# CHAPTER III
# EXPERIMENTAL

## 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), vinyltriethoxysilane (VTES) (97%), 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (BEM), acetic acid (99.7%) and azobisisobutyronitrile (AIBN) (99%) were 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). Methacryloxymethyltrimethylsilane (MSi) (>95%) was purchased from Gelest Inc., (USA). Ethanol (99.8%), dimethylacetamide (99.5%), methyl ethyl ketone (99.5%), HPLC-grade acetonitrile (99.9%), dichloromethane (99.8%) and sodium chloride (99%) were purchased from Labscan Company (Ireland). All chemicals were used without further purification.

## 3.2 Equipment

UV-visible spectrophotometer 2550 (Shimadzu) with integrating sphere attachment ISR-2200 was used to measure the percent transmittance for wavelengths from 200 to 400 nm in intervals of 2 nm.

Nuclear Magnetic Resonance Spectrometer (NMR) spectra were collected from a Mercury NMR spectrometer (Bruker) with a proton frequency at 400 MHz. Deuterated chloroform was used as a solvent.

Fourier Transform Infared Spectrometer (FTIR) spectra were obtained from a Nexus 670 spectrometer (Nicolet) with 32 scans at a resolution of 4 $cm^{-1}$ and a frequency range of 4000-400 $cm^{-1}$.

Scanning Electron Microscope (SEM), model JSM 2590 (JEOL) was used to study surface morphology of the cotton fabric.

Contact angle was measured by DSA10 contact angle measuring instrument, model DSA10-MK2 TIC (KRUSS. Germany)

High Performance Liquid Chrmotography (HPLC) was carried out using Perkins Elmer series 200, equipped with a $C_8$ column 15.0 cm × 4.6 mm (Supelco) using a solution of acetonitrile:water of 60:40 ratio by volume as a mobile phase and a UV detector (759 A-Applied Biosystem) operating at 224 nm.

## 3.3 Methodology

### 3.3.1 Synthesis of 2-hydroxy-4-acryloyloxybenzophenone (HAB)

2,4-dihydroxy-benzophenone (15 mmol), triethylamine (15 mmol), methyl ethyl ketone (MEK, 75 mL), and hydroquinone (1 g) were placed in a round-bottom flask and the contents were cooled in an ice bath. Acryloyl chloride (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 at this point 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. The reaction scheme is shown in Figure 3.1.

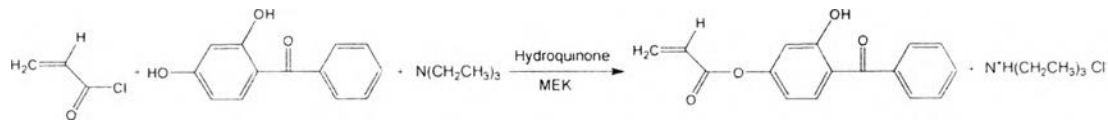


**Figure 3.1** Synthesis of 2-hydroxy-4-acryloyloxybenzophenone (HAB).

3.3.2 Determination of DBSA adsorption on cotton

A solution of DBSA of the desired DBSA and salt concentrations was first prepared. The pH of the solution was adjusted to 4 with HCl solution. 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 thermostatted water bath at the desired temperature and shaken at 120 rpm for a fixed time. The adsorbed DBSA on cotton was calculated by taking the difference between the initial and final concentration of DBSA in the vial. The 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 a molar extinction coefficient of $1.1 \times 10^4$ L $mol^{-1}$ $cm^{-1}$ obtained from the calibration curve.

3.3.3 Determination of the adsorption isotherm

The 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 mixture was equilibrated at 30°C for 15 h or 70°C for 1 h in a sealed 40-mL vial. The pH of the solution was pre-adjusted to 4 and 0.15 M NaCl was added. The concentration of the supernatant was determined by UV spectrophotometer at 224 nm. The initial DBSA concentration in this experiment was varied from 0.05 to 10.00 mM, which covered the regions below and above the CMC of DBSA. In the case where the isotherm was obtained in the presence of HAB, 2.5 mL of HAB in dimethylacetamide was pipetted into a vial containing 31.5 mL of DBSA solution and a piece of cotton fabric, the final concentration of HAB is 0.6 mM. Then the vial was sealed, and the system was allowed to equilibrate. Since HAB also absorbs UV radiation strongly, the initial and final concentrations of DBSA and HAB were determined by HPLC using a $C_8$ 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.

Adsorption isotherms of the DBSA on HAB-treated cotton were obtained by exposing a 6.5 cm × 6.5 cm cotton fabric treated by 1.5 mM HAB 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. The sealed vial was then placed in a thermostatted water bath at 30 °C and shaken at 120 rpm for 15 h. Concentrations of supernatant were determined by Shimadzu UV spectrophotometer 2550 at 224 nm. The adsorbed DBSA on cotton was calculated by taking the difference between the initial and final concentrations of DBSA in the vial. The initial DBSA concentration in this experiment was varied to cover the regions below and above the CMC of DBSA.

3.3.4 Determination of the amount of HAB adsolubilized in admicelle

Experiments were carried out using 2.5 mL of 8.4 mM HAB in dimethylacetamide, 25 mL of 0.84 mM DBSA and 6.5 mL of 0.81 mM NaCl solution, to give the final concentrations of HAB and DBSA of 0.6 mM and NaCl of 0.15 M, in a 40-mL vial containing a 6.5 cm × 6.5 cm cotton fabric at pH 4 and at 70°C for a set time. For equilibrium adsolubilization, the set time was 6 h. The initial and final concentrations of DBSA and HAB were determined by HPLC using the same procedure as described above.

3.3.5 Adsolubilization of comonomer system

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.

3.3.6 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 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 polymer 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:

$$A_{280} = \varepsilon_{BEM,\,280}\, bc_{BEM} + \varepsilon_{HAB,\,280}\, bc_{HAB} \qquad (3.1)$$

$$A_{300} = \varepsilon_{BEM,\,300}\, bc_{BEM} + \varepsilon_{HAB,\,300}\, bc_{HAB} \qquad (3.2)$$

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:

$$\%\ conversion = \{(c_{initial} - c_{final})/c_{initial}\} \times 100 \qquad (3.3)$$

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 (2.11), 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.

### 3.3.7 Admicellar polymerization of HAB

Polymerization of HAB on cotton was carried out in 31.5 mL of 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. Before the start of the experiment, 2.5 mL of HAB in dimethylacetamide with the desired concentration was added to allow the adsorption and the adsolubilization to occur simultaneously. The HAB concentration in the system was varied from 0.6 to 5.0 mM. The set time was 6 h for equilibrium adsorption and adsolubilization. Then 1 mL of the ammonium persulfate solution was injected to initiate the polymerization to give a 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 outer-layer DBSA. The fabric was finally placed in an oven at 60°C until dry.

3.3.8 Admicellar polymerization of HAB-BEM copolymer

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.

3.3.9 Admicellar polymerization of MSi

Polymerization of MSi on an untreated cotton fabric and the HAB treated cotton was carried out in a vial containing a 6.5 cm × 6.5 cm cotton fabric and 0.6 mM DBSA solution with 0.15 M NaCl at pH 4. MSi and AIBN in ethanol with the desired concentrations were added into the aqueous solution and the volume of ethanol was kept to be 10%. An initiator:monomer molar ratio was kept at 1:2. The sealed vial was then placed in a water bath at 30°C and shaken at 120 rpm for 24 h to allow surfactant adsorption and monomer adsolubilization to occur simultaneously. The temperature was then raised to 70°C to initiate the polymerization reaction. 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 upper-layer surfactant. The treated fabric was finally dried in an oven at 60°C.

3.3.10 Characterization of polymer 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 reflection 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 frequency 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 of 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.

For copolymer, 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.

The film thickness was determined from the amount of polymer extracted. The surface area of cotton as determined from BET with nitrogen was found to be 4 $m^2/g$ (Pongprayoon *et al.*, 2002). 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 film thickness was calculated using the following equation:

$$\text{Thickness} = \frac{\text{amount of polymer (g/g cotton)}}{\text{polymer density (g/cm}^3\text{)} \times \text{surface area of cotton (m}^2\text{/g cotton)}} \qquad (3.4)$$

3.3.11 Modification of cotton fabric by VTES-BEM

VTES was hydrolyzed in aqueous solution in the concentration range of 1 – 15 %vol. The pH of the silane aqueous solution was adjusted to 4 by using acetic acid. The hydrolyzation was carried out at room temperature for 2 h. After the VTES was completely hydrolyzed, the solution became homogeneous. A 6.5 cm × 6.5 cm piece of cotton fabric weighing 0.73 g was soaked in the silane solution at the

required concentration for 24 h at room temperature. The ratio of the fabric to solution was 1:20. The fabrics obtained were dried in an oven for 5 h at 120°C in order to allow condensation of the adsorbed silane to occur.

Polymerization of BEM on cotton was carried out in a 40-mL vial containing a 6.5 cm × 6.5 cm piece of untreated or VTES-treated cotton fabric, BEM with the concentration varied from 1.0 to 10.0 mM, and ammonium persulfate, at the temperature of 70°C. Ammonium persulfate was used to initiate the polymerization at the initiator:monomer molar ratio of 1:2. BEM and ammonium persulfate were dissolved in a mixture of water and DMAC. In a total volume of 35 mL, the amount of DMAC was varied from 5 to 30 mL in order to study its effect on the coated film. After 15 h of polymerization, the fabric was taken out from the vial and placed in an oven at 90°C until dry. After that it was washed with water and dried once again.

3.3.12 Washing fastness test

The durability of the UV-protection property of the treated fabric was determined by the washing fastness tests. The washing was carried out in water in the dyeing machine DAELIM DL-6000 at 30 °C with the speed of 30 rpm and 30 min/time. The fabric to water ratio was 1:100.

3.3.13 Determination of UV-protection properties of fabric

The two major steps in determination of UV protection are transmittance measurements and calculations based on the transmittance data collected. In this study, the percentage transmittance of the cotton fabric was measured according to the AATCC Test Method 183-2004 using 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, on warp, weft, and 45° diagonal directions. The results are the mean values obtained from two specimens with three measurements for each specimen. The data are then used to calculate the %UV blocking and the ultraviolet protection factor (UPF).

3.3.14 Water contact angle measurement

The water contact angles of the treated surface were measured using a KRÜSS contact angle measurement instrument, DSA 10-Mk2. A water droplet with the volume of 10 μL was placed onto the tested surface. The contact angles of the droplet were measured at 15 and 25 s for VTES-treated fabric and at 0 and 5 min for MSi/HAB-treated fabric. Five measurements were carried out on a sample at 5 different positions and the average value was reported.