

PRELIMINARY STUDY ON SYNTHESIS AND CHARACTERIZATION
OF THE STAR-SHAPED POLY(ETHYLENE GLYCOL)
THROUGH POLYCONDENSATION REACTION

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การศึกษาเบื้องต้นของการสังเคราะห์และคุณลักษณะของพอลิเอทิลีนไคคอลที่มีรูปร่างแบบดาว
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ัญชนก วงศ์จันทร์ : การศึกษาเบื้องต้นของการสังเคราะห์และคุณลักษณะของพอลิเอ
ทิลีนไกลคอลที่มีรูปร่างแบบดาว โดยปฏิกิริยาการเกิดพอลิเมอร์แบบควบแน่น. (
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SHAPED POLY(ETHYLENE GLYCOL) THROUGH POLYCONDENSATION REACTI
ON) อ.ที่ปรึกษาหลัก : รศ. ดร.อนงค์นาฏ สมหวังธนโรจน์

พอลิเอทิลีนไกลคอลที่มีรูปร่างแบบดาวถูกสังเคราะห์ขึ้นจากกรดเพนเตดิก และ พอลิเอ
ทิลีนไกลคอลโดยใช้ปฏิกิริยาการเกิดพอลิเมอร์แบบควบแน่น เพื่อนำไปแก้ปัญหาความแข็งแรงของ
พอลิเมอร์ขณะหลอมเหลวของพอลิแลคติกแอซิด ในส่วนของการสังเคราะห์จะใช้พอลิเอทิลีนไกล
คอลที่มีน้ำหนักโมเลกุลแตกต่างกันคือ 200, 400 และ 600 กรัมต่อโมล จากนั้นโครงสร้างทางเคมี
ของพอลิเอทิลีนไกลคอลที่มีรูปร่างแบบดาวจะถูกนำไปวิเคราะห์โดยเทคนิค FTIR และ NMR ผล
ของสเปกตรัม FTIR ของผลิตภัณฑ์พอลิเอทิลีนไกลคอลแสดงพีคใหม่ขึ้นซึ่งเป็นพีคของคาร์บอนิล
เนื่องมาจากการทำปฏิกิริยาระหว่างหมู่ไฮดรอกซิลของพอลิเอทิลีนไกลคอลและหมู่คาร์บอกซิลของ
กรดเพนเตดิก สเปกตรัม NMR ของผลิตภัณฑ์พอลิเอทิลีนไกลคอลแสดงโปรตอนของกรดเพนเตดิกใน
โครงสร้างของสายโซ่และยังพบอะตอมคาร์บอนของหมู่คาร์บอนิลเกิดขึ้นอีกด้วย นอกจากนี้ น้ำหนัก
โมเลกุลเฉลี่ยของผลิตภัณฑ์พอลิเอทิลีนไกลคอลมีค่าเพิ่มมากขึ้นเมื่อเทียบกับพอลิเอทิลีนไกลคอลสาย
โซ่ตรง หลังจากนั้นมีการศึกษาสมบัติทางกระแสวิทยาของผลิตภัณฑ์พอลิเอทิลีนไกลคอล พบว่า
ผลิตภัณฑ์พอลิเอทิลีนไกลคอลมีความหนืดเพิ่มมากขึ้นเมื่อเทียบกับพอลิเอทิลีนไกลคอลสายโซ่ตรง
พฤติกรรมการไหลของพอลิเอทิลีนไกลคอลน้ำหนักโมเลกุล 200, 400 กรัมต่อโมลและผลิตภัณฑ์พ
อลิเอทิลีนไกลคอลเป็นการไหลแบบนิวโตเนียน ส่วนพอลิเอทิลีนไกลคอลน้ำหนักโมเลกุล 600 กรัมต่อ
โมลแสดงพฤติกรรมการไหลเป็นแบบนอนนิวโตเนียน ดังนั้นการสังเคราะห์ผลิตภัณฑ์พอลิเอทิลีนไ
กคอลโดยปฏิกิริยาการเกิดพอลิเมอร์แบบควบแน่นประสบความสำเร็จ

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The synthesis of star-shaped poly(ethylene glycol) was synthesized from pentetic acid (PA) and poly(ethylene glycol) (PEG) by polycondensation reaction in order to solve the problem of the melt strength of the molten polymer of poly(lactic acid). In this study, the star-shaped poly(ethylene glycol) were synthesized with a different molecular weight of neat poly(ethylene glycol) of 200, 400 and 600 g/mol. After that, the chemical structure of product-PEG was investigated by FTIR and NMR techniques. FTIR spectra of the product-PEG exhibited carbonyl peak due to the reaction between hydroxyl groups of PEG and carboxyl groups of PA. The NMR spectra of the product PEG displayed the proton of PA in chain structure and carbon atom of carbonyl group, respectively. Moreover, viscosity average molecular weight of the product-PEG was higher than that of linear PEG. For the rheological properties, the viscosity of product-PEG was higher than that of linear PEG. The flow behavior of PEG with Mw of 200, 400 g/mol and the product-PEG exhibited Newtonian behavior. PEG with Mw of 600 g/mol showed Non-Newtonian behavior. Thus, the synthesis of product-PEG by polycondensation reaction was successful.

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Advisor's Signature



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CHAPTER I

INTRODUCTION

1.1 General Introduction

Poly(lactic acid) (PLA) is a biopolymer as well as a linear aliphatic thermoplastic polyester which can be produced from renewable resources such as tapioca, sugarcane and corn [1]. It has some advantages such as transparency, biodegradability and high mechanical properties. Thus, it is widely used for eco-friendly packaging applications [1]. Blown film process is one of the processes for making film packaging which has several factors that should be concerned [2]. PLA has some limitations for blown film process due to its brittleness, low thermal stability, and poor melt strength [2]. From those limitations, this work will focus on improving the thermal stability and melt strength of PLA blown film by blending it with star-shaped poly(ethylene glycol) to increase the entanglement of a polymer chain in PLA blown film.

There are some researches that try to improve mechanical, thermal and rheological properties of PLA by blending it with other polymers, such as poly(butylene adipate-co-terephthalate), poly(butylene succinate) and poly(ethylene glycol) [3-5]. For example, Schneider et. al. [3] studied the blends of PLA and poly(butylene adipate-co-terephthalate) (PBAT) which were immiscible by adding the amount of epoxy functionalized-poly(lactic acid) as a compatibilizer. The blend with compatibilizer showed higher thermal, mechanical properties, and better processability of the blown

film product [3]. Moreover, Sungsanit *et al.* [5] used poly(ethylene glycol) (PEG) as a plasticizer and blended it with linear PLA (L-PLA) with varied PEG contents. It was found that the impact resistance and crystallinity of L-PLA were increased with increased PEG loading, but the glass transition temperature (T_g) and stiffness were reduced.

In term of melt strength improvement, many researches reported that the change of the chain architecture of PLA from linear to the star or branched structure could affect the melt strength of PLA [6-10]. They revealed that PLA blended with a multifunctional epoxide by reactive extrusion resulted in the improvement of thermal stability and melt strength over shearing and stretching measured by rheometer [6, 9, 10]. Several researchers were interested in the preparation of carboxylic acid terminated PLA through polycondensation due to the simplicity of polymer preparation [7-10]. Hiltunen *et al.* [7] synthesized the L-lactic acid polymer, hydroxyl- and carboxyl-terminated telechelic prepolymers by the addition of small amounts of 1,4-butanediol and adipic acid, respectively. However, these studied only presented the synthesis of linear bifunctional product and other article represented multifunctional pentetic acid (PA) for the synthesis of star-shaped, COOH-terminated telechelic of PLA modified chain architecture [10]. Thus, star-shaped polymers, consisting of a core, have received more attention because of their highly branched structures and unique rheological properties [11]. However, the star-shaped of polymer with carboxylic functionalized PEG has not been reported yet.

In this work, the synthesis of star-shaped carboxylic terminated with PEG by polycondensation was studied. The synthesized polymer was characterized by Fourier Transform-Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR) and viscosity average molecular weight. The rheological properties of star-shaped PEG were also investigated.

1.2 Objectives

1.2.1 To synthesize and characterize of the star-shaped carboxylic acid terminated poly(ethylene glycol) through polycondensation reaction.

1.2.2 To study the effect of PEG molecular weight of star-shaped PEG on its rheological property.

1.3 Research Scope

1.3.1 Synthesis the multifunctional pentetic acid (PA) as a star-shaped, COOH-terminated poly(ethylene glycol) with varied weight average molecular weight of PEG at 200, 400 and 600 g/mol.

1.3.2 Confirmation of the star-shape terminated PEG by using FTIR, $^1\text{H-NMR}$ spectroscopy, $^{13}\text{C-NMR}$ spectroscopy, and viscosity average molecular weight.

1.3.3 The viscosity, storage modulus and loss modulus of star-shaped terminated PEG will be evaluated.



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CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter described the literature survey of poly(lactic acid), poly(ethylene glycol) and branched polymer architectures.

2.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is an aliphatic thermoplastic polyester that can be produced from renewable resources. It is an eco-friendly polymer which has been considered as a replacement polymer for the petroleum-based polymers such as polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) [2]. PLA has biocompatibility, composability, good mechanical and physical properties such as high strength, high modulus, transparency, and low permeability and transparency [12]. The life cycle of PLA is shown in Figure 2.1 [12].

PLA is synthesized from alpha-hydroxy (α -Hydroxy acid) subunit or 2-hydroxy propionic acid through the direct condensation reaction of its monomer to produce lactic acid as an oligomer. The polymerization reaction is obtained by a ring-opening mechanism of cyclic lactide dimer [12]. The chemical structure of PLA is displayed in Figure 2.2.



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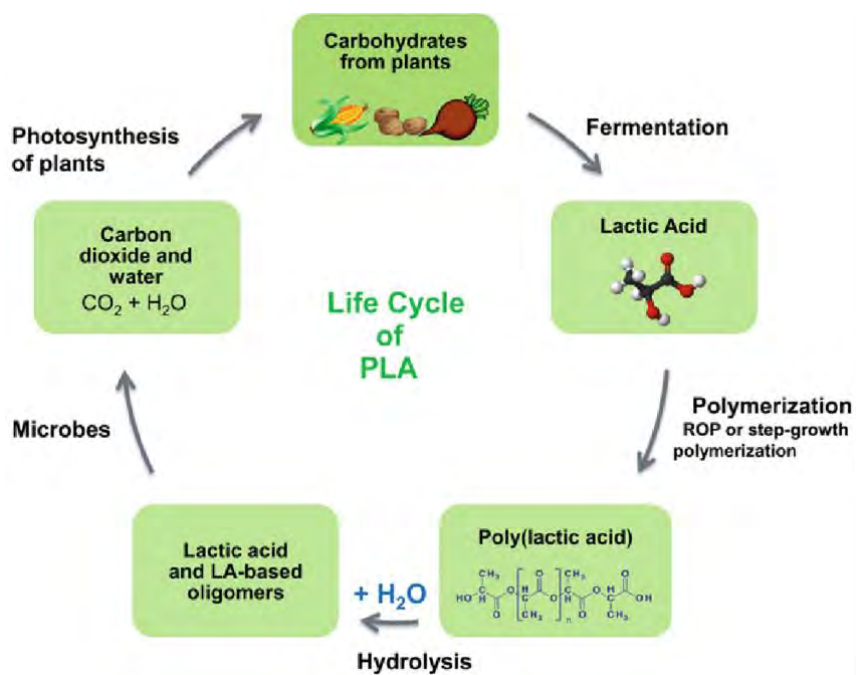


Figure 2.1 Life cycle of PLA [12]

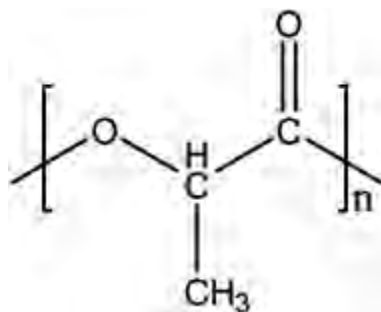


Figure 2.2 Chemical structure of poly(lactic acid) [13]

PLA products can be processed by several techniques such as injection molding, thermoforming, compression molding, extrusion, blow molding and blown film techniques [2]. It has been used as food packaging and biomedical devices due to its environmentally friendly nature, transparency and biodegradability [5]. However, it has some usage disadvantage such as brittleness, low thermal stability, and poor melt

strength [2, 13]. To improve these properties, PLA was enhanced by blending it with plasticizer or with a second polymer including branched polymer and copolymer [5]. Schneider et al. [3] found that blends of PLA with poly(butylene adipate-co-terephthalate) exhibited immiscible blend, but the addition of a small amount of epoxy functionalized-poly(lactic acid) as a compatibilizer could solve this problem and improved thermal and mechanical properties and processability of PLA blown film product.

2.2 Poly(ethylene glycol) (PEG)

Poly(ethylene glycol) (PEG), also known as poly(ethylene oxide) (PEO), is a synthetic polyether that is readily available in a range of molecular weights. It is called PEGs if it has a molecular weight less than 100,000 g/mol, while the ones with a molecular weight higher than 100,000 g/mol are classified as PEOs [14]. These polymers are amphiphilic and soluble in water as well as in many organic solvents (e.g., methylene chloride, ethanol, toluene, acetone, and chloroform). The chemical structure of poly(ethylene glycol) is shown in Figure 2.3 [15].

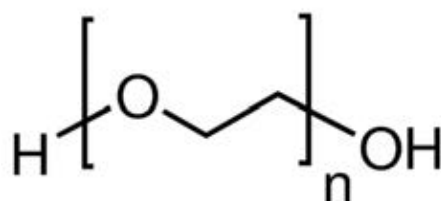


Figure 2.3 Chemical structure of poly(ethylene glycol) [16]

There are several researches reporting the properties of PLA and PEG blends. For example, Jasim *et al.* [17] revealed that good compatibility existed between PLA and PEG. PEG influenced the reduction of dynamic moduli and complex viscosity of PLA/PEG blend. Moreover, Sungsanit *et al.* [5] found that linear PLA (L-PLA) plasticized with PEG, with PEG having MW of 1,000 g mol⁻¹ and at various PEG concentrations, showed higher impact resistance and crystallinity than those of L-PLA, but the glass transition temperature (T_g) and stiffness were decreased. In addition, at 10 %wt of PEG, there was a phase separation between PEG and PLA matrix leading to poor mechanical and thermal properties of PLA/PEG blend. The study of the dynamic behavior and rheological properties of PLA/PEG blend had shown that the plasticized PLA possessed lower viscosity and elastic properties than neat PLA [5].

2.3 Branched Polymer Architectures

Branched polymer affects many of physical properties including the polymer solution viscosity, melt viscosity, solubility in various solvents, glass transition temperature and the size of individual polymer coils in solution. The branched polymer architectures are shown in Figure 2.4. Branched polymers include star, hyperbranched and dendritic-like polymers, dendrimers, graft copolymer, brush, and comb-like polymers as well as polymer networks [18]. In this work, the star-shaped polymer was focused.

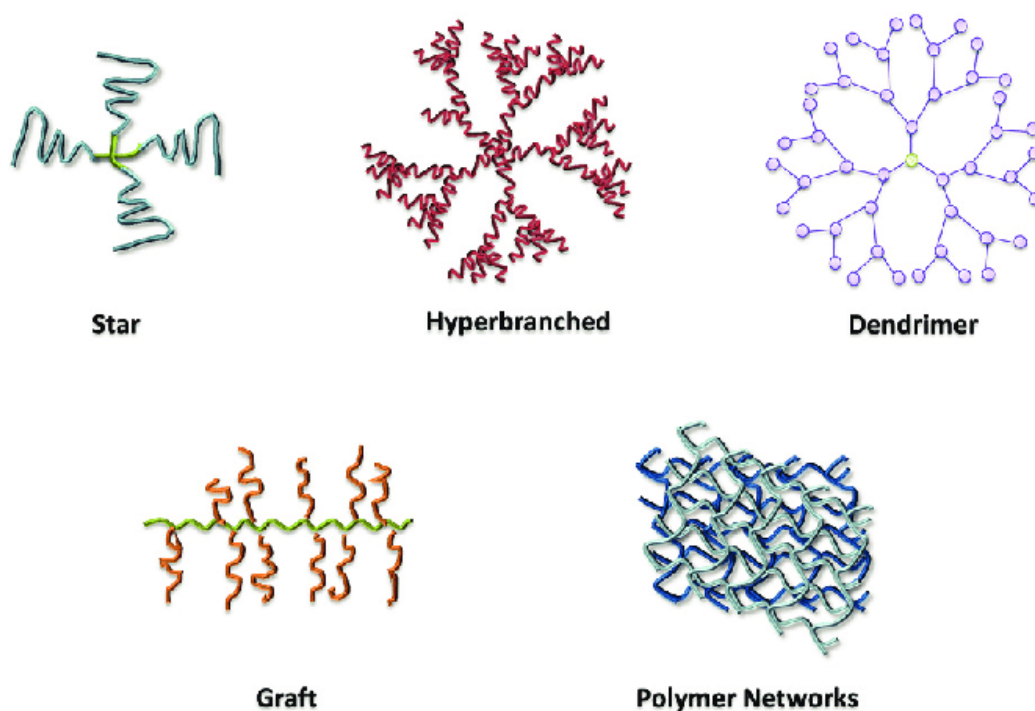


Figure 2.4 Examples of branched polymer architectures [18]

2.3.1 Star-shaped Polymer

The star-shaped polymer is a branched polymer molecule in which a single branch point gives rise to multiple linear chains or arms. If the branches are the same linear chains, they are named “symmetric stars or homostars”. For the branches that have different molecular weights or topology, it is called “asymmetric stars”, or “miktoarm stars” owing to different chemical structure. These arms can be constituted by one-block or multiblock copolymers [11, 18]. The arms of the star-shaped polymer may be modified by choosing the specific chemical structure of an arm and core, depending on the required application. The viscosity of star-shaped polymer does not depend on the total molecular weight but only on the molecular weight of each arm

[19]. The star-shaped polymer is an interesting material for improving PLA properties owing to its rheological behavior and dilute solution properties [19]. Viscosity and other properties depend on the molecular weight of arms. In comparison with dendrimers, the star-shaped polymers show the better advantages of accelerated and tunable methods of synthesis than dendrimer [19].

There are three approaches for the preparation of star-shaped polymer, namely the core-first approach, the arms-first approach, and the core-crosslink approach, as shown in Figure 2.5. The core-first approach is formed by using a multifunctional initiator as a core that initiates the polymerization of several arms simultaneously. The major limitation of this methodology is the difficult characterization of the obtained star-shaped polymer because the molecular weight of its arms cannot be directly measured [11]. The arms-first approach is to form the core of the star macromolecule by coupling the monofunctional living polymeric chains with a difunctional reagent that served as a core [11]. The main advantage of this approach is the relative ease of characterization since the living arms can be characterized in a previous step before linkage. However, this method also has some disadvantage which is the steric hindrance which could limit the number of linkage arms that can be linked together during crosslink reaction [18]. The core-crosslink approach which consists of the reaction of living macroinitiators (MI), also named macromonomers, with multifunctional molecules acting as cross-linkers giving rise to star-shaped architectures, is the best choice for this work [18].

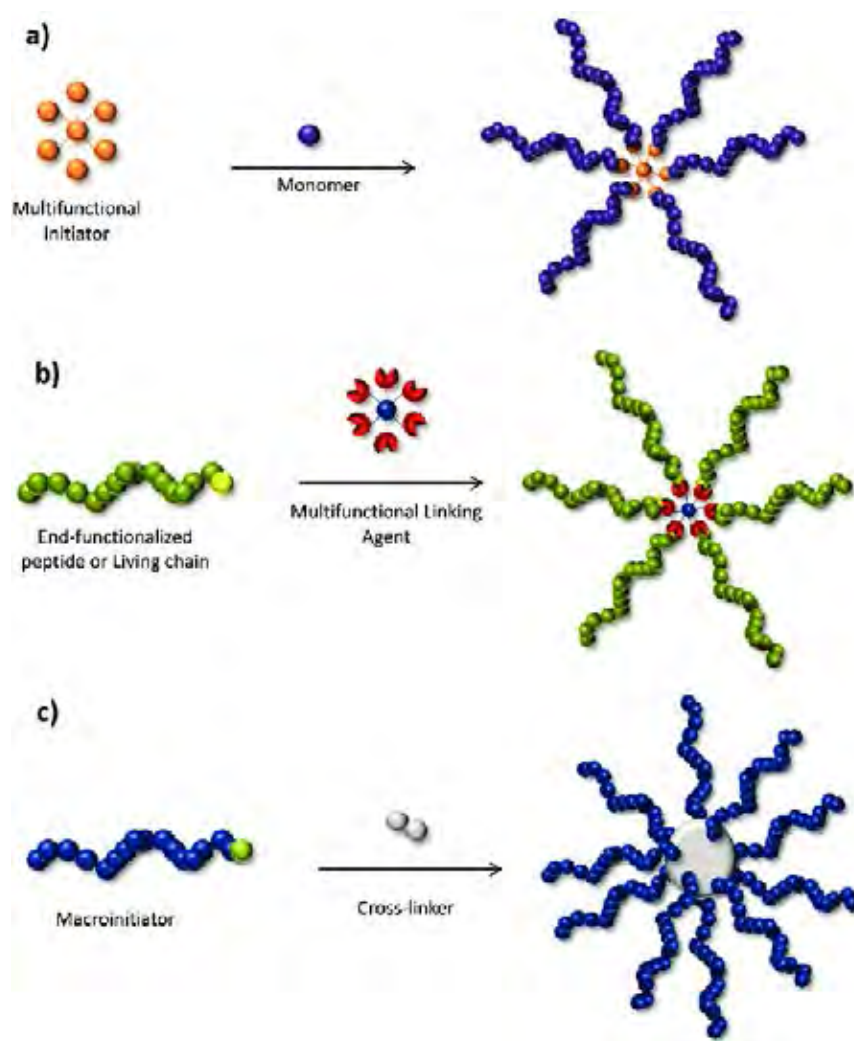


Figure 2.5 The synthetic approach of the star-shaped polymer [18]

2.3.2 Synthesis of Star-Shaped Polymer using Carboxylic Acid as a core molecule

molecule

The synthesis branch structure of tricarboxylic acid-functionalized polylactic acid (PLA) through polycondensation of lactic acid (LA) and citric acid (CA) was reported by Kucharczyk *et al.* [9]. LA and CA (0, 1, 3, 5, 7, 10, 15 and 20 wt% related to LA) were add into a double-necked flask. The temperature was set at

160 °C. After that, the reactor was disconnected from the vacuum pump and 0.05 wt% related to initial mass of the reactants of $\text{Sn}(\text{Oct})_2$ was added dropwise under continuous stirring. The obtained product was filtrated, washed with methanol, and dried at 45 °C for 48 h. The chemical structure of lactic acid and tricarboxylic acid functionalized polylactic acid (PLA) were displayed in Figure 2.6. The result showed the reduction of molecular weight of the branch structure of tricarboxylic acid-functionalized PLA due to the presence of the CA unit in branched structure chain leading to termination of the product chain. The branched structure was detected at low CA concentration (up to 1 wt%).

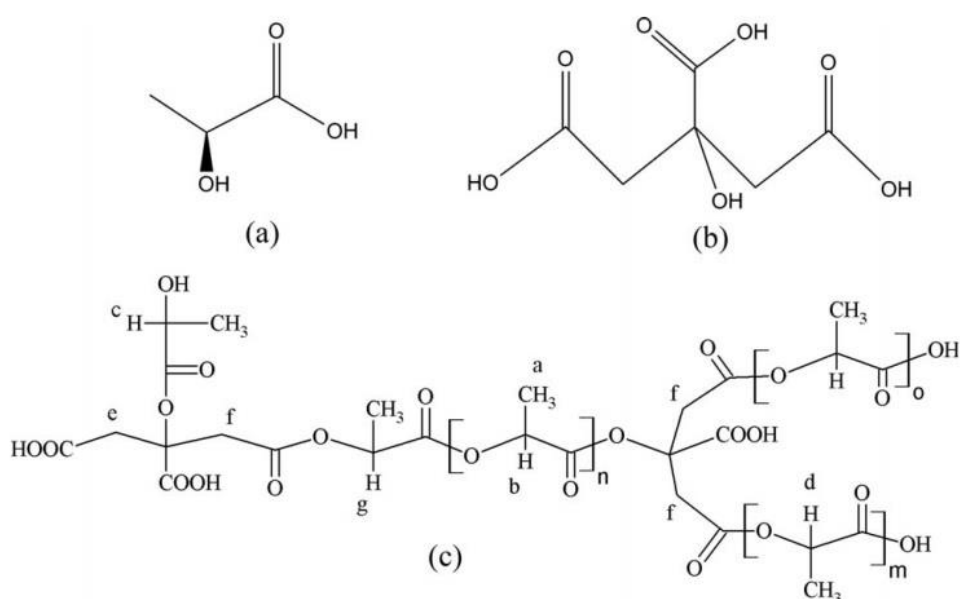
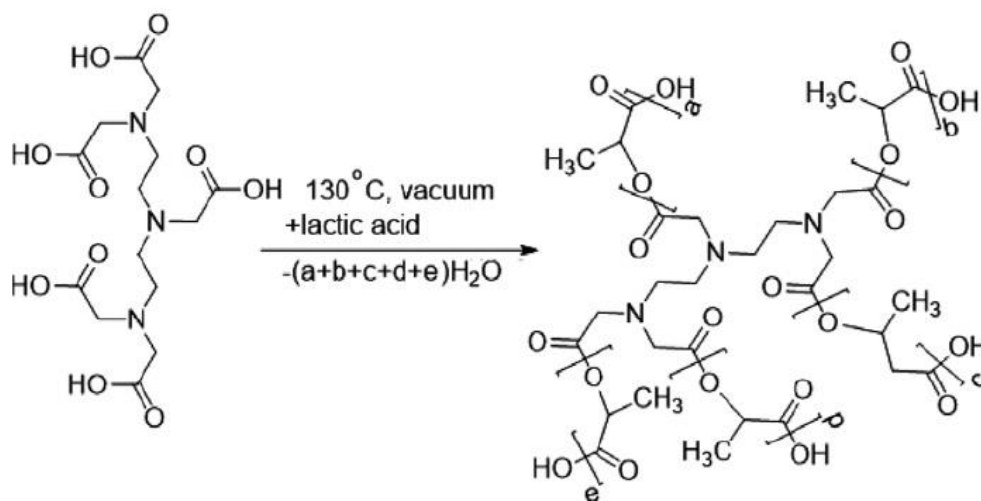


Figure 2.6 The chemical structure of (a) lactic acid, (b) tricarboxylic acid and (c) tricarboxylic acid-functionalized polylactic acid (PLA) [9]

Furthermore, Kucharczyk *et al.*[10] also synthesized the star-shaped carboxyl functionalized poly(lactic acid) by a polycondensation reaction and used pentetic acid (PA) as a core. The possible chemical structure of the product is shown in Figure 2.7. After the polycondensation reaction, the star-shaped PLA was successfully synthesized with five functional PA. However, the synthesis of star-shaped carboxyl polymer having poly(ethylene glycol) arms and had PA as a core have not been reported yet. Thus, the synthesis of star-shaped poly(ethylene glycol) with PA as a core molecule by polycondensation reaction will be focused in this work.



Pentetic acid

star-shaped carboxyl functionalized poly(lactic acid)

Figure 2.7 Chemical structure of the star-shaped carboxyl-functionalized poly(lactic acid) [10]

2.3.3 Effect of Star-shaped Polymer on Thermal Properties

Star-shaped polymers have a lower melting temperature (T_m), crystallization temperature (T_c) and degree of crystallization (x_c) than linear polymer. It depends on the length and number of arms of the star-shaped polymer. In previous work, Wang *et al.*[19] synthesized the three-arm star-shaped poly(ethylene glycol) (TMP-(SK-PEG)₃) having 1,1,1 trihydroxymethyl- propane - sebacic acid diacetic anhydride (SK) (TMP-SK₃) as a core and stannous octoate was used as a catalyst [20]. T_m and T_c of three-arm star-shaped PEG were lower than those of linear PEG because the crystallization process of PEG arms was disturbed by a core and resulted in decreased T_m and T_c . Moreover, the star-shaped carboxyl functionalized poly(lactic acid) was synthesized by using pentetic acid (PA) as a core [10]. The star-shaped carboxyl functionalized poly(lactic acid) exhibited semi-crystalline behavior. The addition of PA content in PLLA matrix resulted in lower T_g which could be due to the presence of branched structure and the increment of D-lactide molecules which increased the free volume and enhanced chain mobility of PLA [10].

2.3.4 Effect of Star-shaped Polymer on Rheological Properties

Numerous researches have shown that branched polymers display significantly different rheological properties compared to linear polymers and polymer networks. The rheological properties of star-shaped polyisoprene having 3 and 4 arms stars were reported by J. Fetters *et al.*[19]. The viscosity of star-shaped polyisoprene having 3 arms was lower than that 4 arms with by approximately 20%. In addition, Perse *et al.* [21] reported that branched polymers displayed significantly different characteristic in rheological properties compared to linear polymers and polymer network. The result showed that the addition of polycaprolactone (PCL) to hyperbranched polyester Bolton (BH40) decreased the viscosity of copolymer with increasing molar mass; but it only showed this phenomenon below the ratio of BH40:PCL at 1:4 wt/wt. Above this amount, the increased of the amount of PCL increase both molar mass as well as the complex viscosity [21]. This might be due to the long enough branched molecules to entangle together with the matrix polymer in accordance with the restrict of chain mobility of polymer molecules [22].



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CHAPTER III

EXPERIMENTS

This chapter contained materials, sample synthesis of star-shaped poly(ethylene glycol), characterization of the synthesized polymer. The schematic diagram of the experimental procedure was illustrated in Figure 3.1. For the synthesis of star-shaped poly(ethylene glycol), poly(ethylene glycol) of molecular weight 35,000 g/mol, 10,000 g/mol, 4,000 g/mol and 1,000 g/mol were chosen. The synthesized product was confirmed by Fourier Transform-Infrared Spectroscopy (FTIR). It was found that the FTIR spectra of the synthesized product did not show the carbonyl peak (C=O) caused by the reaction. Therefore, the star-shaped PEG was unsuccessfully synthesized which could be due to the steric hindrance of a large molecule of PEG. Thus, PEG of molecular weight 200 g/mol, 400 g/mol, and 600 g/mol was chosen to further synthesize star-shaped PEG in this work.

3.1 Materials

Poly(ethylene glycol) (PEG, Mw 200, 400, 600 and 1,000 g/mol) were purchased from Merck, Germany. Poly(ethylene glycol) Mw 1,500 g/mol was purchased from ACROS, BELGIUM. Poly(ethylene glycol) Mw 2,000 g/mol was purchased from TCI, Japan. Pentetic acid (PA) or diethylenetriaminepentaacetic acid (DTPA), Mw 393.35 g/mol, was purchased from Sigma Aldrich, Germany. The solvent which was sulfuric

acid and toluene were bought from RCI Labscan Limited, Thailand. The chemical structure of PLA, PEG and PA were shown in Table 3.1.

3.2 Synthesis of Star-shaped Terminated Poly(ethylene glycol)

by Polycondensation Reaction

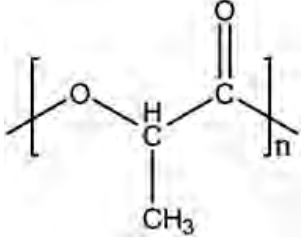
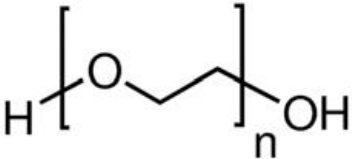
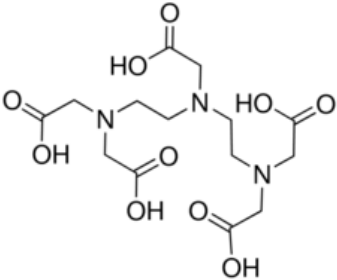
Synthesis of star-shaped terminated poly(ethylene glycol) was adapted from the procedure reported by Kucharczyk *et al.* [10]. Pentetic acid and poly(ethylene glycol) were added into a 100 ml round-bottomed flask containing toluene with a magnetic stirrer. The ratio of PA: PEG was 1:5 mol/mol. First, the mixture was heated at 110 °C for 1 hour. PA was dissolved during this stage in the reaction mixture. After that, the temperature was raised to 130 °C at 1 atm and 0.4 wt% of sulfuric acid was added dropwise under continuous stirring. The reaction was then continued for 6 hours at temperature of 130 °C. The temperature of 130 °C was chosen in order to prevent PA degradation and suppress anhydride reaction between terminal COOH groups. The resulting product was cooled down to room temperature. DI water was added. The product separated into two phases; i.e., toluene is an upper phase and polymer solution is a lower phase. The toluene phase was removed. The polymer solution was filtered by filter paper no.42 to remove unreacted PA from the product. Unreacted PA collected from filter paper was also characterized by FTIR to confirm that there was only unreacted PA on filter paper. The obtained product was filtered, washed with water several times, and dried at 80 °C for 48 hours in a vacuum oven at 20 kPa.



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Table 3.1 The chemical structure of PLA, PEG, and PA

Chemicals	Chemical structure
Poly(lactic acid) (PLA)	 <chem>*OC(C)C(=O)*</chem>
Poly(ethylene glycol) (PEG)	 <chem>*OCCO*</chem>
Pentetic acid (PA)	 <chem>OC(=O)CN(CC(=O)O)CCN(CC(=O)O)CC(=O)O</chem>



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3.3. Characterization

3.3.1 Fourier Transform-Infrared Spectroscopy (FTIR)

The functional group of synthesized star-shape terminated PEG was by FTIR techniques. IR spectra were collected using a Perkin Elmer model Spectrum GX. All samples were placed on KBr plates.

Fourier Transform-Infrared Spectroscopy is a technique for analyzing the functional group of organic compounds [23]. Molecular vibrations can be related directly to the symmetry of molecules, and so it is often possible to determine precisely how a molecule is bonding on surfaces or as a component in a solid phase from its infrared spectrum [23].

3.3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR and ^{13}C -NMR spectra were recorded in the solution of (DMSO- d_6) using a Varian, model Mercury-400 Nuclear Magnetic Resonance spectrometer (USA) operating at 500 MHz. Chemical shifts were reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent signal as a reference.

NMR is a spectroscopic technique to observe local magnetic fields around atomic nuclei [24]. The principle NMR is that many nuclei have a spin and all nuclei are electrically charged. The energy transfer takes place at a wavelength that

corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency [24].

3.3.3 Viscosity Average Molecular Weight

The molecular weight of neat poly(ethylene glycol) and the synthesized star-shaped poly(ethylene glycol) were measured by the viscosity of polymer solution using Ubbelohde viscometer according to ASTM D445 and D446. Using two parameters Mark-Houwink relationship, the intrinsic viscosity had been related to the average molar mass of the polymer. For 0.05M sodium sulfate at 30 ± 2 °C, $K = 0.00104$ dL/g and $a = 0.57$ [25].

3.4.4 Rheological Properties

Rheological properties of star-shaped poly(ethylene glycol) was characterized using a parallel plate and cone and plate fixture with strain-controlled rheometer (model AR-G2 manufactured by TA instrument). The parallel-plate diameter and cone and plate diameter are 25 mm and 40 mm, respectively. The angle of the truncated cone is 2° . The viscosity of sample was measured as a function of shear rate. The strain sweep test was also performed to identify the linear viscoelastic regime of polymer and to identify the strain for the frequency sweep test to evaluate the crossover frequency which showed the entanglement character of the polymer chain. The temperature was set at 25 ± 2 °C and 50 ± 2 °C.



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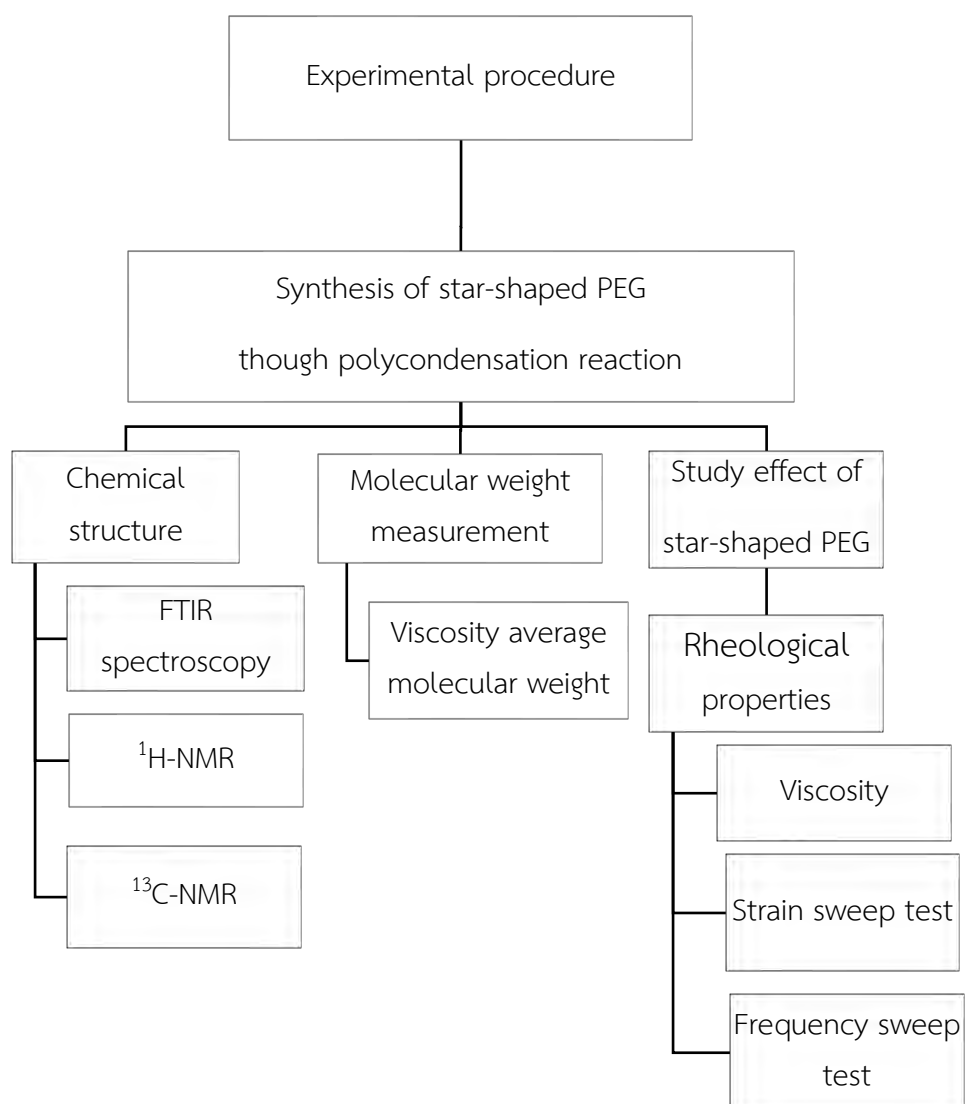


Figure 3.1 The schematic diagram of the experiment procedure

CHAPTER IV

RESULTS AND DISCUSSION

In this section, the characterization of the star-shaped poly(ethylene glycol) synthesized with different molecular weight of poly(ethylene glycol) ranging from 200-600 g/mol by polycondensation reaction was discussed. The chemical structure of neat PEG and the synthesized star-shaped PEG were investigated by FTIR, ^1H NMR, and ^{13}C NMR. The possible chemical structure of the synthesized star-shaped PEG was considered in this part. Finally, the rheological properties including viscosity, storage and loss moduli of neat PEG and the synthesized star-shaped PEG were investigated.

4.1 The Chemical Structure Of Star-shaped Poly(ethylene glycol)

The star-shaped poly(ethylene glycol) (star-shaped PEGs) with different molecular weight varied at 200, 400 and 600 g/mol were synthesized by a polycondensation reaction. The chemical structure of star-shaped PEGs was verified by FTIR, ^1H -NMR, and ^{13}C -NMR. The name of product-PEG200, product-PEG-400 and product-PEG-600 represented the synthesized star-shaped poly(ethylene glycol) with different PEG molecular weight. Pentetic acid (PA) was used as a core of synthesized star-shaped poly(ethylene glycol). The product-PEG200, product-PEG400, and product-PEG600 consist of the star-shaped PEG200 with remaining PEG200, the star-shaped PEG400 with remaining PEG400, the star-shaped PEG600 with remaining PEG600, respectively.

4.1.1 FTIR

The FTIR spectra of pentetic acid (PA), poly(ethylene glycol) with Mw 200 g/mol (PEG200), poly(ethylene glycol) with Mw 400 g/mol (PEG400), poly(ethylene glycol) with Mw 600 g/mol (PEG600) and the synthesized star-shaped PEGs are shown in Figure 4.1-4.3. Figure 4.1 compares the FTIR spectra of PA, PEG400 and the product-PEG400. The absorption peak of PA at 1728 cm^{-1} , 1689.5 cm^{-1} and 1628.9 cm^{-1} corresponded to C=O groups. The peak at 1442.4 cm^{-1} belonged to CH_2 scissoring. The C-N stretching was appeared at 1233.8 cm^{-1} , 1201.3 cm^{-1} , 1142 cm^{-1} , 1087.7 cm^{-1} and 1043.1 cm^{-1} . For neat PEG, the broad peak between 3392 cm^{-1} and 3401 cm^{-1} is O-H stretching. The C-H stretching vibration and C-OH stretching were displayed at $2864 - 2877\text{ cm}^{-1}$ and 1106.96 cm^{-1} , respectively. The peak of product PEG at 2876 cm^{-1} and 3400 cm^{-1} represented the C-H bending and the O-H stretching in the repeating unit of PEG chain. Moreover, the new peak exhibited at 1735 cm^{-1} for product-PEG400, 1737 cm^{-1} for product-PEG 200 and 1735 cm^{-1} for product-PEG600 were attributed to ester group due to the reaction between hydroxyl groups of polyethylene glycol and carboxyl groups of pentetic acid. These results were in accordance with previous researches [26, 27]. It was found that the peak of PEG at 3441 cm^{-1} , 2878 cm^{-1} and 1094 cm^{-1} were O-H stretching, C-H stretching and C-OH stretching, respectively. Moreover, the obvious peak at 1730 cm^{-1} could be attributed to vibrations of C=O stretching of the carboxylic group for PA [26, 27]. This indicated that the synthesis of product-PEGs was successful. The similar synthesized peaks were observed for product-PEG200 and product-PEG600 as

represented in Figure 4.2 and Figure 4.3. To further confirm the synthesis, the NMR analysis was evaluated, and the possible mechanism of our synthesis was proposed as followed.

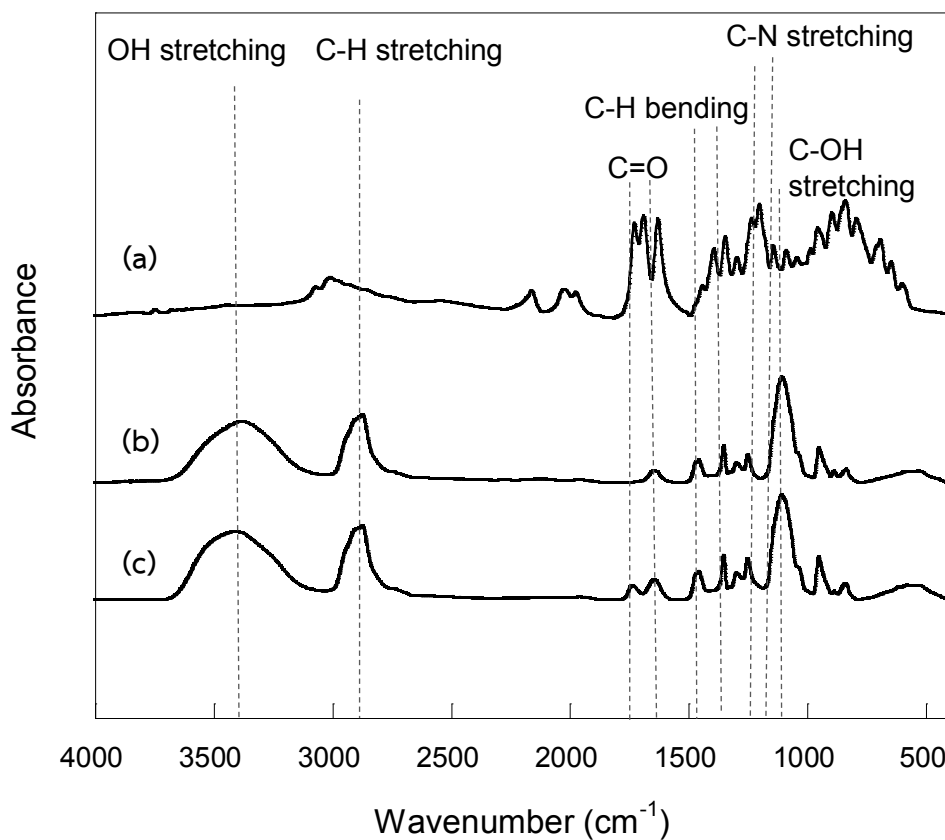


Figure 4.1 FTIR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 200 g/mol and (c) the product-PEG200

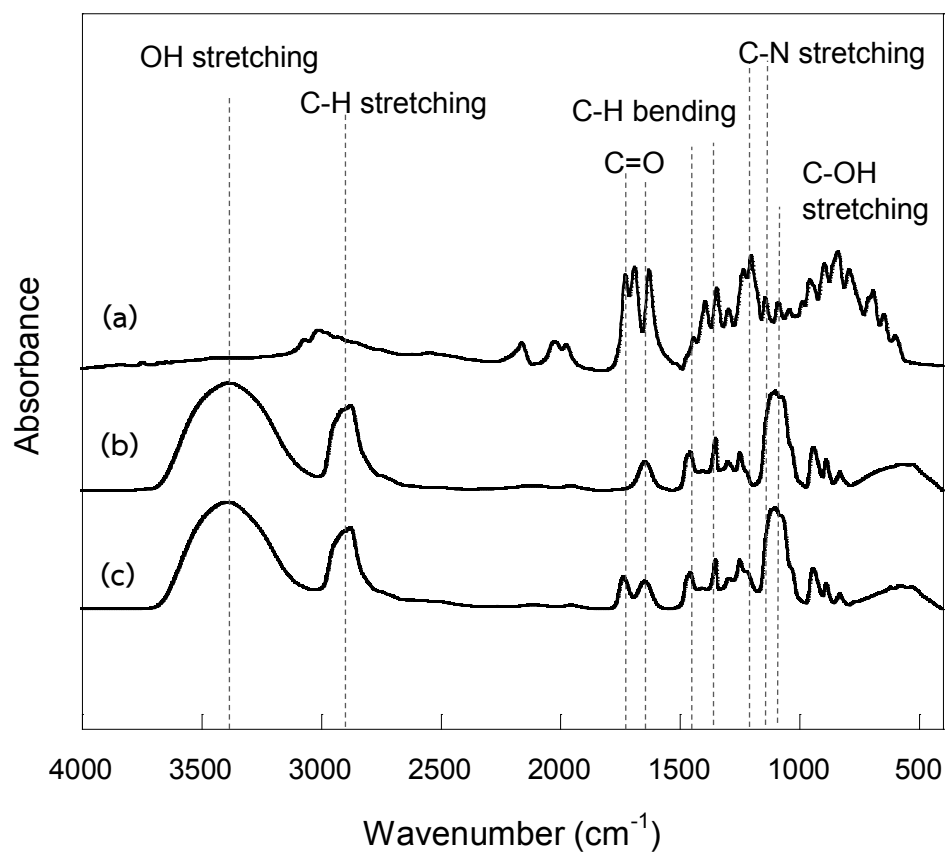


Figure 4.2 FTIR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 400 g/mol and the (c) product-PEG400

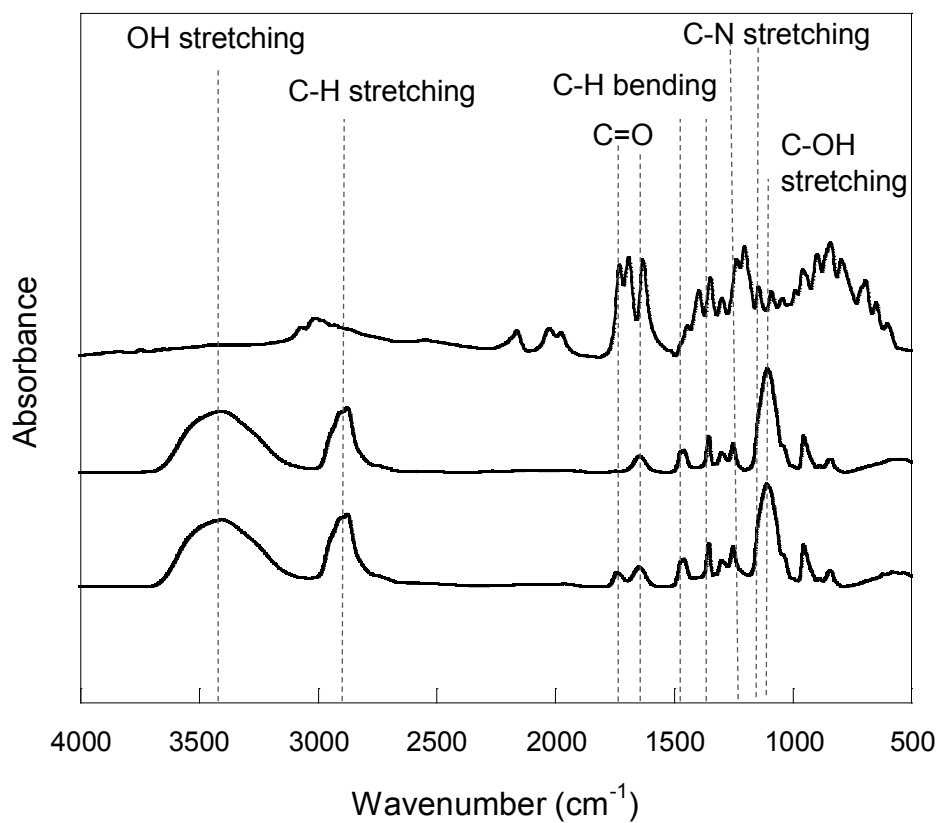


Figure 4.3 FTIR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 600 g/mol and (c) the product PEG 600



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4.1.2 NMR

The product-PEG with PA as a core synthesized via polycondensation reaction was analyzed by NMR spectroscopy. Figure 4.5 showed the ^1H NMR of pentetic acid, poly(ethylene glycol) with molecular weight 400 g/mol and the product-PEG400. The other set of synthesized star-shaped with a different molecular weight of PEG also showed similar results as those of PEG400. Thus, the product PEG400 was shown as a representative sample in Figure 4.5. The ^1H NMR of product-PEG200 and product-PEG 600 were revealed in Figure 4.4 and Figure 4.6. For pentetic acid, the signals at 3.54 ppm and 3.42 ppm belonged to CH_2 close to carboxyl groups. The CH_2 group in the PA molecule was observed from the signal at 2.96 ppm and 2.86 ppm. The result of ^1H NMR for PA was similar to that reported by Kucharczyl *et al.* [10]. The signal at 2.5 ppm was dimethyl sulfoxide- d_6 (DMSO- d_6) solvent [28]. Moreover, the peak at 4.55 ppm and 3.32-3.51 ppm indicated the $-\text{OH}$ and $\text{O}-\text{CH}_2$ functional group of PEG structure, respectively. The peak at 3.05 ppm and 3.40 ppm of the product PEG represented CH_2 in PA chains. The CH_2 of PEG structure was observed at 3.46-3.50 ppm. The hydroxyl proton ($-\text{OH}$) synthesized of the product-PEG400 was shifted from 4.14 to 4.16 ppm. This observation indicated that most of the $-\text{OH}$ groups took part in the polycondensation reaction [29]. To further confirm the formation of the carbonyl group, ^{13}C -NMR was also used to determine the chemical structure of the synthesized star-shaped PEG.

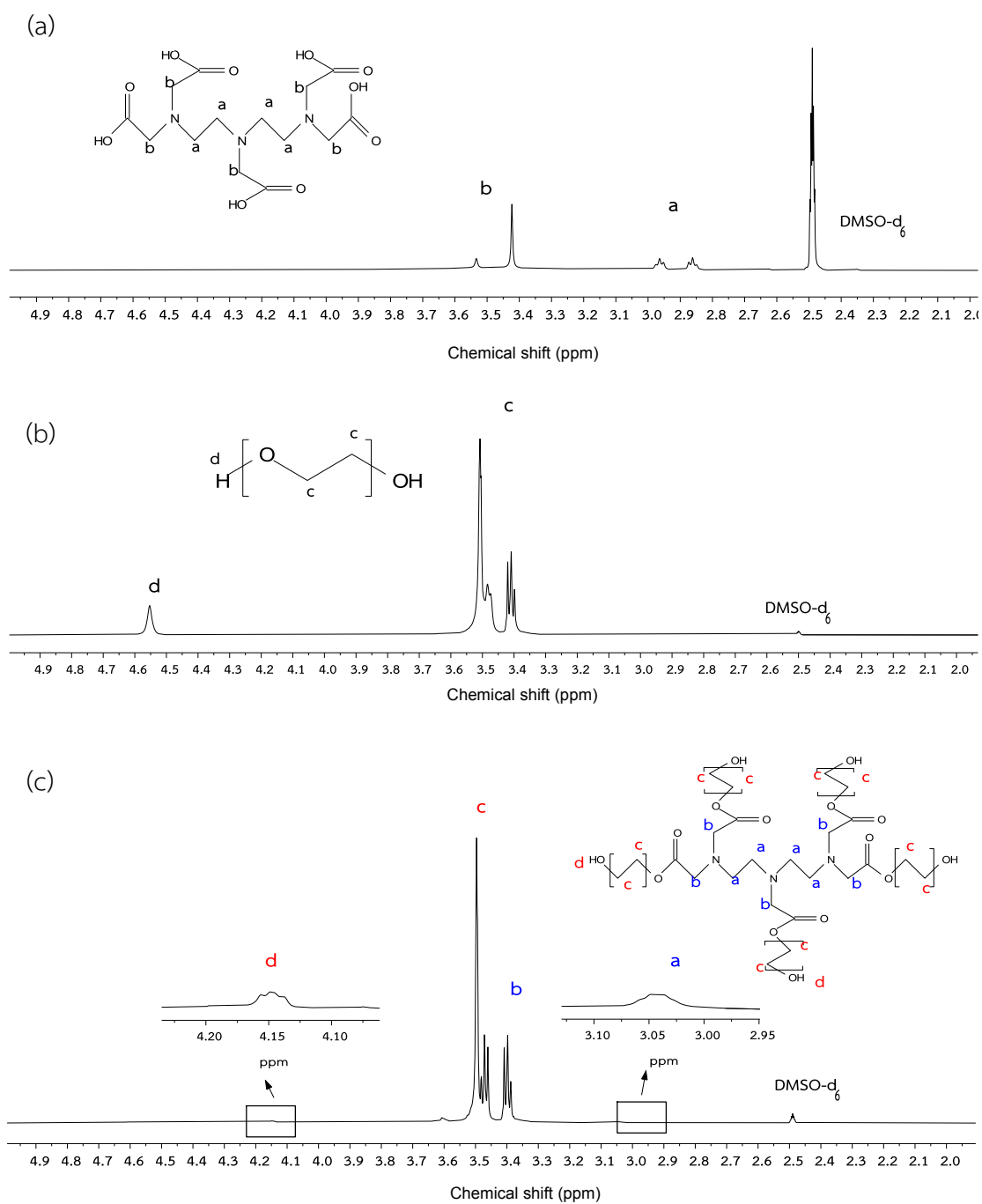


Figure 4.4 ^1H NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 200 g/mol and (c) the product-PEG200

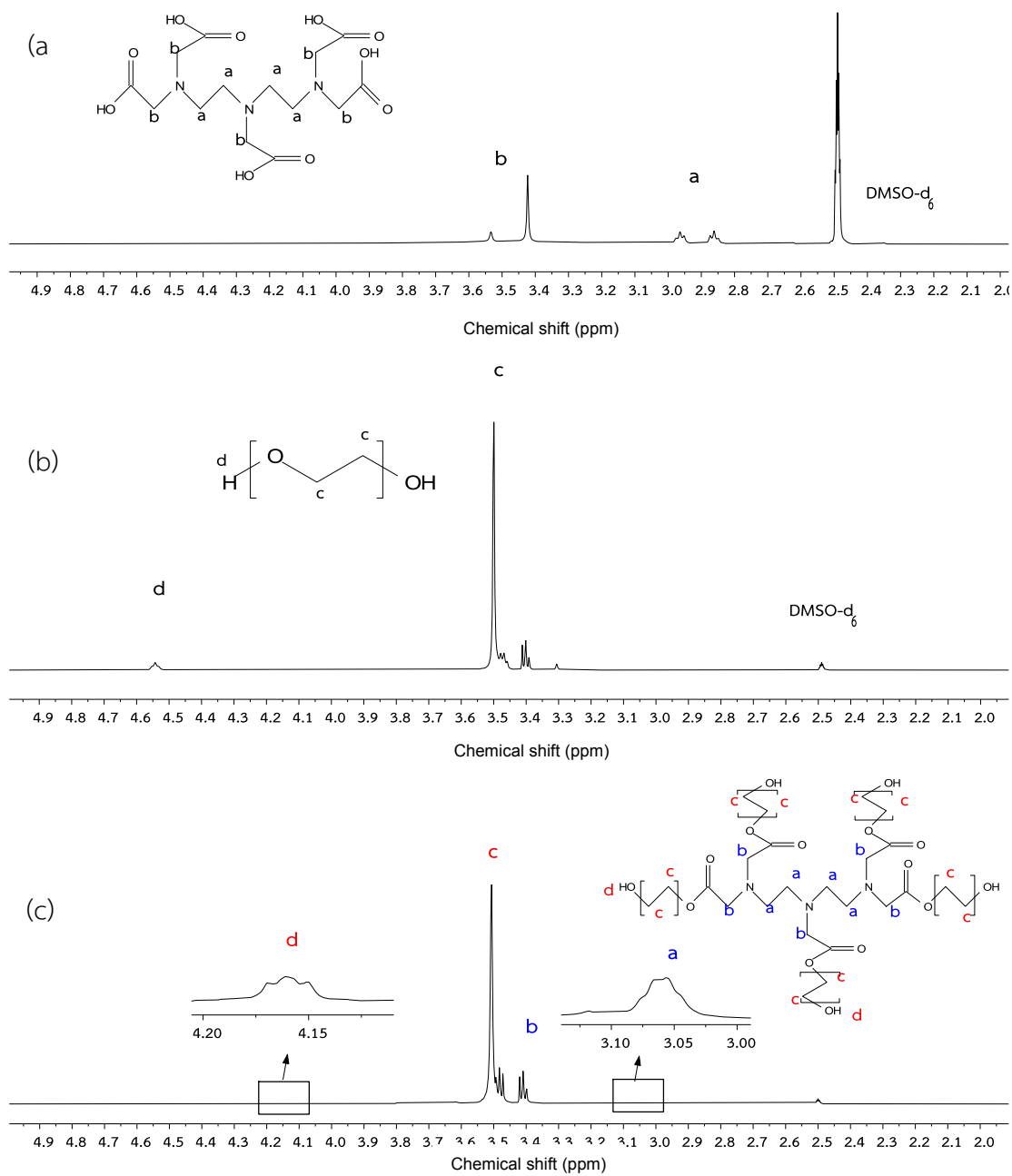


Figure 4.5 ^1H NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 400 g/mol and (c) the product-PEG400

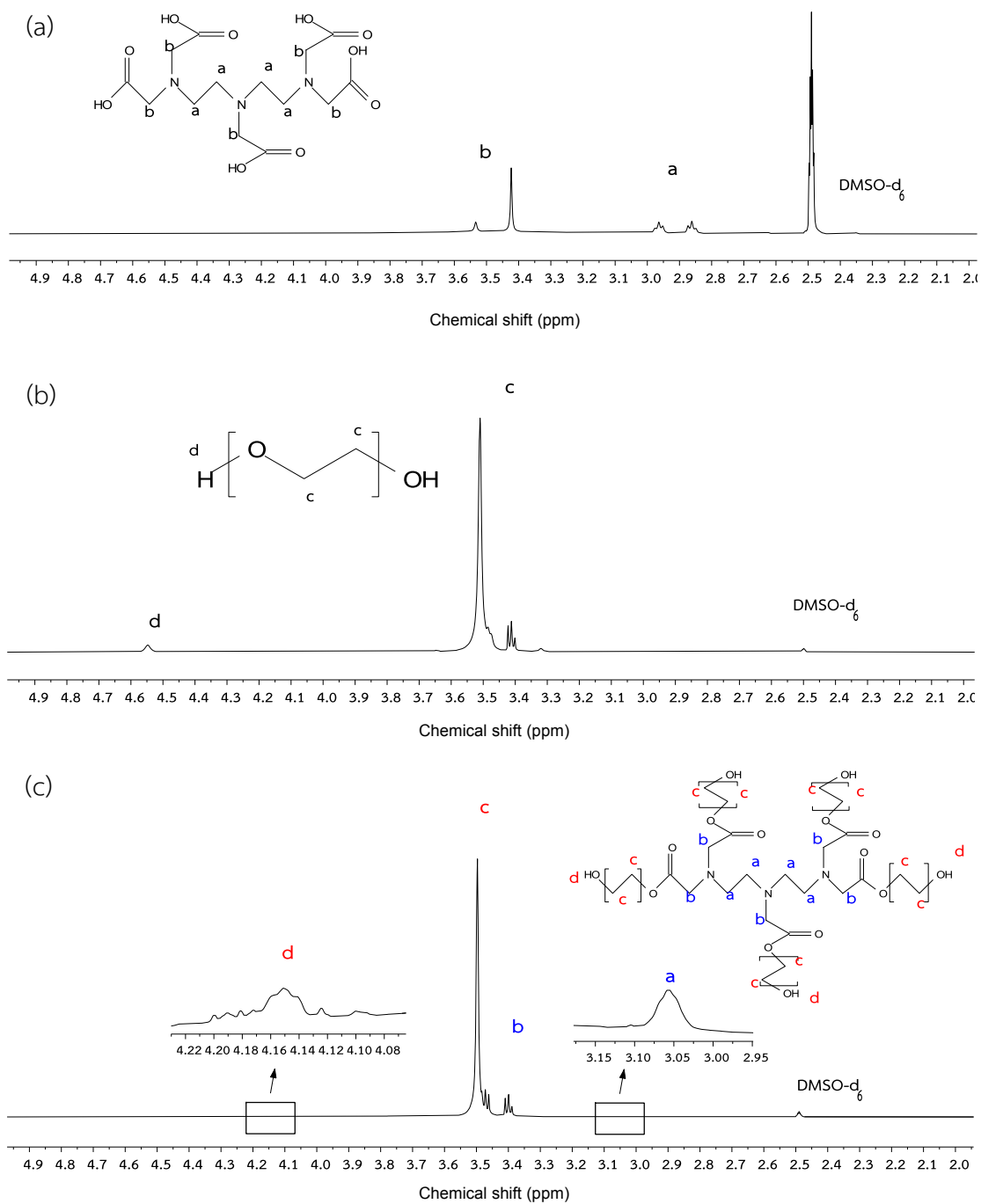


Figure 4.6 ¹H NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 600 g/mol and (c) the product-PEG600

The ^{13}C -NMR of PA, PEG400, and product-PEG400 was revealed in Figure 4.8. For the ^{13}C -NMR of product PEG200 and product-PEG600 were shown in Figure 4.7 and Figure 4.9. The signal of PEG repeating units represented at 69.768 ppm and 72.325 ppm. The signal of PA displayed at 50-60 ppm. The signal of PEG at 70.03 ppm and the signal of PA at 50-60 ppm were observed in the ^{13}C NMR spectrum of product-PEG400. Furthermore, the new peak of carbonyl (C=O) was found at 173.04 ppm for the product-PEG. The carbonyl signal was similar to work reported by Kucharczyk *et al.* [10] that the signal observed at 173 ppm confirming the presence of the carbonyl group. Due to the reaction between the hydroxyl group of poly(ethylene glycol) and the carboxyl group of pentetic acid. The appearance of this new peak confirmed the successful polycondensation of PEG and PA as a synthesized the product-PEG.

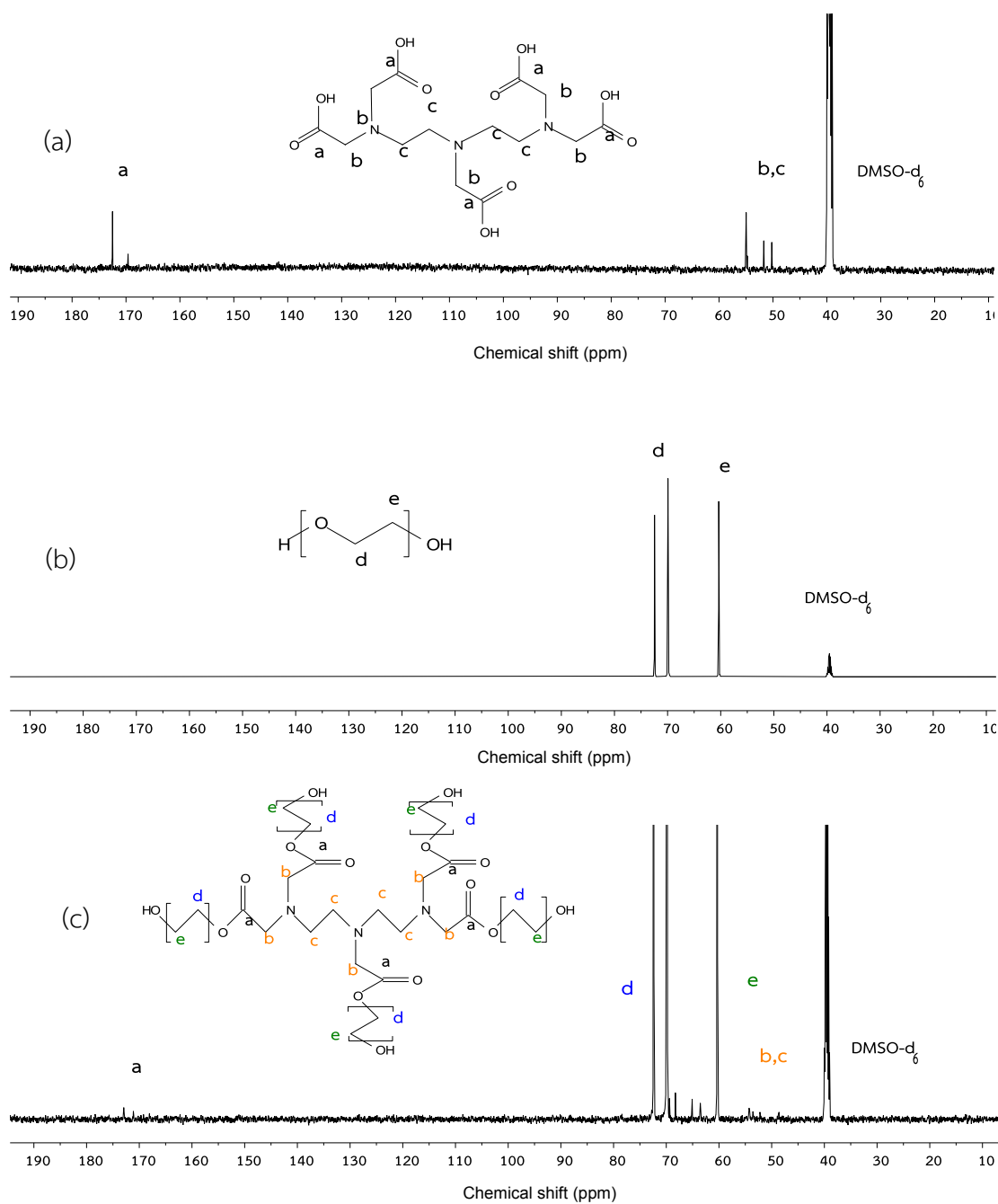


Figure 4.7 ^{13}C NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 200 g/mol and (c) the product-PEG200

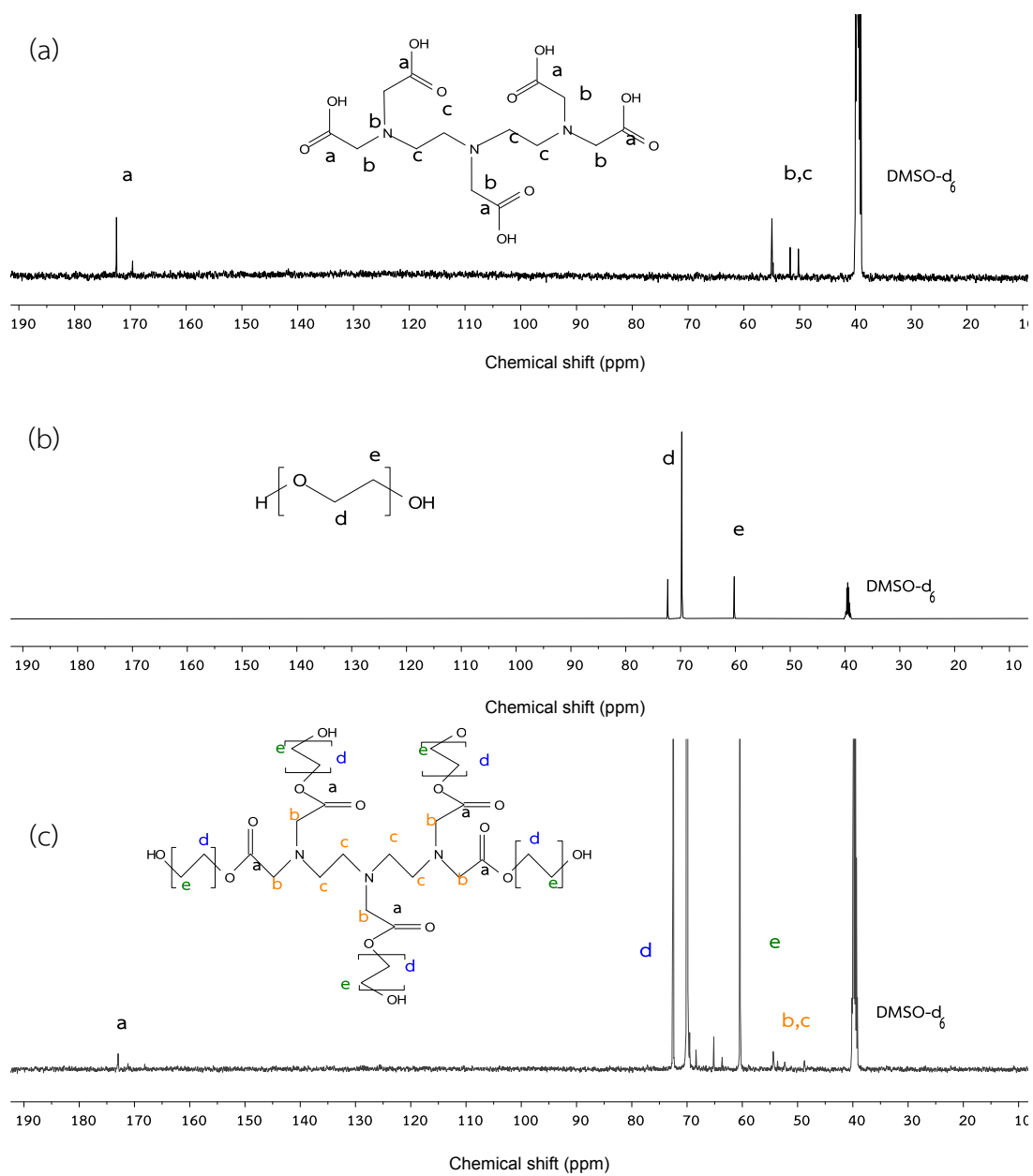


Figure 4.8 ^{13}C NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol) Mw 400 g/mol and (c) the product-PEG400

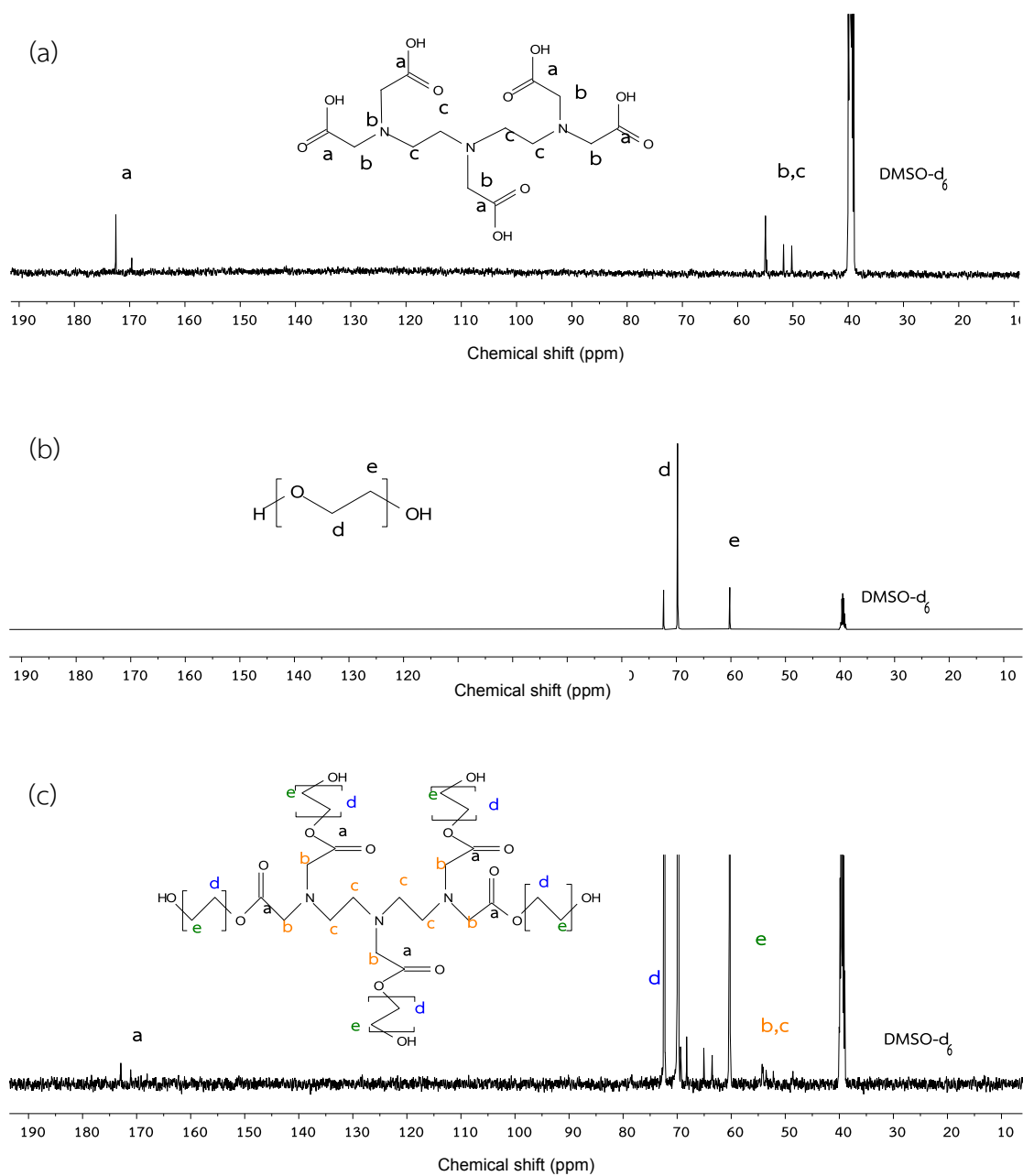


Figure 4.9 ¹³C NMR spectra of (a) pentetic acid, (b) poly(ethylene glycol)

Mw 600 g/mol and (c) the product-PEG600

4.2 Possible Mechanism

Polycondensation reaction is a step-growth polymerization, which is simply formed by the reaction of two monomers and releasing of by-product after synthesis [30]. In this research, poly (ethylene glycol) (PEG) with a various molecular weight at 200, 400 and 600 g/mol and pentetic acid (PA) were used to synthesize star-shaped poly(ethylene glycol) by a polycondensation reaction. Pentetic acid was used as a core structure of the star-shaped polymer. The reaction condition would be deployed from the previous work by Kucharczyk *et al.* [10]. From the previous work, PA was self-catalyst because PA had the potential to be affected by the presence of three nitrogen atoms in the PA molecular structure [10]. In this reaction, sulfuric acid was used as an acid catalyst for polycondensation reaction to increase the possibility of this reaction. The reaction temperature was set at 130 °C to prevent PA degradation [10] and suppress the anhydride reaction between the terminal carboxyl group [10]. Toluene was chosen as a solvent at azeotrope condition to help eliminate water from the reaction [10]. The possible mechanism of synthesized star-shaped poly(ethylene glycol) was shown in Figure 4.10. Briefly, the hydroxyl group of PEG chains was reacted with a carboxyl group of PA chains. The reaction was typically based on esterification in which an ester was formed from alcohol or compounds containing the hydroxyl group and a carboxylic acid [30]. The ratio of pentetic acid and poly(ethylene glycol) was set at 1:5 mol/mol. Through this reaction, linear oligomers could be formed



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together with the polymers as a star-shape architecture which can be seen in Figure 4.10.

The mass yield of the synthesized product poly(ethylene glycol) as shown in Table 4.1. After the polycondensation reaction, the product-PEG400 had the highest yield among other molecular weight. The yield value was calculated from the total mass of reactant and mass of the desired product. The example of yield calculation was shown in Appendix A.

Table 4.1 Composition of the synthesized product poly(ethylene glycol)

Samples	Feed mass ratio (mol/mol) PA: PEG	Mass Yield (wt%)
Product-PEG200	1:5	77.65
Product-PEG400	1:5	87.01
Product-PEG600	1:5	67.55

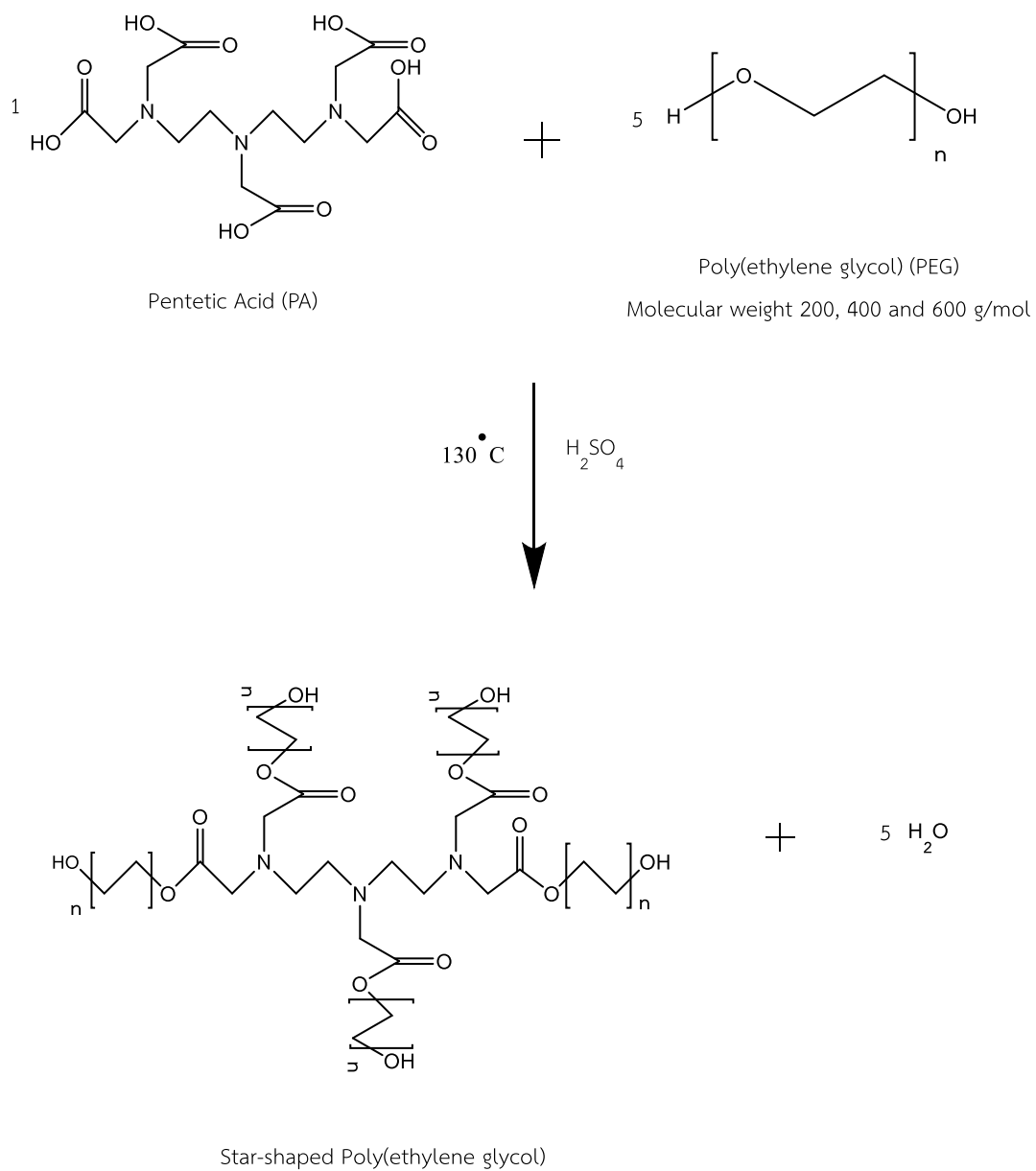


Figure 4.10 The possible mechanism of star-shaped poly(ethylene glycol)

4.3 Viscosity Average Molecular Weight

The viscosity average molecular weight (M_v) was used to find the molecular weight of the synthesized product-PEG. The viscosity average molecular weight of product-PEG was measured by Ubbelohde viscometer. The viscosity average molecular weight of the product-PEG was illustrated in Table 4.2. The viscosity average molecular weight of the star-shaped polymer was calculated using the Mark-Houwink equation [31].

$$[\eta] = KM_v^a$$

where $[\eta]$ was the intrinsic viscosity, M_v was the viscosity average molecular weight, K and a were constants for a particular polymer-solvent system. For PEG, 0.05M sodium sulfate at 30 ± 2 °C was used as a solvent in which are $K = 0.00104$ dL/g and $a = 0.57$ [25]. In general, relative viscosities (η_r) were derived as the flow time of the polymer solution (t_0) divided by the flow time of the pure solvent (t) and the specific viscosity (η_{sp}) was reciprocal to (η_r). Data for reduced viscosity against concentration ($\ln \eta_r/C$) and inherent viscosity against concentration (η_{inh}/C) were plotted and regressed to provide the intrinsic viscosity $[\eta]$ as the intercept of the graph. The intrinsic viscosity of PEG 400 was displayed in Figure 4.11. The viscosity average molecular weight of PEG is consistent with the molecular weight reported by the supplier. For the synthesized product-PEG, M_v of all the product-PEG had higher molecular weight than linear PEG. The viscosity average molecular weight of product-PEG200, product-PEG400 and product-PEG600 increase from 198.98 g/mol to 1030.20 g/mol, 390.34 g/mol to 1782.44

g/mol and 554.20 g/mol to 2199.93 g/mol, respectively after polycondensation reaction. The increment of the viscosity of the product-PEG was caused by the branch structure of PEG with PA as a core structure. Although all the product-PEG had a higher molecular weight than linear PEG, it showed low molecular weight when compared with the expected molecular weight from the theoretical calculation. These results can be explained that there were less than 5 arms in the product PEG. Some PEG chains might not be able to react with the chain end of PA due to the steric hindrance effect of the PEG chain. This finding was consistent with Fukul *et al.* [32] whose demonstrated that the tetra-armed functional coupling agent gave three-arm star polymer due to the steric hindrance effect. The expected molecular weight of star-shaped PEG was directly calculated from its structure shown in Figure 4.10 based on that 5 arms of PA were completely connected with PEG. However, the increase of viscosity average molecular weight of the product-PEG represented a successful synthesis of product-PEG that was consistent with the analysis from FTIR and NMR techniques. The calculation and other parameters of PEG of molecular weight 200 – 600 g/mol, the product-PEG200, the product-PEG400, and the product-PEG600 were illustrated in Appendix B. To further confirm the arms of the synthesized product-PEG, the number of arms in product-PEG was also calculated.

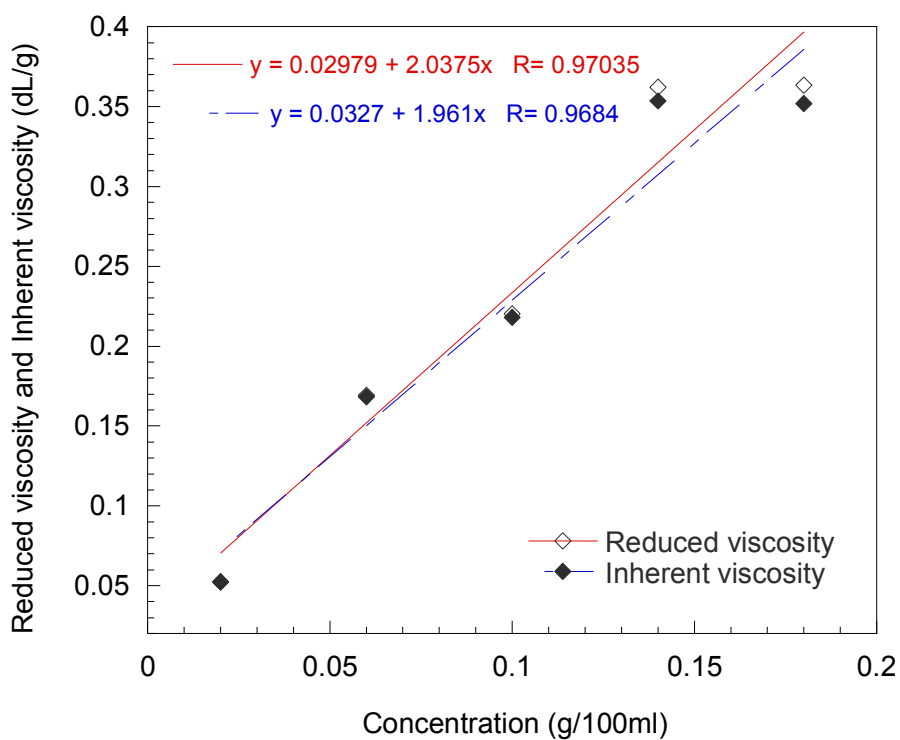


Figure 4.11 The intrinsic viscosity of neat PEG400

Table 4.2 The expected molecular weight, viscosity average molecular weight (M_v) and intrinsic viscosity $[\eta]$ of PEG and the product-PEG

Samples	Expected M_w (g/mol)	M_v (g/mol)	$[\eta]$ (dL/g)
PEG200	-	198.98	0.0213
Product-PEG200	1386	1030.20	0.0543
PEG400	-	390.34	0.0312
Product-PEG-400	2341	1782.44	0.0742
PEG600	-	554.20	0.0381
Product-PEG600	3476	2199.93	0.0836

The number of arms in product-PEG was calculated by viscosity average molecular weight (M_v) of the product-PEG and linear PEG. The calculation of the number of arms in the product-PEG was displayed in the equation below [11, 33].

$$f_n = \frac{M_v(\text{Product-PEG}) \times \text{WF(PEG)}}{M_v(\text{linear PEG})}$$

where f_n was the number of arms, M_v was the viscosity average molecular weight and WF was the weight fraction of PEG arms in the product-PEG. The number of arms of the product-PEG200, the product-PEG400 and the product-PEG600 were approximately 3 to 4 after calculation by this equation. This was consistent with Fukul *et al*, who indicated that four-arms core star polymer could not react with all arms of the living chain owing to steric hindrance [33].

4.4 Rheological Properties of Poly(ethylene glycol) And The star-shaped Poly(ethylene glycol)

The rheological properties of poly(ethylene glycol) and the synthesized product poly(ethylene glycol) were measured using parallel-plate and cone-plate rheometer. The properties including viscosity, loss modulus (G'') and Storage modulus (G') were characterized. Rheological properties play an important role in polymer processing. Thus, the result of rheological properties is discussed in this part.

4.4.1 Steady-State Measurement

The viscosity of neat poly(ethylene glycol) and the product-PEG were measured using parallel-plate 25 mm and the temperature was set at 25 ± 2 °C and 50 ± 2 °C. The relationship between viscosity and shear rate was presented in Figure 4.12 and Figure 4.13. The viscosities of neat PEG, molecular weight ranging from 200, 400 and 600 g/mol, were 0.04565 Pa·s, 0.0791 Pa·s, and 0.1787 Pa·s at the shear rate 10 - $1,000$ s^{-1} , respectively. The relationship between viscosity and the molecular weight was direct variation. The flow behavior of PEG molecular weight of 200 and 400 g/mol displayed a Newtonian fluid. Flow of PEG molecular weight of 600 g/mol behaved as a shear-thinning because it has long chain structure. Polymer showed non-Newtonian behavior due to structure reorganization of the fluid molecules [34]. PEG molecular weight of 600 g/mol had the highest viscosity among all PEG, that was used in this research.

In the case of the synthesized product poly(ethylene glycol), all synthesized product-PEG showed higher viscosity than linear PEG. Viscosities of product-PEG200, product-PEG400 and product-PEG600 were 0.0845 Pa·s, 0.1723 Pa·s, and 0.2439 Pa·s, respectively. The enhancement of viscosity was related to the increment of molecular weight. This was supported with the previous discussion that the product-PEG had higher viscosity average molecular weight than linear PEG.

The viscosity of pure PEG, the molecular weight of 200, 400, 600, 1000, 1500, 2000 g/mol, and the product-PEG measured at 50 ± 2 °C was shown in Figure 4.13. The viscosity of pure PEG and the product-PEG at 50 ± 2 °C were lower those the viscosity at 25 ± 2 °C because the viscosities of PEG decrease with increasing temperature because of chain relaxation at high temperature [35]. In addition, the viscosity of product-PEG was higher than that of linear PEG due to increasing the molecular weight. All pure PEG and the synthesized product-PEG exhibited as a Newtonian fluid which consistent with the study by *Hee et al.* [35] showed that the behavior of pure PEG at high temperature was a Newtonian fluid. The viscosities of all the product-PEG were lower than those linear PEG of the same molecular weight. This can be seen while comparing the product-PEG with a similar molecular weight of linear PEG. For example, the viscosity of the product-PEG 200 with Mw of 1030 g/mol was lower than that of linear PEG 1000 because the number of the entanglements of the PEG was not high enough to account for an increased viscosity compared to that of linear molecules



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with the same molecular weight. This result was consistent with Hepperle *et al.* [36] who found that the viscosity of grafts of the branched polystyrene was lower than that of linear polystyrene with similar molar mass which is caused by the number of the entanglements and their smaller coil size. Therefore, the structure of the product-PEG was not a linear structure. Moreover, all the results confirmed that the synthesized product-PEG were achieved.

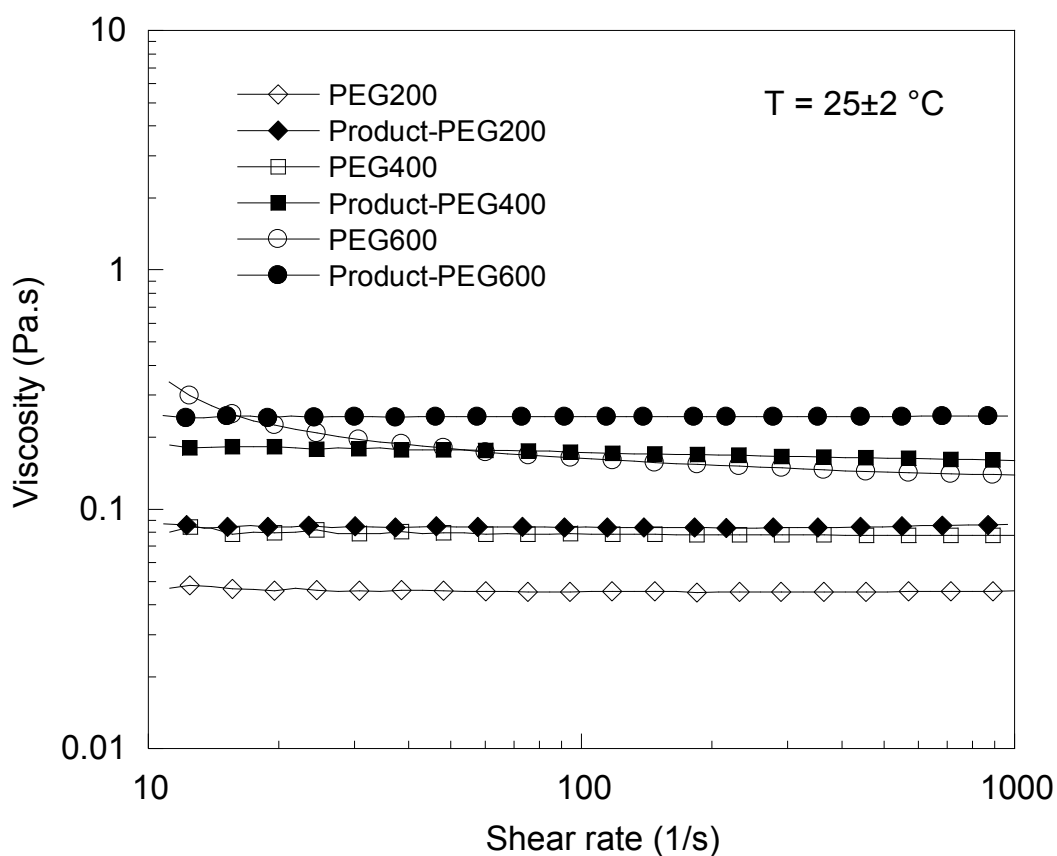


Figure 4.12 Viscosity as a function of shear rate for pure poly(ethylene glycol) and the synthesized product poly(ethylene glycol)

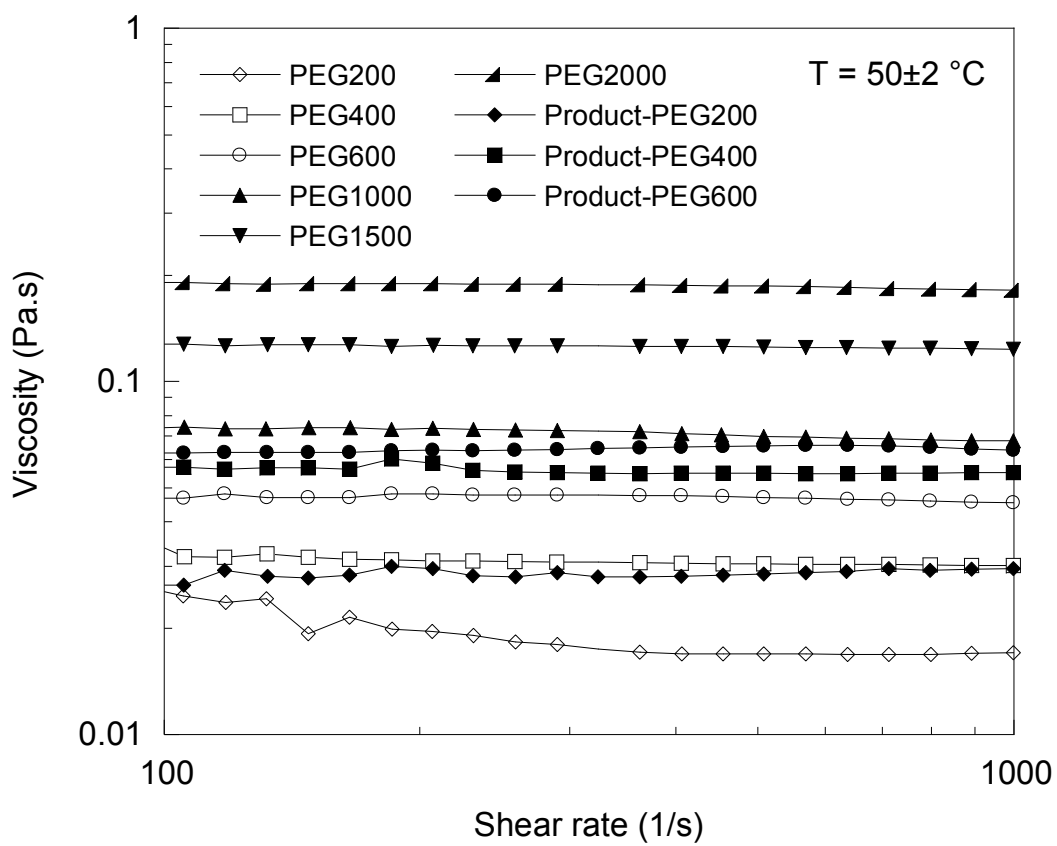


Figure 4.13 Viscosity as a function of shear rate for pure poly(ethylene glycol) and the synthesized product poly(ethylene glycol)

4.4.2 Oscillatory Measurement

In this part, oscillatory strain sweeps of poly(ethylene glycol) with the molecular weight 600 g/mol and the product-PEG600 were measured at the frequency 1 Hz and various %strain from 0.001-1,000 to find linear viscoelastic (LVE) region as shown in Figure 4.13 and Figure 4.14, respectively. The temperature was set at 25 ± 2 °C. The strain sweep test for neat PEG with Mw of 200 and 400 g/mol could not be measured due to the minimum torque oscillation limitation of rheometer. The minimum torque oscillation of rheometer is $0.003 \mu\text{N.m}$, in which the lowest measured torque of pure PEG 600 was $0.002 \mu\text{N.m}$.

For the linear viscoelastic (LVE) region of PEG with Mw of 600 g/mol and the product-PEG600, the strain limit was approximately at 0.01% and 1%, respectively. The LVE region indicated the range in which the test could be carried out without destroying the physical structure or the physical bonding of the polymer [37]. In addition, it also displayed that loss modulus (G'') of PEG600 was higher than storage modulus (G') as shown in Figure 4.13. This indicated that poly(ethylene glycol) Mw 600 g/mol showed a liquid-like character more obvious than elastic solid character [37]. For oscillation frequency sweep, poly(ethylene glycol) with Mw of 600 g/mol and product-PEG600 were tested at constant 0.01 of %strain and 1 of %strain in which was the LVE region with various frequency as shown in Figure 4.16. Poly(ethylene glycol) with Mw of 600 g/mol and the product-PEG600 exhibited crossover frequency between storage modulus (G') and loss modulus (G'') at approximately 11.22 Hz and 3.55 Hz.

The crossover frequency can be used to estimate the relaxation time (τ) which is the time of the longest polymer molecules relaxes and movement during the process [38]. It could be calculated by the equation; $\tau=1/f$ in which f was regular frequency [31, 38]. The relaxation times of PEG600 and the product-PEG600 were 0.09 s and 0.28 s, respectively. The product-PEG600 had longer relaxation time than PEG600. This result illustrated that there are chain entanglements between polymer molecules from the branch architecture of star-shaped PEG. This result could be explained by Rouse's theory [39] that long relaxation time had slow motion of the entire molecule showing that the polymer had entanglement and at short relaxation time meant unentangled polymer.

The strain sweep test of PEG with Mw of 200, 400, 600, 1,000, 1,500, 2,000 g/mol, the product-PEG200, the product-PEG400 and the product-PEG600 could not be at temperature of 50 ± 2 °C because it did not show the linear viscoelastic region as shown in Appendix C. Therefore, the rheological behavior of linear and star-shaped PEG at the same molar mass cannot be compared in this study.

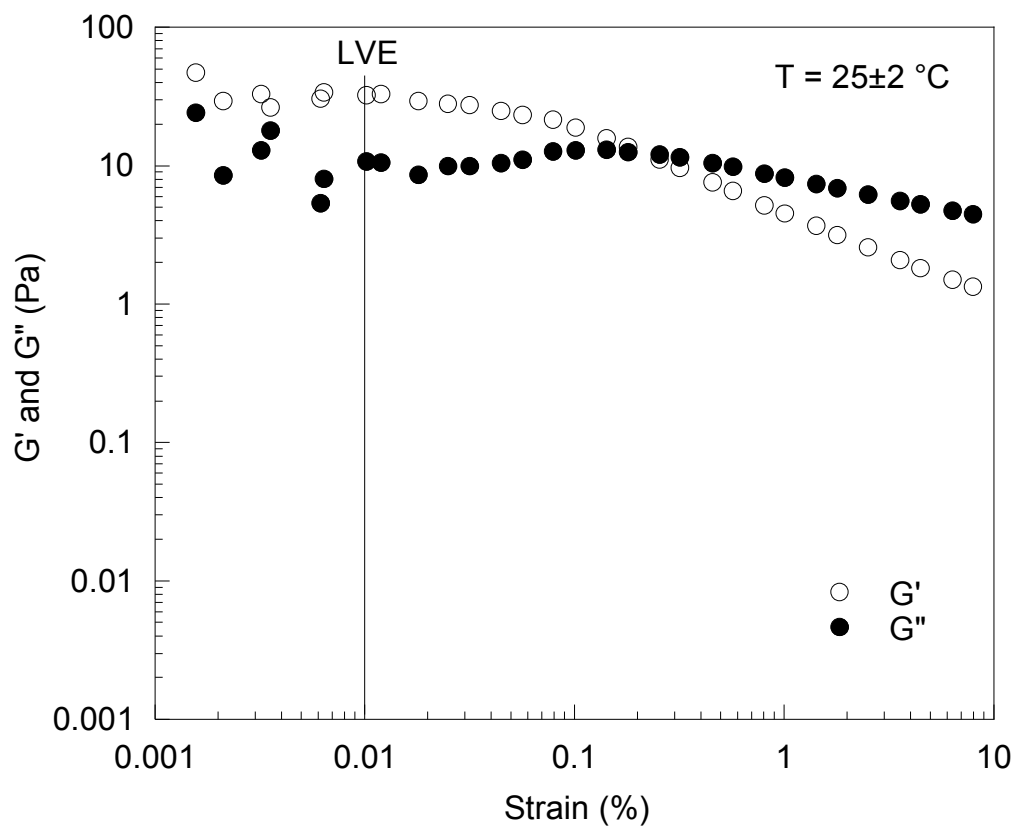


Figure 4.14 Strain sweep test of poly(ethylene glycol) Mw 600 g/mol

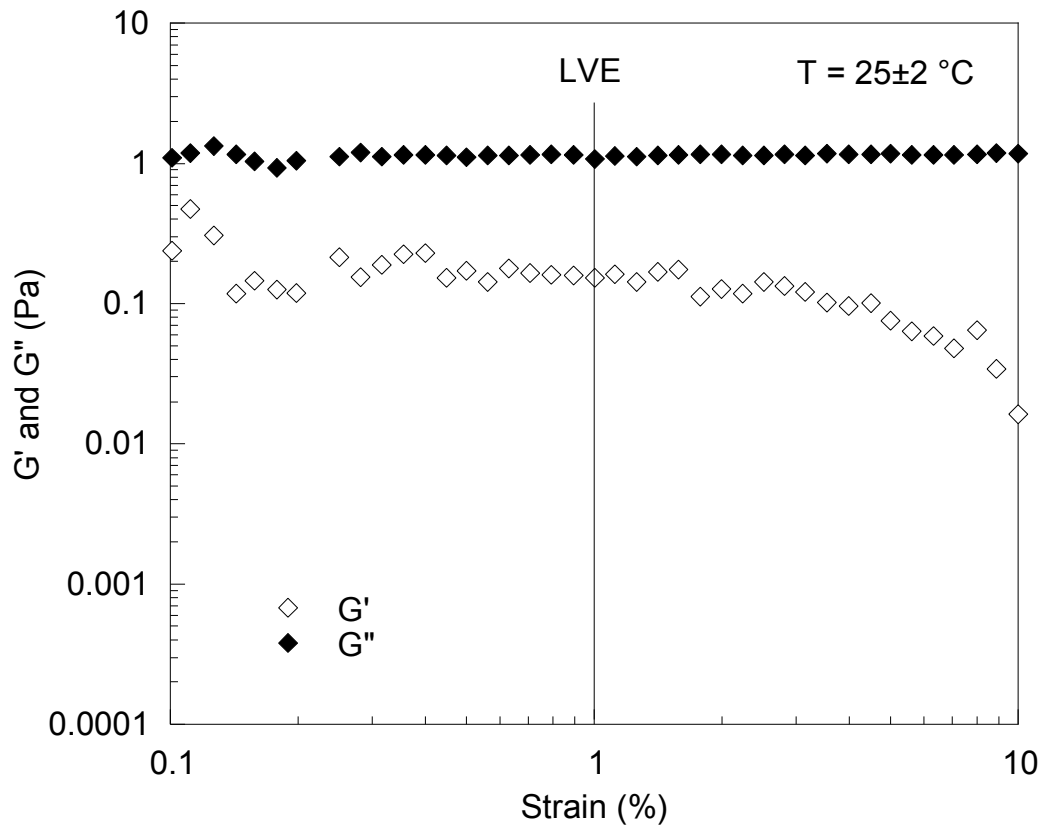


Figure 4.15 Strain sweep test of the product-PEG600

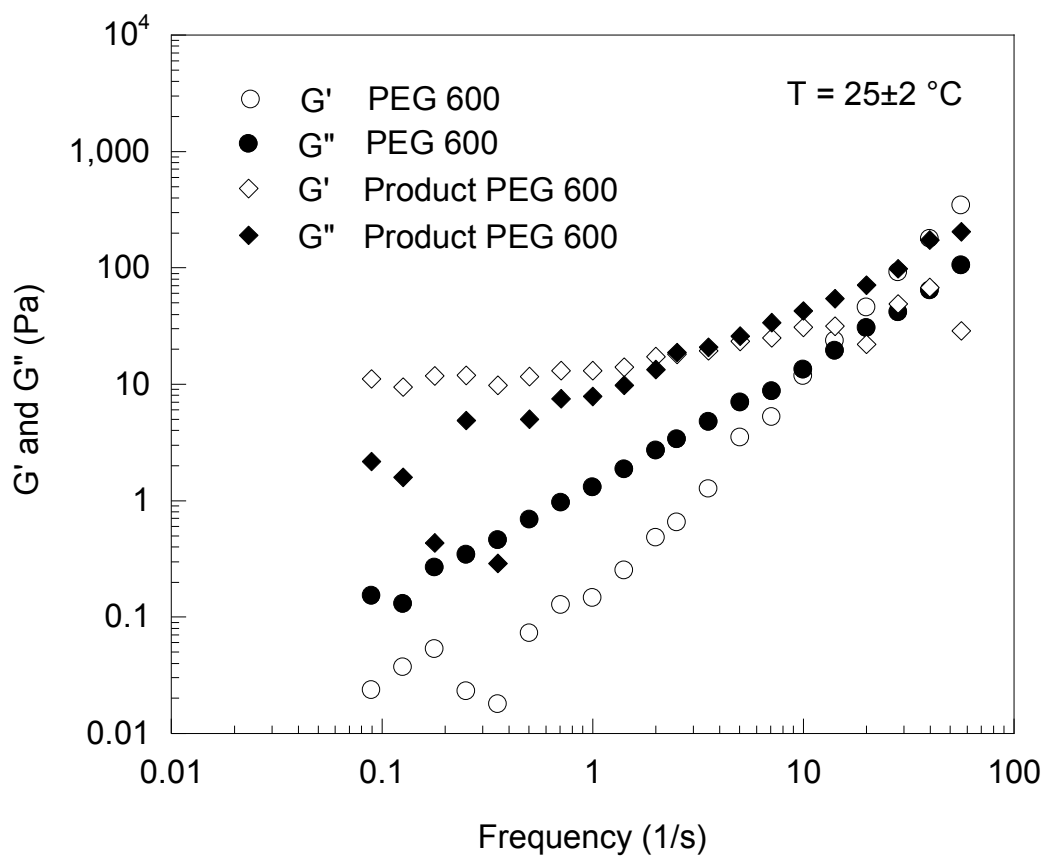


Figure 4.16 Frequency sweep test of poly(ethylene glycol) Mw 600 g/mol and the product-PEG600

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The star-shaped poly(ethylene glycol), which various molecular weight of PEG at 200, 400 and 600 g/mol, were synthesized by a polycondensation reaction and pentetic acid (PA) was used as a core. Sulfuric acid was used as a catalyst. After the reaction, pentetic acid has been removed from the product. The unreacted PEG has not been removed after the reaction; therefore, the product-PEG200, product-PEG400, and product-PEG600 would include star-shaped PEG and unreacted PEG. After the polycondensation reaction, all the product PEG showed the new FTIR spectrum of the carbonyl group at 1730 cm^{-1} . Because the carboxylic group of PA could be reacted with the hydroxyl group of PEG. The NMR results represented the signal of PEG and PA which was observed in the product-PEG200, the product-PEG400 and the product-PEG600. The new signal of carbonyl group was observed in the product-PEG as well.

Furthermore, the viscosity average molecular weight of the product-PEG was higher than that of linear PEG. Although the product-PEG had a high molecular weight, it was lower than the expected molecular weight due to the steric hindrance effect of the PEG chain. The number of arms of product-PEG200, product-PEG400 and product-PEG600 were approximately 3 to 4 arms.

From shear rate sweep test, the viscosity of all product-PEG was higher than that of linear PEG. The enhancement of viscosity was a result of the increment of

molecular weight of the product-PEG. The flow behavior of linear PEG with Mw of 200, 400 g/mol and product-PEG displayed Newtonian fluid. The PEG with Mw of 600 exhibited shear-thinning behavior because it had the long chain structure. The viscosities of neat PEG and the product-PEG decreased with increasing temperature because of chain relaxation at high temperature. The viscosities of all the product-PEG were lower than those of linear PEG of the same molecular weight because the number of the entanglements of the PEG was not high enough to account for increased viscosity. This was confirmed that the structure of the product-PEG was not a linear structure. The linear viscoelastic regime of PEG with Mw of 600 g/mol and product-PEG600 was in the region with %strain at 0.01% and 1%, respectively. The product-PEG 600 presented longer relaxation time than linear PEG600.

From the overall results mentioned, the synthesis of product-PEG with pentetic acid as a core molecule by polycondensation reaction was successful.

5.2 Recommendations

1. The synthesis of star-shaped poly(ethylene glycol) should have excess poly(ethylene glycol) to increase the possibility of polycondensation reaction.
2. The reactant of this reaction should be optimized such as the concentration of catalyst because it may affect the reaction.
3. Residues of PEG should be removed in the final product.



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Appendix



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APPENDIX A

MASS YIELD (%)

The calculation of mass yield (wt%) is as follows

$$\text{Mass yield (wt\%)} = \frac{\text{The total mass of the product (g)}}{\text{The total mass of reactant (g)}} \times 100$$

where the total mass of the product is the mass of product-PEG and total mass of reactant is mass of PA and PEG. The mass of reactant and mass of product were displayed in Table A.1.

Table A.1 The mass of reactant and mass of product

Samples	Total mass of reactant (g)	Total mass of product (g)	Mass yield (wt%)
Product-PEG 200	3.6567	2.8396	77.6547
Product-PEG 400	6.0845	5.2941	87.0096
Product-PEG 600	8.9700	6.0598	67.5563

APPENDIX B

VISCOSITY AVERAGE MOLECULAR WEIGHT

Determination of Viscosity Average Molecular Weight of Polymer the Mark-Houwink equation;

$$[\eta] = KM^a$$

Where $[\eta]$ is the intrinsic viscosity, M is molecular weight, K and a are constants for a particular polymer-solvent system

Terms Related to Viscosity Measurements

$$\text{Relative Viscosity} = \frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r$$

$$\text{Specific Viscosity} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 = \eta_{sp}$$

$$\text{Reduced Viscosity} = \frac{\eta_{sp}}{C} = \eta_{red}$$

$$\text{Inherent Viscosity} = \frac{\ln \eta_r}{C} = \eta_{inh}$$

$$\text{Intrinsic Viscosity} = \left(\frac{\eta_{sp}}{C} \right)_{C \rightarrow 0} = \left(\frac{\ln \eta_r}{C} \right)_{C \rightarrow 0} = [\eta]$$

Where t_0 = The flow times of solvent

t = The flow time of the solution sample

Table B.1 Flow time of 0.05M sodium sulfate

Flow time of solvent (sec)	1	2	Average (sec)
Sodium sulfate	477	476	476.5

Table B.2 Flow time of poly(ethylene glycol) Mw 200 g/mol

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	477	476	477	476.67
0.06	480	479	481	480.00
0.10	485	485	484	484.67
0.14	491	490	490	490.33
0.18	496	497	497	496.67

Table B.3 Flow time of poly(ethylene glycol) Mw 400 g/mol

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	477	477	477	477.00
0.06	482	482	480	481.33
0.10	487	487	487	487.00
0.14	501	501	500	500.67
0.18	508	507	508	507.67

Table B.4 Flow time of poly(ethylene glycol) Mw 600 g/mol

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	478	478	477	477.67
0.06	483	484	484	483.67
0.10	496	496	495	495.67
0.14	517	517	517	517.00
0.18	538	539	538	538.33

Table B.5 Flow time of the product-PEG200

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	479	478	477	478.00
0.06	481	480	482	481.00
0.10	491	493	492	492.00
0.14	507	508	509	508.00
0.18	525	526	526	525.67

Table B.6 Flow time of the product-PEG400

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	475	479	477	477.00
0.06	486	487	486	486.33
0.10	504	505	504	504.33
0.14	517	519	519	518.33
0.18	534	535	538	535.67



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Table B.7 Flow time of the product-PEG600

Concentrations (g/100ml)	Flow time (sec)			Average (sec)
	1	2	3	
0.02	478	478	478	478.00
0.06	486	488	489	487.67
0.10	512	511	511	511.33
0.14	538	539	538	538.33
0.18	566	563	569	566.00

Table B.8 The calculation of Reduced viscosity and Inherent viscosity
for poly(ethylene glycol) Mw 200 g/mol

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	476.67	1.0003	0.0003	0.0175	0.0175
0.06	476.50	480.00	1.0073	0.0073	0.1224	0.1220
0.10	476.50	484.67	1.0171	0.0171	0.1714	0.1699
0.14	476.50	490.33	1.0290	0.0290	0.2074	0.2044
0.18	476.50	496.67	1.0423	0.0423	0.2351	0.2303

Table B.9 The calculation of Reduced viscosity and Inherent viscosity
for poly(ethylene glycol) Mw 400 g/mol

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	477.00	1.0010	0.0010	0.0525	0.0524
0.06	476.50	481.33	1.0101	0.0101	0.1691	0.1682
0.10	476.50	487.00	1.0220	0.0220	0.2204	0.2180
0.14	476.50	500.67	1.0507	0.0507	0.3623	0.3534
0.18	476.50	507.67	1.0654	0.0654	0.3634	0.3520

Table B.10 The calculation of Reduce viscosity and Inherent viscosity
for poly(ethylene glycol) Mw 600 g/mol

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	477.67	1.0024	0.0024	0.1224	0.1223
0.06	476.50	483.67	1.0150	0.0150	0.2507	0.2488
0.10	476.50	495.67	1.0402	0.0402	0.4022	0.3944
0.14	476.50	517.00	1.0850	0.0850	0.6071	0.5827
0.18	476.50	538.33	1.1298	0.1298	0.7209	0.6778

Table B.11 The calculation of Reduce viscosity and Inherent viscosity
for product-PEG200

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	478.00	1.0031	0.0031	0.1574	0.1572
0.06	476.50	481.00	1.0094	0.0094	0.1574	0.1567
0.10	476.50	492.00	1.0325	0.0325	0.3253	0.3201
0.14	476.50	508.00	1.0661	0.0661	0.4722	0.4572
0.18	476.50	525.67	1.1032	0.1032	0.5732	0.5456

Table B.12 The calculation of Reduced viscosity and Inherent viscosity
for product-PEG400

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	477.00	1.0010	0.0010	0.0525	0.0524
0.06	476.50	486.33	1.0206	0.0206	0.3439	0.3404
0.10	476.50	504.33	1.0584	0.0584	0.5841	0.5677
0.14	476.50	518.33	1.0878	0.0878	0.6271	0.6011
0.18	476.50	535.67	1.1242	0.1242	0.6898	0.6502

Table B.13 The calculation of Reduced viscosity and Inherent viscosity for product-PEG600

Concentration (g/100ml)	Average flow time of solvent	Average flow time of sample	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
0.02	476.50	478.00	1.0031	0.0031	0.1574	0.1572
0.06	476.50	487.67	1.0234	0.0234	0.3906	0.3861
0.10	476.50	511.33	1.0731	0.0731	0.7310	0.7055
0.14	476.50	538.33	1.1298	0.1298	0.9269	0.8715
0.18	476.50	566.00	1.1878	0.1878	1.0435	0.9563

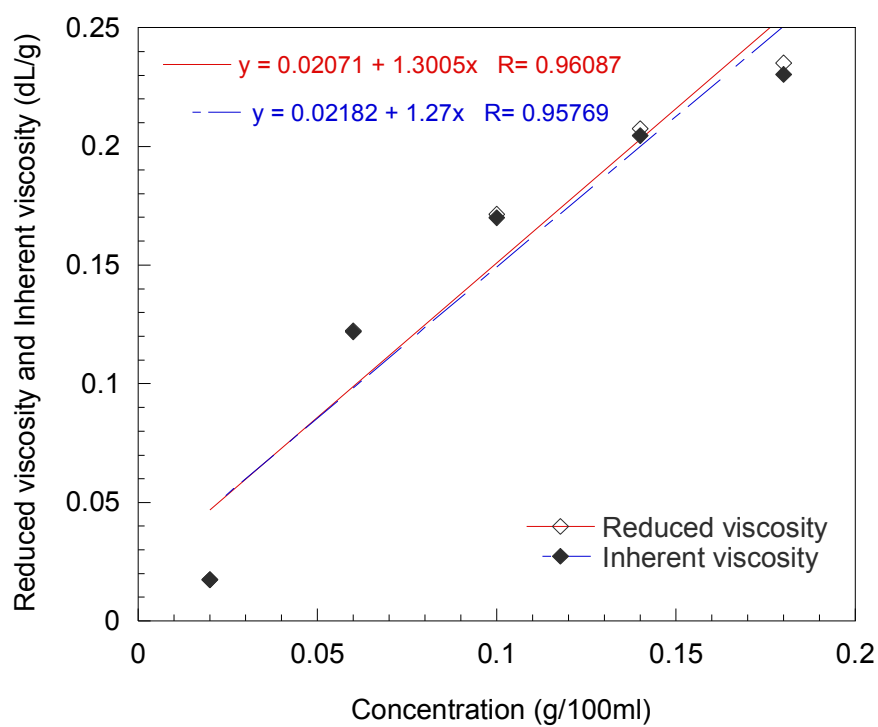


Figure B.1 Reduced and Inherent viscosity of poly(ethylene glycol) Mw 200 g/mol

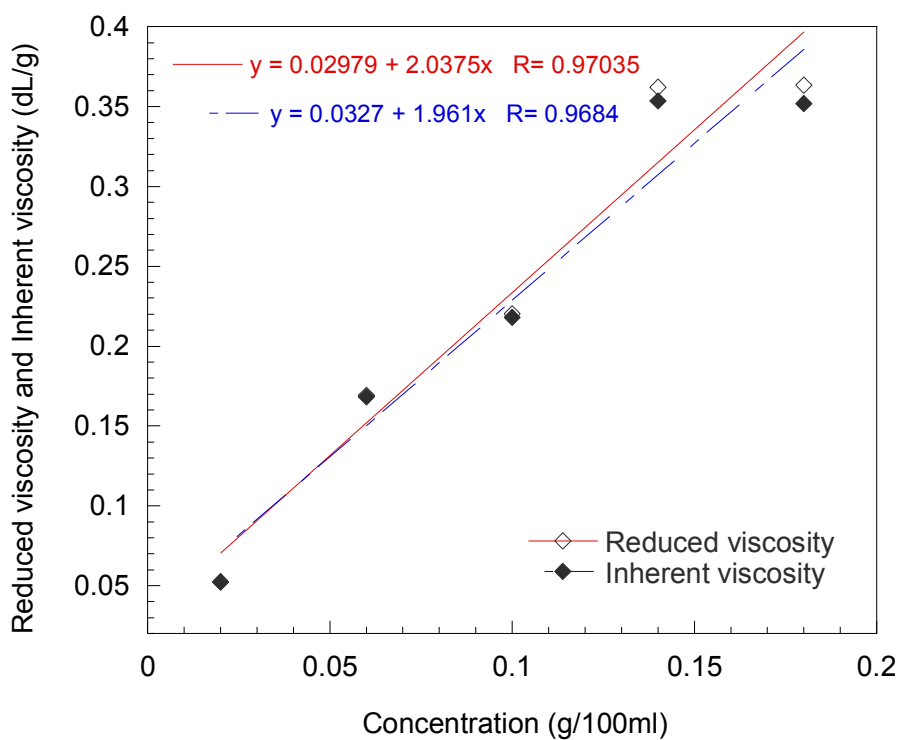


Figure B.2 Reduced and Inherent viscosity of poly(ethylene glycol) Mw 400 g/mol

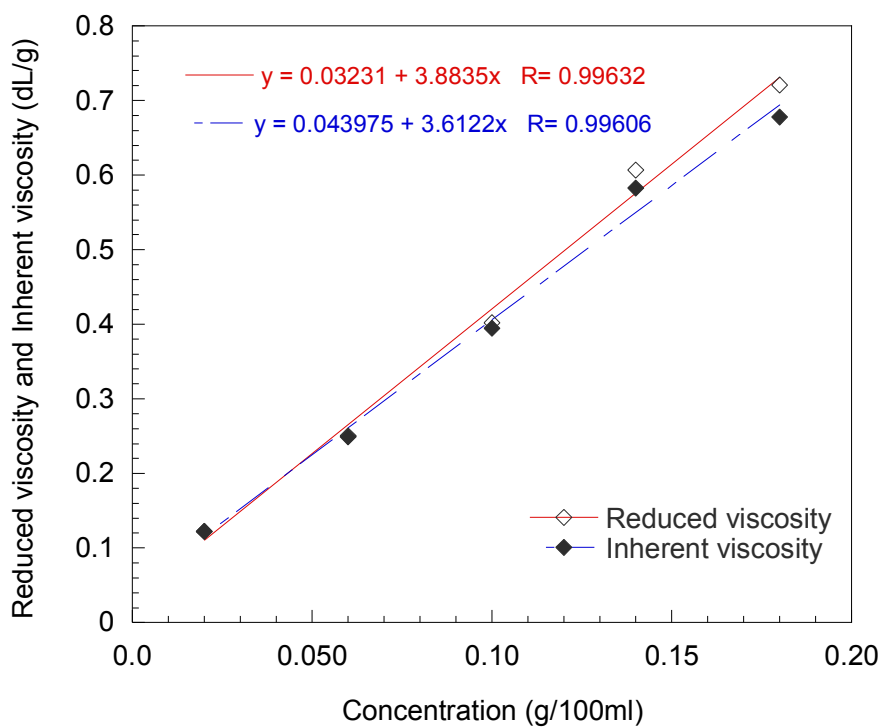


Figure B.3 Reduced and Inherent viscosity of poly(ethylene glycol) Mw 600 g/mol



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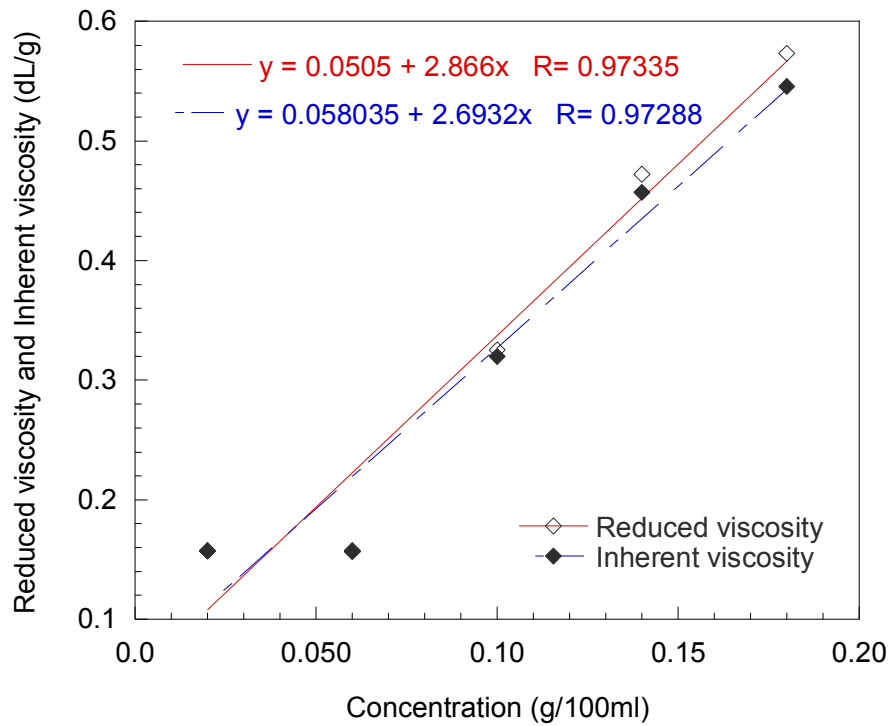


Figure B.4 Reduced and Inherent viscosity of product-PEG200

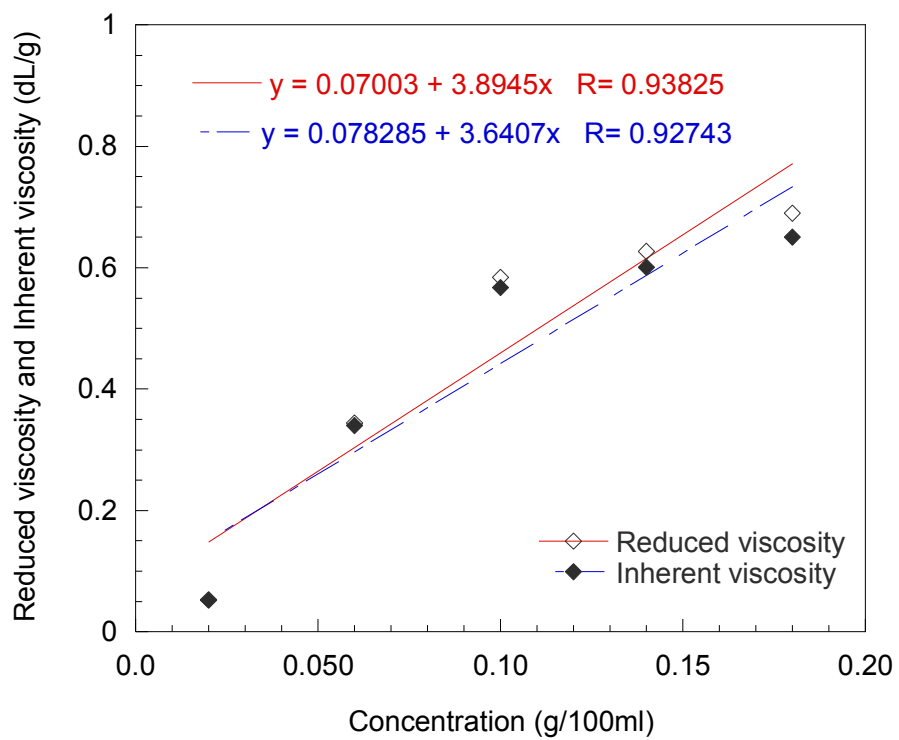


Figure B.5 Reduced and Inherent viscosity of product-PEG400



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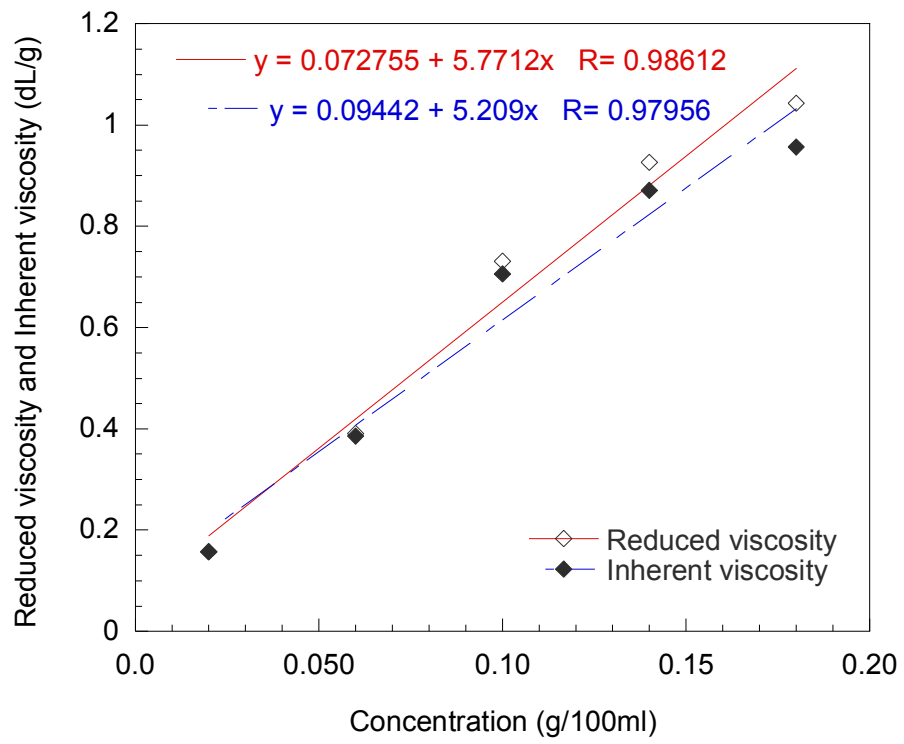


Figure B.6 Reduced and Inherent viscosity of product-PEG600

Appendix C

The number of arms of star-shaped PEG

The number of arms in star-shaped PEG was calculated using the equation below.

$$fn = \frac{M_v(\text{star PEG}) \times WF(\text{star PEG})}{M_v(\text{linear PEG})}$$

Where fn is the number of arms.

M_v is the viscosity average molecular weight.

WF is the weight fraction of PEG arms in star PEG.

The Weight fraction of PEG arms in star PEG (WF star PEG) was considered from the equation below.

$$WF(\text{star PEG}) = \frac{W(\text{PEG}) \times \text{Yield of star PEG}}{[W(\text{PEG}) \times \text{Yield of star PEG}] + W(\text{PA})}$$

Where W is weight of PA and PEG in solution.

APPENDIX C

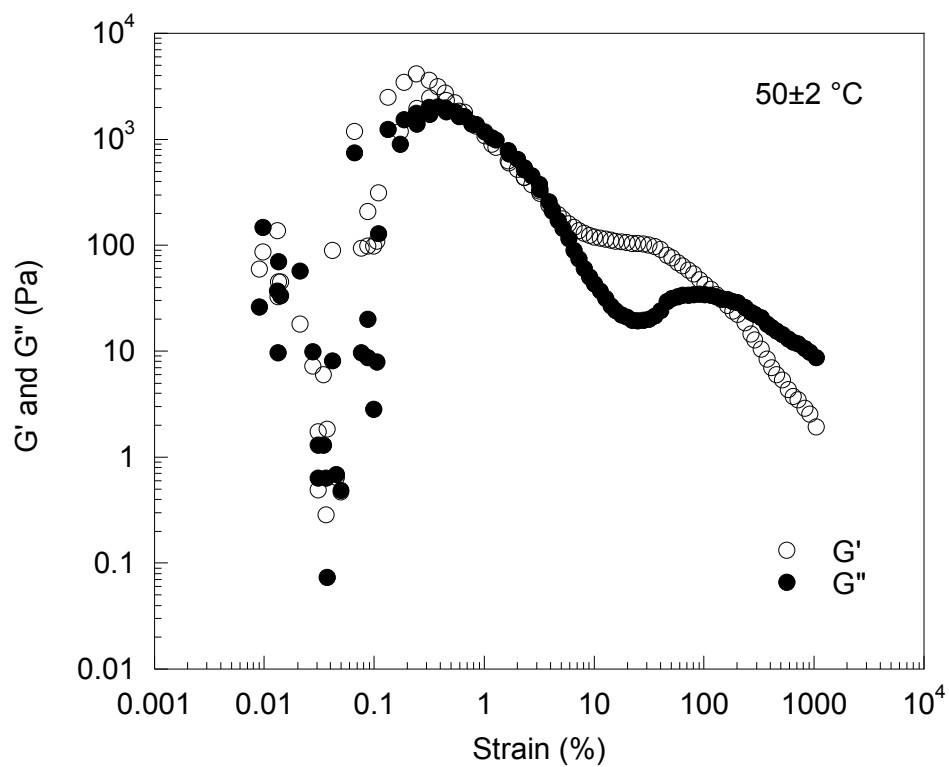
THE STRAIN SWEEP TEST AT TEMPERATURE OF 50 ± 2 °C

Figure C.1 The strain sweep test of poly(ethylene glycol) Mw 1,000 g/mol

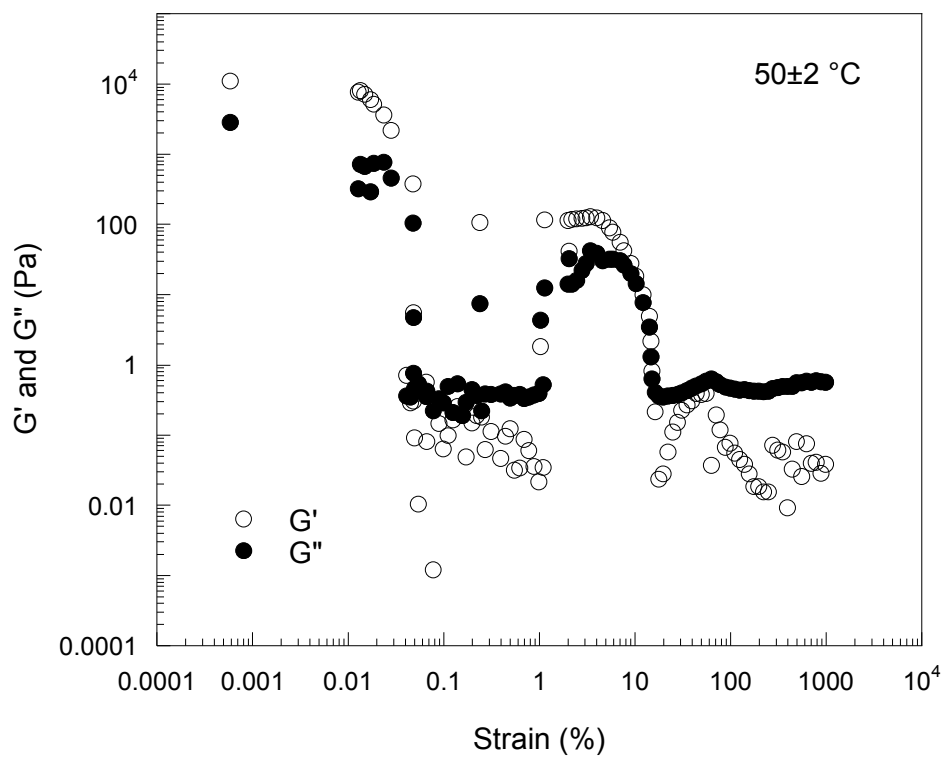


Figure C.2 The strain sweep test of poly(ethylene glycol) Mw 1,500 g/mol

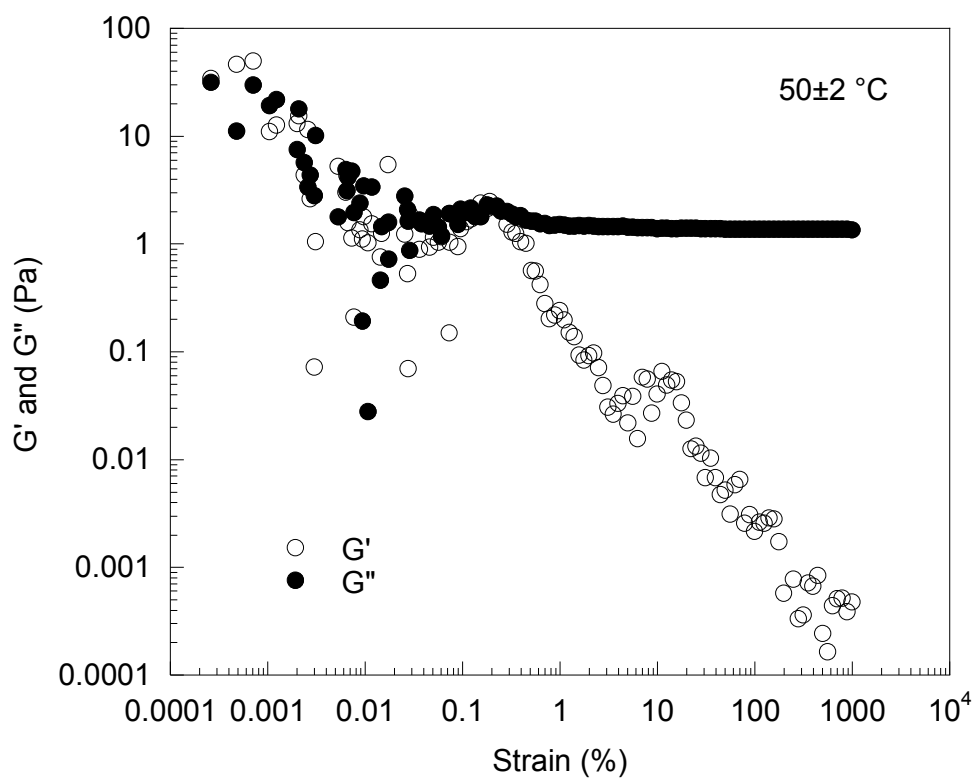


Figure C.3 The strain sweep test of poly(ethylene glycol) Mw 2,000 g/mol



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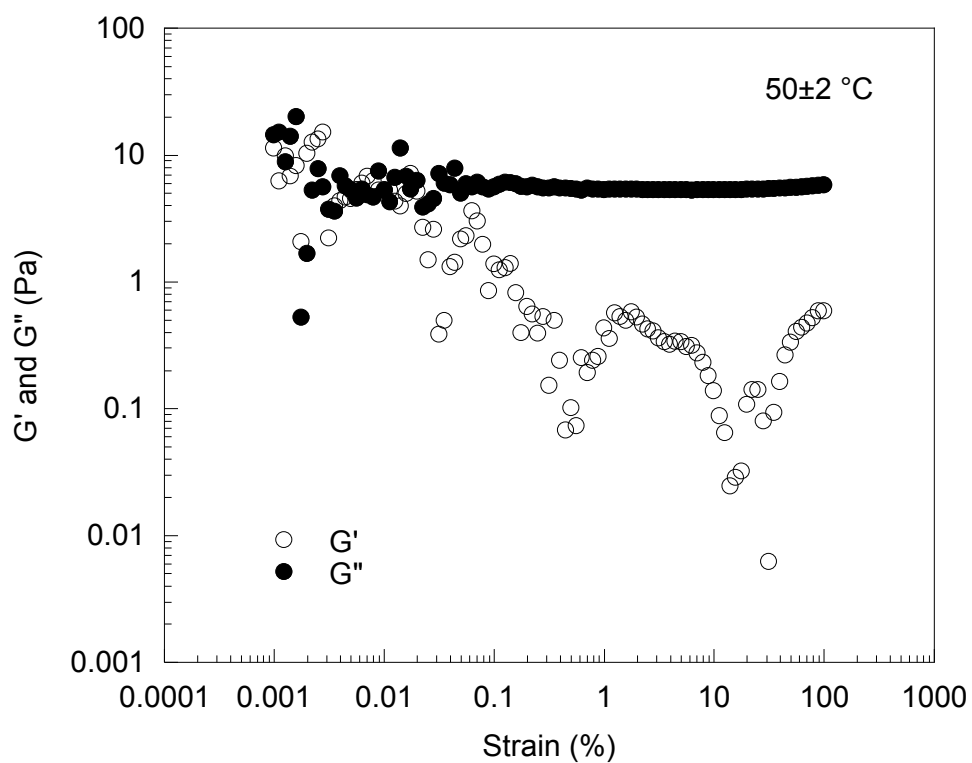


Figure C.4 The strain sweep test of the product-PEG400

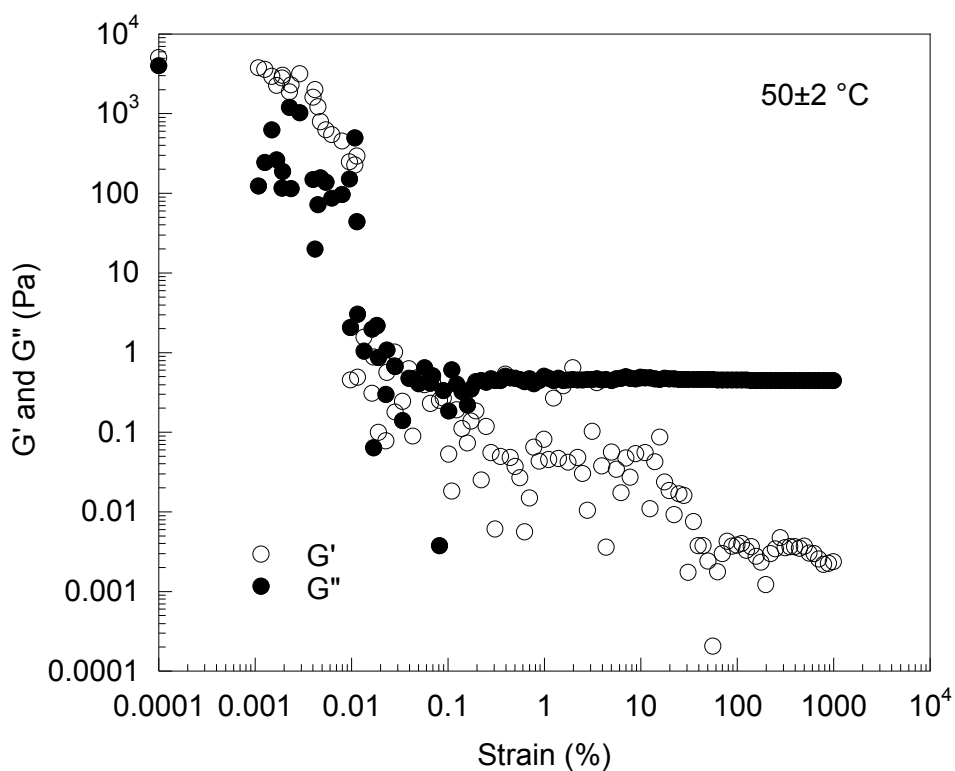


Figure C.5 The strain sweep test of the product-PEG600



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