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นางสาวนฤมล กาญจนภิญโญพงศ์



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF HYDROPHILIC-HYDROPHOBIC COPOLYMER
AS FINISHING AGENT FOR POLYESTER FABRIC



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งานวิจัยนี้ได้ทำการสังเคราะห์โคพอลิเมอร์ชนิดไฮโดรฟิลิก-ไฮโดรโฟบิกเพื่อนำไปตกแต่งสำเร็จผ้าพอลิเอสเตอร์ การสังเคราะห์โคพอลิเมอร์ทำได้โดยการทำปฏิกิริยาแบบแทนที่หมู่ไฮดรอกซิลของสารพอลิ(2-ไฮดรอกซีเอททิลเมทาไครเลท) ด้วยเบนโซอิลคลอไรด์ ซึ่งเป็นสารที่มีสมบัติไฮโดรโฟบิก การตรวจสอบปฏิกิริยาการสังเคราะห์โคพอลิเมอร์ อาศัยเทคนิคฟูเรียรทรานสฟอร์มอินฟราเรดสเปกโตรสโกปีและเทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโกปี

โคพอลิเมอร์ที่สังเคราะห์ได้สามารถกระจายตัวในน้ำในรูปคอลลอยด์สั่น จึงนำไปเคลือบผิวผ้าพอลิเอสเตอร์ด้วยกระบวนการย้อมเส้นใยที่ใช้กันในปัจจุบัน เพื่อคัดแปรสมบัติที่ผิวของผ้าพอลิเอสเตอร์ให้มีสมบัติการชอบน้ำอย่างถาวร เนื่องจากส่วนไม่ชอบน้ำของโคพอลิเมอร์ฝังตัวเข้าไปในเส้นใยพอลิเอสเตอร์ และส่วนชอบน้ำของโคพอลิเมอร์จะเกาะอยู่บนผิวของพอลิเอสเตอร์ การทดสอบความสามารถของการยึดเกาะของโคพอลิเมอร์บนผิวเส้นใยสามารถทำได้โดยการสกัดผ้าที่ผ่านการตกแต่งสำเร็จแล้วด้วยตัวทำละลายเมทานอล จากนั้นจึงตรวจสอบผิวผ้าด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ผลปรากฏว่าสารตกแต่งสำเร็จสามารถยึดเกาะบนผิวเส้นใยได้อย่างคงทน เมื่อเปรียบเทียบกับผ้าที่ยังไม่ตกแต่งสำเร็จ เมื่อตรวจสอบสมบัติการเปียกน้ำ พบว่าผ้าพอลิเอสเตอร์ที่ผ่านการตกแต่งสำเร็จสามารถดูดซับน้ำได้ดีขึ้น สมบัติที่สำคัญอีกประการหนึ่งคือผ้าพอลิเอสเตอร์ที่ผ่านการตกแต่งสำเร็จเมื่อนำไปย้อมด้วยสีย้อมเทอร์สมและทดสอบสมบัติความคงทนของสีต่อความร้อน พบว่ามีความคงทนต่อความร้อนดีกว่าผ้าที่ไม่ได้ทำการตกแต่งสำเร็จ ทั้งนี้เป็นเพราะชั้นของส่วนชอบน้ำของโคพอลิเมอร์ที่เคลือบผิวพอลิเอสเตอร์ช่วยป้องกันการแพร่ออกของสีเมื่อถูกความร้อน

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ลายมือชื่อนิติคุณ.....นฤมล กาญจนภิญโญพงศ์
ลายมือชื่ออาจารย์ที่ปรึกษา.....ผศ.ดร. กาวิ ศรีกุลกิจ

AN ABSTRACT

##4072490823: MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEY WORD: hydrophilic-hydrophobic copolymer / wettability / polyester fabric / surface modification

NARUMON KANCHANAPINPONG : SYNTHESIS OF HYDROPHILIC-HYDROPHOBIC COPOLYMER AS FINISHING AGENT FOR POLYESTER FABRIC. THESIS ADVISOR : ASST. PROF. KAWEE SRIKULKIT, Ph.D. 104 pp. ISBN 974-334-873-5.

A hydrophilic-hydrophobic copolymer for surface modification of polyester fabric was prepared by a partial substitution of hydroxyl groups of poly(2-hydroxyethyl methacrylate) with benzoyl chloride. FT-IR and NMR spectroscopy were employed to follow the chemical reaction.

Such synthesized copolymer was applicable to polyester fabric by conventional dispersion dyeing methods. By applying such textile finishing agent, it was aimed to impart durable hydrophilicity to polyester fabric by anchoring hydrophobic segment and hydrophilic segment on the polyester surface. Surface analysis of treated fabrics before and after solvent extraction using scanning electron microscopy (SEM) indicated that the finishing agent adhered firmly on the fiber surface. Wettability of treated fabrics was evaluated by measuring complete wetness time by standard methods of AATCC and Du Pont. It was found that wetness of treated fabrics improved significantly when compared to untreated polyester fabric. Furthermore, it was found that treated fabrics dyed with disperse dyes had better heat fastness than untreated fabric. An improvement of heat fastness was due to the barrier effect of hydrophilic layers of modified polyester surface on the migration of hydrophobic disperse dyes.

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CHAPTER I

Introduction



Thermoplastic synthetic fibers, typically polyester are widely used mainly for clothing and industrial applications since they are excellent in mechanical properties, chemical resistance, heat resistance, etc. However, due to the hydrophilicity of polyester in nature, the properties associated with hydrophilic characteristic such as antistatic property, sweat-absorbing properties and soil-releasing property which are suitable for producing clothes are restricted⁽¹⁾.

Polyester fabrics used in direct contact with or near the skin as innerwear, intermediate wear, sports wear, are inferior to natural fibers in the feeling of comfort since perspiration from the skin makes the wearer feel stuffy and sticky. Moreover, polyesters are more electrostatic than other fibers in the heat-sensitive group⁽²⁾. Static is characteristic of fibers that have low absorbency. Static is very annoying since it causes clothes to cling to each other. The disadvantage of static causes lint fiber attract to the surface of fabric so that it is difficult to keep dark-colored fabrics looking neat.

To eliminate these disadvantages, many methods have been proposed. For example, the controls of static build-up on polyester fabrics were done by increasing humidity and using lubricants but these controls were not adequate with the thermoplastic fibers. Antistatic finishes were developed to (1) improve the surface conductivity so that excess electrons move freely to the atmosphere or ground; (2) attract water molecules, thus increasing the conductivity of the fiber; or (3) develop a charge opposite to that on the fiber, thus neutralizing the electrostatic charge. The most effective finishes should produce all three effects combined. Most antistatic finishes are not durable and must be applied repeatedly during care to maintain the fabric performance. Most finishes are quaternary ammonium compounds, commercially available as fabric softeners to help controlling static⁽³⁾.

Recently research and development activities for improving the surface of polyester such as the production of multicomponent fibers or sheath/core fibers⁽⁴⁻⁶⁾, sea/land fibers⁽⁷⁻⁹⁾ have attracted much attention. The cross-section of these fibers indicates two layers. The outer layer (sheath) is hydrophilic-hydrophobic copolymer which is more hydrophilic in order to absorb moisture and dissipate static charge, where as, the inner layer (core) has only hydrophobic properties. The production of this kind of fibers requires sophisticated technology. The other disadvantages of this fabrics are the problem of dyeing due to the difference in hydrophilic-hydrophobic copolymer and the problem of reduction in color fastness.

Alternative approach in improving hydrophilicity of polyester is by hydrolysis of polyester using alkali such as sodium hydroxide⁽¹⁰⁾, or enzyme such as lipase⁽¹¹⁾. Coating polyester surface by antistatic layer such as silver halide also improves⁽¹²⁻¹³⁾.

In addition, the method of grafting hydrophilic polymer or hydrophilic copolymer onto the surface of polyester, for example, the grafting of acrylic acid, poly (acrylic acid) or ethyl acrylate onto polyester using benzoyl peroxide initiator⁽¹⁴⁻¹⁶⁾ or the grafting of methyl methacrylate using azobisisobutyronitrile initiator⁽¹⁷⁾ or the grafting of acrylamide using hydrogen peroxide initiator⁽¹⁸⁾ are widely studied.

An improved efficiency of graft copolymerization may be achieved by pretreatment of polyester prior to grafting. Study of glow discharge plasma⁽¹⁹⁾ or swelling assist treatment⁽²⁰⁾ of polyester shows the better wettability and dissipability of static charge. However, the disadvantages of graft copolymerization by some techniques are that it consumes treatment time and is not appropriate for applying to polyester fabrics in the view of commercial interests.

Thus, the purpose of this thesis is to improve wettability of polyester fabrics by coating hydrophilic-hydrophobic copolymer onto the surface of polyester fabrics in order to achieve the permanent hydrophilicity. The copolymer used in this study is poly(hydroxyethylmethacrylate-co-benzoyl ethylmethacrylate), poly(HEMA-co-BEMA), whose characteristics are hydrophilic and adherent to polyester fiber.

Poly(HEMA-co-BEMA) is synthesized by the partial reaction of poly(hydroxyethylmethacrylate), poly(HEMA) with benzoyl chloride. It is expected that this copolymer can be dispersed in water without the requirement of dispersing agent. This characteristic is preferable since the application media is water. Therefore, this finishing agent can be called water-based finish. The application will be carried out using exhaust dyeing machine. It is anticipated that during treatment at temperatures higher than T_g of polyester, the polymer chain will open-up and allow hydrophobic part of the copolymer to penetrate fiber surface. The hydrophilic part which differs from the polyester in terms of hydrophobicity still attaches onto the fiber surface. By anchoring the hydrophobic segment inside the fiber, it is believed that the copolymer can be adhered firmly onto the fiber surface, resulting in imparting the permanent hydrophilic property to the fiber surface.

The scope of this research will be focused on the synthesis and characterization of the hydrophilic-hydrophobic copolymer, poly(HEMA-co-BEMA), the effect of application factors affecting the adhesion capability of the copolymer on the polyester surface, and finally the evaluation of surface properties of modified polyester such as moisture regain, wettability and adhesion ability of the copolymer.

CHAPTER II

Literature Review

2.1 Polyester fibers

Polyester fibers are long chain polymers produced from elements derived from coal, air, water, and petroleum. As defined by the Federation Trade Commission (FTC), these fibers are chemically composed of "at least 85 percent by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted hydroxybenzoate units⁽²¹⁾."

2.2 History of polyester fibers

The groundwork for the development of polyester fibers was laid by Dr. W. H. Carothers in his experiments with giant molecular structures. Dr. Carothers had published research information on polyesters, and after studying his works, British research chemists decided to examine the possibilities of polyesters. During the period from 1939 to 1941, investigations were conducted in the laboratories of the Calico Printers Association, Ltd., by J. R. Whinfield, J. T. Dickson, W. K. Birtwhistle, and C. G. Ritchie. The work resulted in the development of a polyester fiber known in Britain as Terylene. In 1946, E. I. Du Pont de Nemours & Co., purchased the exclusive rights to produce this polyester **fiber in the United States**. Having conducted intensive development work, by 1951, Du Pont was commercially producing the fiber, which is called Dacron.

Subsequently, other companies became interested in polyester fiber. In 1958, Eastman Chemical Products, Inc., announced its own version of polyester, which is called Kodel. The following year, the Celanese Corp. of America obtained licenses to use certain patents owned by Du Pont and entered the market with a polyester called Fortrel, which is now sold by the Celanese affiliate, Celanese Fibers Marketing Co.

In 1966, American Enka Co. announced its Enka polyester fiber and Chemstrand Co., now Monsanto Textiles Co., introduced its Blue "C" polyester fiber, but subsequently discontinued this and other filament fibers in favor of certain staple polyester fibers such as Spectran. In 1967, the American Viscose Division of FMC Corp. (now Avtex Fibers Inc.) introduced its Fiber 200 polyester with the trademark Avilin, and Hoechst Fibers, Inc., (now Hoechst Fibers Industries) an outgrowth of an alliance between Hercules, Inc., and Farberwerke Hoechst AG, presented its Trevira polyester fiber. Since then, additional companies entered the polyester competition. The polyester fibers may be primarily divided into two varieties: PET poly(ethylene terephthalate) and PCDT poly(-1,4-cyclohexylene-dimethylene telephthalate)⁽²¹⁾. The comparison of PET and PCDT fiber may be written in Table 2.1⁽³⁾.

Table 2.1 Comparison of PET and PCDT fibers⁽³⁾

Fiber	PET	PCDT
Formula	$[-OC-\text{C}_6\text{H}_4-\text{COO}-(\text{CH}_2)_2\text{O}]_n$	$[-OCH_2-\text{C}_6\text{H}_{10}-\text{CH}_2\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}]_n$
Commercial names	Avilin, Dacron, Fortrel, Kodel IV, Trevira	Kodel II
Processing	Filaments are hot drawn	Drawn at higher temperature
Type of fiber produce	Filament or staple Textured yarns	Staple and low pilling
Physical properties	Stronger, resistant to abrasion Higher density, 1.38 Lower melting point, 480°F	More elastic Greater bulking properties Greater resiliency Lower density, 1.22 Higher melting point, 540°F

2.3 Polyester manufacture

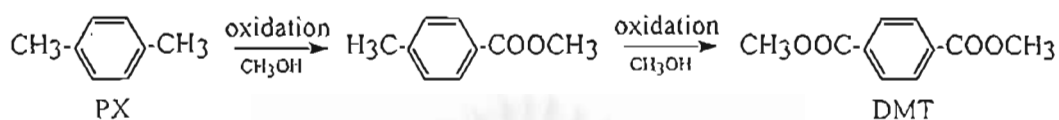
Terephthalic acid (TA) or its dimethyl ester (DMT) and ethylene glycol form a diester monomer which is polymerized to PET. The polymer is melted and extruded (spun) through a spinneret, forming filaments that are solidified by cooling in a current of air. The spun fiber is drawn by heating and stretching the filaments to several times their original length, forming an oriented semicrystalline structure and imparting the desired physical properties. For copolyesters or other polyesters such as poly(butylene terephthalate) (PBT), similar steps are followed with only minor modifications to standard PET processes.

2.3.1 Raw materials.

Before 1965, only DMT was used in the large-scale production of polyester fibers because it was easier to obtain the high degree of purity required to produce a high molecular weight polymer without color-forming bodies. Later, development of direct p-xylene oxidation followed by purification made pure TA (PTA) commercially available. TA now accounts for a 40% and 55% share of the polyester raw material business in the United States and worldwide, respectively. In Japan, the more recent installations do not incorporate a separate purification step, and a medium purity TA (MTA) is found to be satisfactory. In some cases, color is improved by addition of a blueing agent such as divalent cobalt or an optical brightener.

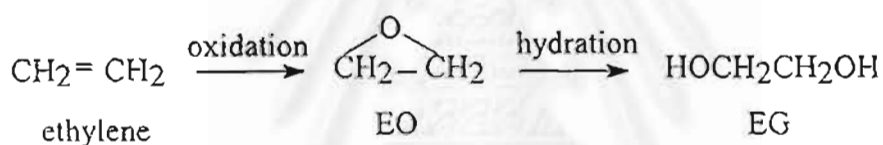
The most widely used TA process is based on catalytic air oxidation of p-xylene (PX) in acetic acid by means of bromine and other promoters or activators. The crude TA is dissolved in water at 250 °C under high pressure and purified by catalytic hydrogenation followed by crystallization. The purification step is expensive with respect to capital costs and therefore the Japanese MTA process is based on a single-step purification of the TA in acetic acid. The main difference between MTA and PTA is a higher content of p-carboxybenzaldehyde impurity in the former, which can be tolerated with minor adjustments. The DMT is obtained by methanol esterification of

the crude TA derived from p-xylene oxidation or by the Witten process, where p-xylene is oxidized and esterified at the same time. The crude ester is purified by crystallization and distillation. The DMT process is shown in Scheme 2.1⁽²²⁾.



Scheme 2.1 The DMT process⁽²²⁾

Ethylene glycol (EG) is derived from ethylene by catalytic oxidation with air to ethylene oxide (EO) followed by acid hydrolysis in Scheme 2.2⁽²²⁾.



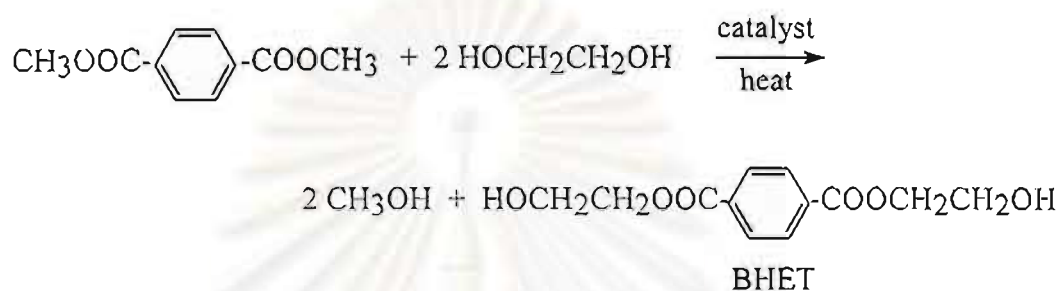
Scheme 2.2 The process of acid hydrolysis for producing ethylene glycol (EG)⁽²²⁾

The ethylene glycol must be pure and free from color-forming impurities and traces of strong acids or bases. An alternative route based on acetoxylation of ethylene failed because of corrosion-related problem.

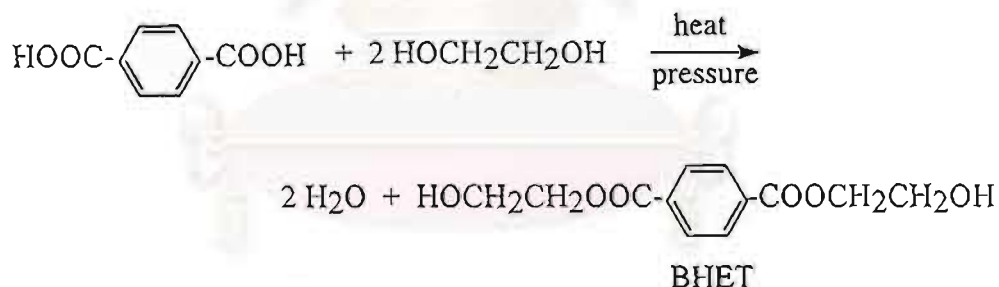
Other raw materials, used in small amounts, are titanium dioxide as a delusterant pigment, optical brighteners, colored pigments or dyes, and comonomers designed to impart special properties to the fibers. Many of these additives, such as PEG, adipic acid (ADA), isophthalic acid (IA), and titanium dioxide, are common commodity materials used in other industrial areas. However, optical brighteners, antioxidants, and some comonomers, such as sodium-5-sulfo-isophthalic acid (5-SIA), are specialty chemicals.

2.3.2 Polymerization

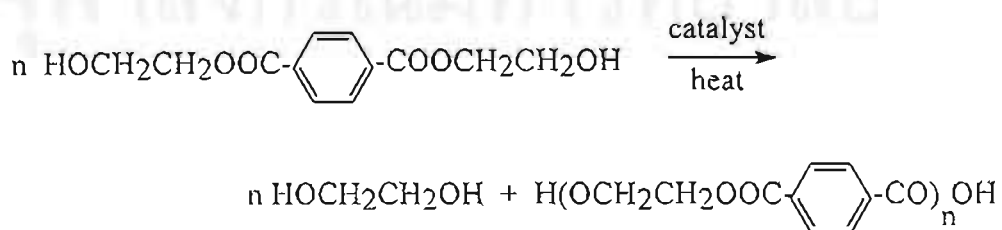
The polyester is produced commercially in two steps: monomer formation by ester interchange of DMT with glycol or esterification of TA with glycol, followed by polycondensation by removing excess glycol to promote chain extension (Schemes 2.3, 2.4 and 2.5)⁽²²⁾



Scheme 2.3 Ester interchange⁽²²⁾



Scheme 2.4 Esterification⁽²²⁾



Scheme 2.5 Polymerization⁽²²⁾

The monomer is formed by the catalyzed ester interchange reaction between molten DMT and glycol at 200 °C and atmospheric pressure. A mixture of mostly bis-β-hydroxyethyl terephthalate (BHET), very low molecular weight polymer, and by-product methanol is obtained; the methanol is distilled off and recovered. Catalysts include divalent salts of manganese, cobalt, magnesium, zinc, or calcium. In the direct esterification of TA, the carboxyl groups of TA catalyze the reaction and no added catalyst is required. Higher temperature and pressure increase the reaction rate. The monomer, which is the same from both methods except for some small end-group differences, is polymerized, usually in the presence of an antimony catalyst; other catalysts, such as compound of titanium and germanium, are used to a limited extent. Additives such as TiO₂ can be added at the different steps of the process. To promote chain extension, the excess glycol is removed from the highly viscous melt at ca 280 Pa (1.5 mm Hg). Heating is continued at this temperature until the desired degree of condensation is obtained. The molecular weight is usually controlled by determination of melt viscosity, frequently using the power input to the agitator as an indicator. Side reactions also occur; the esterification of ethylene glycol gives 3-oxapentamethylene glycol (diethylene glycol), which becomes incorporated into the polymer chain and lowers the softening point of the polymer. By product formation of cyclic oligomers such as trimer and tetramers of TA and glycol also occur in minor amounts, depending on reaction conditions.

More recently, pure terephthalic acid (PTA) has replaced DMT as the raw material because of advantages in processing, handling, and polymer quality, as well as reduced production costs. Capital costs and energy consumption are lower, and there is less excess glycol. Reaction efficiencies are better. The storage life of PTA is practically indefinite, and storage and inventory costs are lower (15% less on a weight basis). No catalyst or methanol is needed. However, the choice is also influenced by availability of the raw materials and the size of the operation; small-scale plants tend to favor DMT.

The starting products are polymerized at high temperatures and then filtered to remove any impurities. The molten polymer may be spun directly, or it may be extruded, cooled, and cut into small pellets or chips, which can be stored for later extrusion.

During the extrusion step, the molten polymer (or remelted chips) is metered through a spinneret. The filaments solidify in cooling air and are taken up on large bobbins, or pirns. The filaments must be drawn to orient the polymer and develop the fiber properties of the filament. The fiber may be completely drawn after extrusion, or it may be partially drawn to form a partially oriented yarn (POY). Filaments intended for staple fibers or untextured yarn are fully drawn. Yarns to be textured at later processing step may be produced as POY. Careful control of the drawing process is required to produce the tenacity and elongation required by the customer. The processes in polyester manufacture are shown in Figure 2.1⁽²²⁾ and Figure 2.2⁽²³⁾.

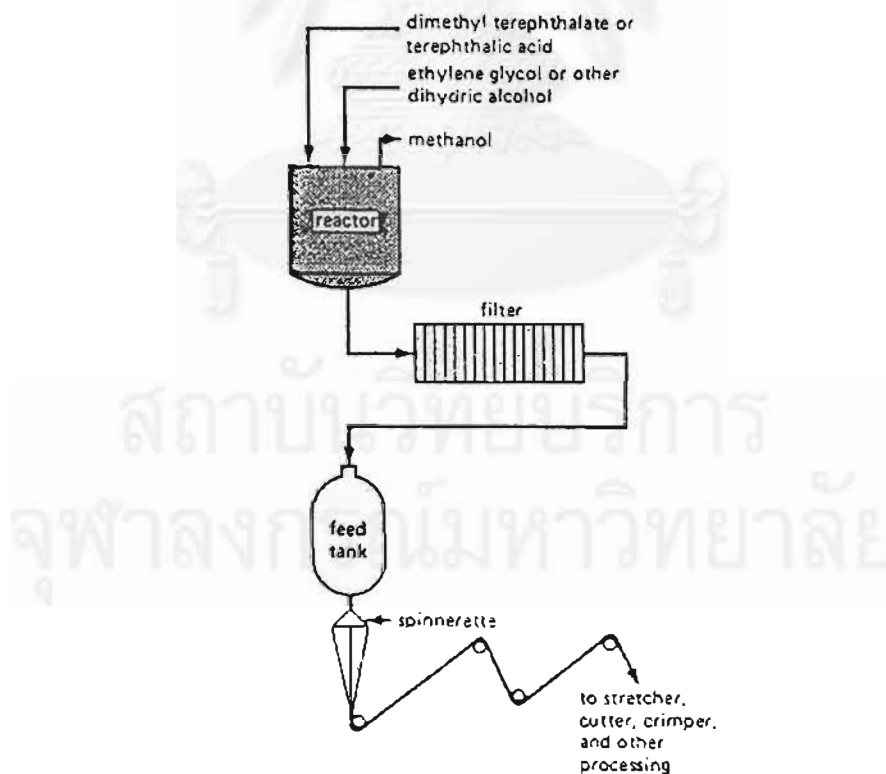


Figure 2.1 Flow diagram for the process used to manufacture polyester

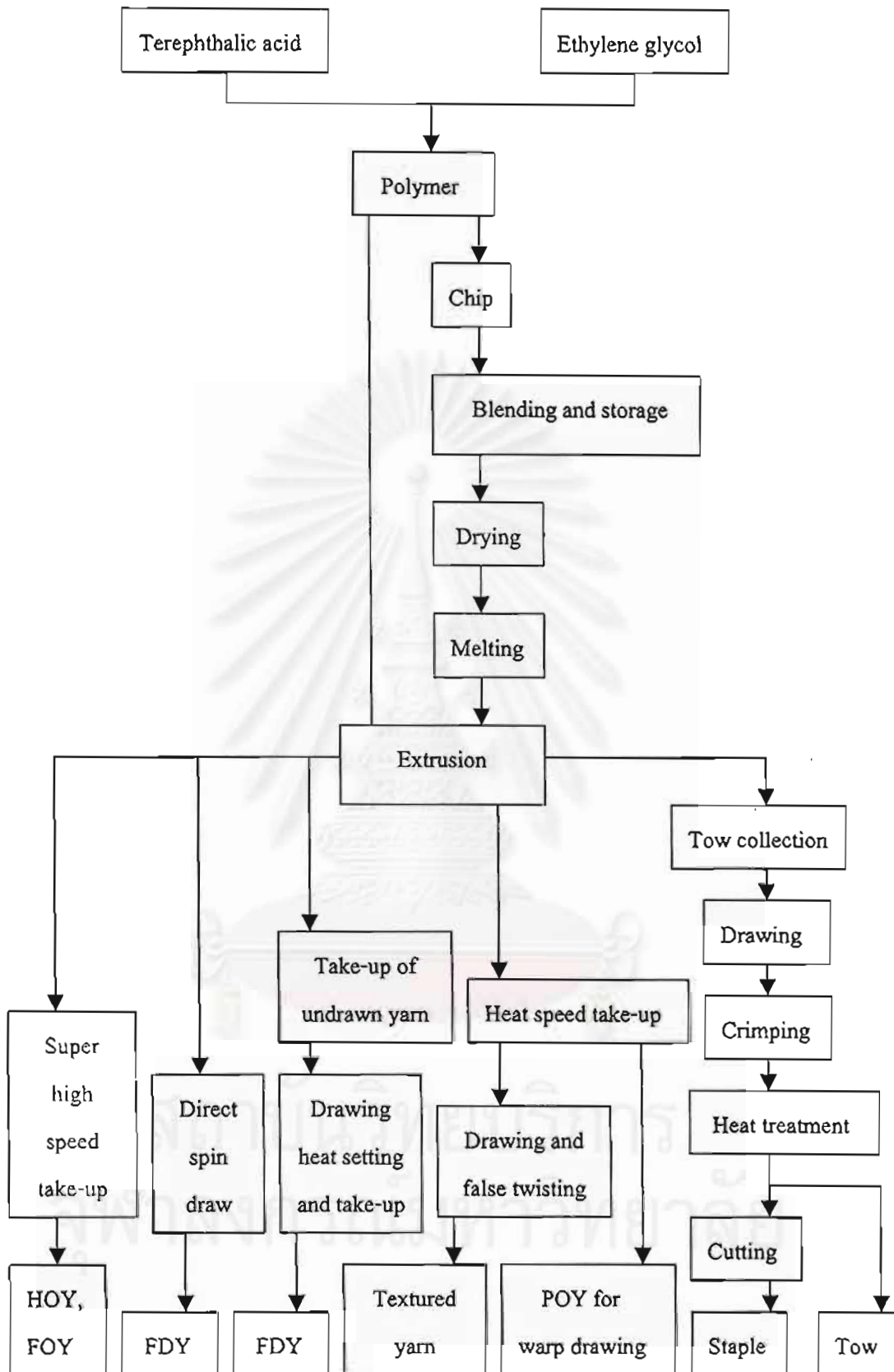


Figure 2.2 Polyester fiber manufacturing processes. HOY = highly oriented spun yarn;

FOY = fully oriented spun yarn; POY = partially oriented spun; FDY =

fully drawn yarn⁽²¹⁾

2.4 Properties of polyester

The important properties of polyester fiber are shown in Table 2.2⁽²⁴⁾.

Table 2.2 The important properties of polyester fiber⁽²⁴⁾

Chemical properties	Physical Properties	Biological properties	Fabric properties
1. Stability towards Acids Bases Bleaches Solvents Sunlight Aging	1. Mechanical properties Elongation Stiffness Flex life Abrasion resistance Work recovery Tensile recovery	1. Toxicity 2. Resistance to Bacteria Molds Insects	1. Appearance Feel Luster 2. Comfort Warmth Moisture - retention Wicking
2. Flammability	2. Thermal properties Melting point Softening point Glass transition - Temperature Decomposition Temperature		3. Stability Shape Shrinkage Felting Pilling Crease - resistance
3. Dyeability	3. Electrical properties Surface resistivity		

2.4.1 Morphology

2.4.1.1 Fineness

Like other manufactured fibers, polyester fibers are available in many lengths and deniers. Very fine-denier or microdenier fibers are now available: some approach 0.5 denier⁽²³⁾. Microdenier fibers probably will become increasingly important in the apparel sector, as their hand more closely resembles that of silk.

2.4.1.2 Color and luster

The fiber is partially transparent and white or slightly off-white in color. As with other manufactured fibers, various degrees of luster can be produced by the addition of delusterants. The delusterants may produce grainy or pitted microscopic appearance.

2.4.1.3 Microscopic features

Polyester fibers are melt-spun and so are available in a wide range of cross-sectional shapes. Several fibers are spun with hollow cores for use in pillows and battings. The most common types are shown in Figure 2.3⁽²³⁾.

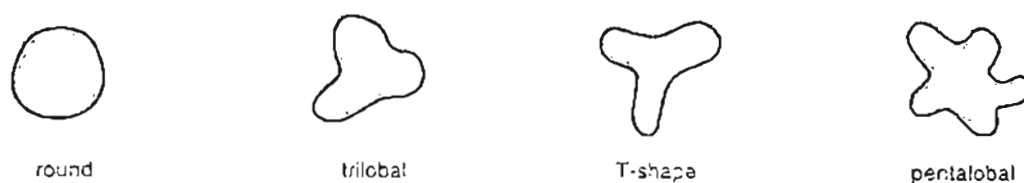


Figure 2.3 The major cross-sectional shapes of polyester fibers⁽²³⁾

2.4.2 Stress-strain relationships

2.4.2.1 Tenacity

The strength of the fibers ranges from 2.5 to 9.5 grams per denier (g/d). The tenacity of polycarbonate is approximately 4.5 g/d. Fibers with tenacities of 2.5 to 3.5 g/d are used almost exclusively for apparel. Yarns made from microdenier fibers have lower tensile strength than comparable denier yarns made from conventional polyesters. The fibers with tenacity over 7 g/d are used in industrial fabrics. Polyester fibers do not lose strength when wet⁽²³⁾.

2.4.2.2 Elongation

Elongation varies with the type of fiber and ranges from about 10 to 60 percent; polycarbonate fiber elongation is 20 to 45 percent. In general, fibers with high tenacity have low elongation, and low-strength fibers have higher elongation. Elastic recovery of polyesters is very good. Most of the high tenacity polyesters exhibit 100 percent recovery after 2 percent elongation. Most other fibers have 95 to 97 percent recovery. Some Kodel fibers have lower (75 to 95 percent) recovery⁽²³⁾.

2.4.3 Density

The density of most polyesters is 1.38 g/cm³. The 200-series Kodel fibers have lower density (1.23 g/cm³). The density of PEB polyesters is about 1.34 g/cm³, and that of the polycarbonates is 1.23 g/cm³. Fiber that has been heavily delustered with TiO₂ may have a density of about 1.4. The low mass of polyester means that fabrics made from it will be light in weight. Because heavier fabrics tend to give a better drape, some attempts have been made to increase the weight of polyester. Kuraray of Japan has added a ceramic component to one of its fibers to produce a specific gravity of about 1.5⁽²³⁾.

2.4.4 Moisture

Polyester fibers have very low moisture regain of 0.4 percent at standard conditions. Even at 95 to 100 percent relative humidity, the moisture content is only 0.6 to 0.8 percent. The low moisture pickup of the fibers makes them quick-drying and at times difficult to process. Low moisture levels are also associated with a high buildup of static electricity. As with nylon, care must be taken with polyester fibers in environments where static buildup will present the problems⁽²³⁾.

2.4.5 Thermal properties

Polyester fibers melt at temperatures from 238 to 290 °C (460 to 554 °F). As the fiber melts, it forms a gray or tawny-colored bead that is hard and noncrushable.

When it burns, the fiber produces dark smoke and acrid odor and (like nylon) exhibits a melt-drip characteristic. The burning polymer falls away from the unignited material and self-extinguishes.

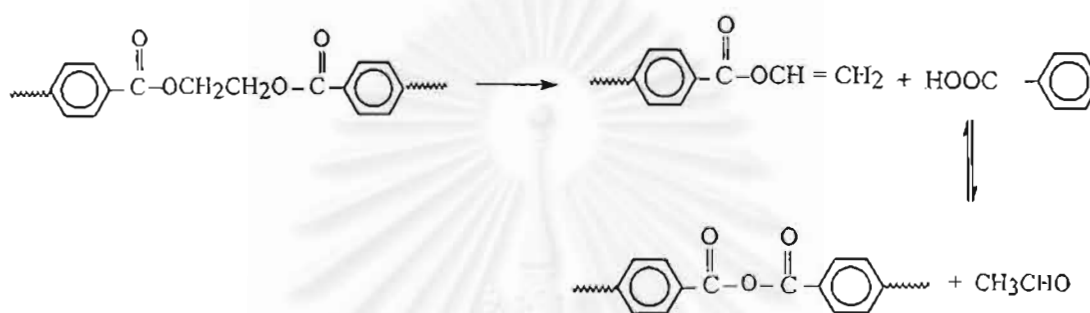
The T_g of polyester is 80 °C. The fiber is easily molded with heat, a property that has made it the ideal fiber for producing textured yarns. Care must be taken in heat-setting polyester yarns and fabrics. Materials that are not properly heat-set will shrink in laundering and lose creases that were thought to have been permanently set in place.

Polyesters retain 70 to 80 percent of their strength following prolonged exposure to 150 °C (250 to 300°F); at lower temperatures there is minimal or no loss of strength. At temperatures above 150°C, strength loss occurs rapidly. Some polymer types may be more heat-resistant than others.

The safe ironing temperatures of polyester are listed as 120 to 150°C (250 to 300°F). Lightweight fabrics should be ironed at the lower temperature⁽²³⁾.

The thermal degradation of PET and model compounds proceeds by a molecular mechanism with random chain scission at the ester links, although a radical mechanism has also been proposed.

The degradation product can undergo further changes, but at ordinary processing temperatures, a certain proportion of carboxyl end groups is introduced into the polymer structure. Color formation upon degradation has been attributed to the formation of polyenaldehyde and from a further breakdown of poly(vinyl ester). A chain scission scheme is shown below (Scheme 2.6)⁽²²⁾.



Scheme 2.6 A chain scission scheme of PET⁽²²⁾

2.4.6 Chemical properties

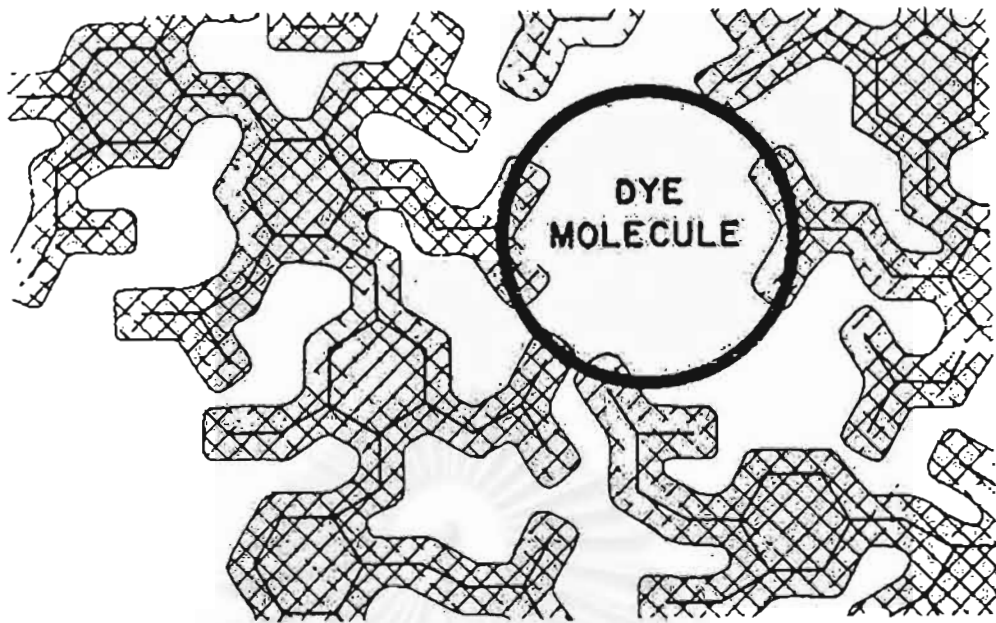
Polyesters have very good resistance to weak acids and alkalies, even at high temperatures. Strong alkalies weaken the fiber at room temperature and quickly degrade it at elevated temperatures. The resistance to strong acids at room temperature is good. Prolonged exposure to boiling hydrochloric acid or 96 percent sulfuric acid disintegrates the fiber. The Kodel 200 fibers are more resistant to acids and alkalies than the others. Hot m-cresol is used to dissolve the fiber in fiber identification tests, and certain mixtures of phenol with trichlorophenol or tetrachloroethane also dissolve it.

2.5 Dyeing of polyester

Polyesters have offered considerable difficulties in dyeing. These have been due to the lack of hydrophilic properties and of reactive groups such as those that abound in the cellulosic fibers and in the protein fibers. For similar reasons cellulose acetate, when it was first made, presented the same difficulty, and it was eventually overcome by the introduction of the disperse dyes, which are applied from an aqueous dispersion, not from solution, and which, having greater affinity for the organic fiber than for the water of the dyebath, eventually migrate to the fiber and form a solid solution in it. This technique has been applied to most of the synthetic fibers as they have come along, and notably to nylon. It was the obvious line of approach to polyester dyeing, but it did not prove to be very easily applicable to this fiber. The reason for this is that the polymer chains in polyester is much more closely packed than in cellulose acetate.

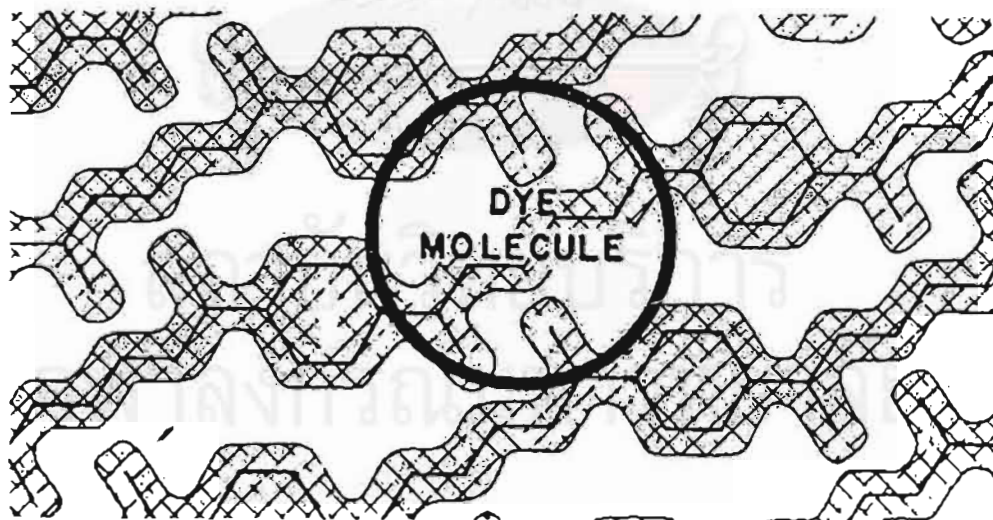
A representation of cellulose acetate fibers based upon information gained from x-ray diffraction studies in Figure 2.4⁽²⁵⁾ represents a magnification of about 100 million times. It can be seen that the dye molecule is drawn approximately to scale and that there are gaps between the chains which can particularly accommodate the dye molecule, because the chains are fairly free to change their positions.

Figure 2.5⁽²⁵⁾ is similar to Figure 2.4 in the magnification but it is the representation of polyester fibers instead. It can be seen that the long-chain molecules are neatly packed in a zig-zag pattern, and there are no gaps which can suitably accommodate the dyestuff molecule, and furthermore, the chain molecules are very reluctant in changing their positions, i.e., to lose their orientation. The result is that the dyestuff particles cannot penetrate the fiber easily and in fact, the process is so slow that it takes a matter of days or even weeks to dye a polyester fiber at a dyeing temperature of 85 °C.



[E. I. du Pont de Nemours & Co., Inc.]

Figure 2.4 Cellulose acetate chains and dye molecule⁽²⁵⁾



[E. I. du Pont de Nemours & Co., Inc.]

Figure 2.5 Polyester chains and dye molecule⁽²⁵⁾

This difficulty has been overcome in four ways:

1. Selection of dyestuffs: The only dyestuffs with measurable affinity for polyester under ordinary conditions are those which may be applied from aqueous dispersion. Some of these will give light to medium shades in about 1.5 hours at the boil; it is necessary to use a temperature of practically 100 °C, as the affinity even of the selected dyestuffs is low at 85 °C (selected dyestuffs for use with polyesters are disperse dyes).

2. High-temperature dyeing: By using higher temperature, e.g., 100 °C, the polyester molecules are more free to move and the dyestuff molecules can penetrate faster and pale shades can be dyed fairly satisfactorily in a reasonable time at this temperature ; even so, penetration is poor and most of the dyestuff is located on the surface of the fibers. If, however, the temperature is continuously increased to 120 °C, the polyester molecules are much more free to move and the dyestuff can penetrate the fibers well; therefore, good medium and heavy shades can be obtained within a reasonable dyeing time such as one hour. This method, however, involves the use of pressure equipment (water or aqueous dyebath cannot be maintained at a temperature higher than 100 °C at atmospheric pressure).

3. Carrier dyeing : By using a carrier ; this in effect is a swelling agent. A small quantity of it is included in the dyebath. It swells the fibers and this enables the polyester molecules to move out more easily and to increase the distance between them. The dimensions of the chain molecules themselves are not changed (they do not swell), the molecules move farther apart so that the diameter of the fiber increases and thus there are spaces to accommodate the dyestuff molecules. The carriers that are used are the known swelling agents for polyester fibers.

4. Thermosol method of dyeing : This method of dyeing consists essentially of the following stages:

4.1 The polyester is thoroughly scoured as a preparatory step, a wetting agent being used to ensure complete removal of warp size, etc. This scouring is most suitably carried out in a beck.

4.2 The polyester is padded in a dispersion of an acetate color; the Latyl class of colors are very suitable. A thickening agent such as salt-free CMC (carboxymethyl cellulose, sodium salt) and an organic solvent such as Cellosolve to help spreading the dispersion on the fabric should also be present.

4.3 The polyester fabric is dried in a flue dryer at about 70 °C with good air circulation (steam-heated cylinders are unsatisfactory because they cause excessive marking off).

4.4 The fabric is passed through an oven at 175-200 °C, the time of passage being about one minute. The dyestuff which has been applied to the fabric in 4.2 and dried on the surface in 4.3, dissolves in and penetrates throughout the fabric in 4.4.

4.5 The fabric is given a good scour to remove traces of loose color and is then finished and dried normally.

2.6 Difficulties of polyester in processing and use of polyester textiles⁽²⁶⁾

Despite the many and generally acclaimed desirable properties of polyester fibers, many requirements of the finishers and consumers have not as yet been satisfied; the accomplishment if these will determine the research and development program in all stages from raw material to end-product for many years to come.

The ever-increasing tendency for using polyester fibers in widely different spheres of application places definite demands on certain variations of some of the typical characteristics of polyester fibers. Even if many of these characteristics were designated as advantages this is merely a relative assessment, since a property which may constitute a definite advantage for certain uses can be positively disadvantageous in other respects; moreover, these characteristics themselves are variable because they are also relative, i.e. they depend on external influences. (e.g. factors such as temperature, duration of action, the concentration of chemicals).

Since it is not possible to give a comprehensive description of the still existing difficulties in the processing of polyester filaments, the following are some of the characteristics which presented problems and were or still are difficult to solve.

2.6.1 Electrostatic charges

The occurrence of electrostatic charges in the processing of some fiber substances is generally known, although different causes for their origin will be found in the relevant literature. However, more recent investigations have ascertained that, particularly with hydrophobic materials with low electrical conductivity, the objectionable effects of static electricity (clinging to parts of the machine, spreading apart of polyfilaments) can reach such proportions that they seriously interfere with production or even bring it to a halt.

Polyester fibers emphasize the disadvantages of electrostatic charges in a special degree; this is based on two characteristics which constitute advantages in other

directions: low water sorption (advantage: rapid drying) and low electrical conductivity (advantage: good insulating power).

In order to obviate these difficulties, comprehensive investigations have been carried out with respect to the sites of maximal charging during textile finishing processes and precautions have been devised which can keep these charges within tolerable limits so as to ensure the undisturbed processing of the textile material. In this connection, those measures which promote dissipation of the charges by conducting them along the textile products and by dissipation into the surroundings are of special significance. The best way of preventing electrostatic charges is to apply preparations which have an antistatic effect.

2.6.2 Low moisture absorption

The low moisture sorption of polyester fibers is generally enumerated as one of its advantages and this is not without justification, since this property ensures very rapid drying of garments after washing, so long as the fabric structure does not contain many capillaries.

However, the strong hydrophobic character of polyester fibers frequently is a disadvantage. The low moisture sorption or absorbtivity of polyester textiles, however, gives rise to a further disadvantage which must be taken into account in the manufacture of garments: polyester fabrics impair or inhibit perspiration, since they do not absorb this and thus cannot conduct it towards the exterior where it can evaporate. This phenomenon is especially pronounced with pure, i.e. 100%, tight polyester fabrics. This disadvantage must and can be surmounted by the textile manufacturers namely by producing garments which are worn near to the body (underwear) in a very loose woven or knitted construction or, in the case of outer garments, by not using pure polyester yarn but polyester blended with other yams; this will satisfy the physiological requirements of normal body perspiration.

2.6.3 Dyeing difficulties

The main difficulties consisted, on the one hand, in discovering suitable dyestuffs and, on the other, in finding a satisfactory process with which to apply the dyestuffs to polyester fibers so as to ensure the necessary durability, light and wash fastness.

Even though many coloring difficulties which existed a few years ago have been surmounted and it is nowadays possible to produce dyeing or printing on polyester or polyester-blend fabrics in the various stages of manufacture which satisfies fastness requirements, a polyester fiber must still be regarded as one of the fibers which it is difficult to dye. The necessity to the manufacturer of polyester textiles for material and installation; they are thus, e.g., higher than those incurred by textile finishers of natural fibers. However, one consideration must be taken into account: dyeing processes for natural fibers have been developed in the course of centuries, whilst experience with dyeing of polyester fibers has accumulated only within the last 5-10 years. In view of the brief duration of this development, the achievements are very considerable because nowadays it is possible to carry out adequate dyeing of polyester-wool or polyester-cotton blends in a one-bath process. In the course of the vigorous development of our modern science and technology, new possibilities will be found to reduce the still relatively high expenditure involved in the dyeing of polyester textiles.

2.6.4 Wet crease behavior

A high degree of insensitiveness to creasing and the relatively good washing resistance can be singled out from among the advantages of polyester textiles. For instance, to wear a polyester suit in a downpour or to wade through water without the suit losing its pleats or trouser creases; moreover, no unintentional creases will be imparted. Apparel made from polyester will keep its perfect appearance after several washes without needing additional pressing.

Thus rigorous washing tests on tafetta made from continuous polyester filaments have shown that this fabric can suffer very considerable wet creasing; this depends on the temperature and composition of the wash liquor. It is mainly meant to point to the necessity for all users of synthetic fiber products to be provided with the appropriate washing instruction.

2.6.5 Pilling

One of the most unpleasant deficiencies which had not been predicted when first using synthetic fibers for textile purpose by which presented manufacturers of synthetic fibers and textile experts with problems and which is still not completely resolved, is 'pill' formation. 'Pilling' denotes formation of pills or small fiber balls, also called neps or slubs, which form on the textiles due to the migration of fiber ends from the fiber texture and which are particularly annoying with apparel textiles. They impair the appearance of garments so markedly that the wearer, for aesthetic reasons, ultimately dispenses with them, although there is plenty of wear still left in them. Fabrics made from polyamide blends exhibit more pronounced pill formation than other blended yarns.

2.7 Previous research works on an attempt to improve the wettability of polyester fibers

It is known that, because of their excellent physical properties, polyester fibers are recently utilized for a wide variety of purposes not only for manufacturing innerwears and outerwears but also for making household goods such as bed sheets and carpets. However, polyesters are disadvantageous in that they are hydrophobic and, when used in the form of apparel, they present only a limited sweat absorbing property and hence give a stuffy easily, and are readily charged with electricity so that they attract dust⁽²⁷⁾.

To eliminate these disadvantages, surface wettability of polyester leads to changes in surface performance particularly water absorbency and antistatic dissipation. Several methods including multicomponent fiber production, hydrolysis of polyester fibers, hydrophilic coating, and graft polymerization etc. have been studied.

2.7.1 Multicomponent fibers

Japanese Patent Laid-Open No. 51-136924⁽²⁸⁾ proposed a sheath-core type conjugated staple fiber with a hydrophilic polyester as the core component and a non-hydrophilic polyester as the sheath component. The hydrophilic polyester used was a polyalkylene glycol copolymer or a polyalkylene glycol copolymer mixed with sulphonic acid or acid phosphonic ester derivatives, and it was intended to increase enhancing water absorbability **for both ends** of the staple fiber. However, the present inventors found that even though the staple fiber was improved in water absorbability, it was not improved in moisture absorbability.

Japanese Patent Laid-Open No. 53-11116⁽²⁹⁾ proposed an antistatic conjugated fiber of sheath-core type with a specific polyether ester as the core component. However, the intended effect was to make the fiber antistatic, and since a polyester obtained by copolymerizing a polyalkylene glycol alone was used as the core

component, the physical properties (strength-elongation characteristic) of the fiber changed with the lapse of time disadvantageously. Furthermore, the polyether ester was remarkably colored and this impaired the quality of the final product obtained disadvantageously.

The research and development by Robert H Blackwell, Candler, N.C.⁽⁴⁾ who introduced a process for producing multicomponent fibers provides a dispersion of a particulate additive or chemical compound such as antistatic agent in a nonaqueous liquid carrier, forms a blend of a first thermoplastic polymer such as polyester fibers and the dispersion by injection the dispersion into an extruder which is part of a fiber extrusion apparatus and which extruder is extruding the first thermoplastic polymer. Then forming a blend of the additive in the first thermoplastic polymer. They provides a second thermoplastic polymer to the fiber extrusion apparatus, in the fiber extrusion apparatus, arranges the blend and the second thermoplastic polymer in a preselected, mutually separate relative arrangement, directs the arrangement of blend and the second thermoplastic polymer to two spinneret which is a part of a fiber the extrusion apparatus while maintaining the preselected, mutually separated relative arrangement. Extrudes the directed arrangement of the blend and the second molten polymer through the spinneret to form multicomponent fiber, and additives the multicomponent fibers.

Tanoke et al.⁽⁶⁾ introduced the conductive composite filament and process for producing the same. A highly oriented, undrawn, conductive, composite filament was provided. This filament was white or colorless and had antistatic properties durable over a long period when clothing utilizing the fiber were actually put on and washed. The filament was a sheath-core composite filament comprising a sheath of a fiber-forming thermplastic polymer (polyester) and a core of a composition comprising a conductive material which comprised a conductive metal oxide.

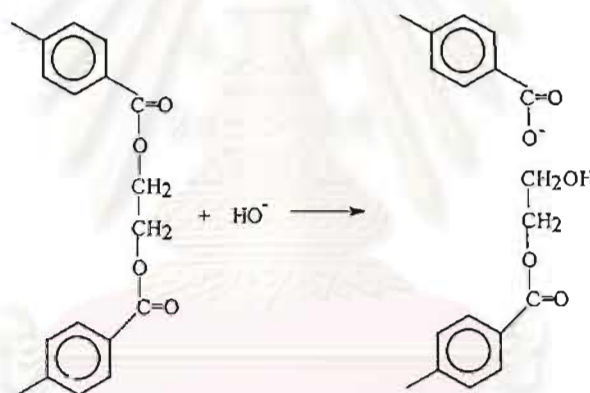
Reinehr et al.⁽⁸⁾ studied the process for producing cross-sectionally stable, hygroscopic fibers and filaments having a core-jacket structure. The objective of invention is to study a process for the production of hygroscopic filaments or fibers having a core-jacket structure and uniform round to oval cross-sectional profiles from hydrophobic, filament-forming synthetic polymers by a dry-spinning process which process comprised an addition of a substance to the spinning solvent which

- (a) has higher boiling point than the spinning solvent used,
 - (b) is readily miscible with the spinning solvent and with water,
 - (c) is a non-solvent for the polymer to be spun,
- and an addition of another substance which
- (a) is soluble in the non-solvent for the polymer to be spun,
 - (b) is soluble in the solvent for the polymer
 - (c) remains dissolved in the non-solvent for the polymer during solidification of the filaments,
 - (d) is insoluble in water, and
 - (e) does not evaporate to any significant extent during the spinning process.

Reinnehr and Frank⁽⁹⁾ investigated the process for the production of hydrophilic filaments and fibers by the dry jet wet-spinning method. The invention related to a process for the production of hydrophilic filaments or fibers having a sheath/core structure, a porosity of at least 10% and a water retention capacity of at least 10% and having a fiber swelling factor which was lower than the water retention capacity. The process was carried out by spinning polymer solution that can be formed into fiber by the dry jet wet-spinning method wherein immediately on leaving the spinning jet and prior to coagulation in the precipitation bath. The filaments or fibers were contacted with steam or with the vapor of another liquid which coagulated the filaments.

2.7.2 Hydrolysis treatment of polyester fibers

Du Pont Co., 1958 et al.⁽²⁸⁾ proposed the surface hydrolysis described as a method to increase the hydrophilicity of polyester fabric. Through the action of a caustic solution at elevated temperatures, portions of the polyester molecules are cleaved to produce terminal hydroxyl and carboxylate groups, as depicted in Scheme 2.7⁽³⁰⁾. The reaction can be accelerated by the addition of quaternary ammonium salts to the bath. Even if further hydrolysis were to occur in laundering, the new groups generated would be identical with those initially present, so no net change would result. As was mentioned earlier, hydrolyzed polyester provides better adhesion for a variety of topical finishes.



Scheme 2.7 Caustic hydrolysis of poly(ethylene terephthalate)⁽²⁸⁾

Hsieh YL, Cram LA⁽¹⁰⁾ studied the enzymatic hydrolysis to improve wetting and absorbency of polyester fabric. The ability of six hydrolyzing enzymes to improve the hydrophilicity of several polyester fabrics was studied. Five of the six lipases improved the water wetting and absorbent properties of regular polyester fabrics more than alkaline hydrolysis under optimal conditions (3N NaOH at 55 °C for 2 hours). Compared to aqueous hydrolysis, the enzyme reactions were highly effective under

more moderate conditions, which were relatively low concentration (0.01 g/l), shorter reaction time (10 minutes), at ambient temperature (25 °C), and no buffer. Improved water wettability is accompanied by full strength and mass from alkaline hydrolysis. The wetting and absorbent properties of sulfonated polyester and microdenier polyester fabrics were also improved by lipases.

Hsieh YL, Miller A, Thompson J⁽¹¹⁾ proposed the basic hydrolysis by studying the wetting, pore structure, and liquid retention of hydrolyzed polyester fabric. This study investigated the contributions of surface wetting and pore structure to liquid retention of fibrous materials using regular and microdenier poly(ethylene terephthalate) (PET) fabrics with aqueous sodium hydroxide. Increasing levels of weight loss, porosity, and thickness reduction were observed with increasing hydrolysis temperatures (3N NaOH for 2 hours). The effects of hydrolysis temperature on wetting and pore structure were different for the two PET fabrics. Varying lengths of hydrolysis time (3N NaOH at 55 °C) also impose different effects on wetting and the pore structure of the microdenier fabric. With considerably varied wetting contact angles and pore structure, water retention of all PET fabrics was inversely related to water wetting contact angles. Data on hydrolysis of regular and microdenier PET fabrics showed that improved water wettability played a primary role in increasing water retention of these hydrophobic fabrics. Pore size distribution and pore connectivities can be limiting factors in liquid retention of hydrolyzed PET fabrics with modified wetting properties and porosity.

2.7.3 Coating antistatic agent

Van Paesschen et al.⁽¹²⁾ studied the adhesion of hydrophilic layers on polyester filament. The adhesion of hydrophilic layers on a dimensionally stable polyester film support was improved by applying after longitudinal stretching of the polyester film a single adhesive layer thereon. The thus covered polyester film was stretched in

transverse direction and heat-set at 180°-220°C. The adhesive layer comprised 30 to 80% by weight of a chlorine-containing copolymer, 5 to 30% by weight of a gelatin, 5 to 40% by weight of a plasticizer for the gelatin and 0 to 30% by weight of a metal-complexing antistatic agent. The polyester film may be a film of poly(ethylene terephthalate) and the hydrophilic layer applied to the single adhesive layer may be a light-sensitive gelatin silver halide emulsion layer.

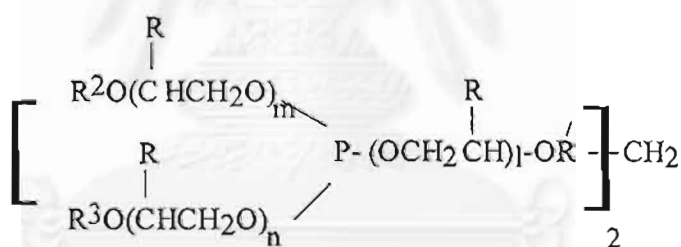
Van Paesschen et al.⁽¹³⁾ proposed the process of applying antistatic coating compositions to polyester film. In this study, a process was provided for adhering an antistatic layer to a dimensionally stable polyester film support, e.g. a film of poly(ethylene terephthalate). An unstretched or only monoaxially stretched polyester film is applied an antistatic layer from an aqueous coating composition. After drying of the antistatic layer, it was stretched biaxially or in a direction perpendicular to the first stretching operation, together with the polyester film support and thereafter the polyester film was heat-set. The aqueous coating composition comprises 30 to 80% by weight of an electroconductive product, 10 to 40% by weight of a stretch-improving agent and 10 to 40% by weight of an inert filler material. The polyester film support may be provided on its opposite side with a subbing layer and one or more light-sensitive gelatin silver halide emulsion layers.

Lark⁽²⁹⁾ studied the process for warp sizing and hydrophilic finishing of polyester filaments and fabric which comprised (1) coating, polyester with the water-soluble polyester of a dihydric alcohol having two to six carbon atoms and an aromatic polycarboxylic acid compound having three, four or five carboxyl groups and (2) drying, polyester onto filament or (3) curing, polyester fabric. The field of this invention had two aspects. The first aspect related to a filament coating process to coat polyester filaments so as to protect the warp yarn from abrasive forces during weaving by means of a warp size. The second aspect related to a fabric coating process, to

modify the surface properties of polyester fibers and fabrics so as to improve their hydrophilic characteristics with consequent improvement in antisoiling and antistatic properties under standard laundering conditions. The general objective of this invention was to provide a simple process of warp sizing 100% polyester filament. Another objective was to obtain these improved properties with minimum modification of the hand of the material. Another objective is to provide a process which utilized the treating additive at a low level of application, thus obtaining an economic; efficient rate of use of the treating additive.

Caldwell et al.⁽²⁹⁾ proposed a textile hydrophilic treatment process which functioned by applying a polymeric coating. The polymeric coating adhered to the fiber by cross-linking a high molecular coating which provided a structured composition with an insoluble exterior that had the desired hydrophilic properties under conditions of wearing and laundering. The process described in this patent provided a hydrophilic insoluble coating having antistatic and antisoiling properties by coating the fabric with a soluble or solutions containing a polyhydric alcohol and addition polymers of α , β - ethylenically - unsaturated acids. Under the proper conditions, the polyhydric alcohol reacted with the aliphatic polyacid to partially cross-link the polymer to provide an external coating of the fiber. The patentee stated that ester linkages were formed to provide a partially cross-linked, flexible polymeric material which functioned very much as an ion exchange resin. The polymeric polybasic acid was cross-linked to the extent that it is no longer soluble but some of the acidic ions were available to furnish ions for conducting static charges. The esterification was necessary to provide an insoluble coating with durability to standard laundering conditions. The patentee stated that the hand of the fabric was affected by the amount of the polymeric additive applied so a minimum amount consistent with effective surface characteristics was desirable.

Chimura et al.⁽³⁰⁾ studied a durably antistatic polyester comprising a poly(ethylene terephthalate)-based polyester and an antistatic agent including a phosphorous acid triester derivative therein containing a polyalkylene oxide chain in the molecule. This invention was attained as a result of the studies made in an attempt to obtain antistatic agents which eliminated the disadvantage of the conventional ones, especially polyalkylene oxide type compounds, and now provided a polyester composition which contained an antistatic agent having no adverse effects on the operation of molding the polyester composition and, further, allowed polyester articles molded therefrom to have a durable antistatic property while they retained the original, satisfactory physical and chemical properties of the polyester base. The polyester compositions of this invention thus comprise a polyester wherein at least 80 mol % of the component units was ethylene terephthalate, with 0.1 to 10 % by weight of an antistatic compound of the general formula.



Wherein R is hydrogen or methyl; R' is phenylene with or without hydrocarbon radical substituents; R² and R³ are each C₁₋₁₈ alkyl, or phenyl with or without hydrocarbon radical substituents, and l, m and n are each an integer of from 1 to 200.

2.7.4 Grafting method

Grafting technique is the technique that introduces different polymer onto any polymeric substrate to achieve additional properties.

Sacak M, Oflaz F⁽¹⁴⁾ studied benzoyl-peroxide-initiated graft-copolymerization of poly(ethylene terephthalate) fibers with acrylic acid. The grafting of acrylic acid

onto poly(ethylene terephthalate) fibers subjected to no-swelling treatment using benzoyl peroxide was investigated. The temperature was found to increase the graft yield. The graft yield increased up to a benzoyl peroxide concentration of 4.0×10^{-3} M and slightly decreased at higher initiator concentrations. The effect of solvents such as dimethylformamide, dimethylsulfoxide, pyridine, and some alcohols upon the grafting were examined by carrying out the graft copolymerization at various water/solvent ratios. Pyridine was found to inhibit the grafting totally. The properties of the grafted fibers such as density, diameter, dyeability, and moisture regain were also investigated. It was concluded due to the observations made in these properties that the grafting took place mainly in the subsurface regions of the fibers and a diffusion barrier occurred after the grafting value of 8-9%. The overall activation energy for grafting was calculated to be 9.9 kcal/mol.

Buchenska J⁽¹⁵⁾ proposed the modification of polyester fibers by grafting with poly(acrylic acid). The grafting of acrylic acid on PET using benzoyl peroxide was investigated. The influence of the main parameters of grafting, the effect of additives on the degree of grafting, and the amount of homopolymer formed during the process were determined. Furthermore, the values of apparent activation energy was calculated. Also, the influence of the degree of grafting on the moisture sorption and swelling of modified fibers were determined. By an additional treatment of the grafted fibers with antibiotics, it was possible to provide the fibers with antibacterial properties.

Meral Karakisla, Mehmet Sacak⁽¹⁶⁾ studied the grafting of ethyl acrylate onto monofilament polyester fibers using benzoyl peroxide. Ethyl acrylate was grafted onto monofilament poly(ethylene terephthalate) fibers using benzoyl peroxide as a chemical initiator. Breaking tenacity and densities of grafted fibers decreased while breaking elongation increased with the graft yield. Scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting.

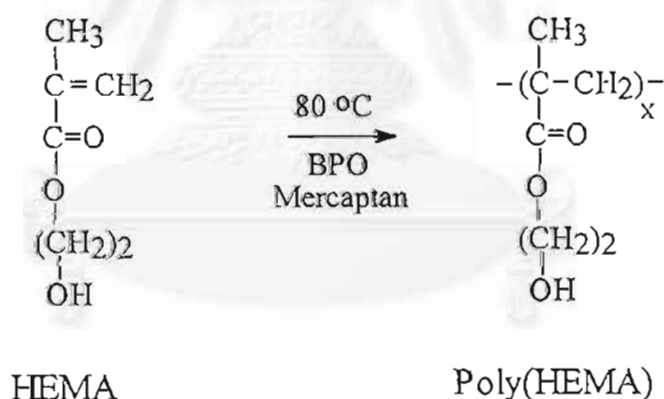
Sacak M, Bastug N, Talu M⁽¹⁷⁾ studied azobisisobutyronitrile-initiated graftcopolymerization of methylmethacrylate onto poly(ethylene-terephthalate) fibers. The study was reported that an increase in temperature and monomer concentration were found to increase the graft yield. The graft yield increased up to an initiator concentration of 0.90×10^{-2} mol/L and decreased at higher initiator concentrations. The fiber densities decreased, and fiber diameters and intrinsic viscosities increased with increasing graft yield. Moisture regain values showed a slight increase with the grafting. Fiber orientation decreased the graft yield to an important extent. The overall activation energy for grafting was calculated to be 11.9 kcal/mol.

Mehmet Sacak and Meltem Celik⁽¹⁸⁾ studied the grafting of acrylamide onto poly(ethylene terephthalate) fibers using hydrogen peroxide as the redox initiator was investigated. Benzyl alcohol was found to be the favorite medium for this grafting. Maximum graft yield (7.6%) was reached at 95°C; the graft yield decreased at higher temperatures, and finally was inhibited at 120°C. The effect of monomer and initiator concentrations on grafting was also studied.

2.8 Concept of synthesis of hydrophilic-hydrophobic copolymer to use as finishing agent for polyester fabric

In this experiment, the idea on how to improve surface performance of polyester fabric by coating application of the synthesized copolymer having hydrophilic/hydrophobic moieties was explored. The main purpose of this work is to develop simple as well as practicable technique of polyester surface modification, when compared to sophisticated process of multicomponent fibers production and graft polymerization.

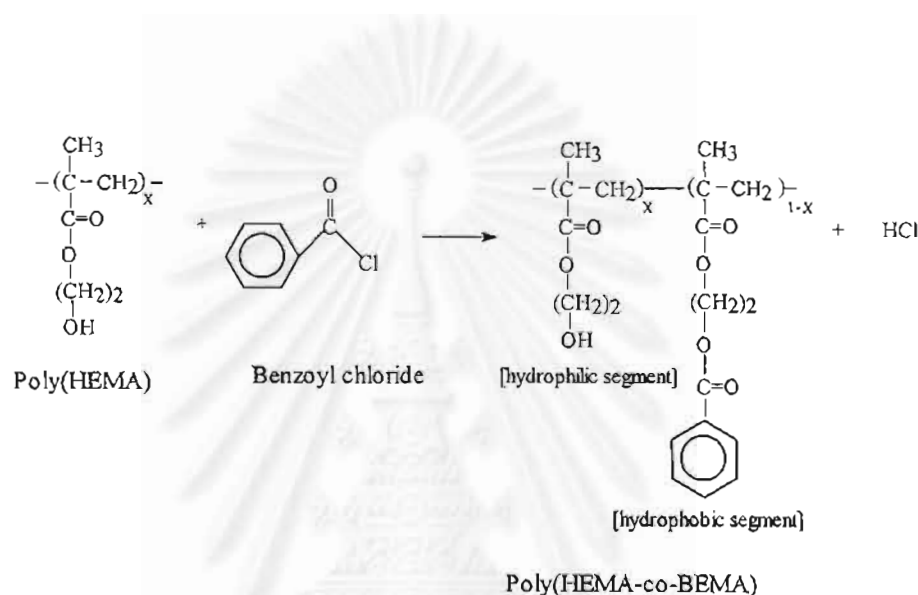
Firstly, poly(hydroxyethylmethacrylate), poly(HEMA), the hydrophilic homopolymer was synthesized by radical polymerization of HEMA monomer using benzoyl peroxide as an initiator. Lauryl mercaptan was employed as chain transferring agent. The polymerization will be carried out in ethanol medium. The polymerization of HEMA can be schematically shown in Scheme 2.8.



Scheme 2.8 The synthesis of poly(HEMA)

This polymer is hydrophilic, since it contains pendant hydroxyl groups so that its attachment ability onto polyester surface is weak. This type of polymer is water insoluble due to strong hydrogen bonding interaction between hydroxyl side groups. In order to make the poly(HEMA) suitable for modifying polyester's surface, the functionalization of poly(HEMA) by incorporation of hydrophobic segment was

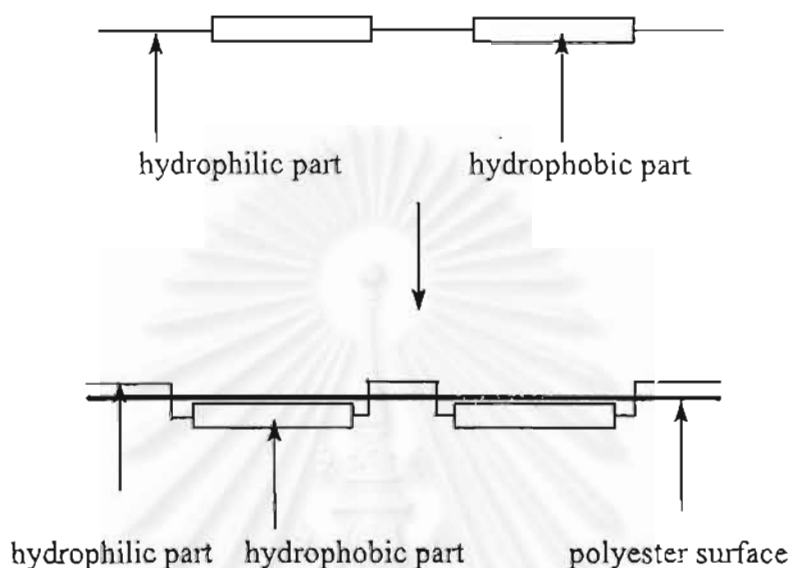
carried-out to partially reduce hydrogen bonding with benzoyl chloride, hence rendering the modified poly(HEMA) to suspend in water. The functionalized poly(HEMA) so called poly(HEMA-co-BEMA) can penetrate partially into polyester surface by anchoring the hydrophobic segment inside fiber surface. It is expected that permanent wettability modification of polyester could be achieved by using solvent free application method. The functionalization reaction may be written in Scheme 2.9.



Scheme 2.9 The functionalization reaction of poly(HEMA)

The prepared poly(HEMA-co-BEMA) will be further employed as the finishing agent for polyester fabric. This finishing agent can be called water-based finish. The application can be carried out using exhaust dyeing machine. It is anticipated that during treatment at temperatures higher than T_g of polyester, the polymer chains open-up and allow hydrophobic part of the copolymer to penetrate fiber surface. The hydrophilic part which differs from the polyester in terms of hydrophobicity still attaches firmly onto the fiber surface. By anchoring the hydrophobic segment inside the fiber, it is believed that the copolymer can be adhered firmly onto the fiber surface, resulting in imparting the permanent hydrophilic property

to the polyester fiber surface. Scheme 2.10 illustrates the attachment mechanism of poly(HEMA-co-BEMA).



Scheme 2.10 Attachment of poly(HEMA-co-BEMA) onto polyester surface.

The penetration of hydrophobic segment into polyester surface occurred during high temperature treatment. It is believed that the hydrophobic part could be absorbed by polyester due to hydrophobic attraction, hence leaving hydrophilic segment onto fiber surface. As a result, surface performance properties of treated polyester would be notably enhanced. After treatment the surface modification polyester fabric was subjected to evaluation of moisture regain, percent add on of modifying agent onto polyester fabric, wettability, surface analysis, and heating fastness of modified dyed polyester fabric.

CHAPTER III

Experimental

3.1 Materials and chemicals

- Polyester fabric from Teijin Polyester Company.
- All chemicals used throughout this work were reagent grade.

Table 3.1 Chemicals used in this project.

Chemicals	Formula	Company
2-hydroxyethylmethacrylate	$C_6H_{10}O_3$	Siam Chemical Industry
Tetrahydrofuran	C_4H_8O	Carlo Erba
N,N – dimethylformamide	$HCON(CH_3)_2$	Carlo Erba
Toluene-4-sulphonic acid	$CH_3C_6H_4SO_3H.H_2O$	Fluka AG
Benzene	C_6H_6	J.T. Baker
Benzoyl peroxide	$C_{14}H_{10}O_4$	Fluka AG
Benzoyl chloride	C_6H_5COCl	Carlo Erba
Lauryl mercaptan	$CH_3(CH_2)_{11}SH$	Fluka AG
Ethyl alcohol	CH_3CH_2OH	P.P.M. Chemical
Methyl alcohol	CH_3OH	P.P.M. Chemical
Isopropyl alcohol	$(CH_3)_2CHOH$	BPH Laboratory
Pyridine	$N(CH)_4CH$	Carlo Erba
Acetone	CH_3COCH_3	Bank Trading
Sulfuric acid	H_2SO_4	BPH Laboratory
Sodium Hydroxide Pellet	$NaOH$	J.T. Baker

Dyes used in this experiment.

Disperse dye, Sumikaron Red E - RDD(A)

Basic dye, Maxilon Red GRL 200%

3.2 Equipment

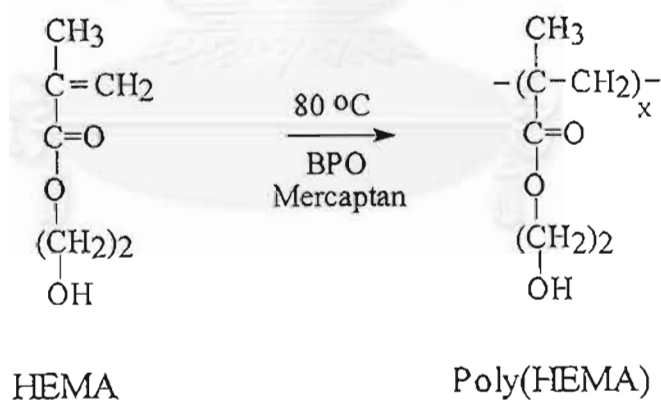
1. Electrical analytical balance, Mettler AB204
2. Rotary dyeing machine & steel pots, Ahiba AG CH-4127 (Ahiba Polymat®)
3. Magnetic stirrer, Framo-Geratetechnik M21/1
4. Fourier-Transform Infrared spectrometer, Omnic Nicolet Impact 400D
5. Nuclear Magnetic Resonance spectrometer, JEOL JNM-A500
6. Macbeth reflectance spectrophotometer, Color-eye 7000
7. Scanning electron microscopy (SEM), Philips XL30CP
8. Rotary vacuum evaporator, Tokyo Rikakikai Co., Ltd.
9. Hot plate, Framo-Geratetechnik M21/1
10. Desiccator, SCHOTT GL32
11. Heating mantles, Electromantle MA
12. Thermal Tester, Daiei Kagakuseiki Seisakusho Co., Ltd No. A-2580
13. Glasswares
 - four-necked round bottom flasks
 - beakers
 - pipettes
 - burettes
 - condensers
 - volumetric flasks
 - separatory funnels
 - erlenmeyer flasks
 - evaporating dishes
 - cylinders
 - stirring rod

3.3 Synthesis of poly(2-hydroxyethylmethacrylate), poly(HEMA)

Four-necked round bottom flask was placed on a heating mantle equipped with a condenser. 10 g. (0.077 mole) of 2-hydroxyethylmethacrylate and 300 ml. of ethyl alcohol were added and stirred well to dissolve before adding 6.18 g. (0.026 mole) of benzoyl peroxide. Heat was supplied through the heating mantles and temperature was raised from room temperature to 80 °C. The reaction was continued for 30 minutes. After that lauryl mercaptan 0.33 g. (0.002 mole) was added. The reaction was continued at this temperature for 24 hours. The flask was removed and cooled down to room temperature.

The polymer solution was poured into benzene and stirred well to precipitate the polymer product. Solvent was poured out and the polymer was left to dry in open air for one week. The characterization was carried out using FT-IR and ¹H-NMR spectroscopy.

The polymerization reaction may be written as follow:



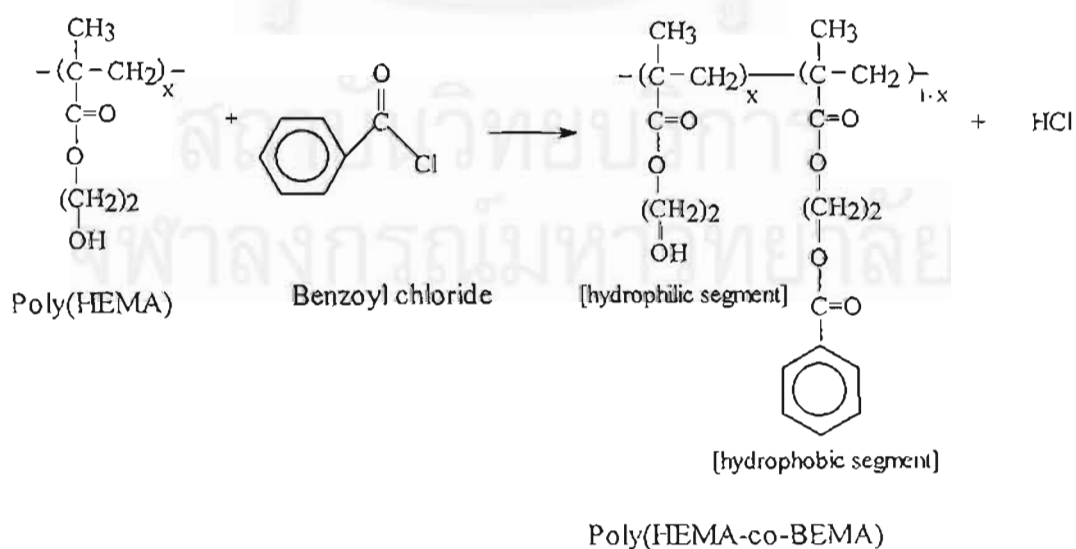
Scheme 3.1 The polymerization reaction of 2-hydroxyethylmethacrylate

3.4 Functionalization of the poly(HEMA) with benzoyl chloride

50 g. of poly(HEMA) obtained from Section 3.3 was dissolved in 200 ml. of N,N - dimethylformamide containing in four-necked round bottom flask. Various amounts of benzoyl chloride were added to the above solution and stirred well. The temperature was raised to 100 °C and maintained at this temperature for 30 minutes. Then sulfuric acid and toluene sulfonic acid (1 ml. each) were added to catalyze the reaction. Pyridine (1 ml.) was added to ensure the complete reaction. This reaction copolymer was expected to give of poly(hydroxyethylmethacrylate-co-benzoylethyl methacrylate), poly(HEMA-co-BEMA). The reaction was continued 30 minutes. The flask was removed and cooled down to room temperature.

Precipitation of the copolymer was followed using the same method as described in Section 3.3.

In this experiment, poly(HEMA-co-BEMA) with varying degree of benzoyl residue at 2.5%, 5%, and 7.5% of BEMA content in Series 1 and 10%, 20%, 30%, 40% and 50% of BEMA content in Series 2 were prepared respectively. The characterization of poly(HEMA-co-BEMA) were carried-out using FT-IR and ¹H-NMR spectroscopy and the reaction of poly(HEMA) with benzoyl chloride may be written as follows.



Scheme 3.2 The functionalization of poly(HEMA) with benzoyl chloride

3.5 FT-IR Analysis

Infrared spectroscopy is the most widely used technique for identification of organic compounds. Principally, infrared spectroscopy is based on the interaction of infrared radiation with molecular dipole moment in the sample. When a sample compound is placed in the IR beam, it absorbs particular frequencies.

For the Fourier Transform Infrared Spectrometer (Figure 3.1), infrared light from suitable source (electrical heated to near 1800 °C) passes through a scanning Michelson interferometer and Fourier Transformation gives a plot of intensity versus frequency. The interferometer splits a radiation beam into two paths and recombines them so that the intensity variation of the exit beam can be measured by a detector as a function of path difference. The computer controls optical components, collects and stores data, performs computations on data, records the data and displays spectra.

In this experiment, identification of poly(HEMA) and poly(HEMA-co-BEMA) by FT-IR technique was carried out using the transmission technique to obtain IR spectra. The method of sample preparation used in this experiment was performed by dissolving the sample in a methyl alcohol solvent. Solid films of sample could be achieved by casting polymer solution onto KBr plates and then allowing solvent (methyl alcohol) to evaporate, if necessary, hair drier was used to quicken evaporation of solvent. The infrared spectra of polymer films were recorded by Omnic Nicolet FT-IR spectrometer. The following parameters were employed; scan range 4000-400 cm^{-1} , scan number : 30, and resolution 4 cm^{-1} . All the spectra were transferred to the computer for further analysis and plotting by Omnic Software.

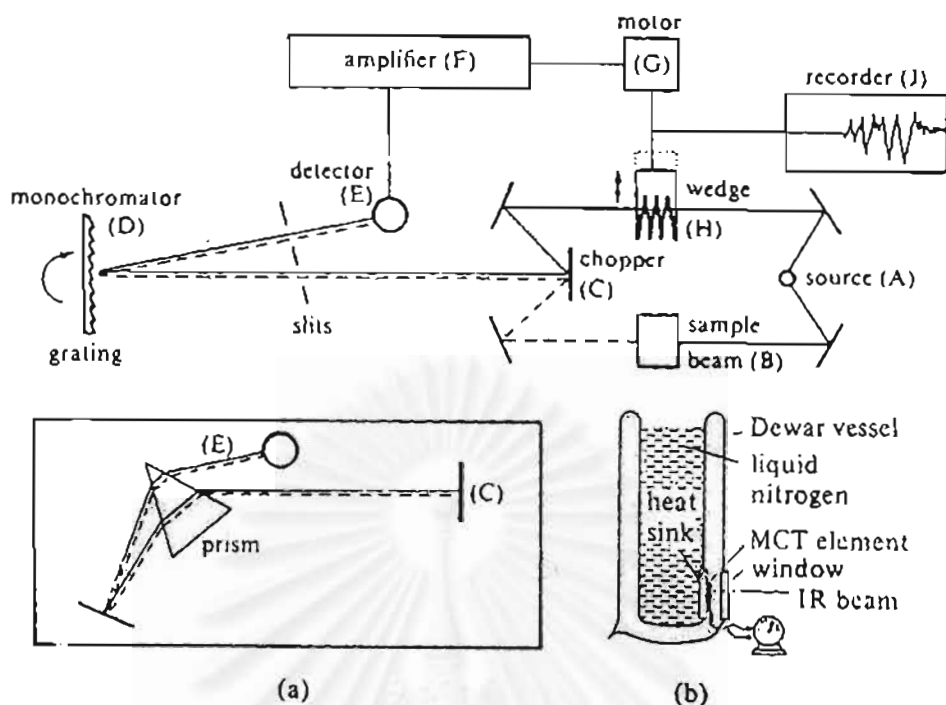


Figure 3.1 Schematic diagram of Fourier Transform Infrared Spectroscopy

3.6 NMR Analysis

Nuclear Magnetic Resonance Spectroscopy (NMR) (Figure 3.2) and is the form of spectroscopy concerning with radio-frequency induced transition between magnetic energy level of atomic nuclei. NMR is an important method for material characterization and for the study of polymer structure-property relationships. NMR signals can be assigned to specific atoms along the polymer backbone and side chains.

The properties of the NMR signals depend on the magnetic environment of the NMR active nuclei, and the local field that they experience.

NMR equipment comprising a magnet, radio frequency oscillator, sample holder and a detector that is capable of producing an electrical signal suitable for display on a recorder or an oscilloscope, or which is suitable for input to a computer.

NMR spectra are absorption spectra which are the results of sample absorbing electromagnetic radiation at radio frequency (typically a few hundreds MHz. - 10^8 Hz) region, the energy absorbed by nuclei.

Principal of the instrument is that a magnetic field, H_0 is being regulated to generate a magnetic field. This H_0 induces the rotation of dipoles at a specific Larmor frequency for each spinning nucleus and external oscillating magnetic signal, H_1 is equal to the Larmor frequency, resonance can occur. The instrument detects the absorption frequency of the sample.

For identification of the chemical structure of poly(HEMA) and poly(HEMA-co-BEMA) with various BEMA contents in this experiment, the NMR sample tube containing a mixture of sample and dimethyl sulfoxide (DMSO-D_6) solvent was placed in FT-NMR spectrometer (JEOL JNM-A500). ^1H -NMR spectra were measured at the radio frequency of 500 MHz.

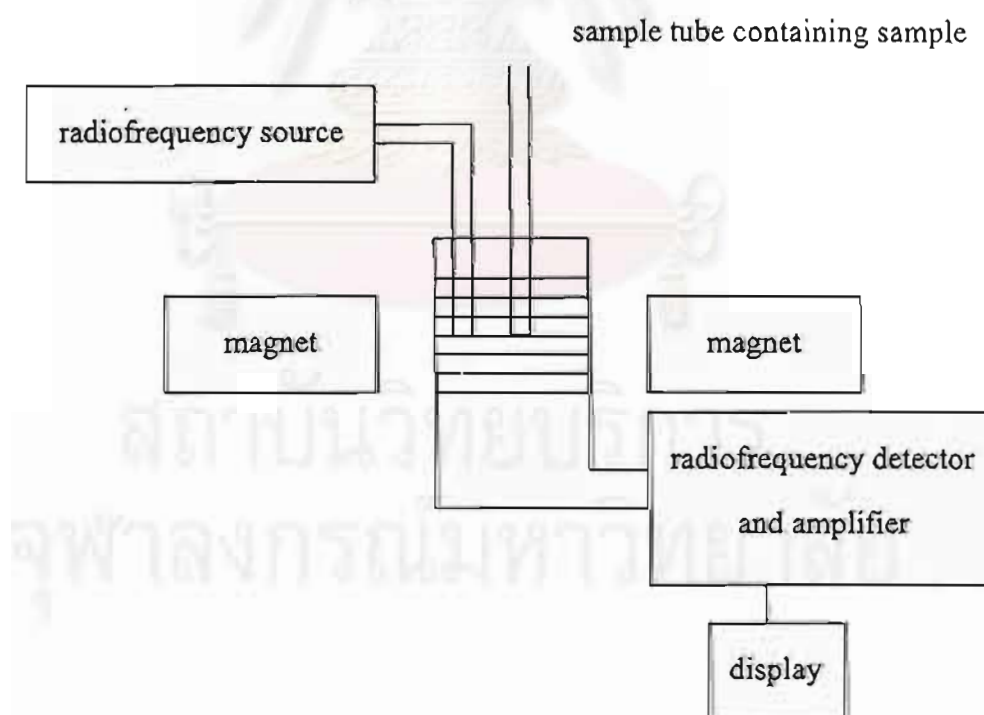


Figure 3.2 Schematic diagram of Nuclear Magnetic Resonance Spectroscopy

3.7 Application of synthesized poly(HEMA-co-BEMA) on polyester fabric

The obtained copolymers were applied onto polyester fabric as modifying agent or finishing agent to improve wettability of polyester carried out by exhaustion method. Application profile was shown on Diagram 3.1 Following factors on the properties of modified polyester fabric were investigated.

3.7.1 Effect of the degree of hydrophobic content (BEMA pendant group)

In this experiment, poly(HEMA-co-BEMA) with varying degree of BEMA content; 2.5%, 5%, and 7.5% in Series 1 and 10%, 20%, 30%, 40%, and 50% in Series 2 were prepared respectively from section 3.4 were used for polyester fabric to study effect of the degree of BEMA content. Modifying x g/l of poly(HEMA-co-BEMA) solution was prepared and polyester fabric was then added into dye tube containing prepared solution.

3.7.2 Effect of finishing agent concentration

Undyed polyester fabric was cut into rectangular shape with 4 cm wide by 20 cm long. Poly(HEMA-co-BEMA)'s concentration of 25%, 50%, 75%, and 100% on weight of fabric (o.w.f.) were prepared. The polyester fabrics were treated in the prepared solutions at the liquor ratio of 1:50. The treatment was carried-out using the Ahiba Polymat[®] machine (Figure 3.3). The treatment procedure was followed according to the Diagram 3.1. After running at 130 °C for 60 minutes, the dyeing vessels were removed and rinsed in tap water. One piece of treated fabrics was refluxed in methyl alcohol for 6 hours to remove some of poly(HEMA-co-BEMA) which might just deposit on the fiber surface. After extraction, treated polyester fabrics were taken-out and rinsed in running tap water and followed by drying in open air. Then, the surface modified fabrics were subjected to the evaluation of surface performance. Such as wettability, moisture regain and durable property.



Figure 3.3 The Ahiba Polymat® machine

The application method was followed according to the following application profile.

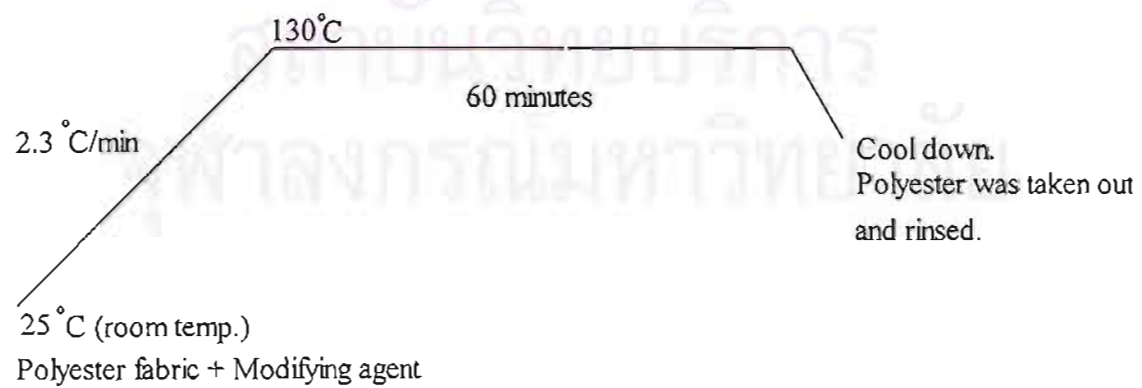


Diagram 3.1 A single-step exhaust treatment of polyester fabric

3.8 Evaluation of properties of treated polyester fabrics

3.8.1 Determination of Percent add on of polyester fabric

Weight of fabric before treatment with exhaustion method was compared with the weight of fabric after treating with exhaustion method and drying for 1 day. The percent add on of the fabric can be calculated from :

$$\% \text{ Add on of fabric} = \frac{(W_2 - W_1)}{W_1} \times 100$$

W_1 = weight of fabric before treat by exhaustion method

W_2 = weight of fabric after treat by exhaustion method and dried for 1 day

3.8.2 Determination of moisture regain

Moisture regain is the percent weight of moisture based on the oven-dry weight of the material. The regain of the material is considered to be the amount of moisture at the time test⁽³¹⁾.

$$\text{Percent of moisture regain} = \frac{\text{Original weight} - \text{Dry weight}}{\text{Dry weight}} \times 100$$

3.9 Evaluation of wettability of treated polyester fabric

In order to assess the efficiency of poly(HEMA-co-BEMA) as the wetness modifier of the polyester fabric, two standard test methods, AATCC test method and Du Pont water drop test, were adopted.

3.9.1 AATCC test method ⁽³²⁾

All tests were conducted in standard atmosphere. The fabric sample was mounted in the embroidery hoop so that the surface was free of wrinkles, but without distorting the structure of the material. The hoop was placed about 1.0 cm below the tip of the burette, and one drop of distilled water was allowed to fall on the surface of fabric. The burette containing distilled water was adjusted so that it delivered one drop of water approximately every seconds. The time was measured for the surface of the liquid to lose its specular reflectance by means of a stop watch. The point was determined by having the hoop between the observer and a source of light at such an angle that the specular reflectance of the light from the surface of the flattened drop can be plainly seen. As the drop was gradually absorbed, the area of this tiny mirror diminished and finally vanished entirely, leaving only a dull wet spot. At this instant the watch was stopped and elapsed time was recorded.

3.9.2 Water drop test by Du Pont ⁽³³⁾

This test determines a finished fabric's resistance to wetting by aqueous liquids. Drops of water-alcohol mixtures of varying surface tensions are placed on the fabric and the extend of surface wetting is determined visually.

This test provides a rough index of aqueous stain resistance. Generally, the higher the water repellency rating, the better the finished fabric's resistance to staining by water-based substances. The composition of standard test liquids is shown in Table 3.2.

Table 3.2 The composition of standard test liquids

Rating	Composition volume %		Surface tension at 25 °C Dyne / cm
	Isopropyl alcohol	Distilled water	
1	2	98	59
2	5	95	50
3	10	90	42
4	20	80	33
5	30	70	27.5
6	40	60	25.4

Procedure

Placed fabric face up on white blotting paper on a flat horizontal surface. Began with test liquid No.1 carefully placed drop approximately 5 mm. in diameter or 0.05 ml. in volume on the test fabric in three location. Step 2, observed the drop for 10 sec. from an approximate 45 °C angle. If at least two of three was not penetrated or wet the fabric and was not show wicking around the drops, place drop of test liquid No.2 on an adjacent site, and repeated step 2. Continued the procedure until at least two of the three drop were wet or show wicking into the fabric within 10 sec. The fabric water repellency rating is the highest number liquid for which at least two of the three drops was not wet or wick into the fabric.

3.10 Color drop's spreading test

Water spreading on polyester fabric in the indication of wettability of the test sample. The solution of 2% w/v basic dye was prepared and spotted on the modified fabric. The spreading of color drop was observed and photographically illustrated.

3.11 Surface analysis of modified polyester fabric by Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) (Figure 3.4) forms an image by scanning probing across the specimen, the probe is focused electron beam. The probe interacts with a thin surface layer of the specimen, a few micrometers thick at most. The detected signal used to form the TV-type image in the number of low energy secondary electrons emitted from the sample surface⁽³⁴⁾.

Table 3.3 Properties of SEM

Lateral Resolution	4 nm.
Magnification	20-10 ⁵
Can observe	Surfaces
Specimen environment	High vacuum (30 torr in H PSEM)
Radiation damage	Rarely serious
Specimen preparation	Easy
Chemical analysis	By X-ray

In this experiment, sample of modified polyester fabric was put on the stub attached by carbon adhesive, then pure gold was sprayed on the sample for 15 seconds, specimen was taken into JSM-5410 scanning microscope instrument, and was scanned picture until the image was clearly seen by using 750 magnification. The resulted picture was printed out and recorded.

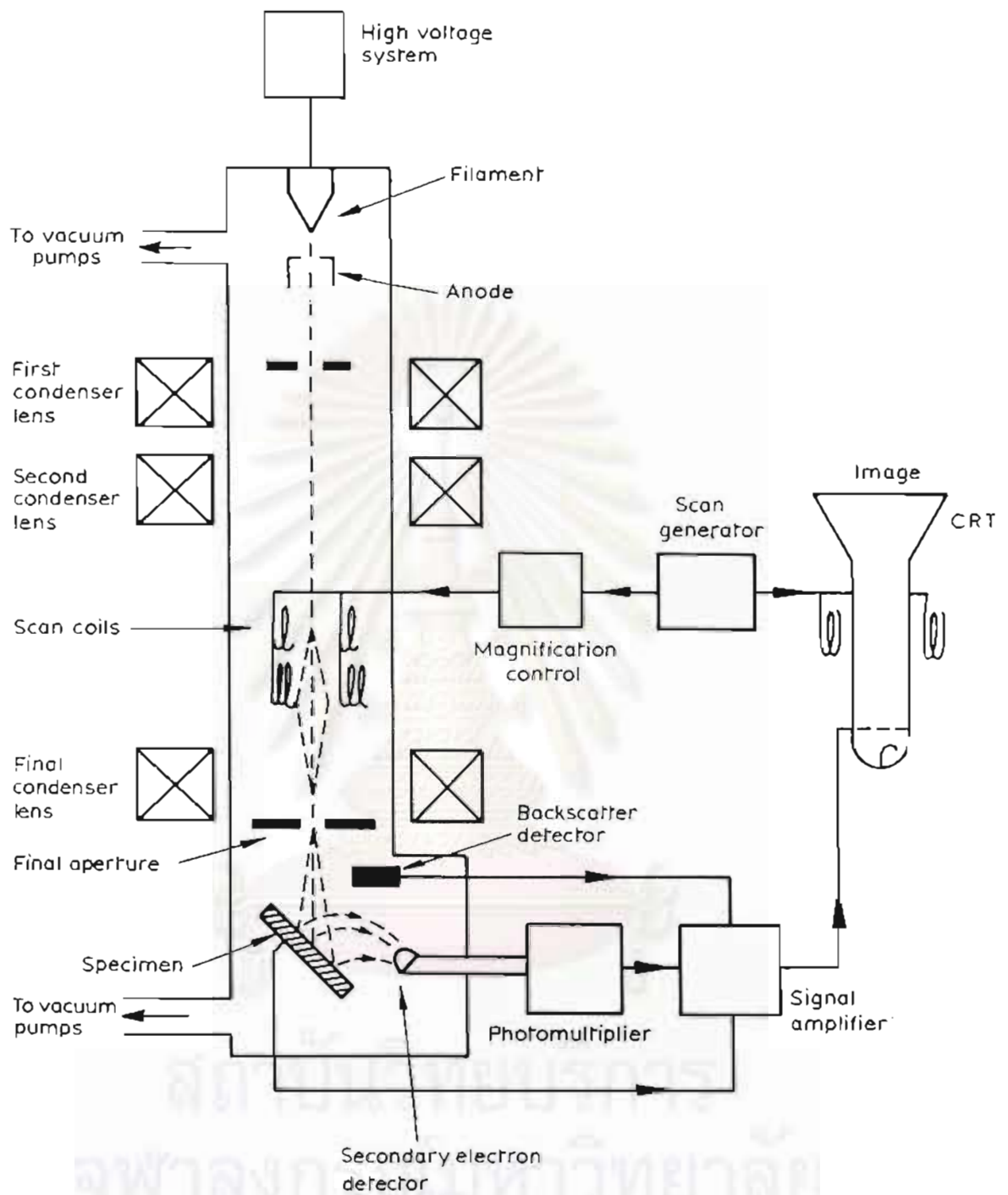


Figure 3.4 Schematic diagram of a scanning electron microscope. Two pairs of deflection coils are shown in the SEM column. The double deflection allows the scanning beam to pass through the final aperture. Four pairs are actual used, for double deflection in the x- and y-directions

3.12 The effect of poly(HEMA-co-BEMA) on improving fastness to heat of dyed polyester fabric

Pieces of polyester size 4 cm. by 20 cm. were weighed and numbered. Prepared fabrics were dyed with 2% owf disperse dye (Sumikaron Red E-RDD[a]) in the Ahiba Polymat® dyeing machine.

Each of dye vessel containing fabrics were weighed and the dyeing was carried out at liquor ratio 1:20. The dyeing temperature was raised to 130 °C at the rate of 2.3 °C/min and the dyeing was continued for 60 minutes, then cooled down. The dyed fabrics were removed from dyeing vessels, rinsed in tap water before soaping with nonionic surfactant at 100 °C , 15 minutes. Dyeing profile is given in Diagram 3.2.

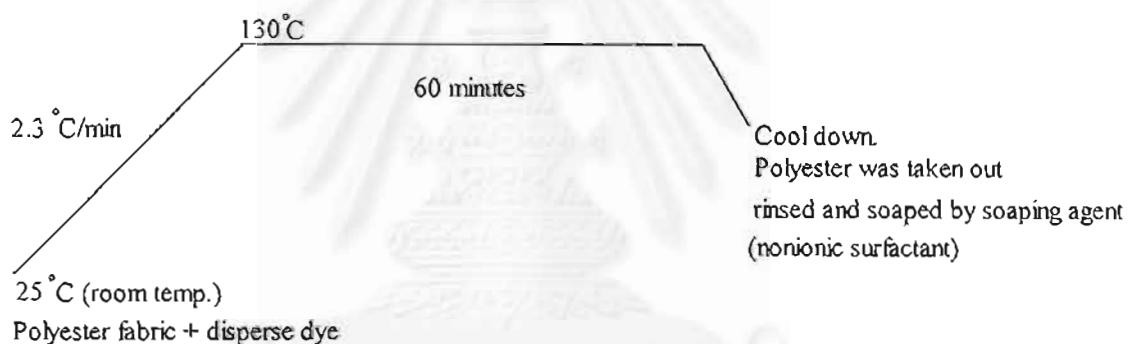


Diagram3.2 Dyeing profile of polyester fabric using exhaustion method

3.13 Treatment of dyed polyester fabric with poly(HEMA-co-BEMA)

Dyed polyester fabrics from Section 3.12 were treated with poly(HEMA-co-BEMA) of different degree of BEMA content. Dyed polyester fabrics were treated with poly(HEMA-co-BEMA)'s concentrations of 10%, 20%, and 30% (o.w.f.) at liquor ratio of 1 : 20. The treatment procedure was carried out using the same procedure as described in section 3.7.

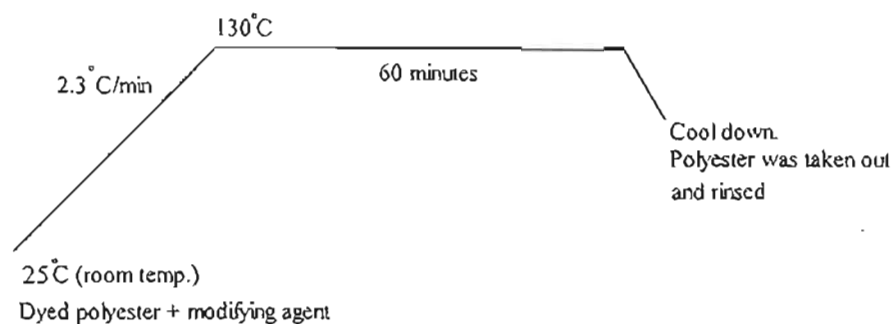


Diagram 3.3 Exhaust treatment of dyed polyester fabric with poly(HEMA-co-BEMA)

3.14 Evaluation of color fastness to heat by hot pressing⁽³⁵⁾

Color fastness is the resistance of dyed materials to change in any of its color characteristics, to transfer of its colorant to adjacent materials, or both, as a result of the exposure of the material to any environment that might be encountered during the processing testing, storage or use of the material.

This test method was intended for determining the resistance of the color of dyed polyester fabric to color change and color transfer when subjected to hot pressing. If used dried fabric, it is called dry pressing. The dried specimen was pressed with a heating device at specific temperature of 200 ± 2 °C.

Heating device in this laboratory is THERMO TESTER, Model T-10M, voltage AC 100 V., maximum power 1400 W., operating temperatures 100 °C-250 °C.

Heating device provides even heat transfer to the specimen from the bottom plate by close contact at a controlled temperature of 200 ± 2 °C and gives pressure of 40 ± 10 g/cm² on the specimen. The sample was cut into the size of 12 cm. x 4cm. Specimen of materials that were subjected to any heat or drying treatment must be allowed to expose to air at 65 ± 2 % relative humidity and temperature of 20 ± 2 °C before test. Undyed polyester fabric was placed on the top of the specimen (modified dyed polyester fabric and unmodified dyed polyester fabric) on the hot plate of heating device and was left for 15 seconds at 200 ± 2 °C. Assessment of the color change and color stain of dyed fabric treated with poly(HEMA-co-BEMA) and dyed fabric without treatment was performed using Macbeth spectrophotometer.

3.15 Measurement of color change and color stain

Measurement of color change was done by using I.C.S. Micromath spectrophotometer (Figure 3.5). After hot pressing treatment, evaluation of color change and color stain was carried out by using an I.C.S. Micromath color measurement (Macbeth 700), the reflectance values was measured at λ max 520 nm.

The color strength of the fabrics before and after heat treatment were expressed as K/S values calculated by the Kubellka-Munk equation.

$$K/S = \frac{(1-R)^2}{2R}$$

K is the absorption coefficient

S is the scattering coefficient

R is the reflectance of the fabric at the wavelength of maximum absorption (λ max)

This effect of poly(HEMA-co-BEMA) on improving fastness to heat was then assessed by comparison between K/S values of dyed polyester fabric before and after heat treatment.

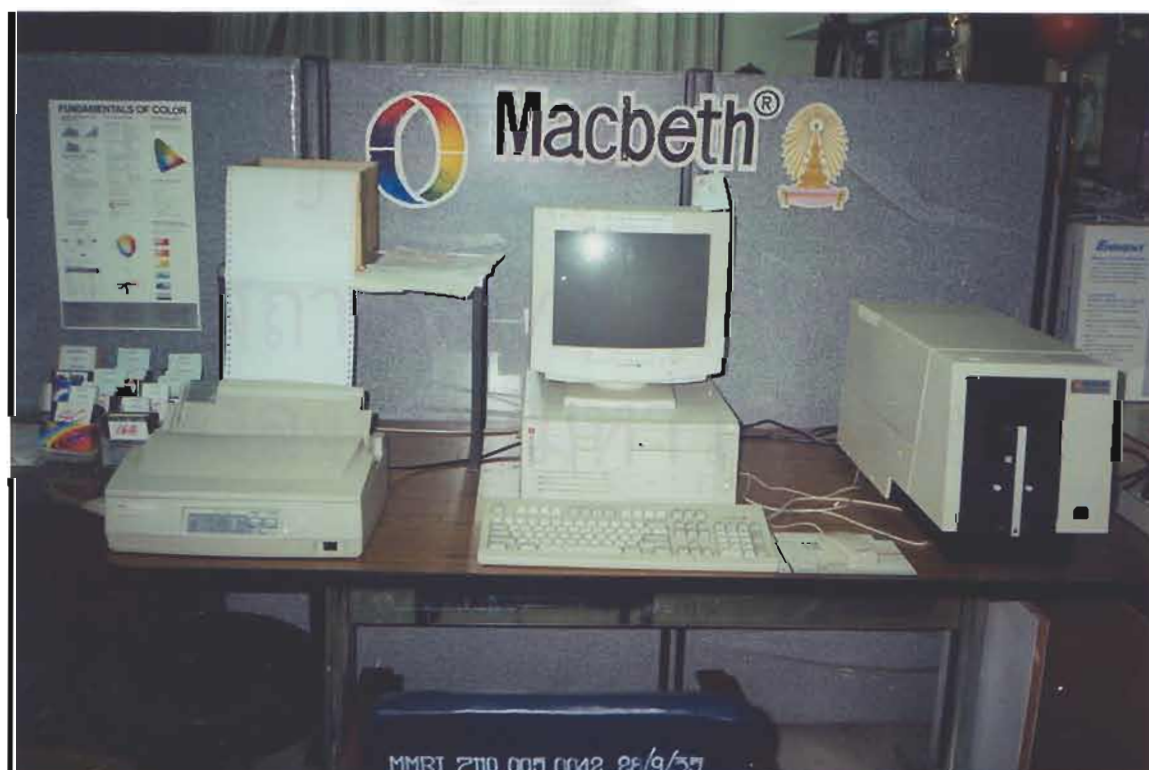


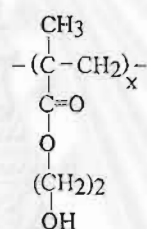
Figure 3.5 I.C.S. Micromath spectrophotometer

CHAPTER IV

Results and Discussion

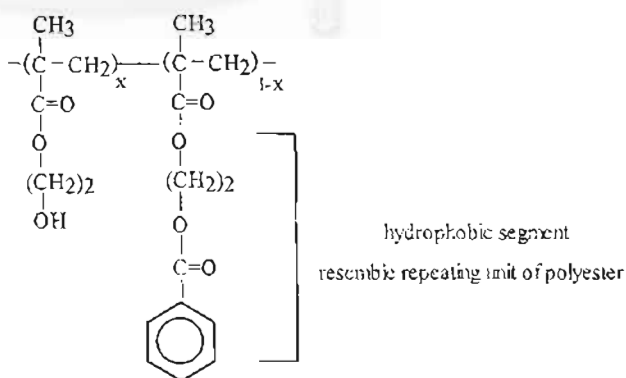
4.1 Synthesis of poly(2-hydroxyethylmethacrylate), poly(HEMA) and poly(2-hydroxyethylmethacrylate-co-benzoylethylmethacrylate), poly(HEMA-co-BEMA)

The poly(2-hydroxyethylmethacrylate), poly(HEMA) has the chemical structure as shown in Figure 4.1. Poly(2-hydroxyethylmethacrylate-co-benzoylethyl methacrylate), poly(HEMA-co-BEMA) was prepared by reacting the poly(HEMA) with benzoyl chloride. Figure 4.2 represents the chemical formula of poly(HEMA-co-BEMA).



Poly(HEMA)

Figure 4.1 Poly(HEMA), this compound was prepared by the method described in Section 3.3



Poly(HEMA-co-BEMA)

Figure 4.2 Poly(HEMA-co-BEMA), this compound was prepared by the method described in Section 3.4

Considering poly(HEMA), it contains hydroxyl groups along polymer backbone which contributes to its hydrophilic characteristic. On the other hand, the hydrogen bonding interaction between adjacent polymeric chain is so large that it renders the polymer water-insoluble. Apart from its poor solubility in water, poly(HEMA)'s ability to adhere on the hydrophobic surface is rather poor.

The modification of poly(HEMA) by partial reaction with benzoyl chloride is interesting in terms of making this compound suitable for improving wettability performance of polyester fabric. The introduction of hydrophobic segment in poly(HEMA) backbone would not only reduce cohesive force between polymeric chains but also favors the good adhesive ability onto the polyester surface. Reduced cohesive force among polymeric chains assists water to separate polymer molecules apart from each other to be suspendable in water medium. As a result, the application of this compound from water is feasible.

The hydrophobic part is crucial to achieve permanent adherence property onto the polyester surface. It can be noticed that hydrophobic pendant group was designed to have chemical structure which resemble to the repeating unit of polyester. It, therefore, was expected that upon heat treatment at certain temperature the hydrophobic segment would be able to penetrate inside polyester surface. So that the hydrophilic part would attach firmly on the surface.

4.2 FT-IR study of poly(HEMA) and poly(HEMA-co-BEMA)

4.2.1 FT-IR study of poly(HEMA)

The Fourier Transform Infrared Spectroscopy (FT-IR) was carried out to identify the chemical structure of the poly(HEMA). The FT-IR spectrum of the poly(HEMA) is shown in Figure 4.3 and some absorption bands of poly(HEMA) are summarized in Table 4.1. The main characteristic absorption bands are found at 3500-3300 cm^{-1} and 2900-2800 cm^{-1} , respectively, which are attributable to the OH-stretching and CH-stretching of methyl group, respectively.

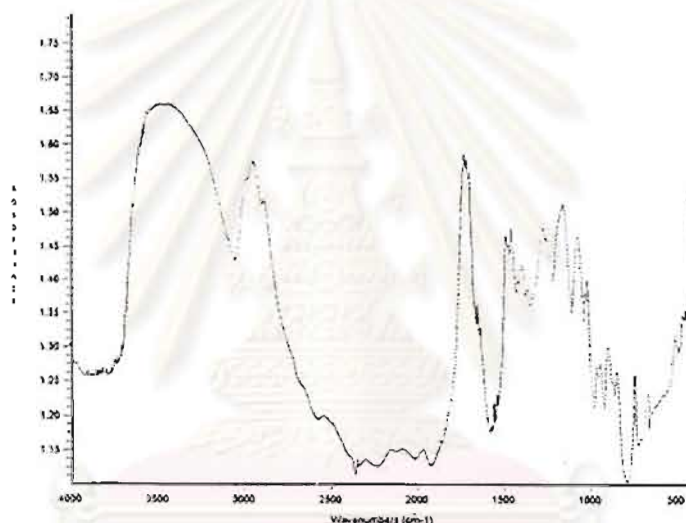


Figure 4.3 FT-IR spectrum of poly(HEMA)

Table 4.1 FT-IR absorption bands of poly(HEMA)

Wave number (cm^{-1})	Assignments
3500-3300	OH-stretching
2900-2800	CH-stretching of methyl group
1700	C=O-stretching
1300-1100	C-O -stretching
800-700	Ar-H-stretching

4.2.2 FT-IR study of poly(HEMA-co-BEMA)

FT-IR analysis was carried out in order to confirm the chemical structure of poly(HEMA-co-BEMA). In this experiment, poly(HEMA-co-BEMA) having various degrees of pendant benzoyl groups were prepared. The resulting copolymers with various degree of functionalization of BEMA content at 2.5%, 5%, and 7.5% in Series 1 and 10%, 20%, 30%, 40% and 50% in Series 2, respectively. The IR absorption spectra of the copolymers were obtained from Omnic Nicolet IR instrument as shown in Figure 4.4. The evidence of the characteristic of the poly(HEMA-co-BEMA) is confirmed by the presence of 735 cm^{-1} band. This band could be assigned to C-H stretching of aromatic ring (benzene group). The gradual decrease in the intensity of hydroxyl peak (O-H stretching) in the region of $3500\text{-}3300\text{ cm}^{-1}$ as the degree of functionalization increase indicates that the hydroxyl groups of poly (HEMA) were consumed and subsequently converted into benzoyl groups.

Table 4.2 The absorption bands of poly(HEMA-co-BEMA)

Wave number (cm^{-1})	Assignments
3500-3300	OH-stretching
2900-2800	CH-stretching of methylene proton
1700	C=O-stretching
1300-1100	C-O -stretching
800-700	Ar-H-stretching

The FT-IR spectra of poly(HEMA-co-BEMA) modified with various amounts of benzoyl chloride contents at 2.5%, 5%, 7.5% in Series 1 and 10%, 20%, 30%, 40%, and 50% in Series 2, respectively are shown in Figure 4.4 below.

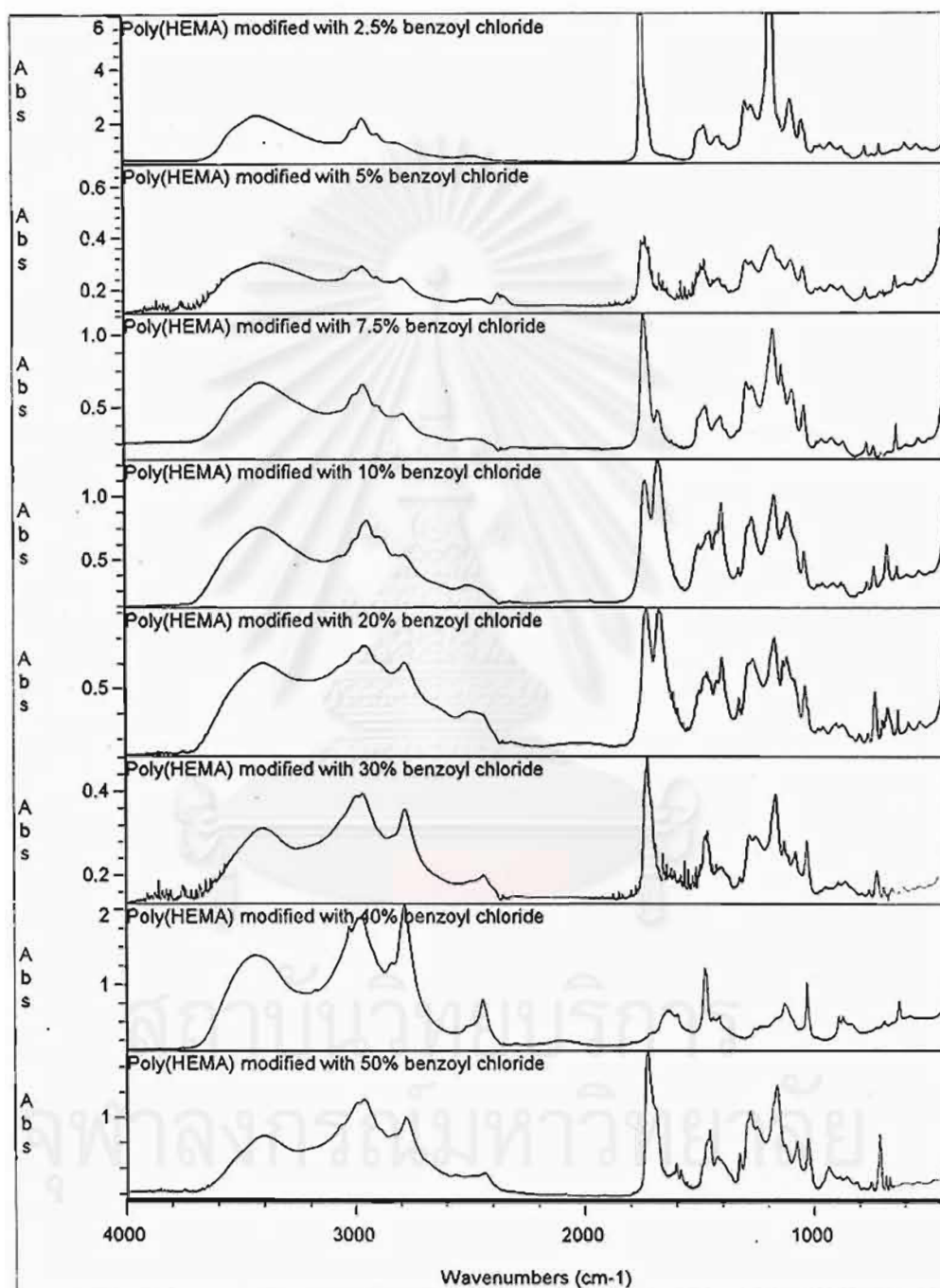


Figure 4.4 FT-IR spectra of poly(HEMA-co-BEMA) modified with different amounts of benzoyl chloride

The actual degree of functionalization can be calculated by comparing change in intensity of OH-stretching with unchanged intensity of CH-stretching at 2900 cm^{-1} according to the following equation.

$$\% \text{ Degree of functionalization} = \frac{(X_2 - X_1)}{X_1} \times 100$$

X_1 = The ratio of OH-stretching intensity to CH-stretching intensity obtained from the spectrum of pure poly(HEMA)

X_2 = The ratio of OH-stretching intensity to CH-stretching intensity obtained from the spectrum of poly(HEMA-co-BEMA)

The calculated results are summarized in Table 4.3

Table 4.3 The calculated degree of functionalization of poly(HEMA)

Theoretical value of degree of functionalization (%)	Actual value of degree of functionalization (%)
2.5	1.05
5	2.11
7.5	4.21
10	13.68
20	17.89
30	33.68
40	45.26
50	50.53

4.3 ^1H NMR study of poly(HEMA) and poly(HEMA-co-BEMA)

4.3.1 ^1H NMR study of poly(HEMA)

The ^1H NMR spectroscopy was used to confirm the chemical structure of the poly(HEMA) as well as poly(HEMA-co-BEMA). The ^1H NMR spectrum of poly(HEMA) in dimethylsulfoxide solvent (DMSO-D_6) is shown in Figure 4.5 and the chemical shifts of all protons are summarized in Table 4.4.

The ^1H NMR spectrum of poly(HEMA) exhibits the peaks corresponding to methylene protons at 0.8-0.9 ppm. The peaks at 3.5-4 and 4.8 ppm. correspond to the signal of $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_2-$ and $-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{CH}_2-$ respectively, from poly(HEMA) backbone. The strong signal at 7.3 ppm. is due to the presence of benzene (solvent) which was not completely removed from poly(HEMA).

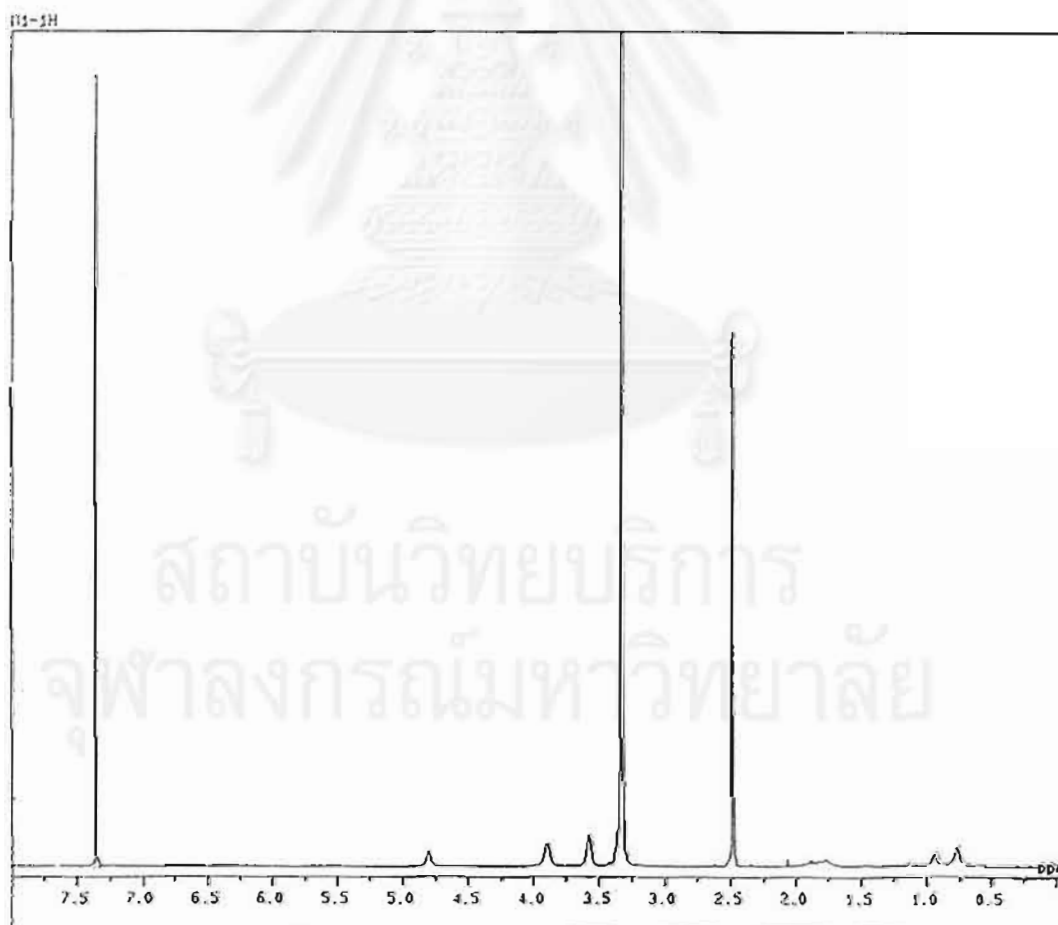


Figure 4.5 ^1H NMR spectrum of purified poly(HEMA) in DMSO-D_6 solvent.

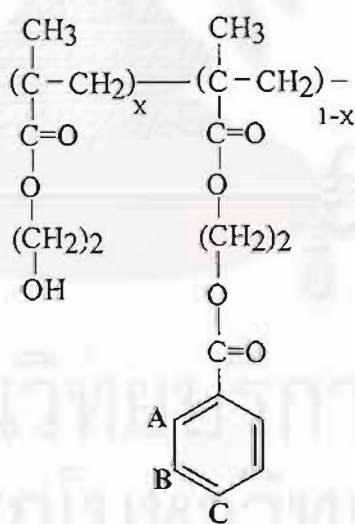
Table 4.4 Chemical shifts of purified poly(HEMA) in DMSO-D₆ solvent.

Chemical shifts (δ)	Multiplicity	Assignments
7.3	singlet sharp	Aromatic protons in benzene residue
4.8	singlet 1 peak weak	$\begin{array}{c} \text{O} \\ \\ \text{-(CH}_2\text{)-} \\ \end{array}$
3.5-4	singlet 2 peaks weak	$\begin{array}{c} \\ \text{-C-CH}_2\text{-} \\ \end{array}$
3.3	singlet	absorbed water of DMSO-D ₆
2.5	singlet	methylene proton of DMSO-D ₆
0.8-0.9	singlet 2 peaks weak	methylene proton of poly(HEMA)

4.3.2 ^1H NMR study of poly(HEMA-co-BEMA)

The ^1H NMR spectra of poly(HEMA-co-BEMA) with various degree of benzoyl pendant contents are shown in Appendix and their proton chemical shifts are presented in Table 4.5.

An example of ^1H NMR spectrum of poly(HEMA-co-BEMA) with the degree of functionalization of BEMA content at 2.5% is illustrated in Figure 4.7. From the spectrum, it is evident that poly(HEMA) was partially converted to poly(HEMA-co-BEMA) from the characteristic of split bands of monosubstituted aromatic protons corresponding to the signals of A, B, and C at 7.9, 7.4, and 7.3 ppm, respectively. The chemical shifts at 3.5-4, and 4.8 ppm. indicated the aliphatic protons attached to carbon at $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_2-$ and $-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{CH}_2-$ in the poly(HEMA) skeleton respectively and the peak at 0.8-0.9 ppm. corresponding to the signal of methylene proton of poly(HEMA).



Poly(HEMA-co-BEMA)

Figure 4.6 The chemical structure of poly(HEMA-co-BEMA)

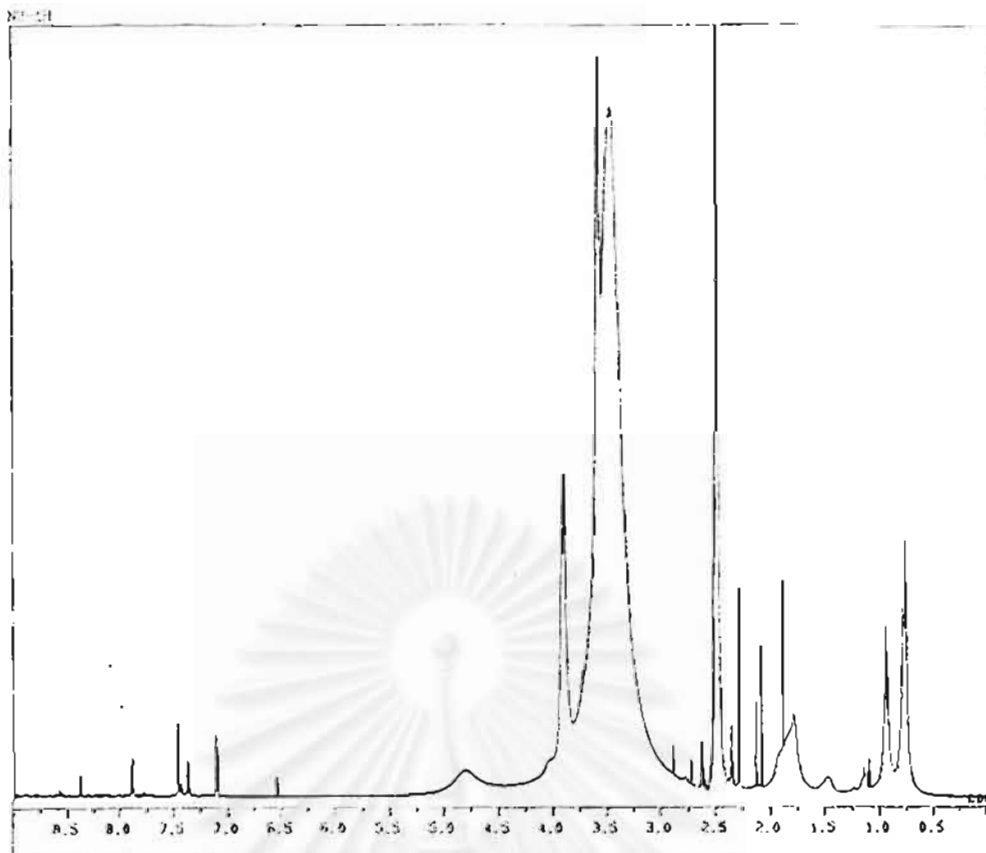


Figure 4.7 ^1H NMR spectrum of poly(HEMA-co-BEMA) with the degree of functionalization of 2.5%

Table 4.5 Chemical shifts of poly(HEMA-co-BEMA) in DMSO-D_6 solvent

Chemical shifts (δ)	Multiplicity	Assignments
7.9	doublet	A
7.4	triplet	B
7.3	triplet	C
4.8	singlet 1 peak (weak)	$\begin{array}{c} \text{O} \\ \\ -(\text{CH}_2)- \\ \end{array}$
3.5-4	singlet 2 peaks (weak)	$\begin{array}{c} \\ -\text{C}-\text{CH}_2- \\ \end{array}$
3.3	singlet	absorbed water of DMSO-D_6
2.5	singlet	methylene proton of DMSO-D_6
0.8-0.9	singlet 2 peaks (weak)	methylene proton of poly(HEMA-co-BEMA)

4.4 Application of poly(HEMA-co-BEMA) onto polyester fabric

4.4.1 Percent add on of modifying agent onto polyester fabrics

Poly(HEMA-co-BEMA) obtained from Section 3.4 was applied to polyester fabric using exhaustion method from Section 3.7. Percent add on of poly(HEMA-co-BEMA) onto polyester fabrics was calculated using method as described in Section 3.8.1. The results of percent add on of modified polyester fabric at various degree of BEMA content of 2.5%, 5%, 7.5% in Series 1 and 10%, 20%, 30%, 40%, and 50% in Series 2 are shown in Figure 4.8 and Figure 4.9, respectively.

The results show that the percent add on of poly(HEMA-co-BEMA) tends to increase with increasing in the degree of BEMA content. This is because of the hydrophobicity of BEMA residue which was capable to penetrating into polyester at the temperature above T_g . Without hydrophobic segment, it is unlikely that pure poly(HEMA) alone would be absorbed into polyester surface, hence durable wettability of poly(HEMA) coated polyester is not obtainable. For % functionalization of poly(HEMA-co-BEMA) with theoretical degree of BEMA content between 2.5%-7.5% and can be seen that there is no significant difference in percent add on. Partly, it may be because the actual percentage of BEMA content was much lower than theoretical value and this also reflects poor efficiency of the reaction between poly(HEMA) hydroxyl groups and benzoyl chloride, then leading to low percent add on.

Apart from the effect of the degree of hydrophobic content, the increase in percent add on is also dependent on the concentration of modifying agents applied. At certain level of concentration such as 100% o.w.f., in the case of 40%-50% degree of BEMA content, uneven precipitation on polyester fabric occurred because excess amount of poly(HEMA-co-BEMA) may affect handleness of treated fabric as well as impractical in view of practical textile chemists. Therefore, the suitable concentration of poly(HEMA-co-BEMA) should be in the range of degree of BEMA content at 10%-30%.

Table 4.6 Percent add on of modifying agent onto polyester fabric, Series 1

Concentration of modifying agent (%)	Percent add on at BEMA content (%)		
	2.5	5	7.5
25	0.64	0.84	0.59
50	0.65	1.36	0.87
75	1.30	1.61	1.15
100	2.24	1.96	1.82

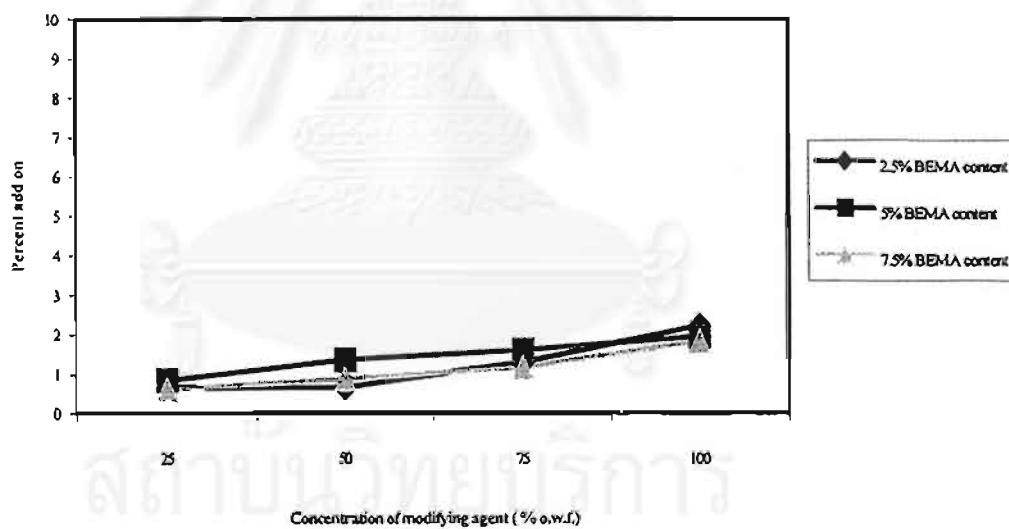


Figure 4.8 Chart of percent add on of modifying agent onto polyester fabric, Series 1

Table 4.7 Percent add on of modifying agent onto polyester fabric, Series 2

Concentration of modifying agent (%)	Percent add on at BEMA content (%)				
	10	20	30	40	50
25	0.28	0.83	0.37	0.37	1.03
50	1.33	1.05	1.28	1.67	3.20
75	3.10	1.68	1.95	16.26	21.15
100	3.48	2.73	2.82	19.73	36.57

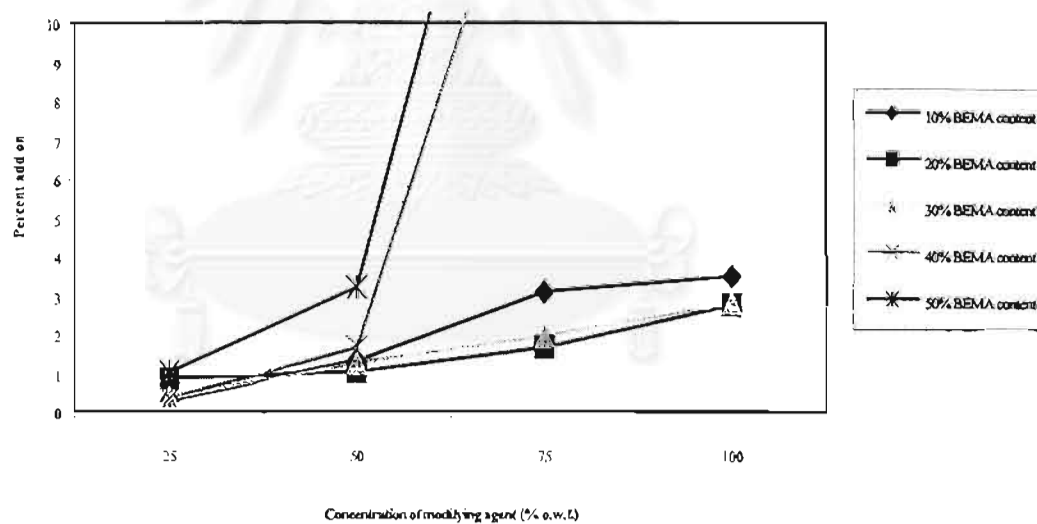


Figure 4.9 Chart of percent add on of modifying agent onto polyester fabric, Series 2

4.4.2 Moisture regain of modified polyester fabric

The moisture regain was calculated from the equation in section 3.8.2. The results are shown in Figure 4.10 and Figure 4.11.

As expected, the percentage of moisture regain is dependent on the percent add on of poly(HEMA-co-BEMA). An increase in percent add on reflects an increase in hydrophilic content (HEMA content) on treated fabric surface so it can retain more moisture from atmosphere than untreated polyester fabric. However, the highest percent moisture regain obtained from 100% (o.w.f.) 50% degree of BEMA content is between 0.4-0.6% in average which still is low when compared to untreated polyester fabric (0.4% moisture regain).



Table 4.8 Percent moisture regain of modified polyester fabric, Series 1

Concentration of modifying agent (%)	Percent moisture regain at BEMA content (%)		
	2.5	5	7.5
25	0.023	0.056	0.031
50	0.038	0.137	0.075
75	0.078	0.161	0.160
100	0.122	0.203	0.756

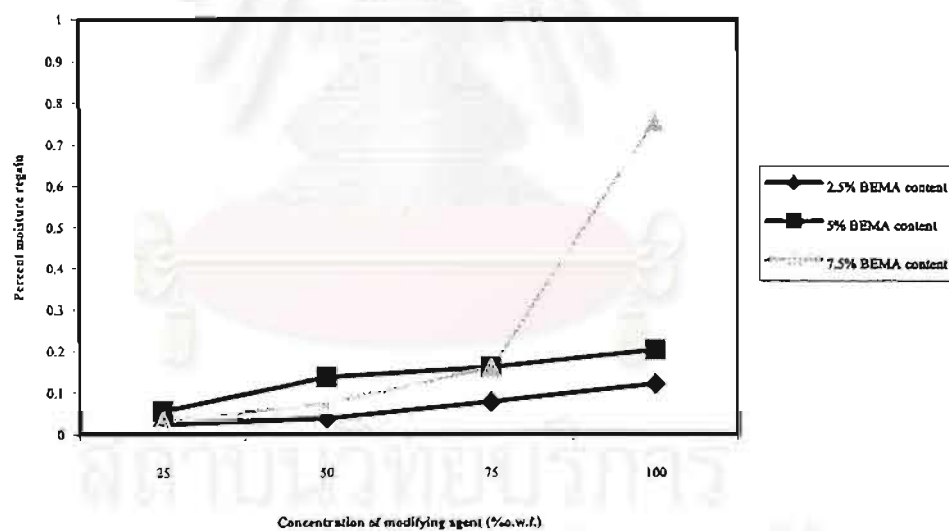


Figure 4.10 Chart of percent moisture regain of modified polyester fabric, Series 1

Table 4.9 Percent moisture regain of modified polyester fabric, Series 2

Concentration of modifying agent (%)	Percent moisture regain at BEMA content (%)				
	10	20	30	40	50
25	0.030	0.122	0.146	0.234	0.250
50	0.074	0.144	0.158	0.199	0.215
75	0.128	0.203	0.247	0.353	0.410
100	0.044	0.212	0.266	0.458	0.679

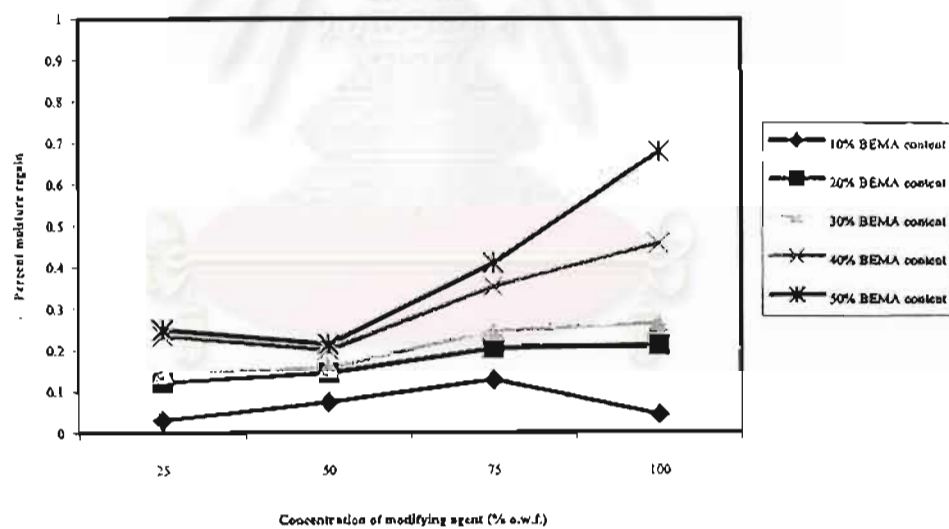


Figure 4.11 Chart of percent moisture regain of modified polyester fabric, Series 2

4.5 Wetness test

The measurement of complete wetness time was performed by drop test method using two different procedures, AATCC standard and Du Pont water drop test as described in Section 3.9.1 and section 3.9.2, respectively.

4.5.1 The time of wetness from AATCC Standard test

Polyester fabric treated with poly(HEMA-co-BEMA) before and after 6 hours methyl alcohol extraction were subjected to wetness test for comparison of durable property of this type of modifying agent. Times of complete wetness are shown in Table 4.10-4.13 Figure 4.12-4.15. Time of complete wetness is the time when water drop on treated polyester fabric completely disappears; the quicker the observed time, the better the wettability of treated fabric. The results show that wettability of treated fabrics is notably improved after being treated with poly(HEMA-co-BEMA). Noting that wettability of treated fabrics is related to the balance degree of hydrophilic content (HEMA) and hydrophobic content (BEMA residue). High ratio of hydrophilic content to hydrophobic content such as 97.5 : 2.5 tends to produce poorer wettability than relatively lower hydrophilic : hydrophobic ratio (92.5 : 7.5). This could be attributed to the poor fixability of poly(HEMA-co-BEMA) with 97.5 : 2.5 hydrophilic : hydrophobic ratio as indicated by low percent add on (see Section 4.4.1).

On the other hand, a further decrease in hydrophilic : hydrophobic ratio tends to produce an adverse effect. Wettability of treated fabric decreases with an increase in the degree of hydrophobic content even though better fixability of the modifying agent on polyester is obtained. Therefore it is important to select the modifying agent with a suitable balance between hydrophilic and hydrophobic contents in order to achieve the optimum results.

Table 4.10 Time of complete wetness (AATCC Standard Method) before methyl alcohol extraction, Series 1

Concentration of modifying agent (%)	Time of complete wetness at BEMA content (%)			
	0	2.5	5	7.5
Control	290	-	-	-
25	-	86	62	68
50	-	73	52	50
75	-	63	30	34
100	-	70	29	25

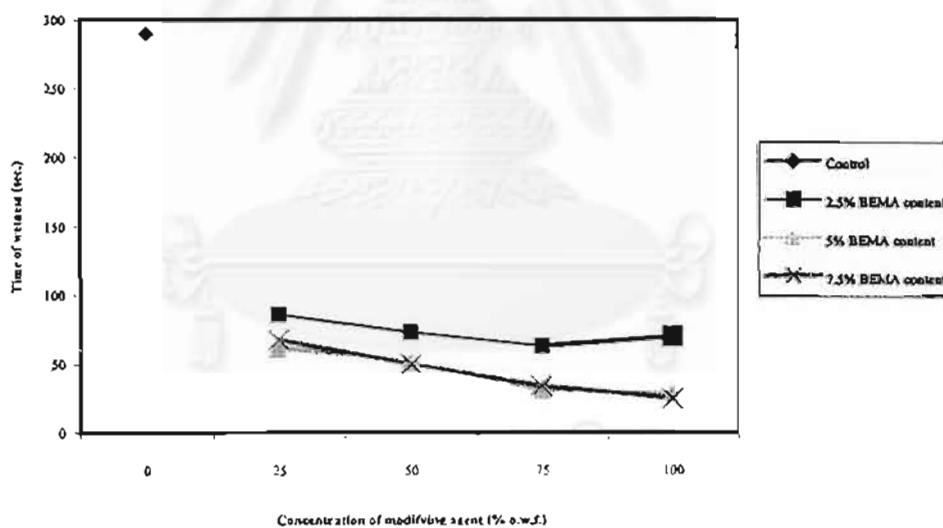


Figure 4.12 Chart of time of complete wetness (AATCC Standard Method) before methyl alcohol extraction, Series 1

Table 4.11 Time of complete wetness (AATCC Standard Method) after methyl alcohol extraction, Series 1

Concentration of modifying agent (%)	Time of complete wetness at BEMA content (%)			
	0	2.5	5	7.5
Control	252	-	-	-
25	-	88	68	65
50	-	85	47	60
75	-	69	44	45
100	-	65	30	35

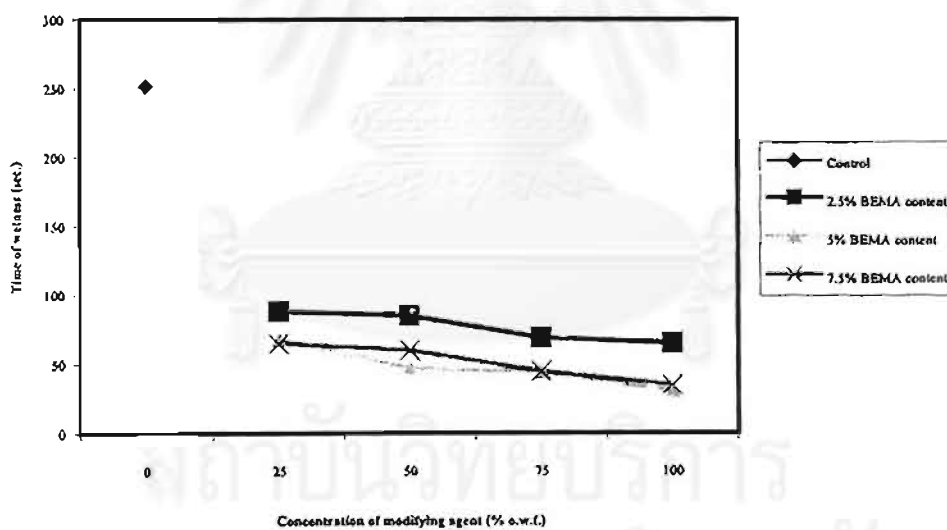


Figure 4.13 Chart of time of complete wetness (AATCC Standard Method) after methyl alcohol extraction, Series 1

Table 4.12 Time of complete wetness (AATCC Standard Method) before methyl alcohol extraction, Series 2

Concentration of modifying agent (%)	Time of complete wetness at BEMA content (%)					
	0	10	20	30	40	50
Control	286	-	-	-	-	-
25	-	50	53	60	83	93
50	-	37	52	42	90	92
75	-	36	36	38	130	147
100	-	34	30	36	220	222



Figure 4.14 Chart of time of complete wetness (AATCC Standard Method) before methyl alcohol extraction, Series 2

Table 4.13 Time of complete wetness (AATCC Standard Method) after methyl alcohol extraction, Series 2

Concentration of modifying agent (%)	Time of complete wetness at BEMA content (%)					
	0	10	20	30	40	50
Control	260	-	-	-	-	-
25	-	38	40	44	51	61
50	-	36	35	40	55	67
75	-	32	34	36	68	74
100	-	28	30	35	72	96

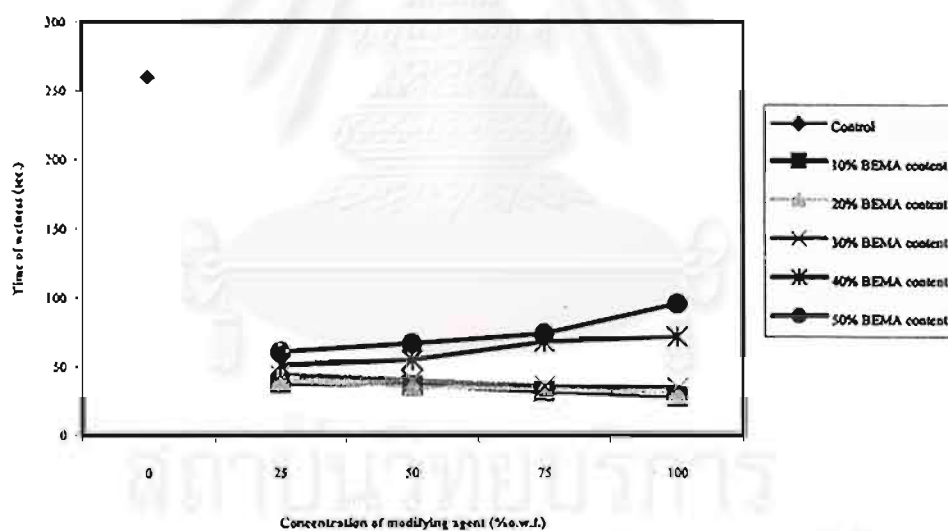


Figure 4.15 Chart of time of complete wetness (AATCC Standard Method) after methyl alcohol extraction, Series 2

4.5.2 Evaluation of wettability from water drop test by Du Pont test method

Unlike AATCC standard, Du Pont wetness test method tentatively provides surface tension data of treated fabrics. Surface tension is indicative of hydrophilic surface. The wettability rating of poly(HEMA-co-BEMA) modified polyester fabric are given in Table 4.14 and Table 4.15. Polyester fabrics treated with poly(HEMA-co-BEMA) with hydrophilic : hydrophobic ratios of 97.5 : 2.5, and 92.5 : 7.5 show the wettability rating of 3 or equivalent surface tension of 42 dyne/cm. A decrease in surface tension of modified fabric reflects the change towards hydrophilic characteristic of polyester surface. The results indicate that a surface treatment with hydrophilic/hydrophobic copolymer would make polyester fabric more hydrophilic. A further increase in hydrophilic/hydrophobic ratios brings about little increase in wettability rating. Comparison of wettability ratings before and after methyl alcohol extraction are virtually unchanged, indicating that removal of depositing agent has no insignificant effect on hydrophilic characteristic of absorbed poly(HEMA-co-BEMA).

Table 4.14 The wettability rating from water drop test by Du Pont, Series 1

Hydrophilic : hydrophobic ratio	Concentration of modifying agent (% o.w.f.)	The wettability rating before methyl alcohol extraction (surface tension, dyne/cm)	The wettability rating after methyl alcohol extraction (surface tension, dyne/cm)
control	-	5 (27.5)	5 (27.5)
97.5 : 2.5	25	3 (42)	3 (42)
	50	3 (42)	3 (42)
	75	3 (42)	3 (42)
	100	3 (42)	3 (42)
95 : 5	25	3 (42)	3 (42)
	50	3 (42)	3 (42)
	75	3 (42)	3 (42)
	100	3 (42)	3 (42)
92.5 : 7.5	25	3 (42)	3 (42)
	50	3 (42)	3 (42)
	75	3 (42)	3 (42)
	100	3 (42)	3 (42)

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Table 4.15 The wettability rating from water drop test by Du Pont, Series 2

Hydrophilic : hydrophobic ratio	Concentration of modifying agent (% o.w.f.)	The wettability rating before methyl alcohol extraction (surface tension, dyne/cm)	The wettability rating after methanol alcohol extraction (surface tension, dyne/cm)
control	-	5 (27.5)	5 (27.5)
80 : 20	25	3 (42)	3 (42)
	50	3 (42)	3 (42)
	75	3 (42)	3 (42)
	100	3 (42)	3 (42)
70 : 30	25	3 (42)	3 (42)
	50	3 (42)	3 (42)
	75	3 (42)	3 (42)
	100	3 (42)	3 (42)
60 : 40	25	4 (33)	3 (42)
	50	4 (33)	3 (42)
	75	5 (27.5)	4 (33)
	100	5 (27.5)	4 (33)
50 : 50	25	4 (33)	3 (42)
	50	4 (33)	3 (42)
	75	5 (27.5)	4 (33)
	100	5 (27.5)	4 (33)

4.6 Illustration of dye drop's spreading on modified polyester fabric

Dye drop's spreading test of modified polyester fabric before and after 6 hours methyl alcohol extraction was carried out. Color drop's spreading before and after methyl alcohol extraction is compared as shown in Table 4.16 and Table 4.17. The wicking capability of the modified fabric was depend on the hydrophilic : hydrophobic ratio. In Series 1, dye drop's spot on the modified fabric increased with decreased in hydrophilic : hydrophobic ratio. However, in Series2, The dye spot tended to decrease with increase in the hydrophilic : hydrophobic ratio. The results are found in good agreement with those obtained from wetness test (Section 4.5). An insignificant difference in color drop spreading before and after methyl alcohol extraction indicate that permanently modified surface of polyester fabric could be achieved with poly (HEMA-co-BEMA). The hydrophilic : hydrophobic ratio of 90 : 10 gave the desired properties including hydrophilic, handle and durability.



Table 4.16 Illustration of color drop's spreading, Series 1



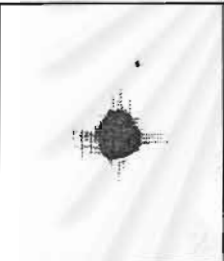
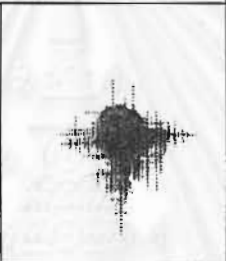
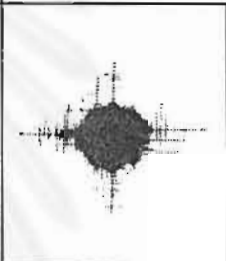




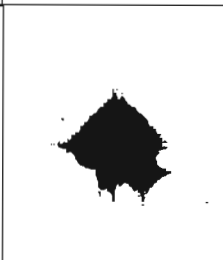
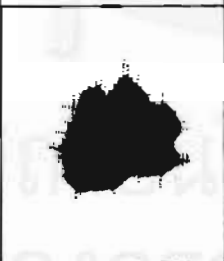
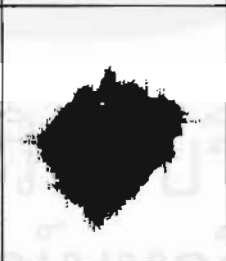
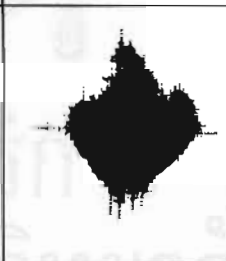
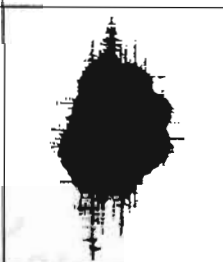




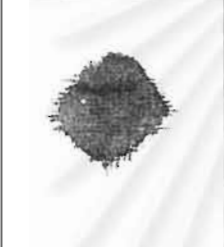


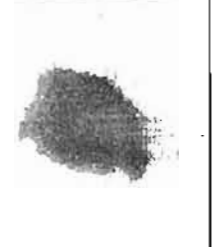
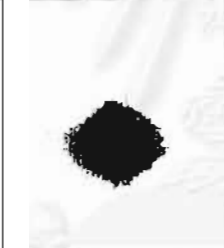











BEMA content in poly(HEMA- co-BEMA) (%)	Concentration of modifying agent before methyl alcohol extraction		Concentration of modifying agent after methyl alcohol extraction	
	25% o.w.f.	50% o.w.f.	25% o.w.f.	50% o.w.f.
Control				
2.5				
5				
7.5				

Table 4.17 Illustration of color drop's spreading, Series 2

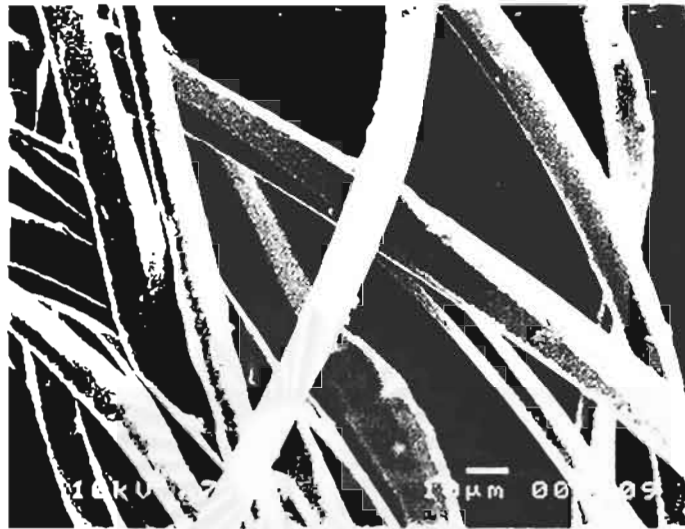
BEMA content in poly(HEMA- co-BEMA) (%)	Concentration of modifying agent before methylalcohol extraction		Concentration of modifying agent after methyl alcohol extraction	
	25% o.w.f.	50% o.w.f.	25% o.w.f.	50% o.w.f.
10				
20				
30				
40				
50				

4.7 Scanning Electron Microscopy of polyester fabric modified with poly(HEMA-co-BEMA)

Scanning Electron Microscopic (SEM) analysis was performed in order to investigate the durability of the modifying agent after surface modification. SEM micrographs of treated fabrics before and after 6 hours methyl alcohol extraction were taken from JSM-5410 scanning electron microscope and compared with those obtained from untreated fabrics. The scanning electron micrographs of uncoated and fabrics modified with poly(HEMA-co-BEMA) before and after methanol extraction with BEMA content of 2.5%, 5%, 7.5% (Series 1) and fabrics modified with poly(HEMA-co-BEMA) after methanol extraction with BEMA content of 10%, 20%, 30%, 40%, and 50% (Series 2) are shown in Figure 4.16, Figure 4.17, and Figure 4.18, respectively.

Scanning electron micrographs results reveal that attachment of poly(HEMA-co-BEMA) onto the polyester surface was not even, probably due to large molecular weight of the copolymer. In order to prevent accumulation of copolymer dispersion, it is important that molecular weight of the copolymer must be as low as 1,000 g/mole.

Before methyl alcohol extraction



After methyl alcohol extraction

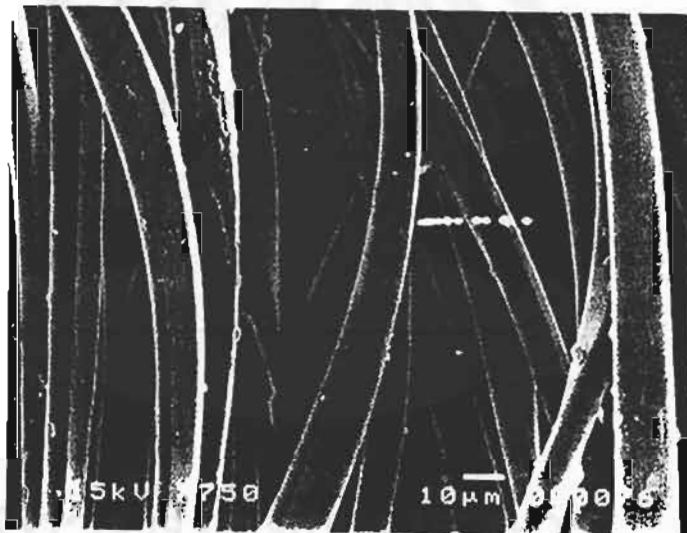


Figure 4.16 Scanning electron micrographs of uncoated fabrics before and after methanol extraction

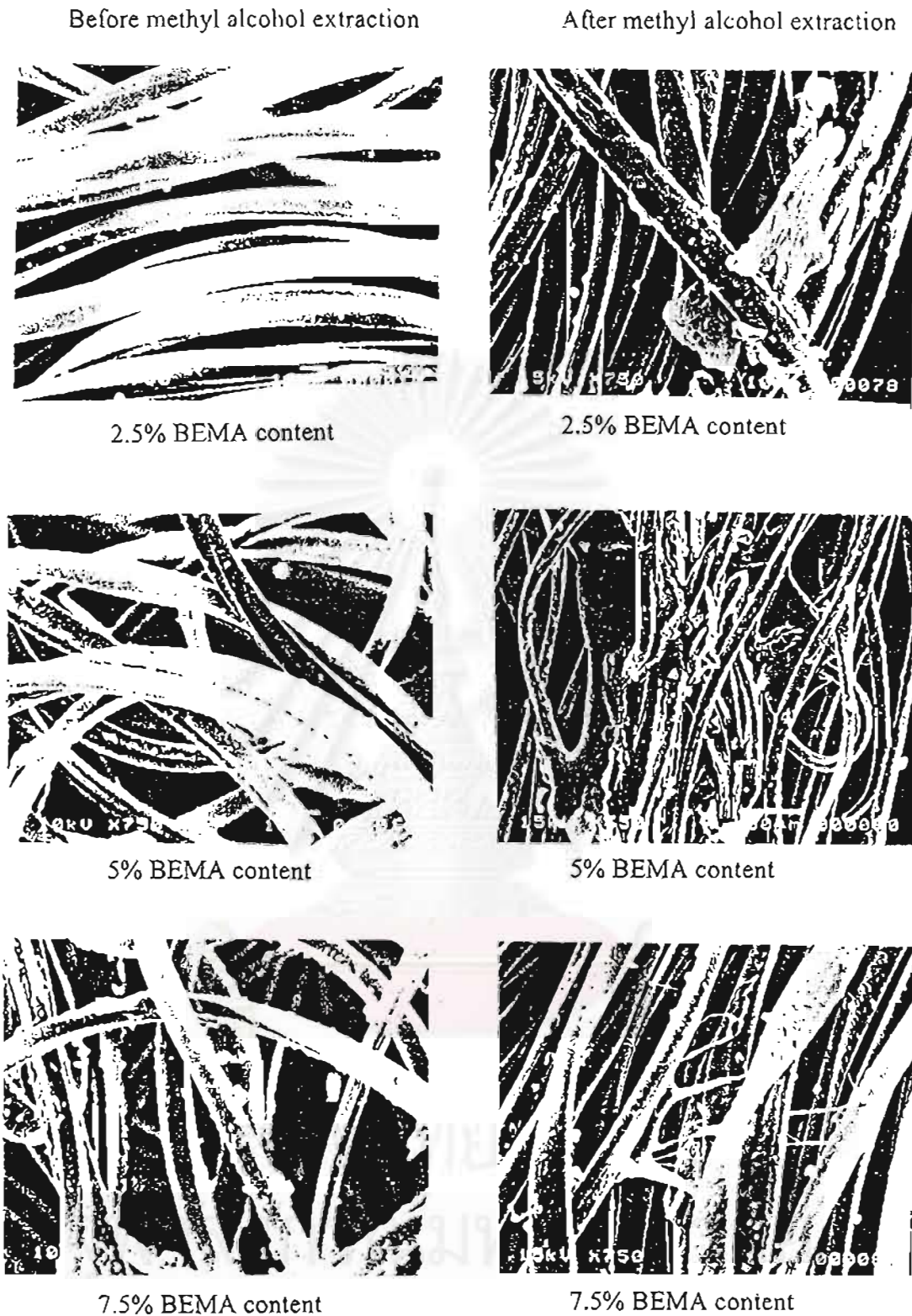


Figure 4.17 Scanning electron micrographs of fabrics modified with poly(HEMA-co-BEMA) before and after methanol extraction with BEMA content of 2.5%, 5%, 7.5% (Series 1)

After methyl alcohol extraction



10% BEMA content



20% BEMA content



30% BEMA content



40% BEMA content



50% BEMA content

Figure 4.18 Scanning Electron Micrographs of fabrics modified with poly(HEMA-co-BEMA) after methanol extraction with BEMA content of 10%, 20%, 30%, 40%, and 50% (Series 2)

4.8 Effect of poly(HEMA-co-BEMA) on heat fastness of disperse dyed fabric

After dyeing polyester fabric with a disperse dyed, dye fabric was then treated with poly(HEMA-co-BEMA) having hydrophilic : hydrophobic ratio of 90 : 10, 80 : 20, and 70 : 30, respectively at 130 °C for 1 hour. Heat fastness property of poly(HEMA-co-BEMA) treated dyed fabric was evaluated using AATCC Standard. Color change and color stain were measured using I.C.S. Macbeth instrument.

Measurement of color change can be determined by K/S values before and after hot-pressing treatment. The percentage of color change was then calculated based on the following equation:

$$\% \text{ color change} = \frac{(A_1 - A_2)}{A_1} \times 100$$

A_1 = K/S of modified dyed polyester fabric before hot-pressing treatment

A_2 = K/S of modified dyed polyester fabric after hot-pressing treatment

The results obtained are shown in Table 4.18. The results indicate that unmodified dyed fabric shows the highest color loss. This was due to during hot-pressing treatment, disperse dye molecules freely migrated out of the fabric surface, resulting in loss of color. In the case of dyed fabric applied with poly(HEMA-co-BEMA) color loss after heat treatment is significantly reduced, depending on the degree of hydrophilic content as well as its concentration. An improved heat fastness of poly(HEMA-co-BEMA) treated dyed fabric is due to the barrier effect of hydrophilic surface on the diffusion of hydrophobic disperse dyes. Gradually increase in hydrophilic content could effectively slow the migration of dye molecules out of fabric. Therefore, the advantages of this hydrophilic / hydrophobic copolymer are not only to modify polyester fabric acquiring hydrophilic characteristic but also to improve fastness property of disperse dyed fabric.

Color stain assessment is an alternative approach in determining color fastness to heat. White polyester fabric was attached to dyed fabric prior to heat treatment. During heating dye molecules migrated and then transferred from dyed fabric to adjacent white fabric. Color on white fabric was then measured and expressed as K/S value and indicative of color stain. The higher the K/S value, the poorer the heat fastness property. The results are shown in Table 4.19.

Obviously, dyed fabric without surface treatment gives highest K/S value on the stained fabric, indicating poor heat fastness. The K/S value of poly(HEMA-co-BEMA) modified dyed fabric decrease with increase concentration of the modifying agent. Higher degree of hydrophilic content (see 10% degree of functionalization) tends to prevent loss of dye. This is due to effective blocking property of hydrophilic surface to hydrophobic disperse dyes.



Table 4.18 Percent color change from K/S value

Hydrophilic : hydrophobic ratio	Concentration of modifying agent (% o.w.f.)	K/S at λ_{\max} 520 before hot-pressing treatment (A_1)	K/S at λ_{\max} 520 after hot-pressing treatment (A_2)	% color change
Unmodified	-	6.193	5.670	8.445
90 : 10	25	5.220	4.939	5.383
	50	5.467	5.209	4.719
	75	5.786	5.729	0.985
	100	6.996	6.971	0.357
80 : 20	25	5.287	4.966	6.071
	50	6.175	5.884	4.713
	75	6.669	6.49	2.684
	100	5.749	5.693	0.974
70 : 30	25	6.371	6.003	5.776
	50	5.159	4.922	4.594
	75	5.84	5.684	2.671
	100	6.557	6.489	1.037

Table 4.19 Color stain from K/S value

Hydrophilic : hydrophobic ratio	Concentration of modifying agent (% o.w.f.)	Color stain of white fabric, K/S at λ_{\max} 520
Unmodified	-	0.458
90 : 10	25	0.151
	50	0.144
	75	0.129
	100	0.125
80 : 20	25	0.153
	50	0.132
	75	0.128
	100	0.121
70 : 30	25	0.302
	50	0.208
	75	0.207
	100	0.206

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CHAPTER V

Conclusions

Results from this experiment may be concluded as follows :

1. Synthesized poly(HEMA-co-BEMA) exhibited hydrophilic and hydrophobic characteristics due to the presence of pendant hydroxyethyl groups as hydrophile and pendant benzoylethyl groups as hydrophobe.
2. The good stability of polymer dispersion in water medium is important in order to be applicable using solvent free system. This could be achieved by control of balance between hydrophilic and hydrophobic segments during synthesis.
3. The resulting polyester fabric treated with poly(HEMA-co-BEMA) using exhaust method showed improved water wettability compared to untreated fabric. Poly(HEMA-co-BEMA) with hydrophilic : hydrophobic ratio of 92.5 : 7.5 to 70 : 30 and their concentration of 25 % and 50 % (o.w.f.) exhibited optimum water wetness.
4. Scanning Electron Microscopic (SEM) results indicated that the attachment of poly(HEMA-co-BEMA) onto polyester fabric was durable. It was believed that hydrophobic segment could diffuse into fiber surface while hydrophilic segment on the fiber surface, resulting in firmed adherence.
5. Additionally, this compound could be used as color protection from heat. Improved heat fastness after surface treatment was attributed to blocking effect of hydrophilic surface on hydrophobic disperse dyes inside the fiber.

CHAPTER VI

Recommendations for future work

1. Solvent should be completely removed during purification of synthesized polymers by oven dry vacuum.
2. Synthesis of poly(HEMA-co-BEMA) by copolymerization of HEMA and BEMA should be investigated to compare with functionalization method.
3. To improve better water dispersion, more hydrophilic parts like acrylamide or acrylic acid should be added to the polymer.
4. Application parameters such as time, temperature, liquor ratio should be investigated.
5. Application by pad-dry-cure method should be included.

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Appendix

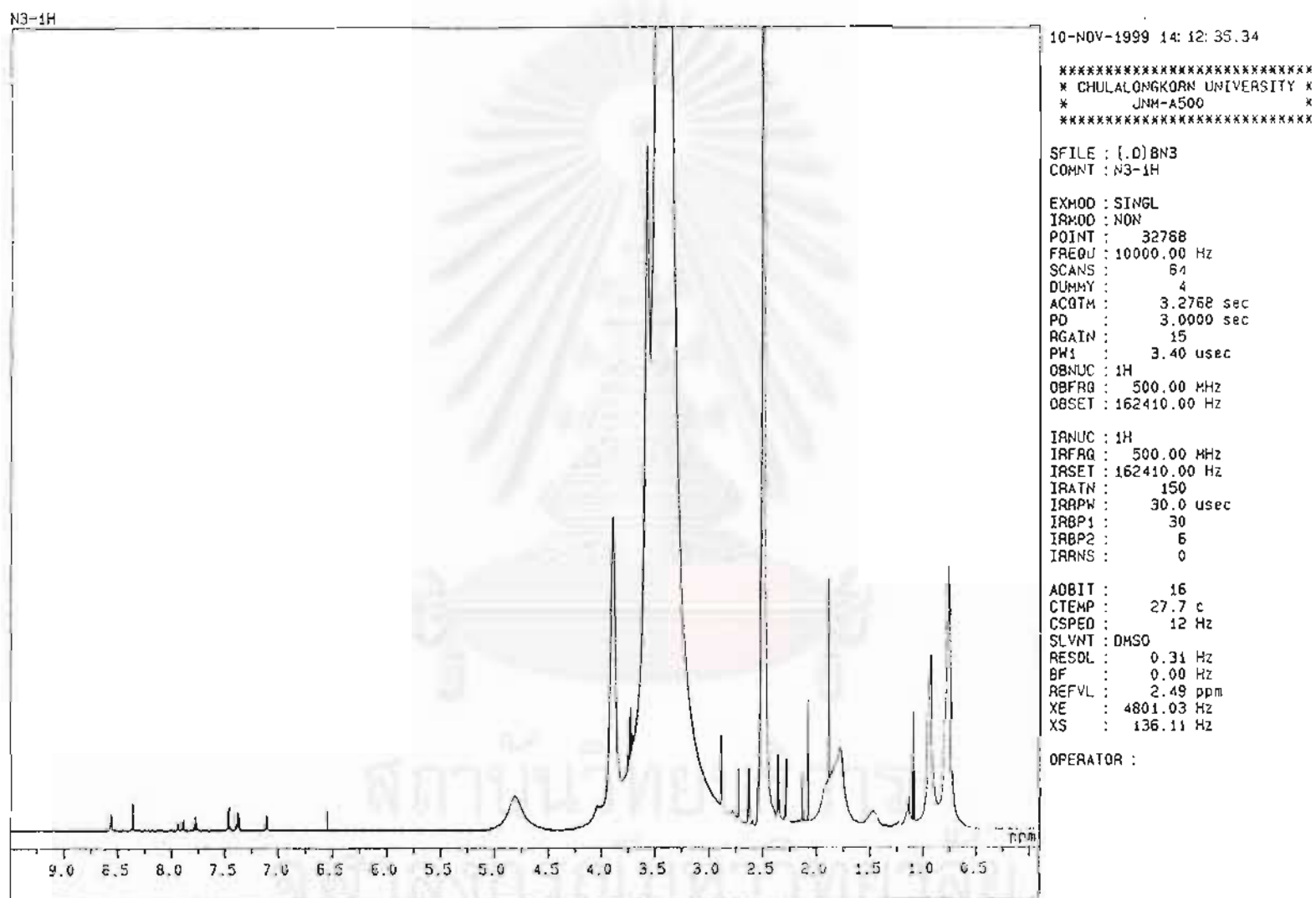


Figure A1 Poly(HEMA-co-BEMA) with the degree of functionalization at 5%

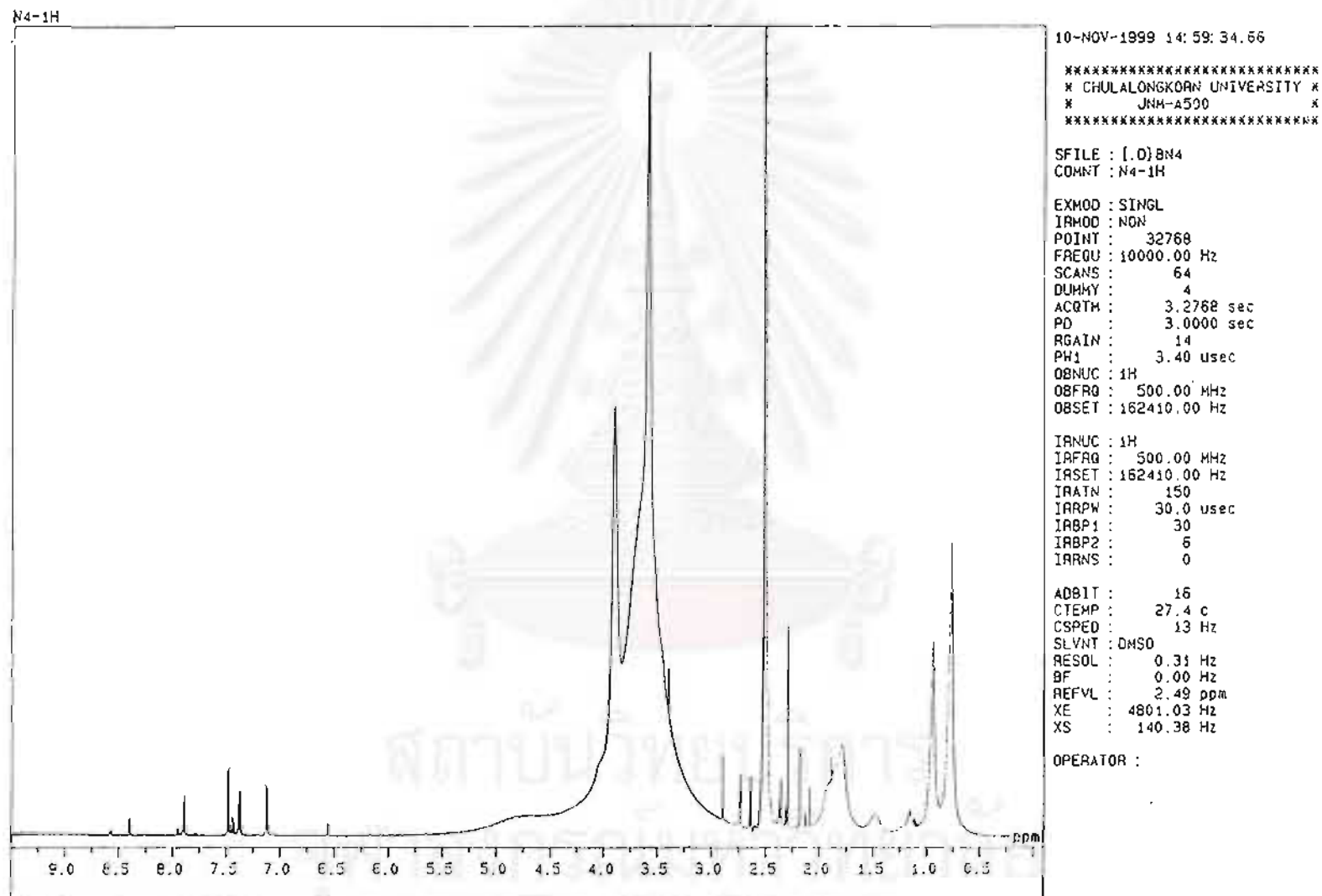


Figure A2 Poly(HEMA-co-BEMA) with the degree of functionalization at 7.5%

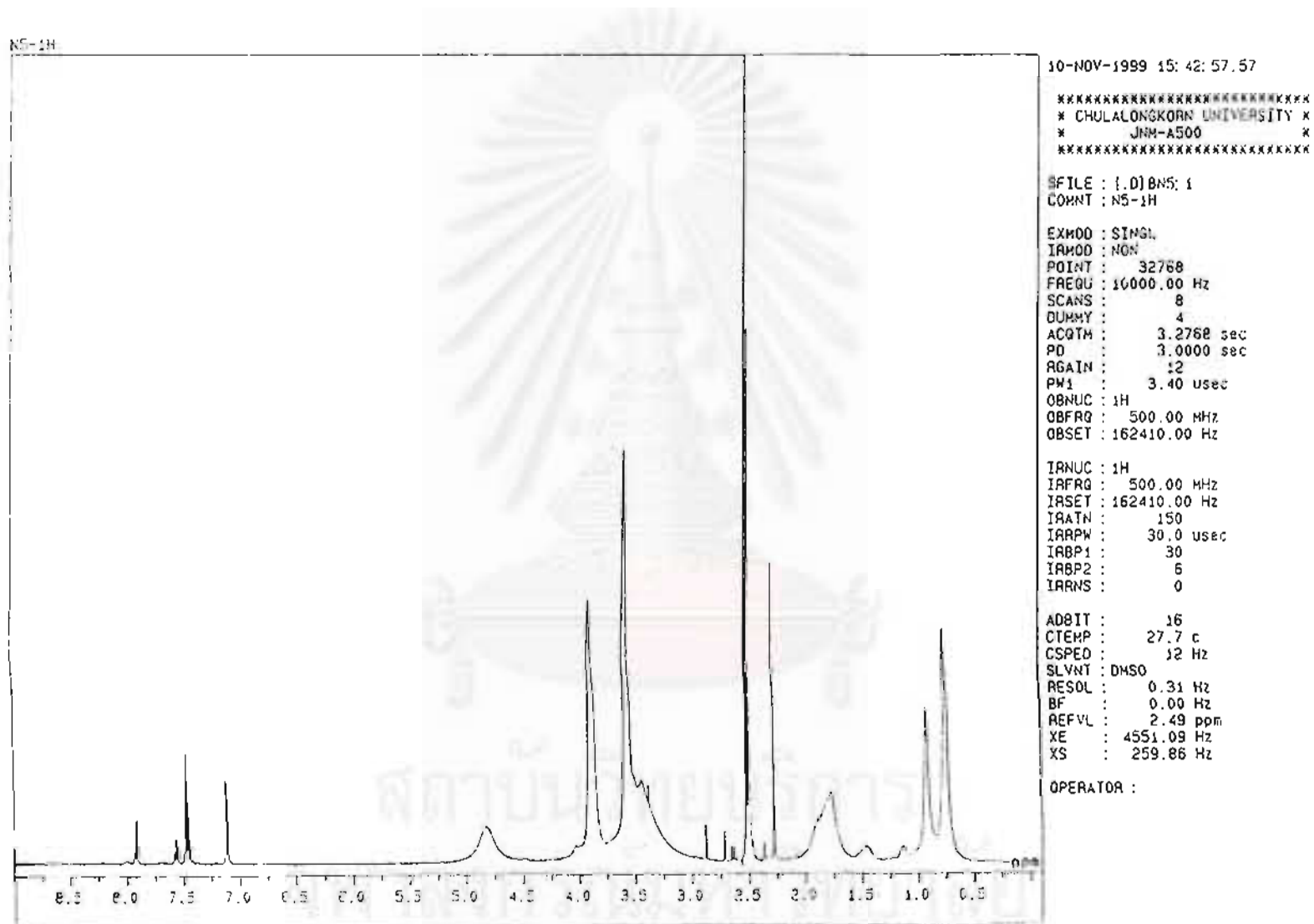


Figure A3 Poly(HEMA-co-BEMA) with the degree of functionalization at 10%

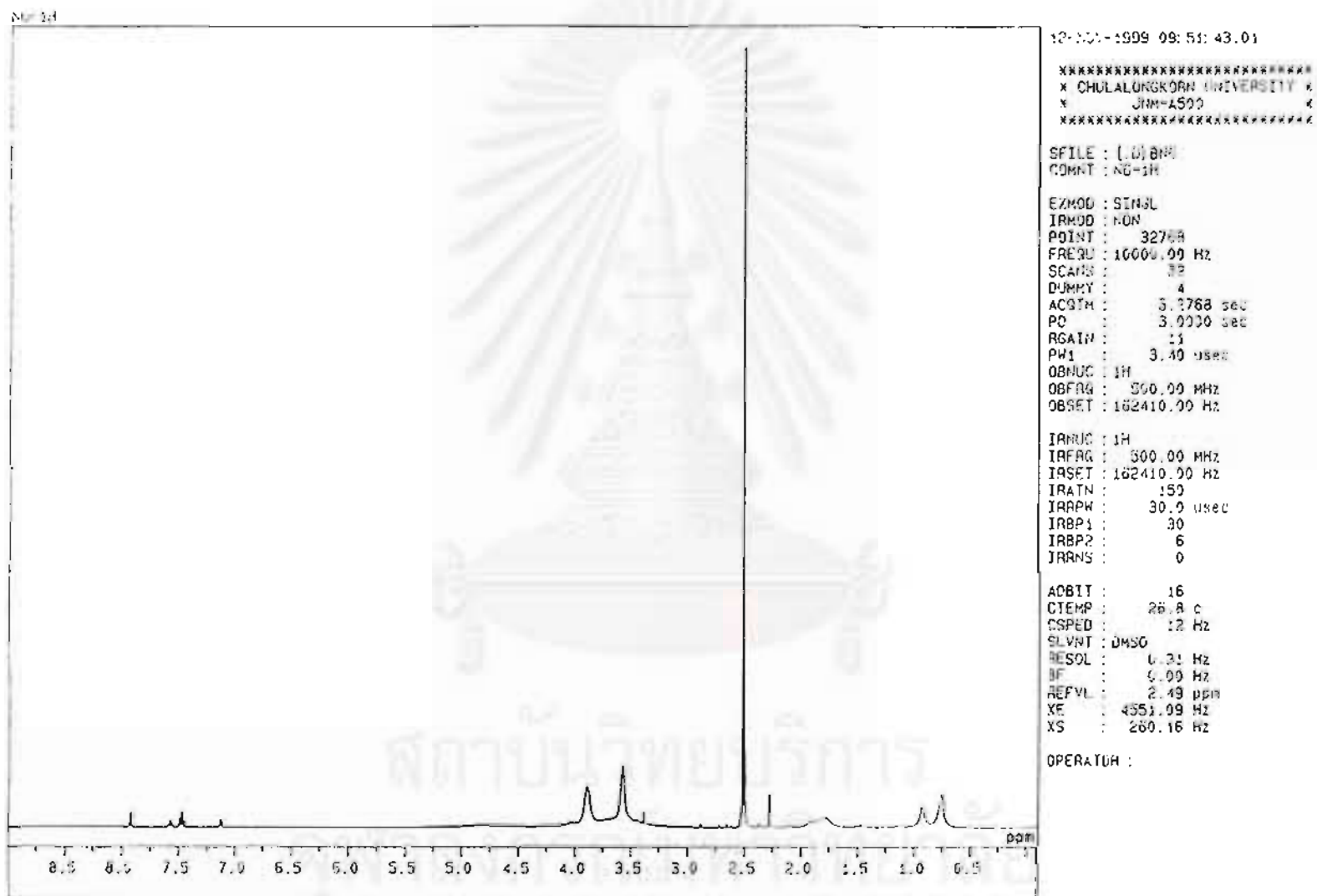


Figure A4 Poly(HEMA-co-BEMA) with the degree of functionalization at 20%

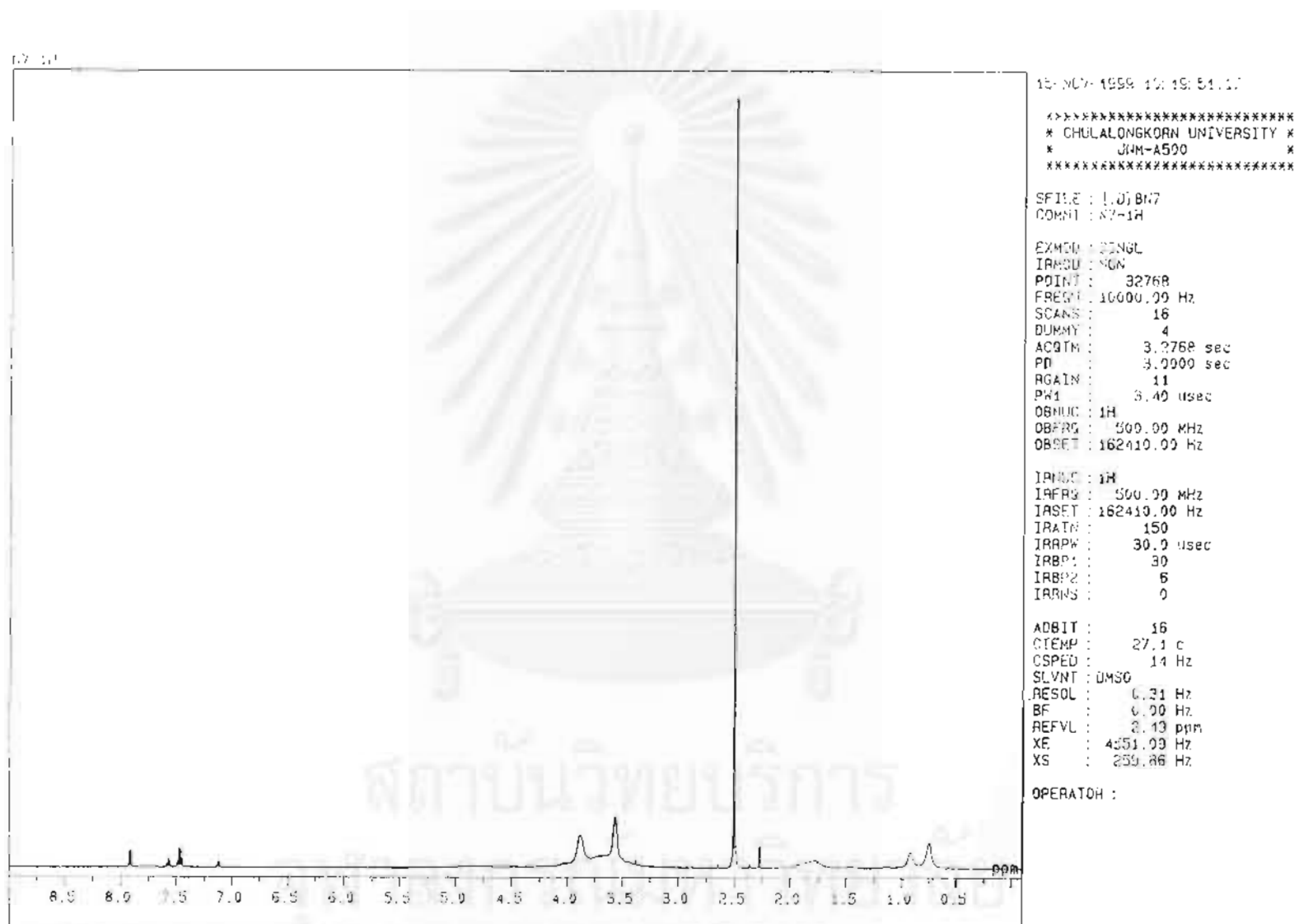


Figure A5 Poly(HEMA-co-BEMA) with the degree of functionalization at 30%

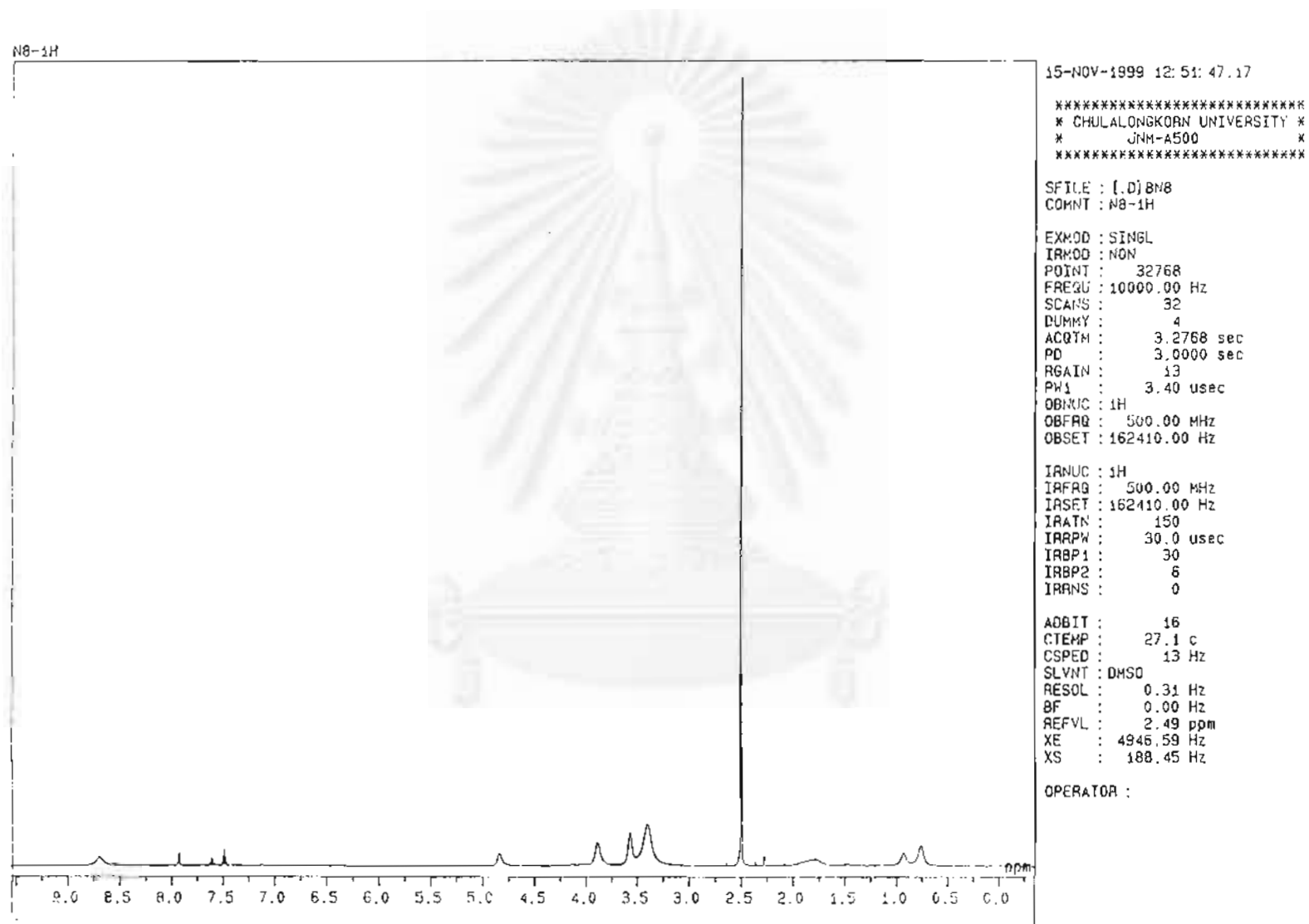


Figure A6 Poly(HEMA-co-BEMA) with the degree of functionalization at 40%

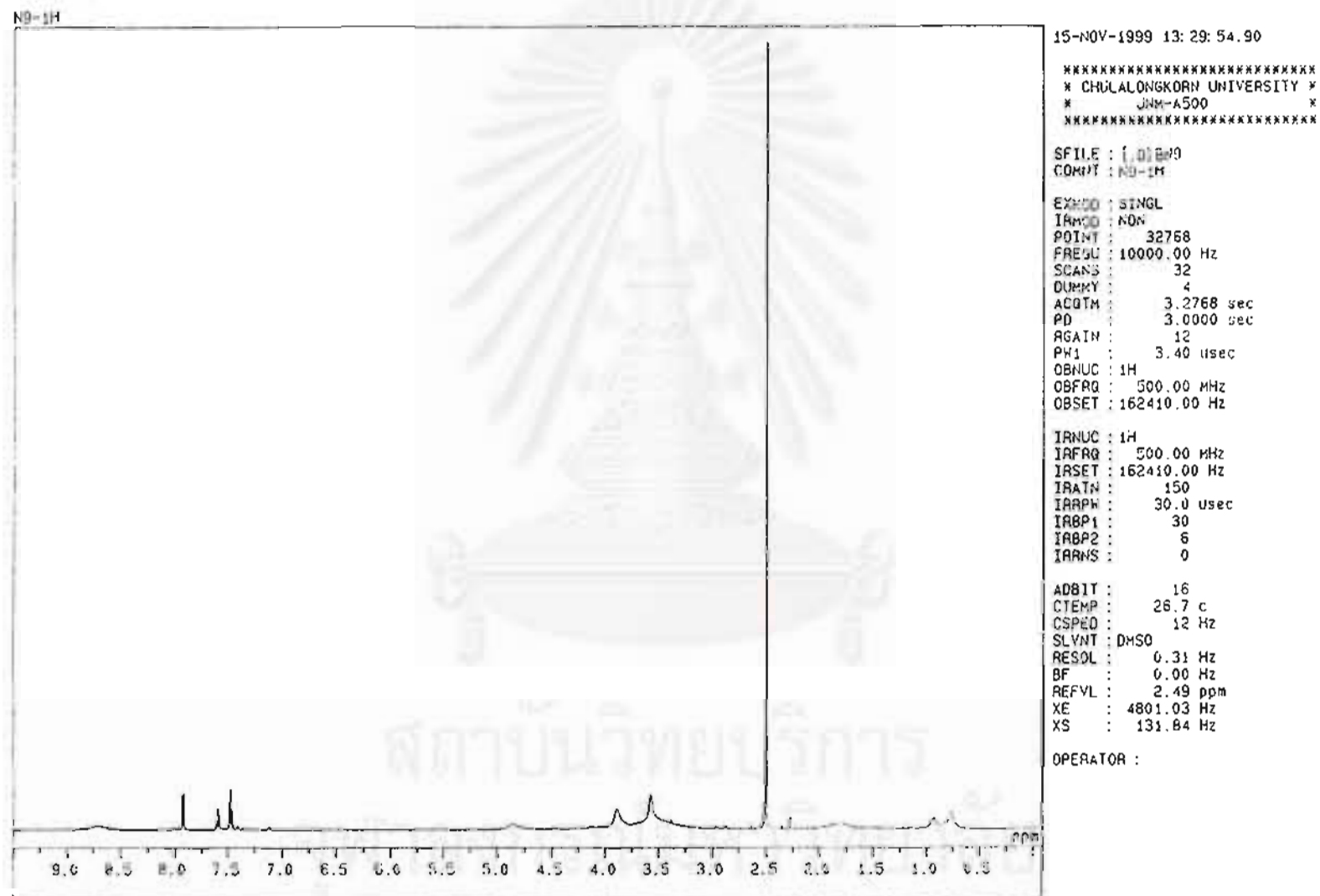


Figure A7 Poly(HEMA-co-BEMA) with the degree of functionalization at 50%

BIOGRAPHY

Miss Narumon Kanchanapinpong was born in Kanchanaburi, Thailand, on May 7, 1975. She received a Bachelor of Science degree with a major in Chemistry from Thammasat University in 1997. She started as a graduate student in the Department of Materials Science with a major in Applied Polymer Science and Textile Technology, Chulalongkorn University in November 1997, and completed the program in May 2000.

