การสังเคราะห์พอลิอีเทอร์พอลิออลกราฟต์ด้วยพอลิ(สไตรีน-*โค*-อะคริโลไนไตรล์-*โค*-ไฮดรอกซีเอทิลเมทาคริเลต)

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SYNTHESIS OF POLYETHER-POLYOL GRAFTED WITH POLY(STYRENE-*CO*-ACRYLONITRILE-*CO*-HYDROXYETHYL METHACRYLATE)

Miss Watcharee Khunwiwat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title SYNTHESIS OF POLYETHER-POLYOL GRAFTED WITH POLY(STYRENE-*CO*-ACRYLONITRILE-*CO*-HYDROXYETHYL METHACRYLATE)
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Field of Study Petrochemistry and Polymer Science
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กราฟต์พอลิ(สไตรีน-*โค*-อะคริโลไนไตรล์-*โค*-ไฮดรอกซีเอทิลเมทาคริเลต) บนพอลิอีเทอร์พอลิออลการค้า (polyol-g-PSAH) โดยกระบวนการเกิดพอลิเมอร์แบบอนุมูลอิสระ และใช้เบนโซอิลเปอร์ออกไซด์เป็นสารริเริ่มปฏิกิริยา เพื่อทำให้กราฟต์พอลิออลมีปริมาณไฮดรอกซิลสูงสำหรับใช้ในการสังเคราะห์โฟมพอลิยูรีเทน ยืนยันโครงสร้างของ polyol-g-PSAH ด้วยนิวเคลียร์แมกเนติกเรโซแนนซ์ (NMR) ฟูเรียทรานสฟอร์มอินฟราเรด (FTIR) และโครมาโทกราฟีแบบซึมผ่านเจล (GPC) ผลิตภัณฑ์ที่ได้มีลักษณะเป็นคอลลอยด์สีเหลืองอ่อน ความหนืดและขนาดอนุภาคของคอลลอยด์อยู่ในช่วง 2,200–19,000 เซนติพอยส์ และ 0.18-0.71 ไมโครเมตร ตามลำดับ การเพิ่มความเข้มข้นของไฮดรอกซีเอทิลเมทาคริเลต (HEMA) ทำให้ความหนืดและขนาดอนุภาคที่ได้ลดลง โดยความเข้มข้นของสารริเริ่มปฏิกิริยาที่ให้ความหนืดของพอลิเมอร์พอลิออลเหมาะสมที่สุดคือ 6 โมลเปอร์เซ็นต์ (mol%) อุณหภูมิในการทำปฏิกิริยาที่สูงทำให้อนุภาคมีขนาดเล็กและความหนืดสูง จากผลการศึกษาปัจจัยที่มีผลต่อการกราฟต์พบว่า ความเข้มข้นของ HEMA และสารริเริ่มปฏิกิริยาที่สูงจะทำให้ประสิทธิภาพการกราฟต์ของ St/AN/HEMA สูงและปริมาณโฮโมพอลิเมอร์ต่ำ อุณหภูมิในการทำปฏิกิริยาที่ให้การกราฟต์ PSAH สูงคือ 115 องศาเซลเซียส การใช้ปริมาณพอลิเมอร์พอลิออล 50 เปอร์เซ็นต์โดยน้ำหนักทั้งหมดของพอลิออลในการสังเคราะห์โฟมพอลิยูรีเทนชนิดยืดหยุ่น (FPU) แสดงความทนแรงอัดได้สูง (240 กิโลปาสคาล) ขณะที่ความหนาแน่นของโฟม FPU ยังอยู่ในระดับเดียวกับโฟมที่ไม่ได้ผ่านการดัดแปร

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..

ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..........................

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WATCHAREE KHUNWIWAT: SYNTHESIS OF POLYETHER-POLYOL GRAFTED WITH POLY(STYRENE-CO-ACRYLONITRILE-CO-HYDROXYETHYL METHACRYLATE. ADVISOR: ASST. PROF. VARAWUT TANGPASUTHADOL, Ph.D., 69 pp.

Poly(styrene-*co*-acrylonitrile-*co*-hydroxyethyl methacrylate) (polyol-g-PSAH) was grafted onto commercial polyether polyol via radical polymerization using benzoyl peroxide (BPO) as initiator to produce the grafted polyol having high hydroxyl group contents for making polyurethane foam. The structure of polyol-g-PSAH was confirmed by NMR, FT-IR, and GPC. The product obtained was pale yellow colloid. The viscosity and particle size of colloid were in the range of 2,200–19,000 cPs and 0.18-0.71 μm, respectively. Increasing hydroxyethyl methacrylate (HEMA) concentration led to a decrease in its viscosity and particle size. The concentration of initiator that yielded the most appropriate viscosity is 6 mol%. At high reaction temperature afforded small particle size and high viscosity. Investigation of factors on grafting properties revealed that high concentration of HEMA and initiator afforded high grafting efficiency of St/AN/HEMA and low free homopolymer content. The optimum of reaction temperature to obtain high PSAH grafting was observed at 115°C. Using polymer polyol of 50% wt based on total polyol in synthesis of flexible polyurethane foam (FPU) showed high compression strength (240 kPa) while the density of FPU foam preserved at the same level with the unmodified foam.

Field of Study: Petrochemistry and Polymer Science Student's Signature ....
Academic Year: 2012 Advisor's Signature ....

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LIST OF ABBREVIATIONS

FPU	Flexible polyurethane
PU	Polyurethane
St	Styrene
AN	Acrylonitrile
HEMA	2-hydroxyethyl methacrylate
BPO	Benzoyl peroxide
PSAH	Poly(styrene-*co*-acrylonitrile-*co*-hydroxyethyl methacrylate)
NMR	Nuclear magnetic resonance spectroscopy
GPC	Gel permeation chromatography
SEM	Scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
OH	Hydroxyl group
°C	Degree Celsius
mg	Milligram
g	Gram
KOH	Potassium hydroxide
µm	Micrometer
α	Alpha
CCl_4	Carbon tetrachloride
%wt	Degree of weight
kGy	Kilogray
Da	Dalton
CN	Cyanide
cPs	Centipoise
$CHCl_3$	Chloroform
THF	Tetrahydrofuran
NCO	Isocyanate
h	Hour
min	Minute

s : Second

rpm : Round per minute

pbw : Part by weight

cm : Centimeter

cm^{-1} : Unit of wave number

KBr : Potassium bromide

$CDCl_3$: Deuterated chloroform

μL : Microliter

nm : Nanometer

mm : Millimeter

ppm : Parts per million (unit of chemical shift)

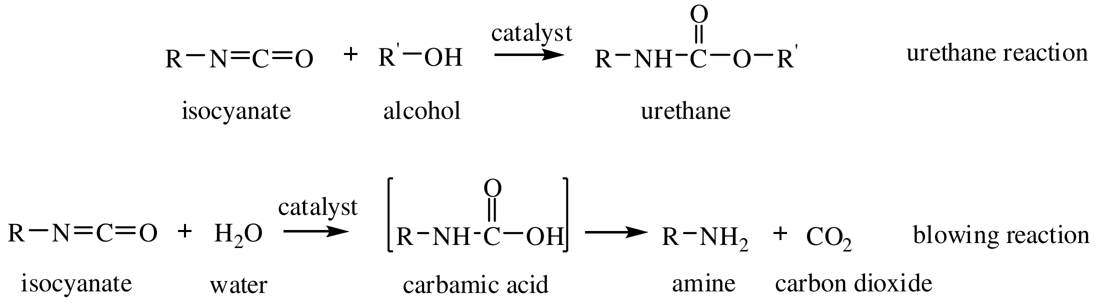
m^3 : Cubic meter

kPa : Kilopascal

CHAPTER I
INTRODUCTION

1.1 Statement of the Problem

Flexible polyurethane (FPU) foams are widely used in various applications for example furniture, mattresses, shoes, and automobile cushion [1]. The FPU foam is produced from the step growth polymerization of diisocyanate macromolecules with polyols, in the presence of blowing agent, catalyst, and other additives (Scheme 1.1).



$$\underset{\text{isocyanate}}{R-N=C=O} + \underset{\text{alcohol}}{R'-OH} \xrightarrow{\text{catalyst}} \underset{\text{urethane}}{R-NH-\overset{\overset{O}{\|}}{C}-O-R'} \qquad \text{urethane reaction}$$

$$\underset{\text{isocyanate}}{R-N=C=O} + \underset{\text{water}}{H_2O} \xrightarrow{\text{catalyst}} \underset{\text{carbamic acid}}{\left[R-NH-\overset{\overset{O}{\|}}{C}-OH\right]} \longrightarrow \underset{\text{amine}}{R-NH_2} + \underset{\text{carbon dioxide}}{CO_2} \qquad \text{blowing reaction}$$

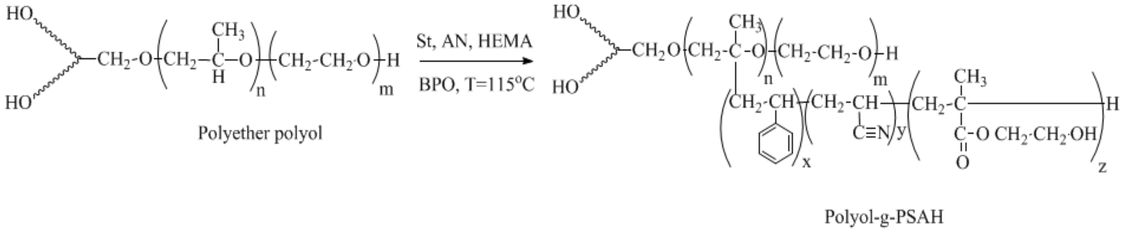
Scheme 1.1 Reaction for preparation of PU foam

The production of FPU foam has been intensively developed in the past years. Reinforcement of FPU foam can be achieved by adding inorganic fillers such as barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and silica (SiO_2) [2]. However, this type of filler promotes an increase in density, permanent deformation, and reduces the resilience of PU foam [3-5]. Therefore, one approach to increase mechanical properties with relatively low foam density is by using organic fillers [6]. These organic fillers are in fact 'polymers' which are grafted onto the polyol part, producing 'polymer polyols'. The polymer polyol is generally mixed with polyols and diisocyanate in the process of FPU foam formation.

The polymer polyol is defined as very fine and stable dispersions of solid polymers in liquid polyether that is synthesized by grafting via radical polymerization of vinyl monomer on polyether. The polymer polyol has many advantages including improving cell opening of foam by destruction of cell membrane during the foam rise and reducing the post-crushing processes [7,8]. It was also reported that polymer polyol was easier to be mixed and disperse in polyol than the inorganic filler [9]. Styrene (St) and acrylonitrile (AN) monomers are most frequently used for grafting polyether polyols. Both monomers are widely used thermoplastic and have excellent properties such as solvent resistance, thermal stability, good transparency, various methods of synthesis, and reproducible composition control [10,11]. Considering that the grafted styrene/acrylonitrile chains do not participate in urethane bonding, it is therefore worth exploring that additional hydroxyl groups on the grafted vinyl polymers would be able to increase the number of linkage between polyol and diisocyanate parts. This should lead to an increase of foam density and thus its mechanical properties can be improved.

This work focused on increasing hydroxyl functional groups (-OH) on the grafted polymer chains with the aim to increase urethane linkages on a single polymer polyol molecule via the reaction between the hydroxyl and isocyanate groups. It was believed that this process would also increase the strength of the PU foam. Hydroxyethyl methacrylate (HEMA) was the selected vinyl monomer to be used for grafting with the conventional styrene and acrylonitrile. HEMA is seen to serve in numerous applications such as hydrogels, controlled drug release, cell adhesion, biosensors, and coating industry [12, 13].

In the present work, polyether polyol grafted with poly(styrene-*co*-acrylonitrile-*co*-hydroxyethyl methacrylate) (polyol-g-PSAH) was prepared via *in situ* radical polymerization initiated by benzoyl peroxide (BPO) (Scheme 1.2).



Scheme 1.2 A representative structure of polyol-g-PSAH

1.2 Research Objectives

The aim of this work is to graft St, AN, and HEMA onto commercial polyether polyol via radical polymerization. The chemical structure, morphology, viscosity, and average particle size of the obtained polymer polyol were investigated. Preparation of FPU foam with the obtained polymer polyol was also studied. It is expected that the mechanical properties of FPU foam would also be increased with the increased hydroxyl groups on the polymer polyol.

1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature survey for method to synthesize polyol-g-PSAH
2. Literature survey for separation of polymer polyol components
3. Literature survey for method of synthesize FPU foam
4. Synthesis of polyol-g-PSAH via radical polymerization. Parameters to be investigated are as follows:
    - HEMA monomer contents (0, 1, 3.6, and 5 mol/mol polyol)
    - Reaction temperature (100, 115, and 130°C)
    - Initiator concentration (6, 11, and 22 mol%)
5. Separation of the polymer polyol components by column chromatography
6. Investigation of the chemical structure of polyol-g-PSAH by using ^{1}H NMR, FTIR and GPC
7. Characterization of the physical properties of polymer polyol (viscosity, morphology, OH number, and average particle size)
8. Preparation of FPU foam
9. Determination of the density and compression strength of FPU foam
10. Result interpretation and summary

CHAPTER II

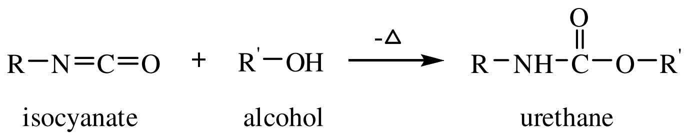
THEORY AND LITERATURE REVIEWS

Nowadays, product of flexible polyurethane (FPU) foam is becoming increasingly important because of its excellent lightweight, easy processing, low cost, and superior comfort characteristics [14,15]. The FPU foam can be divided into two major types that are slabstock and molded foams. Slabstock foams are used in furnishing industry such as mattresses, furniture, and carpet. Molded foams are used in transportation applications such as bumpers, sun visors, and automotives seating [1,8]. The FPU foam is produced from reaction of isocyanate with alcohol, blowing agent, catalyst, and other additives. The two competing reactions (polymerization and gas-producing reaction) are discussed below.

2.1 Principle Chemistry of PU foams

2.1.1 Polymerization Reaction

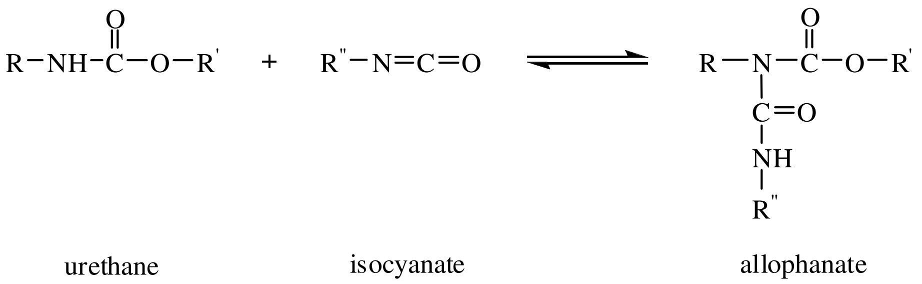
The polymerization reaction is urethane reaction or gelling reaction which is the reaction of isocyanate with hydroxyl groups of polyol (Scheme 2.1). Its heat of reaction is roughly 24 kcal/mol of urethane [7]. This reaction provides urethane bonding between the two parts creating crosslinked polymers.



$$R-N=C=O \;+\; R'-OH \xrightarrow{-\Delta} R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

Scheme 2.1 Urethane reaction [7]

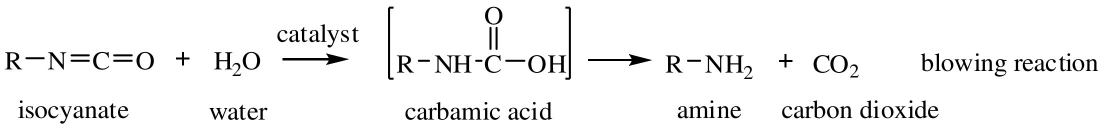
The hydrogen on the nitrogen atom of urethane group is capable of reacting with another isocyanate to form an allophanate group as shown in Scheme 2.2. The formation of allophanate is a reversible reaction and occurring at high temperature. The allophanate linkage can increase crosslink in the polyurethane systems.



Scheme 2.2 Allophanate reaction [7]

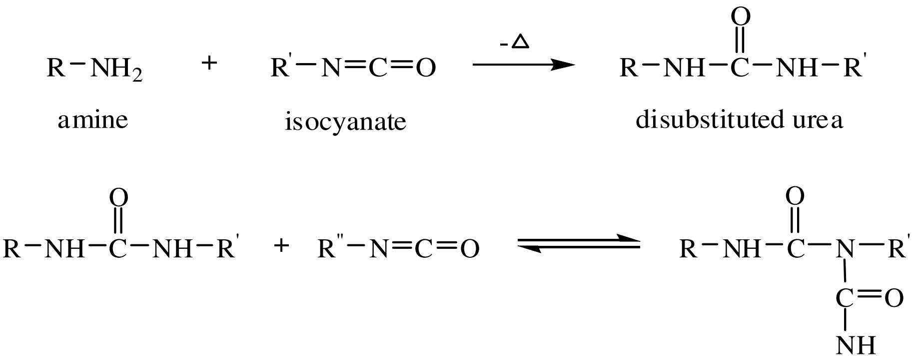
2.1.2 Gas-Producing Reaction

A polymer must be expanded or "blown" by introduction of bubbles and gas to make foam. This blowing reaction occurs as water reacting with the isocyanate (Scheme 2.3). Initially, unstable carbamic acid is formed and then decomposes spontaneously to an amine and carbon dioxide, which expands the polymer into the foam form. In some formulations, a low boiling point blowing agent such as hydrofluorocarbon and trichloroethane is also used to aid gas bubble formation.



Scheme 2.3 Blowing reaction [7]

Further reaction of the amine with another isocyanate gives symmetric urea. The reaction of hydrogen from the disubstituted urea is reacted with free isocyanate group to form a biuret linkage (Scheme 2.4).



Scheme 2.4 Symmetric urea and biuret reactions [7]

The process of FPU foam requires kinetic control over these two competing reactions. If the urethane reaction is faster than the blowing reaction, then formed polymer network will likely entrap the gas and suppress bubble formation. If the blowing reaction is much faster than the urethane reaction, foam will likely to collapse early on [8]. Therefore, the manufacture finds a kinetic balance point for the foaming.

2.2 Polyols

Polyol is an alcohol containing more than two hydroxyl group (-OH) in chain. Processing and properties of the PU foam can be affected by the choice of starting polyol structure. The most polyol used in polyurethane production is polyether polyol and polyester polyol in Figure 2.1. Currently, most commercial polyol used for FPU foam manufacture is polyether polyol. Polyether polyol is mostly used about 90% and the remain is polyester polyol [16,17]. The advantages of polyether polyol are more comfortable and durable than polyester polyol because the ester bond is more susceptible to hydrolysis than the ether bond.

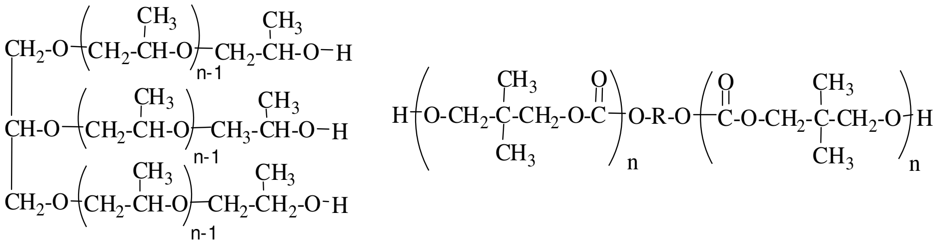
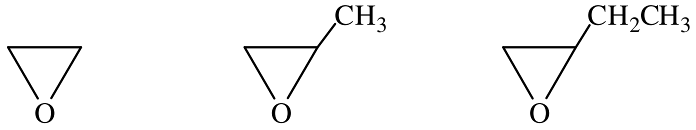


Figure 2.1 Examples of polyether polyol (left) and polyester polyol (right)

2.2.1 Polyether polyol

The polyether polyol used in FPU foam has low functionality (2-3 OH group/mol), OH number range of 28-160 mg KOH/g and molecular weight in the range of 1,000-6,500 Da [18,19]. Polyether polyol can be synthesized by anionic polymerization of alkylene oxide, initiator compound containing two or more active hydrogen atoms and catalyst such as potassium hydroxide (KOH), sodium hydroxide (NaOH), and cesium hydroxide (CsOH) [20]. The alkylene oxides used in synthesis of FPU foam are propylene oxide (PO), ethylene oxide (EO), and butylene oxide (BO) or mixtures of two or more of these (Figure 2.2). The major structure of polyether polyol is copolymer of PO and EO [17]. Initiator is reacted with alkylene oxide monomer by ring-opening reaction and the polymerization process propagates is continued until the desired molecular weight is obtained. To terminate by adding water or acids to obtain hydroxyl at the end chain (Scheme 2.5). If the initiator is two active hydrogen atoms, a diol result. If the initiator contains three active hydrogen atoms, a triol is obtained. The commonly initiators used in the synthesis of polyether polyol are shown in Table 2.1.

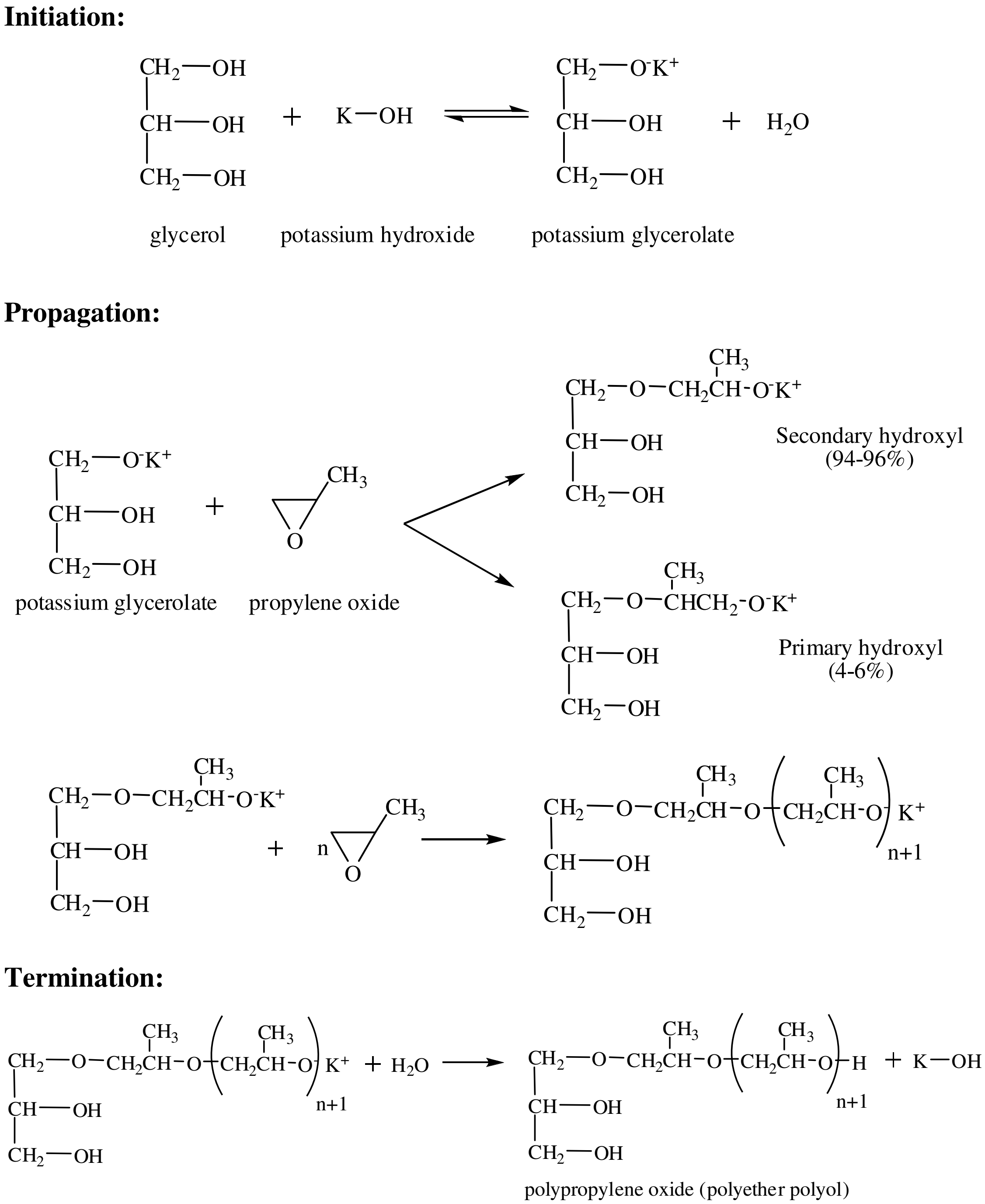


Ethylene oxide (EO) Propylene oxide (PO) Butylene oxide (BO)

Figure 2.2 Chemical structures of alkylene oxide

Table 2.1 Initiators commonly used for polyether polyol synthesis [4]

Initiator	Functionality
Aliphatic Initiators	
Glycols	2
Glycerol	3
Trimethylolpropane	3
Pentaerythritol	4
Amine initiators	
Alkanolamines	3
Ethylene diamine	4
Diethylene triamine	5
Mannich bases	3-7
Carbohydrate source	
Sorbitol	6
Sucrose	8



Scheme 2.5 Synthesis of polyether triol base on glycerol [4]

2.2.2 Graft copolymerization of polyether polyol

Polyether polyol can be modified by grafted with organic polymers. It is known as polymer polyol. The polymer polyol was synthesized from grafting of monomers on polyether polyol via chain radical or step polymerization [7]. The colloid particles are stable dispersion in polyether media. The stability of dispersion obtained by the hydrophobic vinyl polymer part is absorbed and/or chemically built in the particle surface while the hydrophilic polyether part reaches out in the surrounding polyol phase providing a protective shield against coagulation [21] (Figure 2.3). The stabilization of particle dispersion in polyether is based on the principles of steric stabilization [4]. When two particles approach to collapse, the polymeric chains may overlap or compressed [22,23], resulting in the area increase of polymer concentration and osmotic pressure spontaneously appears which the two particles are not to collapse. Mechanism of steric stabilization is shown in Figure 2.4. The solid polymer particle helps increasing the mechanical properties of FPU foam, probably due to the supplementary secondary forces resulting from the interaction between the solid polymer particles and the PU matrix [3].

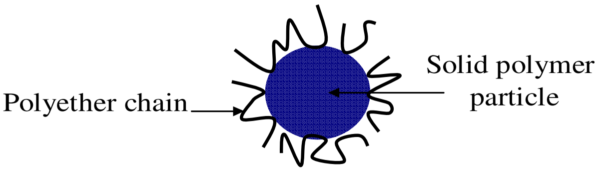


Figure 2.3 A particle formed by the polymer polyol

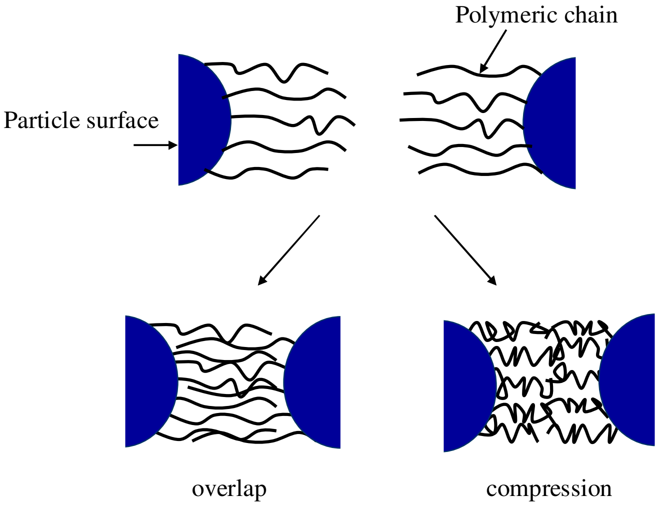


Figure 2.4 Mechanism of steric stabilization: overlap or compression [23]

The following reaction in Scheme 2.6 is proposed for the graft polymerization of vinyl monomer onto polyether polyol. The initiator produce the radicals (I•). The radical might interact with either monomer or polyether polyol, which initiated grafting sites. The H atoms situated in the α-position (-C<u>H</u>-O-) of polyether polyol chain are very susceptibility to radical attack, to become the sites of graft copolymerization [3].

Initiation reaction

$$I{-}I \xrightarrow{\Delta} I^{\bullet} + I^{\bullet}$$

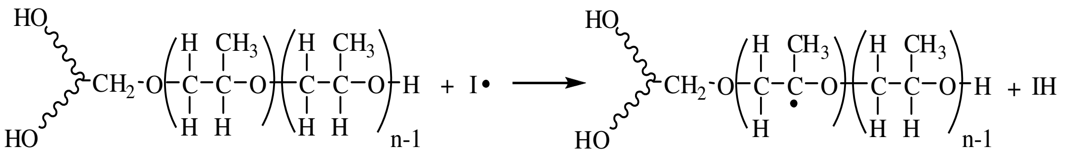
Monomer attack:

$$CH_2{=}\underset{R}{CH} + I^{\bullet} \longrightarrow I{-}CH_2{-}\underset{R}{CH}^{\bullet}$$

vinyl monomer

vinylic monomer radical

Polyether polyol attack:



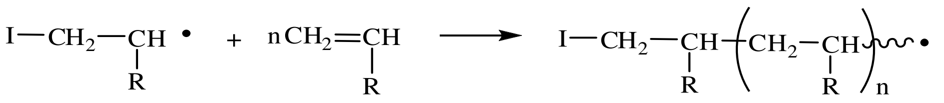
polyether polyol

polyetheric radical

Propagation reaction

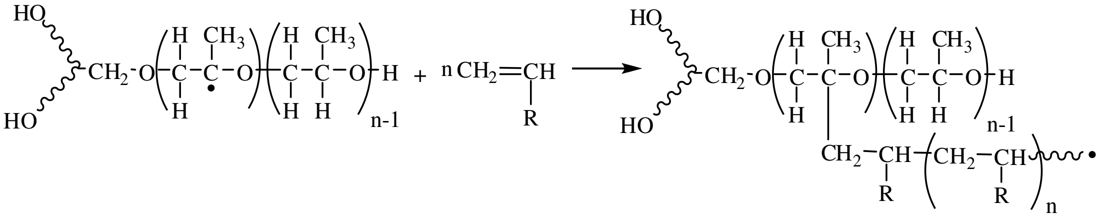
The radical (I•) can attack the α-position of polyether to produce polyetheric radicals that initiate monomers to form the graft copolymers and can also initiate monomers to form free homopolymer radicals.

Propagation of homopolymer:



$$I{-}CH_2{-}\underset{R}{CH}^{\bullet} + n\,CH_2{=}\underset{R}{CH} \longrightarrow I{-}CH_2{-}\underset{R}{CH}{-}\left(CH_2{-}\underset{R}{CH}\right)_n\!\sim\!\sim^{\bullet}$$

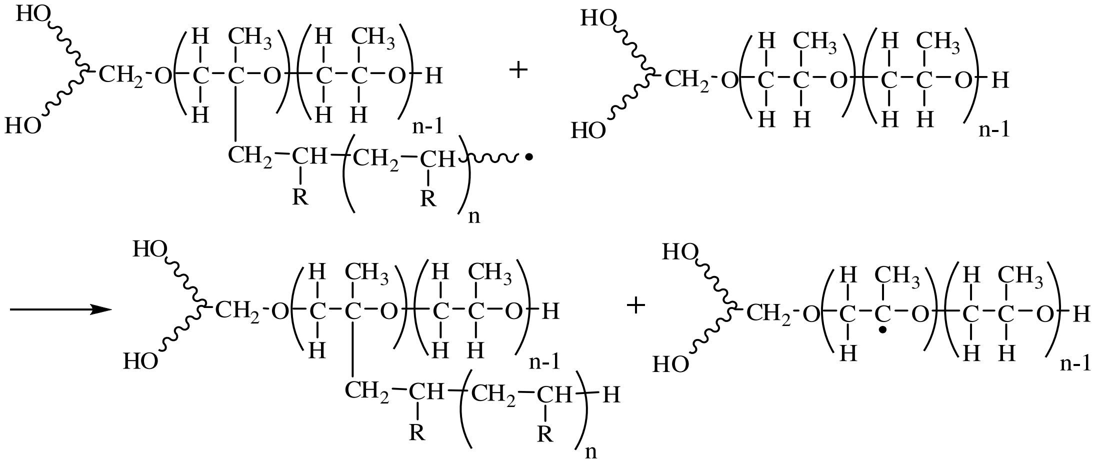
Propagation of graft polymerization:



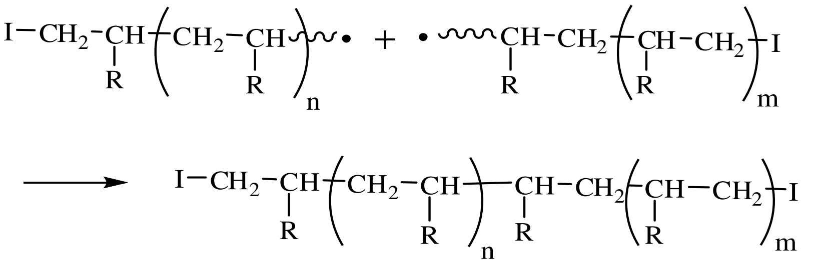
Termination

The product of the graft copolymerization is composed of graft copolymers and free homopolymer.

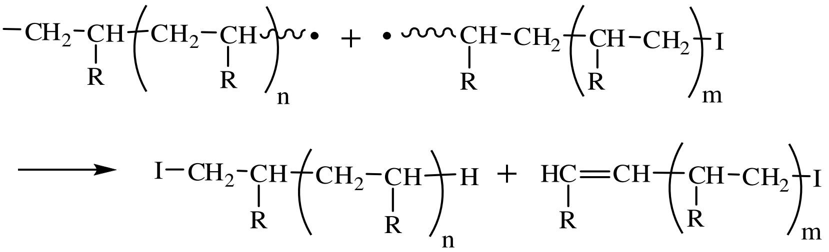
Termination by transfer:



Termination by recombination (coupling of two macroradicals):



Termination by disproportionation:



Scheme 2.6 Mechanism of graft polymerization of vinyl monomer onto polyether polyol

Other grafting method such as by gamma radiation (RKhM-γ-20 unit with ^{60}Co) from Fenin *et al.* [24] was also reported for the styrene grafting on polyol. The grafting on polyol was carried out by irradiation of mixture with 10-40%wt with dose of 10-30 kGy. The product was extracted with isopropyl alcohol and then the precipitate was dried and dissolved in CCl_4. Structures of the polymer polyol was confirmed by IR and NMR. Moreover, the polymer polyol had lower viscosity compared to the initial compound, which is an advantage for the synthesis of polyurethane.

2.2.2.1 Materials

Polyether polyol

The suitable polyether polyol used in synthesis of polymer polyol has molecular weight in the range of from 2,000-14,000 Da and an average functionality at least 2.0. The OH number of polyol has a value of from 25-75 mgKOH/g [25]. Example of favorite polyols include CARADOL SC 36-13, CARADOL SC 56-02, CARADOL SC 36-11 and CARADOL MH 56-03 (CARADOL is a trademark).

Initiators

The initiator was used for the formation of polymer polyol for example peroxide, persulfates, percarbonates, and azo compound. The free radical initiator is usually applied in amount of 0.01-5%wt base on total weight of monomer [26]. Examples of peroxides are benzoyl peroxide, lauroyl peroxide, t-butyl hydroperoxide, and di-t-butylperoxide. Examples of suitable azo compounds are azobis (isobutyronitrile) and azobis(2-methylbutyronitrile).

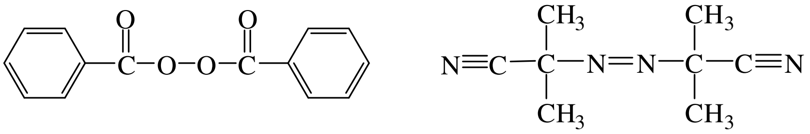


Figure 2.5 Chemical structures of benzoyl peroxide (left) and azobis(isobutyronitrile) (right)

Vinyl monomers

The primary vinyl monomer used in commercial polymer polyol is acrylonitrile (AN) (Figure 2.6). Unfortunately, AN has a disadvantages when used alone in grafting. The products are light brown-yellow color and appear ‘scorching’ in the foaming process [27,28]. This scorch phenomenon is the formation of chromophoric groups due to an intramolecular cyclization of two or more CN groups lead to conjugate polycycloiminic polymer as shown in Scheme 2.7. Thus, the grafting of polyether polyol is avoided by using comonomer such as styrene (St), methyl methacrylate, vinyl chloride, and others. The comonomer is help separation of AN structural units, then phenomenon of intramolecular cyclization is not occur.

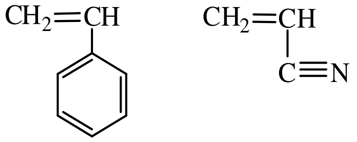
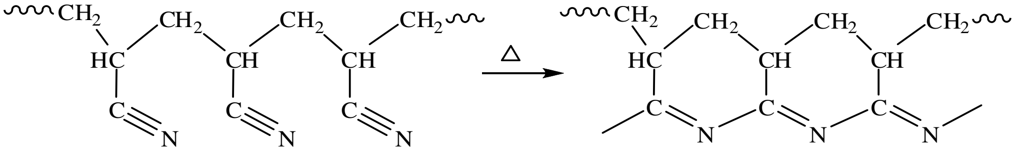


Figure 2.6 Chemical structures of styrene (left) and acrylonitrile (right)



Scheme 2.7 Polycycloiminic polymer of acrylonitrile [3]

Later, St monomer is an interesting choice for use as co-monomer with AN due to lower price. Furthermore, high St content in polymer polyol can improve color and less scorch in PU foam. In 1991, Alexander *et al.* [10] studied the catalysts and conditions to produce stable polymer polyol with the high St/AN ratio. They found that the reaction temperature in the range of 100-130°C and the peroxydicarbonate catalysts led to the stable polymer polyol. However, the ratio of St/AN more than 80/20 resulted in the unstable polymer polyol. In 1993, Simroth *et al.* [29] disclosed that the polymer polyol derived from high styrene content (e.g. about 65-70 %styrene) was unsatisfied in the market, which include stability and increased load bearing characteristics. It was found that it is difficult to make satisfied stable polymer polyol as the high St content. Moreover, polymer polyol with high load bearing characteristics was obtained by increasing of polymer content lead to undesirably high viscosity of polymer polyol. The viscosity of polymer polyol should be sufficiently low for easy of processing, handling and transport. Commercial polymer polyols should have viscosity below 10,000 cPs and preferably viscosity in the range of 2,000-6,000 cPs at ambient temperature, depending on the level of solid [10]. Researchers have been development of polymer polyol to prepare high stability, high polymer content (solid content), and low viscosity polymer polyol. The synthesis of polymer polyol has various methods by adding other additives as shown below.

In 1980, Priest *et al.* [30] synthesized polymer polyol by maintaining a low monomer to polyol ratio throughout the reaction mixture during the process which the diameter of polymer particles were obtained less than one micron. The half life of initiator was no longer than six minutes. The produced polymer polyol can help reduce the scorch of polyurethane foam. In addition, the tensile strength and tear resistance of the modified polyurethane foam with polymer polyol were higher than unmodified foam.

In 1996, Hayes *et al.* [31] prepared polymer polyol which had amount of solid content as 43 %wt by adding small amount of seed (only 1%wt of total feed). The seed is itself a polymer polyol. They were prepared by using the same as the condition for preparing the polymer polyol. The seed particles acted as a nucleus for growth. The particle size obtained by this method has quite broad distribution (Figure 2.7) as compared to polymer polyol prepared in the absence of the seed. This in fact could reduce its viscosity from 10,700 to 8,300 cPs. The particle size of the seed was in the range of 0.2-2 micron. The polymer particle size and distribution in polymer polyol depends on the amount of seed, solid content in the seed, and method of seed addition.

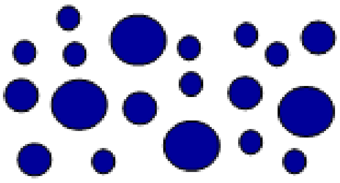


Figure 2.7 Broader distribution of polymer polyol particles can reduce viscosity

In 2003, Heyman *et al.* [32] disclosed the preparation of polymer polyol with solid content of 3-20%. The grafting was carried out by adding 'macromer' in the reaction. The macromer was synthesized by the linkage of glycerine-initiated polyol through coupling with maleic anhydride (Figure 2.8). It contained unsaturation about 0.4 mol/mol polyol which used in synthesis of polymer polyol was 0.1-1.0 mol/mol polyol. The addition of unsaturation into polyol was believed that improved stability resulted due to an increased amount of graft copolymer expected to be formed. Then the agglomerate of particles was decreased.

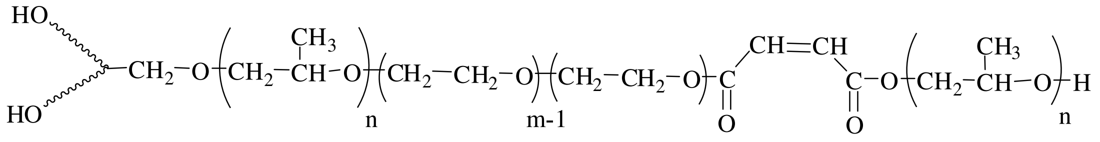


Figure 2.8 Structure of macromer

In 2006, Chauk *et al.* [33] successfully synthesized ultra-high solid polymer polyol which have good stability and low viscosity. The amount of solid content was 60-70%wt in product. It was prepared by using pre-formed stabilizer and chain transfer agent. The term pre-formed stabilizer is defined as an intermediate obtained by reacting macromer with monomers to give a copolymer as shown in Figure 2.9. The pre-formed stabilizer was used in the amount of at least 5%wt based on total weight of feed. The chain transfer agent, iso-propanol, was added in the amount of 6.6-9.5%wt based on total weight of feed to control the molecular weight of the copolymerization. The average particle size of polymer polyol obtained was less than 10 micron. The viscosity of produced polymer polyol was in the range of 14,000-94,000 cPs.

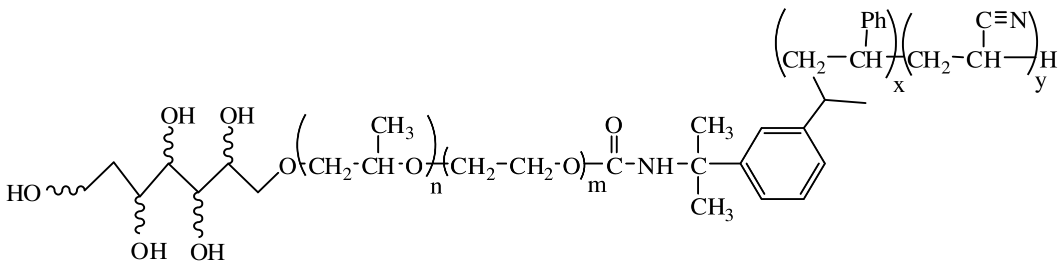


Figure 2.9 Example of structure of pre-formed stabilizer

Other references which describe synthesis of polymer polyol with pre-formed stabilizer for example U.S. patent No. 7,179,882 B2; Adkins *et al.* [1] , U.S. patent No. 7,960,496 B2; Choi *et al.* [34], U.S. patent No. 0041144 A1; Adkins *et al.* [35].

In 2010, Borst and Scheffler [36] studied chain transfer agent used in the synthesis of polymer polyol. They found that the chain transfer agent with carbon from 3 to 9 atoms and at least one thiol and hydrophilic (selected from the group of hydroxyl, amine and carboxyl) moiety effectively controlled the molecular weight and the size of polymer formed from the polymerization. In addition, the chain transfer agent had at least one hydrophilic moiety, and thus the grafted polyol was compatible with polyurethane to help reduce split and degradation on surface of polyurethane. Example of the chain transfer agent is showed in Figure 2.10. The amount of chain transfer agent used was 0.6-1.55 parts by weight per 100 parts by weight of monomer.

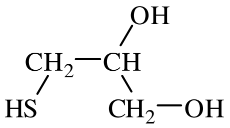
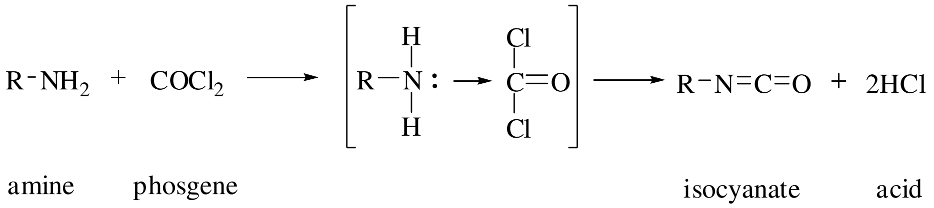


Figure 2.10 Example of structure of chain transfer agent; 3-mercapto-1,2-propanediol

In 2011, Van der wal *et al.* [37] presented method for synthesis of polymer polyol by melting polymer and then blend the molten polymer with polyol under shear. The shearing action breaks the molten polymer into small droplets which become dispersed in polyol phase. When cooling, a dispersion of polymer particles is formed. The polystyrene particles (35%wt solid content) had the average particle size of 4-8 micron and viscosity 6,300-7,400 cPs. Furthermore, they found that the produced foam provided good physical properties.

2.3 Isocyanate

Today, all isocyanates used in industry contain at least two NCO groups per molecule. The most commercially methods of synthesis of isocyanates involve amine phosgenation, as shown in Scheme 2.8



Scheme 2.8 Synthesis of isocyanate [7]

Industrially important diisocyanates include 2,4- and 2,6-toluene diisocyanate (TDI) and 4,4'-methylene diphenyl diisocyanate (MDI). More than 90% of FPU foam is based on TDI [7]. The chemical structures of diisocyanate are shown in Figure 2.11.

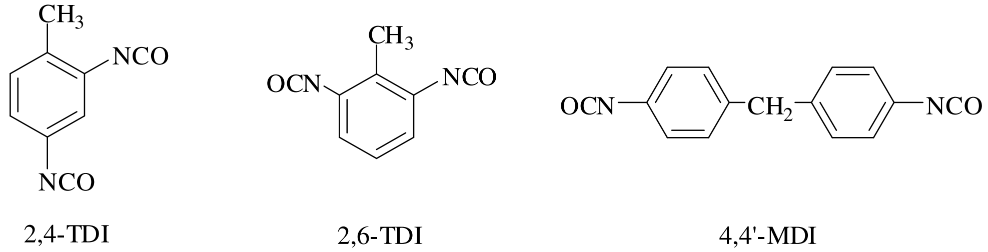


Figure 2.11 Structures of diisocyanates

2.4 Catalysts for PU formation

Catalyst plays an important role in the control and balance between urethane and blowing reaction. The mostly used catalysts for producing PU foam are tertiary amine and organometallic. Tables 2.2 and 2.3 show the applications of tertiary amine and organometallic. The selection of catalyst depends on its activity and performance on physical properties of foam.

Table 2.2 Tertiary amine catalysts and their applications [19]

Catalyst	Formula	Applications
1,4-diazabicyclooctoate (DABCO)	$N(CH_2CH_2)_3N$	All types of foams
N,N-dimethylethanolamine (DMEA)	$(CH_3)_2NCH_2CH_2OH$	Flexible and rigid foams
N,N-dimethylcyclohexylamine (DMCHA)	$C_6H_{11}N(CH_3)_2$	Rigid foams

Table 2.3 Organometallic catalysts and their applications [19]

Catalyst	Formula	Applications
Stannous octoate	$Sn(OCOC_7H_{15})_2$	Slabstock polyether-based FPU foams, molded FPU foams
Dibutyltin dilaurate	$(C_4H_9)_2Sn(OCO(CH_2)_{10}CH_3)_2$	Microcellular foams, elastomer, molding system
Lead octoate	$(C_7H_{15}COO)_2Pb$	Rigid spray foams
Potassium acetate	CH_3COOK	Isocyanurate foams

2.5 Blowing agents

Blowing can be achieved by physical addition of low boiling point liquid to foam formulation. The vaporization of liquid by heat from the exothermic reactions produces gas molecules which diffuse into the nucleated bubbles and contribute to foam expansion. The blowing agent can be divided into two types; chemical and physical blowing agent. The chemical blowing agent such as water expands foams by carbon dioxide gas from the reaction of water with isocyanate. The water level used in the formulation affects on the morphology, density and stiffness of FPU foam. On the other hand, physical blowing agents are cyclopentane, methylene chloride, and trichloroethane.

2.6 Surfactants

The most FPU foams are used with silicone based non-ionic surfactants. The structure of silicone surfactant is shown in Figure 2.12. Surfactants reduce the surface tension of polyol and promote the nucleation of bubbles during mixing. They stabilize the rising foam by reducing stress concentrations in thinning cell walls and prevent the coalescence of rapidly growing cells until those cells have sufficient strength through polymerization to become self-supporting [7]. Cell coalescence lead to total foam collapse. Then, these surfactants help to control the timing and the degree of cell opening.

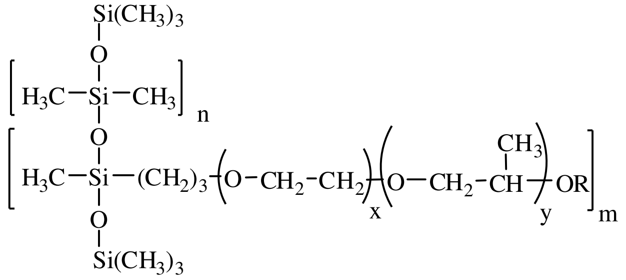


Figure 2.12 General structure of silicone surfactant [19]

CHAPTER III

METHODS AND MATERIALS

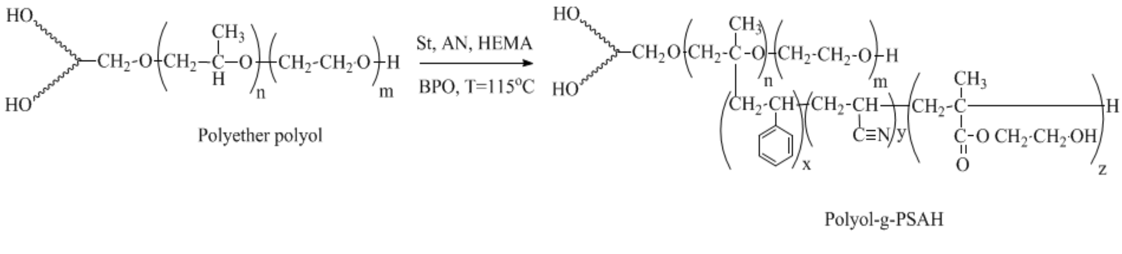
3.1 Materials

The commercial polyether polyol (KONIX®FA-703; hydroxyl number of 30-35 mgKOH/g, viscosity of 860-980 cPs at 25°C), acrylonitrile (AN) and dibenzoyl peroxide (BPO) were kindly supplied by IRPC Public Company Limited, Thailand. Styrene (St; Fluka), 2-hydroxyethyl methacrylate (HEMA; Aldrich), chloroform ($CHCl_3$; Labscan), tetrahydrofuran (THF; Labscan), methanol (Merck), sodium hydroxide (Merck), sodium sulfate anhydrous (Merck) were analytical grade. Silica gel 60 (70-230 mesh ASTM) and thin layer chromatography plates (TLC plates; silica gel 60, GF254) were used for separation of grafted polyol. Polyol (JEFFOL®G-31-35; hydroxyl number of 35 mgKOH/g, viscosity of 800-950 cPs at 25°C), distilled water (blowing agent), Dabco®EG catalyst (mixture of 33% triethylenediamine and 67% monoethylene glycol), Dabco®DC193 surfactant (industry standard silicone), monoethylene glycol (chain extender) and Suprasec®2499 prepolymer isocyanate (diphenyl methane diisocyanate (MDI); %NCO of 18.9) were used for synthesis of FPU foam.

St was purified by extracting twice with 10% sodium hydroxide to remove inhibitor then washing three times with distilled water and drying over sodium sulfate anhydrous. It can be stored in a refrigerator and kept anhydrous with molecular sieves. HEMA was purified by passing the monomer through a column of aluminium oxide and stored in a refrigerator.

3.2 Methods

3.2.1 Synthesis of polymer polyol [30]



Polyether polyol was loaded into a three-necked flask with an addition funnel and in/out of N_2 lines, followed by heating to temperature up to 115 ºC for 30 min to deoxygenate the polyether polyol. A homogeneous mixture of polyether polyol, BPO solution in chloroform, St, AN, and HEMA monomer (total monomer of 20% weight base on polyether polyol) was slowly added to the flask under N_2. The temperature was maintained at 115 ºC throughout the polymerization time of 30 min. The reaction mixture became opaque with pale yellow dispersed solids (Figure 3.1). The unreacted monomers were removed by vacuum at 120 ºC for 2 h. The conversion was determined by gravimetric method and calculated using following equation:

$$\text{Monomer conversion (\%)} = (W_1/W_0) \times 100 \tag{3.1}$$

$$\text{Solid content (\%)} = (W_3/W_4) \times 100 \tag{3.2}$$

where W_0 = weight of the initial monomer
W_1 = weight of the reacted monomer
W_3 = weight of dried solid polymer
W_4 = weight of polymer polyol colloid

Figure 3.1 Product of polymer polyol

The colloid product was precipitated by centrifugation at 10,000 rpm in methanol. This procedure was repeated three times to remove the polyether polyol (starting material) from grafted polyether polyol and free homopolymer. After each centrifugation step the methanol layer was collected and then evaporated to give a viscous liquid. The solid precipitate was vacuum-dried for 24 h.

3.2.2 Separation of the grafted polyether polyol [38]

The column chromatography was performed with a column of diameter 2 cm and length 16 cm packed with a porous silica gel in a suspension form in a solvent mixture of $CHCl_3$ and THF (ratio 4/1 w/w). The $CHCl_3$/THF mixture (4/1 w/w) was the first eluent. Then, THF was added to elute the grafted polyether polyol. And the last eluent was methanol to gather the remains of the grafted polyether polyol. Three fractions from each eluent were collected and dried by vacuum overnight before characterization.

3.2.3 Preparation of flexible polyurethane foam

All of FPU foams were prepared by two-shot methods at room temperature. Polyether polyol, synthesized polymer polyol, catalyst, surfactant, chain extender and blowing agent were homogeneously mixed (component A) by mechanical stirrer and speed at 2,000 rpm. Prepolymer isocyanate as a component B was quickly added to component A and the mixtures were vigorously stirred at 2,000 rpm for 10 second. Then the prepared mixture was poured into a paper cup. The reaction mixture was expanded in a vertical direction. Kinetic rate of polyurethane foam was investigated (cream time, gel time, rise time and tack free time). Tests were performed after the foam had aged for a minimum of 2 days. The formulations used for the preparation of FPU foam are presented in Table 3.1. The amount of each additive was calculated on 100 parts by weight of total polyol components or 1 gram in 100 grams of total polyol components.

Figure 3.2 Flexible polyurethane foam product

Table 3.1 Formulations for preparation of flexible polyurethane foam (part by weight, pbw)

Chemicals	Weight (g)
Polyether polyol	100, 90, 70, 50
Polymer polyol	0, 10, 30, 50
Total polyol components	100
Catalyst	0.5
Surfactant	0.5
Chain extender	5
Blowing agent	0.5
Prepolymer isocyanate*	68.97, 69.17, 69.62, 70.60

* The different OH number of polymer polyol in each formulation caused the need to use different amount of isocyanates to prepare the foams at the same isocyanate index (NCO index = 100).

The flow chart for experiment procedure was summarized and shown in Figure 3.3.

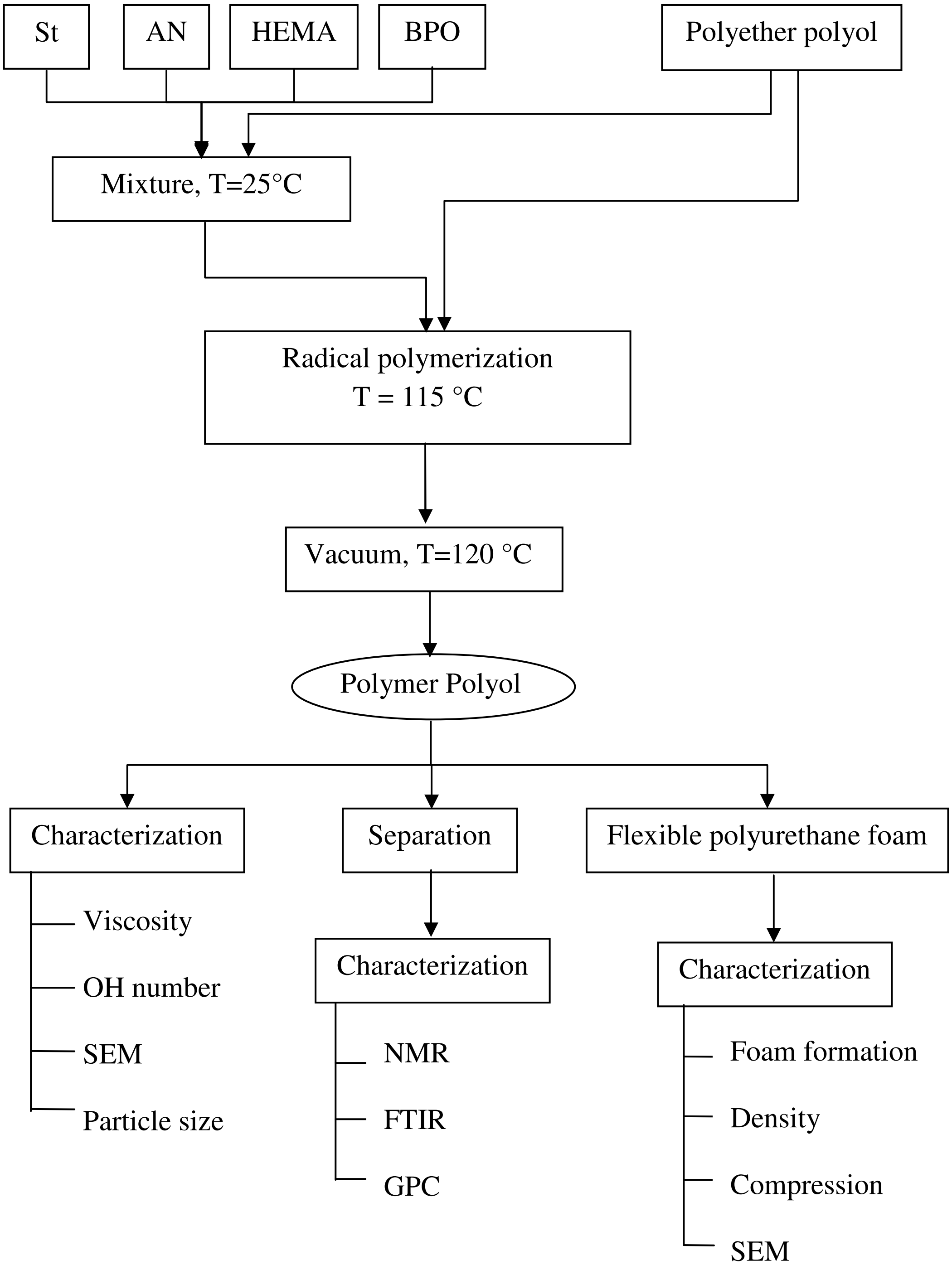


Figure 3.3 Flow chart for experimental procedure

3.3 Characterization of polyol-g-PSAH

3.3.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^1H NMR spectra were recorded on a Varian, model Mercury-400 nuclear magnetic resonance spectrometer (USA) operating at 400 MHz in $CDCl_3$ solution. Chemical shifts (δ) were reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent signal as a reference.

3.3.2. Gel Permeation Chromatography (GPC)

Molecular weight of synthesized polymer were analyzed by GPC using Waters 600 controller chromatograph equipped with HR1 and HR4 columns (Waters, MW resolving range = 100-500,000 Da) at 35 °C and refractive index detector (Water 2414). The THF was used as an eluent and flow rate was 1.0 ml/min. The sample injection volume was 50 μL. The molecular weight of polymer was reported in Dalton unit relative to polystyrene standard (Five polystyrene standards: 996-188,000 Da).

3.3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra were recorded on a FT-IR spectrometer (Nicolet 6700, USA), model impact 410 with 32 scans at resolution 4 cm^{-1}. A frequency of 400-4000 cm^{-1} was collected by using TGS detector. Sample was mixed with KBr powders and pressed into tablets for characterization.

3.3.4 Scanning Electron Microscopy (SEM)

The size and the morphology of particles were determined by scanning electron microscope (SEM, JSM-5410LV). The colloid samples were dropped on cover slip and stained with osmium tetroxide vapor for 1 hour. Then, the substrate on cover slip was dissolved with ethanol to remove original polyether polyol, dried with critical point dryer and coated with gold. The average diameter of particles was calculated by an image analysis of about one hundred particles from the SEM photographs using semafore software.

3.3.5 Particle diameter measurement

Particle size and particle size distribution were measured using laser particle size distribution analyzer (Malvern Instruments, UK) and the range of operational measurements is from 50 nm to 880 μm. The colloid products were dispersed in ethanol before measurement. The colloids were stirred continuously throughout the measurements to ensure they were homogenous. It should also be noted that the theory used to calculate the particle size distribution (Mie theory) assumes that the particles are spherical and homogeneous. Measurements are reported as the volume–length mean diameter: $D[4,3] = \Sigma D_iN_{i4} / \Sigma D_iN_{i3}$, where N_i is the number of droplets of diameter D_i. Span is the width of the distribution based on the 10%, 50% and 90% quantile.

$$\text{Span} = \frac{D[v,0.9] - D[v,0.1]}{D[v,0.5]}$$

3.3.6 Hydroxyl number (OH number)

The OH numbers of the polymer polyols were determined according to ASTM NO C 4274-88 Method D. It is obtained from method of analysis by acetylating the hydroxyl and titrate the resultant acid against KOH [3].

$$\text{OH number} = \frac{56.1 \times 1,000}{\text{Equivalent weight}} \qquad (3.3)$$

where 56.1 is the atomic weight of potassium hydroxide, and 1000 is the number of milligrams in one gram of sample.

3.3.7 Viscosity

The viscosity of the colloid polymer polyol was measured with Brookfield viscometer at the room temperature, spindle number of 31 and speed of 1.5 rpm. The measurement was repeated three times for each sample in order to obtain an accurate average value.

3.3.8 Determination of grafting results

The weight of free homopolymer (free PSAH) and grafted polyol (polyol-g-PSAH) were determined after methanol extraction and column chromatography.

Calculation for %wt of PSAH grafting on the polyol is shown in eq. (3.4). The percentage of free homopolymer PSAH is based on the weight ratio of free PSAH and total PSAH formed (free PSAH and PSAH grafting on the polyol) the following eq. (3.5).

$$\%\text{wt of PSAH grafting on the polyol} = \frac{\text{wt of PSAH grafting on the polyol}}{\text{total wt of product formed}} \times 100 \quad (3.4)$$

$$\%\ \text{wt of free homopolymer PSAH} = \frac{\text{wt of free PSAH}}{\text{total wt of PSAH formed}} \times 100 \quad (3.5)$$

The grafting efficiency (%) of St/AN/HEMA based on amount of reacted monomer was calculated by eq. (3.6). The grafting efficiency of St/AN/HEMA based on fed amount of monomer was calculated by eq. (3.7).

$$\text{grafting efficiency (\%)} = \frac{\text{wt of PSAH grafting on the polyol}}{\text{total wt of PSAH formed}} \times 100 \quad (3.6)$$

$$\text{grafting efficiency (\%)} = \frac{\text{wt of PSAH grafting on the polyol}}{\text{total wt of initial monomer}} \times 100 \quad (3.7)$$

3.4 Characterization of flexible polyurethane foam

3.4.1 Foam formation

Cream time, gel time, rise time and tack free time were investigated by digital stopwatch. The cream time is the start of bubble rise and color of the mixture becomes creamlike from milk. Gel time is the starting point of stable network formation by intensive allophanate crosslinking as well as urethane and urea linkages or the time of begins to gel. Rise time or end of rise time is the time taken for the foam to stop rising as visually observed. Tack free time is the perfect crosslink time and the outer surface of the foam without sticking [19,39].

3.4.2 Density

Density was calculated as the ratio between the weight and volume of foam sample following the procedure of ASTM D 1621-09. The size of specimen was 30×30×30 mm (width×length×thickness) dimension.

3.4.3 Compression strength

Compression strength of FPU foam was preformed according to ASTM D 695. The size of specimen was 30×30×30 mm dimension. The rate of crosshead movement was fixed at 2.54 mm/min and the compression stress at 50% of original thickness.

3.4.4 Statistical analysis

All data obtained from the tests of antibacterial activity are expressed as mean ± one standard deviation (SD) of a representative of three similar experiments carried out in triplicate. Statistical analysis was performed using the Statistical Package for the Social Science (SPSS) version 17.0 software. Statistical comparisons made by One-Way Analysis of Variance (ANOVA) with the Least Square Difference (LSD) tests were used for post hoc evaluations of differences between groups. Statistical significance was associated with the value of $p < 0.05$.

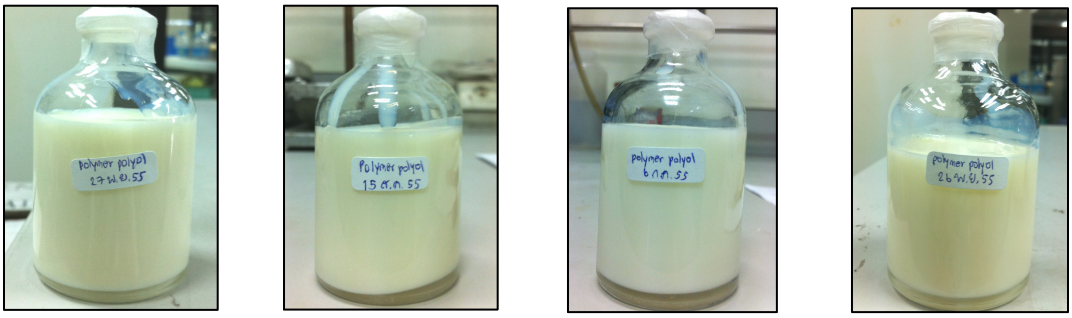
CHAPTER IV

RESULTS AND DISCUSSION

The content in this chapter is divided into 3 parts. The first part focuses on the synthesis of polyether polyol grafted with poly(styrene-*co*-acrylonitrile-*co*-hydroxyethyl methacrylate) (polyol-g-PSAH) via radical polymerization (in the colloid form). The second part reveals details on the separation and characterization of the polyol-g-PSAH. Kinetics of foam formation, density, and compression strength of flexible polyurethane foams by adding with the polymer polyol are presented in the last part.

4.1 Synthesis of polymer polyol

As explained in Chapter 3, the polymer polyol (polyol-g-PSAH) was synthesized by radical polymerization of St, AN, and HEMA monomers in liquid polyether polyol initiated with BPO. The H atoms situated at the α-position (-CH-O-) of the polyol chain are very susceptible to radical attack (hydrogen abstraction by radical mechanism), initiating the graft copolymerization of the vinyl monomers [3]. All polymer polyols obtained are slightly yellow colloids (Figure 4.1). In this study, synthesis conditions including the effect of monomer concentration, initiator concentration, and reaction temperature were investigated.



(a) (b) (c) (d)

Figure 4.1 Products of polymer polyol: (a) 0, (b) 1, (c) 3.62, and (d) 5 mol HEMA/ mol polyol

4.1.1 Effect of HEMA concentration

The effect of HEMA content on grafting process was studied at a fixed reaction temperature of 115 °C, 11 mol% of BPO initiator [30], and the mol ratio of St/AN of 1. It was found that the HEMA monomer content of 0-5 mol/mol of polyol showed no adverse effect when considering the degree of conversion shown in Table 4.1.

Table 4.1 Effect of the mole ratio of HEMA: polyether polyol

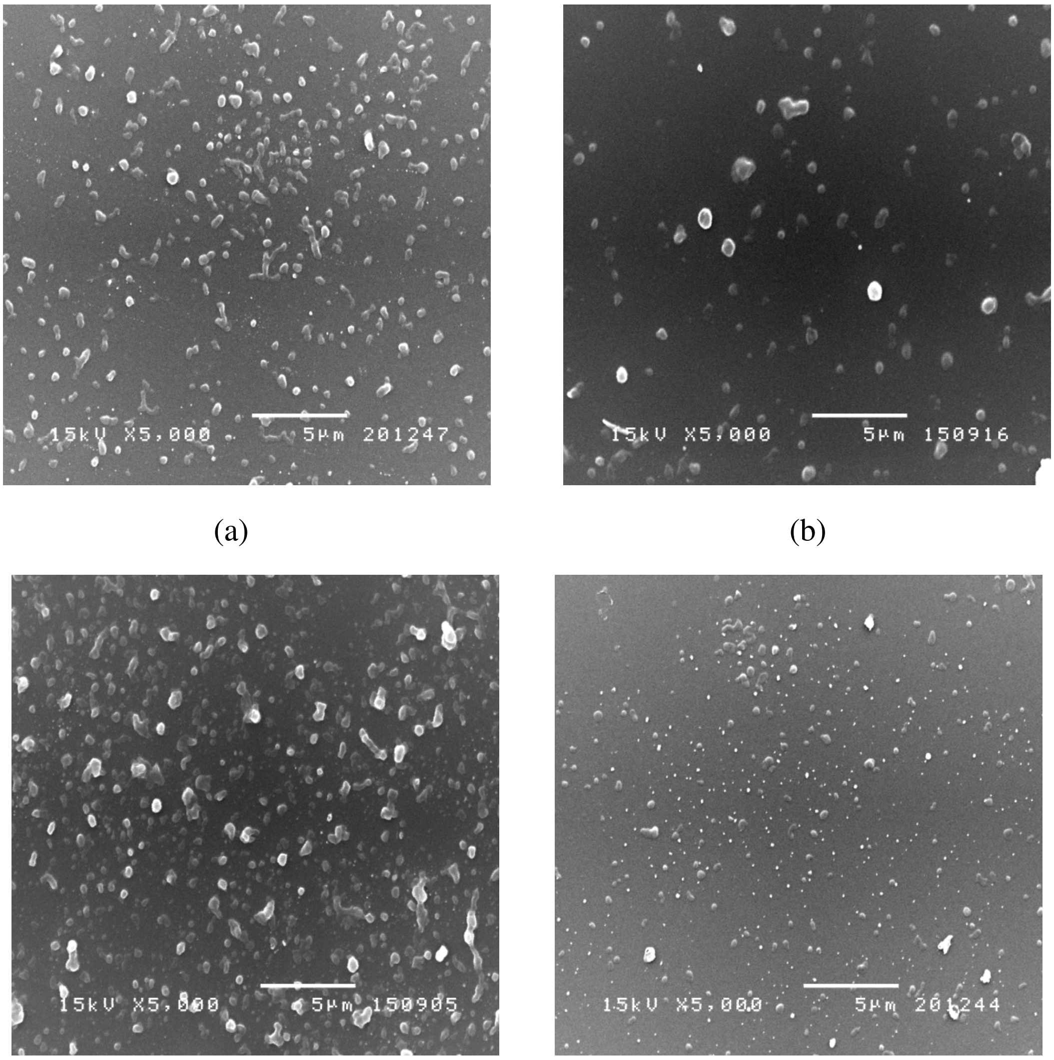
HEMA (mol)	Monomer conversion (%)	OH number (mgKOH/g)	η (cPs)	D^a (μm)	Span	D^b (μm)
original polyol	-	30.0-35.0	860-980	-	-	-
0.00	81.18	30.8	13,530	0.71	0.74	0.43±0.09
1.00	80.21	35.4	9,645	0.71	0.73	0.46±0.15
3.62	81.60	47.2	6,499	0.69	0.72	0.41±0.09
5.00	88.44	-	5,899	0.69	0.71	0.26±0.12

[a] Average particle size measured by laser light scattering

[b] Average particle size obtained by SEM

The hydroxyl number (OH number) of the obtained polymer polyols was analyzed by titrating with standard potassium hydroxide solution to find the amount of hydroxyl groups for the reaction with isocyanates. It is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mgKOH/g) [3]. The increasing HEMA content in the grafting step resulted in the polyols with increasing OH number (Table 4.1). Addition of HEMA at 3.62 mol/mol polyol increased the OH number from 30.8 to 47.2 mgKOH/g. There is no data available for the grafted polyols obtained from adding 5 mol of HEMA/mol polyol, since this sample could not be dissolved in demineralized water (used for hydrolysis in titration).

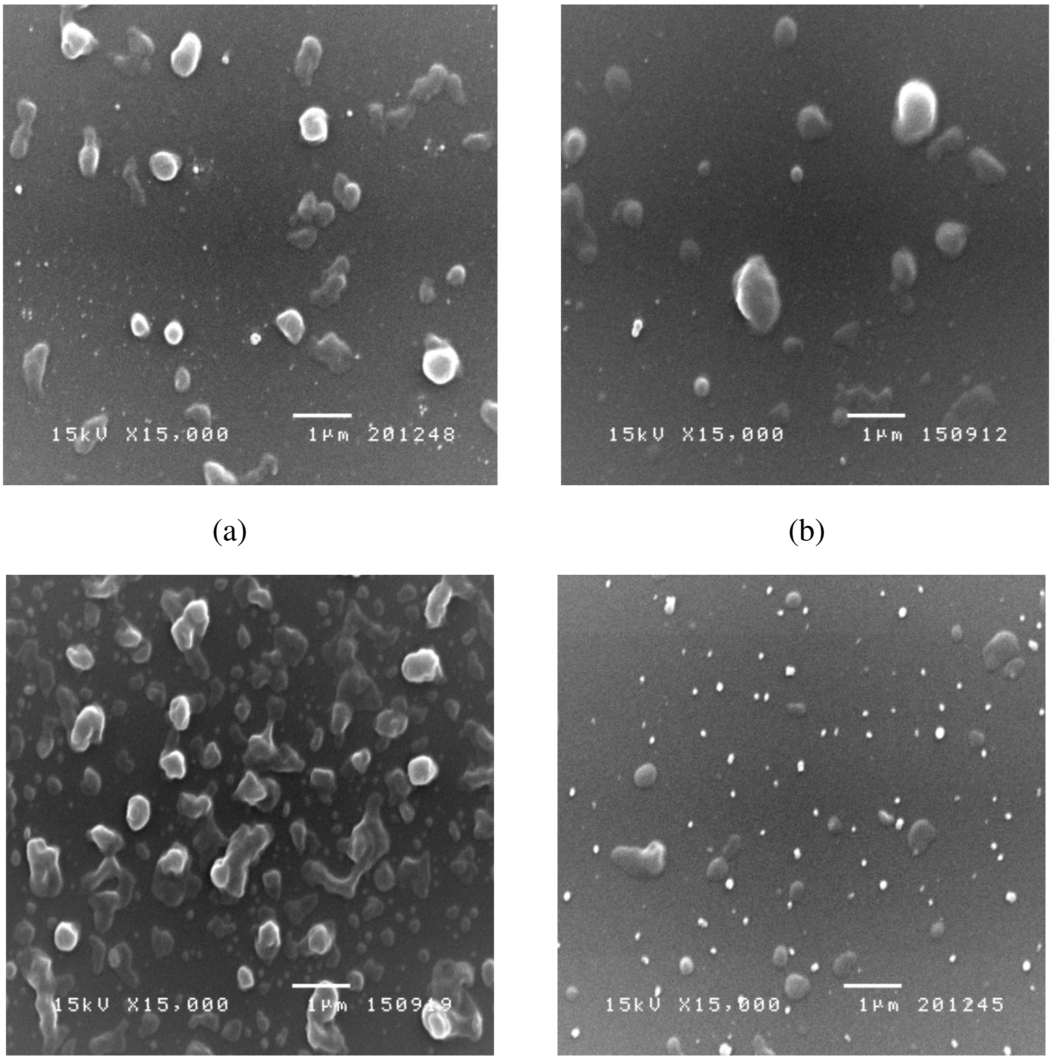
Scanning electron microscopy (SEM) was employed to investigate the morphology of colloid particles obtained (Figures 4.2 and 4.3). Upon close inspection, it is clear that the polymer particles appeared as a quasi-spherical shape. Interestingly, it was found that the smallest polymer particle size was obtained by using the highest HEMA content. Also from laser light scattering analysis, the average particle size decreased when the HEMA content was increased (Table 4.1). In general a non-polar or hydrophobic polymer in a polar environment tends to coil up and appears as spherical particles in order to reduce its interfacial energy. The particle size depends on various factors, including its molecular weight and mass. For the polymer polyols obtained in this study, the polar polyol domain would thus become the ‘shell’ part of each particle while the non-polar polymer part is embedded in the core, as a way to reduce its surface energy. With increasing the relative content of the polar HEMA monomers, the number of particles therefore increased with less non-polar mass in each core (Figure 4.4). The particle size distribution of the polymer polyol was found to be unimodal (Figure 4.5).



(a) (b)

(c) (d)

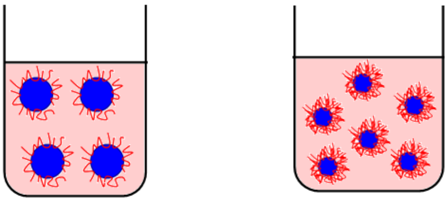
Figure 4.2 Scanning electron micrographs of colloidal particles prepared at (a) 0, (b) 1, (c) 3.62, and (d) 5 mol HEMA/mol polyol at 5,000 magnifications.



(a) (b)

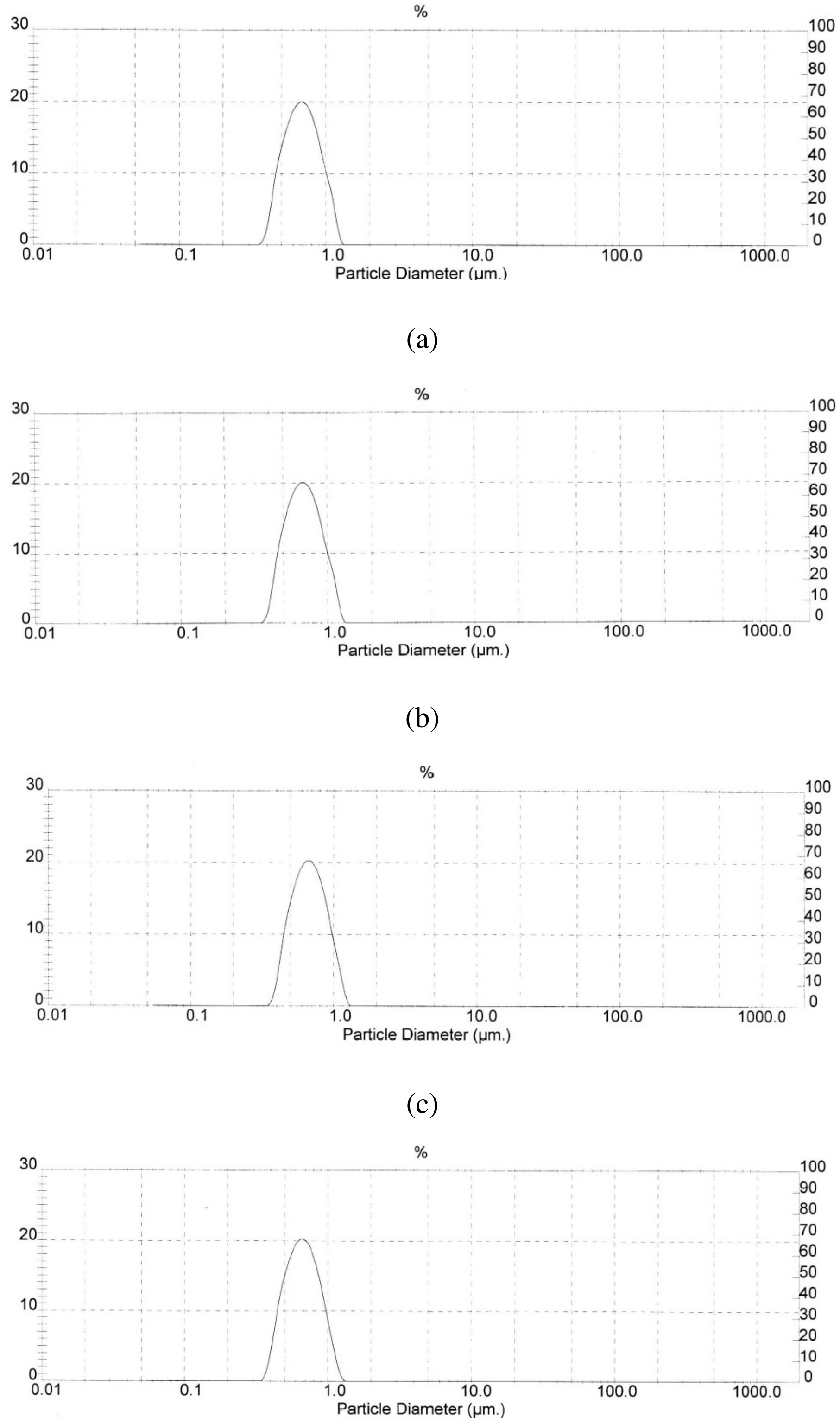
(c) (d)

Figure 4.3 Scanning electron micrographs of colloidal particles prepared at (a) 0, (b) 1, (c) 3.62, and (d) 5 mol HEMA/mol polyol at 15,000 magnifications.



(a) (b)

Figure 4.4 Model of polymer particles dispersed in polyol medium: (a) low and (b) high HEMA contents



(a)

(b)

(c)

(d)

Figure 4.5 Histograms of particle size of polymer polyol: (a) 0, (b) 1, (c) 3.62, and (d) 5 mol HEMA/mol polyol.

Moreover from Table 4.1, when the amount of HEMA added increased, the viscosity of the polymer polyol however decreased from 9,645 to 5,899 cPs. This result is entirely opposite to the theory that small particle size generally resulted in high viscosity because the high surface area of the particles would resist liquid flow [40]. It was probably the increasing polar part of HEMA that helped reduce the phase difference between the grafted polymer and the polar polyol. Furthermore, dispersion of polymer particles was improved result in viscosity decreased [41].

4.1.2 Effect of initiator concentration

The benzoyl peroxide (BPO) was chosen in this work to give free radicals that initiated the grafting sites on polyether polyol backbone. After the radical is formed, it attacks a monomer to grow the polymer chain. Chain termination occurs between two radicals react with each other to create a non-radical species. The amount of BPO studied was ranging from 6-22 %mol of polyether polyol at constant quantities of St/AN/HEMA monomers (1/1/0.5) and reaction temperature (115 ºC) as shown in Table 4.2.

Table 4.2 Influence of mole ratio of BPO: polyether polyol

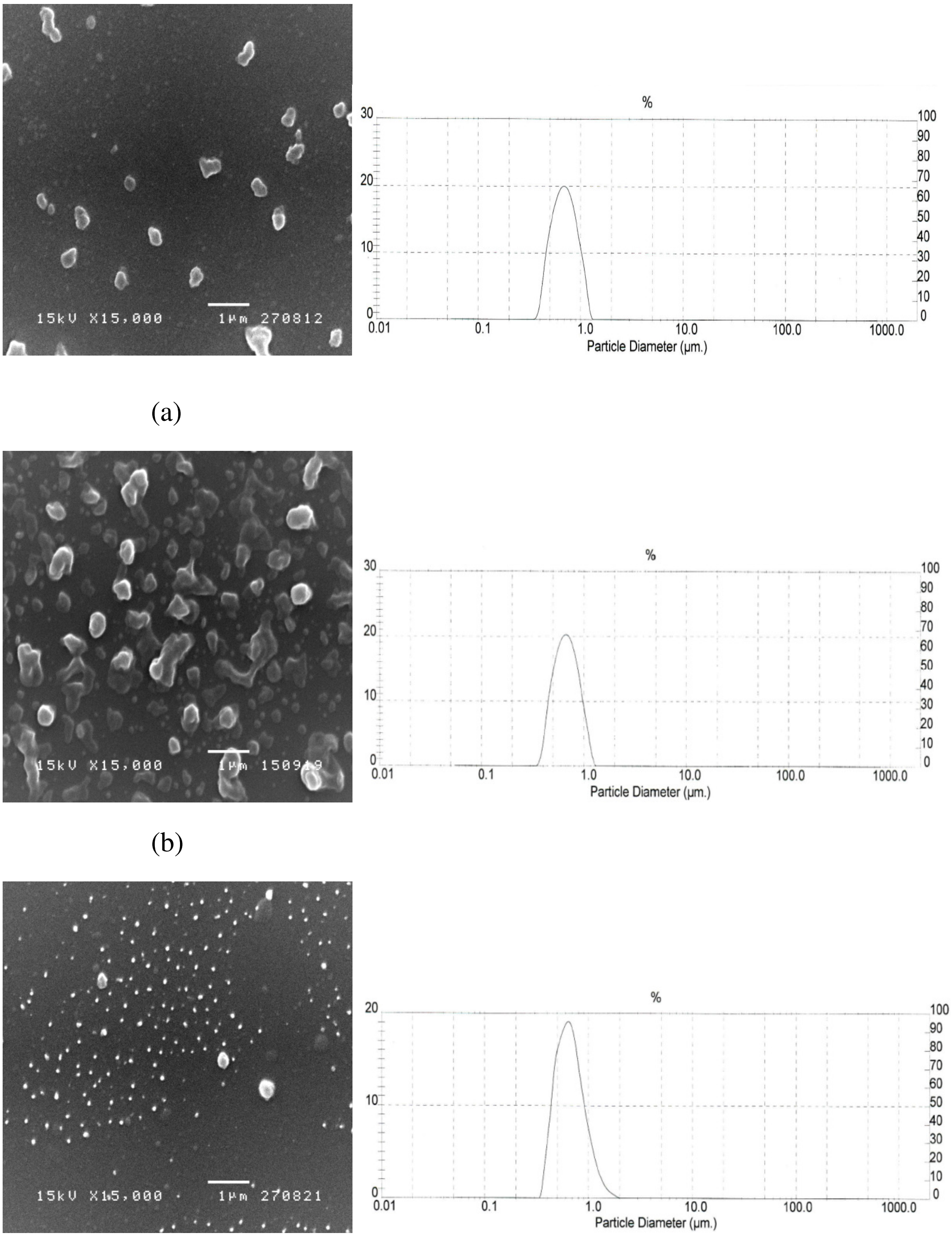
BPO (mol%)	Monomer conversion (%)	OH number (mg KOH/g)	η (cPs)	D[a] (μm)	Span	D[b] (μm)
6	78.86	46.1	2,372	0.71	0.73	0.31±0.09
11	81.60	47.2	6,499	0.69	0.72	0.41±0.09
22	87.77	-*	18,868	0.70	0.85	0.18±0.08

[a]Average particle size measured by laser light scattering

[b]Average particle size obtained by SEM.

* This sample was not analyzed for OH number.

The degree of monomer conversion increased with increasing initiator concentration to 22 mol%. The high initiator concentration generates more radicals (increasing the radical production rate) to consume the monomer molecules then the degree of monomer conversion is increased. No clear effect of initiator concentration on the particle size. High initiator contents usually lead to grafting at multiple sites on the polyether polyol. Then average chain length would decrease and so the particle size. From the experiment it was found that the highest amount of initiator (22 mol%) leads to the smallest particle size (0.18 µm) in which is also shown in Figure 4.6. The small particle size resulted in high viscosity. Adding 22 mol% of BPO resulted in the highest viscosity which was about 3 and 8 times higher than those of the grafted products obtained when the initiator content was 11 and 6 mol%, respectively. Commercial polymer polyols have viscosity in the range of 1,500-6,500 cPs, depending on the level of solid polymers (Sinochem International Corporation). In the investigated range, the reaction at the initiator concentration of 6 mol% provided the most appropriate viscosity used for producing polymer polyol. The OH number of the polymer polyol obtained from 6 and 11 mol% BPO were almost equal since both products were synthesized by using the same amount of HEMA monomer.



(a)

(b)

(c)

Figure 4.6 Scanning electron micrographs of colloidal particles at 15,000 magnifications and histograms of particle size of polymer polyol: (a) 6, (b) 11, and (c) 22 mol % BPO

4.1.3 Effect of reaction temperature

The graft copolymerization of vinyl monomers onto polyether polyol was studied at a fixed mol ratio of St/AN/HEMA of 1/1/0.5, and the BPO initiator concentration of 6 mol%. The reaction temperatures were varied in the range of 100-130°C.

Table 4.3 Influence of the reaction temperature

Reaction temperature (°C)	Monomer conversion (%)	η (cPs)	D^a (μm)	Span	D^b (μm)
100	76.02	2,193	0.73	0.72	0.22±0.14
115	78.86	2,372	0.71	0.73	0.31±0.09
130	76.59	3,399	0.71	0.81	0.19±0.09

[a] Average particle size measured by laser light scattering

[b] Average particle size obtained by SEM

Generally, an increase in temperature results in higher polymerization rate [41]. In addition the temperature increase also leads to initiator decomposition rate increase, more BPO radicals are produced to consume the monomer molecules and hence the degree of conversion should be increased. However, the degree of monomer conversions was the same with increased temperature range investigated in this work (Table 4.3). Noticing that the highest temperature (T = 130°C) leads to the smallest particle size (0.19 μm, SEM). This effect can be explained by the particle size decreased with increasing polymerization temperature, owing primarily to increase of the initiation rate, as was also observed by Kawaguchi *et al.* [42]. The small particle size provided the high viscosity as previously mentioned.

In summary, the investigation of reaction parameters of the graft copolymerization of polymer polyol demonstrated that the increasing HEMA concentrations can be helped reduce the viscosity of polymer polyol. The most suitable initiator content used in the grafting process was 6 mol% because it provided appropriate viscosity for the synthesized polyol-g-PSAH. And the last, the optimum reaction temperature was found to be at 100 to 115°C.

4.2 Separation and characterization of the grafted polyether polyol

During the grafting process, three different components are generally found in the reaction mixture. In this work, they are the starting polyether polyol, the desired grafted polyol (polyol-g-PSAH), and free homopolymers of the added monomers (free PSAH). Consequently, these components must be separated in order to identify their existent in the mixture. First the obtained product after grafting was extracted with methanol and precipitated by centrifugation in order to remove the starting polyether polyol. The methanol layer was evaporated to give a clearly viscous liquid. The precipitated layer was vacuum-dried for 24 hours to obtain solid polymer (Figure 4.7).

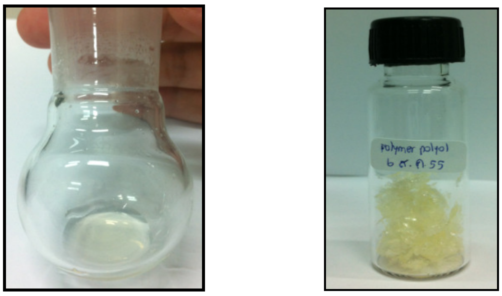


Figure 4.7 Photographs of the obtained polyether polyol after methanol evaporation (left) and slightly yellow solid polymer after vacuum dried (right), from the formulation of HEMA 3.62 mol/mol polyol

The obtained polymer polyols have the percentage of solid content in the range of 10-17 as shown in Table 4.4. The increasing HEMA concentrations however resulted in a decrease of solid content. It should be reminded here that the solid content data was obtained from methanol extraction step. The grafted polyol at high HEMA concentration possessed high content of polar -OH groups and should be therefore dissolved in methanol in a similar manner as the starting polyol. In addition, the small particle size did not completely precipitated (centrifugation at 10,000 rpm) result in solid content decreased.

Then, the solid polymer was separated by means of column chromatography in order to determine the amount of grafted polyol. The $CHCl_3$/THF mixture (4/1 w/w) was the first eluent. Then, THF was added to elute the grafted polyether polyol. And the last eluent was methanol to gather the remains of the grafted polyether polyol.

Table 4.4 Effect of HEMA concentration on the solid content in polymer polyol (initially constant weight of monomers (St, AN, and HEMA) = 20%wt based on polyol)

Entry	HEMA (mol)	Monomer conversion (%)	%Solid content in polymer polyol
1	0.00	81.18	16.5
2	1.00	80.21	13.8
3	3.62	81.60	13.1
4	5.00	88.44	10.2

Table 4.5 shows the effect of HEMA concentration on the degree of polymer recovery after employing the three eluents. It was found that the total recovery of all formulations was less than 100 % because some polymer portions were probably trapped in silica gel stationary phase as evidently shown by FT-IR analysis on the used silica (Figure 4.11). However, it can be concluded that the free homopolymer PSAH and the grafted polyether polyol in this system were 20-48% and 30-48%, respectively.

Table 4.5 Effect of HEMA concentration on the degree of recovery of eluents

Entry	HEMA (mol)	%Recovery			
		$CHCl_3$/THF (4/1 w/w)	THF	Methanol	Total
1	0.00	48.0	34.0	12.6	94.6
2	1.00	39.1	22.0	8.0	69.1
3	3.62	21.8	19.7	15.3	56.8
4	5.00	26.0	26.4	21.6	74.0

From the weights of separated fractions of all components, the amount of grafted polyol can be calculated as shown in Table 4.6. It must be clarified here that both the methanol extraction and column separation processes contained some experimental errors. The methanol extraction originally was intended to extract only the polyol but it was found that the polymer part, probably the low molecular species, was also dissolved in methanol. This would cause the weight of extracted polyol to be higher than it should be. In the product separation step aided by column, the recovery of all polymeric contents was incomplete as shown in Table 4.5, leading to fault calculation of grafting yield. However, these results could give rough information on the grafting behavior of this system.

The effect of HEMA content on grafting performance was also studied with results shown in Table 4.6. The %wt of PSAH grafting on the polyol slightly increased from 5.2 to 13.6 % when the HEMA concentration was increased from 0-5 mol/mol polyol. Both of the grafting efficiency of St/AN/HEMA had the same increasing trend. These results showed that the grafting of copolymer increased with increasing the concentration of HEMA.

Table 4.6 Effect of HEMA concentration on grafting performance

HEMA (mol)	%wt of PSAH grafting on the polyol	% wt of free homopolymer PSAH	Grafting efficiency of St/AN/HEMA* (%)	Grafting efficiency of St/AN/HEMA** (%)
0.00	5.2	60.6	39.4	32.0
1.00	7.9	40.6	59.5	47.7
3.62	11.8	19.5	80.6	65.7
5.00	13.6	16.4	83.6	74.0

* Grafting efficiency of St/AN/HEMA based on amount of reacted monomer

** Grafting efficiency of St/AN/HEMA based on fed amount of monomer

The initiator concentration increased from 6 to 22 mol%, the percent of PSAH grafting on the polyol in each condition was similarity (Table 4.7). The percent grafting efficiency of St/AN/HEMA and the percent of free homopolymer PSAH showed without any correlation with initiator concentration. Interestingly, as the amount of initiator was 22 mol%, the percent of PSAH grafting on the polyol and grafting efficiency of St/AN/HEMA were increased. This is possibly because the high initiator concentration also brought about the higher grafting sites results in grafting process increase. It is consistent with the result of smaller particles size (Figure 4.6), as shown previously. The result of an increase in initiator concentration of 22 mol% seemed to work well due to high grafting efficiency and low free homopolymer PSAH. It was, however, found that at this initiator concentration, the viscosity of product would very high increase (Table 4.2). Thus, the initiator concentration of 6 mol% is the most appropriation.

Table 4.7 Effect of initiator concentration on grafting performance

BPO (mol%)	%wt of PSAH grafting on the polyol	% wt of free homopolymer PSAH	Grafting efficiency of St/AN/HEMA* (%)	Grafting efficiency of St/AN/HEMA** (%)
6	11.8	14.8	85.2	67.2
11	11.8	19.5	80.5	65.7
22	13.1	14.5	85.5	75.1

* Grafting efficiency of St/AN/HEMA based on amount of reacted monomer

** Grafting efficiency of St/AN/HEMA based on fed amount of monomer

The rate of initiator decomposition depends on reaction temperature. When the reaction temperature is increased, more BPO radicals are produced. In the case of PSAH grafting on the polyol (Table 4.8), the reaction temperature of 115°C resulted in high grafting efficiency based on amount of reacted monomer of 85.2%, grafting efficiency of St/AN/HEMA based on fed amount of monomer of 67.2, and low free homopolymer of PSAH. At high temperature a large amount of BPO radicals were produced and reacted with polyether polyol chain to generate the graft copolymers resulting in the decrease of free PSAH.

Table 4.8 Effect of the reaction temperature on grafting performance

Reaction temperature (°C)	%wt of PSAH grafting on the polyol	% wt of free homopolymer PSAH	Grafting efficiency of St/AN/HEMA* (%)	Grafting efficiency of St/AN/HEMA** (%)
100	10.5	21.9	78.1	59.4
115	11.8	14.8	85.2	67.2
130	10.7	21.0	79.1	60.6

* Grafting efficiency of St/AN/HEMA based on amount of reacted monomer

** Grafting efficiency of St/AN/HEMA based on fed amount of monomer

4.2.1 ^{1}H NMR characterization

The compounds obtained from each extraction step were analyzed by ^{1}H-NMR spectroscopy. The methanol extracted viscous liquid was confirmed to be the starting polyether polyol (Figure 4.8). The characteristics ^{1}H NMR spectrum showed intense signals at 1.12 ppm ($-CH_3$), 3.39 ppm ($-CH_2-$), 3.54 ppm (-CH-) of propylene oxide units and 3.64 ppm ($-CH_2-$) of ethylene oxide units in the polyether polyol. Moreover less intense signals of styrene aromatic protons appeared in the region of 6.50-7.59 ppm, the HEMA units at 4.09 ($-CH_2OH$) and 4.44 ($-CH_2-OCO$) ppm, and finally the backbone of vinyl polymers at 1.32-2.02 ($-CH_2$) ppm. The integral area of ortho-St and methyl propylene oxide unit in polyol was 6.50-6.95 and 1.12 ppm respectively. The mole ratio of St/polyol was obtained at 0.13/1 resulted in solid content decreased. This evident confirmed that the starting polyol can be removed by methanol extraction although a small amount of vinyl oligomer was also extracted out.

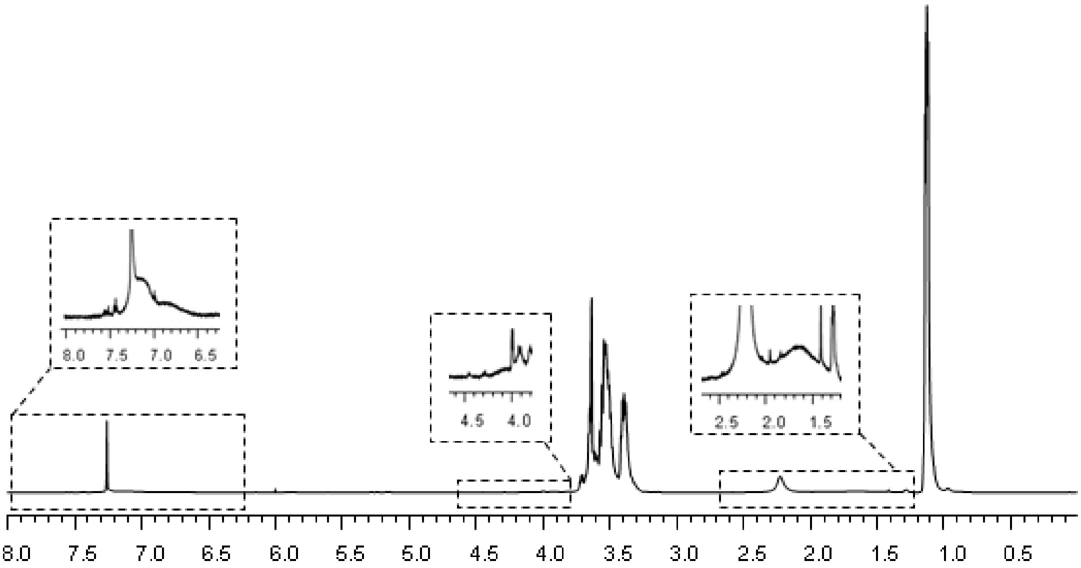


Figure 4.8 ^{1}H NMR spectrum of obtained product after extraction with methanol

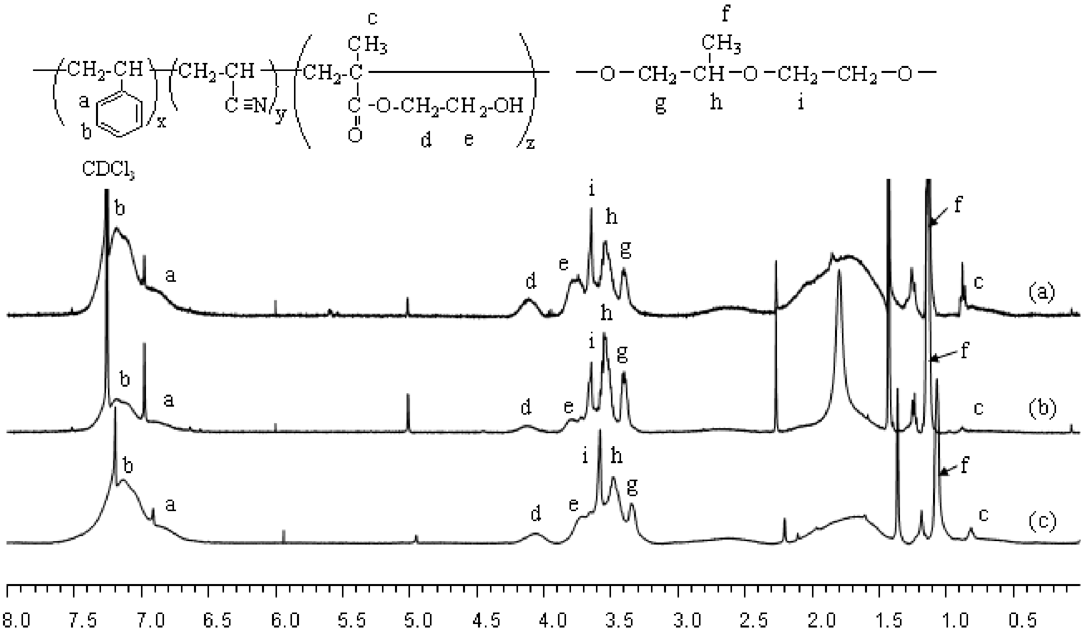


Figure 4.9 ^{1}H NMR spectra of polymer products found in (a) $CHCl_3$/THF fraction, (b) THF fraction, and (c) methanol fraction (Entry 4, Table 4.4)

The polyol-g-PSAH was separated from the free PSAH by column chromatography. All fractions ($CHCl_3$/THF, THF, and methanol) show NMR spectra in Figure 4.9. The ^{1}HNMR spectra show the signals at 1.07 ppm ($-CH_3$), 3.34 ppm ($-CH_2-$), 3.48 ppm (-CH-) of propylene oxide units, and 3.59 ppm ($-CH_2-$) of ethylene oxide units in the polyether polyol, as well as signals at 6.82 and 7.12 ppm corresponding to the aromatic protons of St. The signals at 0.70 ($-CH_3$), 3.73 ($-CH_2OH$), and 4.05 ($-CH_2-OCO$) ppm can be assigned to the HEMA units.

According to the result, the integral area of peak a and peak d were determined to be 6.89 and 4.13 respectively (Table 4.9). Compared to St, HEMA was found in the resulting grafted polymer less than the feed. This suggests that HEMA was less active to a growing grafted polymer chain. Nevertheless from data from NMR analysis the HEMA content in the polymer polyol could be increased from 25-60% when increasing the HEMA feed amount. It is consistent with the increase of OH number discussed earlier in Table 4.1.

Table 4.9 Comparison the mol ratio of HEMA:St before and after the reaction.

Entry	HEMA (by mol polyol)	mol ratio of HEMA : St		%mol HEMA: St
		before reaction (Feed)	after reaction* (Found)	
1	1.00	0.12 : 1	0.03 : 1	25
2	3.62	0.51 : 1	0.22 : 1	43
3	5.00	0.78 : 1	0.46 : 1	59

* The result of THF fraction was calculated from ^{1}H NMR spectrum.

4.2.2 FT-IR analysis

The corresponding FT-IR spectra are shown in Figure 4.10. Absorption of cyano group (in AN) appears at 2240 cm^{-1}. The peak at 1725 cm^{-1} indicates the presence of C=O group in the HEMA unit. The bands at 702, 1602, and 3027 cm^{-1} are characteristics of the St unit. The absorption peak at 1094 cm^{-1} was attributed to the C-O-C stretching vibration of polyol. These results indicated that polyol-g-PSAH contained the polyether polyol grafted with St, AN, and HEMA units.

Furthermore, confirmation the some polymer portion was trapped in the silica gel as showed in Figure 4.11. The spectrum of pure silica gel displays the characterization peak at 1104-1233 cm^{-1}, corresponding to the Si-O-Si stretching of silica (Figure 4.11a). After silica gel was used by column chromatography, new peaks at 2851-2920 cm^{-1} appeared, assigning to the C-H stretching of backbone polymer as shown in Figure 4.11 (b). These result claimed some polymer was trapped in silica gel.

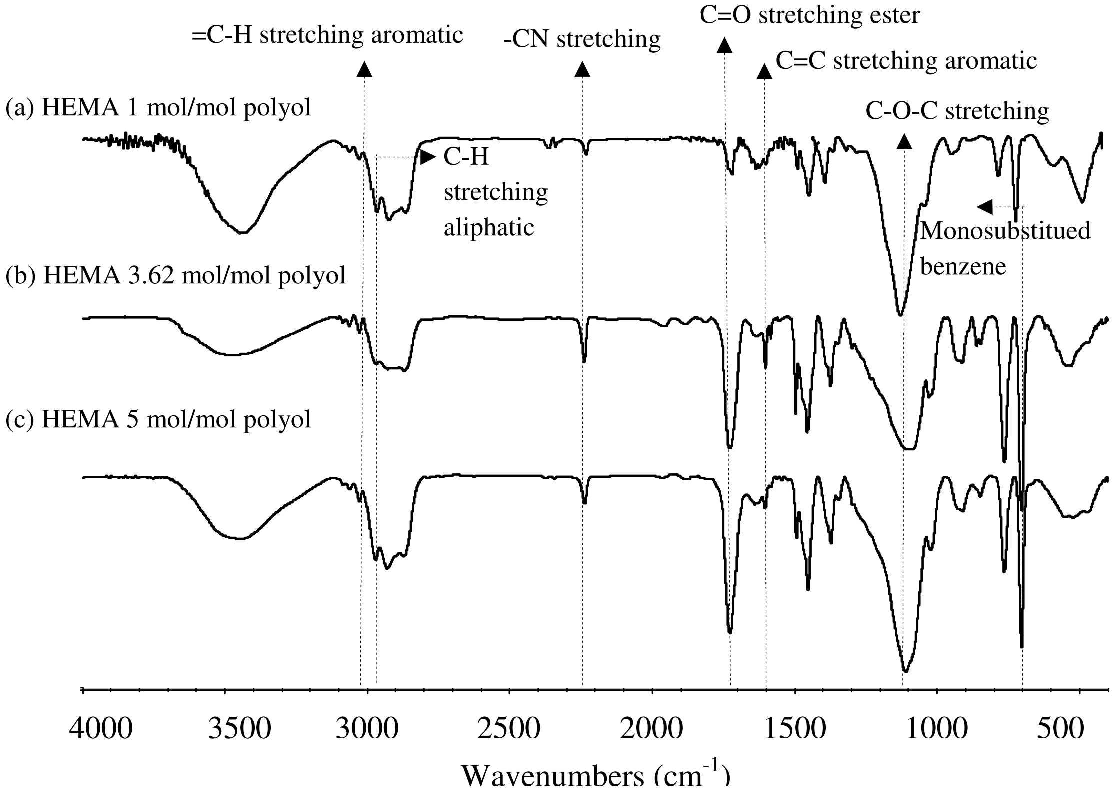


Figure 4.10 FT-IR spectra of polyol-g-PSAH from the THF fraction- HEMA feed amount: (a) 1, (b) 3.62, and (c) 5 mol/mol polyol

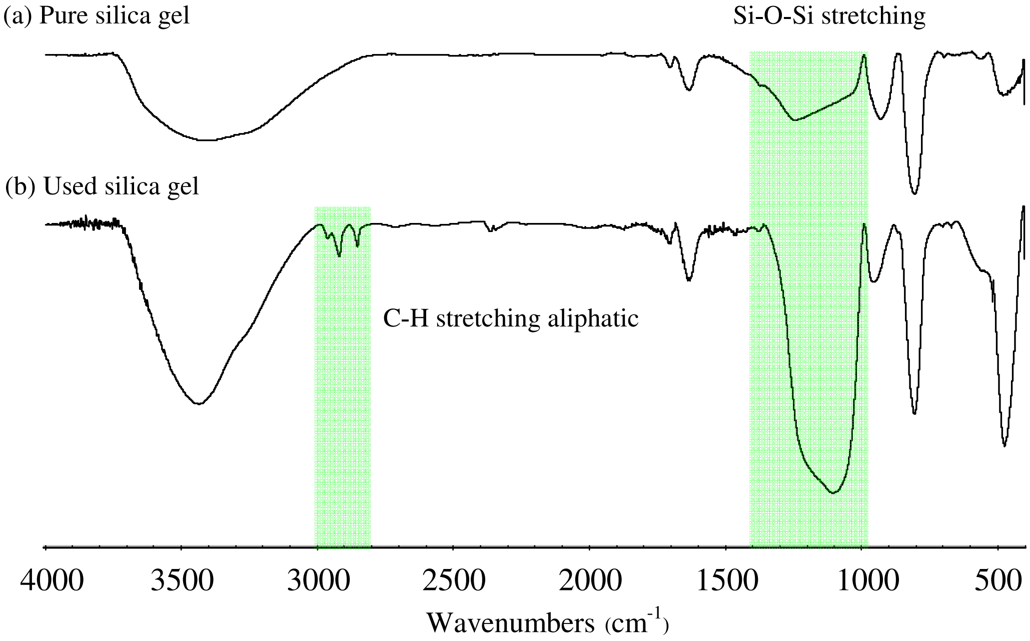


Figure 4.11 FT-IR spectra of (a) pure silica gel and (b) used silica gel

4.2.3 Gel permeation chromatography

The change of molecular weight after grafting was monitored by GPC analysis as shown in Figure 4.12 and Table 4.10. The ungrafted polyether polyol has a molecular weight of 7,610 Da (chromatogram a). The result shown in chromatogram b was believed to be the free PSAH of the fed St, AN, and HEMA having a very high molecular weight (>248,000 Da). Peak shifts in chromatogram c and d clearly indicate molecular weights increase to 43,450 and 25,890 Da, respectively, from the original polyol. This supports the grafting success of the vinyl monomers on the polyether polyol.

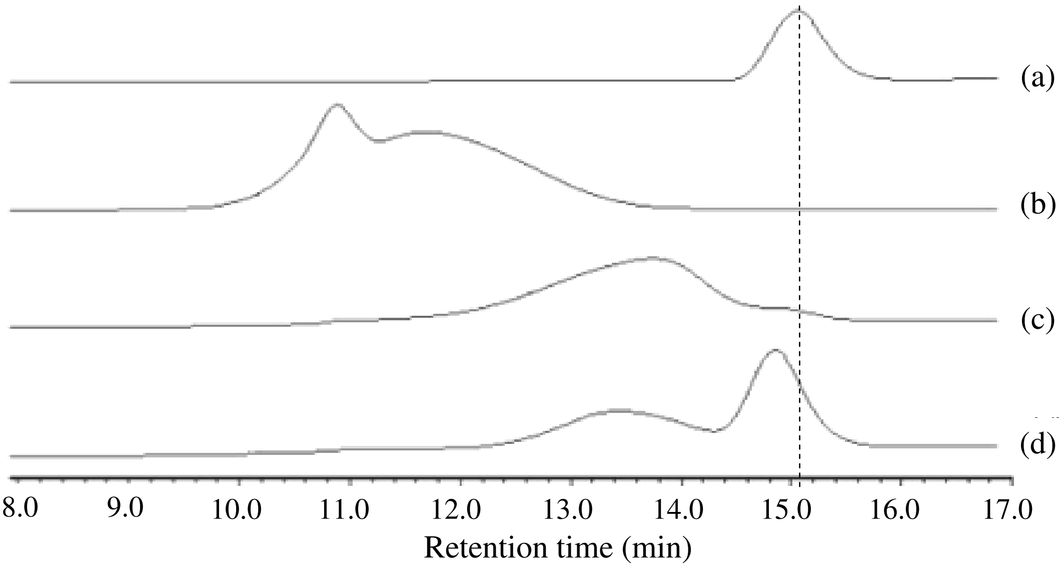


Figure 4.12 Chromatograms from GPC of (a) the original polyether polyol, (b) free homopolymers found in the $CHCl_3$/THF (4/1 w/w) fraction, (c) grafted polyol in the THF fraction, and (d) in the methanol fraction, from polyol-g-PSAH (Entry 2, Table 4.6)

Table 4.10 Molecular weight and polydispersity index of polymer polyol grafted with varied mol HEMA

Entry	HEMA (mol)	$CHCl_3$/THF		THF		Methanol	
		MW (Da)	PDI	MW (Da)	PDI	MW (Da)	PDI
1	0.00	90,723	2.57	40,209	2.45	11,278	1.17
2	3.62	>248,313*	-	43,451	1.78	25,889	2.00
3	5.00	>416,389*	-	54,194	2.29	52,978	1.48

* This sample was dissolved in THF but some high MW portion did not go through filter.

In summary, the evidences of NMR, FT-IR, and GPC can be confirmed the success in the grafting of St, AN, and HEMA onto polyether polyol. From the results of the influential effects on grafting properties by various initiator concentration and reaction temperature, the appropriate grafting condition was obtained when the reaction temperature was used at 115°C and initiator concentration of 6 mol%. The high HEMA concentration can help increase the grafting process.

4.3 Kinetics of foam formation, density, and compression strength of flexible polyurethane foams (FPU)

The kinetic of foaming process, density, and compression strength of FPU foams were studied as a function of HEMA contents in the polyol-g-PSAH at a fixed 10 %wt polymer polyol of the total wt of polyol (component A). The amounts of other chemicals were kept constant. The HEMA concentration was varied from 0, 3.62, and 5 mol/mol polyol. Cream time, gel time, rise time, and tack-free time are the parameters used to determine the kinetics of foaming process. Results are shown in Table 4.11. It was found that when the polyol-g-PSAH was added in to the formulation, the kinetic of foaming process of the FPU foams was not different from the unmodified foam.

Table 4.11 Kinetic of foaming process (at fixed polymer polyol of 10 %wt of total polyol)

Formulation	Cream time (s)	Gel time (s)	Rise time (s)	Tack free time (s)
Unmodified polyol	21±1	38±1	63±2	84±1
Polymer polyol : HEMA (by mol polyol)				
0.00	21±1	32±3	56±1	71±6
3.62	23±1	35±1	59±2	83±3
5.00	22±1	35±1	58±0	74±5

Average n=3, ±SD

Foam density was plotted against HEMA contents as shown in Figure 4.13. At 95% confidence interval, the densities of HEMA 0 and 3.62 mol/mol polyol were significantly different from the unmodified foam. The decreasing density of FPU foam may result from the role of polymer particles to act as nucleating center and as cell opening agents by destruction of cells membranes during the foam rise [3]. But when the HEMA content reached 5 mol/mol polyol, its density was found to be the same as the unmodified foam (see appendix D, Table D-1). This indicates that the polymer polyol without and low HEMA content lags the benefit of having the hydroxyl group which can further covalently link the isocyanate part. At high HEMA content, the hydroxyl groups are located at the hard domain, thus strengthening the foam pore structure.

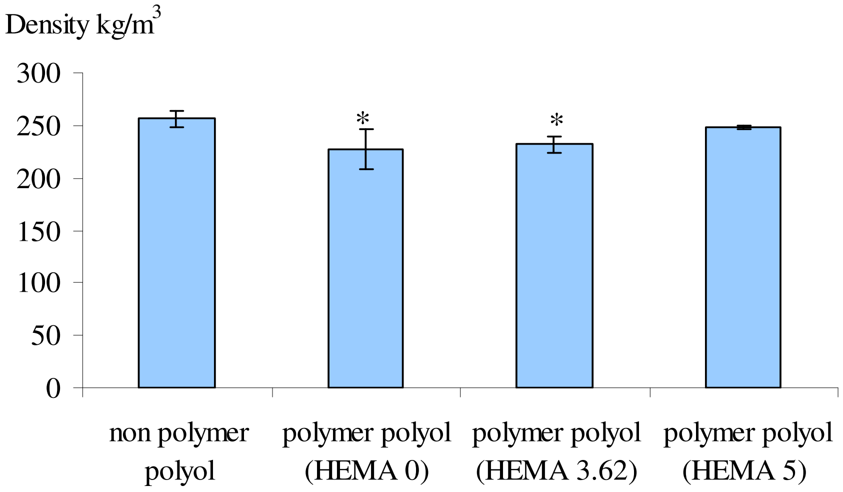


Figure 4.13 Density of FPU foams versus 10%wt of polymer polyol in various formulations $^*p < 0.05$ (compared with non polymer polyol)

The compression strength of FPU foams with various HEMA concentrations in polymer polyol (0-5 mol/mol polyol) is in the range of 115-169 kPa (Figure 4.14). It can be seen that the compression strength increases with an increase in the HEMA concentration, but the values remained lower than the unmodified foam. It is generally known that the mechanical properties of cellular material mainly depend on its density [39]. Therefore, when the HEMA concentration increased, the compression strength increased which may be due to increase of foam density.

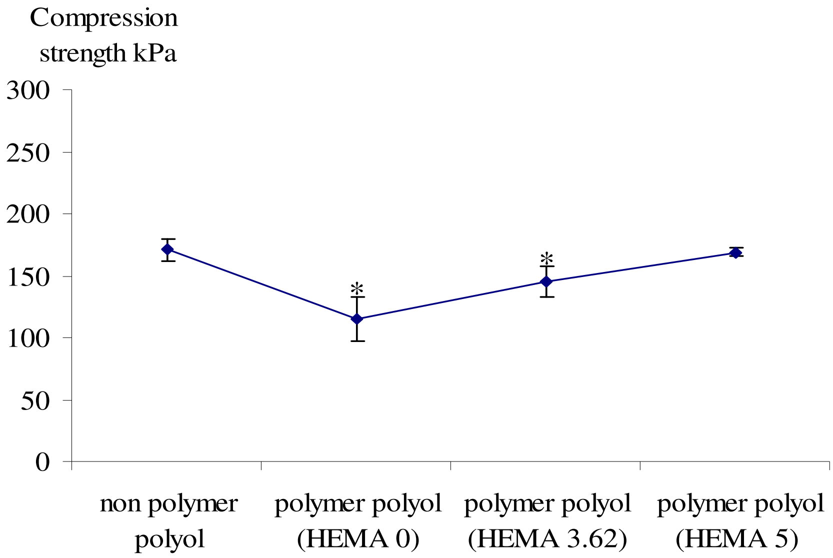


Figure 4.14 Compression strength of FPU foams versus 10wt% of polymer polyol in various formulations $^*p < 0.05$ (compared with non polymer polyol)

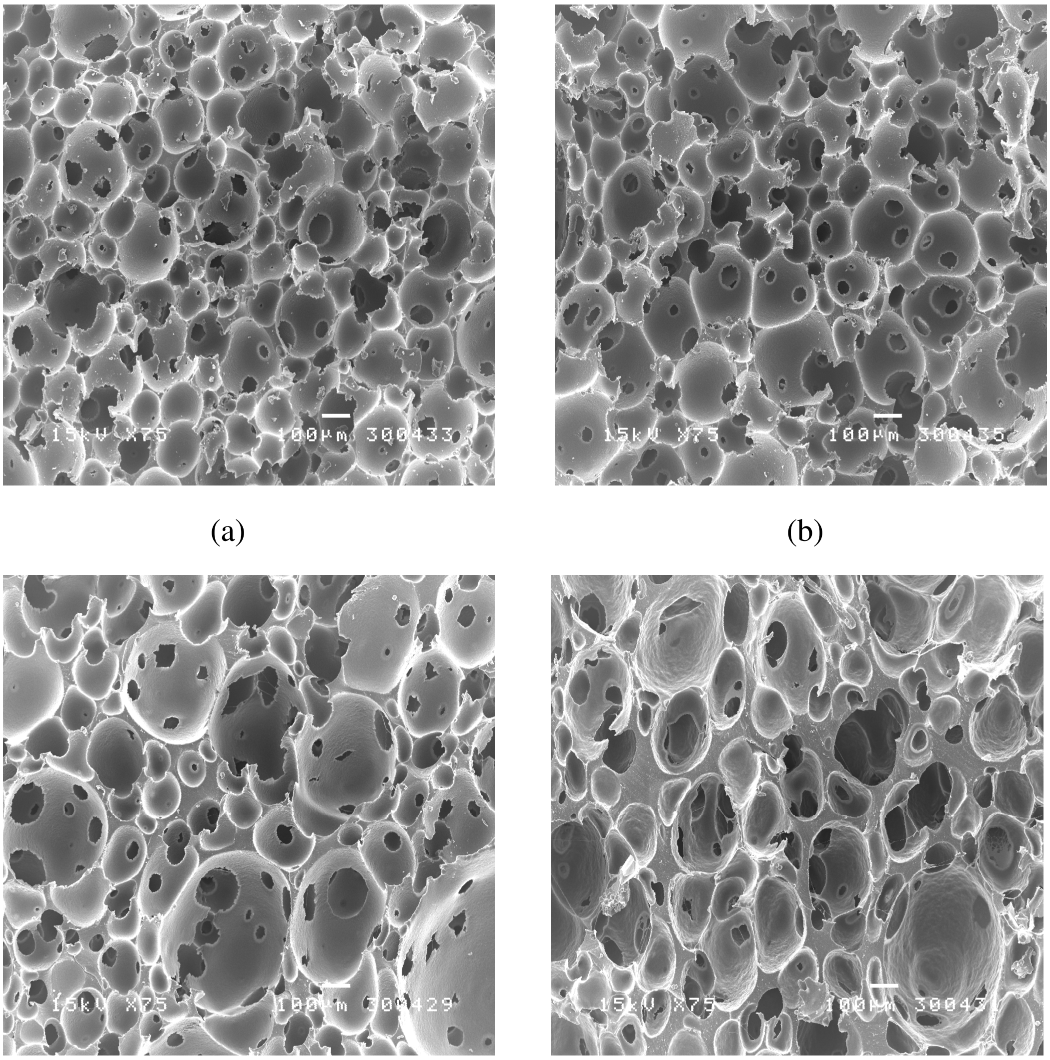
Furthermore, the compression strength of FPU foams were studied with various polymer polyol contents. The polymer polyol content was varied in the range from 0-50 %wt based on total polyol by fixed formulation of polymer polyol (HEMA 3.62 mol/mol polyol). The kinetics of foaming process of all tested samples were also not significantly different (Table 4.12).

Table 4.12 Kinetic of foaming process (at fixed formulation of polymer polyol of 3.62 mol/mol polyol)

Amount of polymer polyol (%wt)	Cream time (s)	Gel time (s)	Rise time (s)	Tack free time (s)
0	21±1	38±1	63±2	84±1
10	23±1	35±1	59±2	83±3
30	20±2	33±3	57^*	70^*
50	22±4	36.5^*	55±2	73^*

All data shown were averaged from 3 sets of experiments, except the ones indicated by * of which only 2 experiments were performed.

The microstructure of foam was observed by SEM. Figure 4.15a shows the microstructure of the unmodified foam. The shape of foam cells is spherical and their sizes are irregular. When the polyol-g-PSAH was included in the foam formulation, the foam cell size increased (Figure 4.15 (b, c, and d)). When the amount of polymer polyol is increased to 50 percent by wt, the cell walls are clearly thicker than without the polymer polyol. The foam density also decreases after the addition of polymer polyol (Figure 4.16), which is mainly due to the increasing size of foam cells.



(a) (b)

(c) (d)

Figure 4.15 Scanning electron micrographs of polyurethane foam samples with varying polymer polyol content (a) 0, (b) 10, (c) 30, and (d) 50 %wt based on total polyol at 75 magnifications.

Foam density was plotted against HEMA contents as shown in Figure 4.16. At 95% confidence interval, the addition of 10 and 30 %wt polymer polyol significantly decreased the density (see Appendix D, Table D-2). Addition of the polyol-g-PSAH at 50 wt% produced the foam with comparable density to that of the unmodified foam. Explanation for this behavior was already mentioned in the Figure 4.13.

The introduction of polyol-g-PSAH at 50 %wt can significantly enhance the compression strength to 240 kPa while the foam density preserved at the same level as the unmodified foam (Figures 4.16 and 4.17). It can be explained that the presence of hydroxyl in the hard 'polymer' part can produce a urethane-linked hard domain which is not the case for the unmodified formulation in which there was no hard domain in the polyol part.

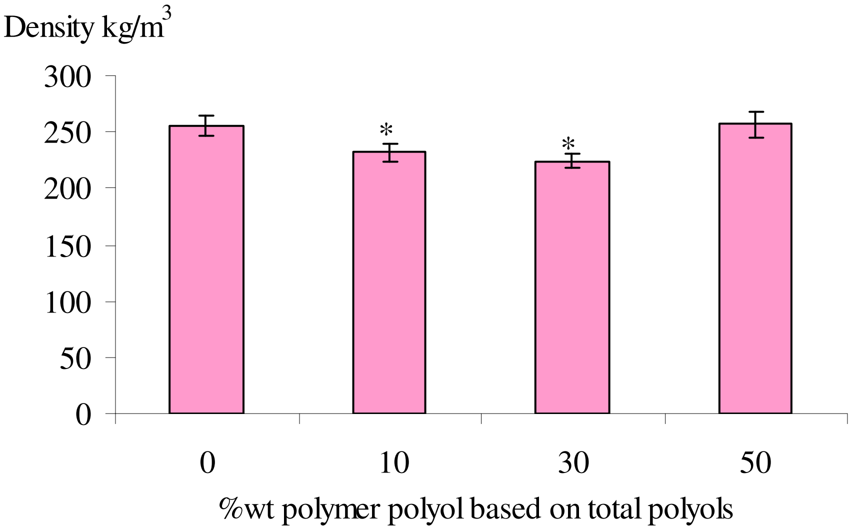


Figure 4.16 Density of FPU foams versus polymer polyol of 0, 10, 30, and 50 %wt based on total polyols at fixed formulation of polymer polyol of 3.62 mol/mol polyol $*p < 0.05$ (compared with non polymer polyol)

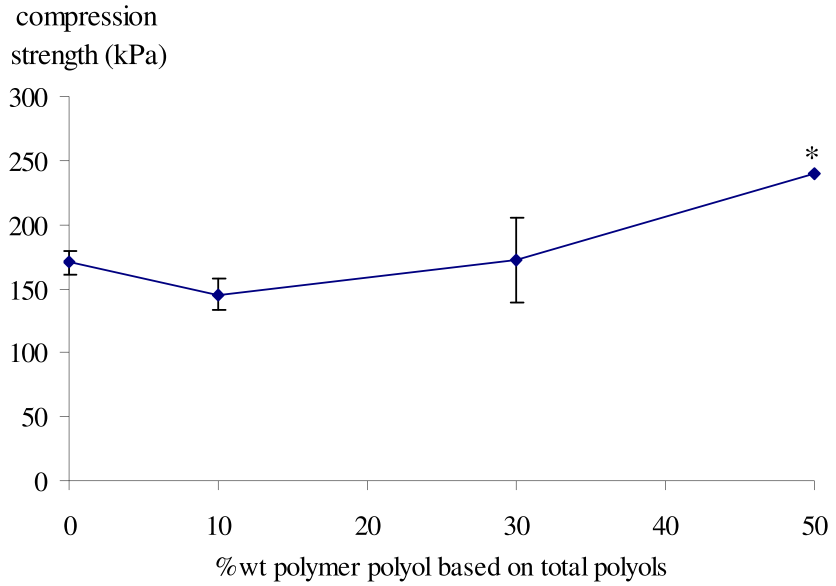


Figure 4.17 Compression strength of FPU foams versus polymer polyol of 0, 10, 30, and 50%wt based on total polyols at fixed formulation of polymer polyol of 3.62 mol/mol polyol *$p < 0.05$ (compared with non polymer polyol)

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusions

Polyol-g-PSAH was prepared by radical polymerization of St, AN, and HEMA in viscous liquid polyether polyol which was also taking a role as the reaction medium. The degree of overall monomer conversion was 76-88%. The addition of HEMA reduced the viscosity of the polymer polyol although its particle size was small as compared to the non-HEMA grafted product. The polymer particle size was determined by SEM imaging and laser light scattering analysis. Methanol extraction and column chromatography in mixture of $CHCl_3$ and THF/THF/methanol with silica as stationary phase were used to separate the grafted polyol from the ungrafted polyol and the subsequent free homopolymer (PSAH). The structure of polyol-g-PSAH was confirmed by NMR, FT-IR, and GPC. Furthermore, the evidence of changing molecular weight from original polyol (7,610 Da) to grafted polyol (43,450 and 25,890 Da) also indicated the successful grafting.

The factors affecting grafting efficiency of the St/AN/HEMA copolymers were studied. It was found that the grafting efficiency of the copolymer increased with increasing concentration of HEMA from 0-5 mol/mol of polyol. Increasing the initiator concentration to 22 mol% led to an increase of grafting efficiency and lowering free homopolymers since higher grafting positions were available. But the BPO initiator concentration which provided appropriate viscosity of polymer polyol was 6 mol% of polyether polyol. The reaction temperature of 115°C was found to be an optimum value for the grafting process.

The size of foam cells were increased when using polymer polyol. The compression strength and density of FPU foam increased with increase in the HEMA concentration due to the increased urethane content. Furthermore, adding polymer polyol at 50% wt based on total polyol in FPU foam showed increase the compression strength while the density of FPU foam preserved at the same level with the unmodified foam. These results lead to confirm that grafting of St, AN, and HEMA on polyether polyol can improve the compression strength of FPU foam.

5.2 Suggestion for future works

A more overview of studies that need to be undertaken and directions that could be further explored are in the following aspects:

- Investigation of other separation techniques such as TREF (temperature rising elution fractionation) for more accurate determination of grafting efficiency
- Investigation of the use other chemicals such as chain transfer agent, stabilizer, and solvent to reduce the viscosity of polymer polyol
- Increasing the amount of vinyl monomer to increase solid content in polymer polyol

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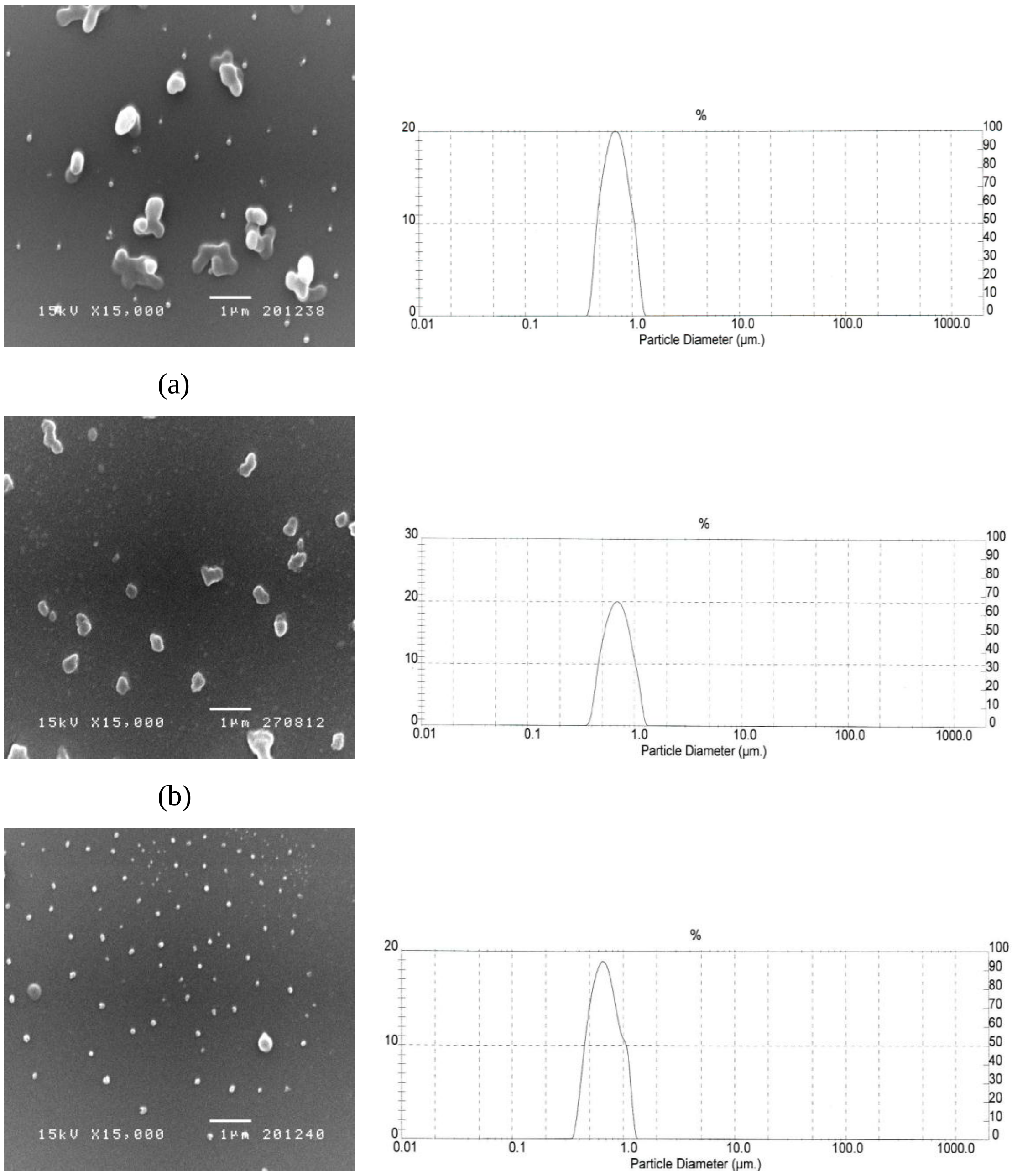
APPENDICES

Appendix A

Colloid particles



(a)

(b)

(c)

Figure A-1 Scanning electron micrographs of colloidal particles at 15,000 magnification and histograms of particle size of polymer polyol at temperature (a) 100, (b) 115, and (c) 130 °C.

Appendix B
NCO Index

NCO Index calculation

Example

Calculation the parts by weight (pbw) of pure MDI (isocyanate value = 18.9) at an isocyanate index 100 required to react with the following formulation.

Table B-1 Formulations for preparation of FPU foam

Chemicals	Weight (g)
Polyether polyol (OH number = 35 mgKOH/g, functionality = 3)	90
Polymer polyol (OH number = 47.18 mgKOH/g)	10
Total polyol components	100
Catalyst (mixture of 33% triethylenediamine and 67% monoethylene glycol)	1.5
Surfactant	0.5
Chain extender (monoethylene glycol)	5
Blowing agent (distilled water, Mw = 18 g/mol)	0.5
Prepolymer isocyanate, NCO index 100	?

1) Find equivalent weight of chemicals

$$\text{Equivalent weight of polyether polyol} = \frac{56.1}{35} \times 1{,}000 = 1{,}603$$

$$\text{Equivalent weight of polymer polyol} = \frac{56.1}{47.18} \times 1{,}000 = 1{,}189$$

$$\text{Equivalent weight of water} = \frac{18}{2} = 9$$

$$\text{Equivalent weight of ethylene glycol} = \frac{62.07}{2} = 31$$

$$\text{Equivalent weight of isocyanate} = \frac{4{,}200}{18.9} = 222.2$$

2) Number of equivalent in formulation $= \dfrac{\text{parts by weight (pbw)}}{\text{Equivalent weight}}$

Equivalent in the above formulation:

$$\text{Polyether polyol} = \frac{90}{1{,}603} = 0.056$$

$$\text{Polymer polyol} = \frac{10}{1{,}189} = 0.008$$

$$\text{Water} = \frac{0.5}{9} = 0.06$$

$$\text{OH groups from chain extender and catalyst} = \frac{(5+1)}{62.07} = 0.19$$

$$\text{Total equivalent weight} = 0.314$$

For the stoichiometric equivalence, MDI pbw is total equivalent weight of OH × equivalent weight of NCO.

Thus:

$$\text{MDI (pbw)} = 0.314 \times 222.2 = 69.78$$

Note: 69.78 defines the isocyanate quantity at 100 index

Where:

$$\text{Isocyanate index} = \frac{\text{actual amount of isocyanate}}{\text{Theoretical amount of isocyanate}} \times 100$$

Thus: (Isocyanate index 100)

$$\text{Isocyanate actual} = \frac{69.78}{100} \times 100 = 69.78$$

Appendix C

Density and Compression of FPU Foam

Table C-1 Density and compression of flexible polyurethane foams (at fixed polymer polyol of 10 %wt of component A)

Formulation	Density (kg/m^3)	Compression (kPa)
unmodified polyol	256±8	170.6±9.457
Polymer polyol :		
HEMA (by mol polyol)		
0.00	227±2	115.4±18.14
3.62	232±8	145.5±12.10
5.00	248±2	168.7±3.536

Average n=3, ±SD

Table C-2 Density and compression of flexible polyurethane foams (at fixed formulation of polymer polyol of 3.62 mol/mol polyol)

Amount of polymer polyol (%wt)	Density (kg/m^3)	Compression (kPa)
0	256±8	170.6±9.457
10	232±8	145.5±12.10
30	224±6	172.3±33.46
50	257±12	239.8*

Average n=3, ±SD

* Average n =2

Appendix D

T-test of density and compression strength of FPU foam

Table D-1 T-test of density of flexible polyurethane foams in comparison between non polymer polyol and various formulations by HEMA 0, 3.62, and 5 mol/mol polyol, respectively (at fixed polymer polyol 10%wt based on total polyols)

HEMA (mol)	Mean Difference	Std. Error	Sig.	95% Confidence Interval	
				Lower Bound	Upper Bound
0	2.90000E1*	9.249	0.014	7.670	5.0330E1
3.62	2.33333E1*	9.249	0.036	2.004	4.4663E1
5	8.00000	9.249	0.412	-1.3330E1	2.9330E1

* The mean difference is significant at the 0.05 level.

Table D-2 T-test of density of flexible polyurethane foams comparison between non polymer polyol and polymer polyol of 10, 30, and 50 %wt based on total polyols (at fixed formulation of polymer polyol of 3.62 mol/mol polyol)

Amount of polymer polyol (%wt)	Mean Difference	Std. Error	Sig.	95% Confidence Interval	
				Lower Bound	Upper Bound
10	23.333*	7.071	0.011	7.03	39.64
30	31.333*	7.071	0.002	15.03	47.64
50	-1.333	7.071	0.855	-17.64	14.97

* The mean difference is significant at the 0.05 level.

Table D-3 T-test of compression strength of flexible polyurethane foams in comparison between non polymer polyol and various formulations by HEMA 0, 3.62, and 5 mol/mol polyol, respectively (at fixed polymer polyol 10%wt based on total polyols)

HEMA (mol)	Mean Difference	Std. Error	Sig.	95% Confidence Interval	
				Lower Bound	Upper Bound
0	55.2441667*	9.812	0.000	32.617475	77.870858
3.62	25.1704333*	9.812	0.033	2.543742	47.797125
5	1.9613667	9.812	0.847	-20.665325	24.588058

* The mean difference is significant at the 0.05 level.

Table D-4 T-test of compression strength of flexible polyurethane foams comparison between non polymer polyol and polymer polyol of 10, 30, and 50 %wt based on total polyols (at fixed formulation of polymer polyol of 3.62 mol/mol polyol**)**

Amount of polymer polyol (%wt)	Mean Difference	Std. Error	Sig.	95% Confidence Interval	
				Lower Bound	Upper Bound
10	25.1697333	1.631E1	0.167	-13.393650	63.733117
30	-1.6351333	1.631E1	0.923	-40.198517	36.928250
50	-69.1375667*	1.823E1	0.007	-112.252740	-26.022393

* The mean difference is significant at the 0.05 level.

VITAE

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