SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE POLY (VINYL ALCOHOL)-*GRAFT*-STEARIC ACID

MS. NANTARIYA PHASUVANICHKUL

A SPECIAL RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF ENGINEERING (CHEMICAL ENGINEERING)
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Abstract

Poly(vinyl alcohol)-graft-stearic acid (PVA-g-SA) copolymers with different degree of substitution (DS) were successfully prepared by one-pot grafting reaction using 1,1'-carbonyldiimidazole (CDI) as a coupling agent, and their structural characteristics were determined by FTIR-ATR and 1H-NMR spectroscopic techniques. In the synthesis step, the yield and DS of the PVA-g-SA copolymer were found to increase with increasing the reaction time. The suitable reaction time in the coupling reaction step was found to be 24 h at which the yield and DS of the obtained PVA-g-SA product were 57.36 % and 49.57 %, respectively. The study on the influence of solvent pretreatment demonstrated that the yield of the PVA-g-SA was improved from 36.53 % to 57.36 % when predried DMSO was used as a solvent. The decompositions of CDI and SA-imidazolide intermediate caused by the water residue in non-predried DMSO were likely responsible for the lower yield. Furthermore, higher DS values were expected to be obtained when increasing the molar feed ratio of SA to PVA. However, it was found that the DS of the PVA-g-SA product increased from 29.13 % to 49.57 %, and then decreased to 41.67 % when the mole of PVA decreased from 37.5 mmol to 18.75 and 12.5 mmol, respectively. The decrease in the yield could be explained by poor mixing of the reaction mixture due to the increase in the viscosity. The preliminary study on the reaction scalability revealed that increasing the reaction scale by 7 and 15 times resulted in the decrease in the yield from 57.36 % to 52.66 % and 44.82 % respectively and the decrease in the DS value from 49.57 % to 45.37 % and 33.24 % respectively. These decreases could be explained by poor mixing of the reaction mixture and undesired reactions due to the presence of water residue. DSC analysis revealed that the PVA-g-SA copolymer with a DS of 30.05 % had a crystalline melting temperature (T_m) of 50.17 whereas the PVA-g-SA copolymer with a DS of 52.68 % had two T_m suggesting two different types of crystal structure being formed. The PVA-g-SA copolymer with a DS of 30.05 % also had glass transition temperature (T_g) of 26.32 °C while no T_g was observed for the PVA-g-SA copolymer with a DS of 52.68 % and 33.24 %. Regardless of the difference in the DS, these graft copolymers possessed similar solubility, which they were completely soluble in the solvents that have the polarity index between 4 and 2.8 but insoluble in high polar and non polar solvents.

Keywords: coupling reaction / Poly(vinyl alcohol)-*graft*-stearic acid / grafting reaction / 1,1'-carbonyldiimidazole / fatty acids

หัวข้อโครงการศึกษาวิจัย	การสังเคราะห์และการวิเคราะห์หาลักษณะเฉพาะของพอลิเมอร์ร่วมแบบกราฟต์ระหว่างพอลิไวนิลแอลกอฮอล์และเสตียริคแอซิดซึ่งสามารถย่อยสลายได้ทางธรรมชาติ
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บทคัดย่อ

PVA-g-SA โดยการใช้ CDI เป็นตัวกระทำในการเชื่อมต่อให้มีค่าการแทนที่ (ค่า DS) ที่แตกต่างกัน 3 ค่า (0.4, 0.8 และ 1.0) ถูกสังเคราะห์ขึ้นด้วยปฏิกิริยาคัพพลิ้ง และ แอคติเวชั่น ค่าการดูดกลืนแสงของเทคนิค FTIR-ATR ที่ตำแหน่ง 1737 cm-1 (C=O stretch), 1230 และ 1160 cm-1 (C-O stretch) แสดงการเกิดพันธะเอสเทอร์ของการกราฟต์ และถูกยืนยันจากค่าการดูดกลืนคลื่นแม่เหล็กไฟฟ้าของเทคนิค ^{1}H-NMR ที่ 5.16 ppm ในการทำปฏิกิริยาพบว่า ปริมาณผลิตภัณฑ์ และค่า DS มีค่าเพิ่มขึ้นเมื่อระยะเวลาในปฏิกิริยาคัพพลิ้งเพิ่มขึ้น นอกจากนี้ ปริมาณของผลิตภัณฑ์ที่ถูกสังเคราะห์จากสารละลายที่ไม่ผ่านการดรายด์ซ้ำมีค่าเพียง 36.53 % ในขณะที่สารละลายที่ผ่านการดรายด์ซ้ำ ให้ปริมาณผลิตภัณฑ์มีค่ามากขึ้นถึง 57.36 % เนื่องมาจาก การสลายตัวของ CDI จากปริมาณน้ำที่ยังคงเหลือในสารละลายที่ไม่ผ่านการดรายด์ซ้ำ นอกจากนี้ การลดจำนวนโมล ของ PVA จะส่งผลให้ค่า DS มีค่าสูงขึ้น แต่พบว่า เมื่อจำนวนโมลของ PVA ที่ถูกใช้มีค่าลดลงจาก 37.5, 18.75 และ 12.5 ให้ค่า DS มีค่าเพิ่มขึ้นจาก 29.13 % ไปยัง 49.57 % และลดลงไปยัง 41.67 % ตามลำดับ เนื่องจาก การปั่นกวนสารละลายผสมซึ่งหนืดมากไม่มีประสิทธิภาพ นอกจากนี้ ปริมาณผลิตภัณฑ์มีค่าลดลงจาก 49.57 % ไปเป็น 45.37 % และ 33.24 % เมื่อขนาดของปฏิกิริยาถูกเพิ่มขึ้นเป็น 7 และ 15 เท่า ตามลำดับ ในการทดสอบคุณสมบัติของผลิตภัณฑ์ พบว่า ค่า DS ที่แตกต่างกันเพียงเล็กน้อยไม่ส่งผลต่อคุณสมบัติทางความร้อนและการละลาย ผลิตภัณฑ์ที่มีค่า DS ต่างกัน ยังคงมีค่าอุณหภูมิการหลอมเหลวที่ใกล้เคียงกัน (50 °C) เช่นเดียวกันกับคุณสมบัติการละลาย นั่นคือ ผลิตภัณฑ์สามารถละลายได้ดีในสารละลายที่มีค่าความมีขั้ว 2.8-4 แต่ไม่สามารถละลายได้ในสารละลายที่มีขั้วสูง และสารละลายที่ไม่มีขั้ว

คำสำคัญ : ปฏิกิริยาคัพพลิ้ง / พอลิไวนิลแอลกอฮอล์-กราฟต์-เสตียริคแอซิด / พอลิเมอร์ร่วมแบบกราฟต์ / 1,1'-คาร์บอนิลไดอิมิดาโซล / กรดไขมัน

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NOMENCLATURES

ABBREVIATIONS

CDI	N,N-carbonyldiimidazole
DS	Degree of substitution
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimrtry
FA	Fatty acid
FTIR	Fourier transform infared spectroscopy
^{1}H-NMR	Proton nuclear magnetic resonance
RT	Room temperature
SA	Stearic acid
PVA	Poly (vinyl alcohol)

GREEK LETTERS

δ	Chemical shift, ppm

SUBSCRIPTS

NMR	Results from nuclear magnatic resonance
exp	Results from experiment
th	Theoretical results

SYMBOLS

T_m	Melting point
T_g	Glass transition temperature
-g-	Grafted copolymer
I	NMR intensities
M_n	Number average molecular weigh

UNITS

^{o}C	Degree celsius
min	Minute
h	Hour
mL	Mililitre
mmol	millimole
g	Gram
cm^{-1}	Per centimeter
ppm	Parts per million
mmHg	Millimetersmercury

CHAPTER 1 INTRODUCTION

1.1 Background

Due to a significant increase in environmental concerns biodegradable polymers (BPs) have increasingly been employed in several applications as a replacement of non-degradable materials. Natural polymers such as starch-based, lignin-based and alginate-based polymers are preferable as they are obtained from naturally renewable resources. However, the properties of natural polymers do not fit the needs of specific applications although their properties can be improved by chemical modification or blending with other polymers or materials. Therefore, synthetic biodegradable polymers have recently become of interest, which have been used in several target applications.

Recently, intensive interests on the self-assembly of amphiphilic block and graft copolymers have been studied extensively from both theoretical and experimental viewpoints, due to their potential applications in drug delivery systems, cosmetics products, and the synthesis of nano-materials, especially controlled release in delivery systems. It has been known that the release behavior of the active agent is strongly influenced by the properties of the polymeric matrix that is used to carry the active agent. Due to these reasons, polymeric materials having amphiphilic characteristics are of interest and therefore focused in the work.

Poly (vinyl alcohol) (PVA) is a water soluble synthetic polymer due to hydroxyl groups along the chain. It is prepared by partial or complete hydrolysis of poly (vinyl acetate) (PVAc) to remove acetate groups. PVA is well known in excellent film forming, emulsifying and adhesive properties. Moreover, it is fully degradable that can reduce the environmental pollution. [1] Nevertheless, PVA is highly hydrophilic in nature due to the presence of the hydroxyl groups on the polymer chains. Such characteristics make PVA less favorable to be used as the polymeric matrix for delivery systems because of the quick release of the active agents. So, balancing between hydrophilic and hydrophobic properties is necessary to form the polymeric matrix that can control the release rate of the active agents, which can be achieved by incorporating hydrophobic molecules into the PVA chain.

In this research, the hydrophilicity of PVA was decreased by incorporating saturated fatty acid (FA) molecules into the PVA chain via grafting technique. Grafting technique was selected as an approach of modifying the PVA structure because the hydrophilicity of PVA can be easily adjusted by varying the degree of substitution (DS) and the chain length of the grafting molecules. Saturated FA was of interest as to avoid undesired side reactions that may occur due to the presence of the double bonds in the unsaturated fatty acid molecules. Accordingly, stearic acid (SA), a long chain saturated FA, was selected as the grafting molecules in this study.

1.2 Objectives

1.2.1 To synthesize and characterize amphiphilic graft copolymers consisting hydrophilic PVA as a backbone and hydrophobic SA as grafting chains.

1.2.2 To investigate the effects of the chemical structure (DS) of the synthesized PVA-g-SA copolymers on solubility and thermal properties.

1.3 Scope of work

1.3.1 PVA-g-SA copolymers were synthesized by grafting the SA molecules onto the PVA backbone using 1,1'-carbonyldiimidazole (CDI) as a coupling agent under various reaction conditions, i.e. mole ratio of SA and PVA and reaction time.

1.3.2 The chemical structure and DS of the synthesized PVA-g-SA copolymers were characterized by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopic techniques.

1.3.3 Thermal properties of the synthesized PVA-g-SA copolymers were characterized by Differential Scanning Calorimetry (DSC).

1.3.4 Solubility of the synthesized PVA-g-SA copolymers in common organic solvents were determined.

1.3.5 Scalability of the grafting reaction was preliminarily investigated.

CHAPTER 2 THEORY AND LITERATURE REVIEW

2.1 General polymer chemistry [2]

A polymer, has normally known as a large molecule (macromolecule) composed of repeating structural units. These subunits are typically connected by covalent chemical bonds. It actually encompasses a large class comprising both natural and synthetic materials with a wide variety of properties.

According to the nature of the repeating unit in the polymer chains, polymers can be classified as homopolymers and copolymers. Homopolymers consist of chains with identical bonding linkages to each monomer unit. This usually implies that homopolymers are made from all identical monomer molecules or one type of monomer molecules. In contrast, copolymers consist of chains with two or more different bonding linkages. Therefore, copolymers are made from two or more different types of monomer molecules. Copolymers can be mainly classified into random, alternating, block and graft copolymers, based on arrangement of the different monomer units along the chain. Random copolymers are copolymers consisting of the different monomer units arranging randomly. In alternating polymers the different monomer units are joined together in a regular alternative fashion. Block copolymers are made up of blocks of different polymerized monomers. Finally, graft copolymers are a special type of branched copolymers in which the side chains are structurally distinct from the main chain. However, the individual chains of a graft copolymer may be homopolymers or copolymers.

Homopolymer: A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

Copolymers:

Random copolymer A-A-B-A-B-B-A-B-A-A-B-A-B-B-A-B-A

Alternating copolymer A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A

Block copolymer A-A-A-B-B-B-B-A-A-A-B-B-B-B-A-A-A

Graft copolymer

```
A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A
        |         |         |
      B-B-B-B   B-B-B-B   B-B-B-B
```

where A = monomer A and B = monomer B

Figure 2.1 Schematic structures of homopolymers and copolymers

2.2 Graft copolymers [3]

The modification of polymers has received much attention recently. Among the methods of modification of polymers, grafting is one of the promising methods. There are two major types of grafting may be considered; grafting with a single monomer and grafting with a mixture of two (or more) monomers. The first type usually occurs in a single step, but the second may occur with either the simultaneous or sequential use of

the two monomers. Generally, polymer chemists employed three strategies including grafting-through, grafting-from, and grafting-onto to synthesize graft copolymers. Graft copolymers can be obtained via the polymerization of macro-monomers using the grafting-through strategy, the resulting graft copolymers via the conventional radical polymerization possessed a broad chain-length distribution, and living polymerization yielded well-defined graft copolymers with low molecular weights. The grafting-from approach utilized the pendant initiation groups on the backbone to initiate the polymerization (generally employing living radical polymerization including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and single-electron-transfer living radical polymerization (SET-LRP) of another monomer to form the side chains. The grafting-onto method is to attach the side chains onto the backbone by a coupling reaction.

2.2.1 Methods of grafting

Considerable work has been done on techniques of graft copolymerization of different monomers on polymeric backbones. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting.

2.2.1.1 Grafting initiated by chemical means

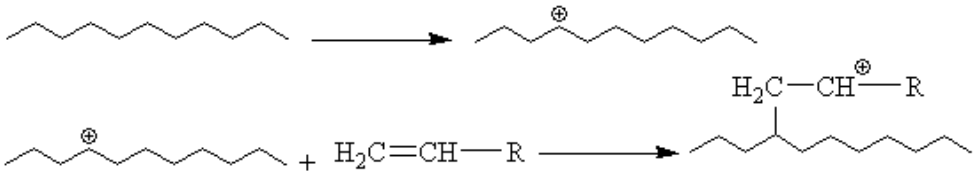
Chemical means of grafting can proceed along two major paths consisting of free radical and ionic. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical mechanism, grafting in the melt and ATRP are also interesting techniques to carry out grafting. In the chemical process, free radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft copolymers. In the same way, the method of living polymerization has developed to provide a potential for grafting reactions. It is defined that it retains its ability to propagate for a long time and grow to a desired maximum size while its degree of termination or chain transfer is still negligible. Furthermore, grafting can also proceed through an ionic mode. Alkali metal suspensions in a Lewis base liquid, organometallic compounds and sodium naphthalenide are useful initiators in this purpose.

2.2.1.2 Grafting initiated by radiation

Radiation technique of grafting can also proceed along free radical and ionic. The irradiation of macromolecules can cause homolytic fission and thus forms free radicals on the polymer. In the radiation technique, the presence of an initiator is not essential. The medium is important in this case, e.g. if irradiation is carried out in air, peroxides may be formed on the polymer. The lifetime of the free radical depends upon the nature of the backbone polymer. Furthermore, the ionic grafting can be performed the radiation grafting with the ions formed through high-energy irradiation. It may be of two different types which are cationic and anionic. The polymer is irradiated to form the polymeric ion, and then reacted with the monomer to form the grafted co-polymer. The

potential advantage of the ionic grafting is high reaction rate. Thus, small radiation doses are sufficient to bring about the requisite grafting. The cationic grafting initiated from the backbone is shown in Figure 2.2 (Path 1). An alternate cationic grafting mechanism can proceed through monomer radical cation, which subsequently forms a dimer. Charge localization in the dimer occurs in such a way that the dimer radical cation then reacts with the radical produced by the irradiation of the polymer (Figure 2.2 (Path 2)).

Path 1



Path 2

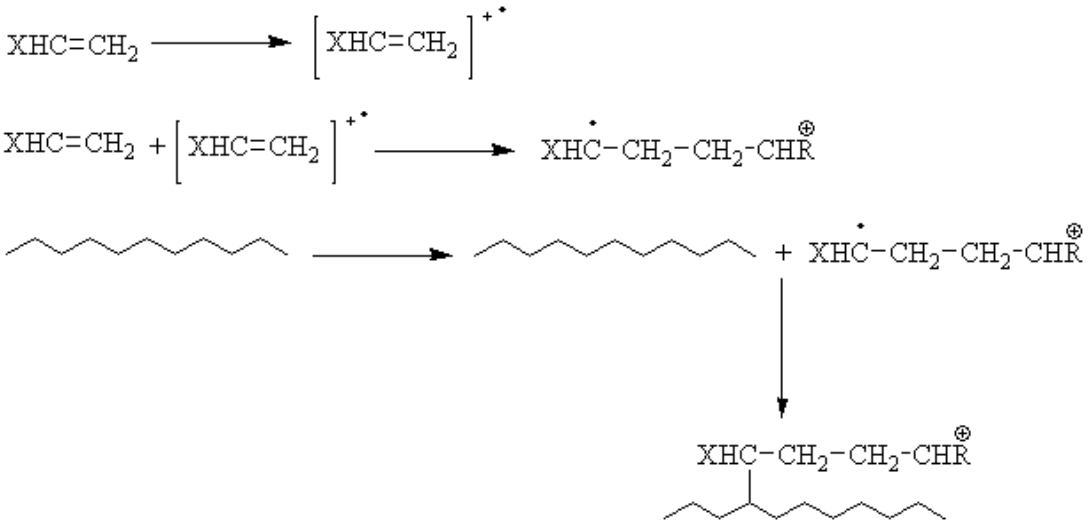


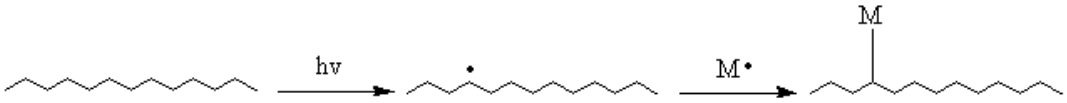
Figure 2.2 Reaction mechanisms of cationic grafting initiated from the backbone (Path 1) and initiated through the monomer (Path 2)

2.2.1.3 Grafting initiated by photochemical technique

When a chromophore on a macromolecule absorbs light, it goes to an excited state, which may dissociate into reactive free-radicals, whence the grafting process is initiated. If the absorption of light does not lead to the formation of free-radical sites through bond rupture, this process can be promoted by the addition of photosensitizers, e.g. benzoin ethyl ether, dyes, such as Na-2,7 anthraquinone sulphonate or acrylated azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions UO_2^{2+}. That means the grafting process by a photochemical technique can proceed in two ways: with

or without a sensitizer. The mechanism without sensitizer involves the generation of free radicals on the backbone, which react with the monomer free radical to form the grafted co-polymer. On the other hand, in the mechanism 'with sensitizer', the sensitizer forms free radicals, which can undergo diffusion so that they abstract hydrogen atoms from the base polymer, producing the radical sites required for grafting (Figure 2.3).

(a)



(b)

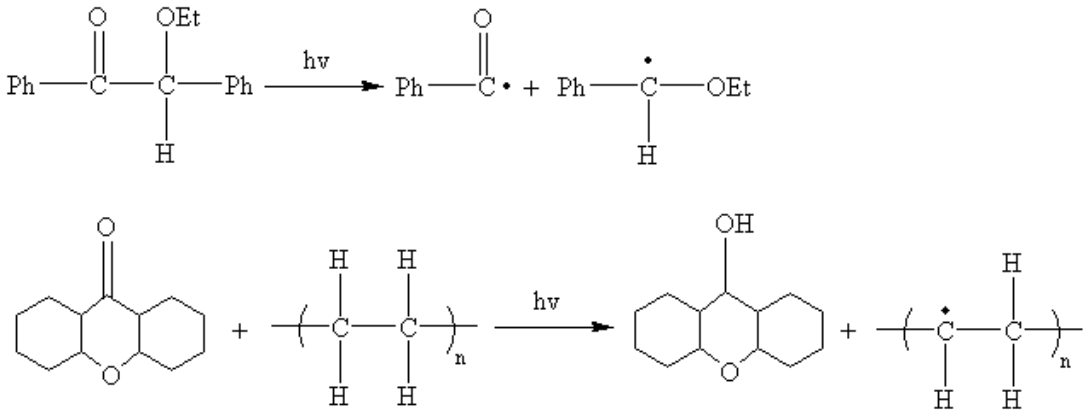


Figure 2.3 Reaction mechanism of photochemical grafting (a) without sensitizer and (b) with sensitizer

2.2.1.4 Grafting initiated by plasma radiation inducement

Plasma conditions attained through slow discharge offer about the same possibilities as with ionizing radiation. The main processes in plasmas are electron-induced excitation, ionization and dissociation. Thus, the accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the polymeric structure, to form macromolecule radicals, which subsequently initiate graft co-polymerization.

2.2.1.5 Enzymatic grafting

The enzymatic grafting method is quite new. The principle involved is that an enzyme initiates the chemical/electrochemical grafting reaction. For example, tyrosinase is capable of converting phenol into reactive o-quinone, which undergoes subsequent non-enzymatic reaction with chitosan.

2.2.2 Controlling factors of grafting

The possible variables that control grafting include the nature of the backbone, monomer, solvent, initiator, additives, temperature, etc.

2.2.2.1 Nature of polymeric backbone

As grafting involves covalent attachment of a monomer to a pre-formed polymeric backbone, the nature of the backbone including physical nature and chemical composition plays an important role in the process [4]. For example, cellulose is resistant to grafting reactions in water owing to its insolubility, due to the immense size of the polymeric chain bonding between the amino residues; the cystine linkages and intramolecular H-bonding in wool are responsible for shaping and setting characteristics. In the presence of UV light, oxidative reactions are initiated and free radicals are formed, leading ultimately to grafting if monomers are present. Even though the backbone of cellulose is highly structured and bulky, swelling of the backbone may take place in the presence of an appropriate solvent, which enhance the mobility of radicals generated in the monomer (e.g. by irradiation) to active sites on the substrate backbone to effect grafting. There are various reports regarding the role of chemical composition on grafting. For example, the presence of lignin (phenolic -OH) in straw affected the grafting of 2-methyl vinyl pyridine, since lignin is a good scavenger of radicals. The presence of functional groups in the backbone also influences the grafting. Styrene is grafted relatively with high efficiency on cellulose acetate-p-nitrobenzoate. This result indicates that the pendant aromatic nitro group is more effective in obtaining a graft co-polymer [5].

2.2.2.2 Effect of monomer

As with the nature of backbone, the reactivity of the monomer is also important in grafting. The reactivity of monomers depends upon the various factors consisting of polar and steric nature, swellability of backbone in the presence of the monomers and concentration of monomers. In general, the grafting efficiency will depend on one monomer concentration. It is often reported that the grafting efficiency increases with monomer concentration up to a certain limit and then decreases with further increase in the monomer concentration [6]. This behavior may reflect an initial increase of the monomer concentration in close proximity to the backbone. After a certain limit, the increase in monomer concentration accelerates the homo polymerization reaction rather than grafting

2.2.2.3 Effects of solvent

In grafting mechanisms, the solvent is the carrier by which monomers are transported to the vicinity of the backbone. The choice of the solvent depends upon several parameters, including the solubility of monomer in solvent, the swelling properties of the backbone; the miscibility of the solvents if more than one is used, the

generation of free radical in the presence of the solvent, etc. The solubility of the monomer depends on the nature of the solvent and the polymer, e.g. alcohols are useful solvents for grafting styrene [7-9]. Diffusion of the monomer controls chain growth and chain termination in the internal structures of the polymer [10]. The solubility parameters δ of the solvents should be close to the polymeric backbone so that the necessary chemical energy to disrupt intermolecular cohesive forces between polymer chains and permit chain mobility.

2.2.2.4 Effect of initiator

The rate of grafting is dependent upon the initiator concentration as well as the monomer and the backbone polymer. There are various empirical relationships regarding the dependence of the grafting efficiency on the initiator concentration. It is apparent from the observations that once a certain initiator concentration is reached, higher levels of initiator do not increase the conversion of grafted monomer. The solubility of the initiator in the grafting medium is another prime factor. Ideally, the initiator should be fully soluble so that it can initiate the grafting reaction through monomers.

2.2.2.5 Role of additives on grafting

Grafting yield or the extent of graft co-polymerization depends on the presence of additives such as metal ions, acids, and inorganic salts. Thus, the reaction between the monomer and the backbone must compete with any reactions between the monomer and additives. Although some additives may enhance the monomer/backbone reaction to augment the grafting efficiency, the reverse will be true if the reaction between the monomer and the additive is dominant.

2.2.2.6 Effects of temperature

The temperature is one of the important factors that control the kinetics of graft co-polymerization. In general, grafting yield increases with increasing temperature, until a limit is attained. One factor in this can be faster monomeric diffusion processes in the backbone increases with increasing temperature, facilitating grafting. One interesting observation is that the maximum graft yield occurs for a temperature near the glass transition temperature.

2.3 Amphiphilic copolymer

Amphiphilic copolymers are composed of two chemically different polymeric segments; one being hydrophilic (water soluble) and the other being hydrophobic (water insoluble). They are used in several applications as nanoreactors, nanotemplates and nanocarriers, especially in delivery systems for drugs and other active agents [1, 2, 10-18].

2.3.1 Poly (vinyl alcohol) grafted with fatty acid

In this study, amphiphilic biodegradable graft copolymers of poly (vinyl alcohol) (PVA) grafted and long-chain saturated FA were synthesized. A general grafting reaction of PVA and saturated FA is depicted in Figure 2.4.

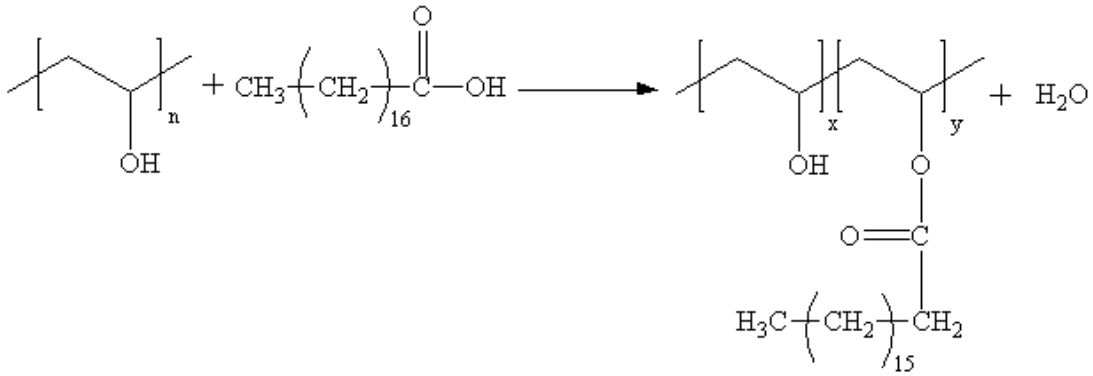


Figure 2.4 A general grafting reaction of PVA and SA

PVA was selected to be a backbone of the graft copolymer due to its desirable properties. PVA is a water-soluble synthetic polymer. It has excellent film forming, emulsifying, and adhesive properties. It also has high tensile strength and flexibility. However, these properties depend on humidity, i.e. the higher the humidity is the more the water is absorbed. The water will reduce its tensile strength, but increase its elongation and tear strength. In addition, PVA is fully degradable that is the most desirable property, which it is expected to be friendly to the environment. Nevertheless, PVA polymeric chain comprises many hydroxyl groups acting as hydrophilic moieties that consequently makes PVA quickly dissolves in water (or any high polar solvents [1]. This nature of PVA leads the matrix to immediately release the active agent, inducing loss of active agent and also other problems mentioned above [12],[13]. Therefore, reducing the hydrophilic character is a necessary method to slow the release rate of the active agent. Saturated fatty acid was chosen to reduce such character due to its hydrophobicity [14]. In other words, this method is balancing between the two characters that support the polymeric matrix to have the degradable and controlled release properties. The reason of using saturated fatty acid is to avoid undesirable side reactions that may occur at the double bonds in the unsaturated fatty acid molecules. In this work, stearic acid (SA) was used as a representative saturated fatty acid. It can be easily found in nature that is beneficial on the cost of the polymeric material.

Typically, PVA-g-SA copolymers can be prepared via the grafting onto approach through the esterification reaction between the hydroxyl groups of PVA and the carboxylic group of SA. As esterification is highly reversible, water generated during the reaction will drive the reaction to reach the equilibrium state, leading to a low yield of the ester product. However, this problem can be avoided by using a coupling reagent. The usage of the coupling agent is also beneficial in speeding the reaction.

In general, there are several coupling agents used to activate carboxylic acids towards ester formation such as N,N'-dicyclohexylcarbodiimide (DCC), N,N'-diisopropyl carbodiimide (DIC), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and 1,1'-carbonyldiimidazole (CDI). In this work, CDI was used as a coupling agent for the esterification reaction between PVA and SA because the application of CDI is much more efficient, avoids equilibrium state of the esterification reaction, and allows the use of DMSO (good solvent for most of carboxylic acids) as solvent. Moreover, oxidation reaction is not observed and no decomposition of DMSO occurs [15]. CDI is an organic compound with the molecular formula $(C_3H_3N_2)_2CO$. It is a white crystalline solid. The esterification reaction using CDI as coupling agent is shown in Figure 2.5

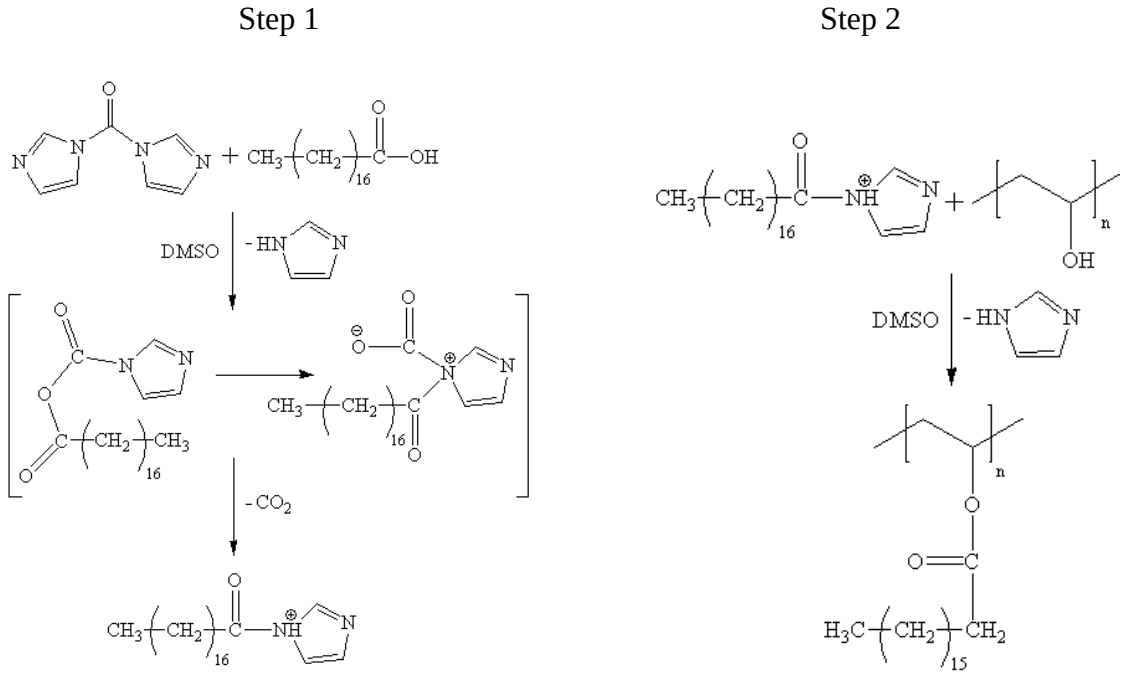


Figure 2.5 A CDI-meadiated esterification reaction of PVA and SA [16]

During the conversion, the reactive imidazolide of the acid is generated and the by-products formed are only CO_2 and imidazole. The reagents and by-products are non-toxic. The imidazole is freely soluble in a broad variety of solvents including water, alcohol, ether and chloroform. In addition, the pH is not strongly changed during the conversion, resulting in negligible chain degradation. To start with, the acid is transformed with the CDI to give the imidazolide. The imidazolide of the carboxylic acid should always be firstly synthesized. The conversion of the alcohol in this first step is also possible for the esterification but yields undesired cross-linking by carbonate formation [15]. Therefore, activation of the carboxylic group of SA with CDI is the first step in the synthesis of the graft copolymer.

2.4 Literature review

PVA grafted with SA at different degrees of substitution (DS) were prepared by Orienti, Zuccari et al. (2001). An acylation reaction was followed, starting from stearoyl chloride as an acylating agent in a molar ratio varying from 0.2-1.0 mole substituent per mole monomer. It was stirred with PVA (Mw = 10,000 D, 80 % hydrolyzed) dissolving in N-methylpyrrolidone at room temperature for 24 h. The solution obtained was supplemented with water to induce precipitation of the substituted polymer. The solid obtained was washed with water and dried under vacuum to constant weight. The degree of substitution of the substituted polymer was determined by using elemental analyser and IR spectrophometer. The infrared spectra of the substituted polymers showed the absorption band of the ester carbonyl at 1730 cm^{-1}, resulting from the linkage of the hydroxyl of PVA with the carbonyl of acyl chloride. Elemental analyses indicated that the experimental DS values always approach the theoretical values (moles of substituent per 100 moles of monomer in the preparative solution). Such values were 100, 80, 60, 40 and 20 % whereas the experimental DS were 95, 74, 57, 39 and 18 %, respectively. This effect correlated with the establishment of a growing steric hindrance on the polymeric chain, with the advancement of substitution which hindered further substitution. At the lower ratio between the moles of substituent and monomer in the preparative solution, almost complete substitution of the polymeric chain can take place. In the presence of lower molecular weight substituents, a higher DS may be achieved before substitution is hindered. [17]

Hydrophobically modified polyvinyl alcohol with fatty acids (FAs) to obtain PVA-FA derivatives for the preparation of lipophilic polymeric nanoparticles able to employ as carriers for active cosmetic ingredients was carried out by Luppi, Cerchiara et al. (2004). PVA (Mw = 10,000 D, 80 % hydrolyzed) was substituted with SA at two different substitution degrees (40 % and 80 %) via acylation reaction using dimethyl aminopyridine as a catalyst. Starting with dissolving PVA in N-methylpyrrolidone, such solution was supplemented with pyridine, dimethyl aminopyridine and stearoyl chloride. The solution was stirred for 48 h at room temperature. The precipitate of pyridinium salt was removed by filtration and the substituted polymer was separated by precipitation into water. The precipitate obtained was purified by re-precipitating twice from ethanol into water, and then dried under vacuum to constant weight. The degree of substitution of the polymer was determined by ^{1}H-NMR in DMSO-d_6. The ^{1}H-NMR spectrum of PVA-SA assigned to the signal at 5.00 ppm, corresponding to the vinylic proton bounded to the acetylic group of PVA. Furthermore, the signals of the methylene protons of the stearoyl were situated at 0.82 ppm. The level of substitution, calculated from the ^{1}H-NMR spectrum, was determined as 37.0 % for PVA-SA40 and 74.9 % for PVA-STEA80. [18]

Grote and Heinze (2005) studied esterification of starch with carboxylic acid imidazolide in DMA/LiCl. Starch materials were allowed to react with saturated and unsaturated fatty acids of varying chain length from C_{14} to C_{18} under homogeneous conditions. By in situ activation of the fatty acids with CDI, stearic acid/DMA solution was added drop wise into CDI/DMA solution under stirring forming the imidazolide and CO_2, which is liberated. Then it was added to the solution of the starch at 80 °C and allowed to react for 24 h at 80 °C. The product was isolated by precipitation into ethanol, filtered, and washed twice with cold ethanol and four times with boiling ethanol and was air-dried over night and then kept for 16 h in vacuum at 50 °C. The esterification of starch with CDI-activated fatty acids was carried out by variation of the molar ratio of starch to stearic acid from 1:1 to 1:4.5. It was found that increasing molar ratio leads to products of increased DS. The DS increases slowly with increasing reaction time (up to 10 h at 80 °C). Variation of the reaction temperature from room temperature to 100 °C shows that DS increases from 0.20 to 1.97. Thus, time and temperature, the temperature being more important, can control the DS. [19]

Synthesis of cellulose furoate with 2-furan carboxylic acid/CDI in DMSO/TBAF was reported by Hussain (2010). CDI was dissolved in DMSO followed by 2-furan carboxylic acid to obtain imidazolide of the 2-furan carboxylic acid. The mixture was stirred overnight then added to the solution of cellulose dissolved in DMSO/TBAF. The reaction mixture was stirred for 24 h at 80 °C under N_2. The homogeneous reaction mixture was precipitated in ethanol and the polymer was collected by filtration. The polymer was dried at 50 °C under vacuum to obtain the product with 61 % yield while 1.91 of DS was received (determined by means of ^{1}H-NMR spectroscopy). The cellulose esters were characterized by means of FTIR spectroscopy, elemental analysis, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The FTIR revealed the carbonyl group of ester at 1728 cm^{-1}. DS was calculated from the ratio of the spectral integrals of the protons of the repeating unit (δ 3.63-5.00 ppm) and the methyl protons of the propionate (δ 0.77, 0.93 ppm). The DS values reached are lower compared to esters prepared using anhydrides, or prepared by imidazolide formation using DMAc/LiCl as solvent. One reason of low reactivity of short chain acid imidazolides (e.g. acetic acid) is due to its high reactivity towards hydrolysis, while long chain aliphatic acids imidazolides were less affected by the water of TBAF in results higher DS values were obtained. Furthermore, cellulose furoate yielded well-resolved ^{13}C-NMR spectrum recorded in DMSO-d_6. Carbonyl of furoate moiety appeared at 157.3 ppm. [20]

Spectrometric characterization of grafted PVA was based on the synthesis of PVA-g-PCL in melt with MgH_2 as catalyst which was reported by Guerrouani, Mas et al. (2009). The occurrence of grafting was shown by the appearance of the signal at 5.08 ppm in ^{1}H-NMR spectra due to the methine proton of the linkage between PVA backbone and PCL side chains. The methine proton of non-grafted PVA units is situated at 4.14 ppm. The signals of the methylene protons of the PVA backbone and those of the 3 methylene protons groups central to CL units of PCL chains are situated between 1.2 and 1.8 ppm. The protons of methylene groups linked to carbonyl or oxygen of ester

groups of PCL chains are shifted to 2.30 and 4.08 ppm respectively. Grafting was confirmed by ^{13}C-NMR mainly from the analysis of methine and methylene carbon signals of backbone chain. The formation of ester linkage resulted in small shift of methine carbon from 64.5 ppm for non-grafted to 66.3-68.3 ppm for grafted repeating units. Besides, characteristics absorption bands in FTIR spectra of ester group was situated at 1727 cm^{-1}. [21]

CHAPTER 3 EXPERIMENTAL

Due to their moisture sensitive nature the grafting reactions were conducted under a N_2 atmosphere (99.999 % purity) using standard high vacuum Schlenk and cannula techniques. In addition, all reagents and solvents were purified and dried via appropriate methods prior to use unless otherwise stated. All reaction glassware and cannula were dried overnight in an oven at 120 °C.

3.1 Materials

Poly (vinyl alcohol) (PVA) (degree of polymerization ~1400, degree of hydrolysis 98-98.8 mol % and M_n~30,000) was purchased from Merck and was pre-dried at 80 °C for 20 h and then at 100 °C for 12 h in a vacuum oven, and kept under N_2 atmosphere. The pre-dried PVA was further dried using a high vacuum Schlenk line at 100 °C for 6 h prior to use. Stearic acid (SA) (98 %) was purchased from Loba while 1, 1'-carbonyldiimidazole (CDI) (97 %) was purchased from Aldrich. Both SA and CDI were dried using a high vacuum Schlenk line at room temperature for 18 h prior to use. Dried dimethyl sulfoxide (DMSO) (99.97 %, max. 0.03% H_2O) purchased from Aldrich was stored over 4 Å molecular sieves under N_2 atmosphere. All other solvents including methanol and chloroform used in precipitation step were AR grade, purchased from Aldrich and used without further purification.

3.2 Measurements

FTIR spectra were recorded in the 500-4000 cm^{-1} range with a Thermo scientific NICLOET iS5 FT-IR spectrometer fitted with a iD5 attenuated total reflection (ATR) accessory. ^{1}H-NMR spectra were recorded on a Bruker spectrometer (500 MHz) at 22 °C, using $CDCl_3$ as a solvent. Chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as an external reference. Differential Scanning Calorimetry (DSC) analyses were carried out with a PERKIN-ELMER DSC 7 in a sealed aluminum pan under N_2 atmosphere. The samples were first heated to 150 °C at a heating rate of 10 °C/min, and then cooled down to -50 °C at a cooling rate of 20 °C/min. The second heating scans were run from -50 to 150 °C at a heating rate 10 °C/min.

3.3 Experimental procedures

3.3.1 Synthesis of PVA-g-SA copolymers

The synthesis of PVA-g-SA copolymers was divided into two reaction steps: (i) Activation of SA with CDI to form activated SA and (ii) Coupling reaction of activated SA and PVA. Approximate amounts of the reactants and solvent that were used for synthesizing PVA-g-SA copolymers are shown in Table 3.1. The following procedure describes the synthesis of Sample 3.

Table 3.1 Approximate amounts of the substances that were used in each synthesis case

Sample	DS^*_{th}	SA:PVA molar feed ratio	PVA		SA		CDI		DMSO
			g	mmol	g	mmol	g	mmol	mL
1-4, 7 and 8	0.8	0.8	0.83	18.75	4.27	15	2.79	17.25	30
5	0.4	0.4	1.65	37.5	4.27	15	2.79	17.25	30
6	1.0	1.2	0.55	12.5	4.27	15	2.79	17.25	30
9	0.8	0.8	5.78	131.25	29.89	105	19.53	120.75	210
10	0.8	0.8	12.38	281.25	64.05	225	41.85	258.75	450

*DS_{th} = theoretical degree of substitution calculated from the molar feed ratio of SA and PVA

In the activation step, SA (4.27 g, 15 mmol) and CDI (2.79 g, 17.25 mmol) were dissolved in 10 and 7 mL of DMSO, respectively. The SA solution was then slowly added to the CDI solution via a cannula. The reaction mixture was heated at 60 °C, upon which a white solid was observed along with CO_2 generation. To ensure the reaction completion, the reaction was allowed to stir for 3 h. Meanwhile, a solution of PVA was prepared by dissolving PVA (0.83 g, 18.75 mmol) in 13 mL of DMSO at 100 °C. The coupling reaction was performed by adding the PVA solution into the activated SA via a cannula. Before the addition the activated SA was heated to 80 °C, at which a clear solution of the activated SA was obtained. The reaction mixture was then stirred at 80 °C for 24 h. After that, the crude product was dissolved in 15 mL of chloroform and then was precipitated in 100 mL of methanol. The white precipitate was filtered, washed with methanol and then dried at room temperature under vacuum for 18 h.

3.3.2 Property analysis

3.3.2.1 Thermal properties

PVA-g-SA sample with known weight (approximately 12 mg) was enclosed in a sealed aluminum pan under N_2 atmosphere. To determine the glass transition temperature (T_g) and melting crystalline temperature (T_m) of the PVA-g-SA sample, the sample was heated to 150 °C at a rate of 10 °C/min and maintained for 10 min to remove previous thermal history, and then cooled to -50 °C at a rate of 20 °C/min. The sample was then re-heated to 150 °C at a rate of 10 °C/min. Data were collected during the second heating run.

3.3.2.2 Solubility

0.1 g of PVA-g-SA sample was introduced into a glass vial containing 1 mL of solvent. The mixture was allowed to stir at room temperature for 3 h. The solubility of the PVA-g-SA sample was evaluated by visual observation, and classified into three categories based on the extent of solubility; soluble, partially soluble and insoluble.

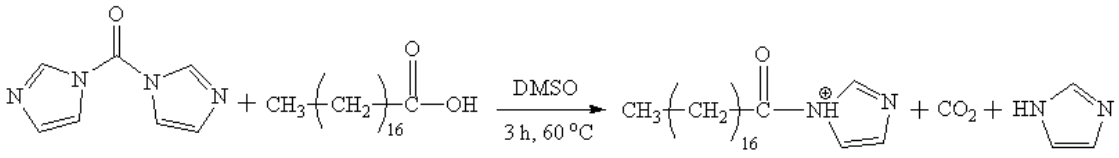
CHAPTER 4 RESULTS AND DISCUSSION

The synthesis of PVA-g-SA copolymers has been already reported using the method of acylation reaction [17, 18]. Nonetheless, there is no report on the structural characterization to ensure such graft product occurrence. The synthesis of PVA-g-SA copolymer by using CDI as a coupling agent is an alternative effective method which the grafting reaction occurs in one pot. Such synthesis method was thus studied. The structural characterization of the synthesized PVA-g-SA copolymers was also performed by means of FTIR-ATR and ^{1}H-NMR spectroscopic techniques. In the synthesis step, the effects of reaction time, solvent pretreatment, molar feed ratio of SA to PVA and scalability on the product yield and DS were discussed. To find out the chemical structure effect, some important properties of the graft copolymers, which are thermal properties and solubility were also investigated.

4.1 Synthesis and characterization of PVA-g-SA copolymers

The synthesis of PVA-g-SA copolymer by graft coupling using CDI was divided into two reaction steps: activation reaction and coupling reaction, as shown in Figure 4.1. Firstly, CDI reacted with SA in DMSO to form activated SA (imidazolide of SA), imidazole and CO_2. Secondly, the coupling reaction was carried out by adding a solution of PVA in DMSO into the activated SA mixture to form the PVA-g-SA product and imidazole. The PVA-g-SA product was then isolated by precipitation in methanol.

Step 1



Step 2

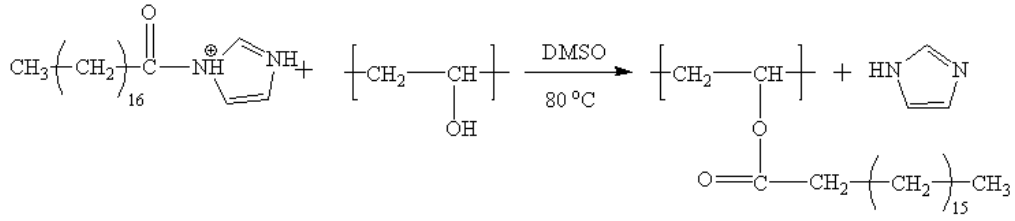


Figure 4.1 Reaction steps for the synthesis of PVA-g-SA copolymer

In the activation reaction step, the addition of SA/DMSO solution into a CDI/DMSO solution gave a precipitate of the SA-imidazolide, which appeared as a foamy mixture (see Figure 4.2 (a)). It could be dissolved by heating up to 80 °C, which was the temperature of the coupling reaction (see Figure 4.2 (b)).

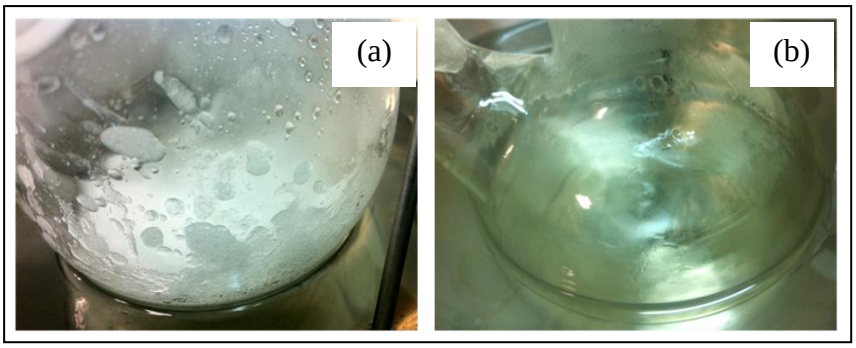


Figure 4.2 The SA-imidazolide mixture at (a) 60 °C, and (b) 80 °C

After the coupling reaction proceeded to the desired reaction time, the reaction mixture was allowed to cool to room temperature, upon which it was partially solidified, giving a heterogeneous mixture (white solid in clear liquid). Such mixture was then dissolved in a minimal amount of chloroform to give a cloudy solution, which was subsequently added slowly into an excessive amount of methanol to give a white precipitate. The yield and degree of substitution of the white precipitate for each reaction condition were shown in Table 4.1. In the characterization step, such white solid was first characterized by FTIR-ATR technique. The FTIR-ATR spectrum of Sample 3 reveals the C=O stretch peak at 1737 cm^{-1} and the C-O stretch peaks at 1230 and 1160 cm^{-1}, which clearly indicates that the ester linkages are present. In addition, the reduction in the intensity of the -OH band around 3350 cm^{-1} was observed. These FTIR-ATR results suggest that some hydroxyl groups in the PVA chains reacted with SA-imidazolide, and then formed the PVA-g-SA copolymers.

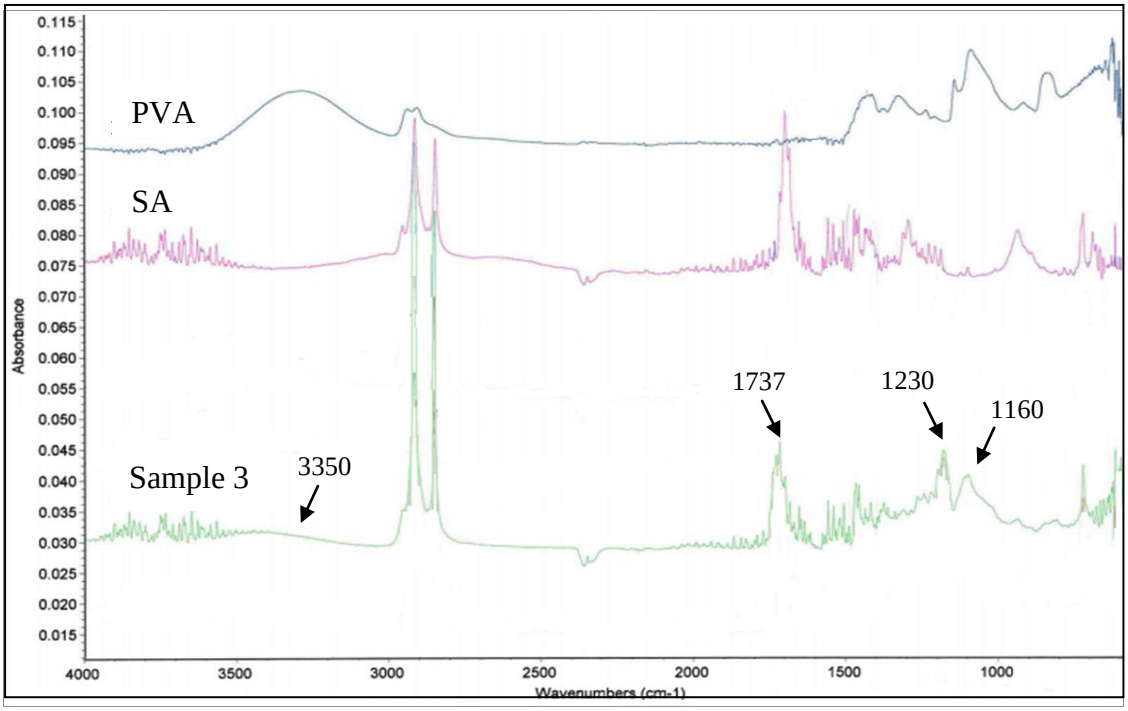


Figure 4.3 FTIR-ATR spectra of PVA, SA and PVA-g-SA copolymer (Sample 3)

Table 4.1 The synthesis results of PVA-g-SA copolymer at several reaction conditions

Sample	DS_{th}	PVA	SA	CDI	DMSO[a]		Time	$Yield^{b}_{exp}$	DS^{c}_{exp}	$Yield^{d}_{cal}$	DS^{e}_{cal}
		mmol	mmol	mmol	mL	Type	h	%	%	%	%
1	0.8	18.75	15	17.25	30	a	12	33.11	30.05	41.43	26.41
2	0.8	18.75	15	17.25	30	a	18	41.92	35.09	45.64	33.39
3	0.8	18.75	15	17.25	30	a	24	57.36	49.57	57.96	44.80
4	0.8	18.75	15	17.25	30	a	48	59.84	52.68	60.44	47.28
5	0.4	37.5	15	17.25	30	a	24	45.77	29.13	48.89	28.30
6	1.0	12.5	15	17.25	30	a	24	42.47	41.67	49.83	42.47
7	0.8	18.75	15	17.25	30	b	24	36.53	-[f]	-[g]	28.75
8	0.8	18.75	15	17.25	30	b	48	47.49	-[f]	-[g]	37.36
9	0.8	131.25	105	120.75	210	a	24	52.66	45.37	54.16	42.50
10	0.8	281.25	225	258.75	450	a	24	44.82	33.24	26.59	35.86

[a] DMSO type a refers to DMSO stored over 4 Å molecular sieve for 24 h while DMSO type b refers to DMSO used as received

[b] The yield percentage of the graft copolymer calculated from $\frac{\text{Weight of product (g)}}{\text{Weight of PVA (g)} + \text{Weight of SA (g)}}$

[c] The degree of substitution of the graft copolymer calculated from the ^{1}H-NMR intensities using Equation (1)

[d] The yield percentage of the graft copolymer calculated from relative DS_{exp} (See Appendix D.1)

[e] The degree of substitution calculated from relative $Yield_{exp}$ (See Appendix D.2)

[f] The degree of substitution cannot be determined due to the inconsistency in the ^{1}H-NMR integrals causing the value of $I_{1.03\text{-}2.09} - I_{2.26} - (14 * I_{2.26})$ being negative number

[g] The yield percentage of the graft copolymer cannot be calculated due to the negative value of relative DS_{exp}

To confirm that the obtained white precipitates are the desired graft copolymer products, every sample was also analyzed by ^{1}H-NMR spectroscopy. Due to the best of our knowledge, the ^{1}H-NMR assignment of PVA-g-SA copolymer has never been reported. In this study assignments of the proton signals of the synthesized graft copolymers were carried out based on the ^{1}H-NMR spectra of the SA and PVA reactants.

The ^{1}H-NMR spectrum of Sample 3 (Figure 4.4) suggests that the PVA-g-SA copolymer was formed since the signals assigned to the methylene protons A and B appear at 2.26 and 1.59 ppm respectively, whereas those in SA are visible at 2.34 and 1.63 ppm (Figure 4.5). The occurrence of grafting was confirmed by the appearance of the signal at around 5.16 ppm, corresponding to the methine group of PVA connected with SA molecule through an ester linkage, while the methine proton of the non-grafted PVA unit is situated at 3.49 ppm. The signals of the methylene protons of the PVA backbone (X, X) are located between 1.03-2.09 ppm, which are partially overlapped with the methylene protons B and C.

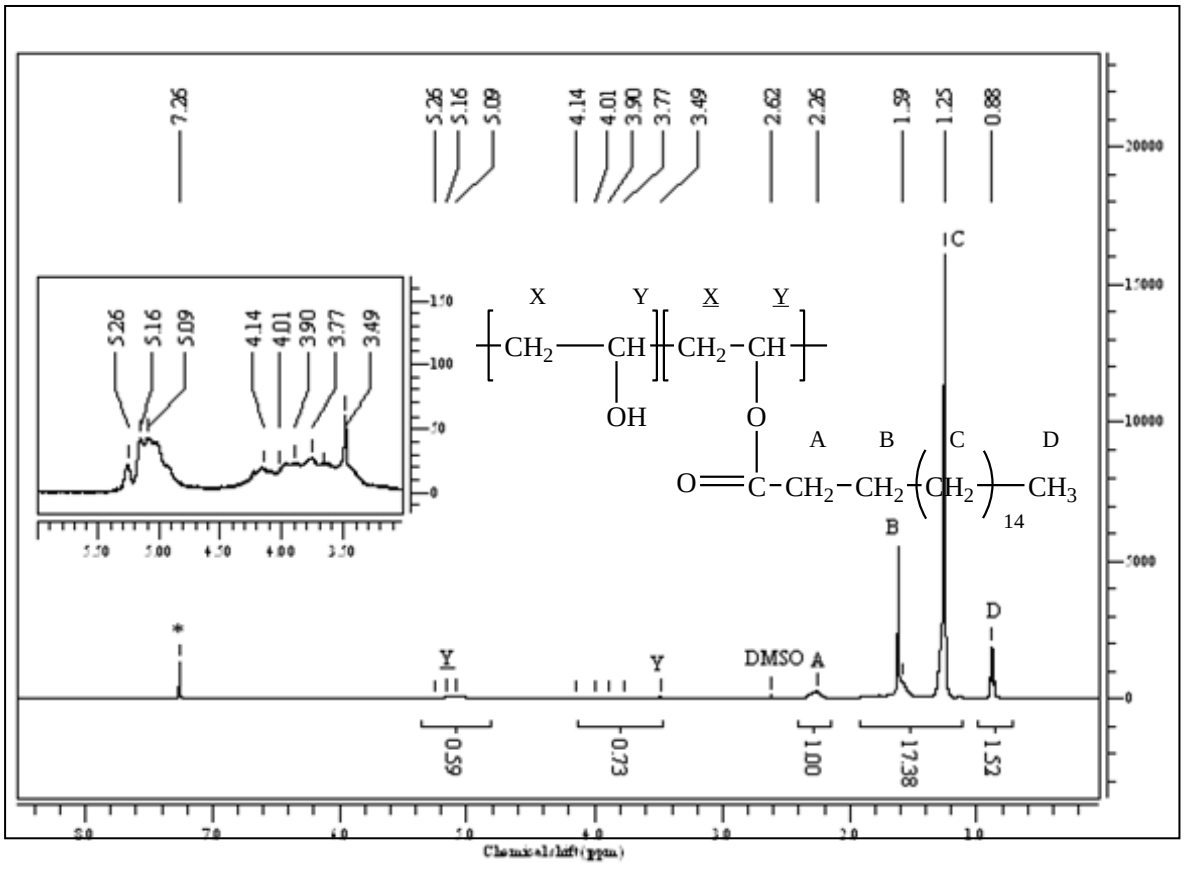


Figure 4.4 ^{1}H-NMR spectrum of PVA-g-SA copolymer (Sample 3)

(22 °C, $CDCl_3$, 500 MHz, δ in ppm: 4.76-5.36 (br, 1H, -CH_2-C<u>H</u>-O-), 3.35-4.24 (br, 1H, -CH_2-C<u>H</u>-OH), 2.26 (t, 2H, -C<u>H_2</u>-COOH), 1.59 (m, 2H, -CH_2-C<u>H_2</u>-$(CH_2)_{14}$-), 1.25 (m, 28H, -CH_2-(C<u>H_2</u>)$_{14}$-CH_3), 0.88 (t, 3H, -$(CH_2)_{14}$-C<u>H_3</u>))

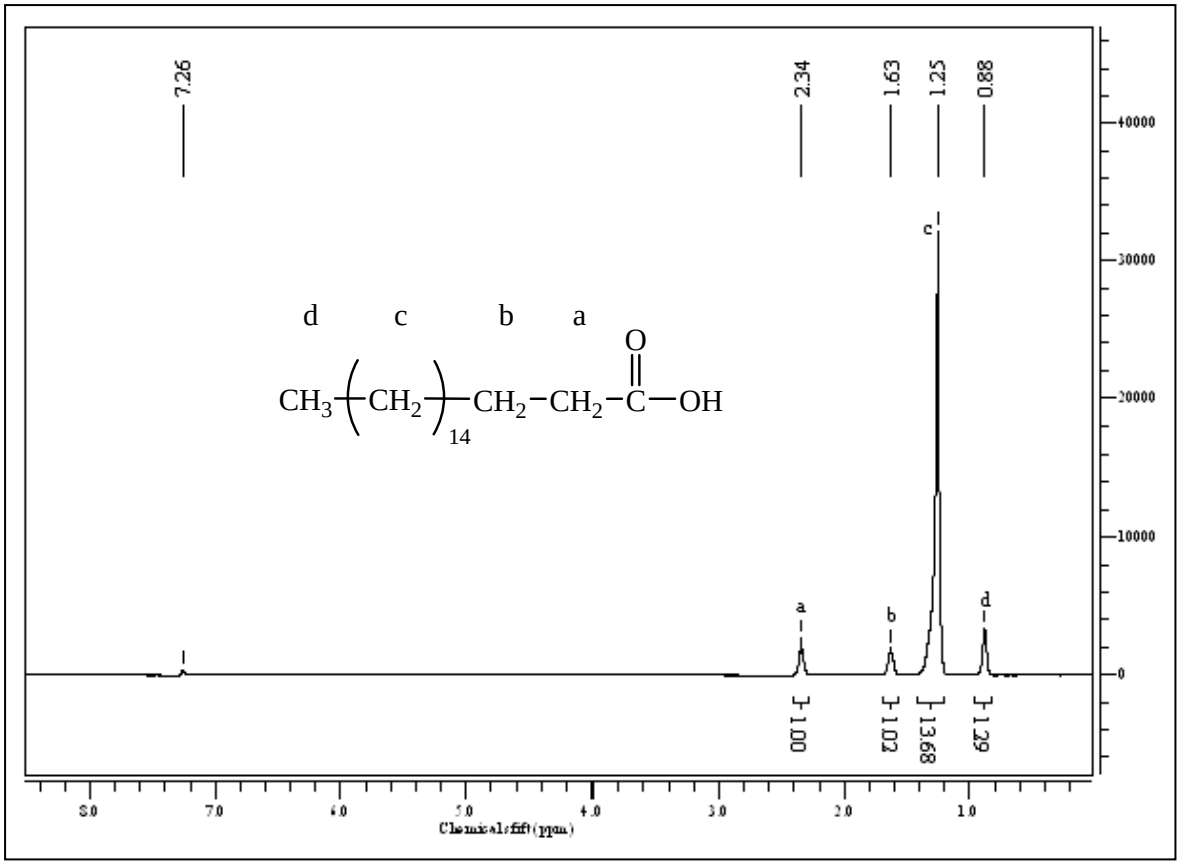


Figure 4.5 ^{1}H-NMR spectrum of SA

(22 °C, $CDCl_3$, 500 MHz, δ in ppm: 2.34 (t, 2H, -C<u>H</u>$_2$-COOH), 1.63 (m, 2H, -CH$_2$-C<u>H</u>$_2$-(CH$_2$)$_{14}$-), 1.25 (m, 28H, -CH$_2$-(C<u>H</u>$_2$)$_{14}$-CH$_3$), 0.88 (t, 3H, -(CH$_2$)$_{14}$-C<u>H</u>$_3$))

Not only the grafting confirmation but also the degree of substitution of the PVA hydroxyl groups with SA molecules can be determined by the ^{1}H-NMR analysis. The experimental degree of substitution (DS_{exp}) was estimated using Equation (1) while the theoretical degree of substitution (DS_{th}) was calculated using Equation (2). The DS_{th} and DS_{exp} values of all samples are shown in Table 4.1.

$$DS_{exp} = \frac{2 \times I_{5.15}}{I_{1.08\text{-}2.09} - I_{2.26} - (14 \times I_{2.26})} \quad (1)$$

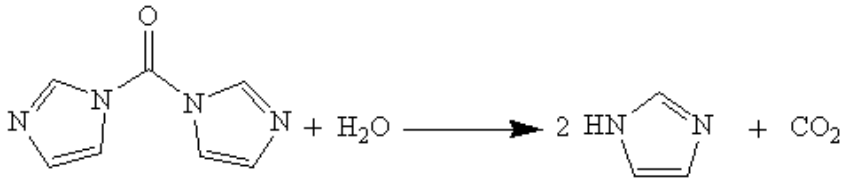
where $I_{2.26}$, $I_{5.15}$ and $I_{1.08\text{-}2.09}$ are the integrals of the signals at 2.26, 5.15 and 1.08-2.09 ppm, respectively.

$$DS_{th} = \frac{\text{Mole of SA}}{\text{Mole of PVA repeating unit}} \quad (2)$$

4.1.1 Effect of reaction time

In order to investigate the effect of reaction time, four PVA-g-SA samples were synthesized as a batch reaction with a molar feed ratio of SA to PVA equal to 0.8 for 12, 18, 24 and 48 h (Samples 1-4). Results presented in Table 4.1 show that the yield and DS of the graft copolymer product were increased with increasing the reaction time from 12 to 24 h and then became almost constant. The highest obtained product yield was only 60 % even though the reaction time was increased to 48 h. The decomposition of CDI, the coupling agent, was suspected to be responsible for the low yield. It is well known that CDI is moisture sensitive. It readily reacts with water (moisture) and then decomposes to imidazole. In addition, activated SA or SA-imidazolide which is a reactive intermediate obtained from the activation reaction is also water-sensitive. When it exposes to water it is quickly hydrolyzed to SA and imidazole [23], causing a low yield was obtained. The hydrolysis reactions of CDI and SA-imidazolide are illustrated in Figure 4.6. Therefore, all the reactants and solvent used in the reaction must be highly dried to ensure the good reaction results.

(a)



(b)

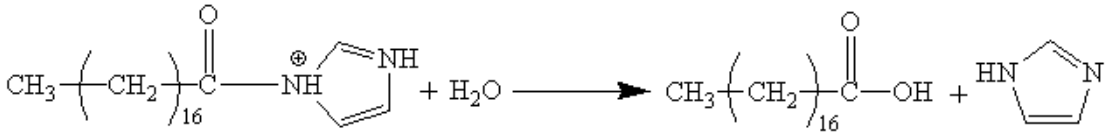


Figure 4. 6 The hydrolysis reactions of (a) CDI and (b) SA-imidazolide

In this work, both PVA and DMSO solvent were dried prior to use. PVA was dried in a vacuum oven at 80 °C for 20 h and then at 100 °C for 12 h in a vacuum oven, and also further dried using a high vacuum Schlenk line at 100 °C for 6 h prior to use. However, it is difficult to completely eliminate water in PVA because of strong hydrogen bonding between the PVA hydroxyl groups and water molecules. On the other hand, the dried grade of DMSO solvent was also predried by storing over 4 Å molecular sieves for at least 24 h before used. Due to its hygroscopic nature, DMSO can attract water molecule from the surrounding rapidly. Since the amount of DMSO solvent used in the reaction was much greater than those of the other reactants, the water residue in the DMSO solvent even in a tiny fraction could greatly affect the reaction, and thus it was considered to be the most possible cause for the poor yield of the graft copolymer product.

It was also found that the yield and DS of the graft copolymer product obtained at the shorter reaction time were considerably less than the calculated values. The maximum differences were observed in the case of Sample 1, which were 20 % and 12 % for the yield and DS, respectively. The lower yield of the obtained product could be explained by poor product recovery in the isolation and purification steps. Sample 1 has the lowest DS which means that the amount of the free hydroxyl groups on the grafted PVA backbone is highest when compared to the other three samples. In other words, Sample 1 is more polar. When it was isolated and purified by precipitating in methanol it is possible that it was partially dissolved in methanol, leading to a lower amount of the graft copolymer product recovered.

In addition, the suitable reaction time in the coupling reaction step was determined in order to be used in the study on the effects of the solvent pretreatment and molar feed ratio of reactants. From Figure 4.6, the suitable reaction time was found to be at 24 h. Although the highest yield was obtained at 48 h, it is definitely not cost effective to run the reaction twice longer in order to afford a slightly greater yield.

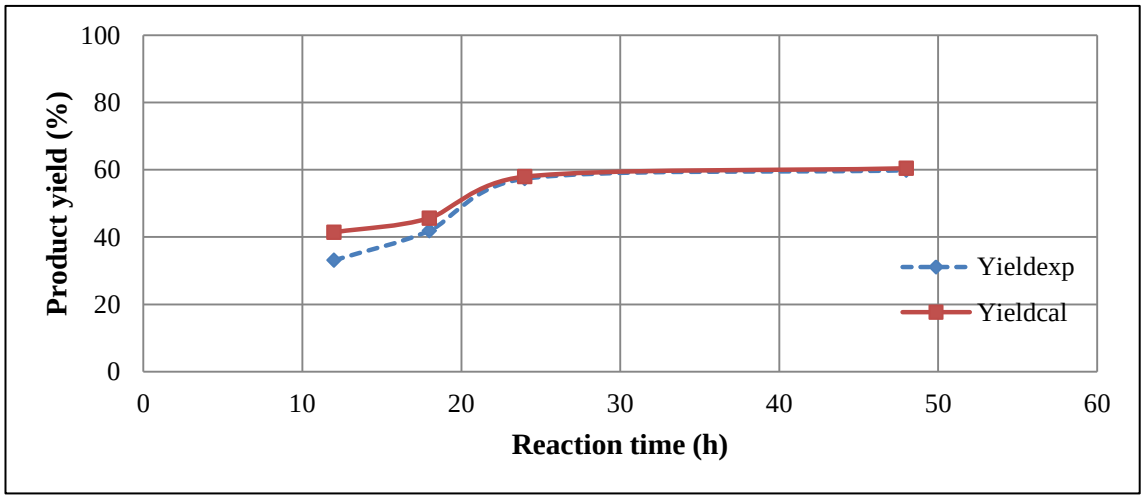


Figure 4.7 A relationship between the PVA-g-SA copolymer yield and reaction time in the coupling reaction step

4.1.2 Effect of solvent pretreatment

As mentioned above, the presence of water in the DMSO solvent can lead to the decompositions of CDI and the SA-imidazolide, which consequently results in a low yield of the PVA-g-SA product. Therefore, DMSO used in this work was a dried grade which contains a maximum water content of 0.03 wt%. In the study on the effect of solvent pretreatment, two types of DMSO solvent were used; DMSO predried by storing over 4 Å molecular sieves for at least 24 h (Type a) and DMSO without predrying (Type b). As shown in Table 4.1, the graft copolymers with lower yield and DS were obtained when using the non-predried DMSO as the solvent. At the same reaction time of 24 h, the yield of the PVA-g-SA product when using the non-predried DMSO was only 36.53 % (Sample 7) whereas 57.36 % yield was obtained when the

DMSO was predried (Sample 3). Similarly, the solvent pretreatment could improve the yield of the graft copolymer product from 47.49 % (Sample 8) to 59.84 % (Sample 4) when the coupling reaction was conducted for 48 h. Furthermore, the NMR integrals of Samples 7 and 8 were not consistent with the theoretical ratio although their signals in ^{1}H-NMR spectrum confirmed the formation of the graft copolymer. It appeared that the intensities of the methylene protons B and C were too low (see Appendix A.7 and A.8). The true cause of the integral inconsistency is not clear, and it requires further investigation. However, one possible explanation is that some side reactions may occur probably due to the high water content in the non-predried DMSO.

Accordingly, the pretreatment of DMSO solvent for the grafting reaction using CDI as a coupling agent is necessary. A higher product yield can be obtained if an anhydrous DMSO is used. Although anhydrous DMSO is commercially available, it is very expensive, and may not suitable for this reaction in terms of cost effectiveness. On the other hand, anhydrous DMSO can be achieved in laboratory by stirring over CaH_2 and then distilling under vacuum. Drying DMSO via this method will take at least two days.

4.1.3 Effect of molar feed ratio of SA to PVA

The effect of the molar feed ratio of SA and PVA on the PVA-g-SA formation was studied by keeping the mole of SA constant at 15 mmol and varying the mole of PVA from 37.5 mmol to 18.75 and 12.5 mmol (Samples 5, 3 and 6, respectively). It is expected that the graft copolymer with a higher DS should be obtained when decreasing the mole of PVA, and Samples 5, 3 and 6 should have a theoretical DS of 0.4, 0.8 and 1.0 respectively. However, it was found that when the mole of PVA decreased from 37.5 mmol to 18.75 and 12.5 mmol, the DS of the PVA-g-SA product increased from 29.13 % to 49.57 %, and then decreased to 41.67 %. The increases in the DS and yield in Sample 3 can be simply explained by a greater rate of reaction due to the higher concentrations of PVA reactant. However, the more the amount of PVA was added, the more the reaction mixture became viscous, leading to a difficulty in stiring, and hence poor mixing of the reaction mixture. As a consequence, the reaction would not proceed well, resulting in the decrease in the yield as were observed in the case of Sample 5.

4.1.4 Preliminary study on scalability

CDI-mediated coupling reaction is considered to be an effective method to synthesize PVA-g-SA copolymer. However, it will be useless if the amount of the synthesized graft copolymer is insufficient to be utilized in either further study or any application. To obtain an adequate quantity of the graft copolymer, the scalability was preliminary studied by scaling up the reaction by 7 and 15 times (Samples 9 and 10 respectively), using the synthesis condition of Sample 3 under which the high yield and DS were obtained. As shown in Table 4.1, the product yield decreased from 57.36 % to 52.66 % and 44.82 % when the reaction was scaled up by 7 and 15 times, respectively.

Similarly, the DS of the graft copolymer product also decreased from 49.57 % to 45.37 % and 33.24 % respectively. These results demonstrated that scaling up the reaction by 7 times slightly affected both yield and DS whereas scaling up by 15 times caused significant decreases. The significant decreases in the product yield and DS when the reaction scale was increased by 15 times could be explained by the poor mixing of the reaction mixture and the undesired reaction due to the water residue in the reaction. It was observed that when the reaction was scaled up by 15 times the magnetic bar that was used to provide the mixing of the reaction mixture could not stir as well as when the reaction was conducted in the smaller scales. The presence of water is also expected to affect the product yield and DS. Although the reactants were freshly dried for at least 18 h before the reactions were carried out, the drying time may not be long enough for drying the large amounts of the reactants resulting in a relatively high amount of water remaining in the reactants.

4.2. Property analyses of synthesized PVA-g-SA copolymers

To investigate the influence of the structural feature of the synthesized PVA-g-SA copolymers on their properties, two PVA-g-SA samples with different DS values, which are Sample 1 (DS_{exp} = 30.05 %) and Sample 4 (DS_{exp} = 52.68 %), were analyzed. The properties that were examined in this study are thermal properties and solubility. Thermal properties of the graft copolymers are interested because they are considered as one of the key parameters to indicate areas of application. On the other hand, knowledge of the solubility of the graft copolymers will be useful for their fabrication/processing and further structural modifications. In addition, the properties of Sample 10 (DS_{exp} = 33.24 %) were also examined because it was the graft copolymer product obtained from the large-scale reaction, which will be used as polymeric carrier for agrochemicals in further study.

4.2.1 Thermal properties

For thermal analysis the glass transition temperature (T_g) and crystalline melting temperature (T_m) of the graft copolymers were determined. Knowledge of T_g and T_m is essential in the selection of materials for various applications. In general, T_g values below room temperature implies elastomeric behavior of the material, whereas values above room temperature define rigid, structural polymers. In other words, as a temperature of a polymer drops below T_g, it behaves in an increasingly brittle manner. While the temperature rises above the T_g, the polymer becomes more rubber-like. On the other hand, T_m is the temperature at which the crystalline regions in the polymer matrix are destroyed and the polymer changes from solid to molten state.

The thermal behavior of the PVA-g-SA copolymers was analyzed by differential scanning calorimetry (DSC). The samples were first heated to 150 °C at a heating rate of 10 °C /min, and then cooled down to -50 °C at a cooling rate of 20 °C/min. The second heating scans were run from -50 to 150 °C at a heating rate 10 °C /min. The T_g was recorded as the midpoint temperature of the heat capacity transition in the second

heating scan whereas the T_m was recorded as the temperature of the endothermic peak. The thermal properties of the PVA-g-SA copolymers (Samples 1, 4 and 10) are summarized in Table 4.2, and their DSC thermograms are shown in Appendix C.

Table 4.2 Thermal properties of the PVA-g-SA copolymers

Sample	DS_{exp} (%)	T_m (°C)	T_g(°C)
PVA	-	230*	85*
SA	-	69.6*	-
1	30.05	50.17	26.32
4	52.68	50.35 and 47.30	N/A
10	33.24	50.60	N/A

* T_m obtained from the material safety data sheet (MSDS) of the chemical

From the DSC thermograms (Figures C.1-C.3), no T_g was observed for Samples 4 and 10. This fact suggests that molecular motion of the grafted polymers is quite restricted because of higher degree of substitution. T_g of Sample 1 was observed at 26.32 °C which it meant that this grafted copolymer was rigid and structural polymer like an obtained brittle powder at the end of the synthesis. On the other hand, endothermic peak at around 50 °C was observed in all graft copolymer samples, regardless of the difference in the DS. This implies that the difference in DS of the graft copolymers did not strongly affect the T_m of the material. Besides, it was also found that the T_m values of the graft copolymers are much lower than the reported T_m value of the pure PVA (230 °C). The low T_m values of the graft copolymers could be explained by the obstruction of the chain packing during the crystallization and the prevention of the hydrogen bonding between the chains by the grafting SA molecules. It is also worth mentioning that the shape of the endothermic melting peak in the DSC thermograms is considerably broad. Moreover, the DSC thermogram of Sample 4 shows two overlapping endothermic peaks at 50.35 and 47.30 °C suggesting that there are two different types of crystal structure occurred and exist in the copolymers. To verify that the above peaks only relate to melt transition, and do not involve any glass transition, DSC thermograms of the quenched samples are required. If that is the case, no endothermic peak should be observed in DSC thermograms.

4.2.2 Solubility

PVA is highly hydrophilic, which is soluble in water and very high polar solvents. Grafting the SA molecules, which are hydrophobic, on the PVA chain will result in a decrease in the hydrophilicity/polarity of the PVA chain, and hence affect the solubility in solvents. In other words, the more the SA molecules grafted on the PVA chain, the lower the hydrophilicity/polarity of the graft copolymer. In this study, ten solvents which have different polarity index were selected for the solubility analysis of Samples 1, 4 and 10 in order to determine the effect of DS on the graft copolymer solubility, which was simply assessed via visual observation. The solubility results of the three graft copolymer samples are presented in Table 4.3.

Figure 4.8 A photograph demonstrating the extent of solubility of the PVA-g-SA copolymers (From left to right: soluble, partially soluble and insoluble)

Table 4.3 The solubility results of the PVA-g-SA copolymers

Solvent	Polarity index	PVA	SA	Sample 1	Sample 4	Sample 10
Water	9.0	-*	-	-	-	-
Dimethyl Sulfoxide	7.2	-*	-	-	-	-
Dimethylformamide	6.4	-*	-	-	-	-
Acetronitrile	5.8	-	-	/	/	/
Ethanol	5.2	-	+	/	/	/
Tetrahydrofuran	4.0	-	+	+	+	+
Dichloromethane	3.1	-	+	+	+	+
Diethyl ether	2.8	-	+	+	+	+
Toluene	2.4	-	+	-	-	-
Hexane	0.0	-	+	-	-	-

Extent of solubility: soluble (+), partially soluble (/) and insoluble (-)

* The solubility of PVA depends on temperature and time

The solubility results in Table 4.3 revealed that the graft copolymer products had different solubility from pure PVA and SA. This confirmed the change in the hydrophilicity/polarity of the graft copolymer products after grafting. The solubility of Samples 1, 4 and 10 was similar; all three samples were found to be completely soluble in the solvents that have the polarity index between 4 and 2.8. On the contrary, the solvents which are considered as high polar solvents (water, DMSO and DMF) and non-polar solvents (toluene and hexane) could not dissolve these three graft copolymer products. However, they could be partially dissolved in acetronitrile and ethanol. They also support the decrease in the hydrophilicity/polarity of the PVA backbone when it was incorporated with the hydrophobic SA. As was observed in the thermal analysis the similarity in solubility of these three samples indicates that a small difference in DS slightly or do not affect the solubility of the graft copolymers. Nevertheless, these data are useful for future work on fabrication/processing and further structural modifications of the synthesized graft copolymers

CHAPTER 5 CONCLUSIONS

5.1 Conclusions

PVA-g-SA copolymers with different DS values were successfully synthesized via the grafting reaction using CDI as a coupling agent. The synthesis was carried out in one pot comprising two reaction steps: activation and coupling reaction. The structural characterization of the synthesized graft copolymers was performed by means of FTIR-ATR and ^{1}H-NMR spectroscopic techniques. The FTIR-ATR spectra revealed the C=O stretch peak at 1737 cm^{-1} and the C-O stretch peaks at 1230 and 1160 cm^{-1}, indicating the formation of the ester linkage between PVA and SA. In addition, the visibility of the ^{1}H-NMR signal at 5.16 ppm, corresponding to the methine group of PVA connected with SA molecule through an ester linkage, clearly confirmed that the SA molecules were successfully grafted onto the PVA chains. In this study three reaction variables, which are reaction time, DMSO solvent pretreatment and the molar feed ratio of SA to PVA, were investigated for their effects on the graft copolymer formation. The results demonstrated that they all had significant effects on the yield and DS of the synthesized graft copolymers. The low yield and DS of the graft copolymer products could be explained by the poor product recovery, undesired reactions due to the presence of water residue and poor mixing of the reaction mixture. The preliminary study on the reaction scalability revealed the significant decreases in product yield and DS value when the reaction scale was increased 15-fold.

To investigate the influence of the graft copolymer structure on the thermal properties and solubility three PVA-g-SA samples with different DS values, Sample 1 (30.05 %), Sample 4 (52.68 %) and Sample 10 (33.24 %) were analyzed. The results revealed that a small difference in the DS slightly affected the above properties. A broad endothermic peak shown in the DSC thermograms, indicating a T_m, was observed at approximately 50 °C for all samples. Interestingly, Sample 4 shows two overlapping endothermic peaks suggesting two different types of crystal structure being formed, and it requires further investigation. In addition, T_g of Sample 1 was observed at 26.32 °C while no T_g was observed for Samples 4 and 10 suggesting that the molecular motion of the grafted polymers is quite restricted because of higher degree of substitution. From solubility analysis all three PVA-g-SA samples gave similar results, which they were completely soluble in THF, dichloromethane and diethyl ether, partially soluble in acetronitrile and ethanol, and insoluble in water, DMSO, DMF, toluene and hexane.

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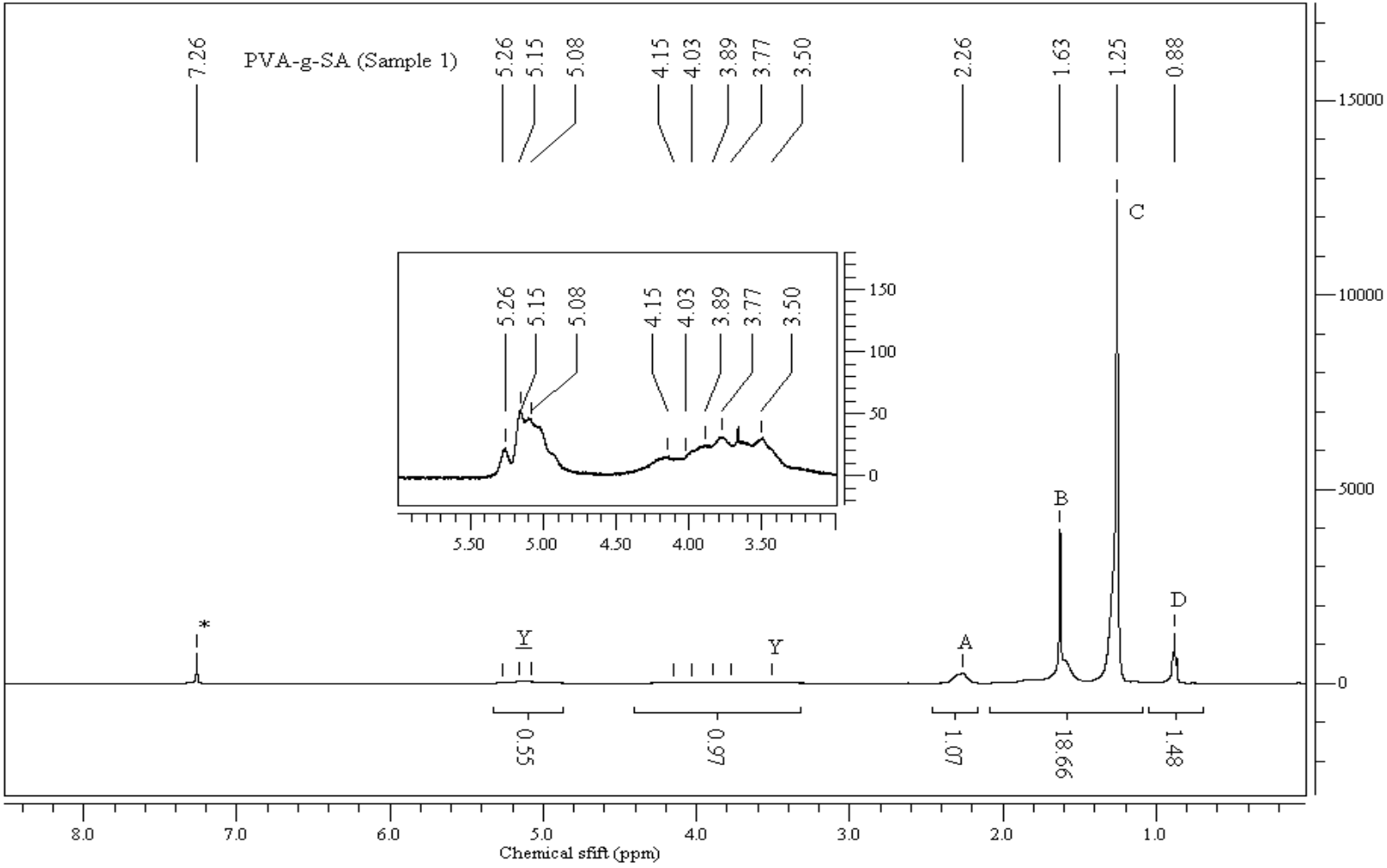
APPENDIX

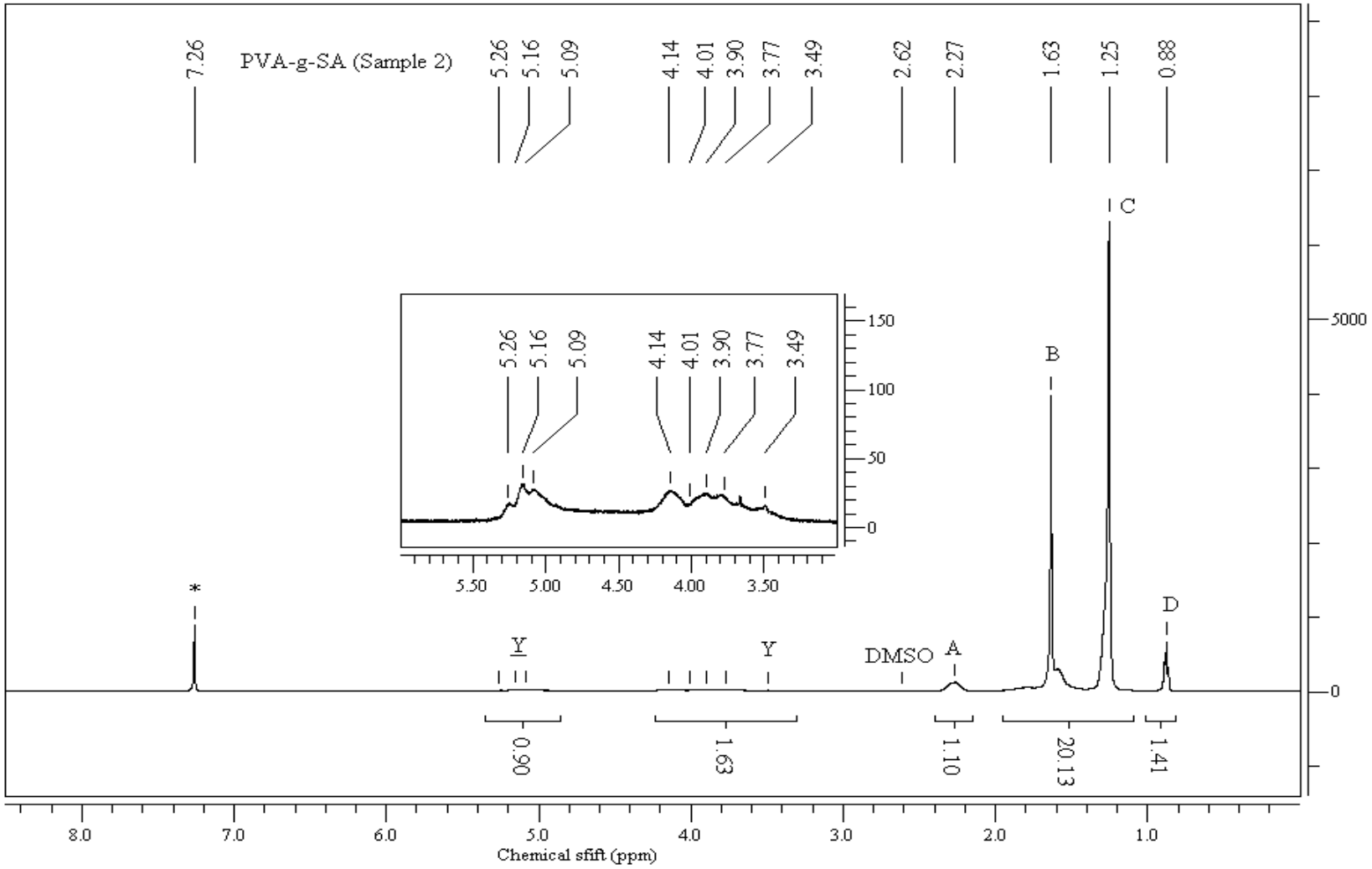
APPENDIX A

^{1}H-NMR SPECTRUM

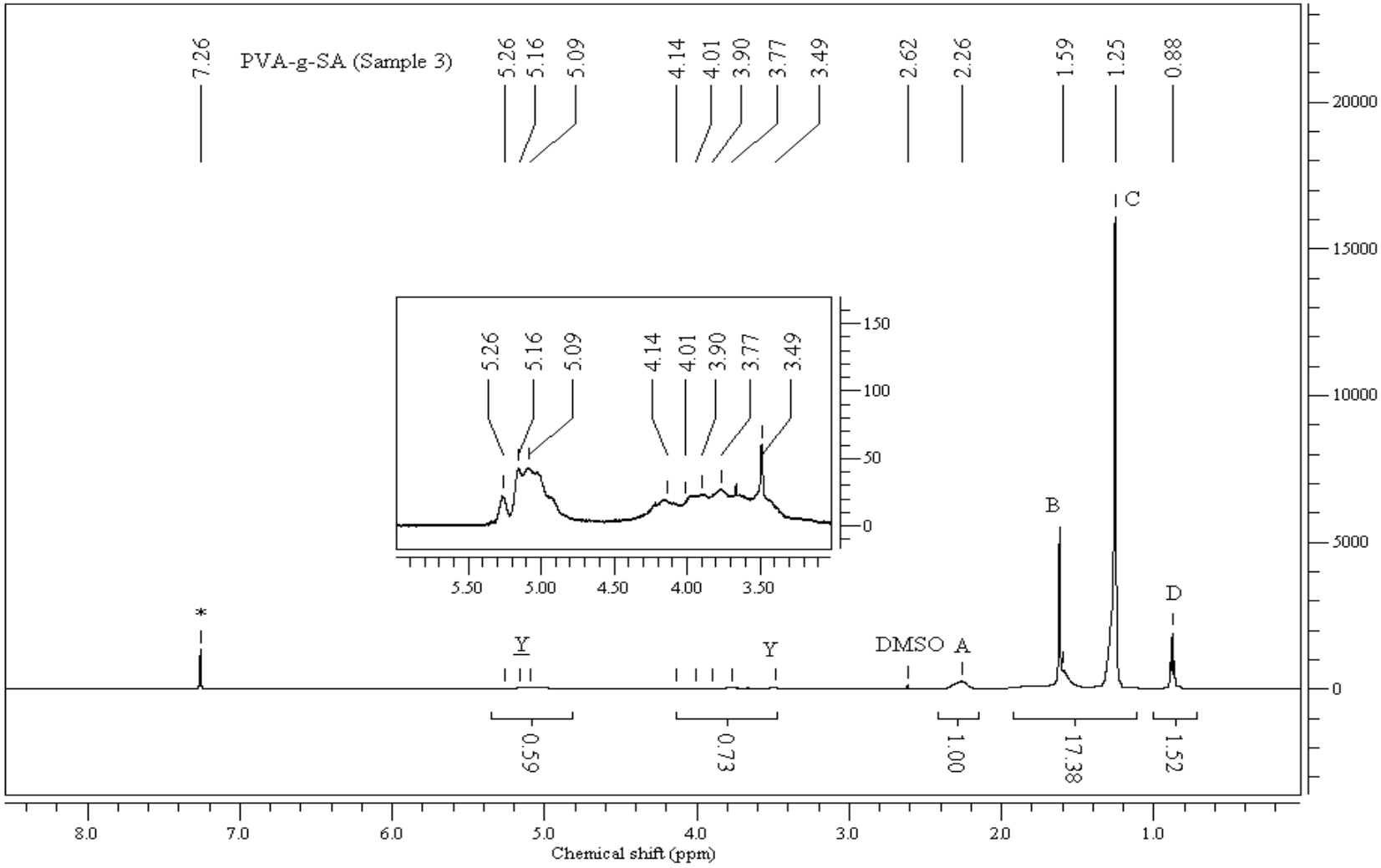
A. 1 ^{1}H-NMR spectrum of Sample 1 (22 ^{o} C, solvent $CDCl_3$)



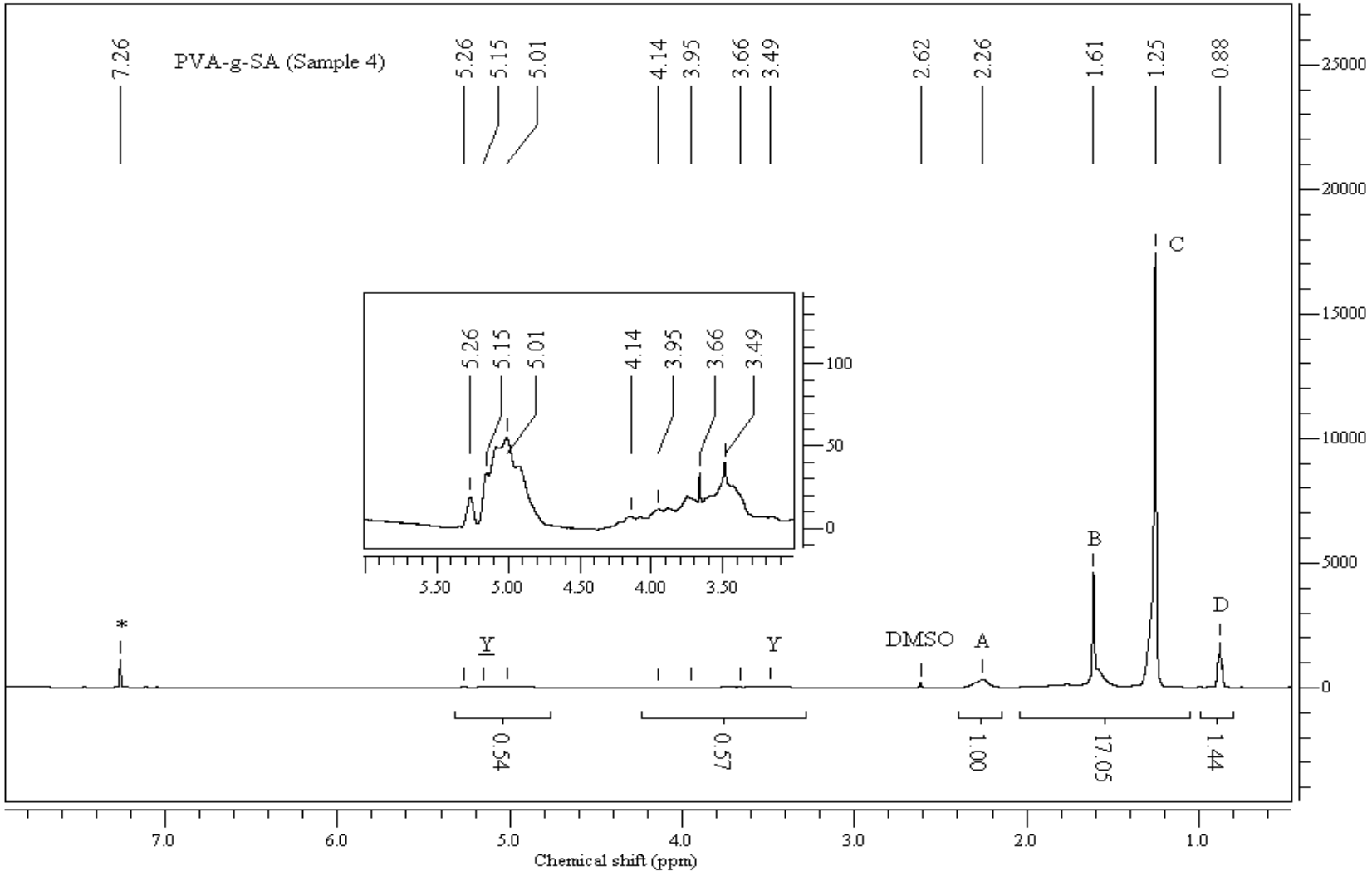
A. 2 ^{1}H-NMR spectrum of Sample 2 (22 ^{o} C, solvent $CDCl_3$)



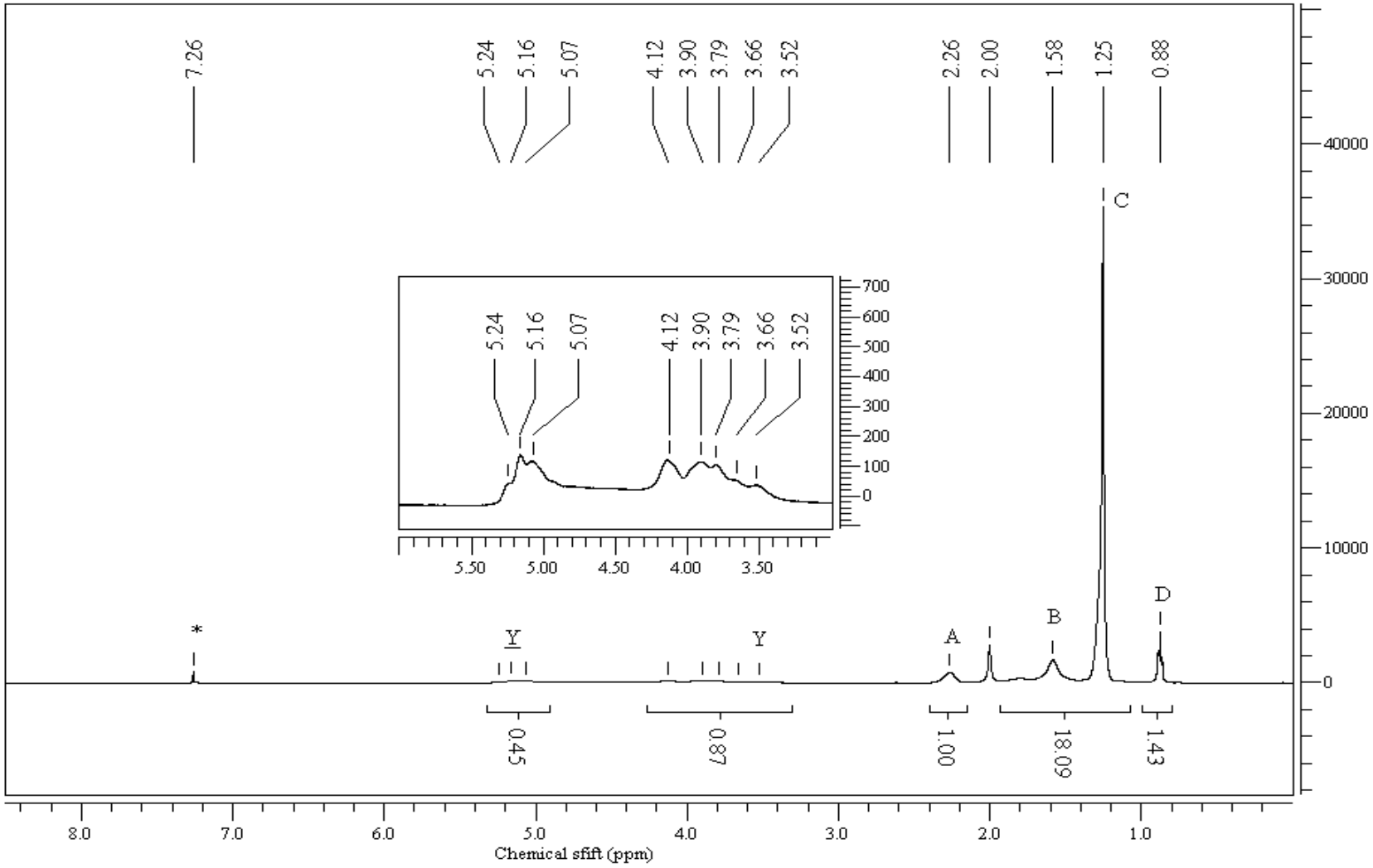
A.3 ^{1}H-NMR spectrum of Sample 3 (22 ^{o} C, solvent $CDCl_3$)



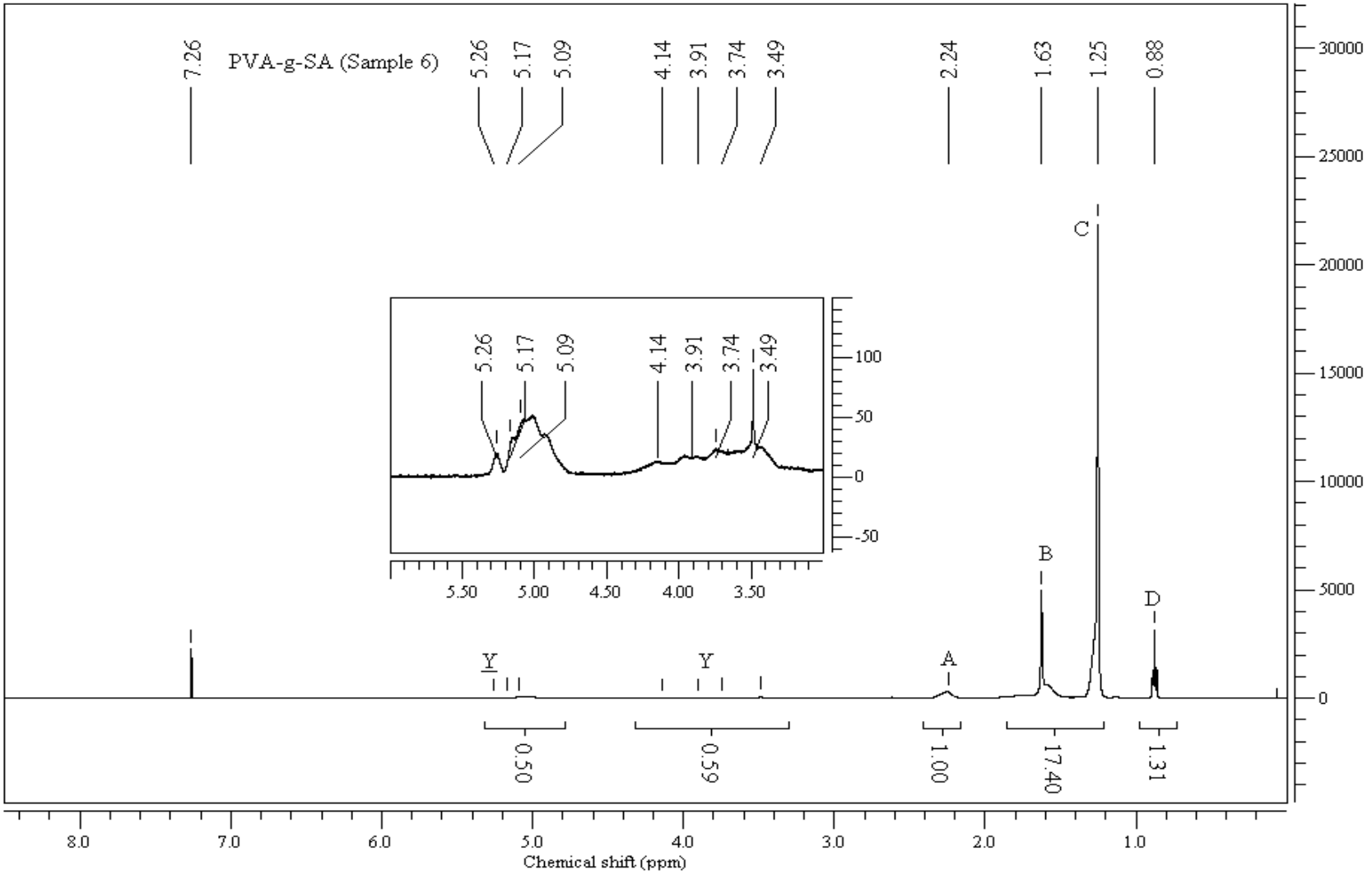
A.4 ^{1}H-NMR spectrum of Sample 4 (22 ^{o} C, solvent $CDCl_3$)



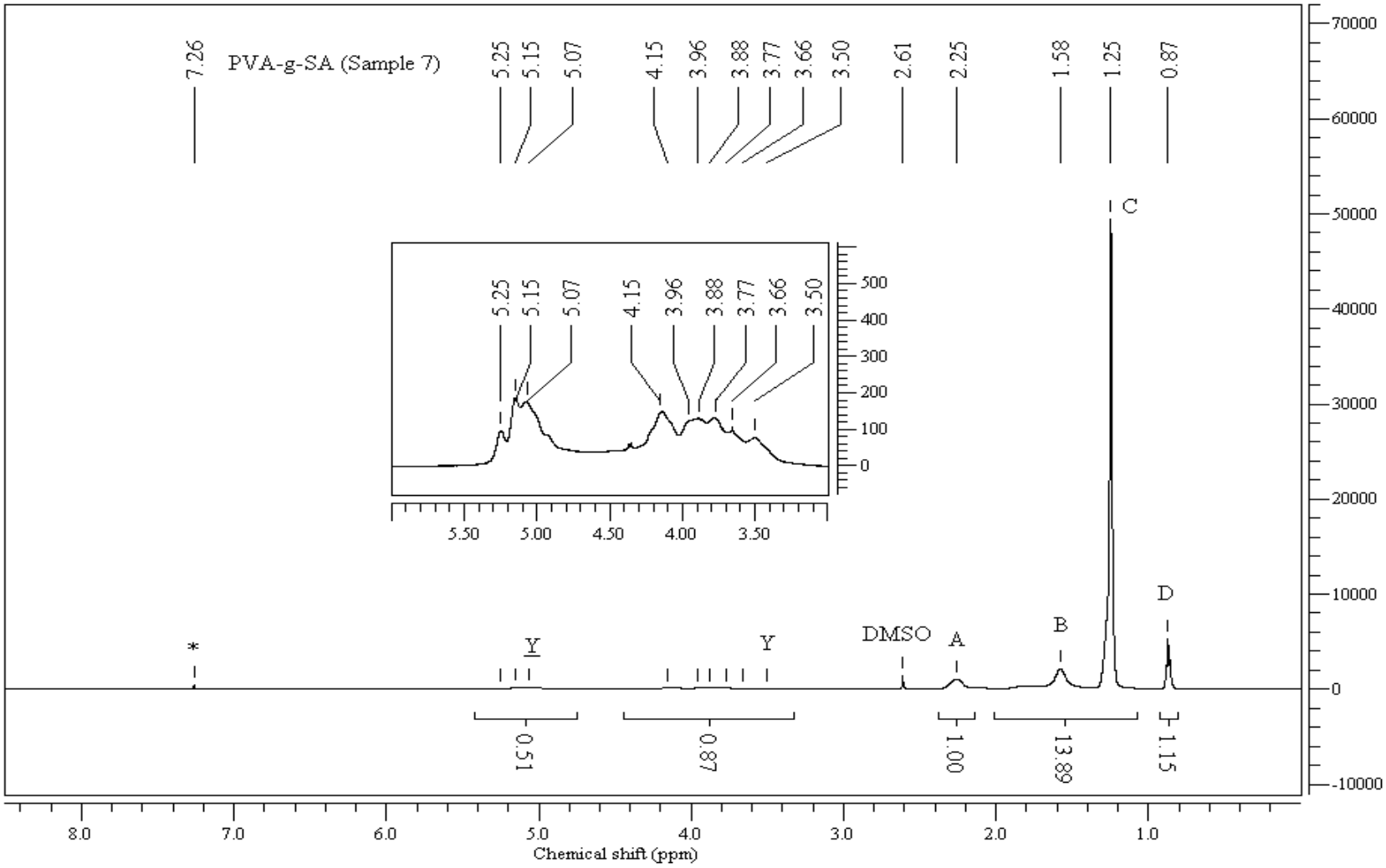
A.5 ^{1}H-NMR spectrum of Sample 5 (22 ^{o} C, solvent $CDCl_3$)



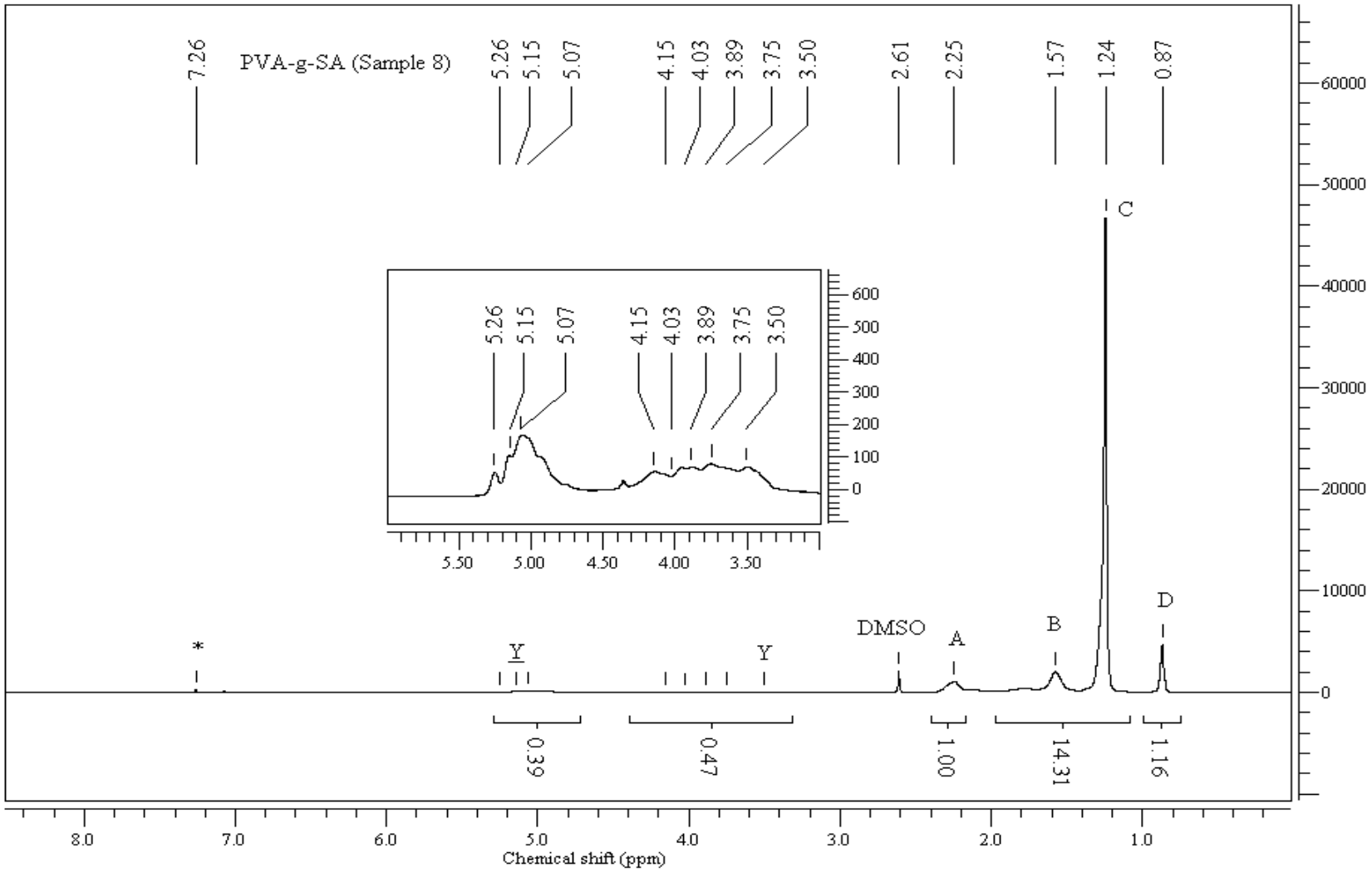
A.6 ^{1}H-NMR spectrum of Sample 6 (22 ^{o} C, solvent $CDCl_3$)



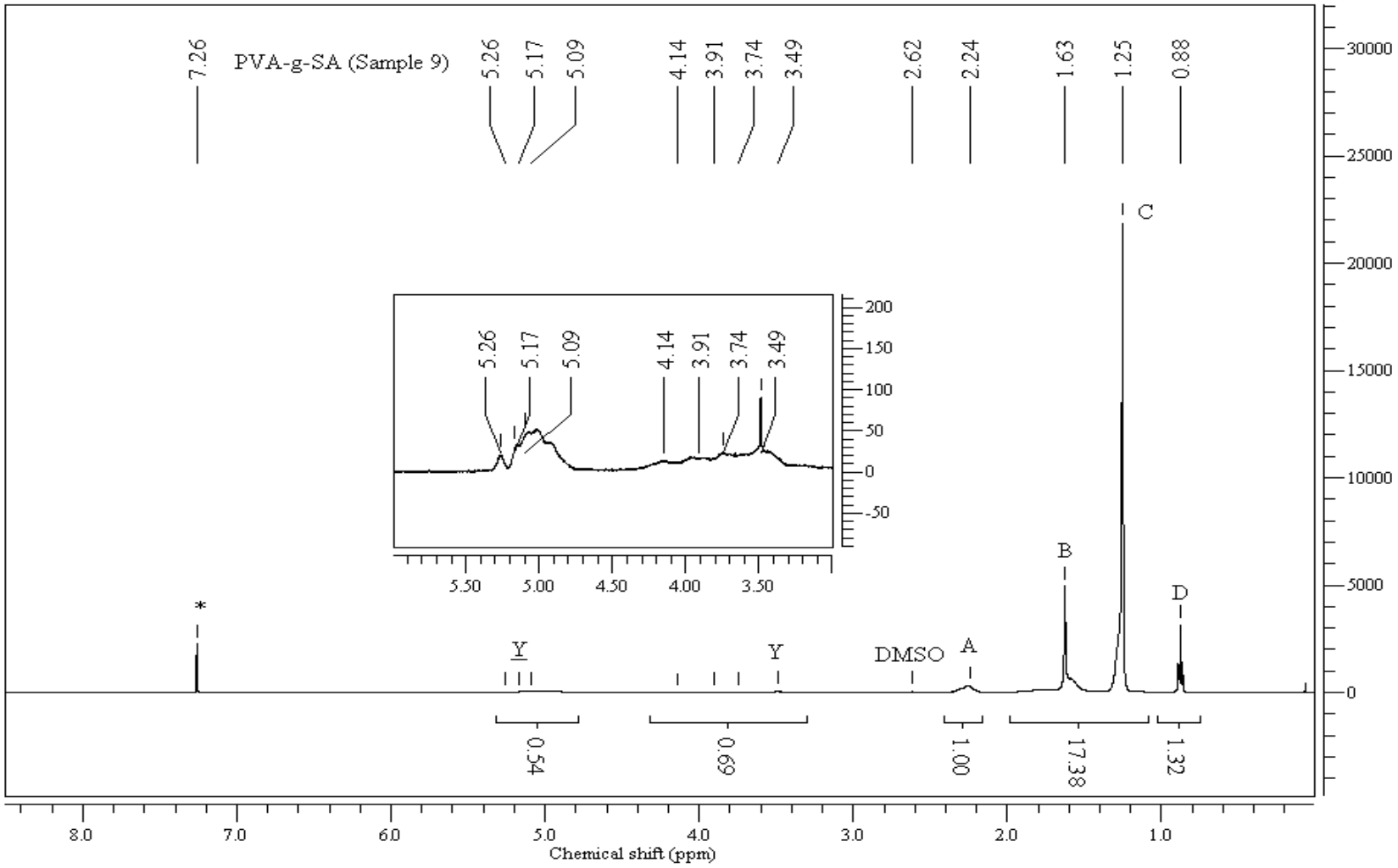
A.7 ^{1}H-NMR spectrum of Sample 7 (22 ^{o} C, solvent $CDCl_3$)



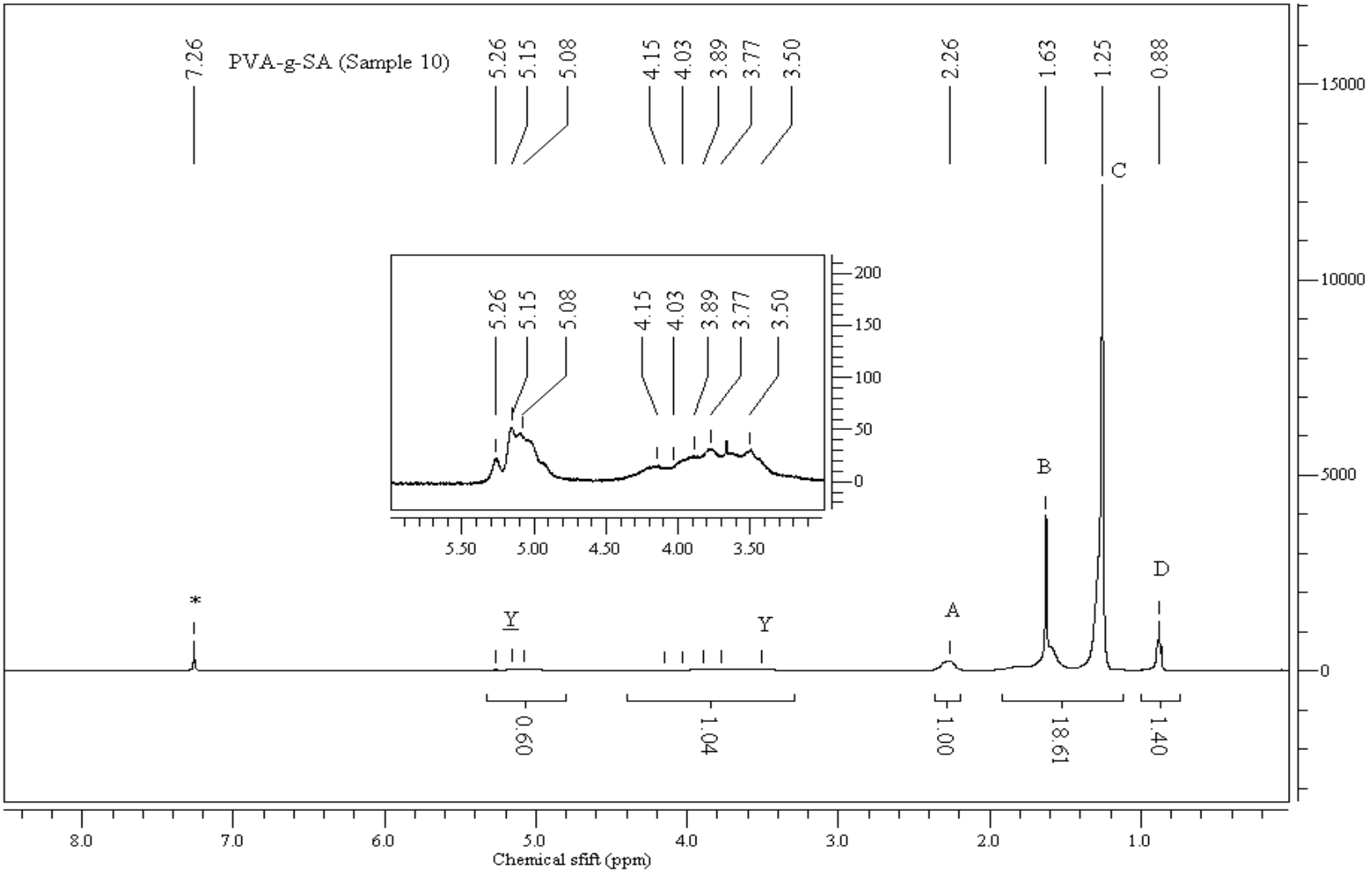
A.8 ^{1}H-NMR spectrum of Sample 8 (22 ^{o} C, solvent $CDCl_3$)



A. 9 ^{1}H-NMR spectrum of Sample 9 (22 ^{o} C, solvent $CDCl_3$)



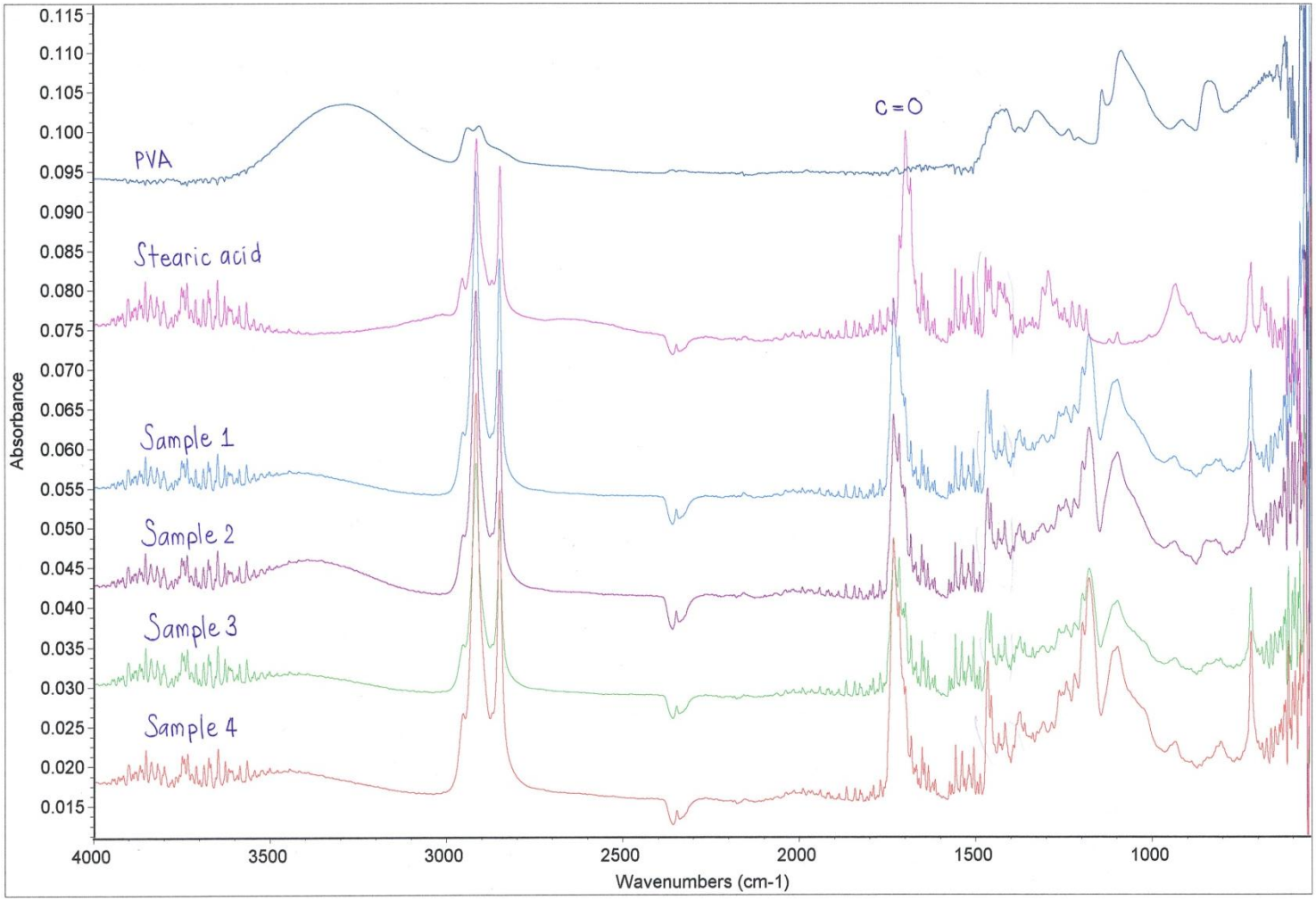
A. 10 ^{1}H-NMR spectrum of Sample 10 (22 ^{o} C, solvent $CDCl_3$)



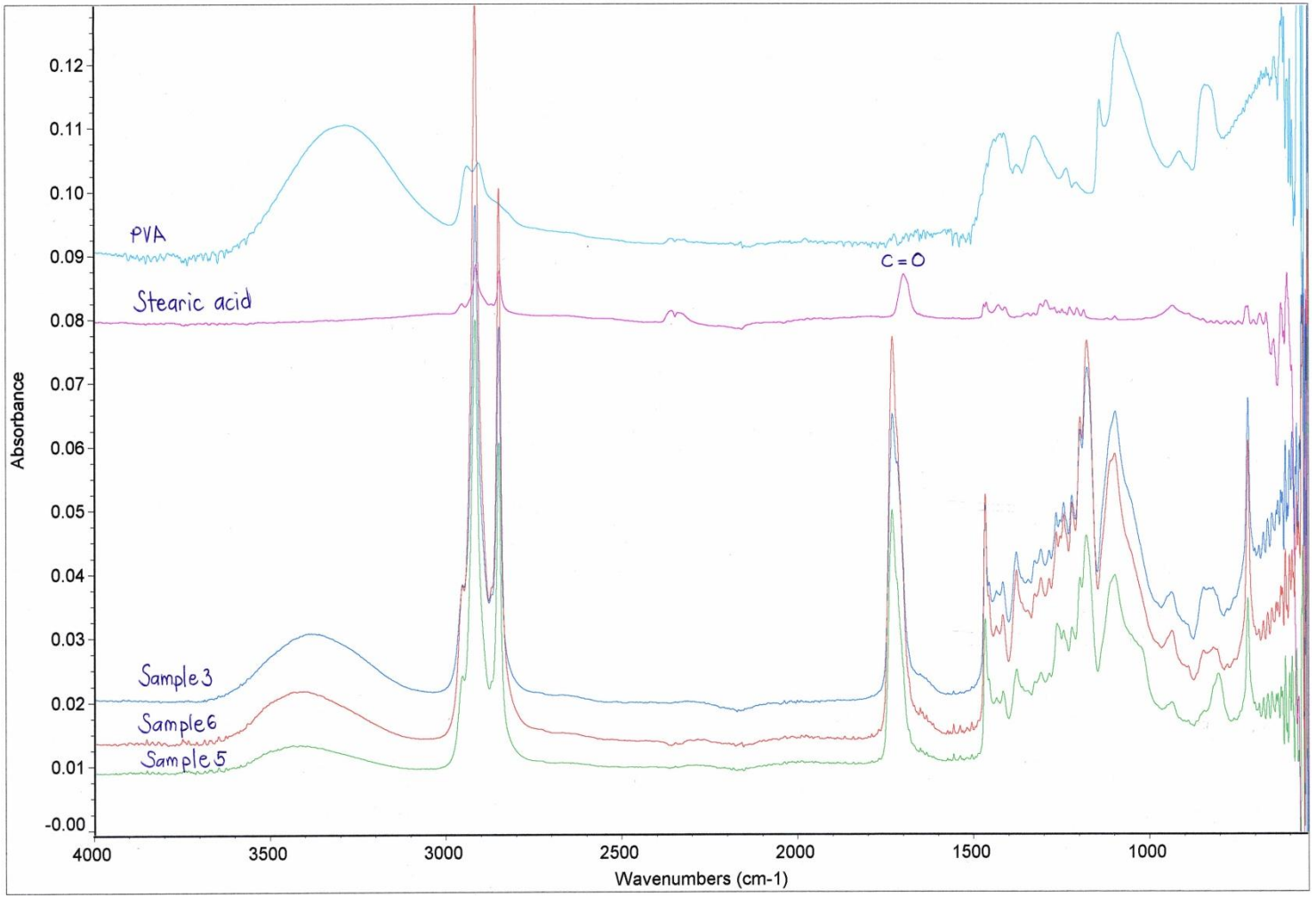
APPENDIX B

FTIR-ATR ABSORPTION PEAK

B.1 FTIR-ATR absorption peak in each coupling reaction time



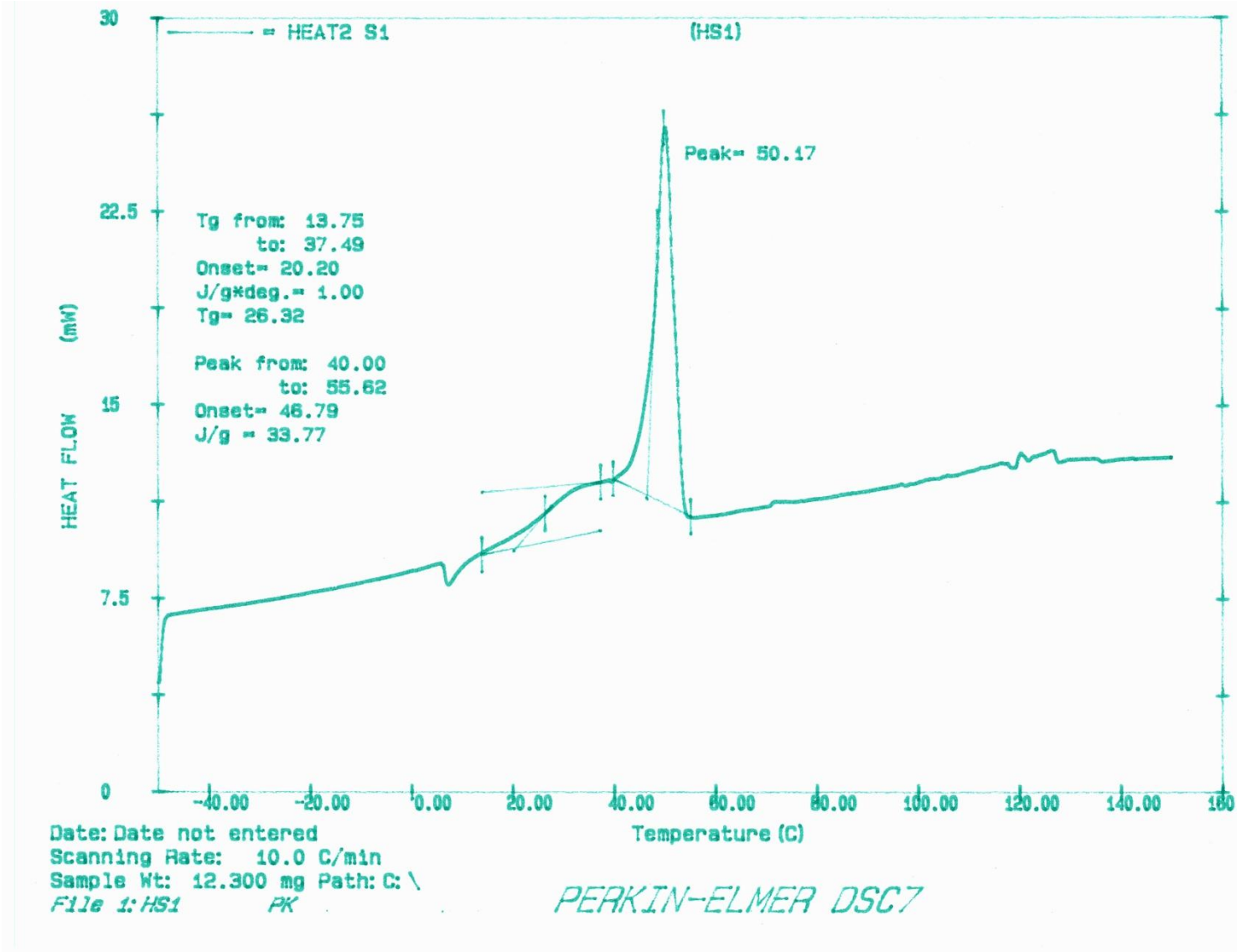
B.2 FTIR-ATR absorption peak in each coupling reaction time



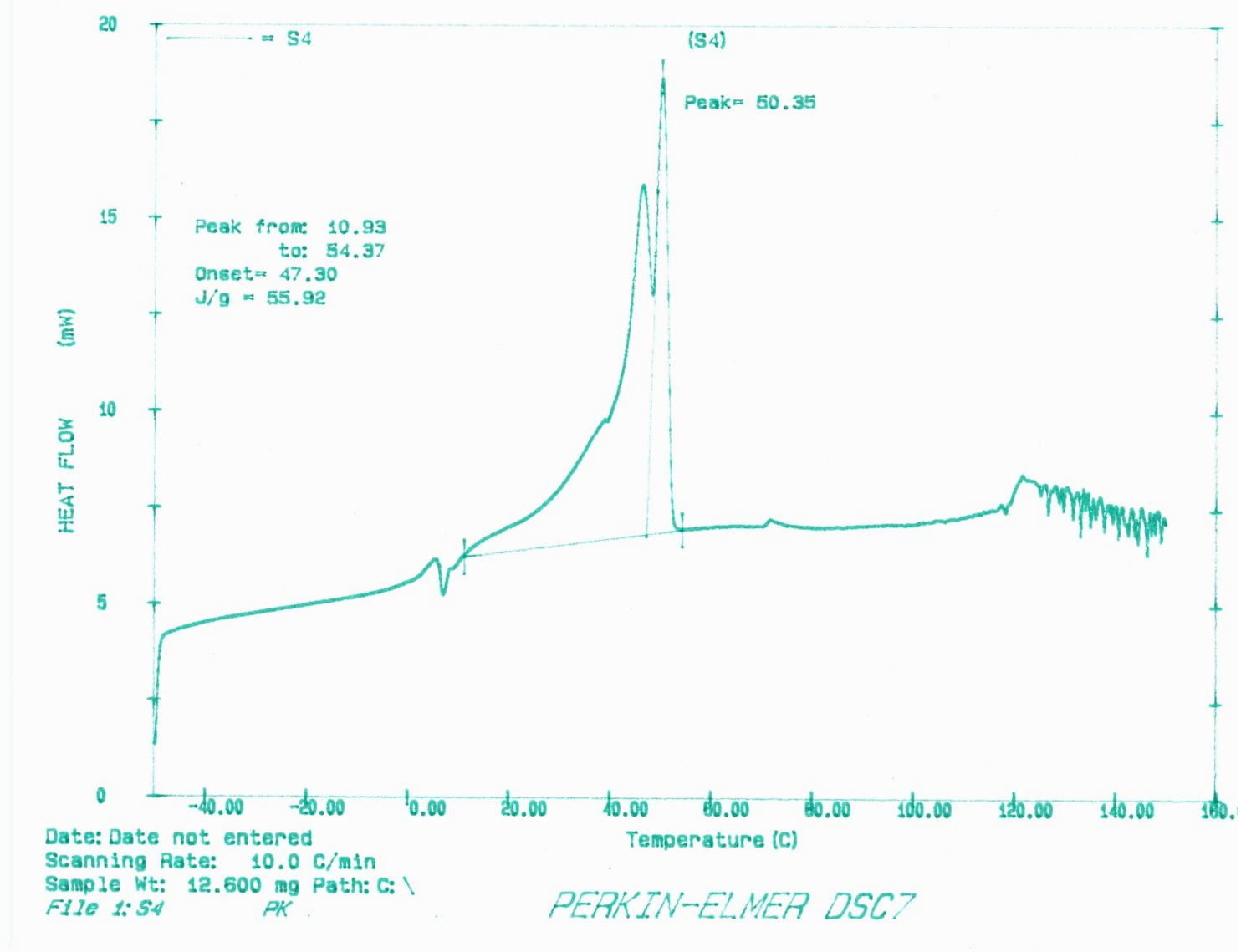
APPENDIX C

Differential Scanning Calorimetry Thermogram

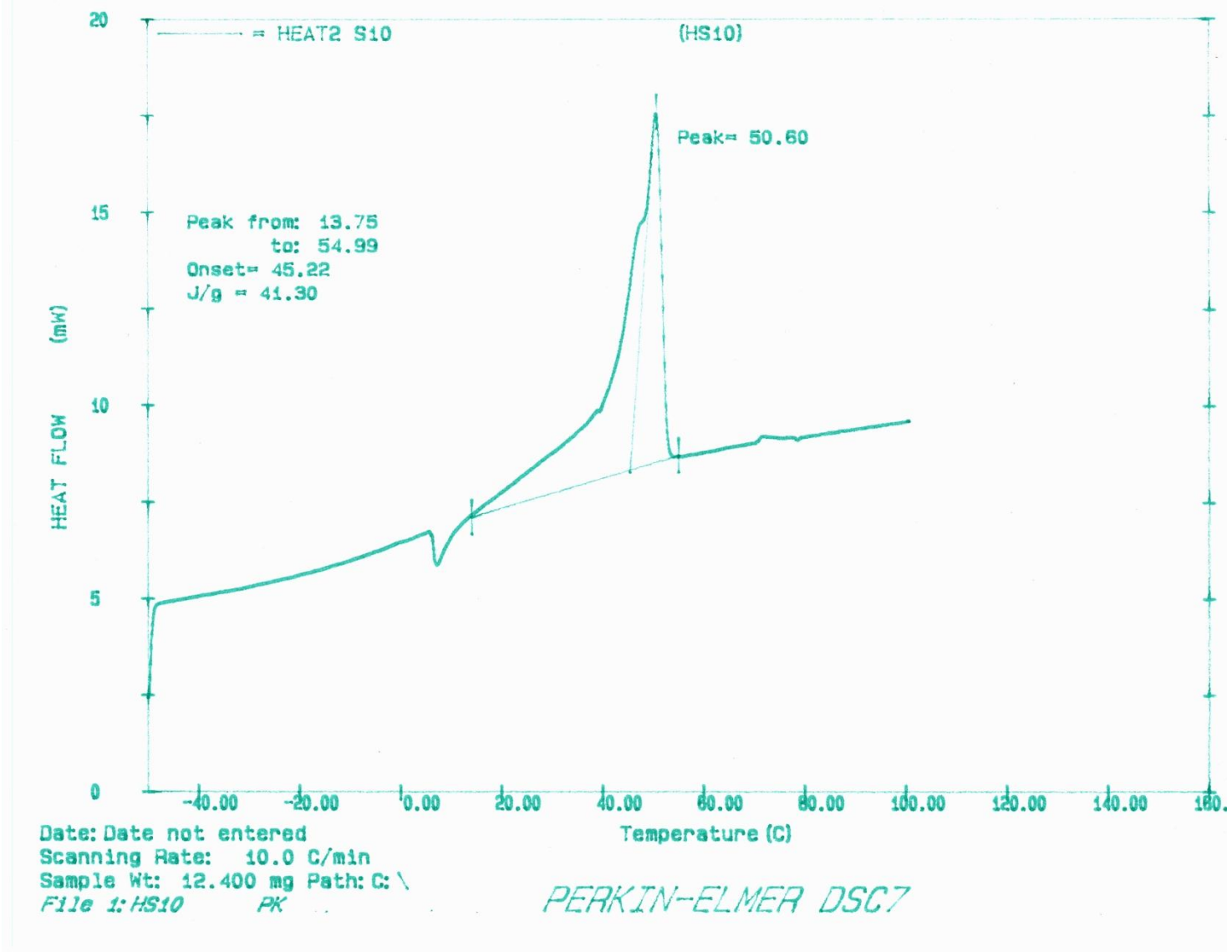
C.1 Differential Scanning Calorimetry thermogram of sample 1



C.2 Differential Scanning Calorimetry thermogram of sample 4



C.3 Differential Scanning Calorimetry thermogram of sample 10



APPENDIX D

Product Yield and Degree of Substitution Estimation

D.1 Calculated product yield ($Yield_{cal}$) estimation

Given: 100 % degree of substitution

Providing: product yield = weight of PVA + weight of SA

In case: degree of substitution = DS_{exp}

Providing: product yield = $\frac{\text{weight of PVA + weight of SA}}{100} \times DS_{exp}$

D.2 Calculated degree of substitution (DS_{cal}) estimation

Known: weight of PVA + weight of SA

Providing: degree of substitution = $DS_{th} = \frac{SA}{\text{PVA unit}}$

Known: weight of product

Providing: degree of substitution = $\frac{DS_{th} \times \text{weight of product}}{(\text{weight of PVA + weight of SA})}$

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