CHAPTER V

BROAD ULTRAVIOLRT PROTECTION BY COPOLYMERIZATION OF 2-[3-(2H-BENZOTRIAZOL-2-YL)-4-HYDROXYPHENYL]ETHYL METHACRYLATE AND 2-HYDROXY-4-ACRYLOYLOXYBENZOPHENONE ON COTTON VIA ADMICELLAR POLYMERIZATION[*]

5.1 Abstract

Two monomers with complimentary ultraviolet absorbing moieties, 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM) and 2-hydroxy-4-acryloyloxybenzophenone (HAB), were copolymerized through admicellar polymerization on a cotton fabric surface in order to improve its ultraviolet protection with broad spectral coverage. Separate and combined adsolubilization of the two monomers in dodecylbenzenesulfonate admicelles were studied and compared. Copolymer composition and monomer reactivity ratio were investigated by FTIR using Fineman-Ross and Kelen-Tüdos methods and it was found that the BEM-HAB copolymer system showed an alternating tendency and exhibited azeotropic polymerization at a particular composition. The copolymerization method used in this study provided a cotton fabric with uniform and complete UV-protection in the most hazardous regions. Ultraviolet Protection Factor (UPF) of the modified cotton was studied with a range of copolymer compositions and it was found that the fabrics coated by copolymer had higher values of UPF than homopolymers, while the monomer ratio of 1:1 gave the highest UPF value.

Key words: Copolymerization; Admicellar polymerization; Benzotriazole; Benzophenone; Cotton fabric; UV Protection

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5.2 Introduction

It is well-known that copolymerization is an effective approach to obtain materials with tailored properties that are usually improved with respect to those of the homopolymers.[1-3] Depending on the utilized monomers, properties of copolymer can be easily varied. In some applications the differences in the radiation emission or absorption of each monomer are being utilized. Recently, copolymerization has been used in the preparation of electroluminescent polymers with the aim of producing easy tuning of emission colors or adjustable light emission.[4-6] The method has also been employed to improve the performance of polymers containing photochromic functional groups, such that the final copolymer will possess photochromophores with uniform distribution.[7,8] In the present work copolymerization was utilized to achieve a broader and more uniform UV absorbance over the entire UV region to improve the performance of UV-protective clothing.

In preparing a UV-protective clothing, normally a UV absorber is applied to the fabric at certain production stage.[9,10] A UV absorber is an organic compound which functions as a blocking agent by taking up UV radiation and converting it to less harmful energy. UV absorbers have been used as photostabilizers to stabilize dyes,[11,12] and employed as the active ingredient in sunscreens.[13] Each such type of the UV blocking species selectively absorbs UV radiation strongly over a certain wavelength range only. In this work, benzotriazole and benzophenone, two types of UV absorbers with complementary UV absorption, were incorporated into monomers which were copolymerized onto fabric via the admicellar polymerization technique. Admicellar polymerization[14,15] is a versatile surface polymerization process using surfactant aggregates adsorbed on the surface to concentrate monomer near to the substrate surface prior to polymerization. It consists basically of 3 steps as shown in Scheme 5.1. First, admicelles are formed on the substrate surface. Second, an organic monomer is allowed to partition into the admicellar layer. Third, polymerization on the surface is initiated. Finally, the surfactant is washed away, leaving a thin polymer film coating. This

technique has been widely studied in many systems. Thin films of polystyrene,[16] poly(pyrrole),[17] poly(2,2,2-trifluoroethyl acrylate),[18] and poly(styrene-isoprene)[19] have been successfully formed on various substrates such as alumina,[16] glass fiber,[19] and mica.[17] More recently, admicellar polymerization has been used to applied various types of polymer thin film on textile fabrics to produce fabrics with wider applications.[20-23] Methachan *et al.*[20] produced water repellent cotton by coating polystyrene thin film on cotton. They showed that good air permeability of the fabric was maintained indicating that there was no blocking of the interstices between fibers and yarns in admicellar polymerization, Compared to pad-dry-cure, the conventional method for applying finishing agent to fabrics, admicellar polymerization is simple with low energy consumption, and the applied film is very thin, so the fabric also retains its pliability and soft touch.

Admicellar polymerization is analogous to emulsion polymerization in that the polymerization takes place in surfactant aggregates, i.e. in admicelle or micelles. In a study, polymerization behavior of styrene in admicelle has been found to be similar to that in micelle.[15] However, there have been very few reports describing admicellar polymerization of copolymers.[19,24] In this work the monomer reactivity ratios in a copolymer system were investigated and the UV-absorbing efficiency of the copolymer was studied based on the analysis of the composition of the comonomers used. The Ultraviolet Protection Factor (UPF) of the modified cotton was studied and comparison was made between the use of homopolymers and copolymer.

5.3 Experimental

5.3.1 Materials

A plain weave, medium-weight (150 g/m^2) cotton fabric was purchased from Boonchauy Co. Ltd. The fabric was desized, scoured, and bleached at the factory. Prior to use, the fabric was washed in a washing machine at 95°C several times until it was free from any remaining surfactant.

Dodecylbenzenesulfonic acid, sodium salt (DBSA) and 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM) were purchased from Aldrich Company (USA). Ammonium persulfate (99%) was purchased from Asia Pacific Specialty Chemicals Ltd (Australia). Dichloromethane (99.8%), dimethylacetamide (99.5%) and sodium chloride (99%) were purchased from Labscan Company (Ireland). All chemicals were used without further purification. 2-Hydroxy-4-acryloyloxybenzophenone (HAB) was synthesized from acryloylchloride and 2,4-dihydroxybenzophenone. Details of materials, synthesis, and identification of the product were described elsewhere.[25]

5.3.2 Adsolubilization

For adsolubilization, experiments were carried out with initial concentrations of 0.25 mM BEM and/or 0.25 mM HAB, 0.6 mM DBSA and 0.15 M NaCl. Dimethylacetamide was used as the solvent for BEM and HAB, and the volume of the organic solvent was kept at 2.5 mL in a total volume of 35 mL. The solution was put in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4. The vial was sealed by aluminium foil and parafilm, and put in a water shaker bath shaking at 120 rpm at 70°C for a set time, varying from 0.25-5 h. The initial and final concentrations of BEM and HAB were determined by UV spectroscopy at 300 and 280 nm respectively.

5.3.3 Determination of % conversion and copolymer compositions

To study % conversion of BEM and HAB in the comonomer system, experiments were carried out using BEM and HAB with the same concentration of 1.5 mM each, 0.6 mM of DBSA, and 0.15 M NaCl in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4. To allow the adsorption and the adsolubilization to occur simultaneously, the solution was kept at 70°C for 6 h. Then 1 mL aqueous ammonium persulfate solution was injected to give a final initiator concentration of 0.75 mM. After a set time, the reaction was stopped by cooling in an ice bath. The fabric was removed and unreacted monomers were washed out using dimethylacetamide, since the polymers

did not dissolve in dimethylacetamide. Then the extracted solution was mixed with the reaction mixture and diluted in dimethylacetamide to 100 mL. The % conversion was determined from the initial and final concentrations of monomers by UV spectroscopy at 280 and 300 nm which are the wavelengths of high absorbance, with least interference from the other component, for HAB and BEM, respectively. According to Beer-Lambert's law, for the 2-component mixture of HAB and BEM, the absorbance of the mixture is given by:

$$A_{280} = \varepsilon_{BEM, 280} \, bc_{BEM} + \varepsilon_{HAB, 280} \, bc_{HAB} \qquad (5.1)$$

$$A_{300} = \varepsilon_{BEM, 300} \, bc_{BEM} + \varepsilon_{HAB, 300} \, bc_{HAB} \qquad (5.2)$$

where A_{280} and A_{300} are the absorbance of the mixture at 280 and 300 nm respectively, $\varepsilon_{x, y}$ is the absorption coefficient of component x at wavelength y nm, b is the path length and c_{BEM} and c_{HAB} are the concentrations of BEM and HAB respectively. From the initial and final concentrations determined by the above equations, the % conversion was calculated using the following equation:

$$\% \, conversion = (c_{initial} - c_{final})/c_{initial} \times 100 \qquad (5.3)$$

To study the copolymerization of BEM and HAB, experiments were carried out using BEM and HAB with a combined total concentration of 3.0 mM, 0.6 mM of DBSA. and 0.15 M NaCl in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4. Dimethylacetamide was used as the solvent for BEM and HAB and the volume of the organic solvent was kept at 2.5 mL in a total volume of 35 mL. The mole fraction of BEM in the comonomer feed was varied to be 0, 0.15, 0.30, 0.45, 0.60. 0.75 and 1.0 in order to determine the monomer reactivity ratios. The solution was kept at 70°C for 6 h, to allow adsorption and adsolubilization to occur simultaneously. Then 1 mL ammonium persulfate solution was injected to initiate the polymerization at a final concentration of 1.5 mM. In order to obey the copolymer equation, the conversions were restricted to less than 10%. From the conversion experiment, a polymerization time of 2

h was set. After the set time, the reaction was stopped by cooling in an ice bath. The fabric was then taken out and washed by deionized water and dried in an oven.

Copolymer composition was determined by extraction of the copolymer from the fabric by dichloromethane. The extraction was carried out at 30°C for 24 h. The copolymer composition was determined by FTIR. The spectrometer used was Nexus 670 spectrometer (Nicolet) with 32 scans at a 4 cm^{-1} resolution in the frequency range of 4000 – 400 cm^{-1}. The copolymer composition was determined from the peak ratios at 1730 and 1760 cm^{-1} by curve fitting using OPUS spectroscopic software version 2.0 from Bruker. The polymer mixtures of poly(BEM) and poly(HAB) with different mole fractions were used to prepare the calibration curve of mole fraction and the FTIR-absorbance ratio.

5.3.4 Admicellar polymerization

Polymerization of BEM and/or HAB on cotton was carried out in 0.6 mM DBSA solution with 0.15 M NaCl in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4 and at the temperature of 70°C. Dimethylacetamide was used as a solvent for BEM and HAB and the volume of the organic solvent was kept at 2.5 mL in a total volume of 35 mL. Before the start of the experiment, monomer(s) with the desired concentration was (were) added into the aqueous solution to allow surfactant adsorption and monomer adsolubilization to occur simultaneously for 6 h. The BEM and HAB concentrations in the system were varied from 0.5 to 3.0 mM. Copolymerization of BEM and HAB was carried out using BEM and HAB with a total concentration of 3.0 mM by varying monomer concentration in the comonomer feed to be 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM. Then 1 mL aqueous ammonium persulfate solution was injected to give an initiator:monomer molar ratio of 1:2. After 15 h of polymerization, the fabric was taken out from the vial and washed with 70°C water for three times to remove the surfactant. The fabric was finally placed in an oven at 60°C until dry. The amount of polymer coated on the fabric was determined by extraction using dichloromethane. The extraction was carried out at 30°C for 24 h. The amounts of poly(BEM) and poly(HAB) or their units in

the copolymer were determined by UV spectrophotometer at 300 and 270 nm respectively.

5.3.5 Determination of UV-protection properties of the fabric

Several national standard test methods have been developed to indicate quantitatively the protection provided by clothing against UV radiation. The first of these was issued in Australia and New Zealand in 1996 as AS/NZS 4399.[26] More recently, a standard has been developed and introduced by the American Association of Textile Chemists and Colorists as the AATCC Test Method 183-2004[27] which has been widely used. In this method the transmittance data is collected by placing the fabric in a spectrophotometer, with all wavelengths in the UV range directed to the fabric. The data are then used to calculate the % UV blocking and the Ultraviolet Protection Factor (UPF).

In this work Shimadzu UV spectrophotometer 2550 with integrating sphere attachment ISR-2200 was used to measure the percentage of transmittance of the cotton fabric according to the AATCC Test Method 183-2004. The percent transmittance for wavelengths from 280 to 400 nm was measured in intervals of 2 nm. Three measurements of the UV transmittance were performed for each specimen, in warp, weft and 45° directions. The results are the mean values of the three measurements of each duplicate specimens.

5.4 Results and Discussion

5.4.1 Adsolubilization and copolymerization

The adsolubilization of BEM and HAB in DBSA admicelles on cotton was investigated by measurement of initial and final supernatant concentrations using UV spectrophotometer. Transient and equilibrium concentrations were calculated from absorbance at 280 and 300 nm. Figure 5.1 (a) shows adsolubilization of 0.25 mM BEM and 0.25 mM HAB versus adsolubilization time when there was only one monomer in

the system and Figure 5.1 (b) shows adsolubilization when both BEM and HAB were present in the system. In the single species systems, the adsolubilization of BEM and HAB increased rapidly during the first hour before leveling off and reaching equilibrium after two hours. The adsolubilization amounts at equilibrium were around 2.2 and 1.0 μmol/g cotton for BEM and HAB, respectively. The higher amount of adsolubilized BEM compared to that of HAB may be due to the more hydrophobic character of BEM. Thus, BEM preferred to be stabilized by hydrophobic tails of DBSA in the admicelle. Aloulou et al.[28] found that the partition coefficient in admicelle depended on the polar character of the molecular structure. The lower the polarity, the higher the amount of molecules adsolubilized. When there were two monomers in the system, the rate of adsolubilization did not change, and surface concentrations of BEM were still greater than HAB. However, the presence of two monomers made the adsolubilization amounts of both increase to 3.8 and 2.0 μmol/g cotton for BEM and HAB, respectively. In the study of styrene-isoprene co-monomer system,[29] it appears that the presence of styrene significantly enhances the adsolubilization of isoprene. Thus, in this case, the adsolubilization of the more hydrophobic BEM in the core of surfactant bilayer could loosen the packing of surfactant molecules and provide more volume for HAB and itself to adsolubilize. Besides, both adsolubilizates should have hydrophobic and π-π interactions with each other, resulting in higher adsolubilizations. Adsolubilization of toluene was also found to promote adsolubilization of acetophenone in cetyltrimethylammonium bromide.[30]

Figure 5.2 shows monomer conversions of BEM and HAB in the copolymerization. A comparison of the rate of conversion between BEM and HAB was studied at low % conversion by using the same initial monomer concentrations. It is clearly seen that the rate of conversion of HAB was higher than that of BEM. This result will be discussed after the presentation of the calculated reactivity ratios (r_1 and r_2) below. It can be seen that the amount of adsolubilization does not necessarily relate to the rate of conversion or the copolymer composition since the amount of adsolubilized BEM was higher than HAB. but the rate of conversion of BEM was lower. When the

polymerization reaction begins, monomers diffuse from supernatant to admicelle to compensate for the loss of monomers by the polymerization reaction.[15]

Spectroscopic methods have been developed to estimate the copolymer composition, such as NMR[31,32] and FTIR.[33,34] FTIR is one of the widely used methods for analysis of copolymers and the determination of r_1 and r_2 because the analyses can be performed quickly and at low cost. FTIR can provide not only qualitative but also very good quantitative analysis.[35-37] Figure 5.3 shows the FTIR spectra of poly(BEM), poly(HAB), and copolymer. For the composition analyses of copolymers, characteristic absorption bands at 1730 cm^{-1} and 1760 cm^{-1} were used. These bands were assigned to $CH_2OC=O$ and $PhOC=O$ carbonyl stretching for BEM and HAB respectively.[38] Mole fractions of monomers BEM and HAB in feed were given as F_1 and F_2 Mole fractions of comonomer units in copolymers (f_1 and f_2) using integrals of absorption bands of 1730 and 1760 cm^{-1} were calculated from the calibration curve shown in Figure 5.4. Absorbance ratio of 1730 cm^{-1} to 1760 cm^{-1} was found to be linearly related to the mole fractions of BEM units.

Copolymerizations were carried out in low conversion conditions (<10%) in order to determine monomer reactivity ratios (r_1 and r_2) in the stationary kinetic stage[39] by using known terminal models of the Fineman-Ross and Kelen-Tüdos equations, respectively:

$$X(Y-1)/Y = r_1(X^2/Y) - r_2 \qquad (5.4)$$

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \qquad (5.5)$$

where X is the mole ratio of monomers in feed, X= [BEM]/[HAB]; Y is the mole ratio of comonomer units in copolymers, $Y = f_1/f_2$; $\xi = (X^2/Y)/(Y^2/Y+\alpha)$; $\eta = [X(Y-1)/Y]/(X^2/Y+\alpha)$; α is an arbitrary constant, $\alpha = [(X^2/Y)_{min}(X^2/Y)_{max}]^{1/2} = 0.6563$. Fineman-Ross and Kelen Tüdos parameters were calculated and shown in Table 5.1.

From the Fineman-Ross plot of $X(Y-1)/Y$ vs X^2/Y in Figure 5.5. the monomer reactivity ratios, calculated from the slope and the intercept of the graph, were $r_1 = 0.6236$ and $r_2 = 0.6751$. From the Kelen-Tüdos plot of η vs ξ, the monomer

reactivity ratios were calculated giving $r_1 = 0.5353$ and $r_2 = 0.5839$. This supports the result in the previous section which showed that the rate of conversion of HAB was higher than that of BEM. The value of $r_1 \cdot r_2$ product was much lower than 1, indicating that the copolymer system showed an alternating tendency. Fineman-Ross and Kelen-Tüdos methods gave the same tendency of the monomer reactivity ratios. Since r_1 and r_2 values were less than 1 and from the curve in Figure 5.6, the BEM-HAB system was found to exhibit azeotropic polymerization at a particular composition. The azeotropic composition can be calculated using the following equation:

$$F_A = \frac{1 - r_2}{2 - r_1 - r_2}$$

(5.6)

The azeotropic compositions calculated from Fineman-Ross and Kelen-Tüdos methods were 0.463 and 0.472, respectively, which were close to that of 0.46 obtained from FTIR analysis in Figure 5.6. When the mole fraction of BEM in feed (F_1) was 0.46, the copolymer formed would have the same composition as that of the feed. When F_1 was lower than 0.46, BEM in the copolymer composition was higher than that in the feed. When F_1 was above 0.46, the copolymer was richer in HAB units. Although the system showed the tendency toward alternating copolymer ($r_1 \cdot r_2 < 1$), there was a wider range of feed composition (0.46-1.0) in which the resulting copolymer was richer in HAB units. Since BEM is larger with a more bulky structure, it has less tendency to homopolymerize, compared to HAB. Thus, both types of propagating radicals reacted somewhat preferentially with HAB monomer. Since the copolymer system showed alternating tendency, the coated fabric had a uniform UV-protection in all areas of the fabric.

For the homopolymers, it can be seen from Figure 5.7 that, at the same monomer concentration, % yield of poly(BEM) was less than that of poly(HAB). This may be due to the greater steric hindrance of BEM as described previously. Moreover, at the same amount of polymer, poly(BEM) gave higher UPF than poly(HAB). This is because, in the UV region 280-400 nm used in UPF calculation, BEM absorbs the radiation more than HAB. For the copolymer, the amounts of extracted polymer shown

in Table 5.2 reflected the mole fraction of BEM in the copolymer and the overall conversion of each (assuming there were no side products). The mole fractions of BEM in the feed were 0.167, 0.333, 0.500, 0.667 and 0.833, and the mole fractions of BEM obtained in the copolymer were 0.165, 0.365, 0.468, 0.529, and 0.653, respectively. Compared to the results from FTIR, these results generally reflect the findings based on FTIR at low conversions as shown in Figure 5.6.

From the amount of polymer extracted, a thickness of the polymer film coated on the fabric can be calculated. The surface area of cotton as determined from BET with nitrogen was found to be 4 m^2/g.[21] It is assumed that the film is evenly distributed over the surface and that all the surface area from BET is accessible. The bulk density of the thinly spread polymer is assumed to be 1.0 g/cm^3. With these assumptions, the maximum thickness of poly(HAB) obtained was 4 nm and that of poly(BEM) was 2 nm. For a copolymer, the film thickness is about 3 nm. From other works, the thickness of polystyrene film on alumina was 3.4-3.6 nm[14] and the thickness of poly(pyrrole) film on mica was 1-3 nm.[17] It can be seen that the polymer films formed by admicellar polymerization are very thin. Thus the coated fabric retains its pliability and soft touch.

5.4.3 UV-protection properties of treated fabrics

Figure 5.8 shows the UV spectra of 0.05 mM BEM and 0.07 mM HAB in dichloromethane. The two monomers complement each other by absorbing UV radiation strongly in different regions. In UV-A region (315-400 nm) both BEM and HAB can absorb the radiation strongly. In UV-B region (280-315 nm) BEM can absorb radiation better than HAB. In UV-C region (200-280 nm) HAB has a strongly absorbing peak in the region 250-280 nm while BEM has strong absorption in the region 200-250 nm. Thus, from the spectra it can be expected that, by using both BEM and HAB, protection in all three regions, covering the whole range of solar UV radiation from 200-400 nm, can be achieved. There is no absorption in the visible range (400-700 nm) which

indicates that the presence of the copolymer would show no color. This will be an advantage when applied to fabrics.

Figure 5.9 shows the UV transmission spectra of untreated and treated cotton using 0.8 mM of BEM and 0.8 mM HAB, and copolymerization of 0.4 mM BEM and 0.4 mM HAB. The untreated cotton showed significant transmission over the whole UV range. In contrast, cotton coated by either poly(BEM) or poly(HAB) could reduce the UV transmission significantly. The transmission of the BEM-treated cotton was almost completely cut off over the range of 290 nm up to 370 nm. For the HAB-treated cotton, the transmission was almost eliminated in 250-290 nm region, where BEM shows less absorption, and in the 320-350 nm region. Further illustrating the complementary properties of BEM and HAB was the higher transmission over the range of 290-320 nm for the HAB fabric, where BEM absorbed well. Thus, as can be seen from Figure 5.9, copolymer of BEM and HAB with both absorbing moieties present helped to provide a treated fabric with protection in the broad UV range of 200-370 nm.

Although the UV transmission of the treated fabric was high at wavelengths greater than 370 nm. the relative erythemal effectiveness in the 320-400 nm region is almost zero as can be seen from Figure 5.10, while that in the 280-300 nm region is equal to 1 and that in the 300-320 nm region has the value ranging from 1 to zero.[40] In other words. the UV radiation in the 320-400 nm region is much less hazardous to skin, and hence the protection in 280-320 nm is more critical. Thus cotton fabric treated by copolymerization in this study can provide complete UV protection in the most hazardous regions. Moreover, UV absorbers which effectively take up radiation in the UV-A region are rare and they are not sufficiently photostable such as butyl-methoxydibenzoylmethane known as avobenzene.[41] In contrast, benzotriazole and benzophenone used in this work have better photostability due to efficient energy dissipation.[42,43] Benzotriazole and benzophenone used in the present work can dissipate their absorbed energy efficiently through a mechanism which involves the reversible rearrangement of a six-membered, intramolecularly hydrogen-bonded ring.[44,45] Hence, they can be expected to be much more photostable.

Ultraviolet Protection Factor (UPF) is the scientific term used to indicate the amount of UV protection provided to skin by fabric. UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the test fabric. According to AATCC Test Method 183-2004,[27] UPF is calculated as follow:

$$UPF = \frac{\sum\limits_{280nm}^{400nm} E_\lambda S_\lambda \Delta\lambda}{\sum\limits_{280nm}^{400nm} E_\lambda S_\lambda T_\lambda \Delta\lambda} \tag{5.7}$$

where:

E_λ = relative erythemal spectral effectiveness

S_λ = solar spectral irradiance in $Wm^{-2}nm^{-1}$

T_λ = average spectral transmittance of fabric

$\Delta\lambda$ = measured wavelength interval in nm

E_λ is the erythema action spectrum developed by International Commission on Illumination (CIE).[40] It indicates the wavelength dependence of the UV radiation in producing erythema in human skin. The calculated UPF value indicates how much longer a person can stay in the sun when fabric covers the skin as compared with the length of time in the sun without fabric covering to obtain the same erythemal response.

The effect of comonomer compositions on the protection properties of the fabric was studied. Figure 5.11 shows the dependence of UPF on BEM and HAB concentrations for the homopolymers, and a comparison between UPF of the copolymer-coated fabric and summation of UPF in the single absorber systems using the same monomer feeds. For the single systems, the higher the monomer concentration, the more UPF the fabric provided, but only up to a certain limit of UPF. Copolymerization can be another way to improve UPF values. When Beer's Law applies to a multicomponent system in which there is no interaction among species, the total absorbance is equal to a summation of the absorbance of the contents.[38] The comparison in Figure 5.11 shows that UPF of the fabric coated by copolymer was close to that of the summation of UPF in

single systems using the same monomer feeds. The slightly lower experimental UPF was due to the fact that the composition in copolymer was not equal to that in the feed as discussed previously. However, at the same total monomer concentration of 3.0 mM, the fabrics coated by copolymer showed a marked improvement in UPF compared to the homopolymers, and the monomer ratio of 1:1 gave the highest UPF value of 97 compared to the values of 73 and 72 obtained from poly(BEM) and poly(HAB) respectively at equal monomer concentration.

5.5 Conclusions

The copolymerization of BEM and HAB via admicellar polymerization on a cotton fabric was studied. The BEM-HAB copolymer system showed an alternating tendency and exhibited azeotropic polymerization at BEM composition of 0.46. The copolymerization method in this study can provide uniform UV-protection over a broad UV range of 200-400 nm. Compared to homopolymer at the same total monomer concentration, the fabric coated by copolymer had a higher UPF, and the monomer ratio of 1:1 gave the highest UPF value.

5.6 Acknowledgments

5.7 References

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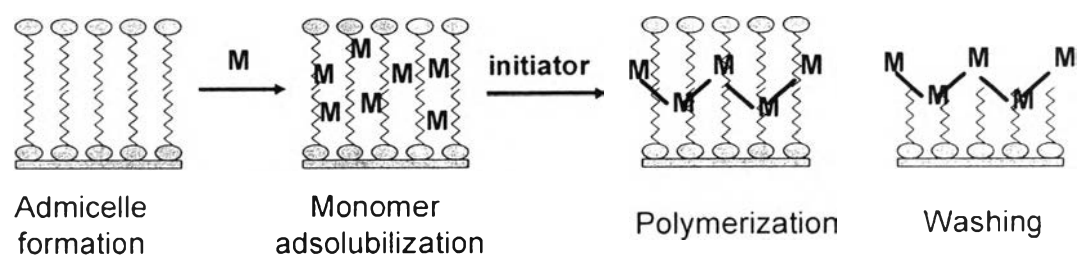
Scheme 5.1 Admicellar polymerization process.
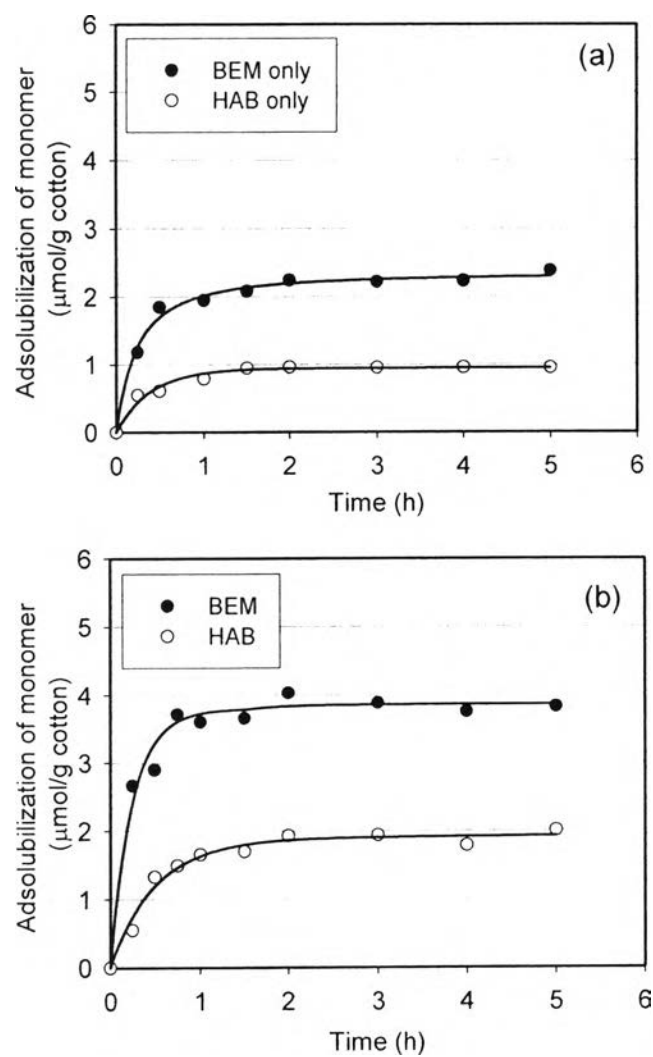
Figure 5.1 Adsolubilization of BEM and HAB (a) in the single system, 0.25 mM BEM/ 0.25 mm HAB, and (b) in the comonomer system, 0.25 mM BEM and 0.25 mM HAB. using 0.6 mM DBSA and 0.15M NaCl at 70 °C.
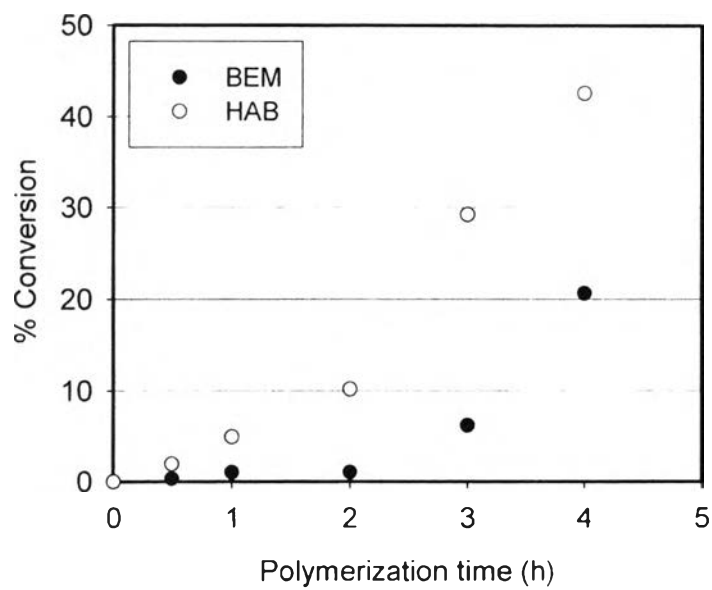
Figure 5.2 The % conversion of the comonomer system. 1.5 mM BEM and 1.5 mM HAB, during polymerization using 1.5 mM ammonium persulfate, 0.6 mM DBSA. and 0.15M NaCl at 70 °C.
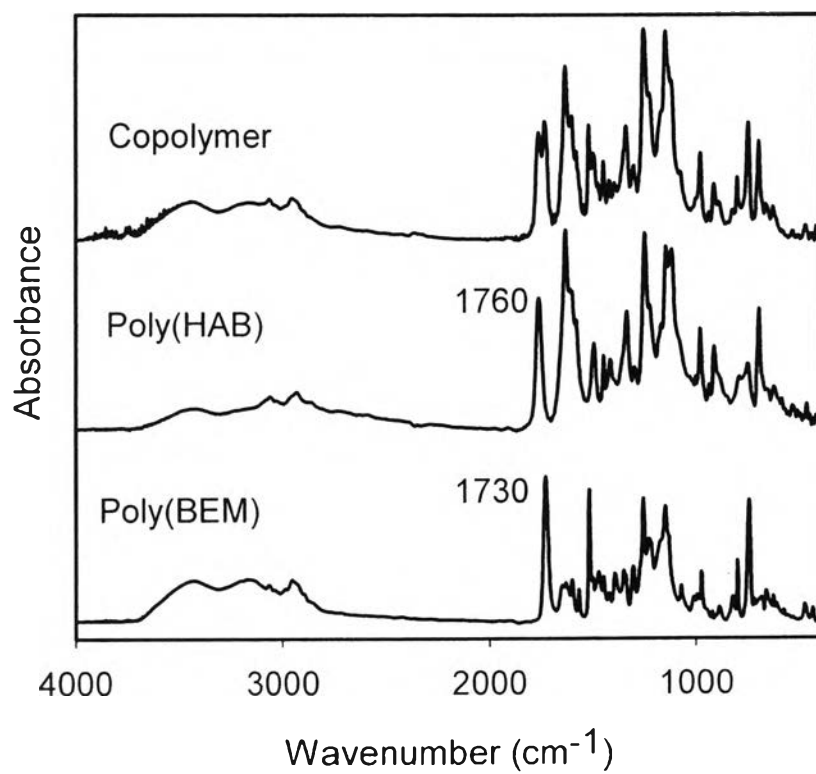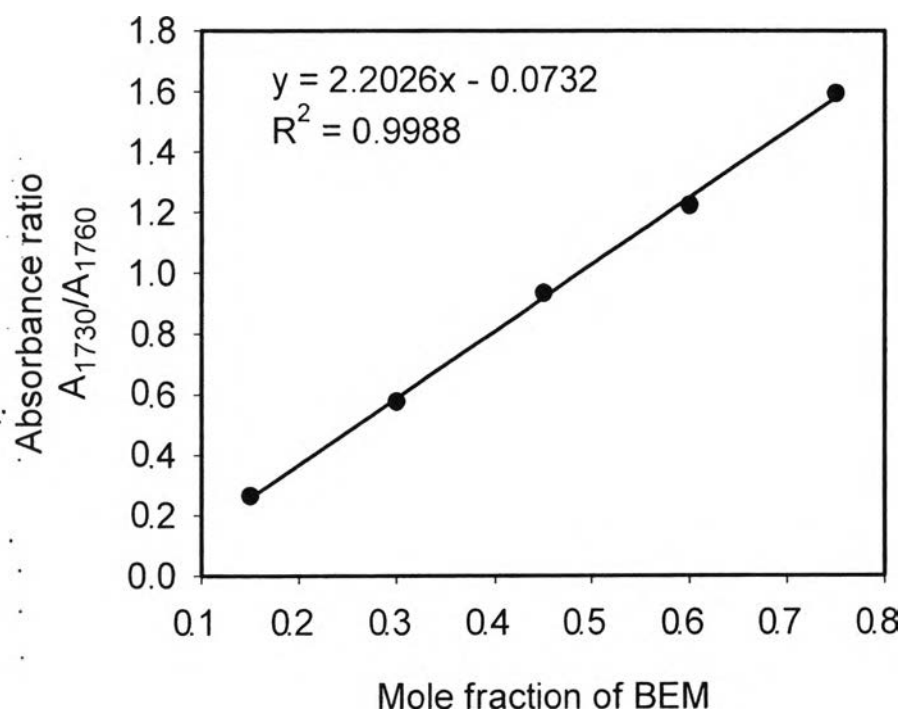
Figure 5.3 The FTIR spectra of poly(BEM), poly(HAB), and copolymer.

Figure 5.4 Calibration curve for FTIR determination of BEM content in BEM-HAB copolymer.
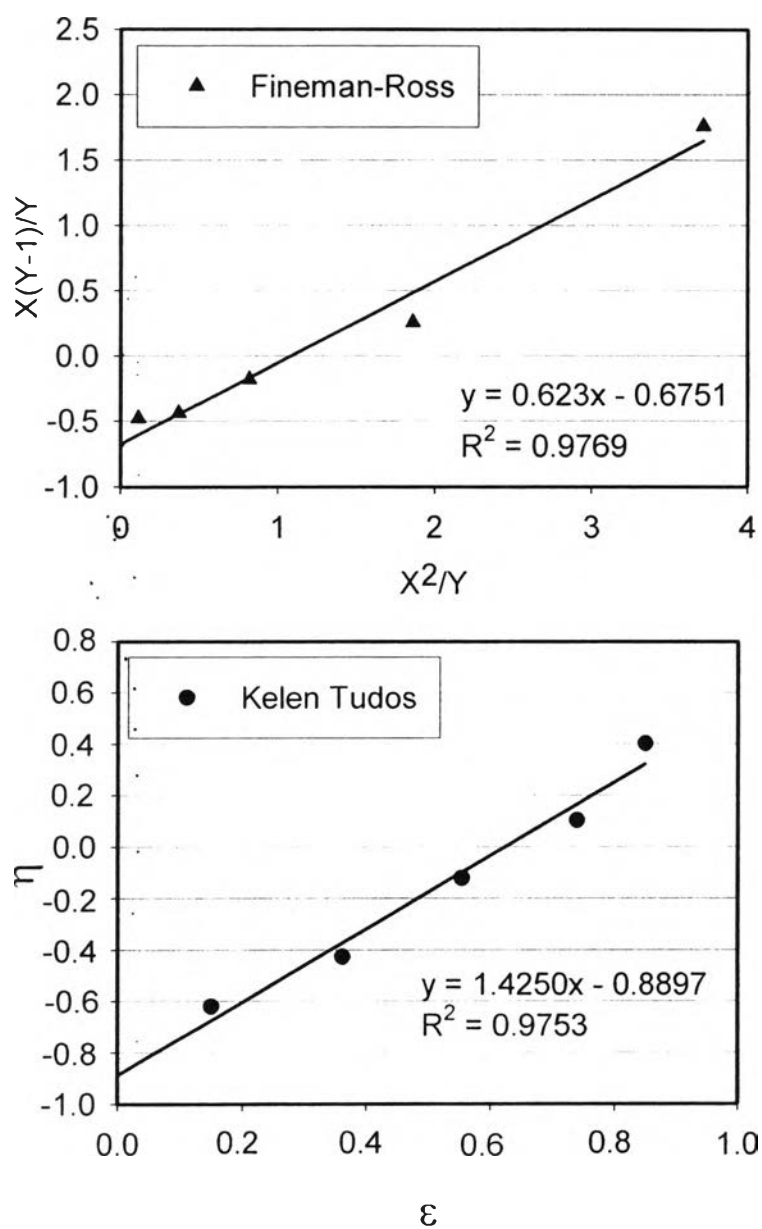
Figure 5.5 Fineman-Ross plot and Kelen-Tudos plot for copolymer of BEM and HAB using BEM and HAB with a combined total concentration of 3.0 mM and mole fraction of BEM in comonomer feed varied from 0.15-0.75.
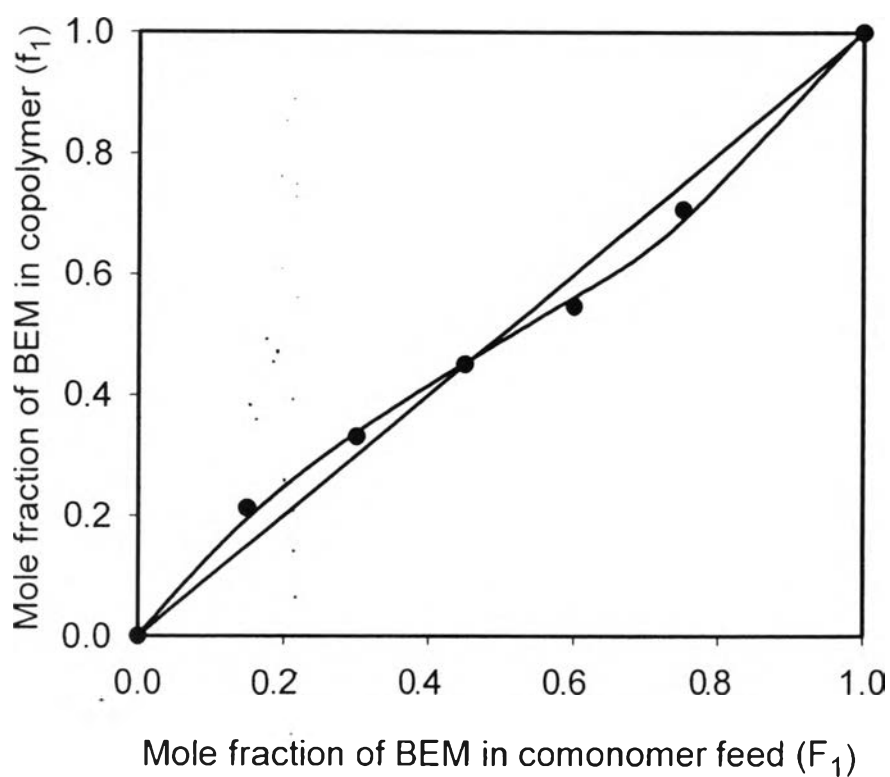
Figure 5.6 Comparison of the mole fraction of BEM in comonomer feed and the mole fraction of BEM in copolymer using BEM and HAB with a combined total concentration of 3.0 mM.
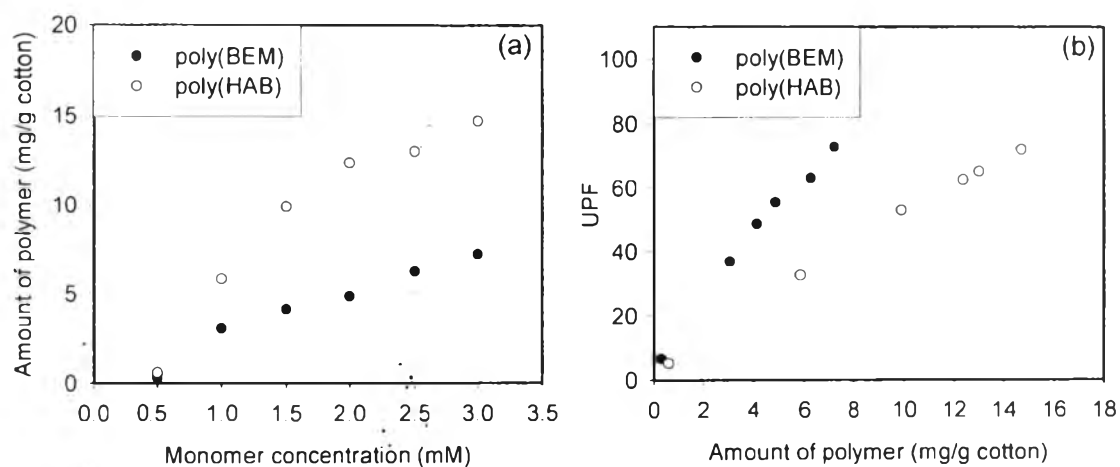
Figure 5.7 Relationship between (a) the amount of polymer and monomer concentration, and (b) UPF and the amount of polymer for poly(BEM) and poly(HAB).
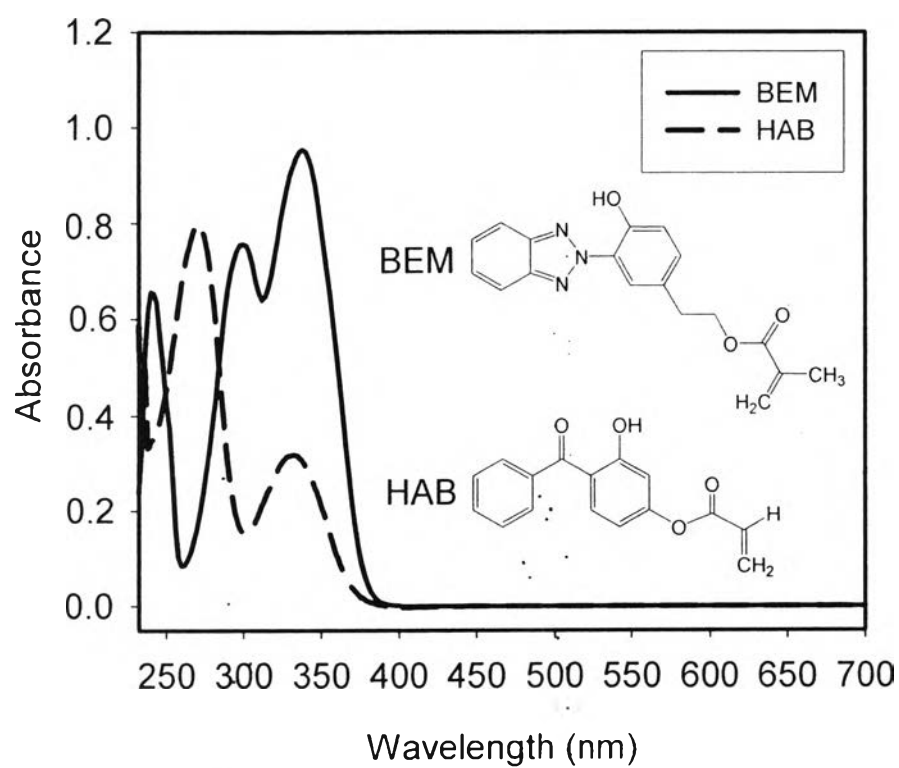
Figure 5.8 UV spectra of 0.05 mM BEM and 0.07 mM HAB in dichloromethane.
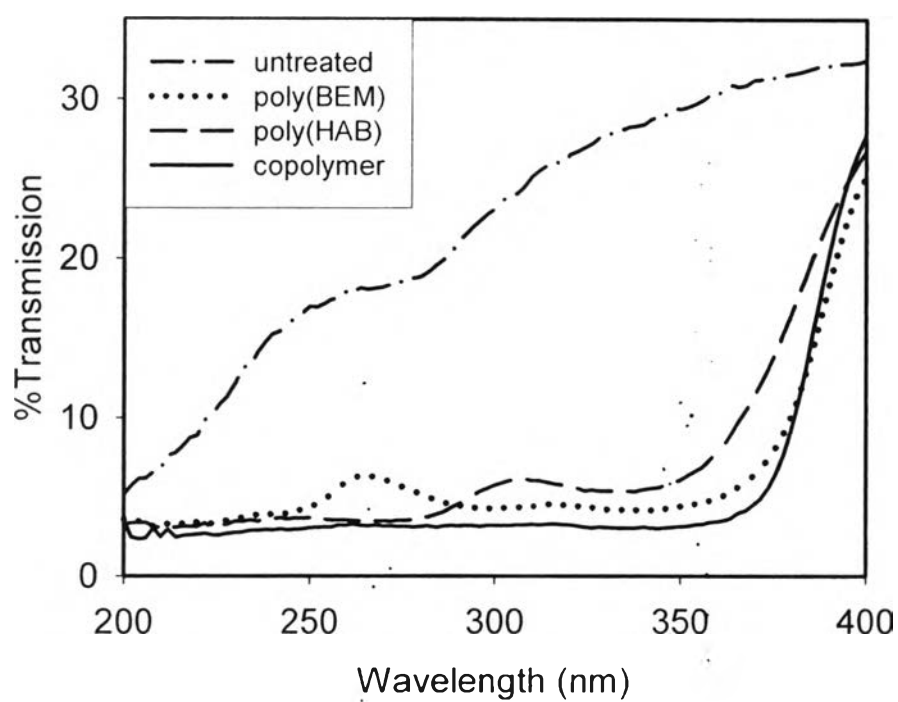
Figure 5.9 The % UV transmission of untreated cotton fabric, cotton fabrics coated by homopolymers using 0.8 mM BEM, and 0.8 mM HAB, and cotton fabric coated by copolymer using 0.4 mM BEM and 0.4 mM HAB.
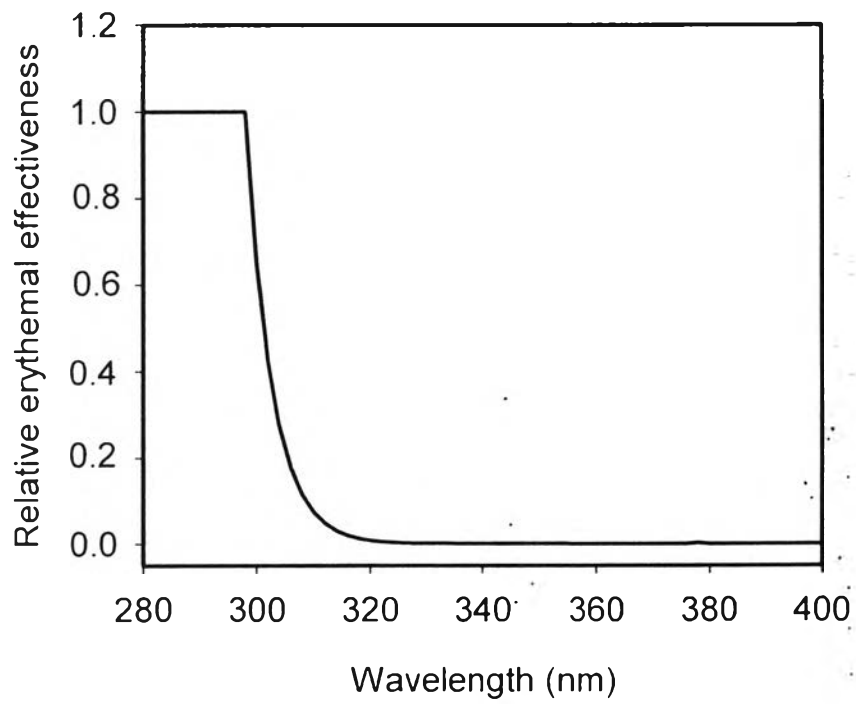
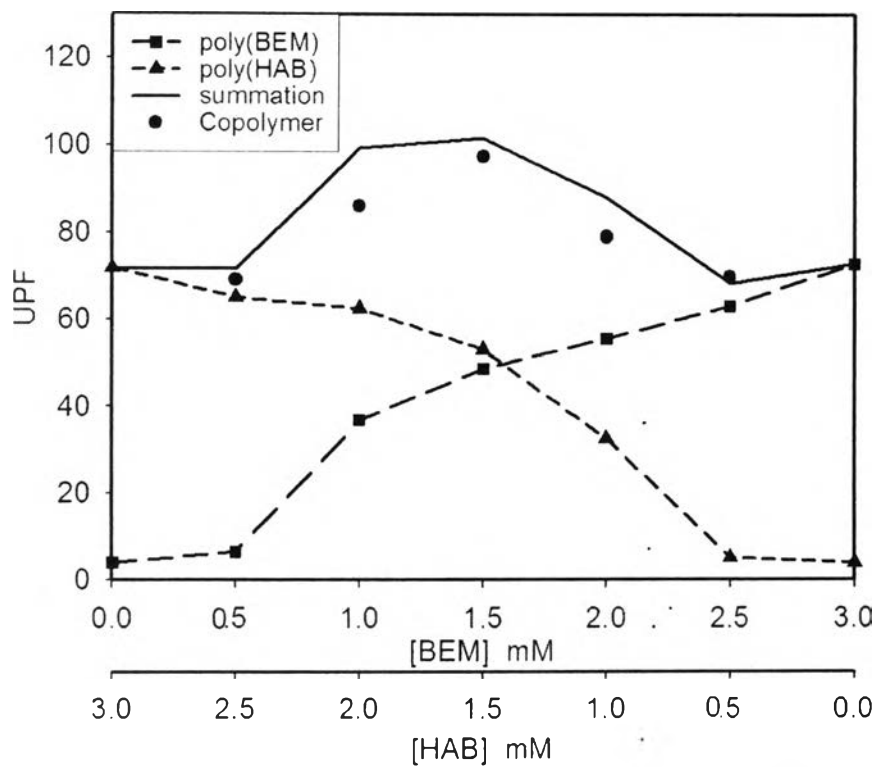**Figure 5.10** Relative erythemal effectiveness in 280-400 nm region.[42]

Figure 5.11 UPF of cotton fabrics coated by homopolymers, poly(BEM), and poly(HAB), using monomer concentration varied from 0.5-3.0 mM and UPF of cotton fabrics coated by copolymer using BEM and HAB with a combined total concentration of 3.0 mM. compared to a summation of UPF in single systems using the same monomer feeds.

Table 5.1 Fineman-Ross and Kelen Tüdos parameters for copolymerization of BEM and HAB

Mole fraction of BEM		Mole ratio		Fineman-Ross		Kelen-Tüdos	
in feed	in copolymer	in feed	in copolymer	(X^2/Y)	$X(Y-1)/Y$	ξ	η
F_1	f_1	X	Y				
0.150	0.212	0.176	0.269	0.1157	-0.4791	0.1499	-0.6206
0.300	0.331	0.429	0.494	0.3718	-0.4390	0.3616	-0.4270
0.450	0.451	0.818	0.820	0.8161	-0.1793	0.5543	-0.1218
0.600	0.547	1.500	1.209	1.8617	0.2589	0.7394	0.1028
0.750	0.707	3.000	2.417	3.7231	1.7590	0.8501	0.4016

Table 5.2 Polymer extraction results and UPF values of cotton fabrics coated by copolymer

BEM (mM)	HAB (mM)	Poly(BEM) or BEM unit (μmol/g cotton)	Poly(HAB) or HAB unit (μmol/g cotton)	Mole fraction of BEM in copolymer	UPF
0.5	2.5	6.82	34.60	0.165	69
1.0	2.0	14.63	25.41	0.365	86
1.5	1.5	17.91	20.34	0.468	97
2.0	1.0	17.91	15.94	0.529	79
2.5	0.5	16.75	8.89	0.653	70