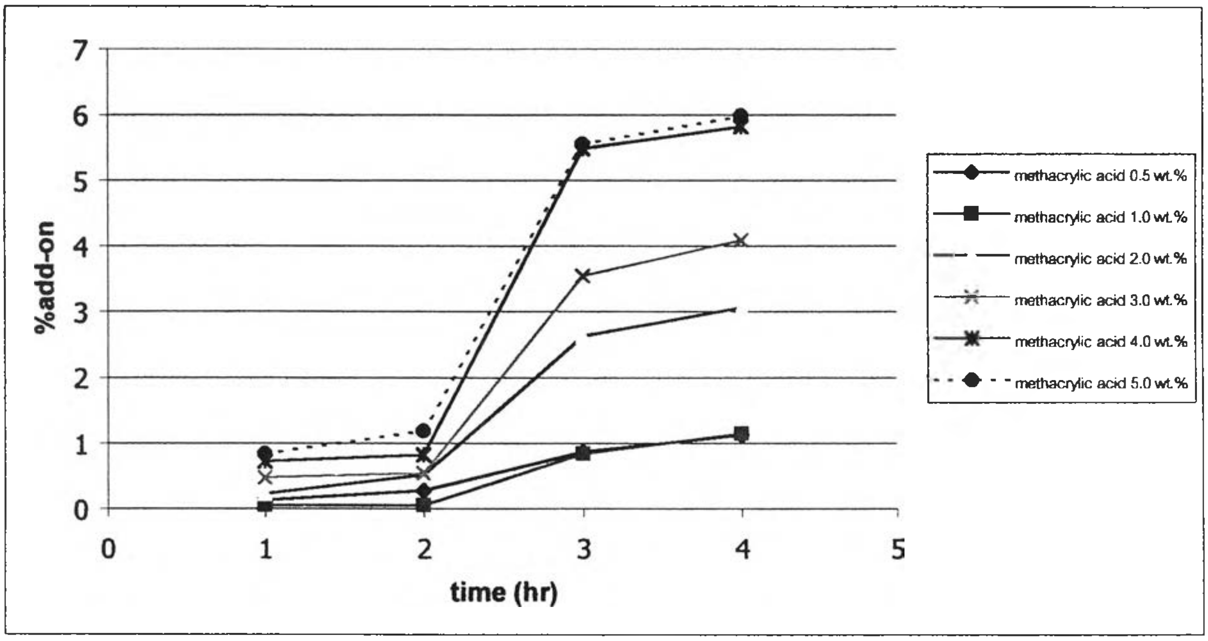


Figure 4.1 Effects of methacrylic acid concentrations and times of polymerization on %add-on

It can be observed that % add-on of polymethacrylic acid was affected by the concentration of methacrylic acid solution as well as times of polymerization. At times of polymerization lower than two hours, percent add-on showed little change compared to untreated cotton fabric. In all cases of methacrylic acid concentrations, a significant increase in percent add-on was obtained when time of polymerization was between 2 and 3 hours, albeit 4 to 5 wt.% of methacrylic acid solutions yielded the most increase in % add-on. Further increase in time of polymerization beyond 3 hours brought about little change in % add-on. It can be concluded that 4 wt.% methacrylic acid solution and polymerization time of 3 hours were the most appropriate conditions for in-situ polymerization reaction of methacrylic acid.

4.2.3 The Effect of Liquor to Fabric Ratio on % Add-on

Effect of liquor ratio in polymerization step on % add-on was studied. The methacrylic acid concentration of 4% and immersion time of 3 hours were fixed. Liquor ratios of 20:1, 30:1, and 40:1 were investigated. The results of % add-on are given in Table 4.3

Table 4.3 The effect of liquor ratio on % add-on of polymethacrylic acid

Liquor ratio	Conc. of methacrylic acid (%w/w)	Time of polymerization (hr)	%add-on
20:1	4	3	4.03
30:1	4	3	4.37
40:1	4	3	4.64

*The raw data were presented in appendix 3

Overall, the most suitable conditions for in-situ polymerization of methacrylic acid as follows:

1) Immersion time of cotton fabric in oil-in-water microemulsion was 2 hr. at liquor ratio of 20:1.
2) The methacrylic acid concentration of 4 wt.%, polymerization time of 3 hr., and liquor ratio of 40:1 were found to produce good results of % add-on of polymethacrylic acid

4.3 Identification of Polymethacrylic Acid in Cellulose Using FTIR

Identification of polymethacrylic acid inside cellulose was carried out using FTIR. The method of sample preparation used in this research was pressed-disc technique by mixing a sample with potassium bromide (KBr). The FTIR spectrum of untreated and treated fabrics before and after ethanol extraction were shown in Figure 4.3 and Figure 4.4

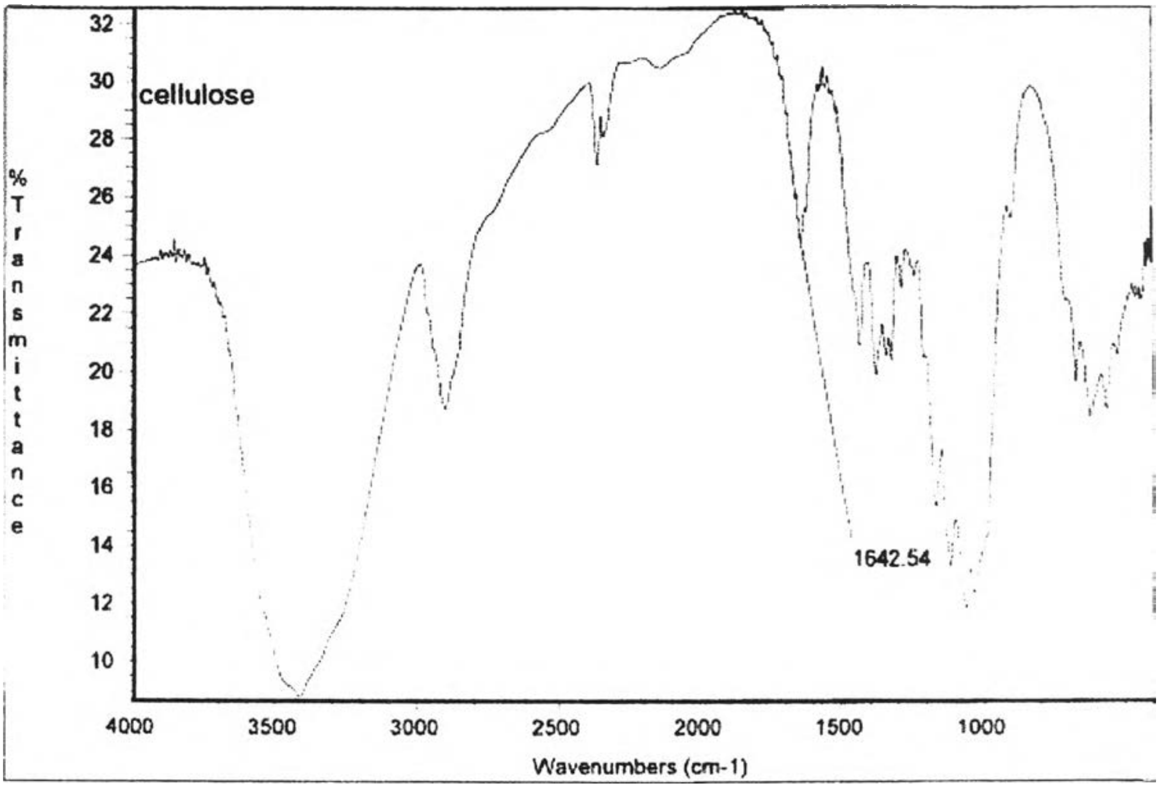


Figure 4.2 FTIR spectrum of untreated cellulose

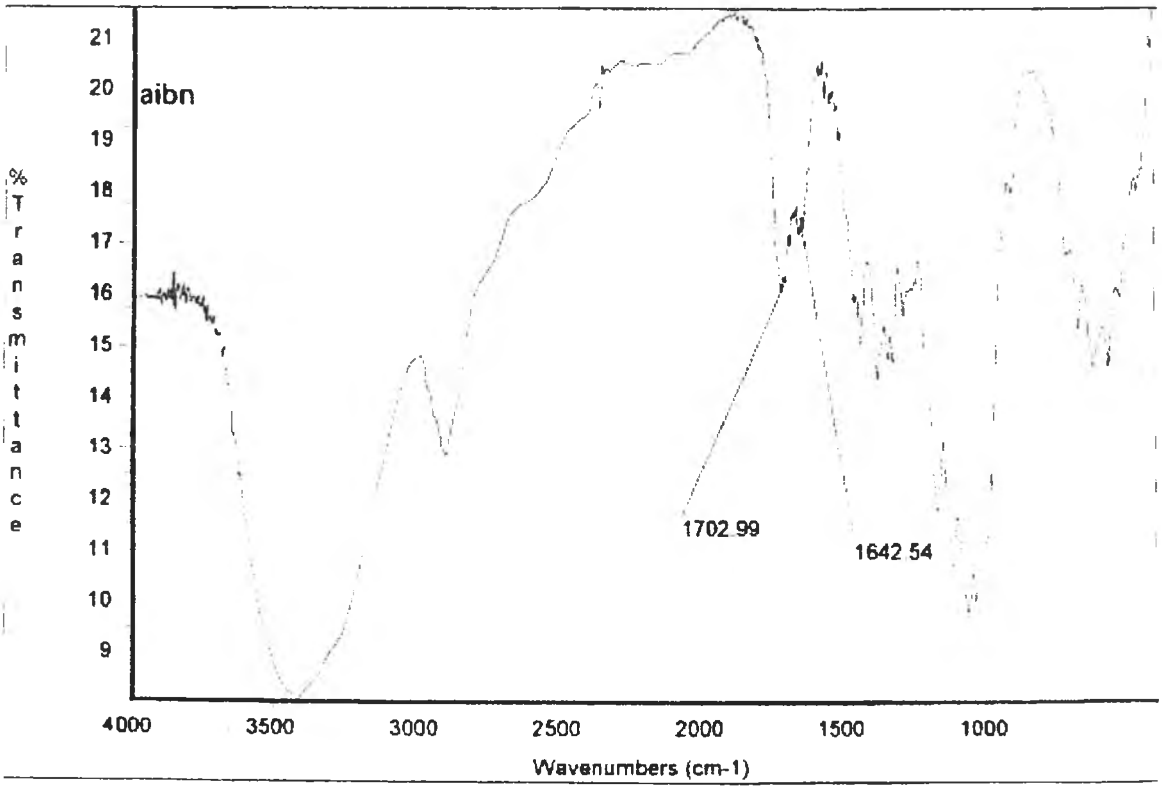


Figure 4.3 FTIR spectrum of polymethacrylic acid modified cotton before ethanol extraction

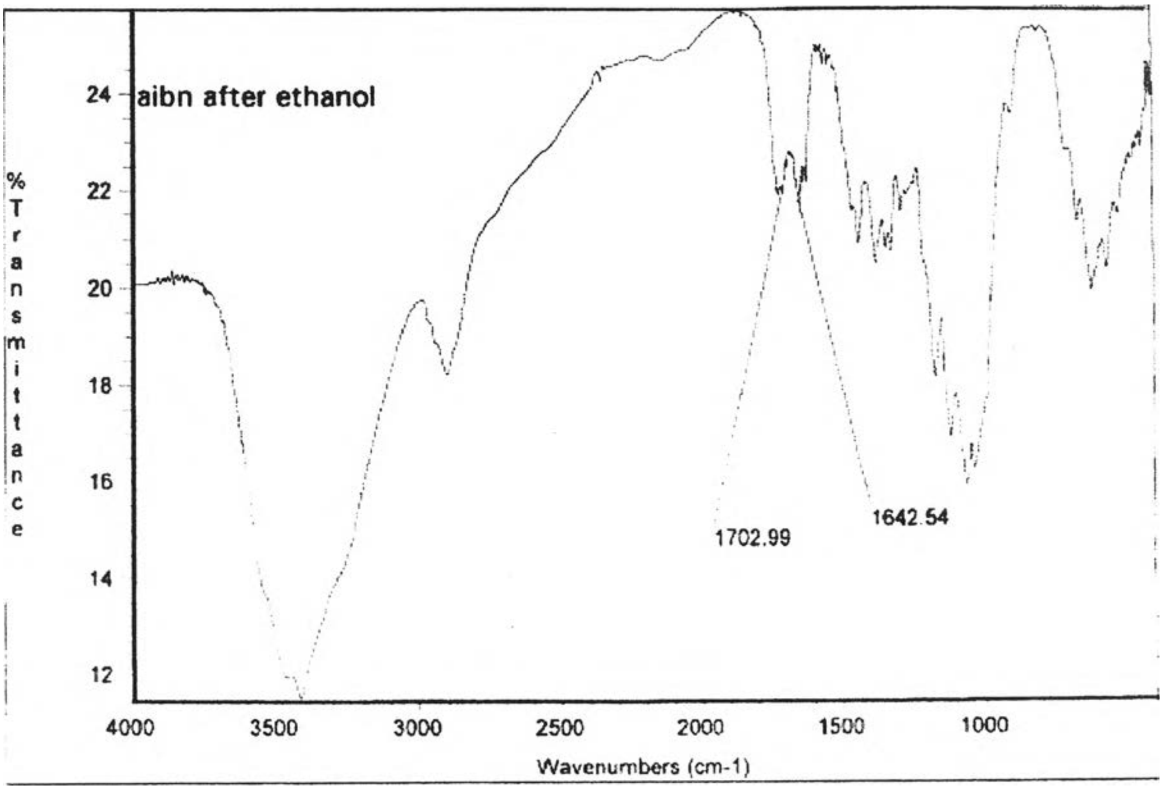


Figure 4.4 FTIR spectrum of polymethacrylic acid modified cotton after ethanol extraction

Figure 4.3 and 4.4, compare the spectra of modified cotton before and after ethanol extraction in order to investigate the durability of in-situ polymethacrylic acid inside cellulose structure, leading to produce entangled polymeric chain held firmly within cellulose fiber. Figure 4.4 confirms that the attachment of polymethacrylic acid to cellulose is permanent, evidenced by the presence of strong intensity of polymethacrylic acid carbonyl group at 1702.99 cm^{-1}. Therefore, it could be possible that permanent fixation of polymethacrylic acid on cellulose is obtainable without graft polymerization.

4.4 The Effect of Different Types of AIBN Containing Systems on % Add-on

Two types of AIBN containing oil-in water microemulsion systems (CTAB-Benzene/propanol-Water) and (SDS-Benzene/propanol-Water) were prepared. Cotton fabrics were treated in both microemulsion solutions according to previous method. In-situ polymerization of methacrylic acid was carried out using the optimum condition found in Section 4.21, 4.22, and 4.23.

The results of % add-on of polymethacrylic acid are presented in Table 4.4 and illustrated in Fig. 4.5. It is obvious that % add-on produced from these two systems are markedly different. As can be seen, % add-on obtained from SDS-benzene/propanol-water system is relatively lower than those obtained from CTAB-benzene/propanol-water system. Since CTAB differs from SDS in that it carries a cationic group which favored the absorption of microemulsion droplets due to the opposite charge attraction between CTAB and fiber surface. On the other hand, SDS and fiber surface tended to repel each other because of same charge interaction. Therefore, the introduction of AIBN initiator by the latter microemulsion system into the interior of cellulose fiber was restricted, reducing the %add-on of in-situ polymethacrylic acid. The finding results also reveal that in order to obtain permanent fixation of polymethacrylic acid inside cellulose it is necessary that AIBN initiator must be introduced to the inner of the fiber to initiate the in-situ polymerization. This could be achieved by using microemulsion system containing cationic surfactant.

Table 4.4 Comparison of % add-on obtained from using CTAB-bezene/propanol-water system and SDS-benzene/propanol-water system

Microemulsion system	Time of polymerization (hr)	%add-on
CTAB-benzene/propanol-water	1	0.71
	2	0.80
	3	5.47
	4	5.80
SDS-benzene/propanol-water	1	0.05
	2	0.03
	3	2.37
	4	3.05

*For CTAB-benzene/propanol-water, the raw data from Table 4.2

*For SDS-benzene/propanol-water, the raw data from Appendix 4

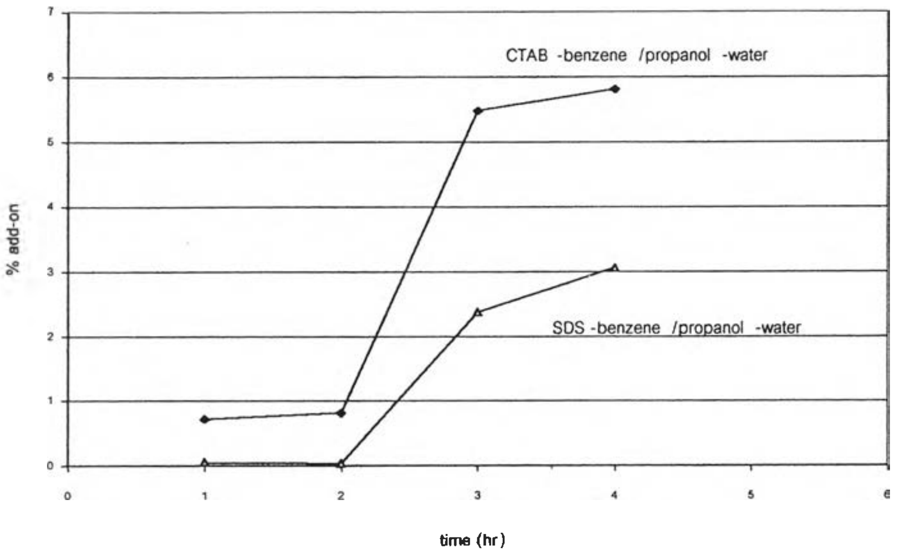


Figure 4.5 Effect of different stock microemulsion solutions on % add-on of polymethacrylic acid

4.5 The Study of Graft Polymerization of Methacrylic Acid Using Potassium Persulfate

Graft polymerization of methacrylic acid onto cellulose was studied for comparison purpose. The graft method was conducted according to literature. In contrast, graft polymerization produced polymethacrylic acid covalently bonded cellulose. Potassium persulfate was a redox initiator, which dissociated itself into $SO_4^{\bullet -}$ radical. Thus produced radical was powerful enough to abstract hydrogen atom from hydroxyl group of cellulose, resulting in cellulose radical (Cell-O•). The overall reaction can be summarized as shown in following Equation:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + \text{Cell-OH} \rightarrow \text{Cell-O}^{\bullet} + HSO_4^{-}$$

The cellulose radical then acted as an initiator for graft polymerization of methacrylic acid. The % add-on of polymethacrylic acid from graft polymerization, from CTAB-benzene/propanol-water, and SDS-benzene/propanol-water systems were compared as shown in Figure 4.6.

Table 4.5 % add-on of polymethacrylic acid prepared by graft polymerization

Time of polymerization (hr)	% add-on
1	0.01
2	3.10
3	4.70
4	5.36

*The raw data were presented in appendix 4

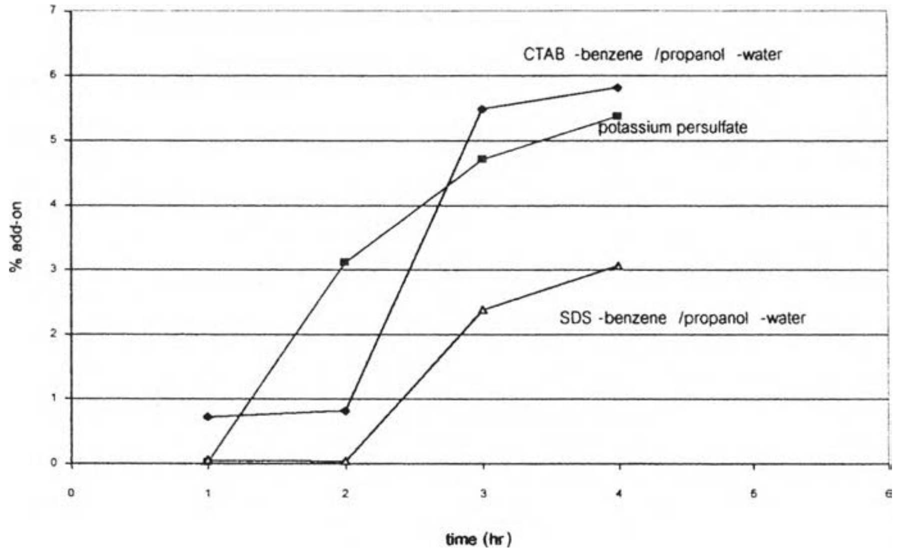


Figure 4.6 The comparison of % add-on of polymethacrylic acid prepared by different stock microemulsion solutions

From the figure, % add-on of graft polymethacrylic acid and % add-on of in-situ polymethacrylic acid are comparable. However, it is believed that their distribution that is one of important factors affecting the properties of modified cellulose might be different. Detailed discussion and properties of modified cellulose from two systems will be found in latter sections.

The presence of polymethacrylic acid inside cellulose structure is confirmed by the absorption band of carbonyl group of polymethacrylic acid at 1702.99 cm^{-1}. The peak intensity could quantitatively represent the amount of polymethacrylic acid content. The results show that the amounts of polymethacrylic acid obtained from IR spectra are found in good agreement with the % add-on.

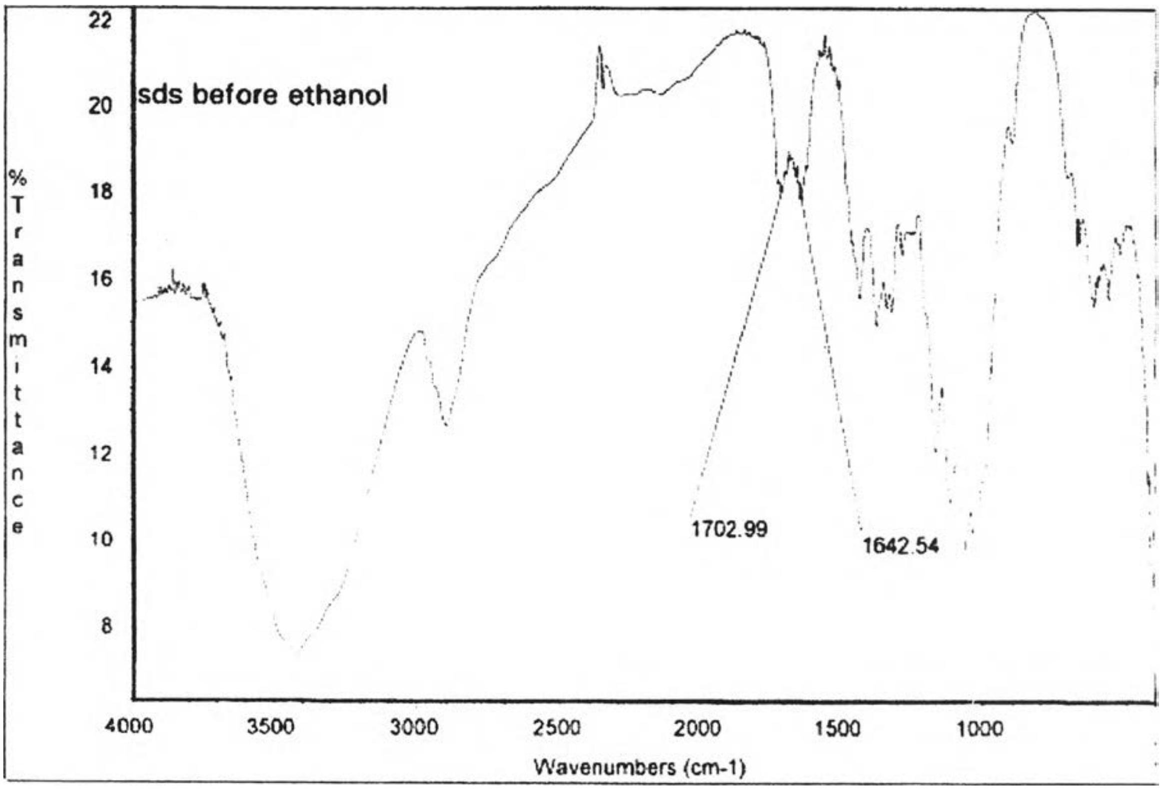


Figure 4.7 FTIR spectrum of polymethacrylic acid modified cotton using anionic surfactant before ethanol extraction

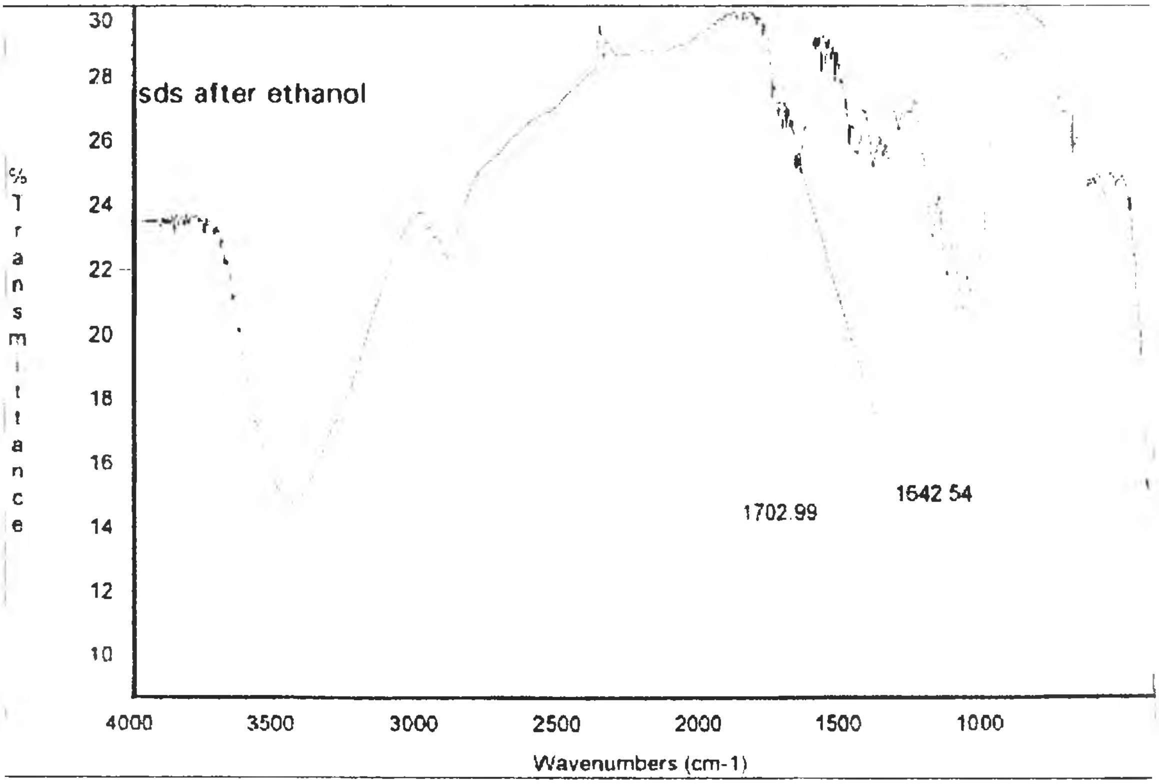


Figure 4.8 FTIR spectrum of polymethacrylic acid modified cotton using anionic surfactant after ethanol extraction

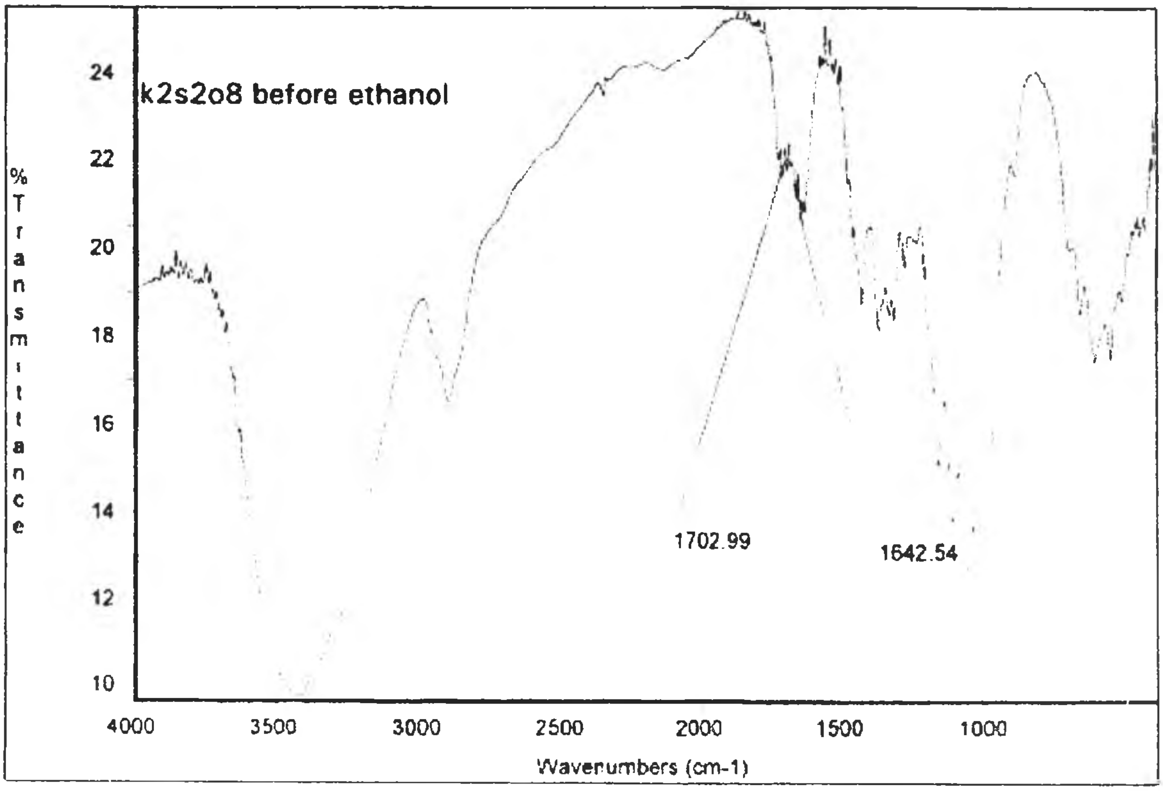


Figure 4.9 FTIR spectrum of polymethacrylic acid modified cotton by graft polymerization before ethanol extraction

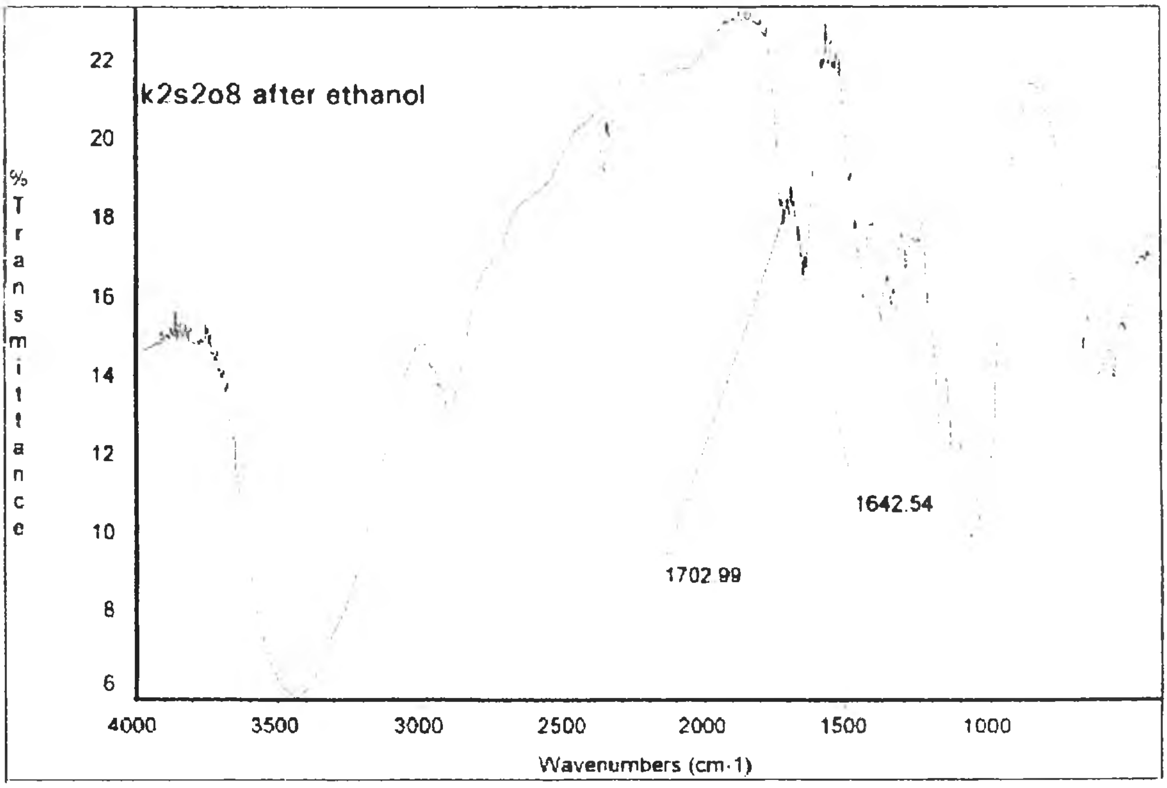


Figure 4.10 FTIR spectrum of polymethacrylic acid modified cotton by graft polymerization after ethanol extraction

4.6 Effect of Polymethacrylic Acid on Moisture Regain of Treated and Untreated Fabrics

The treated fabrics from previous experiment were used for moisture regain measurement. For the samples from CTAB-benzene/propanol-water system, the % add-on was found out by the data in appendix 3. For the samples of SDS-benzene/propanol-water and graft polymerization system, the % add-on was found out by the data in appendix 4. Each sample was weighed after ethanol extraction according section 3.41-3.44. Then these fabrics were placed in the condition of 23 $^{\circ}$C and 62 % humidity measured by hygrometer, BARICO® for 3 days. After that, the weight of samples under this condition was recorded. Thus, the % moisture regain was calculated and presented in Table 4.6.

Table 4.6 %moisture regain of treated and untreated fabrics

Sample	% Add-on	% moisture regain
untreated fabric	-	4.04
CTAB-benzene/propanol-water	4.64	4.50
SDS-benzene/propanol-water	2.37	4.19
graft polymerization	4.70	4.86

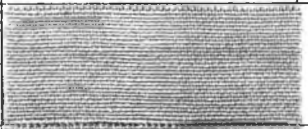
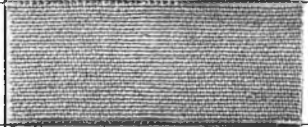
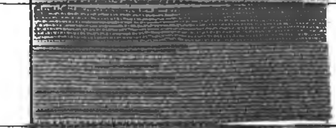
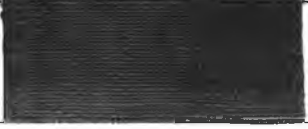
*The raw data were presented in appendix 5

As indication in the above table, the treated fabrics gives higher moisture regain than untreated fabrics because the treated fabrics contained polymethacrylic acid. Theoretically, polymethacrylic acid could absorb moisture because of its anionic characteristic in nature. From the three systems, graft polymerization shows the highest increase in moisture regain while SDS-benzene/propanol-water has the least increase moisture regain due to the lowest amount of % add-on.

4.7 Effect of % add-on of polymethacrylic acid on the Intensity of Dye on Treated Fabrics

Treated fabrics with different concentration of % add-on from 0.1 to 4.0 % were dyed with 2% o.w.f. ASTRAZON BLUE FGLN 200% in the absence of any auxiliaries using exhaustion dyeing method as described in section 3.6. The color strength presented in K/S values of shown in Table 4.7.

Table 4.7 Effect of % add-on (CTAB-benzene/propanol-water system) on dyeability with 2% ASTRAZON BLUE FGLN

Sample No.	% add-on	Dyed sample	K/S value[(a)]
1	0.1		0.170
2	0.2		0.177
3	0.4		0.303
4	0.8		0.361
5	1.1		0.363
6	2.6		0.479
7	3.0		0.484
8	3.5		0.530
9	4.0		0.542

(a) measured at 440 nm

From the results in Table 4.7, color strength increased as the % add-on increased, indicating that the presence of polymethacrylic acid acted as dye sites for basic dye. The more the concentration of polymethacrylic acid the higher the color strength of basic dyes. The absorption behavior of basic dyes are obeyed to the Lang muir absorption isotherm; complete dye exhaustion (clear dye bath solution) is possible as long as the anionic dye site still available such as in the case of low depth of dyeing.

4.8 Dyeing Properties of Polymethacrylic Acid Modified Cotton Fabric with Basic Dyes

The modified cotton fabrics obtained previously were tested for their dyeability with basic dyes. The basic dye range bearing a cationic group is typically attractive to the negatively charged substrate such as; in this case, the polymethacrylic acid modified cotton. Hence, the dyeing of modified cotton with basic dyestuff could produce dyed fabric with high color strength without requirement of additional auxiliaries. Modified fabrics were dyed with basic dyes using dye concentration ranging from 1 to 4 % (o.w.f.) in the absence of any auxiliary by exhaustion method as described in section 3.6.

The results of the color yield from before and after washing test are presented in Table 4.8.

Table 4.8 Color yield of the treated and untreated fabrics which were dyed with various concentrations of ASTRAZON BLUE FGLN 200%

Technique of Modification		Dye Concentration (% o.w.f.)	Color Yield (k/s) (λ=440nm)	
			Before washing test	After washing test
Microemulsion Treatment	CTAB-benzene/propanol-water	1	0.293	0.139
		2	0.545	0.317
		3	0.762	0.355
		4	1.088	0.398
	SDS-benzene/propanol-water	2	0.437	0.254
Graft Polymerization		2	0.645	0.311
Untreated Fabric		1	0.115	0.082
		2	0.191	0.106
		3	0.218	0.125
		4	0.241	0.122

For the treated fabrics, with irrespective to methods of treatment, the results showed that color yield of dyed fabrics before and after washing test increased as the concentration of dye increased. A considerable increase in dye exhaustion compared to those of control was attributed to the attraction between cationic groups of dye and negative groups of polymethacrylic acid. In the case of untreated fabrics, the results of color yield were much relatively lower because unmodified cellulose exhibits weak and temporary negative charge on the fiber surface when immersed under water, leading to weaker dye-fiber interaction. Dyed fabric from anionic microemulsion treatment performed lower color yield than cationic microemulsion. This was due to the fact that cotton fabric treated in anionic microemulsion contained lower amount of % add-on of in-situ polymethacrylic acid. On the other hand, polymethacrylic acid grafted cotton fabric exhibited the highest color yield among the three treatment techniques. It was believed that graft polymer mostly presented on the outer area of cotton yarn since the graft polymerization preferably occurred at the fiber surface. In this case, ring dyeing was expected to be obviously observed (detailed discussion later).

4.9 Evaluation of Fastness Properties of Dyed Fabrics

Light fastness property of dyed fabrics was tested according to ISO 105-B02 standard method, the degree of color fading was assessed referring to standard blue wool scales. The results of light fastness property of dyed treated fabrics were shown in Table 4.9.

Table 4.9 Light fastness (ISO 105-B02) standard test method of treated fabrics dyed with various concentrations of ASTRAZON BLUE FGLN 200%.

Technique of Modification	Dye concentration (%o.w.f.)	Light Fastness
CTAB-benzene/propanol-water system	1	3
	2	3-4
	3	4
	4	4
CTAB-benzene/propanol-water system dyed with ASTRAZON RED 5BL	2	2-3
SDS-benzene/propanol-water system	2	4
Graft polymerization	2	4

Washing fastness property of dyed fabrics was tested according to ISO 105-C01 standard method. The degree of color fading was assessed referring to gray scale.

The results of washing fastness property of dyed treated fabrics were shown in Table 4.10

Table 4.10 Washing fastness assessment of untreated and treated fabrics dyed with various concentrations of ASTRAZON BLUE FGLN 200%.

Method of treatment	Concentration of dye	Color Change	Color staining(a)					
			Ac	C	N	P	A	W
Microeulsion based on CTAB-benzene/propanol-water system	1	2	3	1-2	3	1-2	1	1-2
	2	2	3	1-2	2-3	1-2	1	1-2
	3	1-2	2-3	2	2-3	1-2	1	1-2
	4	1-2	3	2-3	3	1-2	1	2
	2*	1-2	2	1-2	1-2	1-2	1-2	1-2
Microeulsion based on SDS-benzene/propanol-water system	2	2	1-2	1	1-2	1	1	1
Graft polymerization	2	1	1-2	1	1-2	1	1	1
Untreated fabric	1	1	1	1	1	1	1	1
	2	1	1	1	1	1	1	1
	3	1	1	1	1	1	1	1
	4	1	1	1	1-2	1	1	1

* Treated fabric dyed with ASTRAZON RED 5BL

(a) Ac = Acetate adjacent
C = Cotton adjacent
N = Nylon 6,6 adjacent
P = Polyester adjacent
A = Acrylic adjacent
W = Wool adjacent

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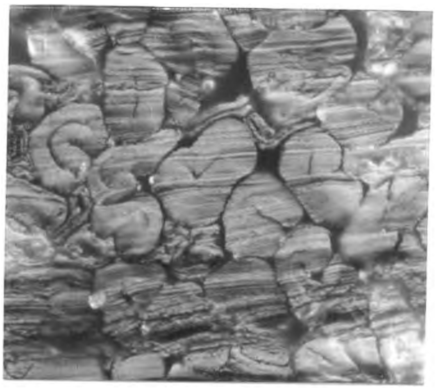

Figure 4.11 Cross section image of treated fabric obtained from graft copolymerization technique

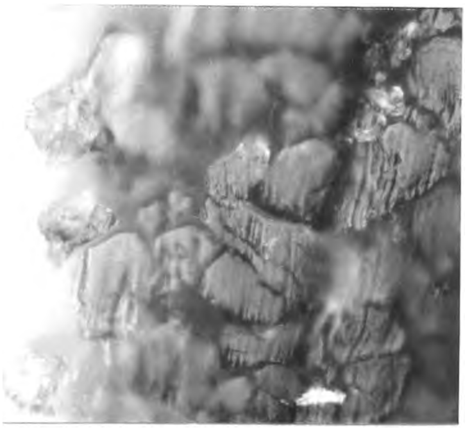

Figure 4.12 Cross section image of treated fabric based on SDS-benzene/propanol-water system

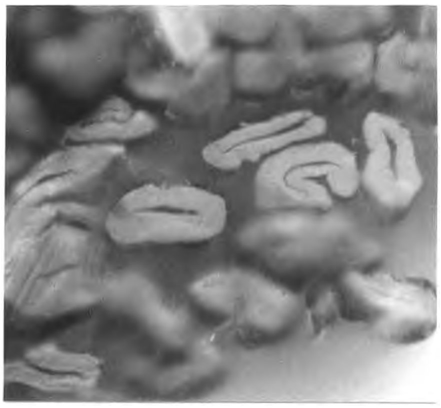

Figure 4.13 Cross section image of treated fabric base on CTAB-benzene/propanol water system

Optical microscope analysis of the cross section of dyed samples was carried out in order to investigate the distribution of polymethacrylic acid inside the cotton yarn. The optical microscopic images are illustrated in Figure 4.11, 4.12,and 4.13. The difference in color distribution across the cross-section If dyed samples was notably observed, reflecting the various level of polymethacrylic acid concentration. Figure 4.11 showed that grafted polymethacrylic acid concentrated mainly on the outer of cellulose yarn, indicating that grafted polymerization preferably occurred on the fiber surface. Figure 4.12 showed the image of dyed sample from anionic microemulsion treatment. It could be seen that the basic dye penetrated into the core of yarn deeper than those of grafted cellulose. This indicated that anionic microemulsion treatment exhibited some degree of the ability of initiator penetration. However, the penetration of AIBN containing anionic microemulsion droplet was retarded due to the repulsive interaction between microemulsion and the fiber surface. In the case of dyed sample from cationic microemulsion treatment based on CTAB-benzene/propanol-water system, very much deeper dye penetration was observable. This indicated that AIBN was successfully introduced into the inner of cotton yarn, inducing the in-situ polymerization of methacrylic acid. Of all three systems, cationic microemulsion treatment was preferable in terms of the possible introduction of water insoluble initiator into the hydrophilic fiber such as cellulose. Cationic characteristic of the microemulsion as well as its nanoscale sizes is very crucial to enhance its diffusion. This work has been aimed at the introduction of new approach to modification of cellulose.