CHAPTER IV

ADMICELLAR POLYMERIZATION OF 2-HYDROXY-4-ACRYLOYLOXYBENZOPHENONE: THE PRODUCTION OF UV-PROTECTIVE COTTON[*]

4.1 Abstract

Admicellar polymerization was used to modify surface of a cotton fabric in order to improve its ultraviolet protection property. A UV-absorbing agent, 2,4-dihydroxybenzophenone, was covalently bonded to a monomer, acryloyl chloride, and the product, 2-hydroxy-4-acryloyloxybenzophenone (HAB), was polymerized on the cotton surface by admicellar polymerization using dodecylbenzenesulfonic acid, sodium salts (DBSA) as the surfactant. Surfactant bilayer adsorbed on the fiber surface was used as the reaction site for the formation of polymer film. The effects of electrolyte, temperature, and adsolubilizate (HAB) on surfactant adsorption were studied. Surface characterization studies confirmed the existence of the poly(HAB) thin film on the fiber surface which significantly reduced ultraviolet transmission through the fabric. Ultraviolet Protection Factor (UPF) of the cotton fabric was greatly improved from a value of 4 for plain fabric to greater than 40 (excellent protection) after treatment with HAB at concentrations greater than 1.2 mM using the admicellar polymerization technique.

Key words: Admicellar polymerization; Adsolubilization; Surfactant; UV-protective cotton

4.2 Introduction

Surface modification of a substrate is an important and versatile method for making materials with enhanced performance in some specific areas. The modified materials will possess surface properties which are different from their bulk properties. Many techniques have been used to modify a substrate surface to alter the mechanical, chemical, or optical properties of a material. More recently, surfactant adsorbed on a surface has been utilized as a template for polymerization in order to modify surface properties of materials. This method has been termed admicellar polymerization. Admicellar polymerization is an *in-situ* polymerization reaction in the core of a surfactant bilayer adsorbed onto the substrate surface to apply a thin polymeric film on the substrate surface.[1,2] There are four main steps, admicelle formation, monomer adsolubilization, polymeric film formation, and surfactant removal. Admicellar polymerization has been successfully used to form various types of polymeric thin films on different substrates such as polystyrene on silica,[3] alumina[4] and cotton,[5,6] styrene-isoprene copolymer on glass fiber,[7] and polypyrrole on mica.[8] This method is simple with low energy consumption and when use with textile fabric, there is no blocking of the interstices between fibers and yarns, thus good air permeability of the fabric is maintained. Since the applied film is very thin, in nano scale,[8] the fabric also retains its pliability and soft touch.

In this work admicellar polymerization was investigated as a thin-film coating technique for making UV-protective fabric. Due to ozone depletion, there has been a progressive increase in the incidence of skin cancers because of exposure to ultraviolet radiation from the sun. Ultraviolet radiation consists of three regions: UV-C (200-280 nm), UV-B (280-315 nm) and UV-A (315-400 nm).[9] The UV-protective properties of clothing have been widely studied and the factors that affect the extent of protection have been reported previously.[10-13] Lightly bleached, uncolored cotton garments, which are very popular in summer, do not provide sufficient protection against UV radiation.[12] To enhance the UV protection, recent research has concentrated on applying UV

absorbing moieties to the fabrics. A UV absorber is an organic molecule which takes up UV radiation and converts it to less harmful energy. The important properties of these molecules are that they strongly absorb UV radiation and rapidly dissipate the energy via some suitable intramolecular rearrangement.[14,15] Due to such effective and reversible reactions, recently organic compounds have been used in a modification of fabrics to enhance their UV protection properties.[9,16,17] UV absorbers can be applied in conjunction with the dyeing process,[13] or incorporated during the synthesis of dyes.[16] The commercial process used to apply dyes and/or UV absorbers on fabrics, which are exhaustion method[9,16] and pad-dry-cure[16,17] have some disadvantages including expensive cost, high energy requirement, and changes to the "feel" of the fabric.

In this study a UV absorbing system, hydroxybenzophenone, was added to an organic monomer structure and the admicellar polymerization of the monomer on the fiber surface was carried out to produce UV-protective cotton fabric. The three important steps of the admicellar polymerization, surfactant adsorption, monomer adsolubilization and polymer film formation, were investigated.

4.3 Experimental

4.3.1 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) was purchased from Aldrich Company (USA). Acryloyl chloride (96%), 2,4-dihydroxybenzophenone (99%) and hydroquinone (99%) were purchased from Merck Company (Germany). Triethylamine (99.78%) was purchased from Fisher Science (UK). Ammonium persulfate (99%) was purchased from Asia Pacific Specialty Chemicals Ltd (Australia). Ethanol (99.8%), methyl ethyl ketone (MEK) (99.5%), dimethylacetamide (99.5%),

HPLC-grade acetonitrile (99.9%) and sodium chloride (99%) were purchased from Labscan Company (Ireland). All chemicals were used without further purification.

4.3.2 Synthesis of 2-hydroxy-4-acryloyloxybenzophenone (HAB)

2,4-dihydroxybenzophenone 3.21 g (15 mmol), triethylamine 2 mL (15 mmol), methyl ethyl ketone (MEK, 75 mL), and hydroquinone (1 g) were placed in a round-bottom flask. Hydroquinone was added in order to prevent polymerization of the vinyl groups. After dissolution, the contents were cooled in an ice bath. Acryloyl chloride 1.2 mL (15 mmol) in 10 mL of MEK was added dropwise with constant stirring and cooling. The reaction mixture was allowed to reach room temperature and was maintained for 2 h. The by-product, quaternary ammonium salt, was filtered off. The filtrate was thoroughly washed with distilled water, dried with anhydrous sodium sulfate, and the solvent was evaporated out. The crude product was recrystallized from ethanol to give 60% yield of pale-green crystal. The chemical structure of the product as shown in Figure 4.1 was confirmed by the following ^{1}H-NMR analysis.[18]

^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 12.3 (s, 1H, m-ArOHOOC), 7.7 (d, 2H, o-HArC=O), 7.65 (d, 1H, m-HArOOC), 7.6 (t, 1H, p-HArC=O), 7.5 (t, 2H, m-HArC=O), 6.9 (s, 1H, o-HArOHOOC), 6.7 (dd, 1H, CH=CH$_2$), 6.6 (d, 1H, o-HArOOC), 6.3 (dd, 1H, CH=CH_2), and 6.1 (dd, 1H, CH=CH_2).

From the FTIR spectrum of HAB shown in Figure 4.2, the medium broad band in the region of 3400-3500 cm^{-1} is assigned to OH stretching of inter and intramolecular hydrogen bonding formed between phenolic-OH and the ketone oxygen. The C-H stretching of aromatic ring is observed at 3080 cm^{-1}. Strong bands at 1740 and 1630 cm^{-1} are ascribed to C=O stretching of ester and ketone groups, respectively. The aromatic C=C stretching is at 1600 cm^{-1}. The peaks at 1150 and 1250 cm^{-1} are due to C-O stretching.

4.3.3 Surfactant Adsorption and Monomer Adsolubilization

The adsorption of DBSA on cotton at different temperatures and salt concentrations was studied. A solution of 5.0 mM DBSA with the desired salt concentration was first prepared. The pH of the solution was adjusted to 4 with concentrated HCl. A 35-mL aliquot of the solution was then pipetted into a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric weighing 0.73 g. The sealed vial was then placed in a thermostated water bath at a set temperature and shaken at 120 rpm for a fixed time, varying for different temperatures. The adsorbed DBSA on cotton was calculated by taking the difference between the initial and final concentration of DBSA in the vial. Final concentration of DBSA in solution was determined by Shimadzu UV spectrophotometer 2550. The wavelength of maximum absorption for aqueous solution of DBSA was found at 224 nm with the molar extinction coefficient of 1.1×10^4 L mol^{-1} cm^{-1} found from the calibration curve.

Adsorption isotherms of the DBSA on cotton were obtained by exposing a 6.5 cm × 6.5 cm cotton fabric to 35 mL of DBSA solution of known initial concentration. The pH of the solution was pre-adjusted to 4 and 0.15 M NaCl was added unless otherwise indicated. The mixture equilibrated at 70°C for 1 h in a sealed 40-mL vial. Concentrations of supernatant were determined by UV spectrophotometer at 224 nm. The initial DBSA concentration in this experiment was varied from 0.05 to 5 mM, which covered the regions below and above the CMC of DBSA. In the presence of HAB the isotherm acquisition proceeded in a similar manner except HAB was dissolved in 2.5 mL of dimethylacetamide before mixing with surfactant solution to yield an HAB concentration of 0.6 mM. Since HAB also absorbs UV radiation strongly, the initial and final supernatant concentrations of DBSA and HAB were measured by HPLC using a C_8 reverse-phase column and a UV detector. The mobile phase was acetonitrile:water of 60:40 ratio by volume. The flow rate of the mobile phase was 1.5 mL/min. The retention times of DBSA and HAB were 1.0 and 3.6 min respectively and the wavelength for UV detection was set at 224 nm.

The rate of HAB adsolubilization was determined in 1.2 mM DBSA with 0.15 M NaCl in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4. The

mixture was equilibrated for 1 h at 70°C for surfactant adsorption. After that, 2.5 mL of HAB in dimethylacetamide was pipetted into 32.5 mL of the above DBSA solution to obtain an HAB final concentration of 0.6 mM. The sealed vial was then placed in a thermostated water bath at 70°C and shaken at 120 rpm for a fixed time varying from 0.25 to 6 h. The initial and final supernatant concentrations of DBSA and HAB were determined by HPLC using the same procedure as described above.

4.3.4 Admicellar Polymerization

Polymerization of HAB on cotton was carried out in a 40-mL vial containing 0.6 mM DBSA and 0.15 M NaCl at pH 4 and the temperature of 70°C. At the start of the experiment, a 6.5 cm × 6.5 cm cotton fabric was placed in the vial and 2.5 mL of HAB in dimethylacetamide with the desired concentration was added into 31.5 mL of the DBSA solution above to allow adsorption and adsolubilization to occur simultaneously. HAB concentration in the system was varied from 0.6 to 5.0 mM. The sealed vial was then placed in a thermostated water bath at 70°C and shaken at 120 rpm for a set time. Equilibration time was set at 6 h for adsorption and adsolubilization. Then 1 mL ammonium persulfate solution, to make up the total volume of the reaction mixture to 35 mL, was injected to initiate the polymerization 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 three times to remove the outer layer of DBSA. The fabric was finally placed in an oven at 60°C until dry.

4.3.5 Characterization of the Poly(HAB) on Cotton Surface

Scanning electron microscopy (SEM) (JEOL, JSM 5200, 15 kv) was used to study surface morphology of the coated fabric. Fourier transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) with a ZnSe plate was used to analyze the chemical groups present in the polymer coating on the cotton surface. The spectrometer used was Nexus 670 spectrometer (Nicolet) with 32 scans at a 4 cm^{-1} resolution in the wavenumber range of 4000 - 400 cm^{-1}.

The amount of poly(HAB) coated on the fabric was determined by extraction with MEK. The extraction was carried out using 20 mL MEK in a vial containing a 6.5 cm × 3.25 cm cotton fabric at 30°C for 24 h. The concentration of poly(HAB) in solution was determined by UV spectrophotometer at 340 nm.

4.3.6 Determination of the UV-Protection Properties of Treated Cotton Fabrics

Two major steps in determination of UV protection are UV transmittance measurements and calculations based on the transmittance data collected. Quantifying the protection provided by clothing against UV radiation has resulted in the development of a number of national standard test methods. The first of these was issued in Australia and New Zealand in 1996 as AS/NZS 4399.[19] Other standard spectral test methods were developed by the American Society for Testing and Materials (ASTM), with Standards D6603-00 [20] and D6544-00.[21] More recently, a standard developed and introduced by the American Association of Textile Chemists and Colorists, AATCC Test Method 183-2004,[22] has been widely used. In this method a fabric is placed in a spectrophotometer, with all wavelengths in the UV range directed to the fabric and the transmittance data collected. The data are then used to calculate the % UV blocking and the Ultraviolet Protection Factor (UPF).

In this study, the percentage of transmittance of the cotton fabric was measured according to AATCC Test Method 183-2004 using a Shimadzu UV spectrophotometer 2550 with integrating sphere attachment ISR-2200. 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 three directions; warp, weft and diagonal. The results are the mean values of the three measurements of duplicate specimens.

4.4 Results and Discussion

4.4.1 Surfactant Adsorption and Monomer Adsolubilization

Electrolytes are known to reduce the electrical repulsion between the ionic head groups of surfactant molecules in micelles.[23] However, there are few studies investigating the interactions of counterions with surfactant surface aggregates.[24-26] In this study the effect of electrolyte on the amount of DBSA adsorbed on cotton fabric was studied by carrying out the experiments in 5.0 mM of DBSA at 30 °C for 24 h, the results are shown in Figure 4.3. It can be seen that the amount of adsorption increased rapidly as NaCl concentration increased in the range 0-0.10 M after which the increase tapered off. The NaCl concentration of 0.15 M was used in further experiments since the amount of adsorption does not increase much by adding more electrolyte. The area occupied per molecule was calculated as $A = 1/\Gamma N_A$, where Γ is adsorption per unit area ($\mu mol/m^2$).[27] The surface area of cotton as determined from BET with nitrogen was found to be 4 m^2/g.[6] From the amount of adsorption in Figure 4.3 and by assuming that DBSA formed a bilayer on cotton, the area per DBSA molecule was calculated and found to decrease from an initial value of 219 $Å^2$ in the absence of NaCl to 57 $Å^2$ after 0.15 M NaCl was added. The result is in good agreement with the area per DBSA molecule on a liquid/air interface which has been quoted as between 46 and 59 $Å^2$ in the presence of 0.1 M NaCl.[23] The decrease in area per DBSA molecule confirms that the presence of electrolyte reduces electrostatic repulsion between the head groups resulting in closer packing of surfactant molecules adsorbed on the substrate.

To study the effect of temperature, experiments were carried out using 5.0 mM of DBSA and temperatures of 30, 50, and 70 °C. Figure 4.4 shows that the equilibrium times at these temperatures were 12, 4 and 1 h, respectively. It can be seen that the equilibrium time of surfactant adsorption can be reduced significantly by increasing the temperature. Thus for surfactant adsorption, the condition of 70 °C for 1 h was used in further experiments. The adsorption rate increases because a temperature increase leads to increases in the kinetic energy of the surfactant molecules and the slightly decrease in adsorption amount of DBSA at the plateau is attributed to the thermal motion of the adsorbed molecules at the interface.[28] Decreased adsorption due to increasing temperature was more obviously seen in the presence of 0.15 M NaCl as

shown in Figure 4.5. In the presence of electrolyte, the more tightly packed surfactant molecules in the admicelles do not as readily accommodate the increased thermal motion so that adsorption decreases.

Adsorption isotherms of DBSA on cotton were studied. The CMC of DBSA at 30 °C is 1.2 mM.[23] From Figure 4.5, the CMC of DBSA at 70 °C with 0.15 mM NaCl was 0.465 mM. The CMC was significantly decreased due to the presence of electrolyte which reduces repulsion between DBSA molecules and enhances micelle formation. In the presence of 0.6 mM HAB, the CMC increased from 0.465 mM to 0.772 mM while the adsorption of DBSA on the fabric decreased. Since the molecule of HAB is large, the adsolubilization of HAB prevents the surfactant molecules from packing closely. Thus, the amount of DBSA adsorbed was reduced. While many species enhance surfactant adsorption on adsolubilization, decreased adsorption is not unprecedented.[25,29] Funkhouser et al.[25] suggested that interaction of hydrogen bonding to surfactant head groups made pyrrole molecules occupy space in the head group region and reduce adsorption. Asvapathanagul et al.[29] found that adsolubilized toluene in the core swells the surfactant bilayer, thus providing more volume for acetophenone to adsolubilize in the admicelles. Salgaonkar et al.[30] found that the addition of aniline caused a decrease in adsorption of hexadecyltrimethyl-ammonium bromide (HDTAB). They proposed that aniline molecules occupied a space closer to the head group region of HDTAB, thus reducing the HDTAB head group packing. From the adsorption isotherm, the area occupied per DBSA molecule was calculated from adsorption of DBSA at the plateau, 70 °C and 0.15 M NaCl. The area occupied per DBSA molecule increased from an initial value of 181 $Å^2$, in the absence of HAB, to 302 $Å^2$ in the presence of HAB. The admicelle becomes swollen by adsolubilized monomer, hence the area per surfactant molecule increases.[31]

The rate of adsolubilization of HAB was studied using HPLC. Surfactant adsorption step was carried out first at 70 °C for 1 h and HAB was then added to the solution. Figure 4.6 shows the amount of adsolubilized HAB and adsorbed DBSA versus adsolubilization time. The adsolubilization of HAB increased rapidly during the first

hour before leveling off and reaching equilibrium after four hours. In the case of DBSA, the initial adsorption before addition of HAB was 7.27 μmol/g cotton. As HAB adsolubilized into the admicelle, the adsorption of DBSA was found to decrease accordingly, reaching equilibrium after four hours. This clearly shows that the adsolubilization of HAB constrains the packing of the surfactant molecules and hence DBSA adsorption decreases. The mole ratio of HAB to DBSA at equilibrium was about 1:2 indicating that one molecule of HAB is adsolubilized by two molecules of DBSA in the admicelle. The HAB:DBSA ratio obtained in this work is very similar to the styrene:sodium dodecyl sulfate ratio on alumina[1] and silica,[3] and the styrene:linearalkylbenzene sulfonate ratio on cotton.[6] The consistent 1:2 ratio of the adsorbed species not only indirectly supports the existence of a bilayer but also implies a location of the monomer within the bilayer.[1]

4.4.2 Characterization of Poly(HAB) Thin Film on Cotton Fabrics

The presence of poly(HAB) on the cotton surface after admicellar polymerization was determined by FTIR-ATR. When the amount of HAB used in admicellar polymerization increased, the characteristic peaks appeared with higher intensity. In Figure 4.7 the strong band at 1630 cm^{-1} is assigned to C=O of ketone groups. The band in the region of 1230-1250 cm^{-1} is assigned to the C-O stretching of a phenolic ester. The peak at 1150 cm^{-1} is due to C-O stretching.

SEM micrograph in Figure 4.8 (a) shows the clean surface of untreated cotton fiber. The poly(HAB)-coated surface in Figure 4.8 (b)-(f) shows that the polymer was uniformly coated on the fiber surface. The polymer on the surface appears as a rough, not smooth, film. This may indicate that the polymerization occurred separately in many initiation sites and the polymer grew until it reached neighboring sites. Yuan et al. also found that admicellar polymerization of poly(pyrrole) resulted in a film with many islands and disks which came from favored reaction sites at which polymerization initiated and spread over the substrate. Higher monomer concentrations showed larger islands compared to lower concentrations.[8] In addition, the micrographs prove that the

coating occurred only on the fiber surface and not in the spaces between fibers and yarns. This is important and it can be concluded that improvement in UV-protection does not come from the physical blocking of the interstices between fibers but from absorption of UV radiation by the benzophenone moiety.

4.4.3 UV Protection Properties of the Treated Cotton Fabrics

The UV spectrum in Figure 4.9 shows that HAB strongly absorbs UV radiation with absorption peaks at 270 and 330 nm. There is no absorption in the visible range (400-700 nm) which indicates that the presence of HAB would show no color. This will be an advantage when it is applied to fabrics. The UV transmission spectra of untreated cotton and treated cotton using 0.6, 1.2, 1.8 and 3.0 mM of HAB are shown in Figure 4.10. The transmission of the treated cotton using 1.8 and 3.0 mM of HAB is almost totally cut off in UV-B region (280-315 nm) and up to 370 nm in UV-A region. The reduction in UV transmission is due to the UV absorption of poly(HAB). The characteristic UV absorption peaks of HAB can be seen from the 0.6 mM HAB curve which still shows substantial absorption around 270 and 330 nm.

According to AATCC Test Method 183-2004,[22] the average A-range ultraviolet (UV-A) transmittance and the average B-range ultraviolet (UV-B) transmittance can be calculated using Equations 4.1 and 4.2, respectively.

$$T(UV-A)_{AV} = \frac{\sum\limits_{315nm}^{400nm} T_\lambda \times \Delta\lambda}{\sum\limits_{315nm}^{400nm} \Delta\lambda} \qquad (4.1)$$

$$T(UV-B)_{AV} = \frac{\sum\limits_{280nm}^{315nm} T_\lambda \times \Delta\lambda}{\sum\limits_{280nm}^{315nm} \Delta\lambda} \qquad (4.2)$$

The percent blocking for UV-A and UV-B are subsequently calculated using Equations 4.3 and 4.4.

$$\% \ UV-B \ blocking = 100\% - T(UV-B)_{AV} \qquad (4.3)$$

$$\% \ UV - A \ blocking \ = 100\% - T(UV - A)_{AV} \qquad (4.4)$$

where T(UV-A) and T(UV-B) are expressed as percentage.

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. UPF is calculated as follows:

$$UPF = \frac{\sum_{280nm}^{400nm} E_\lambda S_\lambda \Delta\lambda}{\sum_{280nm}^{400nm} E_\lambda S_\lambda T_\lambda \Delta\lambda} \qquad (4.5)$$

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

λ = wavelength in nm

E_λ is the erythema action spectrum developed by International Commission on Illumination or CIE.[32] It is a spectral dependence of the ability of UV radiation to produce erythema or an abnormal redness in human skin caused by dilation of blood vessels. Reference values of E_λ and S_λ at each wavelength are provided by AATCC Test Method 183-2004. 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.[13]

The effect of HAB concentration on the protection properties of the treated fabric was studied. The results are reported in Figure 4.11, which indicates that higher HAB concentration provides higher UPF up to 3 mM of HAB and a greater percentage UV blocking up to around 2 mM of HAB. Further increase in HAB concentration does not provide better protection. The percent blocking of UV-B is higher

than that of UV-A for the whole range of HAB concentrations. This is to be expected as HAB strongly absorbs in UV-B region. This corresponds to the requirements of a UV-protective clothing since UV-B is more hazardous to human skin, compared to UV-A. To classify the protection ability of fabrics, the calculations of both the UPF and the percent UV blocking are considered. The percent UV blocking data does not take into account that certain wavelengths in the UV range are more responsible for skin damage than others, while the calculation of UPF concerns erythemal spectral effectiveness and irradiance at a certain wavelength. Thus UPF is preferred in the classification of fabrics compared to the percent UV blocking. According to AS/NZS 4399: 1996,[19] fabrics can be classified according to their UPF values as shown in Table 4.1. From Figure 4.11, it can be concluded that cotton fabric, which has UPF of 4 before treatment, can provide excellent UV protection with a UPF value of more than 40 after admicellar polymerization of HAB with a concentration of 1.2 mM, while a maximum UPF value of about 70 was obtained with an HAB concentration of 3.0 mM.

Based on polymer extraction, the maximum yield of polymer is 47%. The low yield of polymer is probably due to the steric hindrance of the bulky HAB molecule in the confined space of admicelle compared to a smaller monomer. For example, the very high conversion of styrene monomer to polystyrene in the admicelle has been observed.[1] Figure 4.12 is a plot between the amount of the polymer extracted and UPF values. It shows that UPF value increased with increasing amount of polymer up to a polymer amount of 14 mg/g cotton, after which the UPF value leveled off. According to Beer Lambert Law, the amount of UV absorption for a given species is a function of media thickness and UV absorber concentration. In practice, high concentrations of UV absorbers and sufficient thickness of the polymer are required before enough absorption can take place to provide adequate protection. From Figure 4.11 and 4.12, it appears that, up to a certain limit, further increase in polymer amount does not lead to further improvement in UPF or % UV blocking. At high amount of polymer, the transmitted light is essentially independent of polymer film thickness. Probably the amount of UV absorption by poly(HAB) already reaches its maximum. In addition, since the fabric has

a certain amount of porosity, some UV radiation is bound to get through the fiber interstices as shown in Figure 4.13. UPF can be further increased by blocking interstices between fibers and yarns, but air permeability will become worse. Although admicellar polymerization appears to result in an upper limit to UPF, the excellent UV protection with good air permeability can certainly be obtained. The upper limit in UPF may be apparent simply because photodetector sensitivity decreases as the light intensity (transmittance) goes to zero.

From the amount of extracted polymer and the surface area of cotton which was found to be 4 m^2/g determined from BET with nitrogen,[6] a thickness of polymer film is calculated. The bulk density is used to calculate when the structure of such thin layers on the surface undoubtedly is not quite the same and it is assumed to be 1.0 g/cm^3. Assuming that the film is evenly distributed over the surface and that all the surface area from BET is accessible, the thickness of poly(HAB) at the highest amount of polymer coating of 15.3 mg/g cotton is found to be 3.8 nm which, interestingly, is about twice the length of the hydrophobic tail of the surfactant molecule used. The result is also close to the thickness of 3.4-3.6 nm for polystyrene obtained by previous workers.[1] It can be seen that the polymer films formed by admicellar polymerization are very thin. Thus the coated fabric can retain its pliability and soft touch.

By the total carbon content analysis, O'Haver et al.[3] showed that most of polystyrene, formed by admicellar polymerization, remained on silica after washing. In this work the effect of surfactant concentration on UV protection, before and after washing at 70 °C for 3 times, 10 min/time, has been investigated using 1.2 mM HAB. The results of UPF shown in Figure 4.14 agree with the theory that admicellar polymerization works best when the concentration of surfactant approaches the CMC.[30,33] Below CMC, the surface coverage is not saturated. When the surfactant concentration exceeds CMC, UPF is significantly reduced. This implies that HAB will partition into the micelles in solution more than the admicelle when both are present in the system. Polymerization without surfactant was also studied. It was found that UPF of the fabric was as high as 30. It is believed that solution polymerization occurred in this

case, leading to deposition of the polymer on the fiber surface and within the interstices between fibers. However, the polymer could be easily removed as can be seen from the much greater reduction in the UPF value after washing. The resistance to washing was highest when the optimum amount of surfactant of 0.6 mM was used. The results show that surfactant plays a very important role in the coating process.

Figure 4.15 shows the effect of UV-A exposure time on the % UV-A blocking and UPF of the coated fabric using 1.2 mM HAB. A 6W UV-A Hg Philips lamp was used. It was found that the % UV-A blocking and UPF of the fabric remained almost unchanged, even after exposure for 24 h. In general the photostability is due to efficient energy dissipation and a small quantum yield in photodecomposition (10^{-7}-10^{-6}).[15] In the case of hydroxybenzophenone in poly(HAB), upon absorption of UV radiation, the UV energy is dissipated into harmless thermal energy via an intramolecular isomerization cycle (proton-transfer) as shown in Figure 4.16. The period of this photo-tautomerism cycle is extremely short, thus not allowing radical formation or other undesired side reactions to take place. In summary, with hydroxybenzophenone system, the cotton fabrics coated by poly(HAB) could provide a stable UV protection for at least 24 h in this condition.

4.5 Conclusions

UV-protective cotton fabric can be produced via admicellar polymerization technique using 2-hydroxy-4-acryloyloxybenzophenone (HAB) which is synthesized from grafting of 2,4-dihydroxybenzophenone onto acryloyl chloride. With a suitable time, near-CMC surfactant concentration and HAB concentration greater than 1.2 mM, the cotton fabric, which has a low UPF of 4 before treatment, could provide excellent UV protection (UPF > 40) after the admicellar polymerization process and the efficiency is stable even under continuous UV exposure of up to 24 hours.

4.6 Acknowledgements

4.7 References

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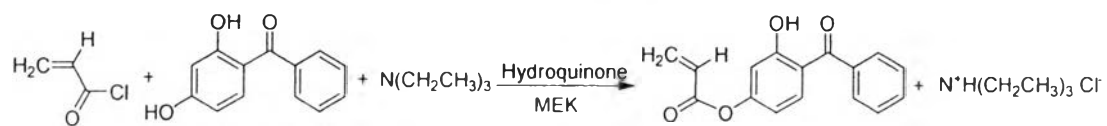
Figure 4.1 Synthesis of 2-hydroxy-4-acryloyloxybenzophenone (HAB).
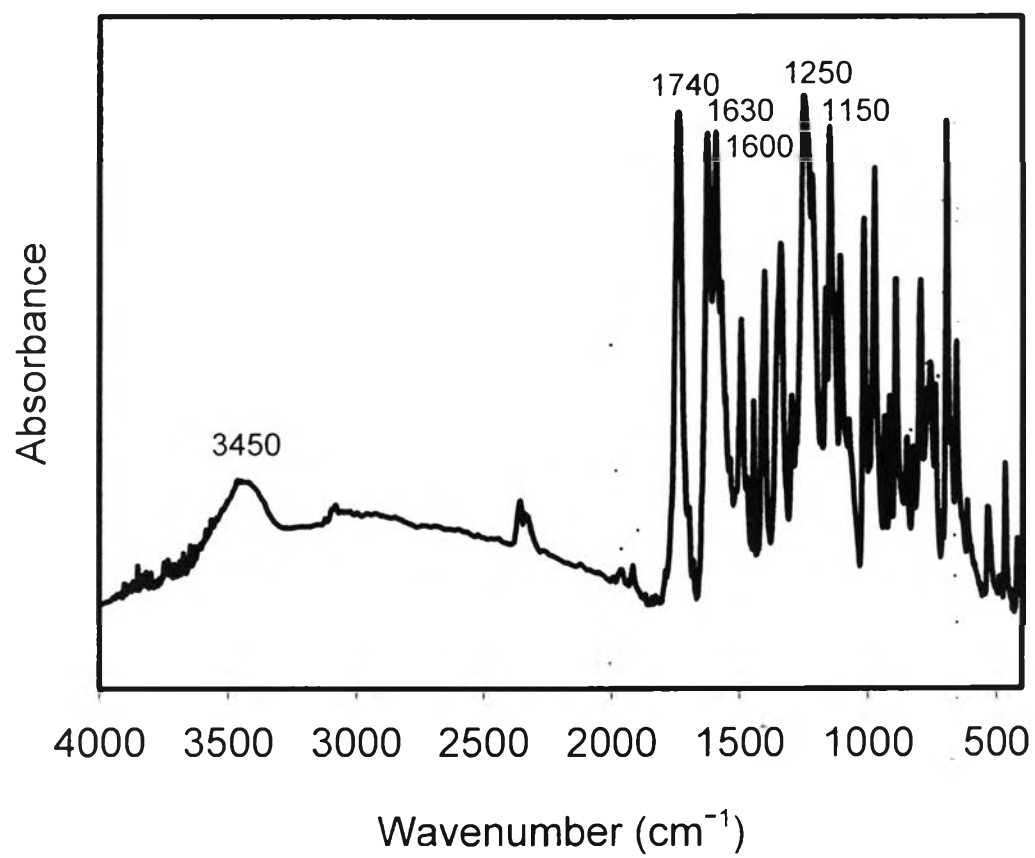
Figure 4.2 FTIR spectrum of 2-hydroxy-4-acryloyloxybenzophenone (HAB).
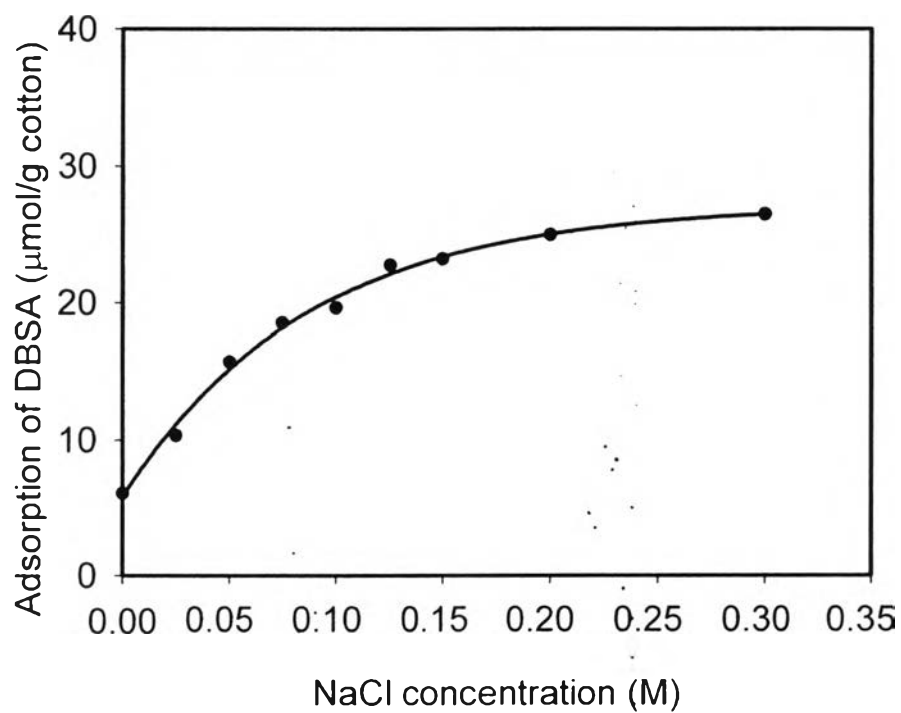
Figure 4.3 Effect of electrolyte on the adsorption of DBSA on cotton fabric using 5.0 mM DBSA at 30 °C for 24 h.
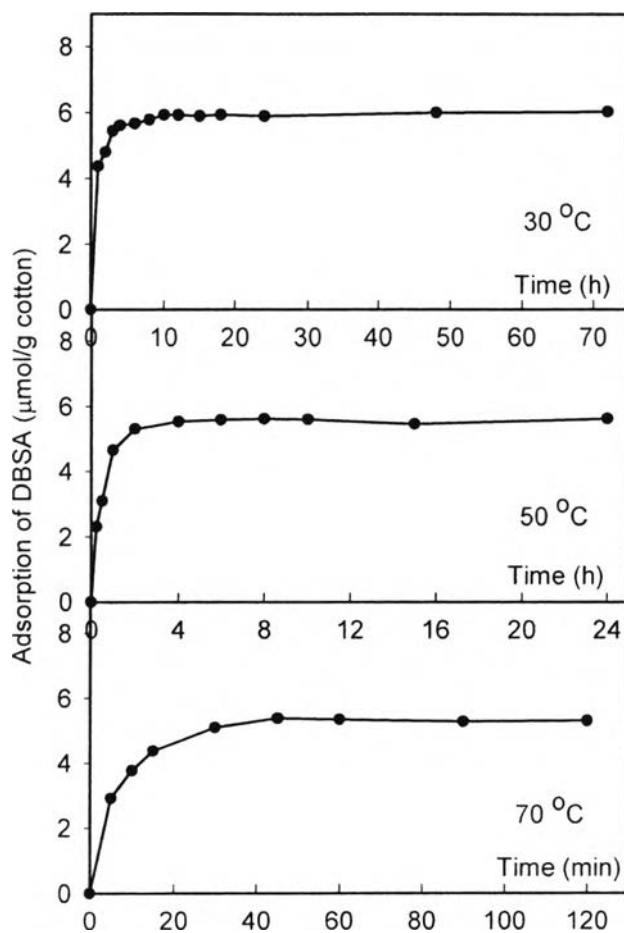
Figure 4.4 Effect of temperature on the adsorption of DBSA on cotton fabric using 5 mM DBSA, without NaCl.
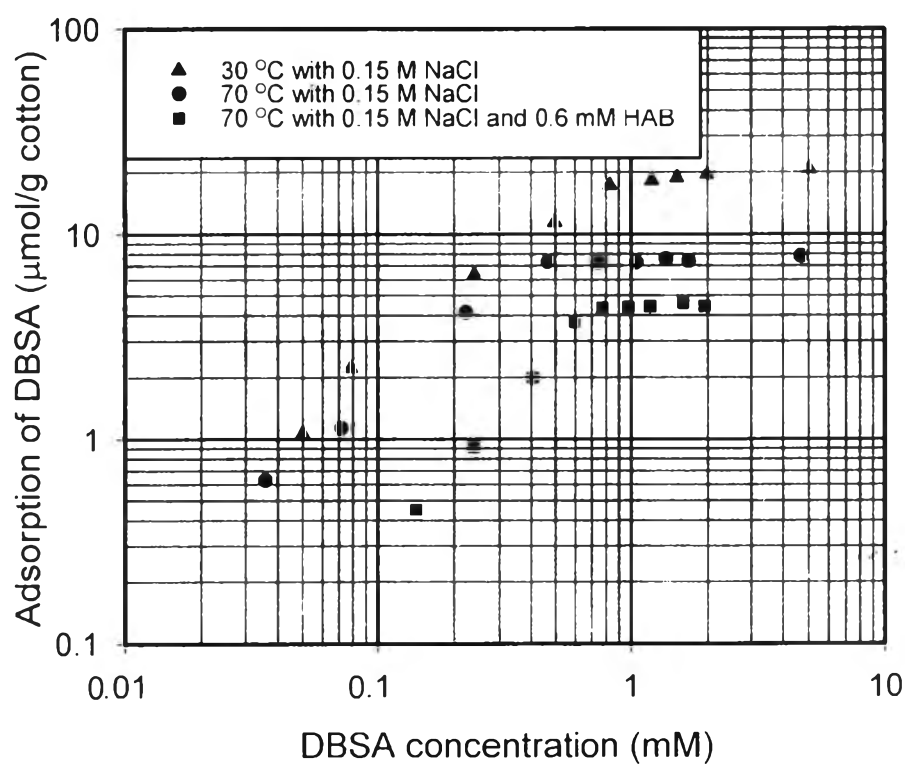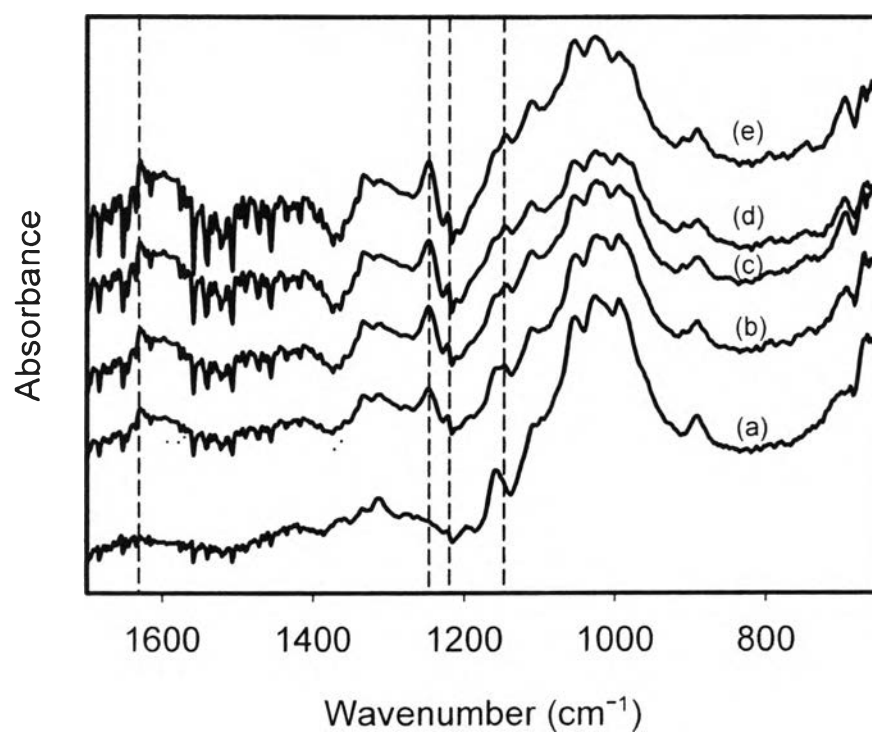
**Figure 4.5** Effect of temperature and adsolubilizate on the adsorption isotherm of DBSA in the presence of salt.
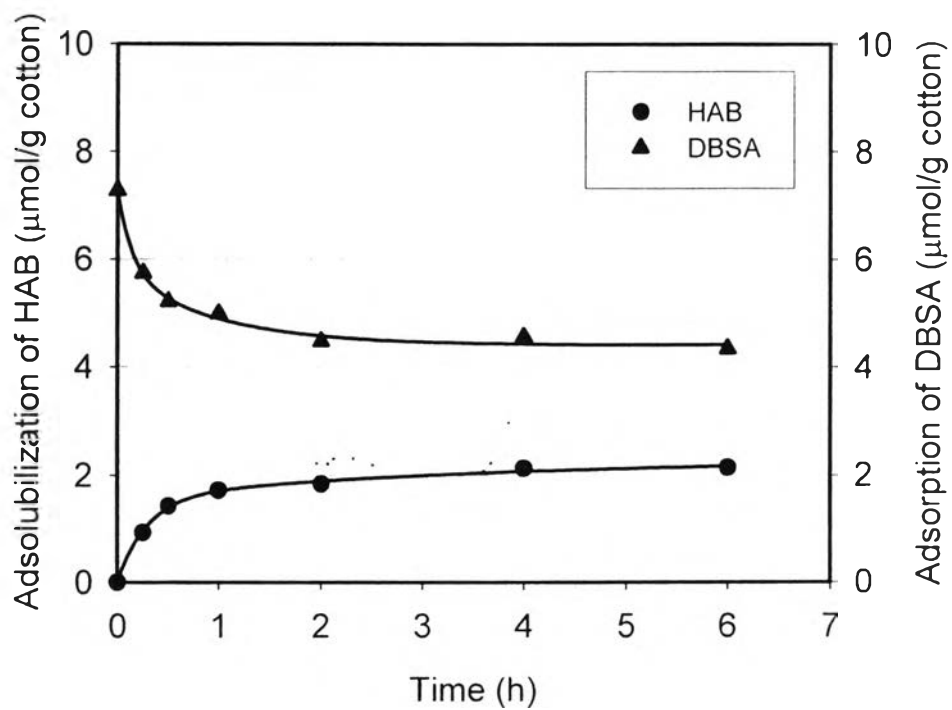
Figure 4.6 Adsolubilization of HAB and adsorption of DBSA on cotton fabric versus adsolubilization time at 70 °C after 1 h-surfactant equilibrium adsorption, using 0.6 mM HAB, 1.2 mM DBSA, 0.15 M NaCl.

Figure 4.7 The FTIR-ATR spectra of (a) untreated cotton, and treated cotton using HAB of (b) 0.6 mM; (c) 1.2 mM; (d) 1.8 mM; and (e) 3.0 mM, 0.6 mM DBSA and 0.15 M NaCl.
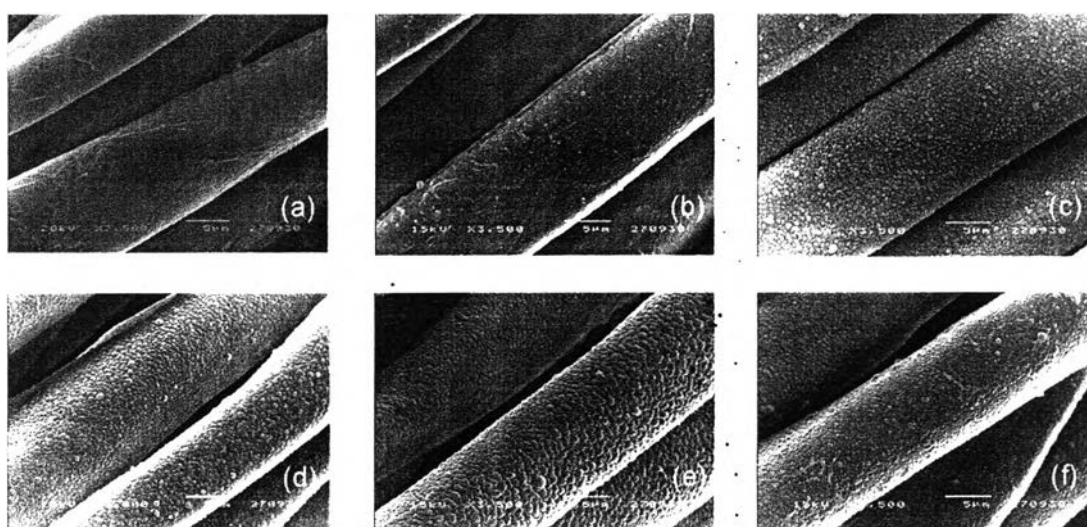
Figure 4.8 SEM micrographs of untreated cotton (a), and treated cotton fabrics by using HAB of 0.6 mM (b); 1.2 mM (c); 1.8 mM (d); 2.4 mM (e); and 3.0 mM (f), 0.6 mM DBSA and 0.15 M NaCl.
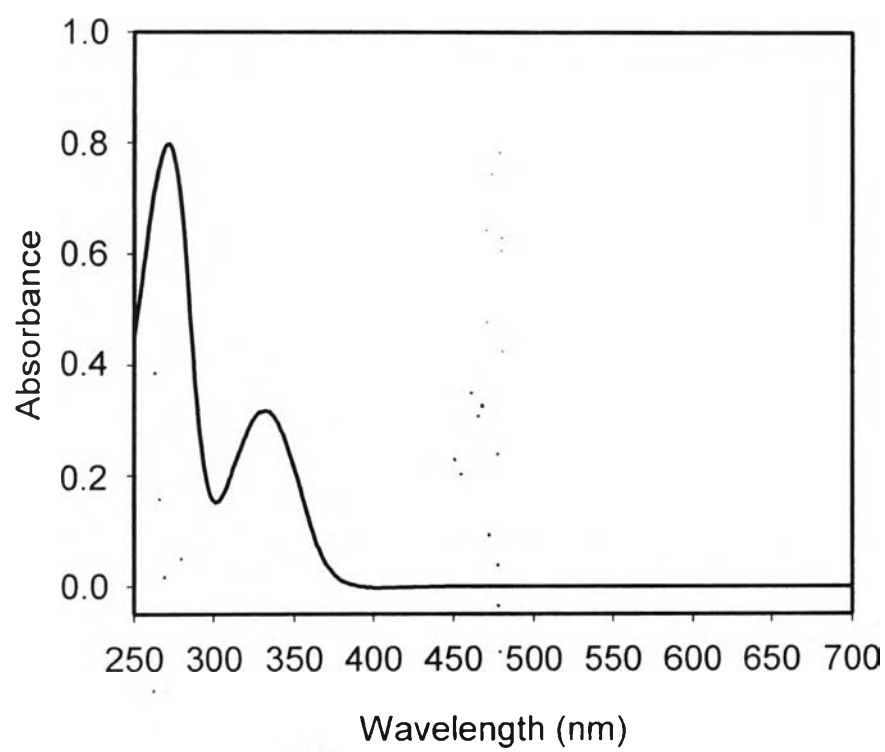
**Figure 4.9** UV spectrum of 2-hydroxy-4-acryloyloxybenzophenone (HAB).
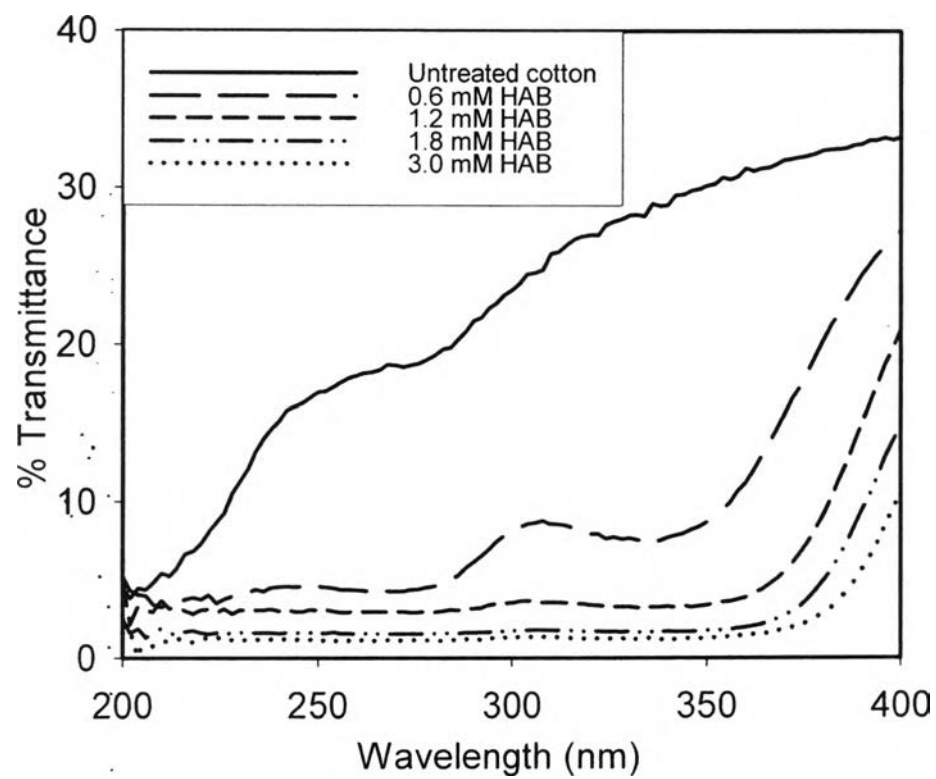
Figure 4.10 The UV transmission spectra of untreated cotton, and treated cotton using 0.6, 1.2, 1.8 and 3.0 mM of HAB, 0.6 mM DBSA and 0.15 M NaCl.
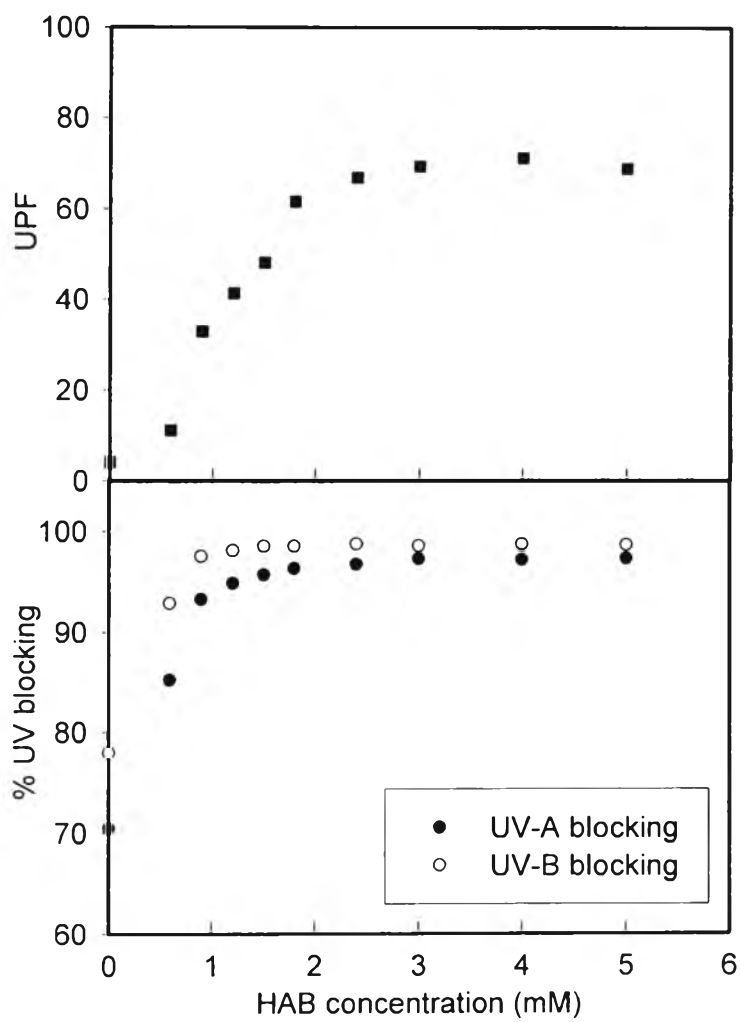
Figure 4.11 The effect of HAB concentration on UPF and % UV blocking of treated cotton fabrics, using 0.6 mM DBSA and 0.15 M NaCl.
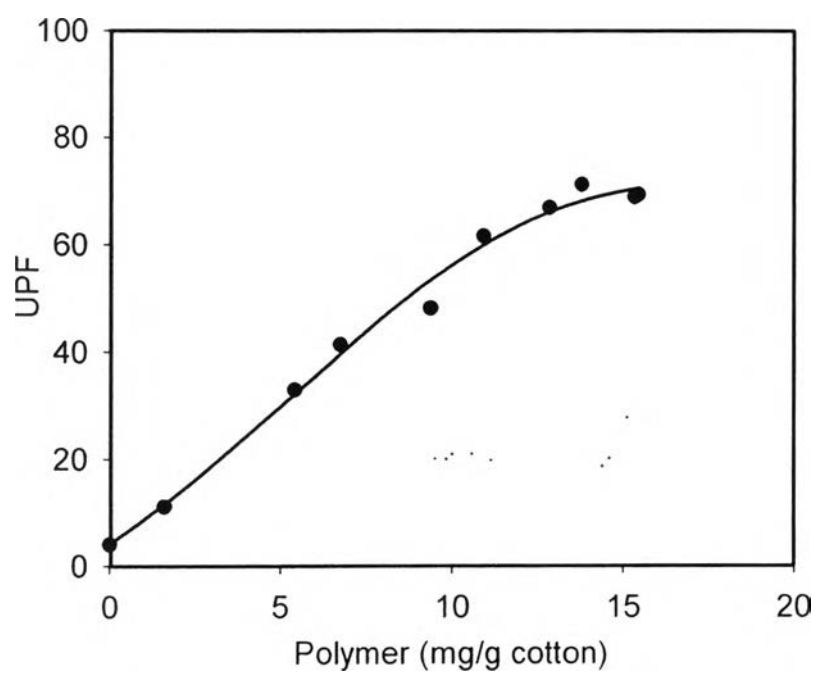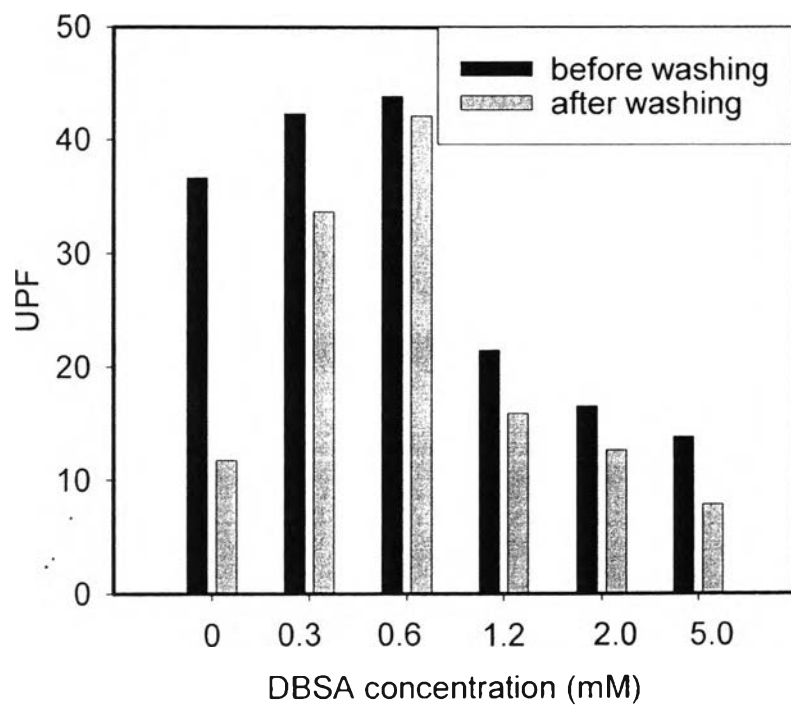
Figure 4.12 The relationship between UPF of treated cotton and the amount of poly(HAB) extracted by MEK.
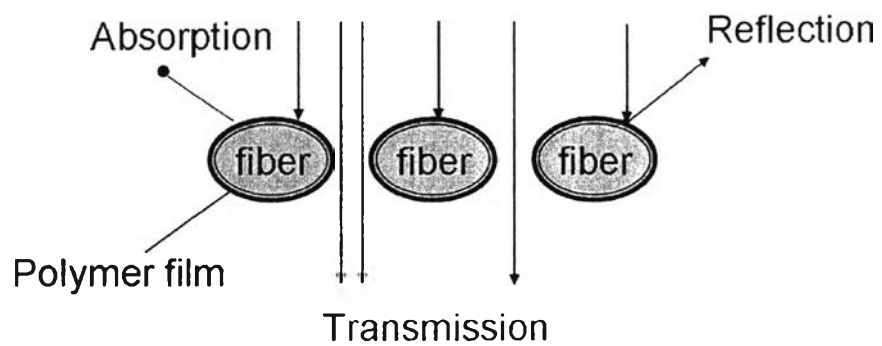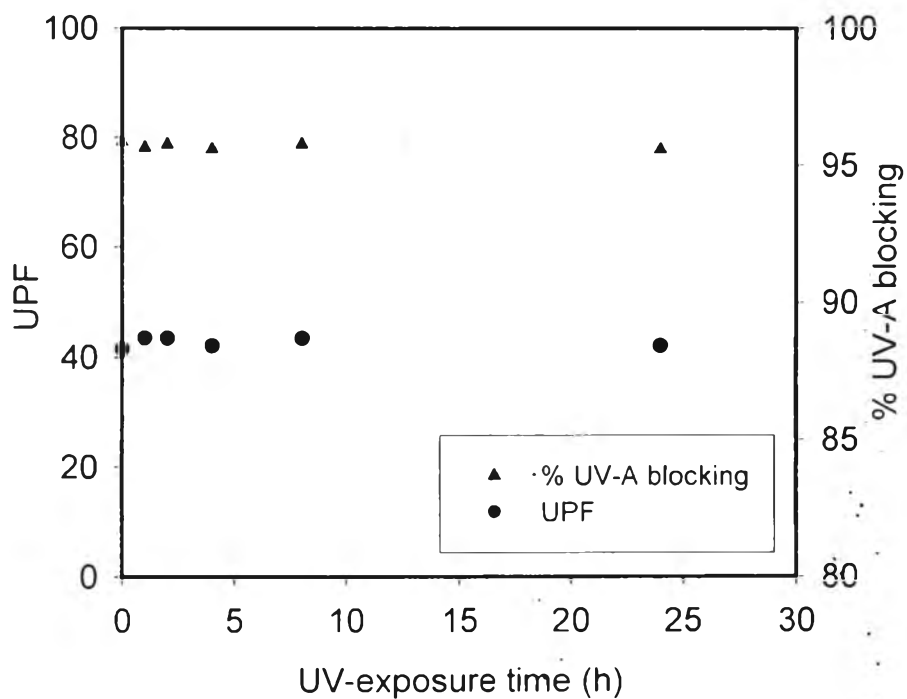
Figure 4.13 Schematic representation of absorption and transmission of UV radiation by fabrics.
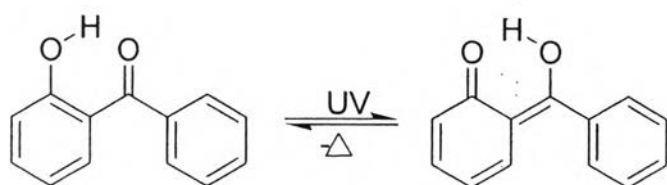
Figure 4.14 The effect of DBSA concentration on UPF before and after washing at 70°C for 3 times, 10 min/time, of the coated cotton using 1.2 mM HAB and 0.15 M NaCl.

Figure 4.15 The effect of UV exposure, using 6W UV-A Hg Philips lamp, on the % UV-A blocking and UPF of the coated cotton using 1.2 mM HAB, 0.6 mM DBSA and 0.15 M NaCl.

Figure 4.16 Intramolecular proton-transfer of hydroxybenzophenone.

Table 4.1 Classification of UV protection level of fabrics based on AS/NZS 4399

UPF	Protection Level
15-24	Good
25-39	Very Good
≥ 40	Excellent