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A STUDY OF HYDROGENATION REACTION OF ISOPRENE-STYRENE BLOCK COPOLYMER

ORASA TAVICHAI

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Thesis
entitled

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for the degree of Master of Science (Polymer Science)
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Polymers with high degree of unsaturation are prone to be thermally and oxidatively unstable, especially when experiencing the melt-mixing process. Hydrogenation is one of the practical reactions used to change chemical structure in order to improve thermal properties. In this study, poly(isoprene-b-styrene) prepared by anionic polymerisation was hydrogenated by non-catalytic method using *p*-toluenesulphonyl hydrazide (TSH) as a hydrogen releasing agent. The block copolymers having various molecular weights and certain equal block composition (50:50) were synthesised in cyclohexane at 40°C using *n*-BuLi as an initiator. Characterisation of the product by ^{1}H-NMR showed that the ratio of cis-1,4, trans-1,4 and 3,4-polyisoprene obtained in polyisoprene block was 70.25.5. For the styrene block, it was likely to be atactic polystyrene because the single broad absorption band was observed in range of 1040-1100 cm^{-1}. Hydrogenation reaction of the block copolymer was carried out in xylene solution at 135°C using TSH The mole ratio of TSH to double bond was varied, i.e. 1:1, 2:1, 4:1, and 6.1 as a preliminary study. It was found that the mole ratio of 4:1 is the optimum ratio, giving rise to high percentage of hydrogenation and rather low content of TSH by-product. Percentage of hydrogenation was determined by three techniques, i.e. IR, ^{1}H-NMR, and Iodine Value Molecular weight and molecular weight distribution of hydrogenated products were measured using GPC. A slight decrease in molecular weight was found which could be due to degradation caused by the relatively high reaction temperature. From DSC measurement, T_g of the hydrogenated product was found to be increased about 10-20°C above that of the original block copolymers. The thermal stability of hydrogenated products was slightly improved as shown by TGA. It was also found that cis-trans-isomerisation took place during the hydrogenation process By-product obtained from dissociation of TSH was also investigated. Purification of hydrogenated products was also carried out.

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อรสา ต๊ะวิชัย . การศึกษาปฏิกิริยาไฮโดรจิเนชันของไอโซปรีน-สไตรีนบล็อกโคพอลิเมอร์ (A STUDY OF HYDROGENATION REACTION OF ISOPRENE-STYRENE BLOCK COPOLYMER) คณะกรรมการควบคุมวิทยานิพนธ์ ปราณี ภิญโญชีพ, Doctorat de l' Universite' du Maine, เสาวรภย์ ลิ้มเจริญ, Dr.rer nat , ชาคริต สิริสิงห, Ph.D 141 หน้า
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พอลิเมอร์ที่มีความไม่อิ่มตัวสูงมักไม่เสถียรต่อความร้อนและเกิดปฏิกิริยากับออกซิเจนได้โดยเฉพาะอย่างยิ่งในระหว่างทำการผสมที่สภาวะหลอมเหลว ปฏิกิริยาไฮโดรจิเนชันเป็นวิธีที่ง่ายในการเปลี่ยนโครงสร้างทางเคมีเพื่อปรับปรุงสมบัติทางความร้อน ในการศึกษานี้นำไอโซปรีน-สไตรีนบล็อกโคพอลิเมอร์ที่เตรียมจากวิธีแอนไอออนิกพอลิเมอไรเซชันมาทำการเติมไฮโดรเจนโดยวิธีไม่ใช้ตัวเร่งซึ่งจะใช้ *p*-tolunesulphonyl hydrazide (TSH) เป็นตัวให้ไฮโดรเจน ได้ทำการสังเคราะห์บล็อกโคพอลิเมอร์ที่มีน้ำหนักโมเลกุลต่างๆกันโดยควบคุมส่วนประกอบของบล็อกให้เท่ากับ 50:50 ขึ้นก่อน โดยใช้นอร์มัลบิวทิลลิเธียมเป็นตัวเริ่มปฏิกิริยาในไซโคลเฮกเซนที่ 40°C การวิเคราะห์ผลโดย ^{1}H-NMR พบ cis-1,4, trans-1,4 และ 3,4-พอลิไอโซปรีน เป็นสัดส่วนประมาณ 70:25:5 ในพอลิสไตรีนบล็อกอาจกล่าวได้ว่ามีโครงสร้างเป็น atactic เนื่องจากพบสัญญาณการดูดกลืนแสงอินฟราเรดที่กว้างเพียงหนึ่งสัญญาณในช่วง 1040-1100 cm^{-1} จากนั้นทำปฏิกิริยาการเติมไฮโดรเจนแก่บล็อกโคพอลิเมอร์โดยใช้ TSH ในไซลีนที่ 135°C ในการศึกษาเริ่มแรกใช้สัดส่วนโดยโมลของสารให้ไฮโดรเจนต่อปริมาณพันธะคู่เป็น 1:1, 2:1, 4:1 และ 6:1 พบว่าสัดส่วนโดยโมลเท่ากับ 4:1 เป็นสัดส่วนที่เหมาะสมซึ่งให้เปอร์เซ็นต์การเติมไฮโดรเจนสูงและให้ผลพลอยได้ที่เป็นสารเจือปนไม่มาก การตรวจสอบเปอร์เซ็นต์การเติมไฮโดรเจนใช้เทคนิค IR, ^{1}H-NMR และ Iodine Value วัดน้ำหนักโมเลกุลและการกระจายตัวของน้ำหนักโมเลกุลใช้เทคนิค GPC พบว่าน้ำหนักโมเลกุลลดลงเพียงเล็กน้อย ซึ่งอาจเนื่องมาจากอุณหภูมิที่ใช้ในปฏิกิริยาค่อนข้างสูง ศึกษาสมบัติทางความร้อนโดยใช้เทคนิค DSC และ TGA พบว่า T_g ของพอลิเมอร์ที่เติมไฮโดรเจนแล้วมีค่าสูงขึ้น 10-20 °C และมีความเสถียรต่อความร้อนมากขึ้น นอกจากนี้ยังพบการเกิด cis-trans isomerisation ในขณะทำปฏิกิริยาการเติมไฮโดรเจน ได้ศึกษาผลพลอยได้จากการแตกตัวของ TSH และทำพอลิเมอร์ที่เติมไฮโดรเจนแล้วให้บริสุทธิ์ด้วย

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LIST OF ABBREVIATIONS

PI	=	Polyisoprene
PS	=	Polystyrene
PB	=	Polybutadiene
IS	=	Isoprene-styrene block copolymer
I	=	Isoprene composition
S	=	Styrene composition
MIS	=	Mixed isoprene-styrene block copolymer
HMIS	=	Hydrogenated mixed isoprene-styrene block copolymer
HPI	=	Hydrogenated polyisoprene
TSH	=	*p*-Toluenesulphonyl hydrazide
db	=	Double bond
%H	=	% Hydrogenation
DSC	=	Differential Scanning Calorimetry
TGA	=	Thermogravimetric Analysis
FT-IR	=	Fourier Transform Infrared Spectroscopy
GPC	=	Gel Permeation Chromatography
NMR	=	Nuclear Magnetic Resonance Spectroscopy
MW	=	Molecular weight
MWD	=	Molecular weight distribution
$\overline{M}_n$	=	Number-average molecular weight
$\overline{M}_w$	=	Weight-average molecular weight

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CHAPTER I

INTRODUCTION

1.1 General Introduction

It has been realised that new molecules are not always required to meet needs for new materials but blending can usually be implemented more rapidly and economically than the development of new chemistry. Mixing of polymers to obtain a fine level is seldom easy. Polymer blends are always thermodynamically immiscible, separate into two or more phases, and give poor practical properties. It is assumed that either the particle size of the dispersed domains is not optimum or the immiscibility of the two phases produces weak interfaces between them, which fail too easily under stress The most popular way of trying to solve these problems is the addition of a third component; if this succeeds, the added ingredient is called a "compatibiliser".

Block copolymers, the prevalent compatibilisers, are unique in that two (or more) homopolymers, which are thermodynamically incompatible, are chemically bonded to each other thus limiting the amount of phase separation that may be occurred in mixtures of homopolymers. Their properties as "surfactants" which can assist the dispersion of polymer blends have been recognised and widely utilised(1)

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The general fashion to select block copolymer to be a compatibiliser is not surprising that block copolymer containing blocks or segments chemically identical to the blend components is the obvious choice. Copolymer structure and molecular weight have paramount influences on the effectiveness as compatibilisers

In the study of PE/PS blends, Fayt.et al.(2) concluded that block copolymers were more effective than graft copolymers, diblock copolymers were more effective than triblock or star-shaped copolymers, and tapered diblock copolymers were more effective than pure diblock copolymers

To obtain block copolymers, anionic polymerisation, a process which can control copolymer architecture, is required. By this method, segments with different properties can be united into one chain, e.g. polar and non-polar segments, crystalline and amorphous units, segments with widely different glass transition temperature (T_g), blocks possessing different conformations (random coil and rod-like), elastomeric and non-elastomeric units, or hydrophilic and hydrophobic blocks(3) For an example, block copolymer containing different segment characteristic, styrene-isoprene block copolymer (SI) whose one block is hard segment of polystyrene (PS) , the other shows rubbery characteristic of polyisoprene (PI) is of interest. Won Ho Jo et.al.(4) studied compatibilisation of SI in PS/PI blends. It was found that SI can reduce interfacial tension of the blends.

Furthermore, chemical modification is considered to be an effortless way to alter and optimise the physical and mechanical properties of polymers The chemical modification is a post polymerisation process producing polymers with desirable physical and chemical properties that are not accessible by standard polymerisation

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techniques. Chemical modifications on unsaturated polymers are of particular interest, for instance, grafting , crosslinking , oxidation , epoxidation and hydrogenation have been successfully carried out, because of the reactivity to perform reaction of the double bond.

Hydrogenation is one of the modifications of diene polymers to which scientists considerably paid attention because of its beneficial products Hydrogenated nitrile rubber (HNBR) was used as an oil resistant polymer possessing ozone , oxygen and chemical resistance at high temperature(5). Hydrogenated styrene butadiene rubber (HSBR) was used as an elastomer with improved thermal properties Mousumi et.al.(6) studied hydrogenation of SBR by diimide reduction in the latex phase. They also found that the glass transition temperature (T_g)of hydrogenated product is increased. Many compatibilisers and impact modifiers are prepared by anionic polymerisation and then chemically modified such as styrene-ethylene-butylene-styrene (SEBS) and ethylene-propylene copolymer (EPR) which are the products of hydrogenation of styrene-butadiene-styrene (SBS) and polyisoprene (PI) , respectively. Plawky et al (7) used SEBS as impact modifiers in PP/PE blends and Laosee(8) investigated the effect of compatibilisers on mechanical properties and morphology of PP/scrap dust rubber blends using SEBS as a compatibiliser.

Styrene-isoprene block copolymer (SI) can prepared by anionic polymerisation at rather milder condition than SEBS, SBS or EP copolymers. In addition, the chemical modification by hydrogenation on the unsaturation moieties will result in one of promising block copolymers that can be employed as an effective

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compatibiliser for polymer blends. Therefore, the preparation of the SI and its hydrogenation reaction at various molecular level are of our interest as well as its characterisation including the determination of hydrogenation level.

1.2 Block Copolymer by Anionic Polymerisation

1.2.1 Anionic Polymerisation

Polymer of uniform chain length and predictable molecular weight are merely produced by the anionic polymerisation. The virtual absence of a termination step in polymerisations initiated by organoalkali compounds gives the useful features. This system is attractive because it is homogeneous, "living" (i.e. without termination and transfer reaction) although handling of these extremely reactive organometallic initiators is difficult and, to obtain reproducible results, one must eliminate almost all traces of impurities such as water, oxygen, acetylene, etc., in the monomer and solvent. Under a proper condition, the termination free process makes feasible for obtaining the narrow molecular weight distribution (Poisson distribution) as forecast by Flory, the formation of linear block polymers containing segments of controlled molecular weight by sequential addition of various monomers, and the reactive end groups which were introduced onto the polymer chain by permitting the polymer-carbanion to react with certain reagents(3).

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The mechanisms of anionic polymerisation are composed of initiation and propagation steps, and it has been recognised that termination and transfer reactions

may not contribute significantly. For butyllithium-initiated polymerisation, the following mechanism was proposed(9)

Initiation: $BuLi + M \longrightarrow BuMLi$

Propagation: $BuMLi + M \longrightarrow BuM_2Li$

$BuM_2Li + M \longrightarrow BuM_3Li$

$BuM_nLi + M \longrightarrow BuM_{n+1}Li$

Polymerisations initiated by alkyl lithiums consist of two major steps, initiation and propagation. The former deals with the addition of a monomer to an alkyl lithium compound such as butyl lithium. The propagation reaction is the growth step which deals with the addition of a monomer to the active polymer chain. During transferless polymerisation, the number of polymer molecules remains constant Since there is no termination, active anionic chain ends are remaining after all momomers have been polymerised. When fresh monomer is added, polymerisation resumes. The name "living polymerisation" was coined by Szwarc because the chain ends remain active until killed. Flory noted that since all of the chain ends grew at the same rate, the molecular weight can be determined by the amount of initiator used versus that of monomer(10).

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$$\overline{M}_n = \frac{\text{gram of monomer}}{\text{mole of initiator}} \quad (1)$$

The key monomer classes that yield to anionic living polymerisation techniques are styrenes, butadienes, methacrylates, acrylates, ethylene oxide, hexa methylcyclotrisiloxane, and lactones. Table1 1, 1 2 and 1.3 show types of monomer, initiator and solvent capable of undergoing anionic polymerisation(11) , respectively.

Table 1.1 Monomers which can be polymerised anionically

Types of monomers	Examples
I) Vinylic and acrylic monomers	- Styrene , α-methylstyrene and electron donating substituted styrenes - Diene (butadiene, isoprene, piperylene, phenylbutadiene , etc.) - Vinylnaphthalene - Vinylpyridine - Alkyl methacrylate - Acrylonitrile and methacrylonitrile
II) Heterocyclic monomers	- Oxirane (ethylene oxide) - Propylene oxide - Isobutylene oxide - Thiirane and substituted thiiranes - Caprolactone

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Table 1.2 Initiators of anionic polymerisation

Types of initiators	Examples
I) Metal organic initiators	- Butyl lithium
	- Fluorenyl-Na
	- Diphenylmethyl-Na
	- Benzyl-Na
	- Cumyl-Na
II) Radical-ionic initiators	- Naphthalene-Na

Table 1.3 Aprotic solvents which can be used in anionic polymerisation process

Types	Examples
- Alkane	- Pentane , hexane , heptane , cyclohexane
- Aromatic	- Benzene , toluene
- Dioxane	
- Oxolane (or THF)	
- Dimethylformamide (DMF)	
- Hexamethylphosphoramide (HMPA)	

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1.2.2 Isoprene-Styrene Block Copolymerisation

Barring premature termination of the active centers, anionic polymerisation can again ensue when the supply of monomer is replenished. If the monomer used in the second addition differs from that polymerised first, a block polymer will be formed. In view of the "living" nature of organolithium polymerisation, it is also possible to synthesis block polymers in which the sequence and length of the blocks are controlled by incremental(or sequential) addition of monomers

Diene-styrene two-phase systems with two distinct glass transition temperatures have received the most attention in recent year(11) They possess unique and novel properties for industrial applications. Their potential has been realised in thermoplastic elastomers where the block copolymer is the principal constituent of the material and in applications where the block copolymer acts as a useful additive, e.g., surfactant and viscosity improver(12). Isoprene-styrene block copolymer (IS) , initiated by buthyl lithium as mention here , also touch the interest of many workers Hsieh et.al(13) studied anionic polymerisation of polydienes and diene-styrene copolymers, using organolithium as initiators in various solvents They summarised that stereochemistry of polybutadiene is sensitive to initiator structures and types of solvent whereas the monomer concentration and conversion have no effect on polymer microstructure. Corbin et al.(14) also prepared multiblock copolymer of styrene and isoprene by interupting styrene polymerisation by step additions of isoprene.

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Kinetic of isoprene-styrene in hydrocarbon solvent has also been studied by Hsieh(9). In the copolymerisation of butadiene or isoprene and styrene, the reactivity ratios are influenced by the type of solvent used . Worsfold(15) studied the isoprene-styrene system in cyclohexane It was shown that $k_{si} > k_{ss} > k_{ii} > k_{is}$, which adequately explains the peculiar behavior of isoprene-styrene system.

$$S^- + S \xrightarrow{k_{ss}} S^-$$

$$S^- + I \xrightarrow{k_{si}} I^-$$

$$I^- + I \xrightarrow{k_{ii}} I^-$$

$$I^- + S \xrightarrow{k_{is}} S^-$$

where S^- and I^- are active polymer chains having styryl lithium and isoprenyl lithium units, respectively, the cross-propagation rate of styryl anion to isoprene monomer, k_{si} is much more rapid than the homopolymerisation rate of styrene, k_{ss}, whereas the opposite is true for the cross-propagation rate of isoprenyl anion to styrene monomer, k_{is}, which is slower than the homopolymerisation rate of isoprene, k_{ii}.

The successful synthesis of block copolymers from styrene and the dienes will be influenced by the following considerations · firstly, influence of solvent on the chain microstructures of the polydienes, secondly, effect of initiator and solvent on the initiation and propagation rates, finally, effect of the solvent on the copolymerisation behavior of styrene and dienes .

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1.2.2.1 Initiation by Alkyl Lithium

The reactivity of metal organic compound as a nucleophile relies on the substituents carried by the carbanionic site (nature, number), on its solubility in the solvent chosen, and on its ability to dissociate into free ions, far more reactive than ion pairs in many cases. Alkyl lithiums are very reactive and versatile reagents They almost spontaneously react with oxygen, carbon dioxide, water, alcohols, ketones, ethers, and so forth, e.g.,(16)

$$RLi + O_2 \longrightarrow ROOLi \longrightarrow 2ROLi,$$

$$RLi + CO_2 \longrightarrow RC(O)OLi,$$

$$RLi + H_2O \longrightarrow RH + LiOH,$$

$$RLi + EtOEt \longrightarrow RH + C_2H_4 + EtOLi.$$

Not astonishingly, alkyl lithiums easily add to C=C bonds, particularly those of styrene , the dienes, and their derivatives, and initiate their anionic polymerisation

$$RLi + \diagup C{=}C \diagdown \longrightarrow R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Li \quad (\text{or } R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}^{-}, Li^{+})$$

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Such an addition is slow compared to the rates of reaction of alkyl lithium with O_2, moisture, and CO_2, hence the monomers and solvents have to be purged even

from traces of these compounds when alkyl lithium are used as initiators. Alkyl lithiums such as methyl lithium and the isomeric butyl lithium are covalent compounds which form rather stable aggregates in which carbon-lithium bond order is maximised by the utilisation of all valence orbitals of lithium(9). The tetrameric and hexameric forms are prefered in most cases. The reactivity of aggregates, not including possible steric effects, would be expected to increase in the order tetramer< dimer< monomer. Many factors such as a change in organic moiety, the solvent, or the concentration range may radically affect the bonding and the reactivity of the lithium species .

Hsieh(9) has shown that the order of reactivity of RLi is slightly different for dienes, where the order is *sec*-BuLi> *i*-PrLi> *t*-BuLi> *i*-BuLi> *n*-BuLi , than for styrene where *sec*-BuLi> *i*-PrLi> *i*-BuLi> *n*-BuLi> *t*-BuLi , both series having been determined from maximum rate data in cyclohexane.

Solvents also affect initiation reaction. The polymerisation initiated by *n*-BuLi proceeded in benzene without induction period. The monomer consumption is the fastest at the onset of the reaction as shown by curve A Figure1.1 It implies that initiating agent is available from the start of the reaction and is replenished faster than consumed by initiation. The initiation is drastically different in aliphatic hydrocarbon, cyclohexane in this case. The S-shaped curve B of Figure1.1 depicts the consumption of styrene. The process started with a substantial induction period and accelerated remarkably as the reaction proceeded. The concentration of the initiating species was low at the onset of polymerisation and the rate of their formation was slower than that of consumption by monomer. This may be the result of a direct slow bimolecular

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reaction of the RLi aggregates with the monomer, or it may reflect the very slow rate of dissociation of the aggregates yielding the initiating fragments . However, the rate of formation of the active species undergoes and autocatalytic acceleration after the polymerisation ensued.

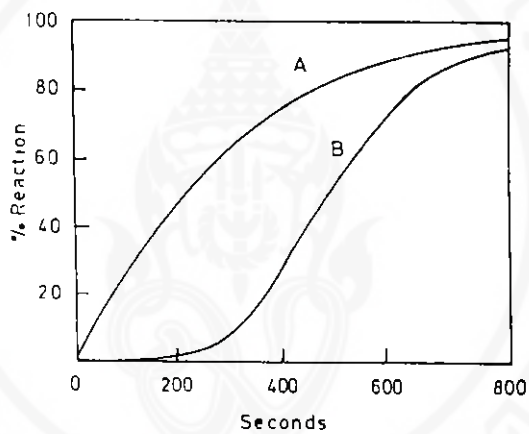

Figure 1.1 Typical plot of styrene consumption vs time in polymerisation initiated by *sec*-BuLi. Curve A in benzene, $[sec\text{-BuLi}]_0 = 1.1\times10^{-3}$ M, $[\text{styrene}]_0 = 5.3\times10^{-2}$ M, T = 30°C. Curve B : in cyclohexane, $[sec\text{-BuLi}]_0 = 1.3\times10^{-3}$ M, [styrene] = 8.7×10^{-2}M , T = 40°C. Note: the instantaneous (no induction period) initiation in benzene and the induction period in cyclohexane(9).

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1.2.2.2 Propagation of Polydienes and Propagation of Polystyrene

The association phenomenon plays a key role in all organo lithium reactions performed in hydrocarbon solvents. To clarify the kinetic of lithium polystyrene propagation proceeding in these solvents, one has to study the polymerisation after complete depletion of the initiator. Otherwise the formation of various mixed alkyl lithium-lithium polystyrene aggregated will distort the kinetic of propagation The propagation was found to be first order in monomer but $\frac{1}{2}$ order in the growing polymers. It appeared that lithium polystyrene in hydrocarbon solvents existed in the form of inactive dormant dimers in equilibrium with a minute amount of the active unassociated polymers(16).

The aggregation of lithium polybutadiene or polyisoprene in hydrocarbon solvents is higher than that of lithium polystyrene. The kinetic of their propagation suggested the tetrameric nature of their aggregates which were in equilibrium with a minute portion of the active monomeric polymers(16)

The measurement of propagation kinetics has shown that the reaction is first order in original monomer concentration. This relationship was true for butadiene, isoprene and styrene in solvent such as heptane, cyclohexane, benzene and toluene Figure1.2 illustrates the first order relationship in cyclohexane. The order of rate of propagation for three monomers was found to be styrene> isoprene> butadiene, and for three solvents toluene> cyclohexane> hexane(9)

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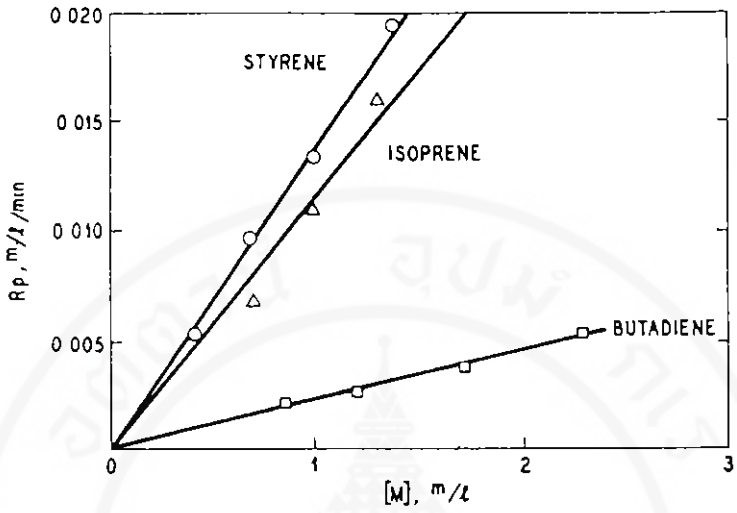

Figure 1.2 Rate of propagation (R_p) in cyclohexane at 30°C as a function of concentration [M](9)

1.2.2.3 Factors Affecting Molecular Structure of Diene

I) Effect of Initiator

In the consideration of organometallic initiators, type of counter ions affects molecular structure obtained. Large counter ions tend to be more effective in stabilisation of living polymer system than small counter ions(10). The microstructures of polybutadiene and polyisoprene produced under different conditions are revealed in Table 1.4 (11)

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Table 1.4 Homogeneous anionic polymerisation of isoprene and butadiene

Isoprene

Counter ion	Solvent	Mole % of units inserted			
		1,4-cis	1,4-trans	1,2	3,4
Li^+	Pentane	~94	-	-	~6
	Pentane/THF(90.10)	~0	~25	~10	~65
	THF	-	-	~25	~15
	Diethyl ether	-	~50	~5	~45
Na^+	Pentane	small	~40	~7	~50
K^+	Pentane	small	~55	~7	~35

Butadiene

Counter ion	Solvent	Mole % of units inserted		
		1,4-cis	1,4-trans	1,2
Li^+	Pentane	~35	~50	~15
	THF	~0	~5	~95
Na^+	Pentane	~7	~25	~67
K^+	Pentane	~12	~38	~50

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It was shown that to obtain polydiene with highest elastomeric properties, the lithium-initiated system in a hydrocarbon solvent should be selected.

Lithium polydienes constitute aggregates in hydrocarbon solutions and only a minuscule fraction of the polymer, leaving in the monomeric form, partake in the propagation. To investigate the cis to trans ratio in the high molecular weight polymer created in hydrocarbon solvents, the following rate constant are essential(16)

— CIS, Li	+	M	⟶	— CIS•CIS, Li	k_1
— CIS, Li	+	M	⟶	— CIS•TRANS, Li	k_2
— TRANS, Li	+	M	⟶	— TRANS•CIS, Li	k_3
— TRANS, Li	+	M	⟶	— TRANS•TRANS, Li	k_4

where M = monomer

Experimental data pertaining to the isoprene polymerisation in the aliphatic hydrocarbons revealed that k_2 and k_4 were negligible compared with k_3, i.e , the addition of monomer to any active end group, whether cis or trans, preferentially yielded a cis end-group Moreover , k_1 is ~$8k_3$(16).

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II) Effect of Solvents

It was shown that solvents to be used in anionic polymerisation must meet the following requirements , they must be aprotic to prevent any transfer or deactivation reactions and they must be free from any electrophilic functions which may react with the carbanionic sites, e.g.nitro-, ester- or ketone-groups(11) Solvent also have a profound influence on the stereochemistry of polydiene when initiated with alkyl lithium. The chain microstructure of polydiene block is of paramount importance, since a high cis 1,4-polybutadiene or polyisoprene is high elasticity (low T_g); on the other hand, a high content of trans-1,4 or 1,2 or 3,4-structure results in poor rubbery properties

Kelly and Tobolsky(17) reported that polymerisation of isoprene in non-polar solvents, or weakly solvating solvents, result largely in cis-unsaturation (70-90 percent) whereas in polar solvents, highly solvating solvents such as ether and THF increase 1,2-polyisoprene , 3,4-polyisoprene and trans-1,4-polyisoprene Aromatic solvents such as toluene tend to increase 1,2 or 3,4 linkages

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1.3 Hydrogenation

Hydrogenation is a common chemical modification method used to change polymer properties into desirable physical and chemical properties. It has been the most widely used process to modify not only properties but also the structures of dienic base polymers since they have reactive groups which resemble that of polyalkenes To improve the photolytic, oxidative and thermal stability of these polymers, hydrogenation is one of the most efficient performances.

The earliest hydrogenation was employed by Okawara et.al.(18) who removed residual double bonds from polyvinyl chloride. Subsequently, hydrogenation of polydienes, both homopolymers and copolymers, has received much attention by many researchers

Hydrogenation of polymers can be attained by both catalytic and non-catalytic methods.

1.3.1 Catalytic Hydrogenation

Catalytic hydrogenation, a hydrogen transfer process, is the reaction of an unsaturated substrate with transition metal-activated hydrogen which is shown by the equation below .

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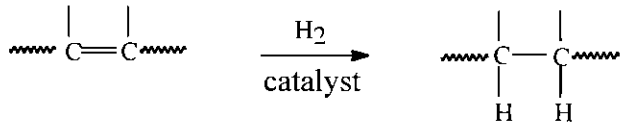

(2)

The classical and the most used hydrogenation catalysts are the noble metals Pt, Pd, Rh and Ru supported on active carbon, Raney nickel and some supported Ni and Cu catalysts(19) .

Catalytic hydrogenation is also divided into two types, homogeneous and heterogeneous hydrogenation, which depend on features of systems(19) Homogeneous hydrogenation employed a soluble transition metal complex whereas heterogeneous hydrogenation relied on an insoluble transition metal catalyst to contribute hydrogen addition to double bonds Catalytic hydrogenation of homopolymers and copolymers was investigated by many workers. Rachapudy et.al.(20) studied homogeneous catalytic (alkylated transition metal salts) hydrogenation compared with heterogeneous catalytic (nickel on kieselguhr , paladium on calcium carbonate) hydrogenation of anionically prepared polybutadiene They found that only the heterogeneous catalysts yield completely hydrogenation products. Gan et.al.(21) examined homogeneous hydrogenation of natural rubber using nickel 2-ethylhexanoate and triisobutylaluminum as catalysts. Moreover, Luo(22) also studied heterogeneous hydrogenation of 1,3-butadiene and isoprene prepolymers with palladium on carbonate as a catalyst. Homogeneous hydrogenation of poly [alkylmethacrylate(-b-styrene)-b-butadiene-b(styrene-b-) alkylmethacrylate] triblock and pentablock copolymers using triethyl aluminium/ cobalt 2-ethyl hexanoate complex as a catalyst was studied by Yu et.al(23) Hydrogenations of

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diene-styrene block copolymers were also studied Heterogeneous catalytic hydrogenation of styrene-isoprene diblock copolymer was performed using two palladium supported catalysts , Pd-$CaCO_3$ and Pd-$BaSO_4$, by Gehlsen and Bates(24) It was found that both styrene and isoprene part were hydrogenated to receive poly(vinyl cyclohexane) whose thermal properties were better than those of its unsaturated precursor In contrast, Velichkova et.al(25) prepared polystyrene-poly(ethylene propylene) block copolymers for being thermoplastic elastomers and viscosity index improvers by selective hydrogenation of styrene-isoprene block copolymers. Only dienic parts of copolymers were hydrogenated with homogeneous catalysts.

Both homogeneous and heterogeneous catalytic hydrogenations require special equipment It is sophisticated that the reactions concern pressure range, pressure control, temperature control and agitation. Additionally, various factors influence the catalytic hydrogenation process are the followings(20)

- types of catalyst which affected selectivity to give the desired products,
- activity of the catalyst (reaction time) and productivity,
- types of support which concerned with catalyst performance,
- solvents which influenced not only solubility of reactants and products but also activity and selectivity of catalysts

Because of specific instruments, severe conditions e.g. high pressure, high temperature which caused degradation and difficulty of removing residual catalysts, a moderate condition using reducing agents is prefered

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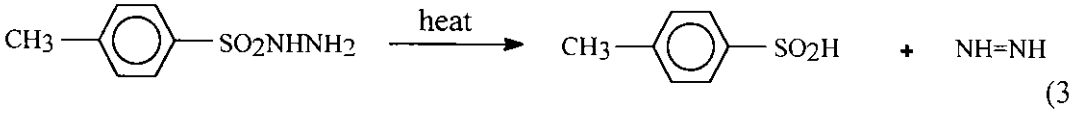
1.3.2 Non-catalytic Hydrogenation

It has been some 20 years ago that di-imide reduction of alkenes and alkynes has become established as an important organic reaction The diimide (HN=NH) can be produced by various ways(26) : 1) the carboxylation of the potassium azodicarboxylate, 2) the oxidation of hydrazine, 3) the thermal decomposition of arenesulphonyl hydrazides, 4) the decomposition of hydroxylamine-o-sulfonic acid or chloramine, 5) the thermal decomposition of anthracene-9,10-bisimine and 6) the photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione. Some examples of diimide producing agents are shown in Table 1.5

Because of its efficiency and instrumental simplicity, diimide reduction has become the most popular method of non catalytic hydrogenation of unsaturated polymers Compounds such as *p*-toluenesulphonyl hydrazide (TSH) decompose at moderate temperature (105 °C) to give diimide (N_2H_2) with proposed mechanism shown in equation 3(27).



(3)

Diimide reduction is unique in that the reaction is homogeneous, conducts at atmospheric pressure at moderate temperature and is highly specific with the hydrogen addition in a syn configuration . It was suggested by Hahn(28) that its

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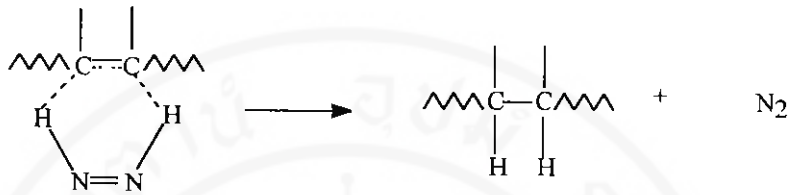
mechanism involved concerted hydrogen transfer from cis-diimide to alkenes as shown in equation 4.



(4)

Table 1.5 Some prevalent diimide releasing agents(29)

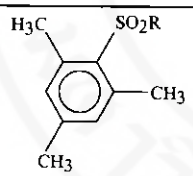
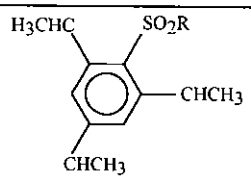
Structure	Nomenclature
	
a . R = $NHNH_2$	2,4,6-trimethylbenzenesulphonyl hydrazide
b · R = Cl	2,4,6-trimethylbenzenesulphonyl chloride
c . R = H	2,4,6-trimethylbenzenesulphinic acid
	
a . R = $NHNH_2$	2,4,6-tri-isopropylbenzenesulphonyl hydrazide
b R = Cl	2,4,6-tri-isopropylbenzenesulphonyl chloride
c R = H	2,4,6-tri-isopropylbenzenesulphinic acid

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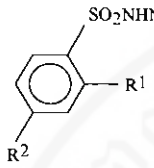
Table 1.5 Some prevalent diimide releasing agents (cont.)

Structure	Nomenclature
$K^+O_2^-C\text{-}N{=}N\text{-}CO_2^-K^+$	potassium azodicarboxylate
	
a $R^1 = R^2 = H$	benzenesulphonyl hydrazide
b $R^1 = H$, $R^2 = Me$	*p*-toluenesulphonyl hydrazide
c $R^1 = NO_2$, $R^2 = H$	*o*-nitro-benzenesulphonyl hydrazide
d $R^1 = R^2 = NO_2$	2,4-dinitro-benzenesulphonyl hydrazide

Harwood et.al.(30) had studied hydrogenation of unsaturated polymers i.e.polybutadiene and polyisoprene by diimide reduction. They found that *p*-toluenesulphonyl hydrazide (TSH) is a reasonably efficient (about 40%) reducing agent when the concentration of unsaturated units is high and the complete reduction obtained only when about five moles of hydrazide per mole of butadiene or isoprene units are employed Their results that the diimide reduction of cis -1,4-polyisoprene is not as efficient as that of cis-1,4-polybutadiene also confirm the mechanism of syn addition of diimide on olefinic unit and the less steric hindrance molecule favor the reaction. There have been several studies of non-catalytic hydrogenation of polybutadiene on various aspects. For example , Edwards et. al.(31) studied diimide hydrogenation of butadiene by using NMR measurements to identify the

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incorporation of an aromatic impurity in the polymer which results from a side reaction during hydrogenation reaction while Poshyachinda(32) had shown some evidence of cis-trans isomerisation of the diimide hydrogenation of cis-polybutadiene by FT-Raman spectroscopic method. Nang et.al.(18) studied the reaction of cis-1,4-polyisoprene with TSH. They found that the rate of hydrogenation was increased with increase in concentration of polyisoprene and of TSH. In addition the reaction caused depolymerisation and cyclisation.

The rate of hydrogenation also depended on the microstructure of polymer, as Mango and Lenz(33) reported in the study of hydrogenation of polyisoprene with different microstructures. It was found that vinyl segment were hydrogenated at a greater rate than either the cis or trans-1,4-units ($k_{vinyl} > k_{cis} \approx k_{trans}$). Poshyachinda and Kanithanon(32) reported that the rate of addition of hydrogens to the butadiene sites in the cis configuration was likely to be faster than that of the trans unit because of having steric only on one side . Several authors reported the use of TSH as reducing agent for copolymers of polybutadiene and polystyrene or polyisoprene and polystyrene which will be mentioned in the next section

1.3.3 Hydrogenation of Isoprene-Styrene Block Copolymer by Diimide Reduction

Hydrogenations of copolymer, especially block copolymer, interest many of the reseachers because of their unparalleled behaviors Diene-styrene block copolymer is one of the most distinctive block copolymers investigated in

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hydrogenation field. The hydrogenated products of styrene butadiene elastomer , styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) triblock copolymers as thermoplastic elastomer with good thermal and oxidative stability were reported(34). Hydrogenation of Styrene-Butadiene-Styrene block copolymer and Styrene-Butadiene random copolymer by TSH were studied by Mango and Lenz(33).

Hahn(28) investigated hydrogenation of poly(styrene-b-butadiene-b-styrene) (SBS) and poly(styrene-b-isoprene-b-styrene) (SIS) with diimide generated by thermal decomposition of TSH. It was found that butadiene and isoprene blocks were hydrogenated while styrene blocks were not affected during this reaction. Additionally, hydrogenation of styrene-isoprene diblock copolymer using TSH was studied by Podesva et.al.(35)

The mole ratio of TSH to double bond of polybutadiene and polyisoprene was claimed by Hahn that at the mole ratio of 2.1, the former was complete hydrogenation and the latter gave partially hydrogenated product because of steric effect The larger amount of TSH was suggested to fulfill complete hydrogenation of polyisoprene because only syn form of diimide effected the hydrogenation of alkenes and it was so reactive that it can disproportionate to give hydrogen and hydrazine or react with oxygen to give water and nitrogen. Moreover, it was mentioned that the mole ratio of 4:1 give rise to a complete hydrogenation of synthetic cis-1,4-polyisoprene(36). The effective hydrogenation was performed under the condition of no more than 2% w/v polymer concentration .

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1.3.4 Secondary Reactions of Hydrogenation Using TSH

Many literatures reported that various side reactions occured together with diimide hydrogenation including cis-trans isomerisation , incorporation of by-products, cyclisation and degradation. It was evident that cis-trans isomerisation appeared in partially hydrogenated dienic polymers during hydrogenation . In hydrogenation of cis-polybutadiene using TSH, even for an addition of the small amount of TSH, the change of some of the cis units in the backbone into the trans configurations was conceived by raman spectroscopy(37)

The incorporation of by-products, TSH-decomposed products, to the olefinic sites was determined by various method. The presence of sulfone functionallity was indicated by the strong IR bands at 1318 and 1148 cm^{-1}(SO_2 asymmetric and symmetric stretching, respectively) and bands at 812 and 1020 cm^{-1} due to the *p*-tolyl aromatic ring(28). From raman scattering, the bands at 1331 and 1152 cm^{-1} were depicted to asymmetric and symmetric -C-SO_2-C- vibration, respectively(31) and a band near 1600 cm^{-1} was claimed for benzene ring of TSH by-products(32). According to ^{1}H-NMR spectra, resonances due to the *p*-tolylsubstituent are obviously exibited at 2.4 ppm. for the para methyl and 7.7 ppm. for the aryl ring protons(28,31) It was claimed by Hahn(28) that addition of tripropylamine (TPA) equimolar to TSH can reduce this side reaction.

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Table 1.6 Vibration wave numbers and assignment of the impurity incorporation during the hydrogenation(29)

Approximate description of band assignments	Wave number observed (cm^{-1})	
	Infrared	Raman
ν(CH)	3075	3062
ν(CC) aromatic ring stretching	1597	1600
	1576	1580
	1490	1500
	1436	1450
		1000
ν_a((C-)SO_2(-C))		1331
ν_s((C-)SO_2(-C))	1314	
δ(C-H) in plane	1147	1152
$\nu_{(s)}$((C-)SO_2(-C))	1088	1090
ρ(C-H) rocking	1060	1040
	814	815

The changes in molecular weight and molecular weight distribution during hydrogenation designated the degradation of polymers which were detected by GPC . Hahn(28) reported that chromatograms of hydrogenated SBS showed no change in MWD compared to that of the starting polymer whereas there are changes in hydrogenated products of SIS. It is unclear whether these changes are due to thermal or catalytic degradation by acid by-products.

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Moreover, cyclisation is also the side reaction of this type of hydrogenation described by Nang(18). The slight shifts of the CH_3 deformation vibration at 1450 cm^{-1} of the hydrogenated polymer were recorded as the occurrence of cyclisation.

1.4 Scope of the Thesis

The inspiration of this work is originated from the interesting characteristics of block copolymers which are potential to be good compatibilisers in polymer blends In the case that block copolymers possess unsaturated parts which are vulnerable to heat, there should be the problems of block copolymer lost or their properties damaged when melt mixing. The object of this work is to improve the thermal properties of block copolymer via hydrogenation

The thesis focused on the diimide hydrogenation of isoprene-styrene block copolymer (IS) prepared by anionic polymerisation. The work can be grouped into three parts In the first part, anionic polymerisation was studied in term of $\overline{M}_n$ controlling. IS of various $\overline{M}_n$ (2000, 2500, 4000, 5000 and 8000) were prepared with a specified block composition of isoprene:styrene of 50:50 For the second part, diimide hydrogenation of IS using TSH was studied to find out the following factors affecting the reaction These included the mole ratio of TSH to double bond in isoprene unit which gave the optimum hydrogenation Side reactions and suitable methods for purification of product were also investigated The last part is the characterisation of original block copolymer compared with the hydrogenated polymers in the following aspects, T_g and thermal stability, chemical structure, molecular weight and molecular weight distribution.

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CHAPTER II

EXPERIMENTAL

2.1 Materials

Table 2.1 Information of materials used in this study

Materials	Grade	Supplier
Isoprene	Purum	Fluka
Styrene	Purum	Fluka
n-BuLi	Commercial	Fluka
2,5-Dimethoxybenzyl alcohol	Purum	Fluka
Calcium hydride	Practical	Fluka
Sodium sulfate anhydrous	Practical	Fluka
p-Toluenesulphonyl hydrazide	Purum	Fluka
Iodine monochloride	Zur synthese	Merck
Iodine resublimed	Analytical	BDH
Sodium thiosulphate-5-hydrate	Analytical	Merck
Potassium iodate	Purum	Fluka
Potassium iodide	Analytical	JT Baker
Soluble starch	G R	Merck

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Table 2.1 Information of materials used in this study (cont.)

Materials	Grade	Supplier
Sodium hydroxide	Purum	EKA
Cyclohexane	Analytical	JT.Baker
Tetrahydrofuran	Analytical	JT Baker
Hexane	Commercial	Fluka
Chloroform	Analytical	JT.Baker
Deuterated Chloroform	Purum	Fluka
Glacial acetic acid	Analytical	JT Baker
Sulfuric acid	Analytical	JT Baker

2.2 Instrumentations

1) IR spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrometer.

2) ^{1}H-NMR and ^{13}C-NMR spectroscopy were performed by a Bruker DPX-300 NMR spectrometer (300 MHz).

3) Raman Spectra were carried out on a Perkin Elmer System 2000 FT-Raman spectrometer using Nd-YAG (a Yittrium Aluminium Garnet crystal doped with triply ionised Neodynium) laser source and InGaAs (Indium Gallium Arsenide) detector.

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4) Averaged molecular weight and molecular weight distribution was determined by a Waters 150-CV Gel Permeation Chromatography (GPC) equipped with two 10 μm mixed-bed styragels (HT3 and HT4 which have the effective molecular weight range from 500 to 600,000 daltons), using refractometer and viscometer detectors Polystyrene standards(Polymer laboratories) were used for calibration and universal calibration was obtained from a PC base software Chromatograms of the samples were achieved by using THF as a mobile phase at a flow rate of 1.0 ml/min. The data of peak molecular weight ($\overline{M}_p$), number averaged molecular weight ($\overline{M}_n$), weight averaged molecular weight ($\overline{M}_w$) and polydispersity index ($\overline{M}_w/\overline{M}_n$) were reported.

5) DSC thermograms were obtained from a Perkin Elmer DSC7 Differential Scanning Calorimeter(DSC) Samples were scanned from -70 to 120°C at a heating rate of 20°C/min

6) TGA thermograms were recorded on Thermogravimetric Analyser (Perkin Elmer TGA 7) Sample were scanned from 50 to 600°C under air atmosphere at a heating rate of 40°C/min.

2.3 Purification of Materials

1) Cyclohexane was dried by refluxing with CaH_2 for 3 h and then distilled under nitrogen gas.

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2) *n*-BuLi was filtered through dry celite packed column under helium gas and titrated with 2,5-dimethoxybenzyl alcohol under nitrogen gas using dry THF as a solvent

3) Isoprene was extracted by 10% NaOH aqueous solution to eliminate inhibitor (4-tert-butyl cathechol). Organic layer was washed with distilled water 2-3 times to remove trace of base and dried with anhydrous Na_2SO_4 for 1 h Then it was distilled under nitrogen gas.

4) Styrene was purified by extraction with 10% NaOH aqueous solution to get rid of inhibitor (4-tert-butyl-cathechol). After removing trace base by washing organic layer with distilled water, it was dried with anhydrous Na_2SO_4 for 1 h. Then, it was distilled under reduced pressure in presence of CaH_2.

5) Tetrahydrofuran (THF) was dried by refluxing with Na using benzophenone as an indicator

6) Methanol and hexane were simply distilled before utilisation

2.4 Preparation of Poly(isoprene-b-styrene) by Anionic Polymerisation.

The equipment for polymerisation of block copolymer is shown in Figure2.1 . A dried 250 ml two-necked round bottom flask, whose one neck was mounted with a septum and the other with a condenser, was equipped with a nitrogen inlet tube and a magnetic bar. Then air inside the flask was removed by vacuum pump and dried nitrogen gas was introduced into the flask several times. The flask was heated in an

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oil bath at about 40°C. Dried cyclohexane, *n*-BuLi and purified isoprene were injected into the flask by syringe, respectively.

Polymerisation of isoprene was first carried out at 40°C for 3 h to give living polyisoprenyl anion. Then purified styrene monomer was added and allowed the reaction to proceed for another 3 h at 40°C.

The amount of initiator and monomer used in the reaction depended on the number averaged molecular weight ($\overline{M}_n$) required which was calculated from the equation 1 given in section 1.2 1

The polymerisation was terminated by an addition of methanol The product was obtained by precipitation in excess methanol and dried in a vacuo at room temperature for 24 h. Block copolymers obtained from anionic polymerisation were stored in a desiccator for characterisation.

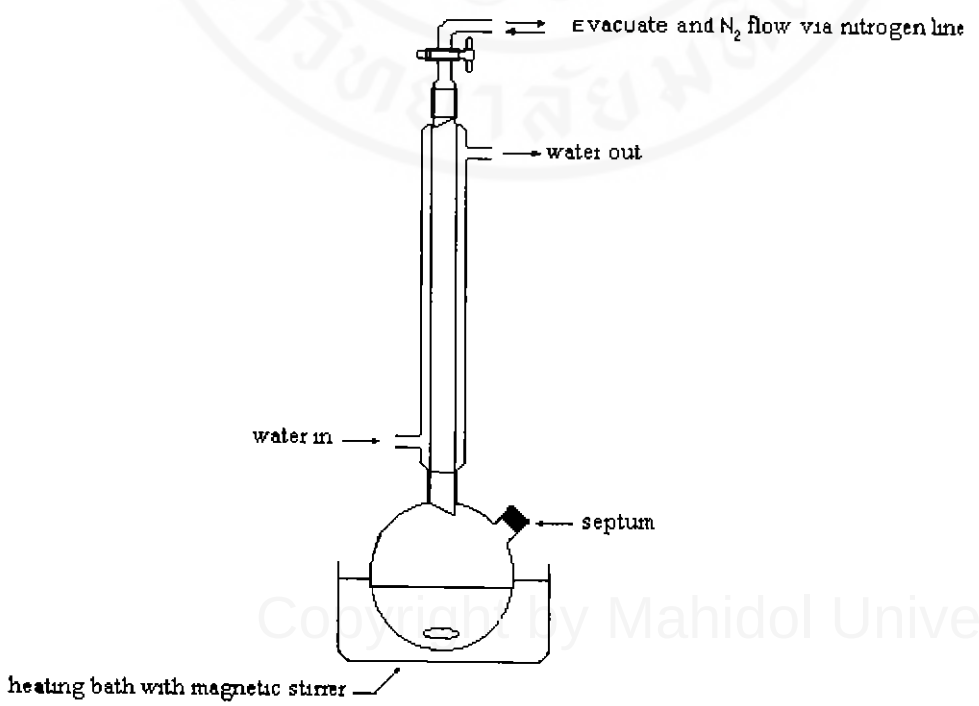

Figure 2.1 The equipment of anionically synthetic block copolymerisation

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2.5 Hydrogenation Procedure

Hydrogenation of Poly(isoprene-b-styrene) was accomplished in a 2L three-necked round bottom flask equipped with magnetic bar, a reflux condenser, a thermometer and a nitrogen gas inlet. Positive pressure of nitrogen was inserted into the equipment (via a mineral oil bubbler) through a gas inlet The top of condenser was mounted with silica gel trap. The equipment was shown in Figure 2.2

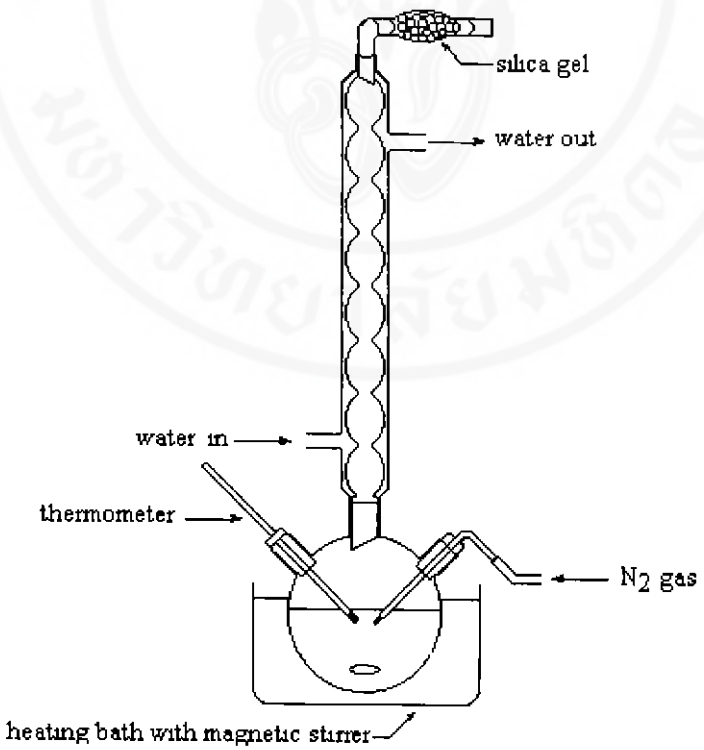

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Figure 2.2 Hydrogenation apparatus

The solution of polymer in xylene, 2%w/v polymer solution which was calculated from w/v ratio of 2 parts of polymer to 100 parts of xylene(28) , was added into the flask. Then, *p*-toluenesulphonyl hydrazide (TSH) was added into the flask. The amount of TSH was 2 times as much as that of unsaturation site in block copolymer (calculated from ^{1}H-NMR). The vessel was heated to reflux (135-140°C) for 4 h. The TSH is solely slightly soluble in xylene at room temperature but totally dissolves upon heating. When the reaction was proceeded, the reaction mixture changed from colorless to deep yellow and a white powder solid emerged as a precipitate.

The reaction mixture was washed with distilled water and filtered through sinter glass funnel packed with aluminum base to remove by-products The mixture was concentrated by evaporating the xylene at 45°C under vacuum using a rotary evaporator. The concentrated mixture was then precipitated in methanol whereas residual acid by-products dissolved in methanol The recovered polymer was dried in vacuo at room temperature. Such the impurity had it that the second time filtration was required after the separation between product and by-products by dissolving in hexane. The pure product was dried in vacuo at room temperature for 24 h before analysed subsequently.

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2.6 Structural Characterisation

2.6.1 FT-IR Spectroscopy

Each sample was dissolved in distilled $CHCl_3$ and then casted onto a NaCl window. After complete vaporisation of the solvent, the sample was recorded on Perkin Elmer system 2000 FT-IR spectrometer by scanning 16 times at a resolution of 4 cm^{-1}.

2.6.2 ^{1}H-NMR and ^{13}C-NMR Spectroscopy

For ^{1}H-NMR analysis, approximate 60 mg of each sample was dissolved in deuterated chloroform ($CDCl_3$, 0.5 ml) using tetramethylsilane (TMS) as an internal reference. The sample was filtered prior to spectrum measurement by DPX-300 FT-NMR (300 MHz). The chemical shift (δ) reported was given in part per million (ppm) down field from TMS.

2.6.3 Raman Spectroscopy

Raman spectra were obtained from a Perkin Elmer system 2000 NIR FT-Raman spectrometer using a Nd-YAG laser source, giving an excitation line at 1064 nm, and a InGaAs detector. Each sample was scanned 16 times over the spectral range 3600 to 200 cm^{-1} at 4 cm^{-1} resolution and laser power output of 400 mW

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2.7 Determination of Isoprene and Styrene in the Block Copolymer

2.7.1 ^{1}H-NMR Spectroscopy

The extent of each block composition can be determined by means of ^{1}H-NMR spectroscopy. Since the area under resonance signals is proportional to the number of specific protons in the sample(37), thus quantitative analysis of block component can be evaluated from integration of the spectrum. Poly(isoprene-b-styrene) revealed characteristic signals of isoprene at δ_H ($CDCl_3$, ppm) : 5 13 (m,1H at C=C of 1,4-PI), 4 70 (m, 2H at C=C of 3,4-PI), and 1.5-2.5 (m, 5H of CH_3 and CH_2) and those of styrene at δ_H ($CDCl_3$, ppm): 6.55-7.04(m, 5H of phenyl ring), 1 0-2.5 (m, CH_2) It is known that signals at δ 6.55-7 04 ppm correspond to the aromatic structure of polystyrene, while those at δ 5.13 ppm and δ 4 75 ppm are belonging to the 1H adjacent to C=C of 1,4-polyisoprenic structure and to 3,4-addition of polyisoprenic structure, respectively. Therefore the amount of polyisoprene, including 1,4- and 3,4-polyisoprene, and polystyrene in the block copolymers synthesised in this study can be assessed from the resonance area (A) of these chemical shifts. The mole percentage of 1,4- , 3,4-polyisoprene and polystyrene can be also calculated from the following equations(38).

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$$\%1,4\text{-PI} = \left(\frac{10A_{(1,4-PI)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (5)$$

$$\%3,4\text{-PI} = \left(\frac{5A_{(3,4-PI)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (6)$$

$$\%PS = \left(\frac{2A_{(PS)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (7)$$

$A_{(1,4\text{-PI})}$: the resonance area of the methine proton adjacent to C=C of PI at $\delta = 5.10$ ppm.

$A_{(3,4\text{-PI})}$: the resonance area of the methylene proton adjacent to C=C of PI at $\delta = 4.75$ ppm.

$A_{(PS)}$: the resonance area of the proton adjacent to benzene ring at $\delta =$ 6.5-7.2 ppm.

1,4-Polyisoprene also shows two different microstructures, cis- and trans-microstructure. The percentage of cis- and trans-microstructure can be estimated from ^{1}H-NMR. The relative amount of cis- and trans-microstructure are calculated from equation below.

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$$\% \text{ cis-1,4-PI} = \left(\frac{A_c}{A_c + A_t}\right) \times 1,4 - PI \quad (8)$$

$$\% \text{ trans-1,4-PI} = \left(\frac{A_t}{A_c + A_t}\right) \times 1,4 - PI \quad (9)$$

A_c : integration of methyl proton signal adjacent to double bond at 1 69 ppm of cis-microstructure

A_t : integration of methyl proton signal adjacent to double bond at 1.60 ppm of trans-microstructure

1,4-PI . % 1,4-PI in copolymer calculated by equation 5

From the ^{1}H-NMR spectra, overlapping of signals at 1.60 and 1 62 ppm belonging to methyl proton signals of trans- and 3,4-microstructure, respectively, is observed. So, the calculation of cis- and trans- ratio is erroneous. Hence only approximate ratio of these microstructures can be estimated To reduce this type of error, signals were amplified to achieve higher intensity of integrated spectrum in the process of calculation In addition, this calculation is confirmed by the ratio of cis-1,4- and trans-1,4-PI to 3,4-PI calculated from ^{1}H-NMR signals at 5 1 ppm and 4.75 ppm which should be close to the ratio of 94:6

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2.7.2 Iodine Value (I.V.) by Wijs Method

The quantitative method to measure the unsaturation present in samples was the determination of iodine value, defined as the number of centigrams of iodine equivalent to the unsaturation present in 1 g. of sample (weight percent of absorbed iodine) [cg(I_2)/g] (39).

A precisely weighed unsaturated sample (near 0.1 mg), whose weight was recommended as shown in the Table 2.2 (40) , relative to the approximate level of unsaturation in sample, was dissolved in chloroform. Then the dissolved sample was added with the exact amount of Wijs solution, iodine monochloride in acetic acid and chloroform mixture, allowed to proceed the reaction for 2 h. After this standard time of reaction, 10% potassium iodide solution was added and then back titration was performed to determine the liberated iodine with a standardised sodium thiosulphate using starch solution as an indicator A blank test was carried out without sample under the same conditions.

Polystyrene in block copolymer sample did not react with the Wijs solution , whereas polyisoprene in the sample did because the reactivity of iodine monochloride solution was not strong enough. If subjected to proper conditions, using bromine in a catalysed bromine solution(41,42) as a reagent, both polyisoprene and polystyrene in copolymer sample would be reacted. Thus total amount of unsaturation including conjugation was obtained.

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The Iodine Value (I V) was given by the formula(40):

$$\text{I.V.} = \frac{12.69 \times N \times (V_B - V_S)}{m} \quad (10)$$

where:

N = the exact normality of the sodium thiosulphate solution, standardised with standard potasssium iodate,

V_B = ml of the standardised sodium thiosulphate required for titration of the blank,

V_S = ml of the standardised sodium thiosulphate required for titration of the sample,

m = mass of the sample in grams.

12.69 = number derived from atomic weight of iodine

Table 2.2 The weight of unsaturated samples to be taken varies according to its expected iodine value.

Expected Iodine Value	Sample weight to be taken for test (g)
< 5	3.00
5 to 20	1.00
21 to 50	0.40
51 to 100	0.20
101 to 150	0.13
151 to 200	0.10

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2.8 Determination of %Hydrogenation (%H)

2.8.1 ^{1}H-NMR Spectroscopy

The percentage of hydrogenation of samples was measured from the ratio of polyisoprene and polystyrene before hydrogenation to that after hydrogenation by the use of ^{1}H-NMR spectroscopy, as described in section 2.7.1 It has been assured that the amount of polystyrene was constant and no side reactions which resulted in the inclination of phenyl ring in the samples.

Percent hydrogenation was calculated as follows:

$$\%H = (1 - \frac{I_A / S_A}{I_B / S_B})x100 \quad (11)$$

where :

I_A/S_A = the ratio of weight percent of polyisoprene to that of polystyrene after hydrogenation.

I_B/S_B = the ratio of weight percent of polyisoprene to that of polystyrene before hydrogenation.

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2.8.2 Iodine Value by Wijs Method

The percentage of hydrogenation of hydrogenated sample can also be obtained by the determination of residual unsaturation in sample by Wijs method as follow 2.7.2. The percent of hydrogenation was calculated as follow, if the iodine value of the base polymer prior to hydrogenation was known (39).

$$\%H = \frac{I.V._{(B)} - I.V._{(A)}}{I\ V._{(B)}} \times 100 \qquad (12)$$

where :

$I\ V_{(A)}$ = iodine value of sample after hydrogenation

$I\ V_{(B)}$ = iodine value of the base polymer

2.8.3 IR Spectroscopy

The percentage of hydrogenation of poly(isoprene-b-styrene) can be determined by means of IR spectroscopy The vibrational peak at 1601 cm^{-1} assigned to the styrene repeating units was used as the internal standard whereas the band at 840 cm^{-1} was the characteristic peak of polyisoprene This peak reduced drastically after hydrogenation. Then , the absorption peak area ratio at 1601 cm^{-1} to 840 cm^{-1} was measured before and after hydrogenation for calculating percentage of hydrogenation (33) using the equation below.

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$$\%H = (1 - \frac{I_A / S_A}{I_B / S_B}) x100 \quad (13)$$

where

I_A = peak area at 840 and 889 cm^{-1} assigned to isoprene units after hydrogenation

I_B = peak area at 840 and 889cm^{-1} assigned to isoprene units before hydrogenation

S_A = peak area at 1601 cm^{-1} assigned to styrene units after hydrogenation

S_B = peak area at 1601 cm^{-1} assigned to styrene units before hydrogenation

2.9 Average Molecular weight and Molecular Weight Distribution

The average molecular weight and molecular weight distribution of block copolymer and hydrogenated block copolymer were acquired by Gel Permeation Chromatography (GPC). GPC, size exclusion chromatography (SEC) employing organic solvents, was a non-interactive technique whereby dissolved macromolecules were seperated on the basis of molecular size

The separation mechanism was contingent on the ability of the different sized solutes to diffuse in and out of the porous structure and on the residence time of them within porous structure of packing column Critical molecular size above which solute molecules would be unable to enter the porous structure was the " exclusive limit". Molecules whose average hydrodynamic radius is larger than that of the gel pores cannot be separated. In similar fashion, "total permeation limit" was the critical molecular size below which the chromatography packing material was unable to

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discriminate among molecules of different sizes. Molecules at or below this critical size were said to entirely permeate the packing for a given column. A region of selective permeation was between the two limits of exclusion and total permeation. The accessibility of the pores by diffusion to different molecules was a function of both molecular and pore size. The smaller the molecules, the deeper they permeated into the pores of the gel. Therefore, smaller molecules had longer residence time within the pore (43).

The relationship between molecular size and elution volume/time was plotted to give the GPC calibration curve. Polymer standards of known molecular weight and monodisperse were used to establish the calibration curve by plotting log molecular weight (logM) against elution volume (V_e). The flow rate through the column should be maintained at the constant value and so log molecular weight can be plotted against time(t)

Because of the variation of the solute sizes of a given molecular weight with both conformation and molecular type, it was difficult to obtain absolute molecular weight data on an unknown polymer sample unless the unknown was known to be of the polymer sample and conformation as the calibrants used. In many instances, molecular weights of unknowns have to be cited, referencing the calibrant type used, as no primary standard are available. However, even when primary standard were not available, it may be possible to obtain absolute data by use of the universal calibration method (44)

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2.10 Thermal Analysis of Polymers by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC is one of the most widely used thermal analysis techniques. It is a thermal techniques in which the physical property, enthalpy, is measured as a function of temperature while the sample and reference materials stayed isothermally to each other, as they are heated or cooled at a linear rate. In this study, thermal behavior, T_g, of block copolymers and hydrogenated products has been investigated using Perkin Elmer DSC7, power compensated DSC at a heating rate of 20°C/min. The sample and reference materials were maintained isothermally by the use of individual heaters The difference in energy inputs to the heaters, $d(\Delta Q)/dt$ or dH/dt was measured directly (45) The thermograms acquired were a recording of heat flow, dH/dt, in mW, as a function of temperature. An endothermic curve peak was indicated by a peak in the positive heat flow direction (increase in enthalpy) whereas an exothermic peak was recorded in the opposite direction. The area enclosed by the DSC curve peak was directly proportional to the enthalpy change.

TGA detects the change in mass of a sample when it is heated. This change may caused by degradation of the sample and volatilisation of substances or moisture in the sample. In this study, thermal stability of poly(isoprene-b-styrene) and hydrogenated products was investigated by Perkin Elmer TGA7. The samples were heated under air atmosphere from 50°C to 600°C at a scanning rate of 40°C/min.

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CHAPTER III

RESULTS AND DISCUSSION

In this chapter, presentation of synthesis and characterisation of polyisoprene and polystyrene via anionic polymerisation process are described in section 3 1. The following section 3.2 is the results and discussion of synthesis of diblock poly(isoprene-b-styrene) via anionic polymerisation process and its characterisation The hydrogenation reaction of the diblock poly(isoprene-b-styrene) is discussed in section 3.3.

3.1 Synthesis and Characterisation of Homopolymer

3.1.1 Synthesis of Polyisoprene and Polystyrene

Monomers that can be polymerised anionically should possess electron withdrawing substituent at the vinylic function. Isoprene and styrene are such molecules that have been used successfully in anionic polymerisation process. In this study, homopolyisoprene (PI) and homopolystyrene (PS) were prepared by using the same condition as Pasiri(38), i.e. *n*-BuLi was used as a mono-anionic initiator except that this reaction was carried out in cyclohexane which is non-polar solvent instead of toluene.

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In anionic polymerisation of isoprene, pale yellow solution was observed when isoprene monomer was added to solution of *n*-BuLi at 40°C. This is the same colour as the initiator solution. The propagation of polyisoprenyl anion was detected by the increase of solution viscosity. After 3 h of polymerisation, the living anionic polymer was terminated by addition of methanol and clear solution was obtained The polyisoprene prepared in this study was viscous and colourless

Homopolystyrene was synthesised in a similar manner. After an addition of styrene monomer into initiator solution for a few minutes, living polystyryl anion was appeared by a sudden change from pale yellow solution into darked-red colour. The polymerisation was carried out at 40°C for 3 h The process of the reaction was observed by an increase of solution viscosity. At the end of reaction, the dark red solution became colourless after addition of excess methanol, indicating that the living chain end was terminated. The obtained product was colourless solid

3.1.2 Characterisation of Polyisoprene and Polystyrene

3.1.2.1 Evaluation of Chemical Structure by Spectroscopic Methods

Isoprene is a monomer containing two conjugated double bonds Generally, eight types of configurations can be obtained when it is polymerised, i.e. cis-1,4- , trans1,4- , 1,2- isotactic, 1,2-syndiotactic, 1,2-atactic, 3,4-isotactic, 3,4-syndiotactic and 3,4-atactic polyisoprenes. Polystyrene is derived from styrene monomer which is

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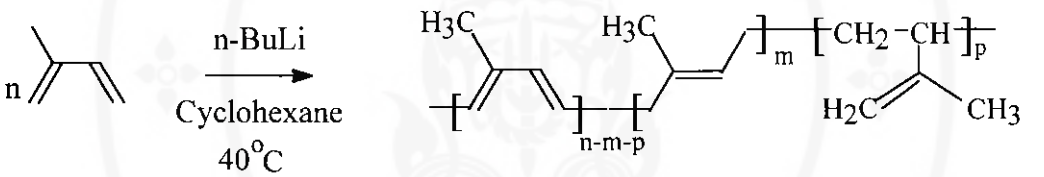
categorised in vinylic group. Isotactic, syndiotactic and atactic configurations are three possible configuration isomers of polymer derived from vinyl monomer

It has been reported that the type of initiator and polarity of the solvent play major role on stereochemistry of polymers(46). In this study, both isoprene and styrene were polymerised using *n*-BuLi as an initiator. It has been known that by the use of *n*-BuLi as an initiator and cyclohexane as a solvent, the cis-1,4-polyisoprene is the major product and the trans-1,4 and 3,4-polyisoprene are also formed as shown in equation 14.



(14)

The IR spectrum of synthesised PI shown in Figure 3 1 exhibited two characteristic absorption bands at 1665 and 1644 cm^{-1} corresponding to cis-1,4 or trans-1,4 and 3,4 polyisoprene respectively.

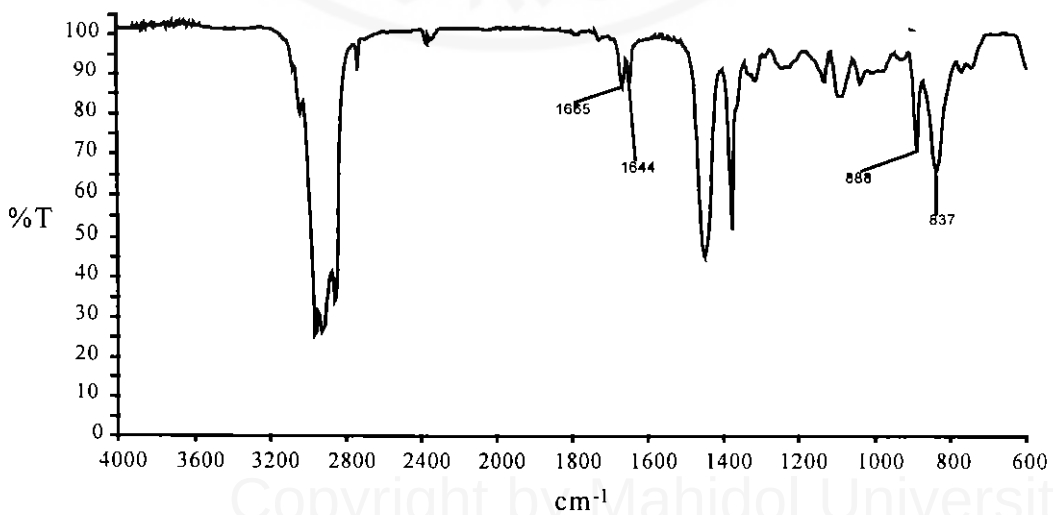


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Figure 3.1 IR spectrum of polyisoprene

Table3.1 The assignment of IR spectrum of polyisoprene

Reference*(cm^{-1})	Observed (cm^{-1})	Assignment	Structure
3100-3000	3100-2900	ν (=CH)	CH vinyl of PI
2969	2961	ν_a (CH_3)	CH_3 of trans -1,4-PI
2929	2925	ν_a (CH_3)	CH_3 of cis -1,4-PI
2853	2853	ν_S (CH_3)	CH_3 of cis -1,4-PI
1662	1665	ν (C=C)	C=C of cis , trans-1,4-PI
1641	1644	ν (C=C)	C=C of 3,4-PI
1445	1448	δ (CH_3)	CH_3 , CH_2 of PI
1380	1376	δ_S (CH_3)	trans-1,4-PI
1323	1329	δ (=C–H)ip	trans-1,4-PI
1321	1312	δ (=C–H)ip	cis-1,4-PI
1038	1028	γ_r (CH_3)	cis-1,4-PI
888	888	δ (=C–H)	3,4-PI
837	837	δ (=C–H)	1,4-PI

* Reference 38 , 46

ν = stretching ν_S = symmetric stretching ν_a = asymmetric stretching δ = deformation

δ_a = asymmetric deformation δ_S = symmetric deformation δ( )ip = in plane deformation γ_r = rocking

It is not possible to differentiate the vibrational frequency of C=C stretching band of cis-1,4 and trans-1,4 microstructures at 1665 cm^{-1} by, infrared spectroscopy technique. It is noted that by the use of high resolution ^{1}H-NMR and ^{13}C-NMR , cis and trans isomers can be detected and evaluated(21, 48). The results of ^{1}H-NMR and ^{13}C-NMR of synthesised PI are shown in Figure 3.2 and Table 3.2.

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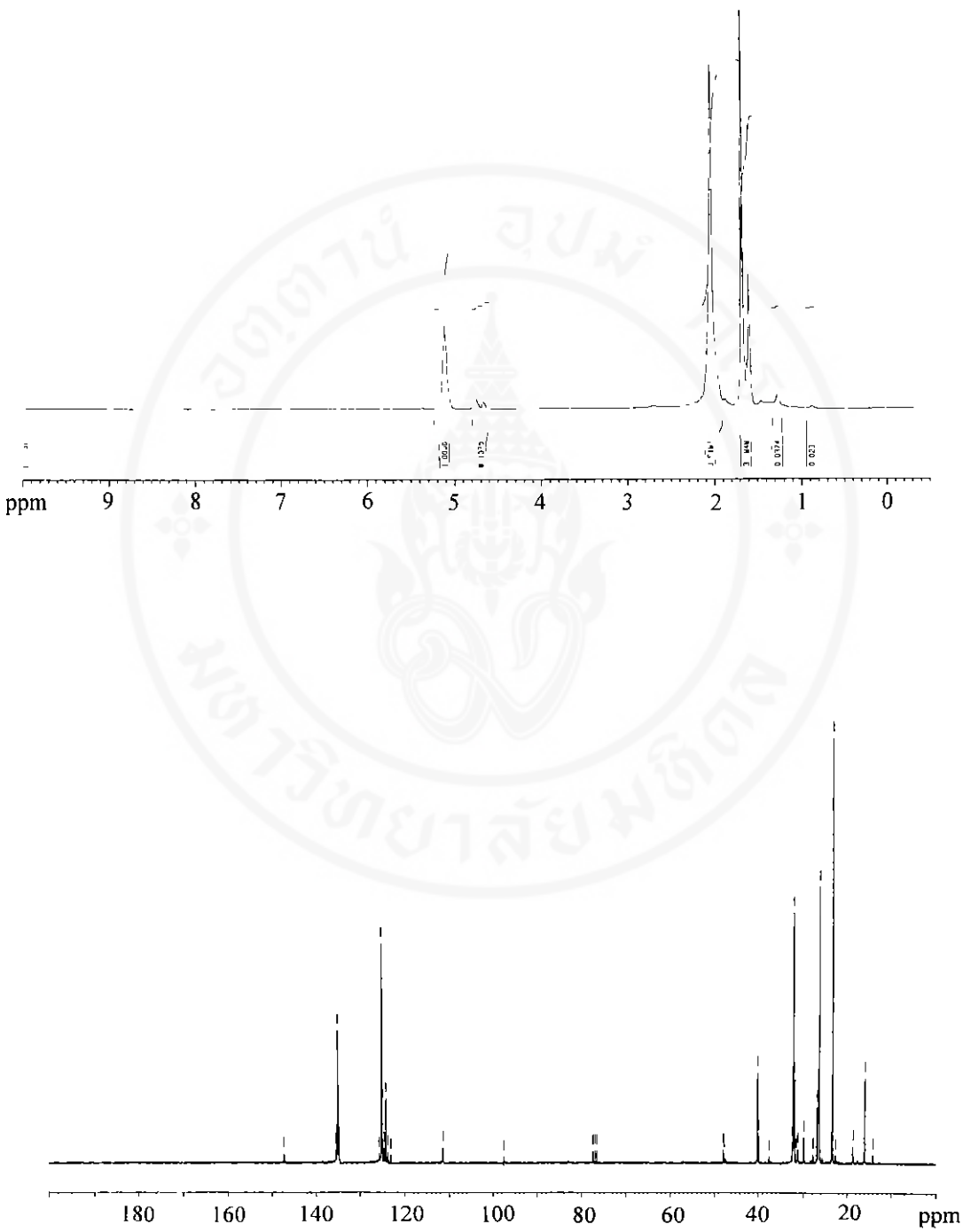

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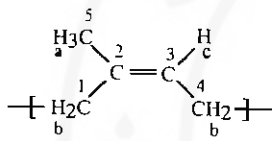
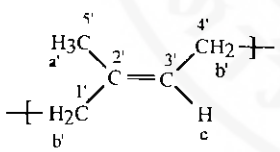
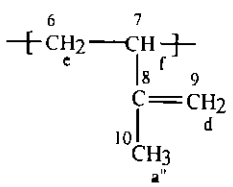
Figure 3.2 ^{1}H-NMR and ^{13}C-NMR spectra of polyisoprene

The characteristic peaks found in ^{1}H-NMR spectrum of the synthesised PI can be assigned that the signals at 5 1 ppm and 4.7-4.8 ppm are of the protons at double bonds of 1,4-PI and 3,4-PI respectively

Table3.2 The ^{1}H-NMR and ^{13}C-NMR assignments of characteristic peaks of various configuration of polyisoprene







^{1}H-NMR (ppm)			^{13}C-NMR (ppm)		
label	reference	observed	label	reference	observed
a	1 68	1 69	1	32 3	32 2
a′	1 60	1 60	1′	39 7	39 8
a″	1 64	1 62	2	135 6	135 3
b	2 03	2 03	2′	135 2	135 2
b′	1 96	1 97	3	125 3	125 0
c	5 11	5 12	3′	124 8	124 2
d	4 75	4 75	4	26 5	26 5
e	2 00	–	4′	28 6	26 6
f	1 36	–	5	23 4	23 4
			5′	16 0	16 0
			6	32 1	32 0
			7	47 5	–
			8	147 4	147 3
			9	111 2	111 4
			10	18 0	18 6

reference 21 , 38 , 47 o overlapped

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The amount of 1,4-PI and 3,4-PI presented in PI can normally be evaluated from the peak area ratio of these two signals by the equations 15 and 16 below

$$\%1,4\text{-PI} = \left(\frac{2A_{(1,4\text{-PI})}}{2A_{(1,4\text{-PI})} + A_{(3,4\text{-PI})}} \right) \times 100 \qquad (15)$$

$$\%3,4\text{-PI} = \left(\frac{A_{(3,4\text{-PI})}}{2A_{(1,4\text{-PI})} + A_{(3,4\text{-PI})}} \right) \times 100 \qquad (16)$$

where $A_{(1,4\text{-PI})}$ integration of signal at 5.1 ppm

$A_{(3,4\text{-PI})}$: integration of signal at 4.75 ppm

In this study, three experiments were carried out using the conditions listed in Table3.5, it was found that about 94 % of 1,4 addition and 6% 3,4 addition were detected.

The difference of cis-1,4 , trans-1,4 and 3,4 microstructures can further detected by methyl proton adjacent to C=C. By enlarging ^{1}H-NMR spectrum of PI shown in Figure 3.3, three different signals of methyl protons were observed. These are two signals of methyl protons adjacent to C=C at 1.68 and 1.60 ppm corresponding to cis-1,4-PI and trans-1,4-PI respectively whereas the methyl proton adjacent to C=C of 3,4- PI is present at 1.64 ppm Therefore the ratio of cis-1,4-PI and trans-1,4-PI can be approximately determined The ratio of cis-1,4 , trans-1,4-PI

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and 3,4 PI calculated from equations 8 and 9 in section 2.7 1 are about 70:25:5 as presented ın Table 3.4

Table 3.3 The microstructure of synthesised polyisoprene (PI) calculated from ^{1}H-NMR spectra.

Sample	cis-1,4-PI	trans-1,4-PI	3,4-PI
PI1	69.71	24.85	5.44
PI2	69.29	24 82	5.89
PI3	72.62	22.48	4.90

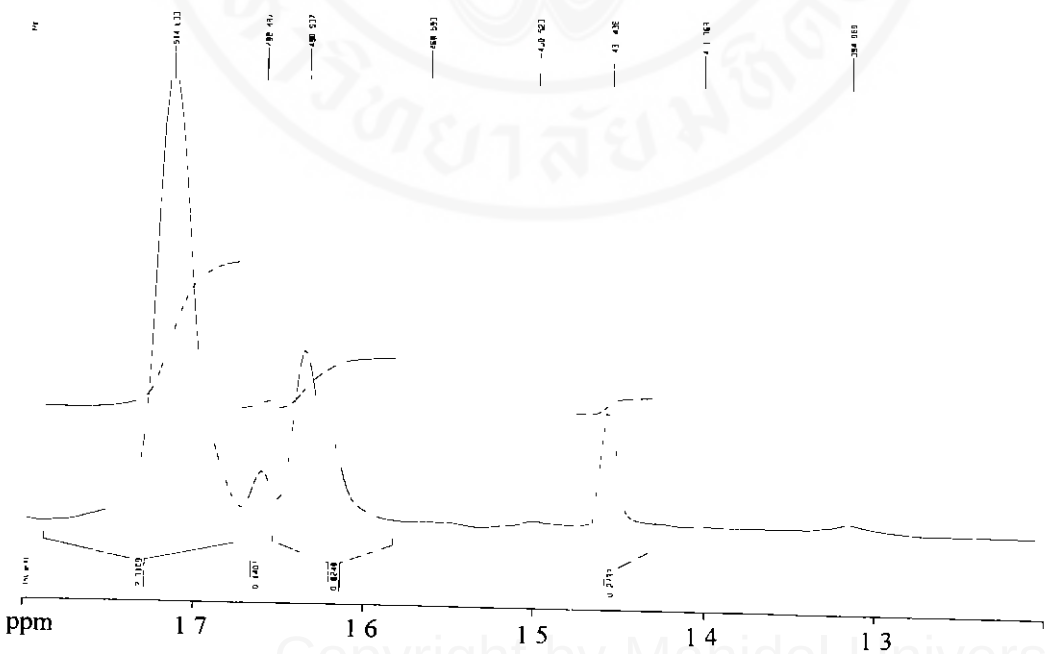

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Figure 3.3 Amplification of ^{1}H-NMR spectrum of synthetic polyısoprene

From ^{13}C-NMR spectrum, dominant peak assignments to methyl carbon of cis-1,4 , trans-1,4 and 3,4-microstructure are as the followings δC(CDCl3, ppm) : 23 4 (CH_3 of cis-1,4), 16.0 (CH_3 of trans-1,4) , 18.6 (CH_3 of 3,4), For the characteristic peaks of C=C , it exhibited 135.3, and 125.0 (C=C of cis-1,4), 135.2 and 124.3 (C=C of trans-1,4), and 147.3 and 111.4 (C=C of 3,4).

For polystyrene, IR spectrum shown in Figure 3.4 and Table 3.4 shows important characteristic peaks at 1600, 1490 and 1450 cm^{-1} corresponding to benzene ring of polystyrene. Another particular vibrational frequencies of the synthesised PS found are =C-H Aromatic(summation bands) at 1943, 1870, 1803 and 1746 cm^{-1}.

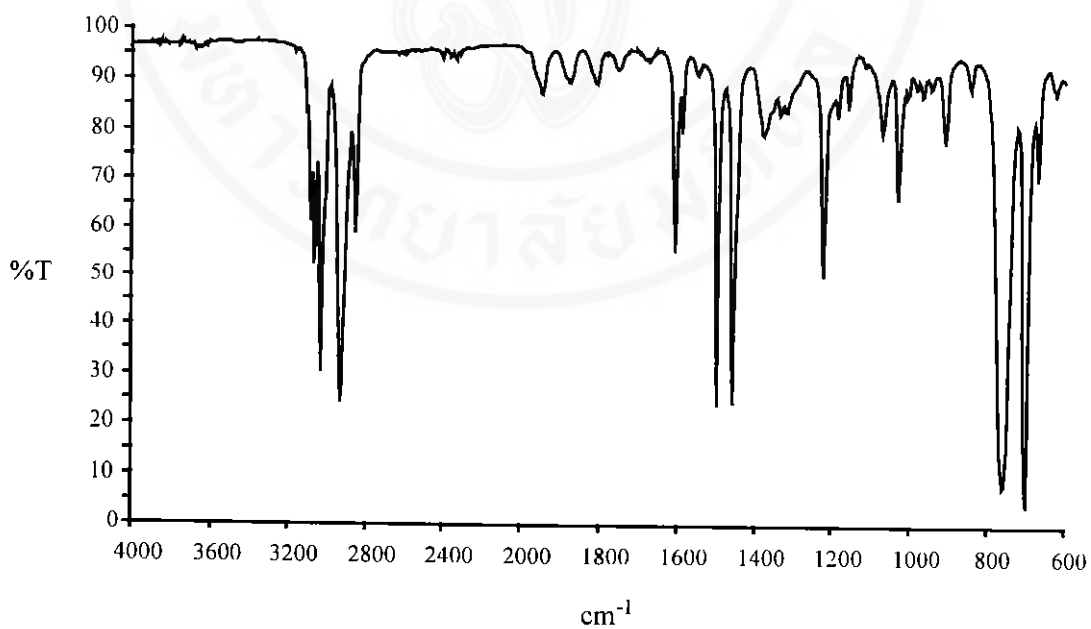

Figure 3.4 IR spectrum of polystyrene

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Table 3.4 The assignment of IR spectrum of polystyrene

Reference*(cm^{-1})	Observed (cm^{-1})	Assignment	Structure
3100-3000	3060, 3026		CH aromatic of PS
1944	1943	δ (=C–H)A_r	summation bands of PS
1871	1870		
1802	1802		
1746	1745		
1600	1601	ν (C=C)A_r	benzene ring of PS
1490	1493		
1450	1452		
1445	1448	δ (CH_2)	CH_2 of PS
1217	1218	δ (C–H)A_r	benzene ring of PS
750	758	δ (=C–H)A_r	monosubstitued aromatic of PS
700	699		

* Reference 38 , 46

ν = stretching ν_a = asymmetric stretching ν_S = symmetric stretching δ = deformation

δ_a = asymmetric deformation δ_S = symmetric deformation $\delta(\ )_{ip}$ = in plane deformation ρ_r = rocking

Zimba et al. (49) showed that isotactic, syndiotactic and atactic polystyrene can be differentiated by infrared spectra obtained using 250 scans and resolution of 2 cm^{-1}. Atactic PS showed a broad band at 1100-1040 cm^{-1}, syndiotactic exhibited a sharp peak in the same region while two small peaks are observed for isotactic PS. In our case, it reveals that atactic PS was synthesised as a broad band at 1100-1040 cm^{-1} was detected. This is not surprising as it is known that anionic polymerisation of

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styrene in non-polar solvent and *n*-BuLi as an initiator, irregular addition of styrene to anionic active center would be occurred.

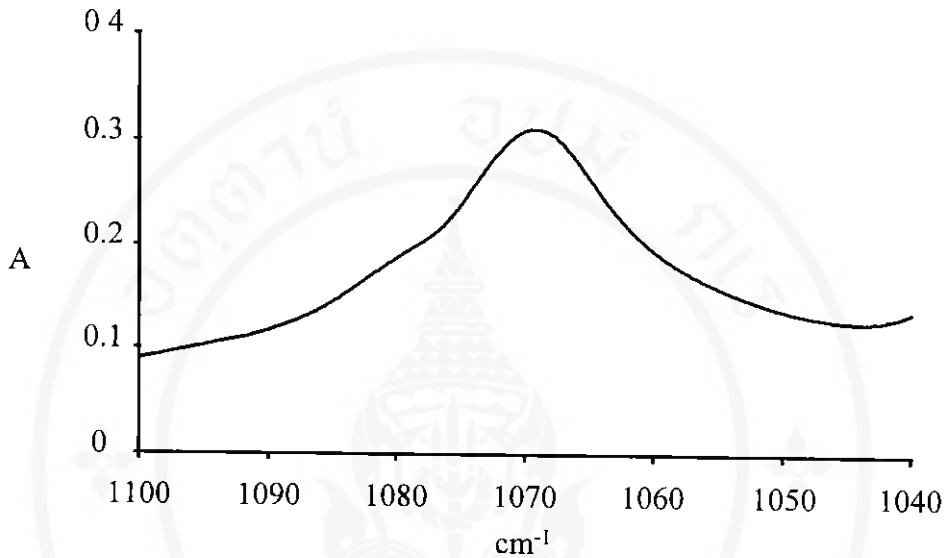

Figure 3.5 Absorption peak of polystyrene at 1100-1040 cm^{-1} with 250 scans and resolution of 2 cm^{-1}

3.1.2.2 Molecular weight (MW) and Molecular Weight Distribution (MWD) of Homopolymer

MW and MWD of polyisoprene and polystyrene synthesised were evaluated by gel permeation chromatography(GPC). Their results are presented in Table 3 5 It was found that the theoretical value of $\overline{M}_n$ differed from the experimental results determined by GPC. The deviation was due to the variation of concentration of initiator which is affected by the humidity, and resulted in decreasing of anionic active species. This phenomena resulted in higher $\overline{M}_n$ than the theoretical calculation

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obtained from the equation 1 in section 1.2.1. However the actual concentration of initiator was not measured prior to use because it can be varied with time depending on the moisture content. In this study, the value of $\overline{M}_n$ measured from GPC was accepted.

Table 3.5 Synthesis condition of polyisoprene(PI) and polystyrene(PS)

Sample	*n*-BuLi (ml[d], mole)	monomer (ml, g)	Calculated $\overline{M}_n$ (x10^3)	$\overline{M}_n^c$ (x10^3)	MWD[c]
PI1[a]	4, 0.0050	15, 10.2	2.0	6.2	1 58
PI2[a]	4, 0.0050	15, 10.2	2.0	3.4	1.96
PI3[b]	2, 0.0026	10, 6.81	2.6	7 5	1.63
PS1[a]	5.4, 0.0068	15, 13 59	2 0	4.2	1 34
PS2[a]	2, 0.0030	15, 13.59	5.0	13.0	1.64
PS3[a]	2, 0.0030	15, 13.59	5.0	14 1	1.57

a · [*n*-BuLi] = 1.25 M, b · [*n*-BuLi] = 1.28 M, c · determined by GPC, d : in hexane

In theoretical point of view, it is accepted that anionic polymerisation is the only process that provides polymer with narrow molecular weight distribution i.e MWD = 1.0-1.01. The results in Table 3.5 and Figure 3 6 exhibited that MWD of the two types of homopolymer synthesised are in the range of 1.3-1.6 This revealed that some impurities might be presented in the experimental process. This is due mainly to

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the presence of moisture or oxygen that effected the activity of the active species which caused the deviation of molecular weight of polymer before termination step.

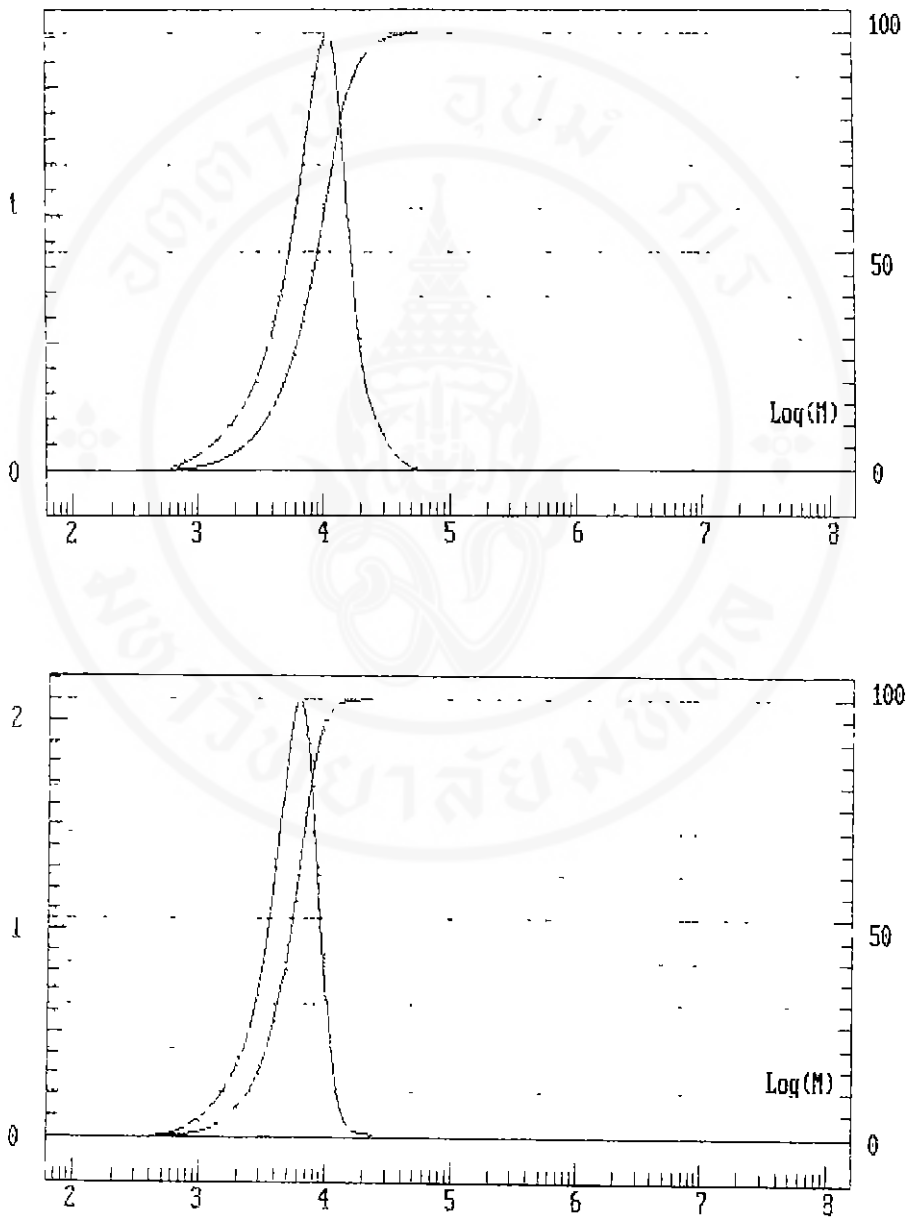

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Figure 3.6 GPC chromatograms of polyisoprene(PI1) and polystyrene(PS1)

3.2 Synthesis and Characterisation of Poly(isoprene-b-styrene)

3.2.1 Synthesis Conditions

One of the most successful method to prepare block copolymer is by anionic polymerisation. Firstly, the preparation of anionic living polymer of one type of monomers should be carried out, then the second monomer is added after the first monomer was totally consumed. This process is a sequential addition of two different types of monomers if diblock copolymer is required In our case, poly(isoprene-b-styrene) was anionically prepared by the sequential addition of isoprene and styrene monomers as described in section 2.4.

In this section, *n*-BuLi was used as a mono-anionic initiator and the reaction was carried out in cyclohexane which is a non-polar solvent as described in section 3.1 The anionic living polyisoprene was prepared by an addition of isoprene monomer into the solution of *n*-BuLi. This phenomenon was observed by the appearance of a pale yellow solution and the increase of solution viscosity. The polymerisation was allowed to take place for 3 h as reported by Pasiri (38) Then, styrene monomer was added to the living polyisoprenyl anion. The reaction of styrene monomer with the anionic species in the reaction mixture was observed by the instant change of pale yellow to a red-orange colour solution The copolymerisation was carried out further for another 3 h. The diblock copolymeric anion was terminated by addition of excess methanol. The red colour solution was changed to

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colourless solution. After purification by reprecipitation in methanol, the colourless solid product of isoprene-styrene dibolck copolymer was obtained.

The preparation of isoprene-styrene dibolck copolymer (IS) could be successfully prepared rather than the occurrence of alternating or random copolymers because of the two reasons. The first reason is due to the different propagation rate constant of isoprene and styrene monomers The homopolymerisation rate constant of isoprene, k_{ii}, is higher than the cross-polymerisation rate of isoprenyl anion to styrene monomer, k_{is} (15). Isoprene should be homopolymerised until depletion, then cross-polymerisation was occurred. The second reason is that allowing time to polymerise isoprene monomer is long enough to complete its homopolymerisation

In order to achieve higher or lower molecular weight of polymer prepared by anionic polymerisation, the amount of monomer as well as initiator play major role. At a given amount of monomer, the higher amount of initiator, the lower molecular weight polymer is obtained. In this study, the amount of isoprene and styrene monomers used is based on the objective to prepare equal length of each block component and various molecular weights of block copolymers. Five different molecular weights were selected, i.e. $\overline{M}_n$ of the two consecutive blocks is 2000, 2500, 5000, 6000 and 8000. Therefore, the amount of *n*-BuLi required is on the basis of half molecular weight, i.e. 1000, 1250, 2500 , 3000 and 4000. The conditions of preparing IS are grouped in Table 3 6. Each condition was carried out repeatedly. The results and discussion of this topic will be presented in section 3.2.3

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Table 3.6 Synthesis conditions of isoprene-styrene diblock copolymer

Sample	*n*-BuLi (mole, ml)	Isoprene (g)	Styrene (g)	Calculated $\overline{M}_n$ (x 10^3)	Calculated I : S(%w/w)
IS1	0.0176[a], 12.5	17.0	18.1	2.0	49:51
IS2	0.0128[b], 10.0	13.6	18.1	2.5	43:57
IS3	0.0064[b], 5.0	13.6	18.1	5 0	43 57
IS4	0.0059[a], 4 2	17.0	18.1	6 0	49.51
IS5	0 0042[a], 3.0	17.0	18.1	8.0	49:51

[a] : [*n*-BuLi] = 1.4070 M , [b] : [*n*-BuLi] = 1.2818 M

3.2.2 Structural Evaluation

Chemical structure evaluation of the synthesised isoprene-styrene diblock copolymer (IS) was implemented using IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Its spectra were illustrated in Figures 3.7, 3.8 and 3.9 respectively. The assignments were also shown in Tables 3.7 and 3.10.

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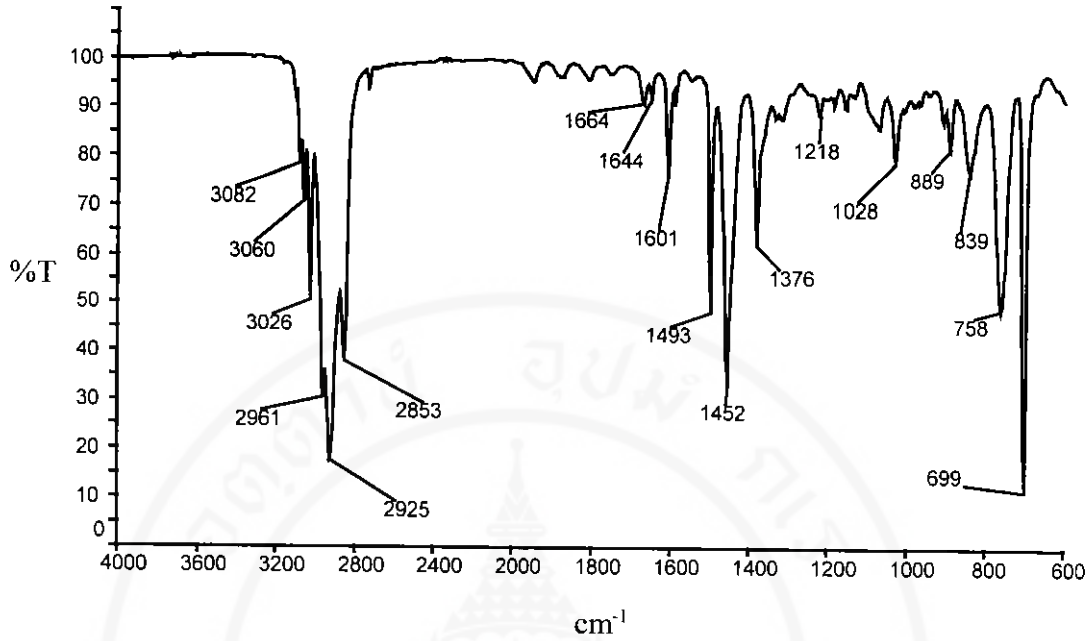

Figure 3.7 IR spectrum of isoprene-styrene block copolymer

The characteristic absorption bands in IR spectrum of the synthesised IS exhibited two important characteristic peaks at 1664 and 1644 cm^{-1} which correspond to C=C stretching of polyisoprene (PI) segment having 1,4 addition and 3,4 addition respectively. The deformation signals of =C-H of 1,4 and 3,4 PI at 889 and 839 cm^{-1} respectively also confirm the existence of 3,4 and 1,4 microstructure. The presence of polystyrene segment in the block copolymer is estimated by characteristic peaks at 1600, 1490 and 1450 cm^{-1} corresponding to benzene ring of polystyrene and vibrational frequencies of =C-H Aromatic(summation bands) at 1943, 1870, 1802 and 1745 cm^{-1}. The microstructure of polystyrene in block copolymer was also atactic polystyrene determined by a single broad absorption band in 1040-1100 cm^{-1} as discussed in the previous section

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Table 3.7 IR characterisation of isoprene-styrene block copolymer

Reference*(cm^{-1})	Observed (cm^{-1})	Assignment	Structure
3100-3000	3082, 3060, 3026	ν (=CH)	CH vinyl of PI
2969	2961	ν_a (CH_3)	CH_3 of trans -1,4-PI
2929	2925	ν_a (CH_3)	CH_3 of cis -1,4-PI
2853	2853	ν_s (CH_3)	CH_3 of cis -1,4-PI
1944	1943	δ (=C–H)A_r	summation bands of PS
1871	1870		
1802	1802		
1746	1745		
1662	1664	ν (C=C)	C=C of cis , trans-1,4-PI
1641	1644	ν (C=C)	C=C of 3,4-PI
1600	1601	ν (C=C)A_r	benzene ring of PS
1490	1493		
1450	1452		
1445	1448	δ (CH_3) , δ (CH_2)	CH_3 , CH_2 of PI , CH_2 of PS
1380	1376	δ_s (CH_3)	trans-1,4-PI
1323	1329	δ (=C–H)ip	trans-1,4-PI
1321	1312	δ (=C–H)ip	cis-1,4-PI
1217	1218	δ (C–H)A_r	benzene ring of PS
1038	1028	γ_r (CH_3)	cis-1,4-PI
888	889	δ (=C–H)	3,4-PI
837	839	δ (=C–H)	1,4-PI
750	758	δ (=C–H)A_r	monosubstitued aromatic of PS
700	699		

* Reference 38 , 47

ν = stretching ν_s = symmetric stretching ν_a = asymmetric stretchin

δ =deformation δ_a = asymmetric deformation δ_s = symmetric deformation

δ( )ip = in plane deformation γ_r = rocking

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In the case of ^{1}H-NMR outstanding resonances around 6-8 ppm are generally referred to as protons of aromatic ring whereas those at around 4-5 ppm are implied to

be the protons adjacent to double bonds The characteristic peaks found in ^{1}H-NMR spectrum of the synthesised IS copolymer can be assigned that the signals at 5.1 ppm and 4.7-4.8 ppm are of the protons at double bonds of 1,4-PI and 3,4-PI respectively. Therefore, the amount of 1,4-PI and 3,4-PI presented in PI block can be normally evaluated from the peak area ratio of these two signals. While those at 6 5-7.1 ppm. are of the proton of benzene ring of PS block. The amount of PS block and PI block can then calculated by using the three signals as shown in equations 5-7 in section 2.7.1.

$$\%1,4\text{-PI} = \left(\frac{10A_{(1,4-PI)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (5)$$

$$\%3,4\text{-PI} = \left(\frac{5A_{(3,4-PI)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (6)$$

$$\%PS = \left(\frac{2A_{(PS)}}{10A_{(1,4-PI)} + 5A_{(3,4-PI)} + 2A_{(PS)}}\right) \times 100 \quad (7)$$

Several types of IS diblock copolymer have been synthesised in this work It was found that in all the samples the polyisoprene segment contained in average 94% and 6% of 1,4 addition and 3,4 addition respectively as shown in Table 3.8 These results are in agreement with that shown in the literature (50) and the results in section 3.1 of synthesised PI.

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The nature of solvents and initiators play a key role affecting microstructure of diene parts of block copolymers. In this study, polyisoprenic lithium propagated in

hydrocarbon solvent. This gave high cis-1,4-PI as reported by Kelly and Tobolsky (17). Because in hydrocarbon media the metal counter-ion-carbon is bound covalently, a six membered ring is suggested for the transition state with the incoming monomer unit fixed in the cis configuration (51).

^{1}H-NMR spectrum also exhibited three different signals of methyl proton adjacent to C=C at 1.69 and 1.60 ppm corresponding to cis-1,4 PI and trans-1,4-PI respectively and at 1 62 ppm of 3,4 PI. Therefore, the ratio of cis-1,4 PI and trans-1,4-PI of PI block can be evaluated. The ratio of cis-1,4 PI to trans-1,4-PI is about 75.25 which were calculated from ^{1}H-NMR spectrum as shown in Appendix A(1A). The results of the amount of cis-1,4 PI , trans-1,4-PI , 3,4 PI and PS are present in Table 3.8.

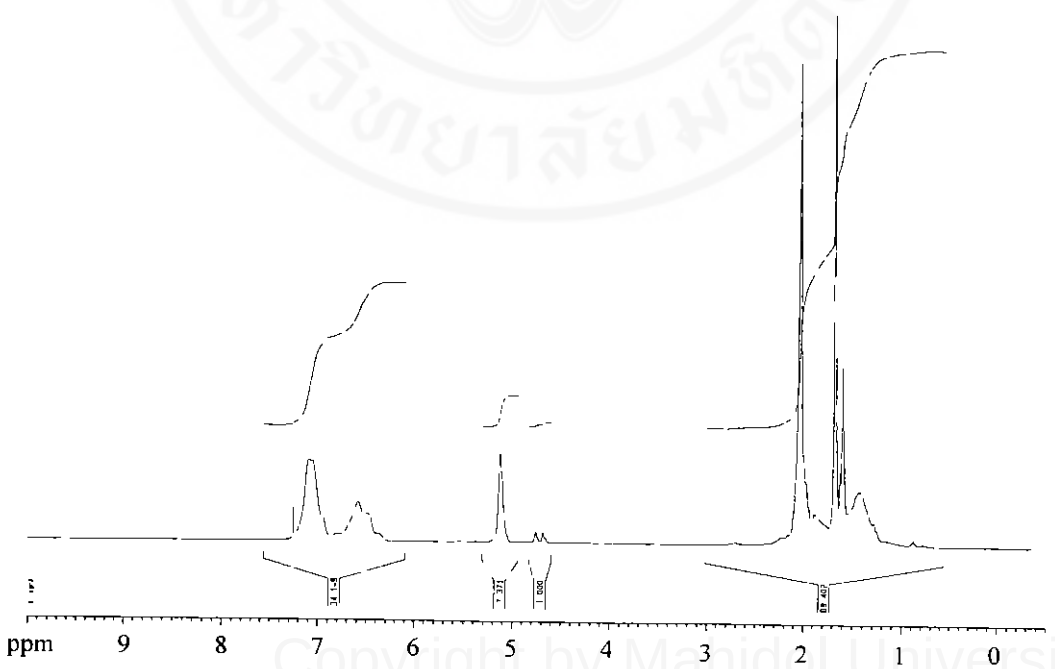

Figure 3.8 ^{1}H-NMR spectrum of isoprene-styrene block copolymer

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Table 3.8 Percentage of microstructure of isoprene-styrene block copolymer

Sample	% cis-1,4-PI	% trans-1,4-PI	% 3,4-PI	% Styrene	1,4-PI 3,4-PI
IS1(1)	38 77	12 58	3 37	45 28	94 6
IS1(2)	43 66	11 52	3 98	40 84	94 6
IS1(3)	41 52	10 25	3 47	44 75	94 6
IS1(4)	40 87	11 88	3 48	43 77	94 6
MIS1	38 44	12 81	3 70	45 05	94 6
IS2(2)	35 01	10 54	2 62	51 83	95 5
IS2(3)	34 73	11 05	3 25	50 97	93 7
MIS2	31 01	9 79	3.20	56 00	93 7
IS3(1)	39 53	12 5	4 02	43 95	93 7
IS3(2)	36 42	9 10	2 80	51 68	94 6
IS3(3)	37.39	11 33	3 42	48 86	93 7
IS3(4)	36.49	11 47	3 70	48 34	93 7
MIS3	36 16	11 77	3 09	48 97	94 6
IS4(1)	38 54	11 38	3 59	46 49	93 7
IS4(2)	35 24	11.47	3 74	49 55	93 7
IS4(3)	33 68	8 42	3 41	54 49	93 7
IS4(4)	30 64	11 91	3 68	53 77	92 8
MIS4	29 88	9 54	3 19	57 39	93 7
IS5(1)	28 96	11 26	2 55	57 23	94 6
IS5(2)	33 98	11 33	2 97	51 73	94 6
MIS5	31 58	10 53	1 44	56 45	97 3

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From ^{13}C-NMR spectrum, dominant peaks at 137.4, 128.2, 127.5 and 126 0 ppm can be assigned to C=C of PI block of various microstructures and benzene ring of polystyrene segment while peaks at 23.4, 18.6 and 15.9 ppm are deduced to be CH_3 of cis-1,4-PI, 3,4-PI and trans-1,4-PI, respectively

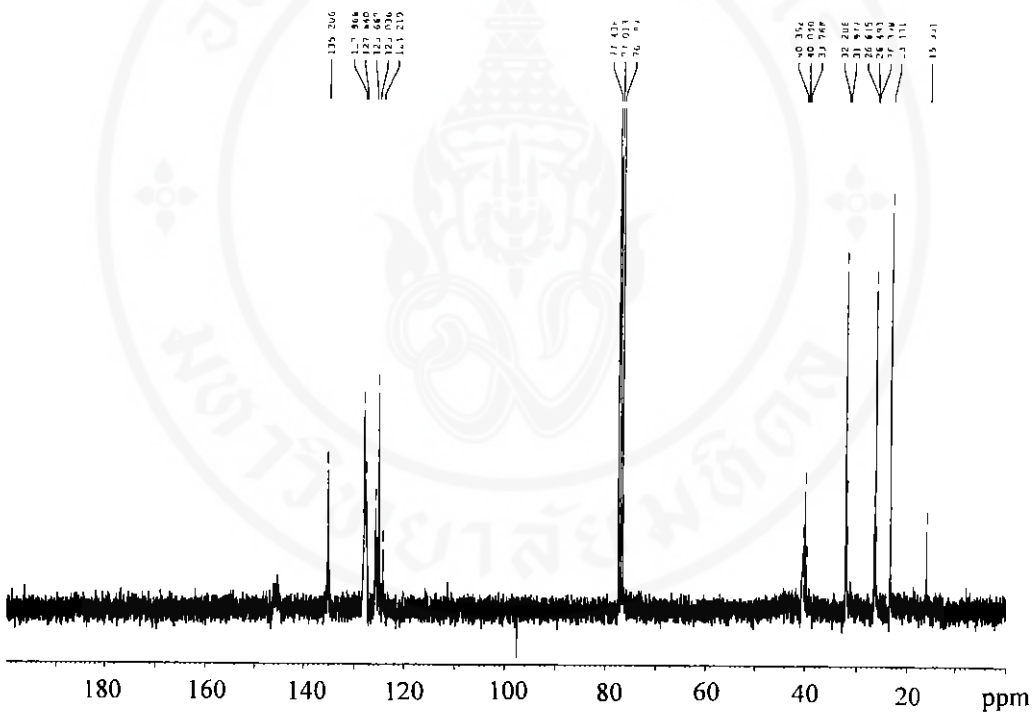

Figure 3.9 ^{13}C-NMR spectrum of isoprene-styrene block copolymer

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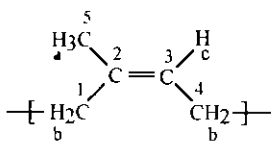
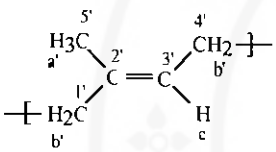
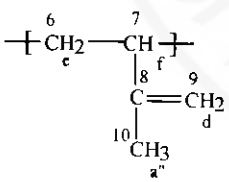
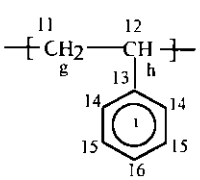
Table 3.9 ^{1}H-NMR and ^{13}C-NMR characterisation of isoprene-styrene diblock copolymer









^{1}H-NMR (ppm)			^{13}C-NMR (ppm)		
label	reference	observed	label	reference	observed
a	1 68	1 69	1	32 3	32 2
a′	1 60	1 60	1′	39 7	39 8
a″	1 64	1 62	2	135 6	135 3
b	2 03	2 03	2′	135 2	135 2
b′	1 96	1 97	3	125 3	125 0
c	5 11	5 12	3′	124 8	124 2
d	4 75	4 75	4	26 5	26 5
e	2 00	–	4′	28 6	26 6
f	1 36	–	5	23 4	23 4
g	1 00-2 50	1 36	5′	16 0	16 0
h	o	–	6	32 1	32 0
1	6 50-7 05	7 02, 6 51	7	47 5	–
			8	147 4	145 2
			9	111 2	–
			10	18 0	–
			11	113 4	–
			12	137 0	135 3
			13	137 4	–
			14	126 0	125 6
			15	128 2	128 0
			16	127 5	127 7

reference 21 , 38 , 48 o overlapped

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3.2.3 Molecular Weight (MW) and Molecular Weight Distribution (MWD) of Isoprene-Styrene Block Copolymer

MW and MWD of isoprene-styrene block copolymers prepared using condition in Table 3.6 are presented in Table 3 10. The results of $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$ were analysed using GPC. Five different $\overline{M}_n$ were prepared i.e. required $\overline{M}_n$ of 2000, 2500, 5000, 6000 and 8000. Similar to the preparation of homopolymer, the theoretical value of $\overline{M}_n$ differed from the experimental results determined by GPC. It could be possible that the initiator could react with moisture and oxygen during storage, leading to a decrease of the initiator concentration Therefore, higher molecular weight of the polymer is obtained. However, acceptable and reproducible molecular weight and molecular weight distributions of these required $\overline{M}_n$ were obtained as repeated experiments were carried out. Additionally, it was found in all experiments that more than 2 times of experimental $\overline{M}_n$ were achieved comparing to the theoretical $\overline{M}_n$. The higher required $\overline{M}_n$, the higher deviation of $\overline{M}_n$ from theoretical value was observed.

The results in Table 3.10 indicated small difference in molecular weights analysed by GPC in the case of calculated $\overline{M}_n$ of 2000 and 2500 i e they are both $\overline{M}_n$ of about 5000. These results were due to the difficulty in employing of small different amount of initiators in the reaction mixture. Similar results were also remarked in the case of calculated $\overline{M}_n$ of 5000 and 6000 that $\overline{M}_n$ of about 11000 were obtained. In this study various molecular weights of block copolymers were

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carried out in the same size of apparatus, therefore it is unable to enlarge the quantity of the monomers To vary $\overline{M}_n$ of a required copolymer, different amount of initiator , higher or lower, is a major parameter to be controlled. Consequently, in the case of calculated $\overline{M}_n$ of 8000 , fairly small quantity of initiator was employed, then error on accuracy might occur inevitably It was found that the experimental $\overline{M}_n$ obtained was about 25000 Therefore, it is necessary to accept the value of $\overline{M}_n$ measured experimentally by GPC. However, it is accepted that the amount of initiators employed in different experiments can be used as a general trend for scaling up the synthesis of the block copolymer.

Because of the unimodal chromatograms obtained as shown in Appendix B(2B), it could be inferred that the synthesised polymers were only block copolymers which were not impured by homopolymers either polystyrene or polyisoprene homopolymers.

Table 3.10 Molecular weight and molecular weight distribution of isoprene-styrene block copolymer

Sample	Calculated $\overline{M}_n$ ($x10^3$)	$\overline{M}_n$ ($x\ 10^3$)	$\overline{M}_v$ ($x\ 10^3$)	$\overline{M}_w$ ($x\ 10^3$)	MWD
IS1(1)	2.0	5.7	7.5	8.8	1.55
IS1(2)	2.0	5.1	7.1	7.8	1.52
IS1(3)	2.0	6.4	7.0	9.4	1.54
IS1(4)	2.0	5.0	7.0	7.6	1.53

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Table 3.10 Molecular weight and molecular weight distribution of isoprene-styrene block copolymer(cont.)

Sample	Calculated $\overline{M}_n$ (x10^3)	$\overline{M}_n$ (x 10^3)	$\overline{M}_v$ (x 10^3)	$\overline{M}_w$ (x 10^3)	MWD
IS2(1)	2.5	4.9	7.0	7 3	1.49
IS2(2)	2.5	5.5	7.8	8 5	1.54
IS2(3)	2 5	4.9	7.0	7.5	1.53
IS3(1)	5.0	10.5	15.0	16.4	1.56
IS3(2)	5.0	11.0	14.9	15.6	1.42
IS3(3)	5.0	15.6	21.3	24.2	1 55
IS3(4)	5.0	11 4	15 8	17.4	1.52
IS4(1)	6.0	10.7	20.3	19 5	1.82
IS4(2)	6.0	11.3	26.1	18.0	1.59
IS4(3)	6.0	10.2	17.5	16.3	1.60
IS4(4)	6 0	12.3	20.9	22.4	1.81
IS5(1)	8 0	20.3	34 0	35.4	1.75
IS5(2)	8.0	25.9	46.2	43.0	1.66

Note (1), (2), (3) and (4) referred to first, second, third and forth preparation, repectively.

3.2.4 Evaluation of Mixed Poly(isoprene-b-styrene)

The IS block copolymers prepared were hydrogenated further. In this case, the large scale of copolymers was required in hydrogenation reaction. Consequently, solution blending of the block copolymers was studied. Their structures, MW and MWD were also characterised. MIS1 was the product of mixing of IS1(1), IS1(2), IS(3) and IS1(4) while MIS2 was the product of mixing of IS2(2) and IS2(3). MIS3

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was obtained by mixing of IS3(1), IS3(2), IS3(3) and IS3(4) and MIS4 was of IS4(1), IS4(2), IS4(3) and IS4(4) whereas MIS5 was obtained by mixing of IS5(1) and IS5(2).

After blending, the copolymers were purified by re-precipitation in distilled methanol and dried under vacuum for 12 h. It was found that comparing to the original copolymers, mixed copolymers showed the same spectral patterns in IR, ^{1}H-NMR and ^{13}C NMR as those of original block copolymers. Peak assignments are also the same as shown in Tables 3 7 and 3.9 Figure 3 10 shows the comparison of IR spectra of the mixed copolymers while ^{1}H-NMR, ^{13}C-NMR spectra of mixed polymer are present in Appendix A(2A) Virtually, solution blending did not affect chemical structures of block copolymers. It is therefore a practical way to synthesis several small batches of block copolymers and blending them to get large amount of block copolymer when limited apparatus is available

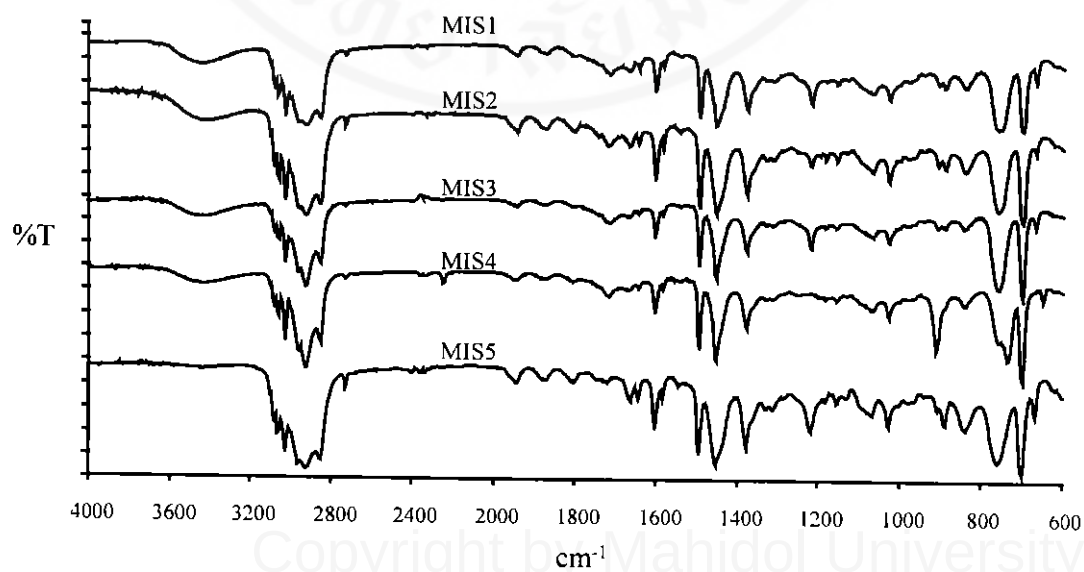

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Figure 3.10 IR spectra of mixed isoprene-styrene block copolymers

Averaged MW and MWD of the mixed copolymers were determined by GPC. Appendix B(3B) demonstrated the chromatograms of all mixed copolymers. Their chromatograms revealed unimodal signals similar to the initial copolymers. However, it was noted that the GPC chromatograms of mixed copolymers were slightly more broaden than those of the initial copolymers. It could be the result of the slight difference in hydrodynamic volume distribution of the various block copolymers prepared. The information of averaged MW and MWD was shown in Table 3.11

Table 3.11 Averaged molecular weights and MWD of mixed isoprene-styrene block copolymers

Sample	$\overline{M}_n$ (x 10^3)	$\overline{M}_v$ (x 10^3)	$\overline{M}_w$ (x 10^3)	MWD
MIS1	6.1	8.9	10.0	1.65
MIS2	4.5	6.6	7.4	1.66
MIS3	8.1	14.2	15 5	1.89
MIS4	16.2	31.9	33 4	2.06
MIS5	21.9	55.2	39.8	1.81

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3.2.5 Determination of Isoprene Block Composition by Iodine Value

Preparation of diblock copolymer by a sequential addition of monomers via anionic polymerisation is the most successful method. The severe condition is strictly required otherwise narrow distribution of molecular weight can not be achieved In this case, isoprene monomer has to be totally polymerised before addition of styrene It is not practical to sampling isoprene monomer to determine MW of isoprene segment before addition of the second monomer. By using the results from ^{1}H-NMR it is acceptable to determined the ratio of isoprene and styrene block composition in the block copolymer. The measurement of unsaturation present in the block copolymer is another method to evaluate the amount of isoprene in the block copolymers. Iodine value, defined as the number of centigrams of iodine equivalent to the unsaturation present in 1 g. of sample (weight percent of absorbed iodine)[cg(I_2)/g](39) It has been used to determine unsaturation of dienic polymers. In our case the sample was dissolved in chloroform and the exact amount of Wijs solution, iodine monochloride in acetic acid were added. These conditions are not sensitive to the unsaturation in polystyrene therefore practically the isoprene segments were dosed

Table 3.12 shows the results of a ratio of isoprene and styrene in various block copolymers and mixed IS determined by means of ^{1}H-NMR as well as their iodine values (I.V.). It was observed that I.V. increased when relative percentage of isoprene composition was higher. Although I V. is an absolute method for determining the amount of unsaturation in polymeric materials, it has still some errors from weighing, pipetting and titration. The interpretation should be done with precaution The I.V

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values obtained can be further used for comparison in hydrogenation in section 3.3.3 2.

Table 3.12 Block composition of isoprene-styrene block copolymer determined by ^{1}H-NMR and Iodine Value(I.V.).

sample	% I:S[a]	I.V.[b]
IS1(1)	55 45	176 ± 1
IS1(2)	59 . 41	183 ± 1
IS1(3)	55 : 45	175 ± 2
IS1(4)	56 : 44	179 ± 1
MIS1	55 : 45	178 ± 1
IS2(2)	48 : 52	163 ± 1
IS2(3)	49 : 51	163 ± 2
MIS2	44 · 56	161 ± 2
IS3(1)	58 : 44	187 ± 1
IS3(2)	48 : 52	169 ± 2
IS3(3)	52 : 48	175 ± 2
IS3(4)	52 : 48	171 ± 2
MIS3	51 : 49	175 ± 2
IS4(1)	54 : 46	173 ± 2
IS4(2)	50 : 50	170 ± 1
IS4(3)	46 : 54	152 ± 2
IS4(4)	46 : 54	166 ± 2
MIS4	43 : 57	151 ± 1
IS5(1)	43 . 57	168 ± 2
IS5(2)	48 : 52	166 ± 1
MIS5	56 : 44	169 ± 1

[a] calculated from ^{1}H-NMR

[b] I V by Wijs method

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3.3 Hydrogenation Reaction

It has been known that dienic polymers such as polybutadiene and polyisoprene are susceptible to oxidation and thermal degradation as these polymers possess double bonds in the molecular chain. Hydrogenation is one of the alternatives to reduce degree of unsaturation, resulting in the increase of thermal resistance of dienic polymers. Diimide derivatives have been widely used as hydrogen donor at mild condition to unsaturated compounds(27). In this section, hydrogenation of isoprene-styrene block copolymers (IS) are investigated in order to alter chemical structure and improve thermal properties of IS. The reaction was carried out in xylene solution at 135°C using *p*-toluenesulphonyl hydrazide (TSH).

3.3.1 Hydrogenation of Homopolyisoprene

Theoretically, stoichiometric ratio of double bond and diimide is needed to hydrogenate 100 % of unsaturation. One mole of TSH generates one mole of hydrogen under suitable condition as shown in equations 3 and 4 in section 1.3.2 In practice, it was shown by Poshyachinda et al(36) that complete hydrogenation of polybutadiene required about 1.6 times of TSH while about 4 times of TSH by mole was required to complete hydrogenation of synthetic polyisoprene(34). In our case, a trial of hydrogenation of homopolyisoprene (PI) was carried out by using 2·1 mole ratio of TSH to PI at 135°C in xylene for 4 h. It was found by ^{1}H-NMR in Appendix C that the existence of signal at 5.1 ppm characteristic of proton adjacent to carbon-

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carbon double bond of cis-1,4 or trans-1,4 PI. This evidence shows that partial hydrogenation was achieved It is not surprising that no signal belonging to proton of 3,4-PI at 4.75 ppm was observed because hydrogenation at side chain double bond of PI is easier than at the position of 1,4-PI(25) because of less steric hindrance. In addition, it has been shown elsewhere that hydrogenation reaction of trans-1,4 PI is more favorable than cis structure as the addition of diimide is syn-addition(34). I.V. has been used to identify degree of hydrogenation reaction as shown in equation 12 in section 2.8.2 It was found that about 80% hydrogenation of polyisoprene was obtained (I.V. of PI = 339±4 and I.V. of HPI = 65±0) However, IR spectrum shown in Appendix C was hardly seen peaks at 1664 cm^{-1} due to 1,4 cis-and trans-PI but the characteristic peak at 860 cm^{-1} corresponding to 1,4-PI can be used to confirm partial hydrogenation of polyisoprene when 2 times by mole of TSH was used comparing to double bond of PI.

3.3.2 Effect of *p*-Toluenesulphonyl Hydrazide Content on Hydrogenation

Hydrogenation of poly(isoprene-b-styrene) (IS, $\overline{M}_n$= 5.7 x 10^3) was then investigated at various ratios of TSH to double bond as shown in Table 3.13. The reaction was proceeded at 135-140 °C for 4 h. The gradual change of reaction mixture from colourless to deep yellow and the appearance of white powder solid indicated the progress of reaction. It was found later that the white solid was TSH by-product. It was removed by filtration. After precipitation of the filtrate in methanol, the hydrogenated block copolymer was obtained.

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Table 3.13 Hydrogenation condition of isoprene-styrene block copolymer (IS1)

Sample	$\overline{M}_n^a$ (x 10^3)	%I:S[b]	TSH/db (mole)	% Hydrogenation[b]
HIS1(1)	5.7	55:45	1 : 1	85.9
HIS1(2)	5 7	55:45	2 : 1	95 8
HIS1(3)	5.7	55:45	4 : 1	98.4
HIS1(4)	5.7	55:45	6 : 1	98.4

a: Isoprene-styrene block copolymer, measured by GPC

b: Calculated from ^{1}H-NMR

The hydrogenated products were analysed using IR and ^{1}H-NMR techniques. Generally, if complete hydrogenation was accomplished, all signals belonging to double bond of isoprenic moiety should be disappeared. However, IR spectra of hydrogenated products illustrated in Figure 3.11 shows the characteristic peaks of isoprene blocks at 1665, and 840 cm^{-1} which belong to C=C stretching and =C-H deformation. New absorption peaks also appear at 810, 1079 and 1141 cm^{-1} which was assigned in the literature as signals of SO_2 belonging to TSH by-product(52).

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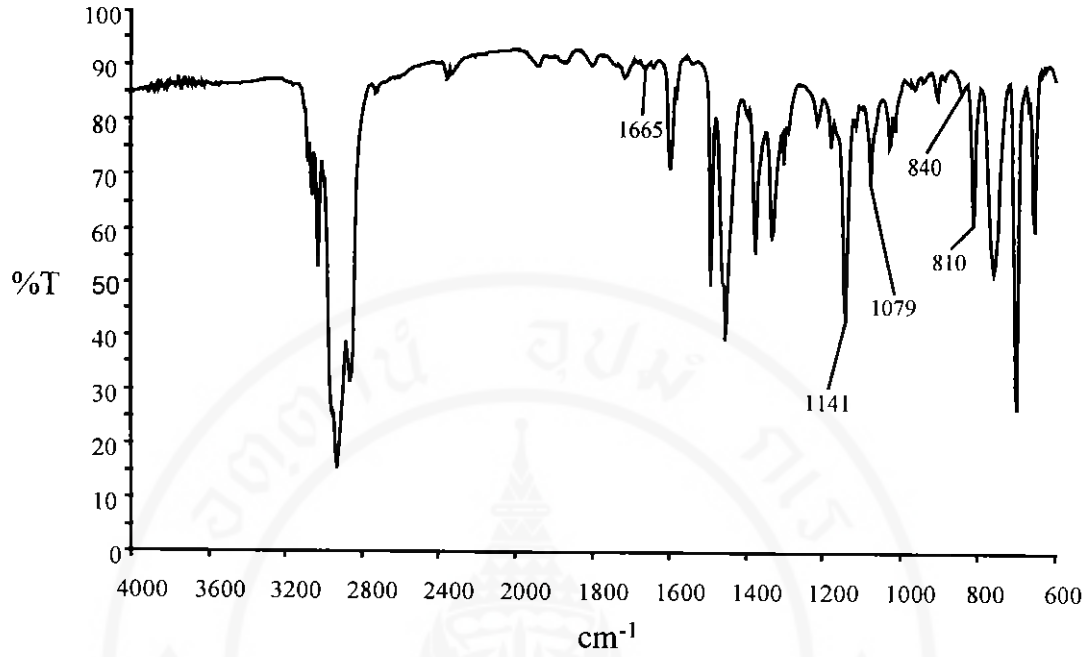

Figure 3.11 IR spectrum of hydrogenated product (HIS1(1))

^{1}H-NMR spectrum of hydrogenated products at different mole ratios of TSH to double bond of isoprene units are illustrated in Figure 3.12. The signal of proton adjacent to C=C was observed at 5.1 ppm . It was found that integration of this signal decreased substantially compared to the signal of aromatic ring of styrene units This results confirmed partial hydrogenation of isoprene-styrene block copolymer obtained from all experimental conditions. However, gradual decrease of the integral signal of proton adjacent to C=C was observed when higher amount of TSH was used as shown in Figure 3.12. It could obviously be seen that there was an impurity contamination which gave ^{1}H-NMR signal at 2.3 ppm. The higher TSH/db mole ratio was used, the stronger the signal appeared

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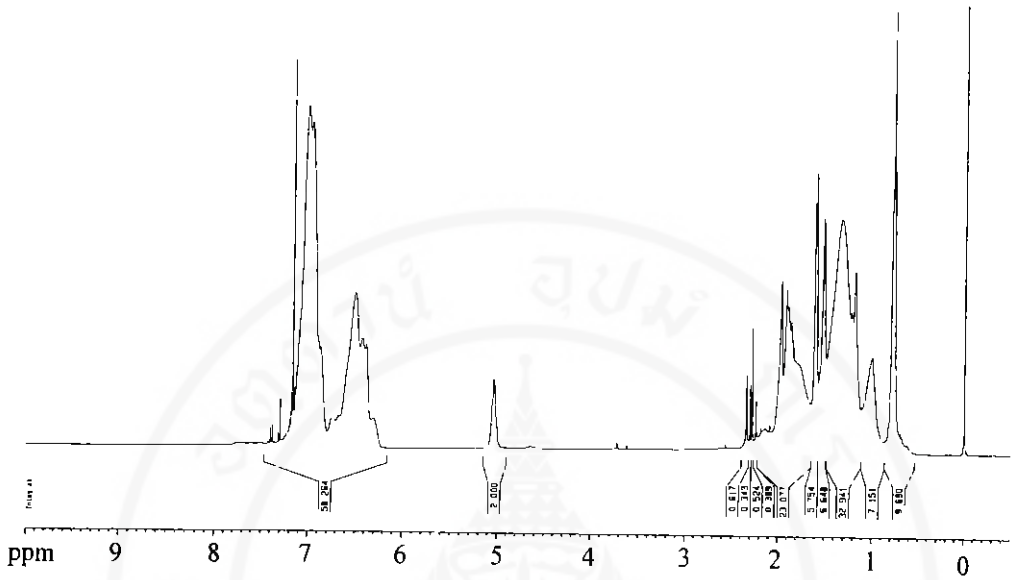
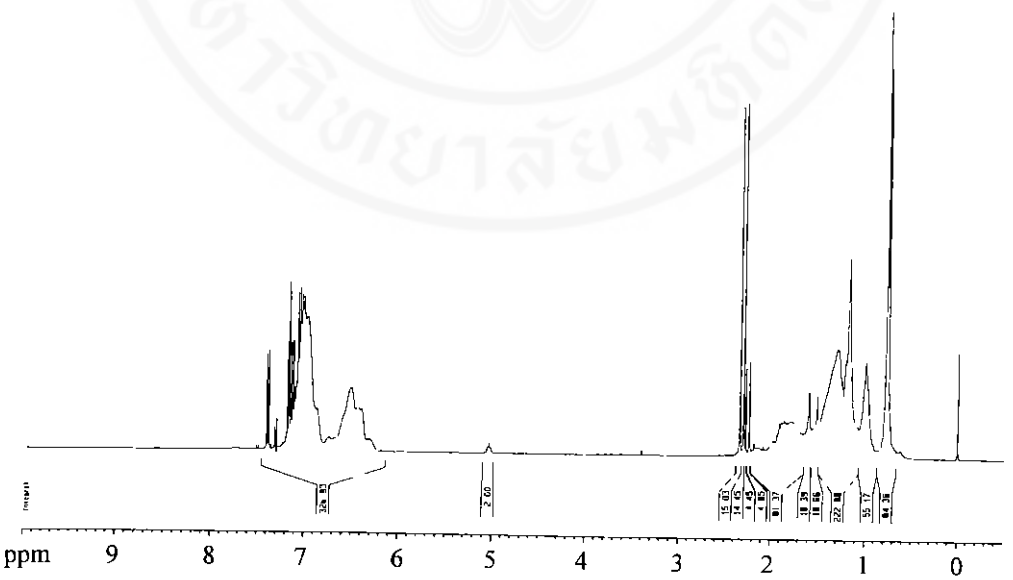


HIS1(1)



HIS1(2)

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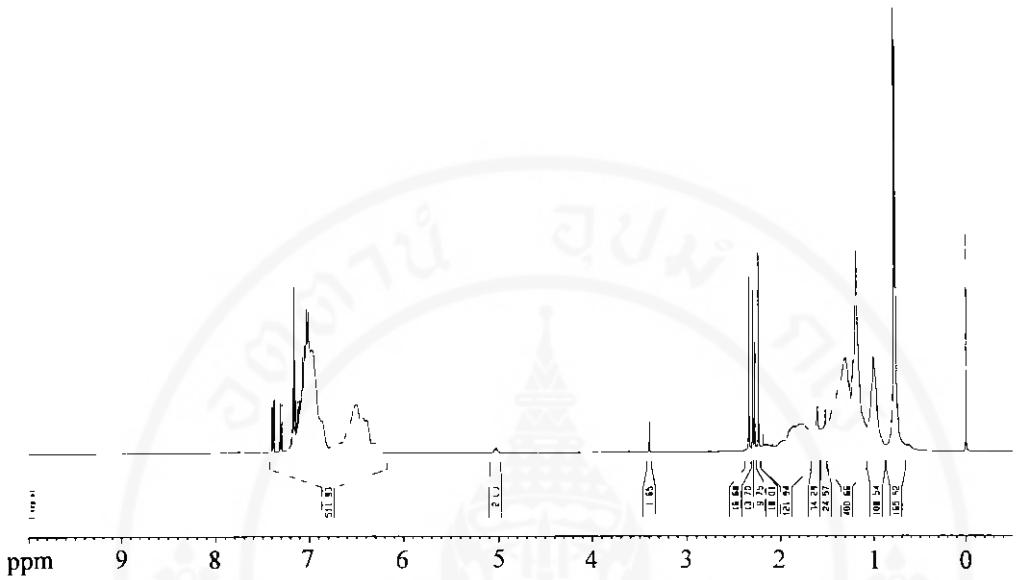
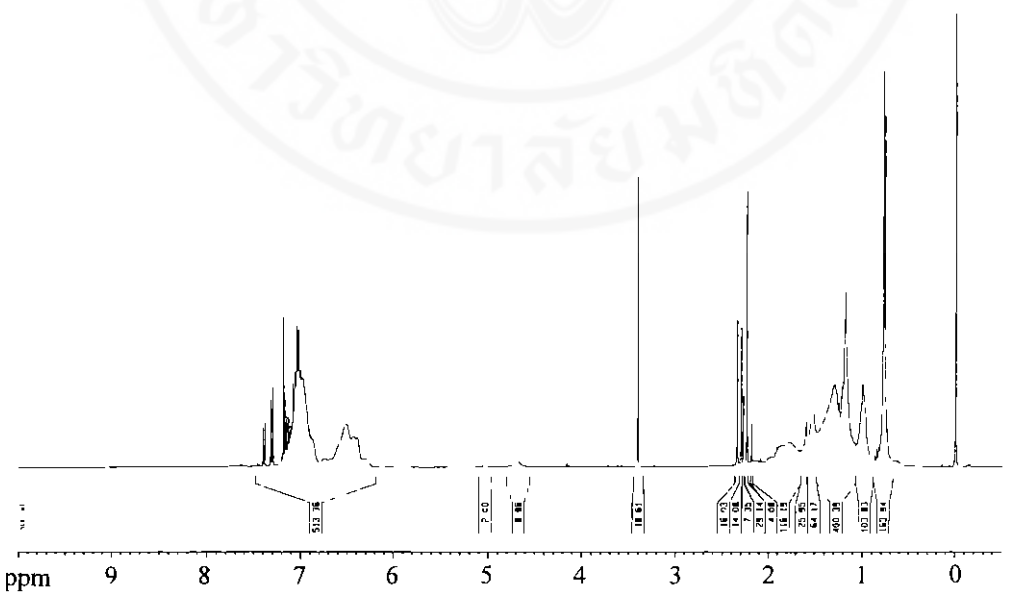
Figure 3.12 ^{1}H-NMR spectra of HIS1(1), HIS1(2), HIS1(3) and HIS1(4)



HIS1(3)



HIS1(4)

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Figure 3.12 ^{1}H-NMR spectra of HIS1(1), HIS1(2), HIS1(3) and HIS1(4) (cont.)

The percentage of hydrogenation was calculated from equation 11 in section 2.8 1. by comparing the relative integral area of proton adjacent to C=C of polyisoprene and aromatic proton of polystyrene. The results of four experiments are also shown in Table 3.13. From these data, it could be deduced that percentage of hydrogenation increase when TSH/db mole ratios were increased. Theoretically, 1 1 mole ratio should give complete hydrogenation but in the case of HIS(1), it gave only about 85% hydrogenation. The reason could be that IS consisted of high amount of 1,4- cis isomer which is much more steric hindrance than the trans-isomer in syn-addition mechanism of diimide generated from TSH. Another reason could be attributed to the high reactivity of diimide and only its syn form can react with C=C of isoprenic unit. For TSH, at the decomposition temperature, the diimide will react with double bonds of polymer in hydrogenation reaction. The diimide can also undergo disproportionation giving nitrogen and hydrazine as shown below. This second reaction is faster than the first one, i e $k_2 > k_1$.

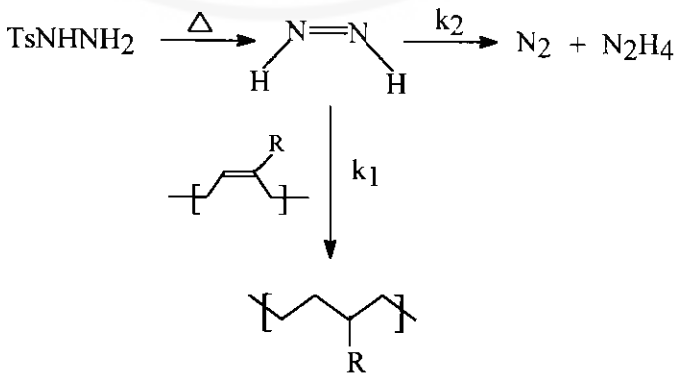

Figure 3.13 Competition reaction occuring in hydrogenation using diimide. k_1 : rate constant of hydrogenation of polyisoprene and k_2 : disproportionation rate of diimide ($k_2 > k_1$)

As it was reported that mole ratio of 4.1 gave a complete hydrogenation of synthetic cis-1,4-polyisoprene(36), in our case hydrogenation of IS gave hydrogenation of 98%. It may be resulted from stiffness of polystyrene parts that restricted the hydrogenation reaction(22). It was likely found that no drastic change of % hydrogenation was observed between mole ratio of TSH/db at 4:1 and 6:1 when IS ($\overline{M}_n = 5.7x10^3$) was used as a starting material. It was found disadventageously that higher amount of TSH caused more appearance of by-product shown by ^{1}H-NMR signal at 2.3 ppm. The higher TSH/db the mole ratio, the stronger the signal Therefore, the mole ratio chosen to hydrogenate further was 4:1 because it gave almost the highest percentage of hydrogenation whereas 6:1 mole ratio gave about the same percentage of hydrogenation as that of 4:1 mole ratio. Additionally, 4:1 mole ratio is more economical than 6:1 mole ratio. Then, the condition of hydrogenation using TSH/db equal 4:1 mole ratio compromised between percentage of hydrogenation and impurity contamination.

3.3.3 Hydrogenation of Various Molecular Weights of Poly(isoprene-b-styrene)

Various ranges of molecular weight of isoprene-styrene block copolymers synthesised in section 3.2.3 have been used in this section, i e. MIS1, MIS2, MIS3 and MIS4. They were hydrogenated using TSH/db mole ratio equal to 4.1, polymer concentration of 2 % and following the procedure described in section 2 5. The hydrogenation conditions of mixed polymers were shown in Table 3.14. The

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hydrogenated products obtained were symbolised as HMIS1, HMIS2, HMIS3 and HMIS4

Table 3.14 Condition of hydrogenation of mixed isoprene-styrene block copolymers using TSH/db mole ratio of 4:1

Sample	$\overline{M}_n$[a] ($\times 10^3$)	% I:S [b]	db (mole)	TSH (mole)	polymer (g)	TSH (g)
HMIS1(1)	6.1	55:45	0.162	0.648	20 0	120.68
HMIS1(2)	6.1	55:45	0.162	0.648	20 0	120.68
HMIS2	4.5	44:56	0.129	0 518	20.0	96 47
HMIS3	8.1	51:49	0.150	0.600	20 0	111 74
HMIS4(1)	16.2	43:57	0 125	0.501	20 0	93.30
HMIS4(2)	16.2	43:57	0.125	0.501	20 0	93.30

a : measured using GPC , b . calculated from ^{1}H-NMR

It was found in section 3 3.2 that the data obtained from ^{1}H-NMR and IR techniques indicated impurity contamination of TSH by-product in the hydrogenated products. This would affected on calculation of the percentage of hydrogenation because benzene ring signal of TSH by-product must have been included in the signal of polystyrene. It is therefore necessary to purify the hydrogenated products. So, the hydrogenated products were repeatedly precipitated in methanol before

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characterisation. It was found that the by-products could be gradually removed from the hydrogenated products. This will be discussed in section 3.3.6.2.

3.3.3.1 Structural Characterisation

The purified hydrogenated products were analysed using IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. IR spectra of hydrogenated products obtained from various molecular weights of starting copolymer indicated the appearance of unhydrogenated isoprene units at the characteristic peaks of 1,4-PI at 1665 and 840 cm^{-1} which belong to C=C stretching and =C-H deformation as shown in Figure 3.14 The disappearence of absorption peaks at 810, 1079, 1141 cm^{-1} due to signal of SO_2 belonging to TSH by-product(52) was detected.

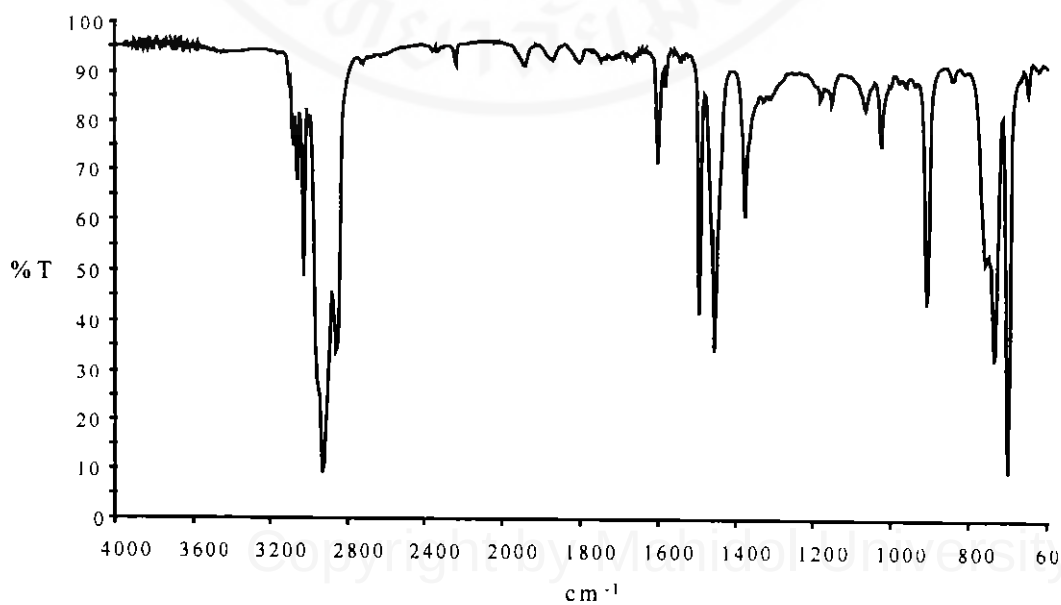

Figure 3.14 IR spectrum of purified hydrogenated product (HMIS3)

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^{1}H-NMR and ^{13}C-NMR spectra of hydrogenated products were illustrated in Figures 3.15 and 3.16 respectively The assignments of ^{1}H-NMR and ^{13}C-NMR were shown in Table 3.15. From ^{1}H-NMR spectra, the signal of proton adjacent to C=C at 5.1 ppm was also observed. It could be seen that no signal of impurity contamination from ^{1}H-NMR signal at 2.3 ppm. was observed.

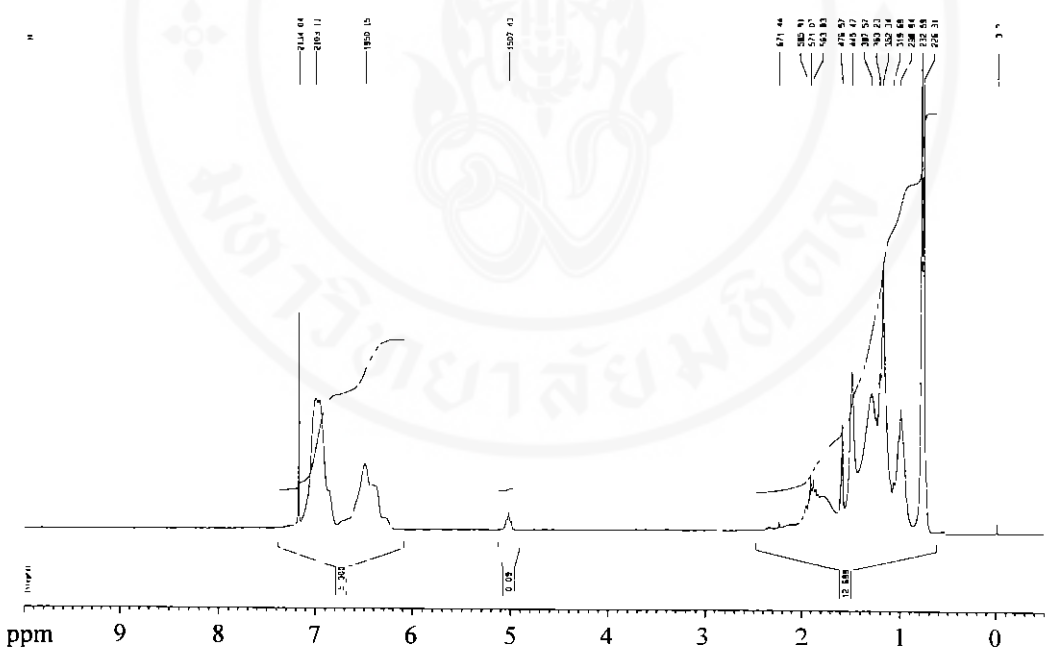

Figure 3.15 ^{1}H-NMR spectrum of purified hydrogenated product (HMIS(2))

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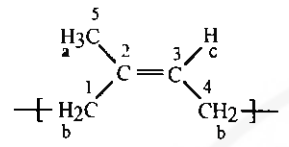
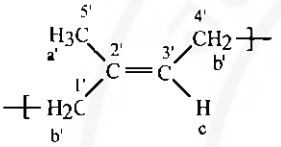
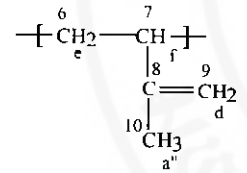
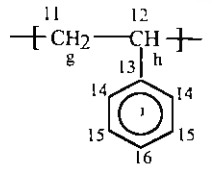
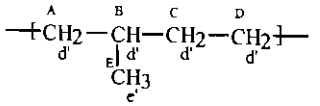
Table3.15 ^{1}H-NMR and ^{13}C-NMR assignments of hydrogenated isoprene-styrene block copolymer

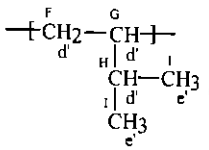












^{1}H-NMR (ppm)			^{13}C-NMR (ppm)		
label	reference*	observed	label	reference*	observed
a	1 68	1 67	1	32 3	32 2
a′	1 60	1 61	1′	39 7	39 8
b	2 03	2 03	2	135 6	135 3
b′	1 96	1 97	2′	135 2	135 2
c	5 11	5 12	3	125 3	125 0
d′	1 25	1 30	3′	124 8	124 3
e′	0 84	0 88,0 91	4	26 5	26 4
g	1 00-2 50	1 36	4′	28 6	26 6
h	o	–	5	23 4	23 4
i	6 50-7 05	7 02,6 51	5′	16 0	16 0
			11	113 4	–
			12	137 0	135 3
			13	137 4	–
			14	126 0	125 6
			15	128 2	128 0
			16	127 5	127 7
			A	37 9	37 5
			B	33 2	32 7
			C	37 9	37 5
			D	24 9	24 5
			E	20 0	19 8
			F-I	o	–

*reference 21, 38 and 47 o overlapped

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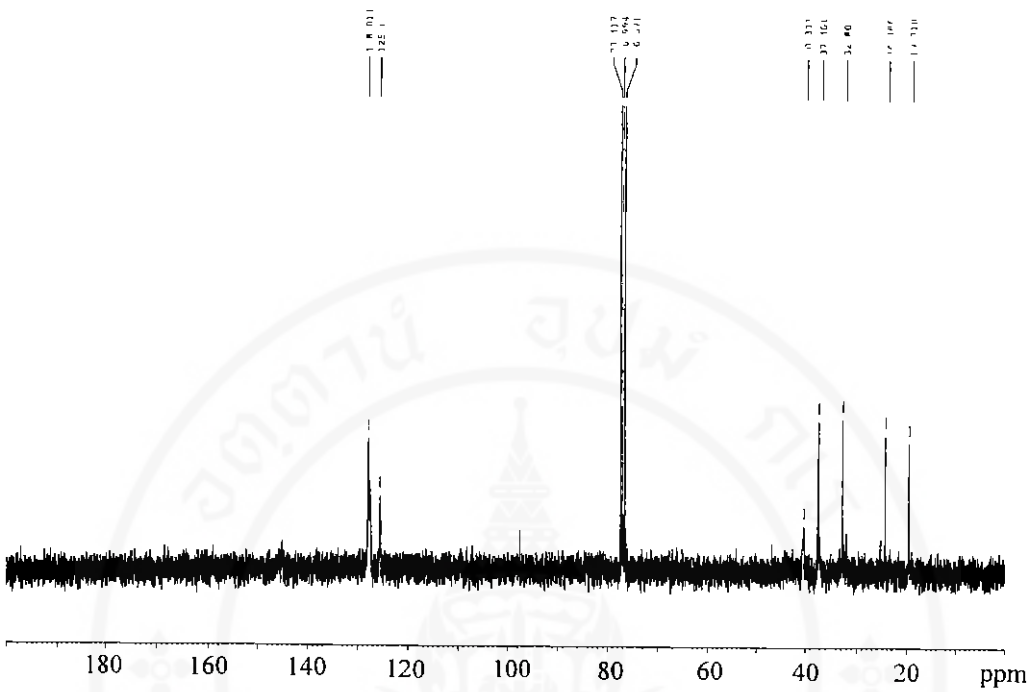

Figure 3.16 ^{13}C-NMR spectrum of purified hydrogenated product (HMIS(3))

3.3.3.2 Comparison of Various Techniques in Determination of Degree of Hydrogenation

The percentage of hydrogenation (%H) of purified hydrogenated products were analysed using ^{1}H-NMR spectroscopy, IR spectroscopy and Iodine value(I.V). The results are given in Table 3.16. %H can be calculated from ^{1}H-NMR spectroscopy by comparing relative signal area of proton adjacent to C=C of isoprene units at 5.1 ppm. with that of aromatic proton of styrene units at 6 5-7.2 ppm before and after hydrogenation using equation 11 described in section 2.8 1 The corresponding data are listed in Appendix D(1D). Comparison of absorption peaks at 840 and 889 cm^{-1}, due to 1,4-and 3,4-isoprene units, with 1601 cm^{-1}, due to styrene

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units, before and after hydrogenation (see Appendix D(2D)) could also be used to determine %H of hydrogenated poly(isoprene-b-styrene). The %H was calculated from equation 13, section 2.8.3.

Section 3.2.4 showed that I.V. can be used to quantify the degree of unsaturation of isoprene unit in the block copolymer. Therefore, the comparison between the I V. of the starting material and that of the modified product should be considered to be another analytical technique to evaluate the degree of hydrogenation of the isoprene-styrene block copolymers. Equation 12 described in section 2.8.2 shows simple calculation of the degree of hydrogenation via I.V. method. All data obtained from I.V. measurements are shown in Appendix D(3D).

Table 3.16 % Hydrogenation of mixed isoprene-styrene block copolymers (MIS) determined by ^{1}H-NMR , IR and Iodine Value (I.V.)

Sample	$\overline{M}_n^a$ (x10^3)	%H by ^{1}H-NMR	%H by IR	%H by I.V
HMIS1(1)	6 1	85.0	92.3	75.5
HMIS1(2)	6.1	83.6	91.3	74.4
HMIS2	4 5	87.7	90.5	67.0
HMIS3	8.1	85.3	85.5	74.3
HMIS4(1)	16.2	67.3	89.9	71.9
HMIS4(2)	16.2	77.3	92.1	72.2

a: Mixed isoprene-styrene block copolymer, measured by GPC

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It is shown in Table 3.16 that the percentage of hydrogenation determined by different techniques are different The results show no significant relationship between %H and MW among all techniques. It was found that %H of HMIS1 and HMIS4 determined by ^{1}H-NMR technique were about 85 and 70 whereas the results from I.V gave %H of 76 and 72 respectively. It seemed that the higher molecular weight of the copolymer, the lower %H was found by ^{1}H-NMR. ^{1}H-NMR and IR techniques used the relative integral area of two different peaks of isoprene and styrene units. Therefore, error from measuring the integral area might be obtained. For I.V. technique, error in determination of degree of unsaturation of isoprene units in the block copolymer can be occurred from titration process, hence three different titration experiments had been carried out and the averaged results were taken in consideration Similar result was obtained by I V. that %H of HMIS4 is lower than HMIS1 even though the same mole ratio of TSH/db were used. Consequently, the comparison of %H can be used in a certain technique but the results could not be compared in different techniques

3.3.4 Molecular weight and Molecular weight Distribution of the Hydrogenated Products

Molecular weight and molecular weight distribution of hydrogenated products were determined by GPC. The comparison of $\overline{M}_n$, $\overline{M}_w$ and MWD is shown in Table 3.17. An example of chromatogram of hydrogenated polymer (MIS3) is shown in Figure 3.17. When hydrogenation reaction of poly(isoprene-b-styrene)

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(MIS) was carried out at high temperature, it was believed that another type of by-product released from TSH is *p*-toluenesulphonic acid. Some side reactions probably could be occurred such as degradation and cyclisation. Both side reactions can affect on the changes of molecular weight and molecular weight distribution Generally, chain cleavage is believed to cause the changes of molecular weight rather than cyclisation as the reaction was investigated at rather high temperature(36). However, if TSH by-product is an acid, protonation of isoprene units by the acid by-product could be possible to form carbonium ion at tertiary carbon which underwent cyclisation(53) but no evidence of cyclised product from IR absorption peak at 1450 cm^{-1} (18) has been detected.

In this study, it was found that molecular weight of hydrogenated polymers were slightly different from those of the original polymers It could not be concluded that the little changes of molecular weight were caused by cyclisation rather than degradation because of no evidence of cyclisation from spectroscopic analysis. Hahn (28) also reported that it was still doubtful whether the changes in molecular weight of hydrogenated polyisoprene from TSH-by product or thermal reaction.

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Table 3.17 Molecular weight and molecular weight distributions of poly(isoprene-styrene) before and after hydrogenation

Sample	$\overline{M}_n$ (x 10^3)		$\overline{M}_w$ (x 10^3)		MWD	
	Before	After	Before	After	Before	After
MIS1(1)	6.1	4.8	8.9	13.4	1.65	2.79
MIS1(2)	6.1	5.2	8.9	11.9	1.65	2.30
MIS2	4.5	5.6	7.4	9.2	1 66	1.64
MIS3	8.1	10.9	15.5	16.4	1.89	1.50
MIS4(1)	16 2	15.1	33.4	36.2	2.06	2.40
MIS4(2)	16.2	14.1	33 4	24.0	2.06	1.69

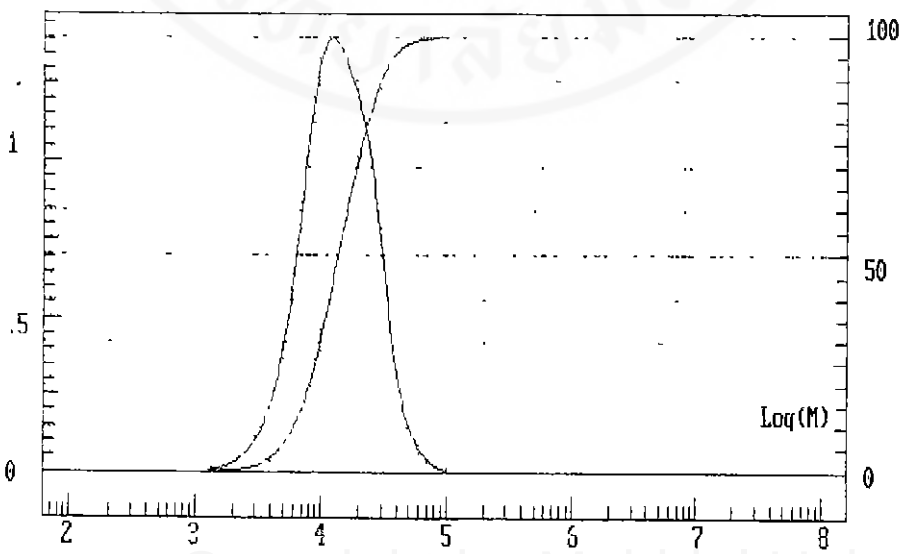

Figure 3.17 GPC chromatograms of hydrogenated polymer (HMIS3)

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3.3.5 Thermal Characterisation

It has been known that dienic polymers cannot resist high temperature treatment because their unsaturation in the molecular structure could initiate degradation reaction through formation of radical at allylic position of the double bonds. In the case of isoprene-styrene block copolymer, the modification by hydrogenation reaction should increase the thermal stability of the modified product as the degree of unsaturation decreased. Thermal behavior of hydrogenated poly(isoprene-b-styrene) was analysed using TGA and DSC techniques. The measurement of resistance to heat before it was decomposed was recorded on TGA and heat required to give molecular deformation of polymers, i.e T_g, was recorded on DSC. It was found that hydrogenated block copolymers possessed higher thermal stability as depicted by the thermograms in Appendix E(3E). T_g of the hydrogenated copolymers is also higher than that of the original products. The results of T_g are shown in Table 3.18 and DSC chromatograms of hydrogenated copolymers and initial block copolymers are shown in Appendix E. It was clearly noticed that T_g of hydrogenated block copolymers increased about 10-20°C when compared with that of original block copolymers. The increase in T_g resulted from the higher amount of saturated chains which allowed close arrangement of polymer chains. Therefore, they required more energy to move. In addition, the trans-microstructure obtained by cis-trans isomerisation of residual double bonds (described in section 3 3 6.1) may also result in the augmentation of T_g.

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Table 3.18 Glass transition temperature of poly(isoprene-b-styrene) before and after hydrogenation.

Sample	T_g (°C)	
	Before hydrogenation	After hydrogenation
MIS1(1)	42	65
MIS1(2)	42	69
MIS2	53	62
MIS3	46	69
MIS4(1)	52	64
MIS4(2)	52	60

However, the influence of molecular weight of hydrogenated block copolymers on thermal property, i.e. T_g was not clearly seen because there was neither much different in molecular weight among hydrogenated block copolymers nor the degree of hydrogenation. There is not any extra-endothermic peak from DSC chromatogram of the hydrogenated block copolymer, therefore this can be used to confirm that no cyclisation reaction is occurred or if it is, it should be very small percentage that could not effect on thermal property of the final products.

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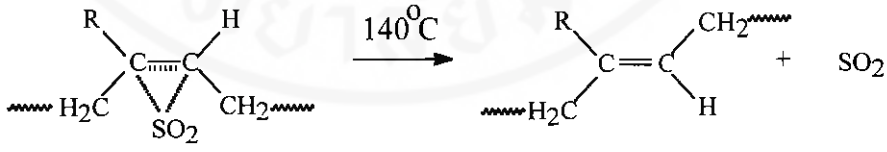
3.3.6 Determination of Secondary Reaction

3.3.6.1 Cis-trans Isomerisation

Cis-trans isomerisation of unsaturated hydrocarbon polymers occurred in many ways such as photo-induced, radiation-induced, catalytic and thermal isomerisation(53). For 1,4-polyisoprene, catalytic cis-trans isomerisation has been carried out using thiol acids, sulfur dioxide and related materials as catalysts. It was also reported that thio-compound catalysts such as SO_2 involved likely as reversible addition to double bonds. Isomerisation was occurred via formation of unstable complex at 140°C as shown below(53). This isomerisation is very clean and uncontaminated by adducts



It has also been reported that 1,4-PB undergoes thermal uncatalysed cis-trans isomerisation whereas 1,4-PI does not (53). Therefore, in our case, it can be deduced that cis-trans isomerisation of residual double bonds in 1,4-PI could be occurred totally from catalysed cis-trans isomerisation by thiol containing by-product. So, the ratio of residual double bonds of isoprene to styrene units in the hydrogenated products were re-analysed to compare with that of the starting materials. The results

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concerning cis-trans isomerisation of the residual double bonds are shown in Table 3.19. It was found that the amount of trans-isomer of isoprene units increased significantly whereas trans-1,4-polyisoprene were hydrogenated more than cis-1,4-polyisoprene as reported by Thanomsilp(36). It can be concluded that there has been cis-trans isomerisation of poly(isoprene-b-styrene) during hydrogenation reaction with TSH. These results are in accordance with several works (28, 31, 32) showing that cis-trans isomerisation of both polybutadiene and polyisoprene could occur during hydrogenation using TSH.

Table 3.19 Determination of cis-trans isomerisation of hydrogenated products calculated from ^{1}H-NMR data (Appendix A(3A))

Sample	Before hydrogenation		After hydrogenation	
	%Cis	%Trans	%Cis	%Trans
MIS1(1)	75.0	25.0	64.5	35.5
MIS1(2)	75.0	25.0	64.5	35 5
MIS2	76.0	24.0	33.3	66.7
MIS3	75.4	24.6	23.1	76.9
MIS4(2)	75.8	24.2	39.7	60.3
MIS4(2)	75 8	24.2	42.9	57.1

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3.3.6.2 Impurity Contamination

Impurity contamination on hydrogenated block copolymer could come from the by-product generated from TSH, i.e. *p*-tolyl *p*-toluenethiosulphonate acid It is not practical to observe the by-product from the signal from ^{1}H-NMR of benzene ring because isoprene-styrene block copolymers are composed of styrene units. Therefore, the contamination can be detected from signals of other groups i.e SO_2 and *p*-tolyl group which were differentiated by IR and ^{1}H-NMR spectra as described in section 1.3.4. In the case of IR technique, the signal of SO_2 can be revealed both asymmetric and symmetric stretching at absorption peaks of 1321 and 1141 cm^{-1} respectively as shown in Figure 3.18. The peak at 1079 cm^{-1} is assigned to C-S deformation and at 810 cm^{-1} is assigned to C-H rocking of *p*-tolyl group(28, 31). These signals are not seen in spectra of original polymers.

From ^{1}H-NMR shown in Figure 3.19, the resonance signals of methyl protons of *p*-tolyl group at 2.3 ppm (28) were detected. Many workers (28, 31, 32) believed that these by products were incorporated to double bonds of isoprene units. In contrast, after purification of hydrogenated products by separating dissolution in hexane in which the by-products could not be dissolved, filtering through sintered glass packed with aluminum base and re-precipitating in methanol, the signal of impurity were reduced. These signals completely disappeared after hydrogenated products were purified twice or three times. So, it could be deduced that by-products did not attack to double bonds but they contaminated to hydrogenated products.

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Figures 3.18 and 3.19 revealed IR and ^{1}H-NMR spectra showing the sequence in purification of hydrogenated IS , respectively

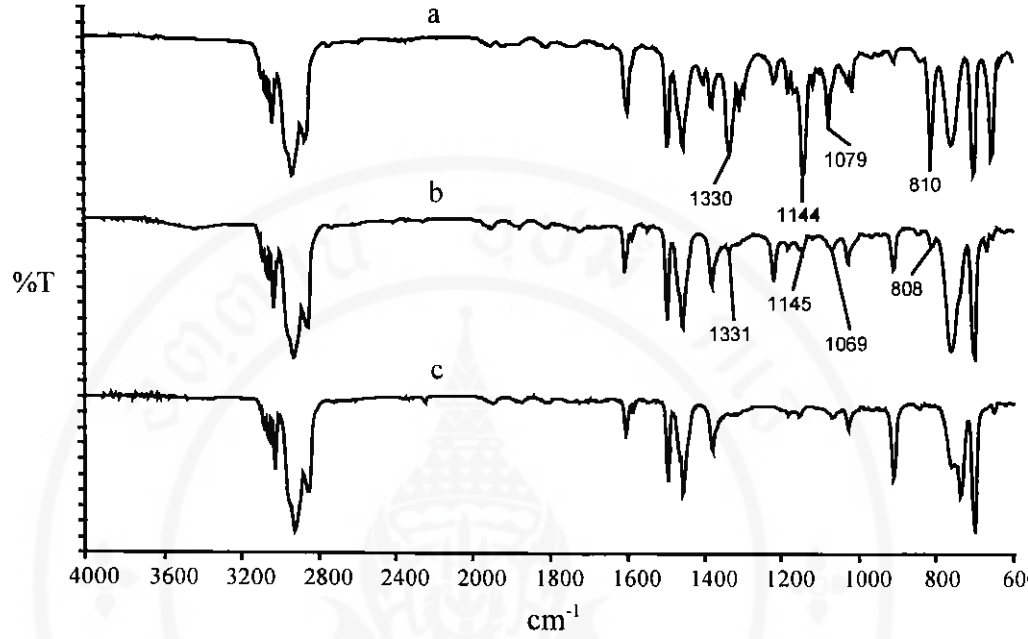
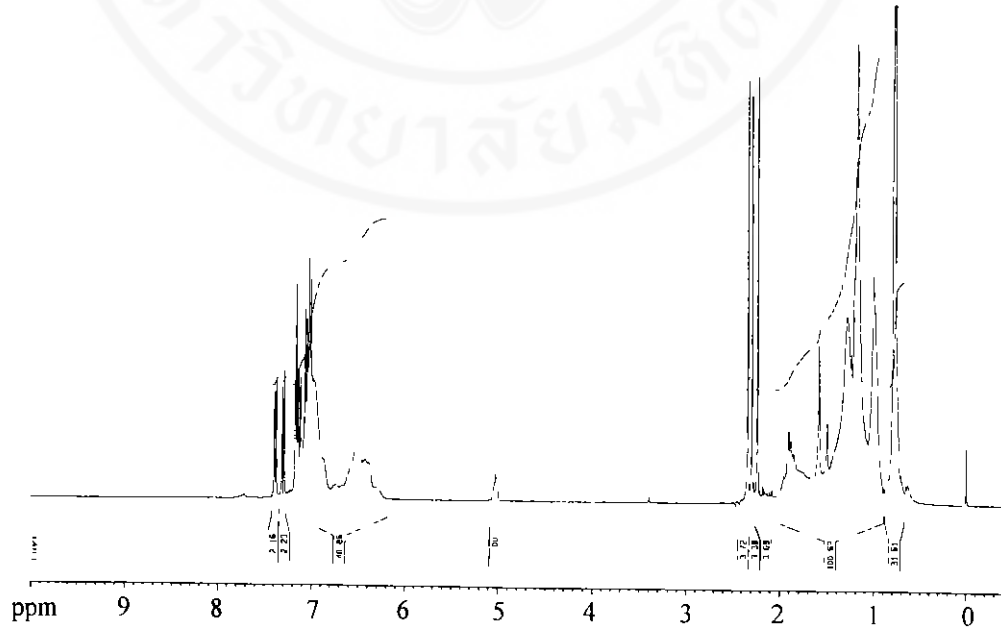


Figure 3.18 IR spectra of hydrogenated product(HMIS3) ; a : before purification, b . first purification, c : second purification.



(a)

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Figure 3.19 ^{1}H-NMR spectra of hydrogenated product(HMIS3) ;(a) :before purification, (b) :first purification, (c) :second purification.

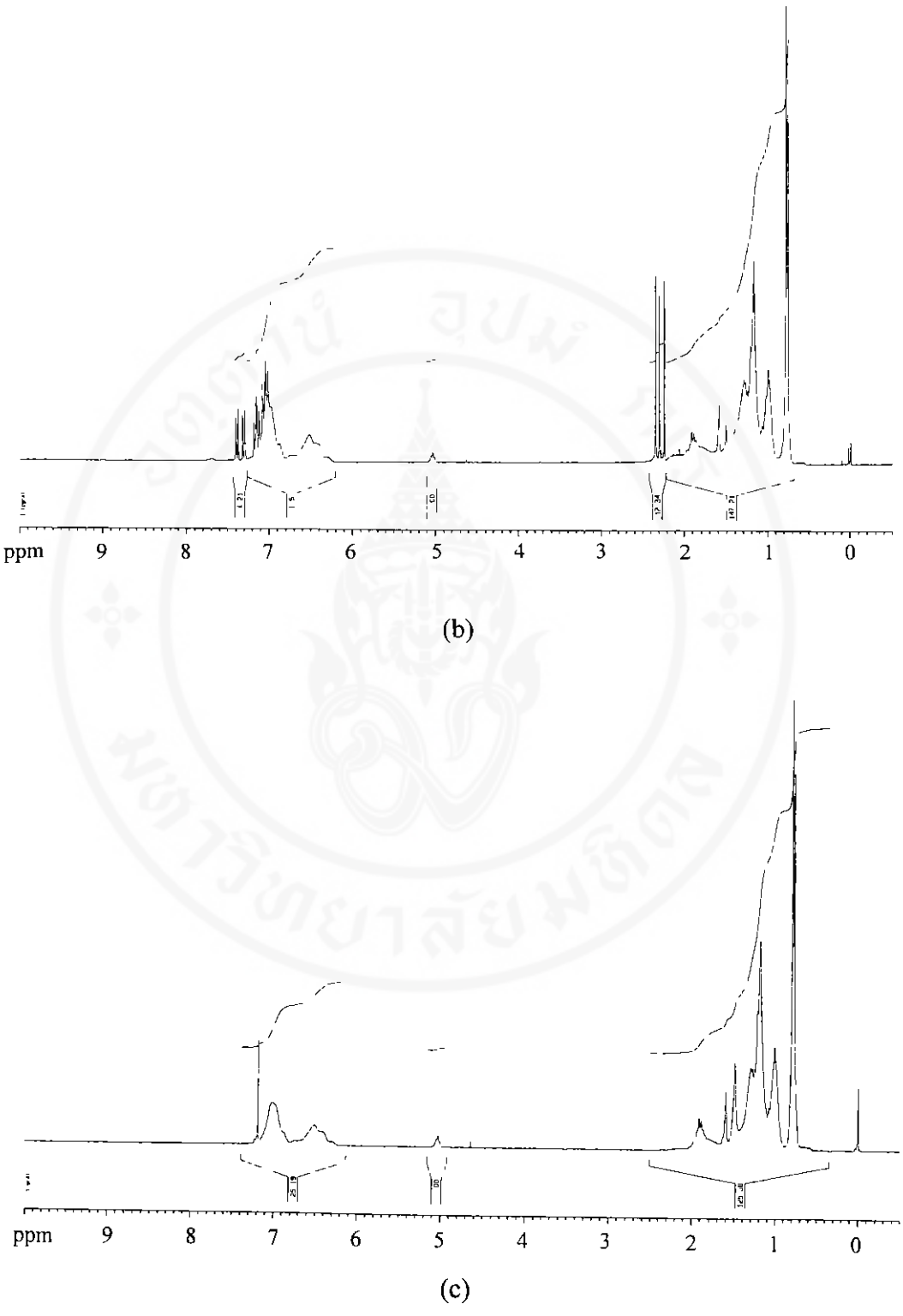

Figure 3.19 ^{1}H-NMR spectra of hydrogenated product(HMIS3) ; (a) :before purification, (b) :first purification, (c) second purification (cont.).

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Another evidence that assured this conclusion was the results from GPC. The chromatogram of unpurified hydrogenated products in Figure 3.20 showed two separate peaks, hydrogenated product's at lower elution time and by-product's at higher elution time. If by-products attacked the molecular chain of the block copolymer during hydrogenation reaction, it would result in bimodal peak because of different hydrodynamic volume of by-product unincorporated and incorporated poly(isoprene-styrene). It was estimated that the elution peak that could be of by-product had molecular weight about 400 daltons which was somewhat close to that of TSH by-product. *p*-tolyl-*p*-toluenethiosulphonate which was believed to be by-product in this study has the molecular weight of 278.4 daltons. However, this evidence gave only preliminary conclusion that there is a small molecule mixed with polymer because of the limitation of separating ability of the GPC column which can separate in the range of 500 to 600,000 daltons.

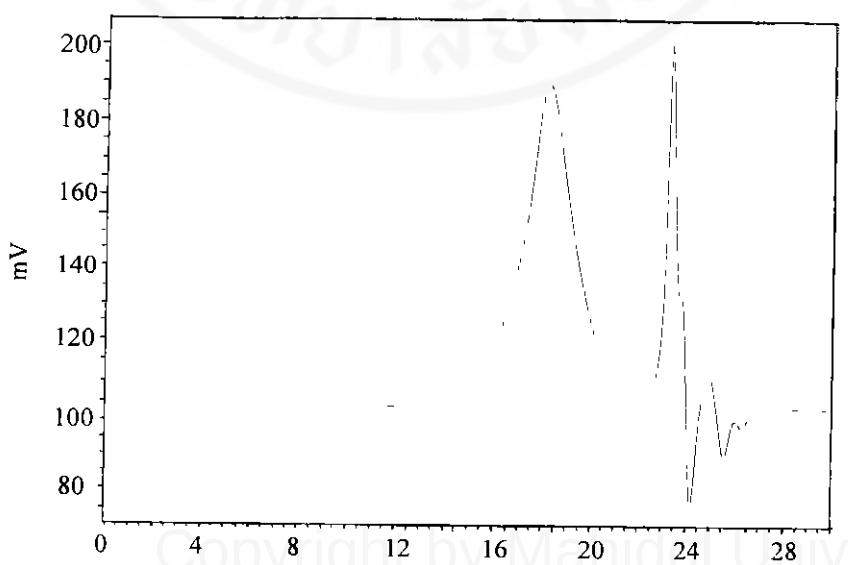

Figure 3.20 GPC chromatograms of unpurified hydrogenated product showing the impurity contamination

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The by-products collected from polymer solution after completion of reaction symbolised as A and seperation by hexane dissolution symbolised as B were analysed using IR, Raman, ^{1}H-NMR and ^{13}C-NMR. From these spectra, it was found that A had the same spectrum patterns as B in all test methods. It could be preliminarily concluded that A and B are alike. Edward et.al (52) investigated decomposition by-product of TSH in hydrogenation reaction of polybutadiene. The pyrolysis of TSH gave *p*-tolyl-*p*-toluenethiosulfonate by disproportionation. This postulation was coincident with the results of hydrogenated by-product in this study. It was deduced that by-product obtaining from hydrogenation of isoprene-styrene block copolymer was *p*-tolyl-*p*-toluenethiosulfonate. The assignment was shown in Table 3.20 and Table 3.21 for IR, Raman and ^{1}H-NMR, ^{13}C-NMR, respectively. The IR, Raman and ^{1}H-NMR, ^{13}C-NMR spectra were also revealed in Figures 3.21, 3 22, 3.23, and 3.24, respectively

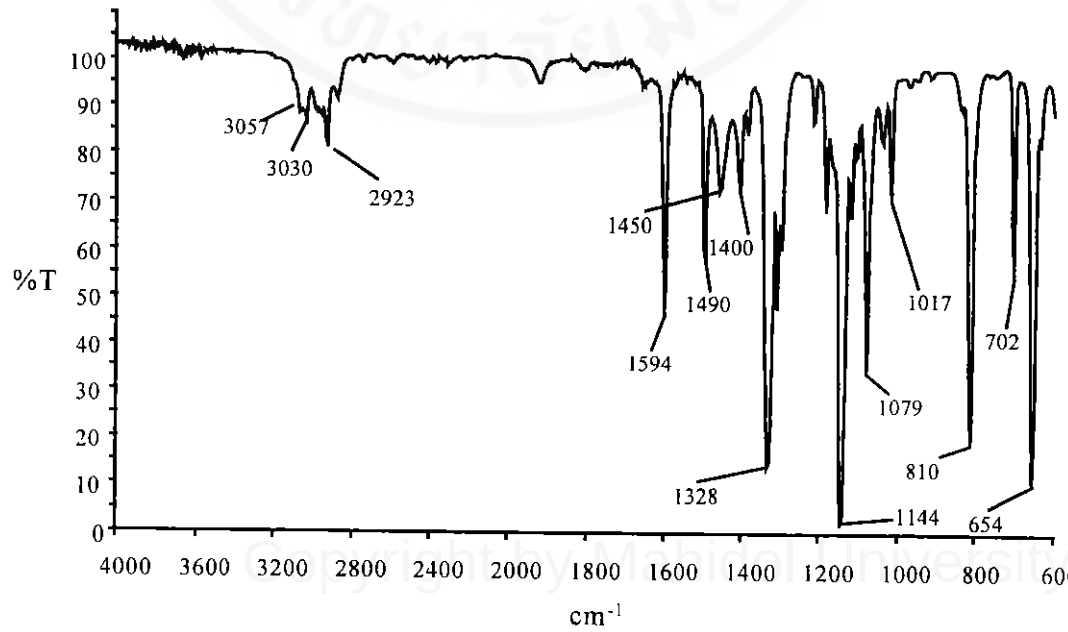

Figure 3.21 IR spectrum of TSH by-product in the hydrogenation using diimide

Table 3.20 IR and Raman assignment of hydrogenated by-product

IR (cm^{-1})		Raman (cm^{-1})		assignment
Reference*	Observed	Reference*	Observed	
3055	3061	3075	3067	ν_s (C-H)
3036	3027	3060	3055	ν_a (C-H)
2918	2923	2900	2919	ν (C-H)
1593	1594	1595	1592	Aromatic ring stretching
1487	1490	1495	1489	Aromatic ring stretching
1450	1450			δ (CH_3)
1401	1400			δ_a (CH_3)
		1380	1373	δ_s (C–CH_3)
1321	1328	1320	1322	ν_a ((C)–SO_2–(S))
		1300	1302	δ (C–H)
		1220	1210	Aromatic ring stretching
1141	1144	1140	1135	ν_s ((C)–SO_2–(S))
1073	1079	1080	1087	ν_s (C–S)
1015	1017	1020	1001	ν_s (C–C)
812	810	800	798	Aromatic ring deformation
703	702			ν (C–S)
653	654			ρ (C–H)
		580	588	δ (SO_2)
		480	485	ν (S–S)
		462	441	δ (CSO)
		380	387	δ (CSS)
		360	364	δ (CSS)
		315	322	δ (CSO)

* . reference 52

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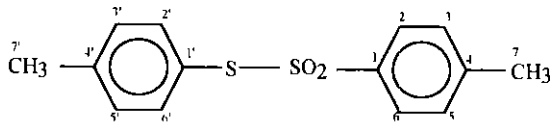
Table 3.21 ^{1}H-NMR and ^{13}C-NMR assignment of hydrogenated by-product

Structure :



Label	^{1}H–NMR (ppm)		multiplicity	Label	^{13}C–NMR (ppm)	
	Reference*	Observed			Reference*	Observed
2-H	7 55	7 50	d	C-1	139.86	140 4
3-H	7 35	7 30	d	C-2	129 74	127 5
5-H	7 35	7.30	d	C-3	131 67	129 3
6-H	7 55	7 50	d	C-4	149 21	144 6
7-H_3	2 48	2 48	s	C-5	131 67	129 3
2′-H	7 26	7 25	d	C-6	129 74	127 5
3′-H	7 21	7 20	d	C-7	22 05	21 6
5′-H	7 21	7 20	d	C-1′	124 27	124 5
6′-H	7 26	7 25	d	C-2′	138 74	136 4
7′-H	2 40	2.39	s	C-3′	132 47	130 2
				C-4′	146 25	142 0
				C-5′	132 47	130 2
				C-6′	138 74	136 4
				C-7′	21 81	21 4

* : reference 52

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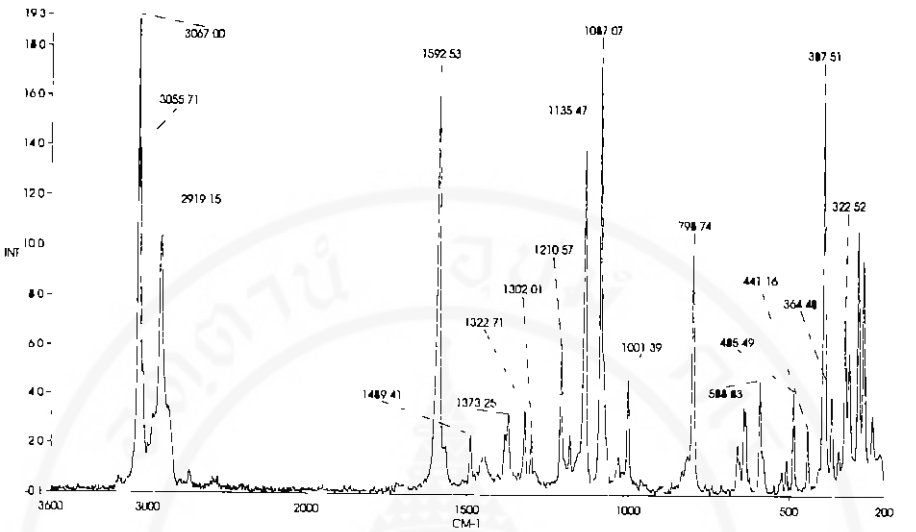

Figure 3.22 Raman spectrum of TSH by-product in the hydrogenation using diimide

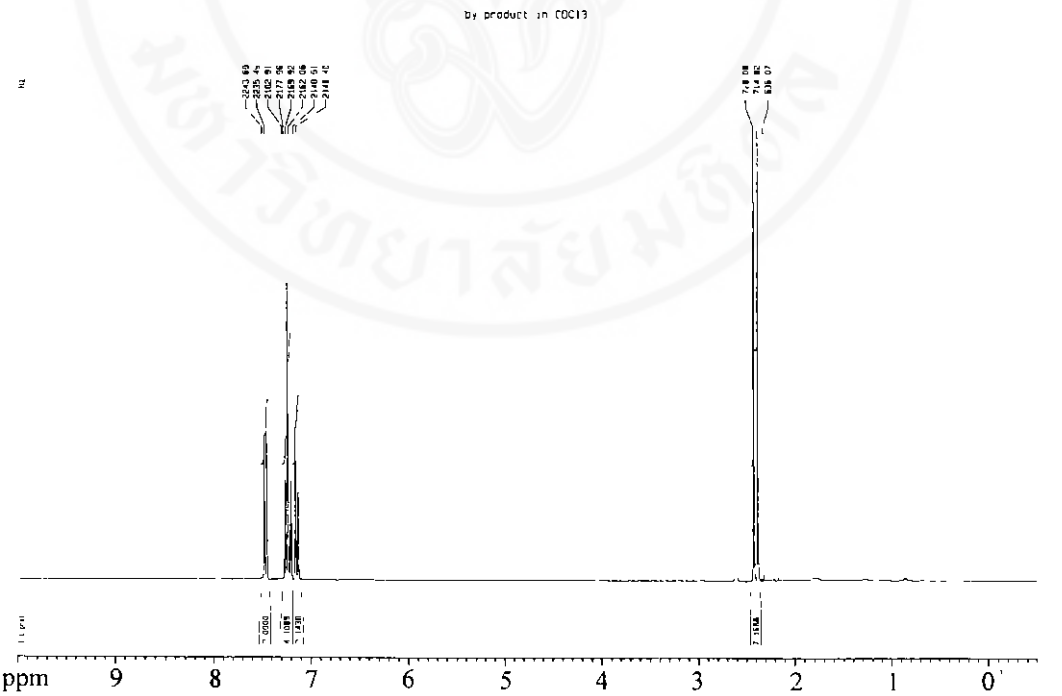

Figure 3.23 ^{1}H-NMR spectrum of TSH by-product in the hydrogenation using diimide

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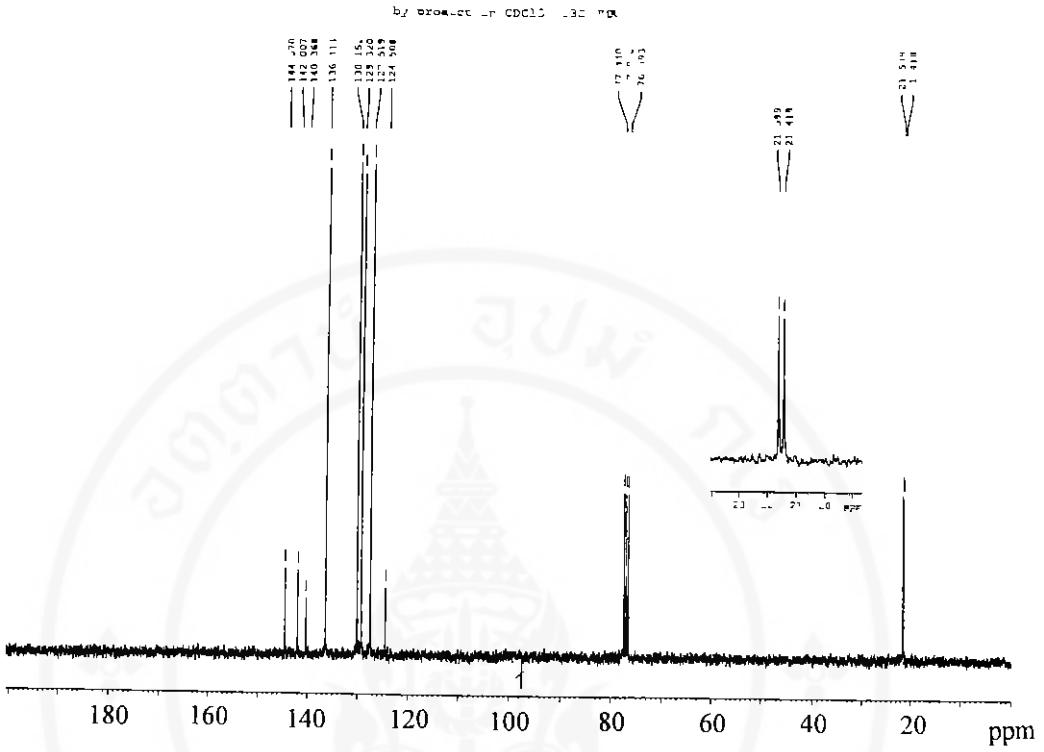

Figure 3.24 ^{13}C-NMR spectrum of TSH by-product in the hydrogenation using diimide

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CHAPTER IV

CONCLUSIONS

1. Homopolyisoprenes, homopolystyrenes and isoprene-styrene block copolymers can be synthesised by anionic polymerisation giving rather narrow MWD. The MW of polymer obtained can be estimated from the amount of monomer and initiator used.
2. The microstructure ratio of cis-1,4: trans-1,4: 3,4-polyisoprene determined using ^{1}H-NMR spectroscopy was found to be 70: 25: 5. Polystyrene prepared in this study was atactic polystyrene examined by IR spectroscopy. MW of homopolymers and block copolymers obtained were higher than the calculated MW. This could be due to the variation of concentration of *n*-BuLi which was reduced by oxygen or humidity.
3. Isoprene and styrene composition in the prepared block copolymer can be estimated from ^{1}H-NMR and I.V. techniques where the former measures the relative signal between isoprene and styrene but the latter measures the amount of double bonds by reacting with I_2. These two techniques gave results.
4. Non-catalytic hydrogenation using *p*-toluenesulphonyl hydrazide (TSH) of PI using TSH/db mole ratio as 2:1 gave partial hydrogenation in agreement.
5. Various mole ratios of TSH/db were investigated for hydrogenation of poly(isoprene-b-styrene). It was found that the ratio of TSH/db of 4:1 was the

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most appropriate to obtain polymer of high degree of saturation but moderate impurity contamination.

6. %Hydrogenation can be investigated from various techniques i.e ^{1}H-NMR, IR, I V. It was revealed that about 67 to 85 % hydrogenation of the modified product were obtained, depending on the technique utilised.
7. It was detected by ^{1}H-NMR that ratio of cis structure decrease after hydrogenation while trans structure is more favorable in this kind of reaction. There should be cis-trans isomerisation caused by SO_2 containing reagent
8. The evidence from IR, ^{1}H-NMR, ^{13}C-NMR and Raman spectroscopy revealed that by-product of hydrogenation using TSH was *p*-tolyl *p*-toluenethiosulphonate.
9. Thermal properties i.e. thermal stability and Tg of hydrogenated block copolymers were improved. T_g of hydrogenated copolymers is 10-20°C higher than that of original block copolymers.

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APPENDICES

APPENDIX A : ^{1}H-NMR and ^{13}C-NMR spectra

Appendix 1A : Amplification of ^{1}H-NMR spectra of polyisoprene(PI) for calculation of microstructure

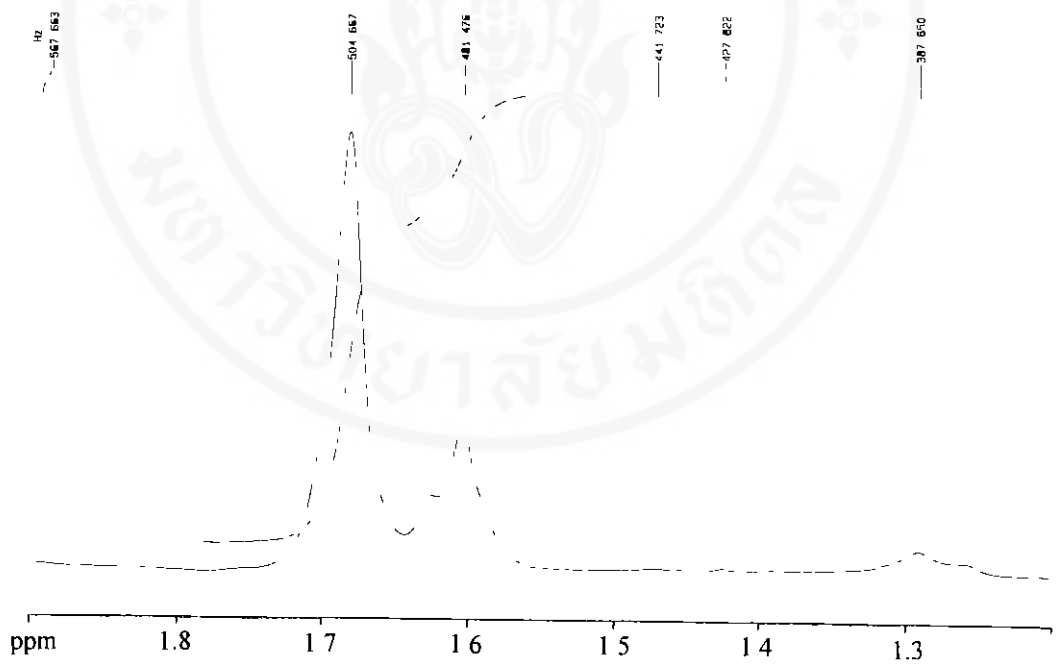

Figure 1A-1 ^{1}H-NMR of PI2

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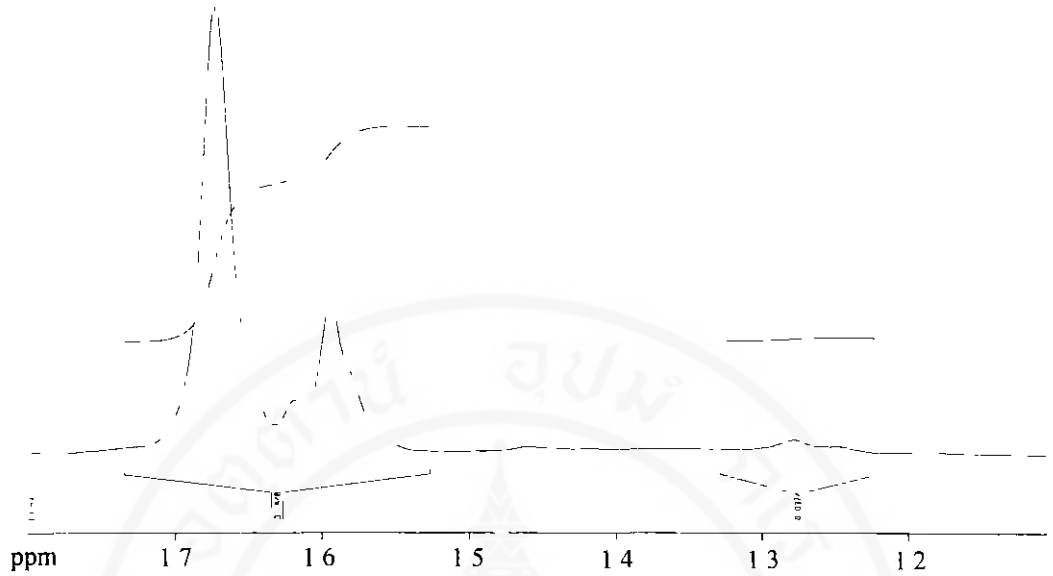

Figure 1A-2 ^{1}H-NMR of PI3

Appendix 2A : ^{1}H-NMR and ^{13}C-NMR spectra of mixed isoprene-styrene block copolymer(MIS)

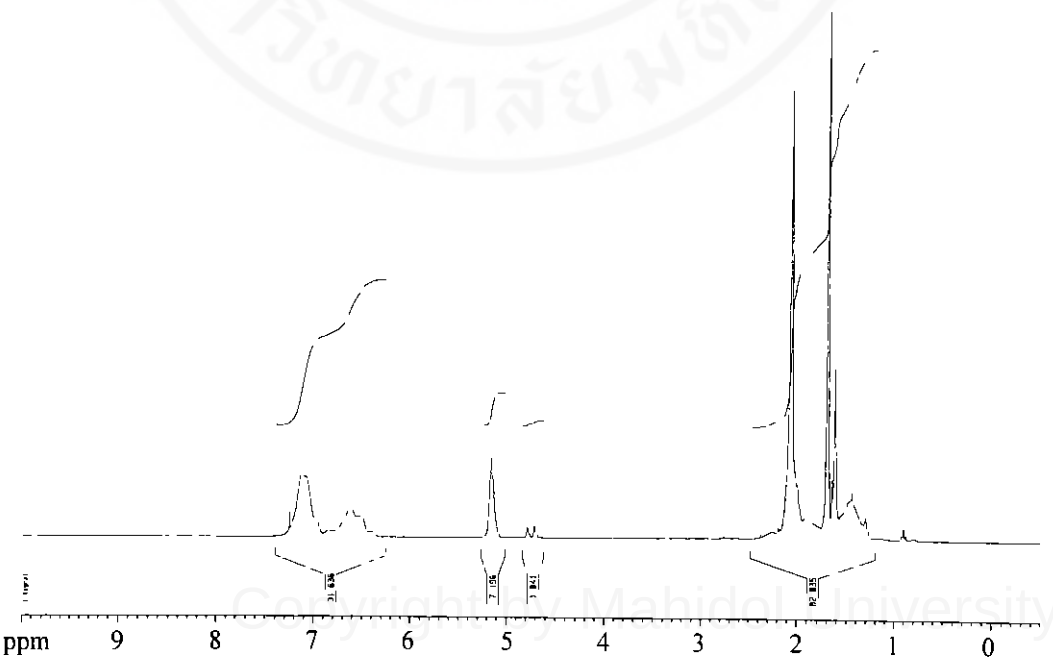

Figure 2A-1 ^{1}H-NMR spectra of MIS1

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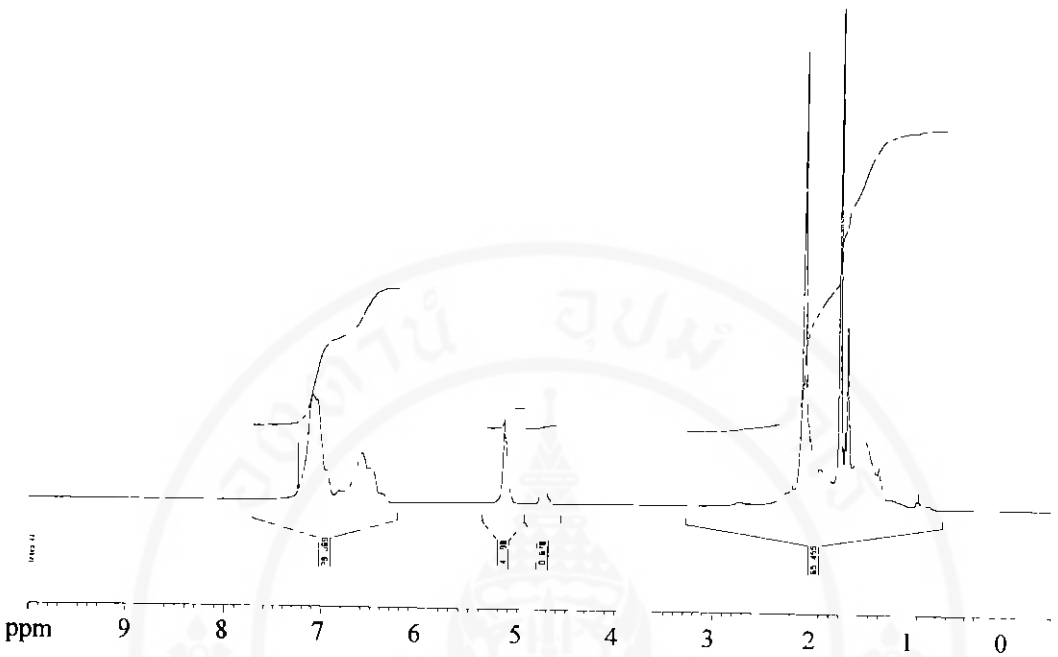

Figure 2A-2 ^{1}H-NMR spectra of MIS2

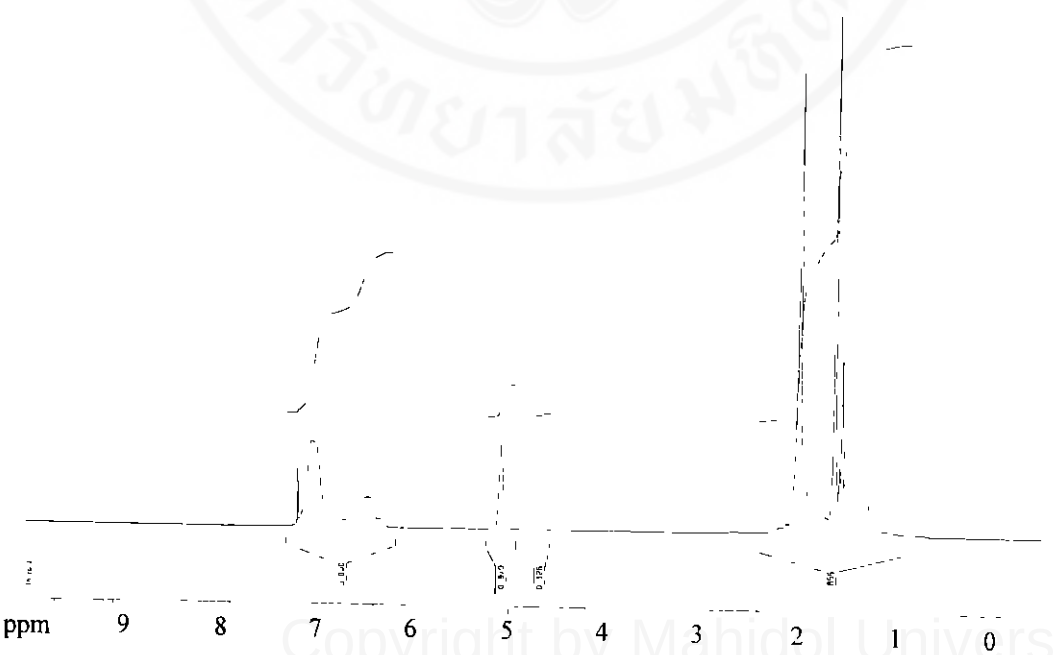

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Figure 2A-3 ^{1}H-NMR spectra of MIS3

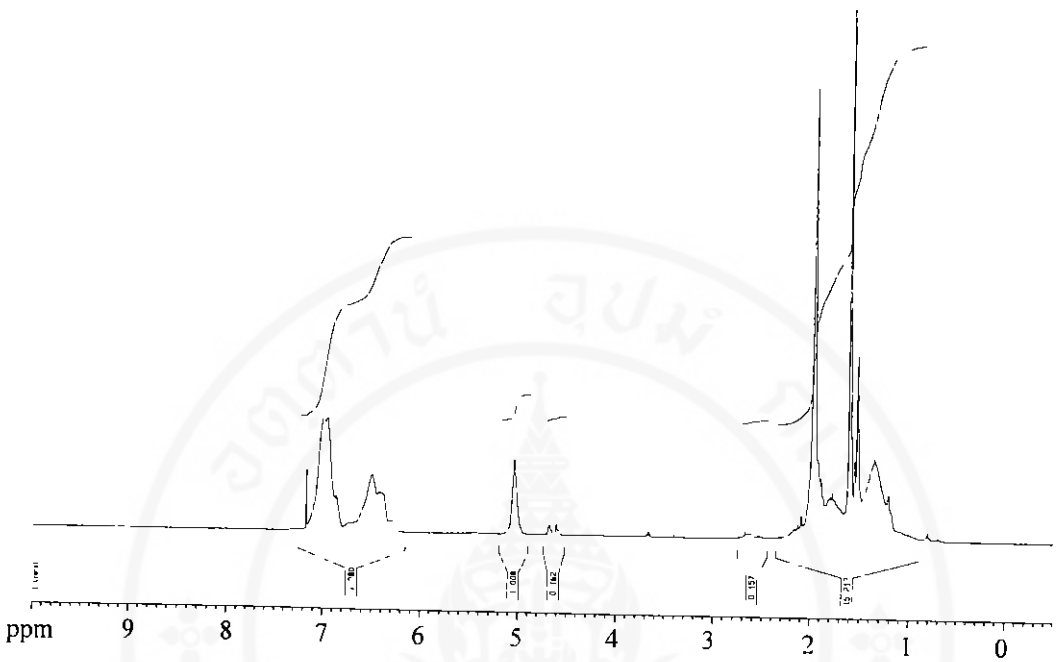

Figure 2A-4 ^{1}H-NMR spectra of MIS4

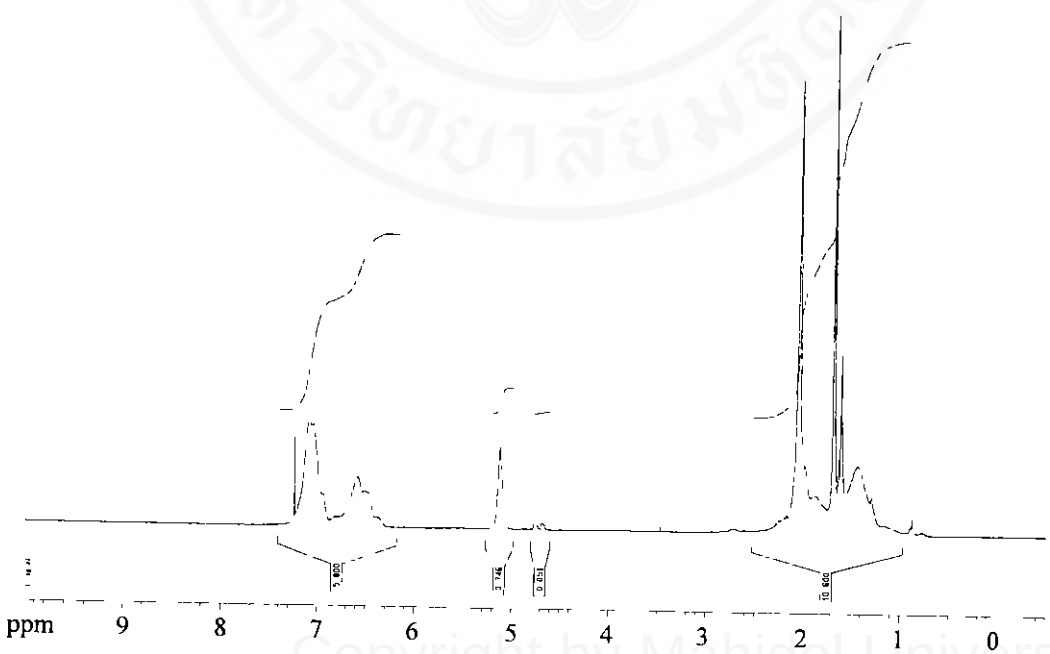

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Figure 2A-5 ^{1}H-NMR spectra of MIS5

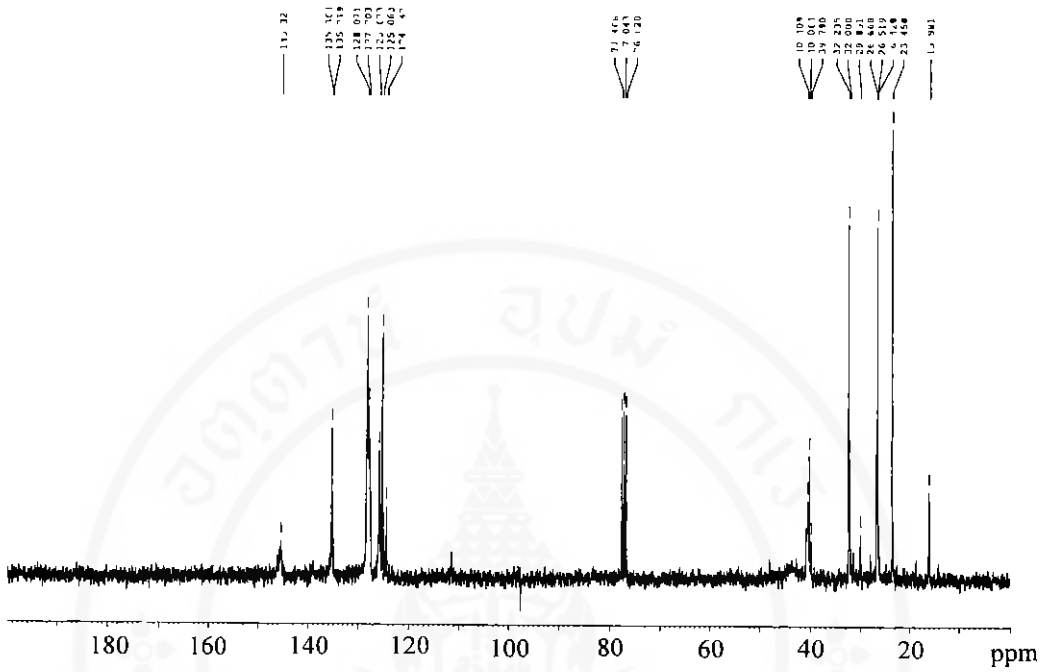

Figure 2A-6 ^{13}C-NMR spectra of MIS1

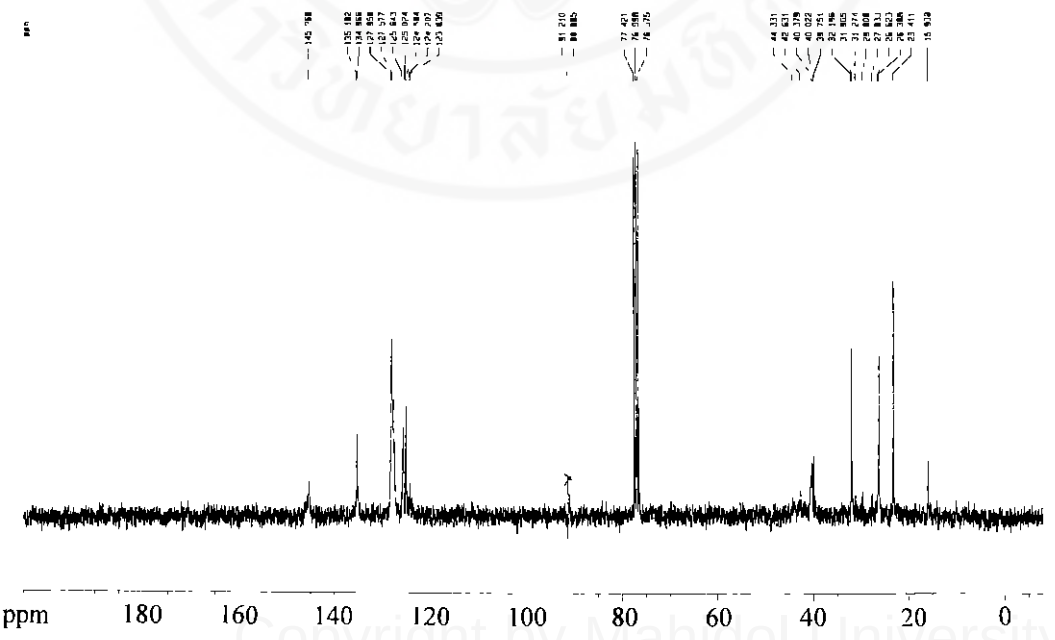

Figure 2A-7 ^{13}C-NMR spectra of MIS2

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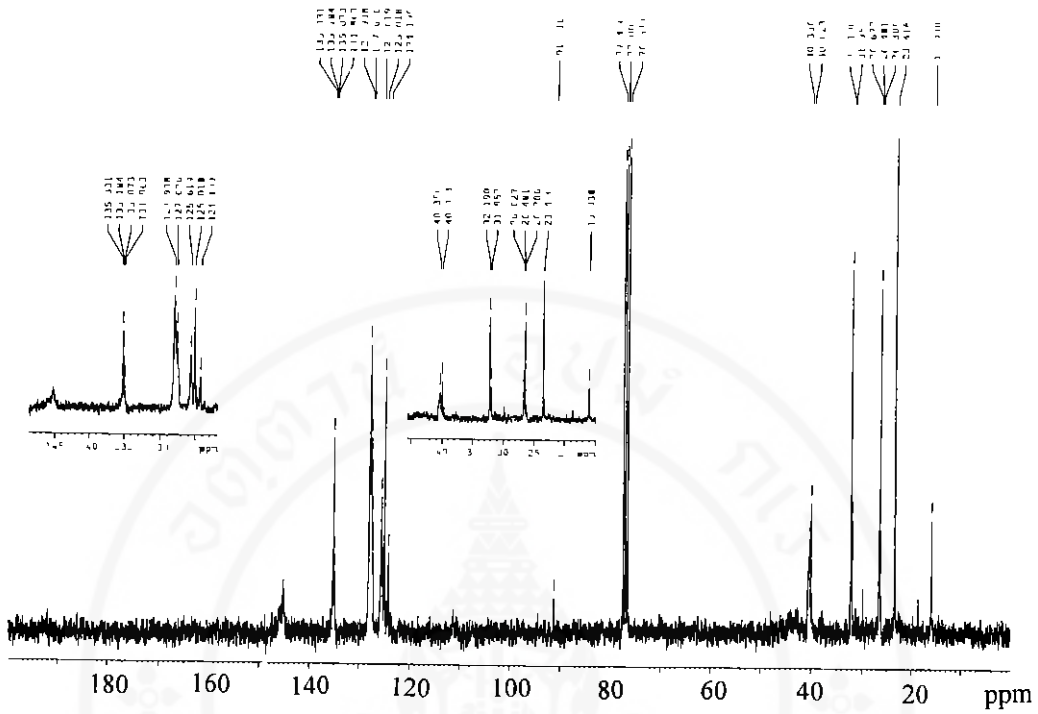

Figure 2A-8 ^{13}C-NMR spectra of MIS3

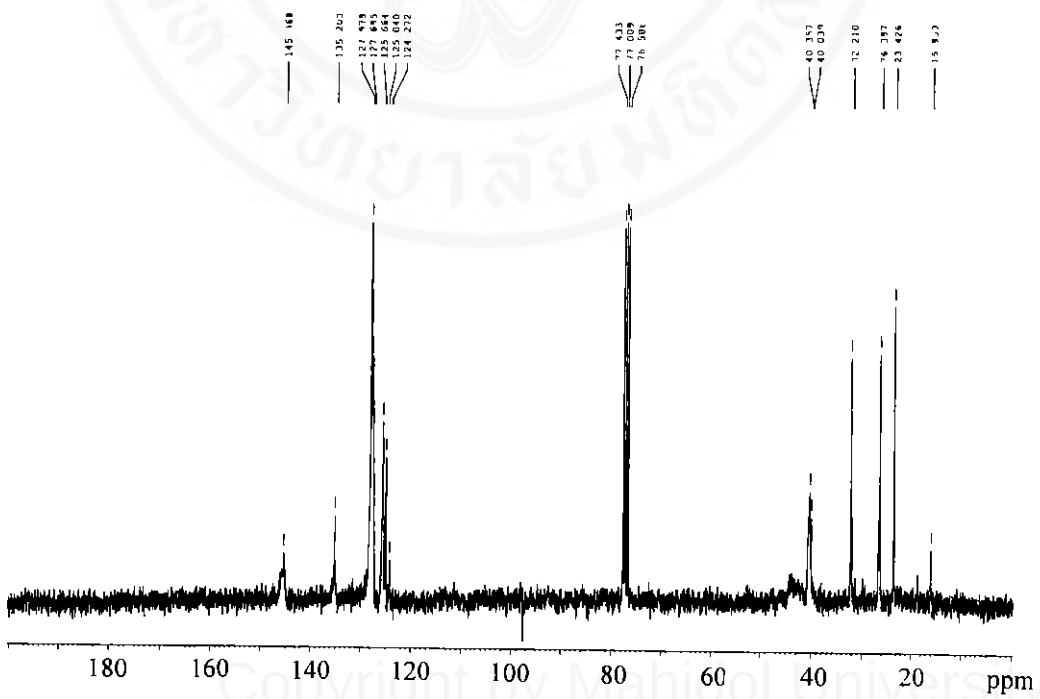

Figure 2A-9 ^{13}C-NMR spectra of MIS4

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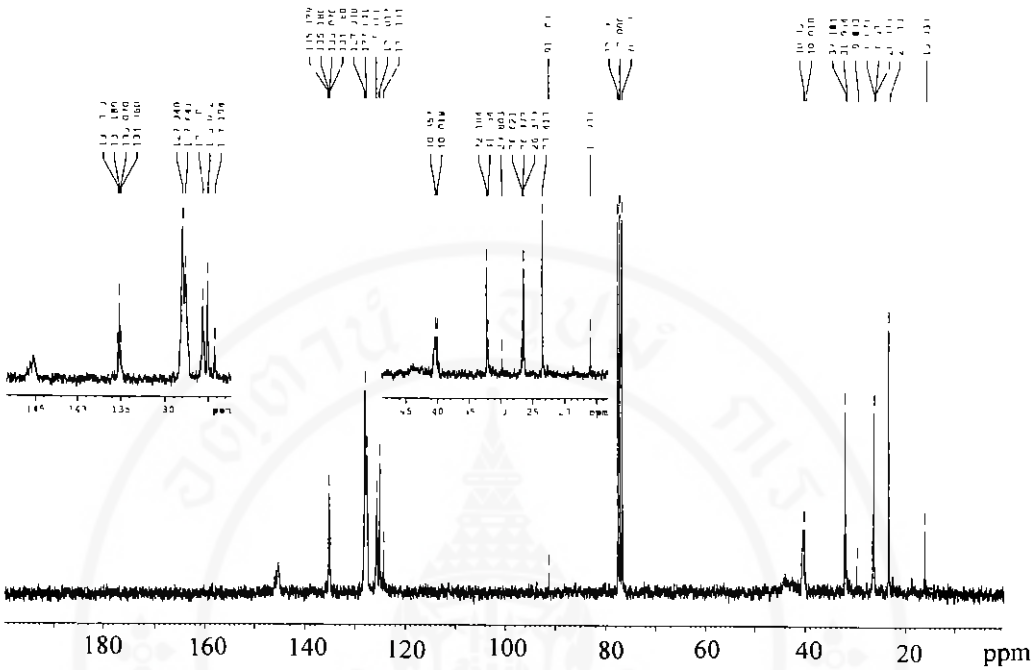

Figure 2A-10 ^{13}C-NMR spectra of MIS5

Appendix 3A : Amplification of ^{1}H-NMR spectra of mixed isoprene styrene block copolymer(MIS) for calculation of microstructure

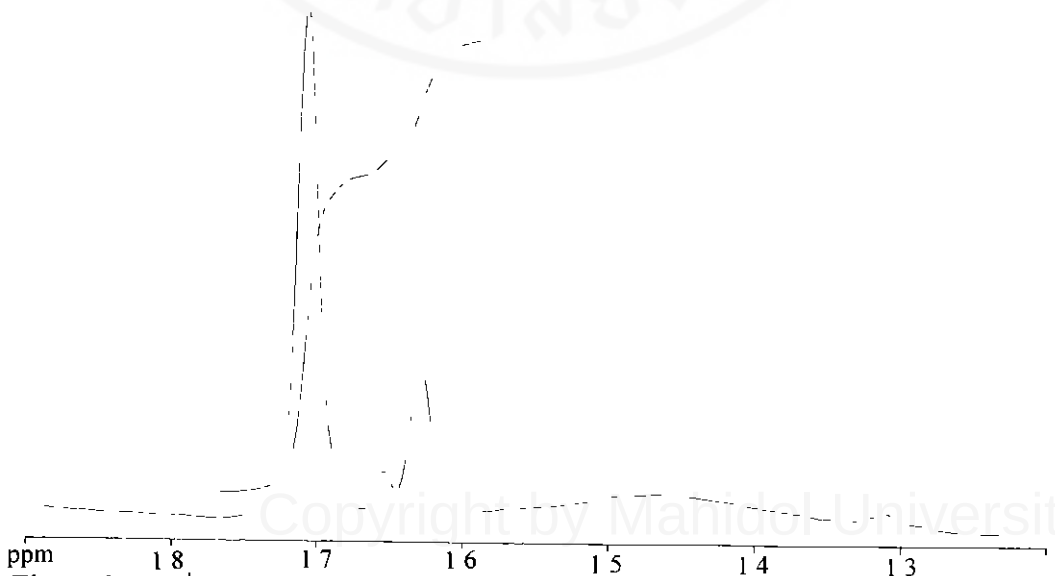

Figure 3A-1 ^{1}H-NMR spectra of MIS1

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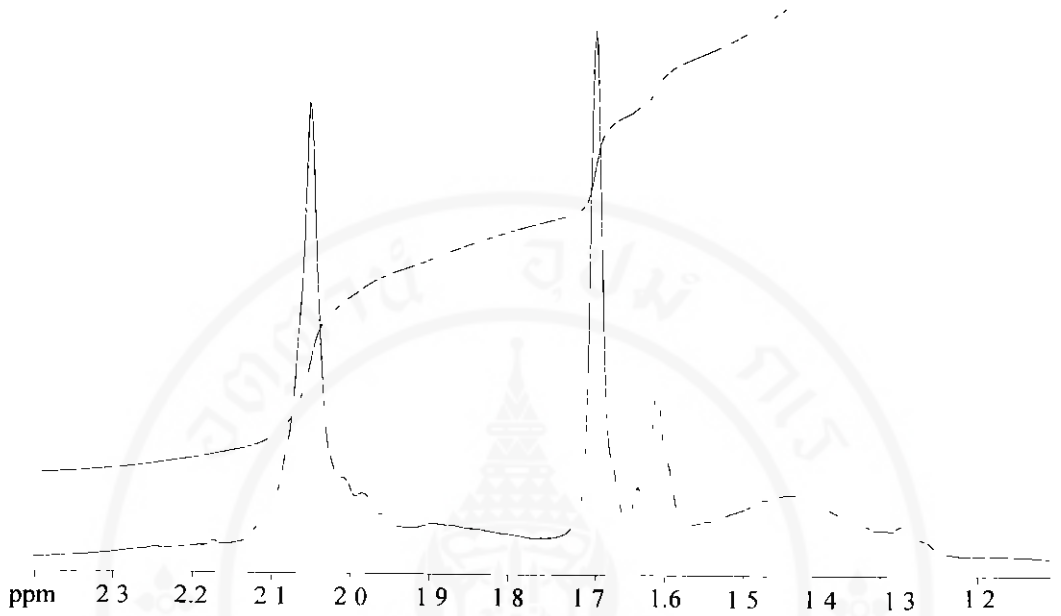

Figure 3A-2 ^{1}H-NMR spectra of MIS2

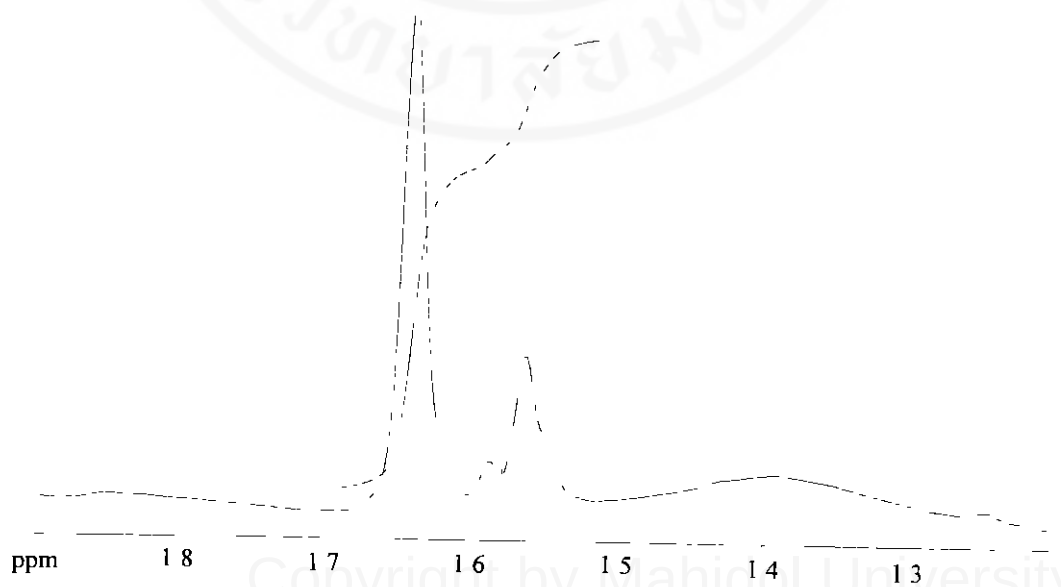

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Figure 3A-3 ^{1}H-NMR spectra of MIS3

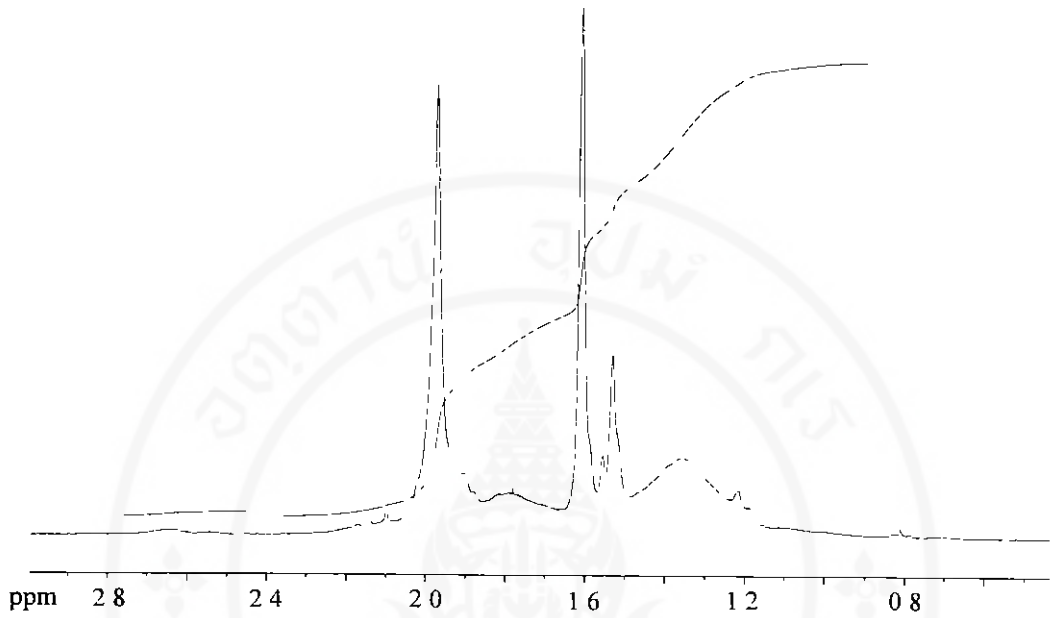

Figure 3A-4 ^{1}H-NMR spectra of MIS4

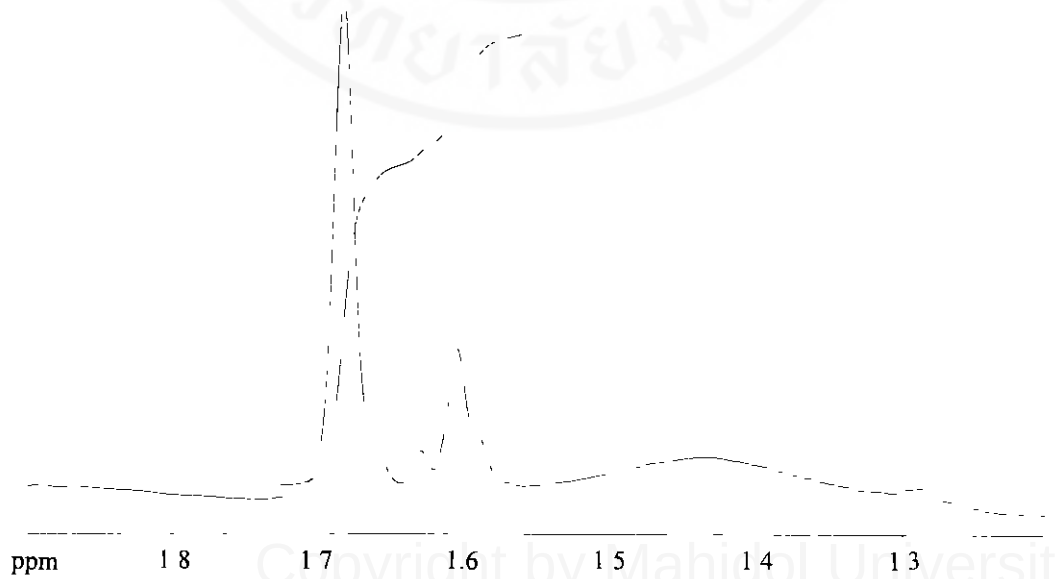

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Figure 3A-5 ^{1}H-NMR spectra of MIS5

APPENDIX B : Gel permeation chromatograms

Appendix 1B : GPC chromatograms of polyisoprene(PI) and polystyrene(PS)

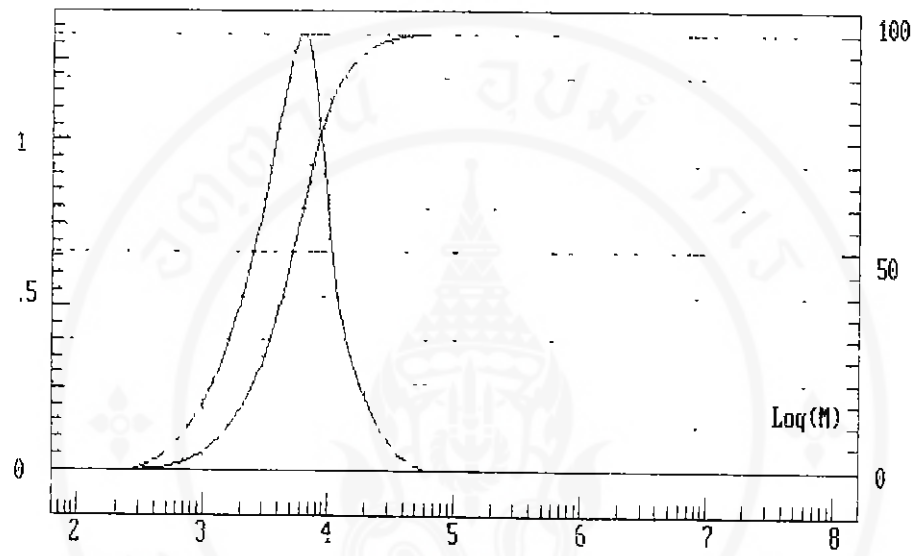

Figure 1B-1 GPC chromatograms of PI2

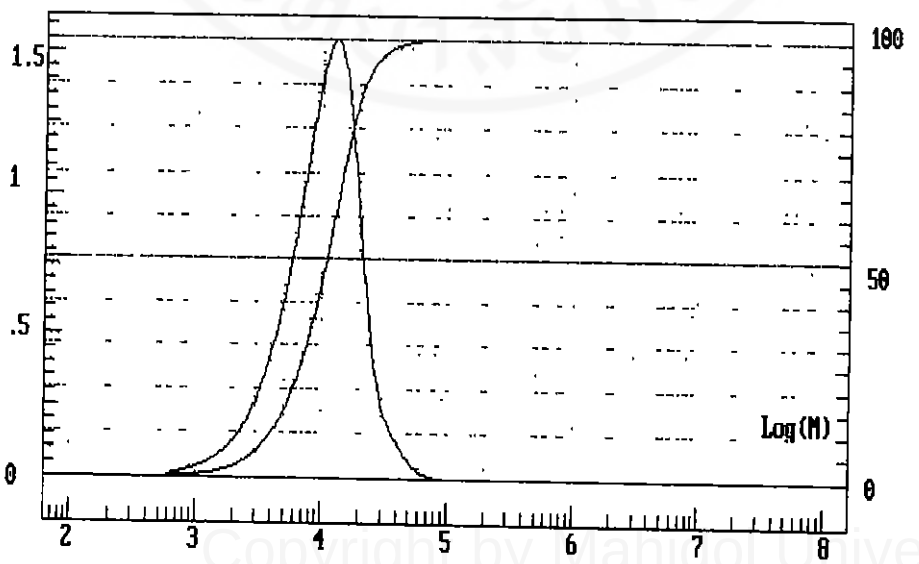

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Figure 1B-2 GPC chromatograms of PI3

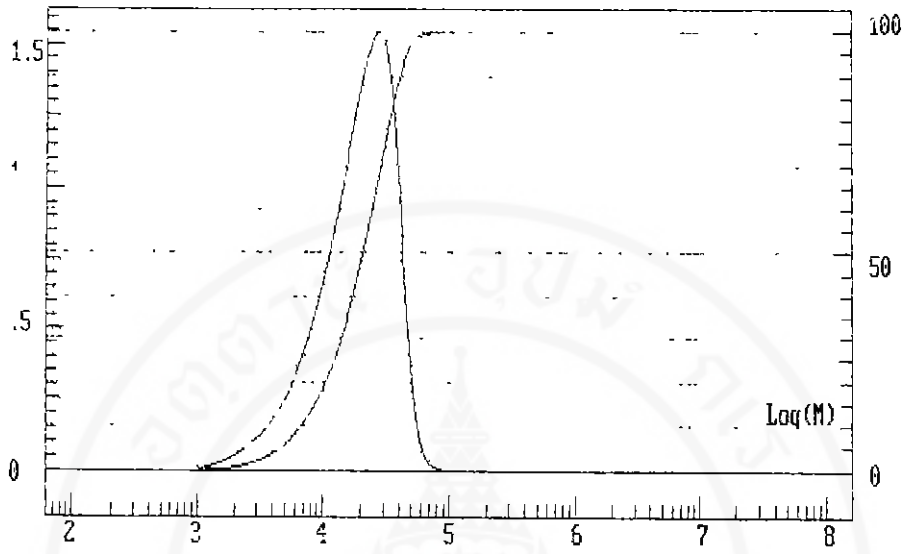

Figure 1B-3 GPC chromatograms of PS2

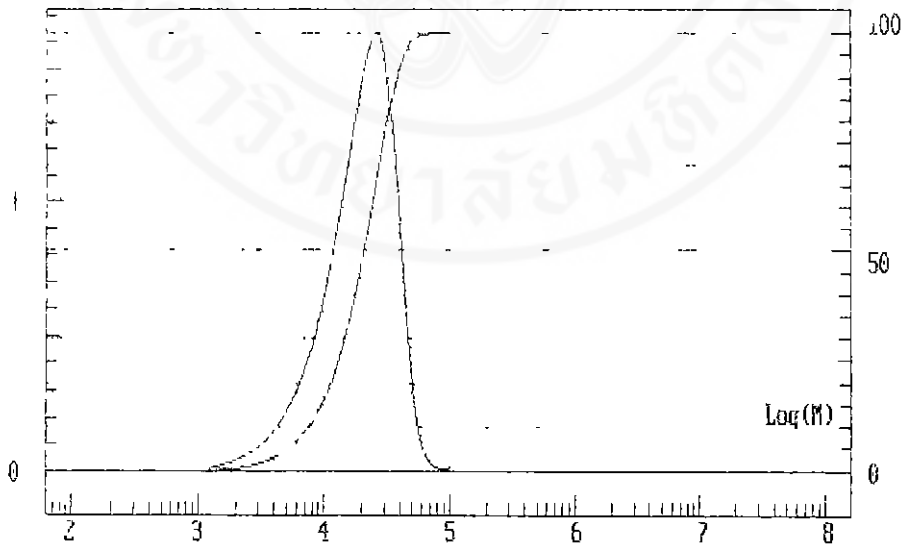

Figure 1B-4 GPC chromatograms of PS3

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Appendix 2B : GPC chromatograms of isoprene styrene block copolymer(IS)

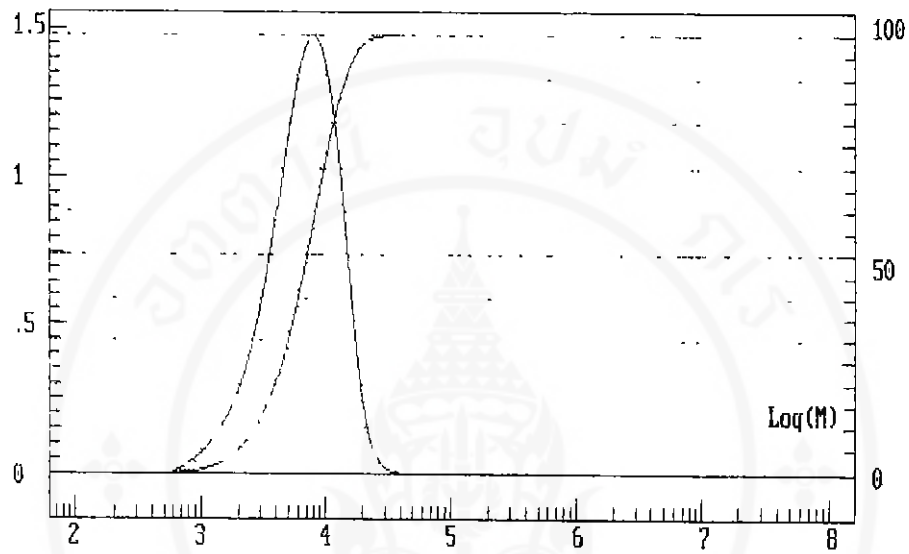

Figure 2B-1 GPC chromatograms IS1(2)

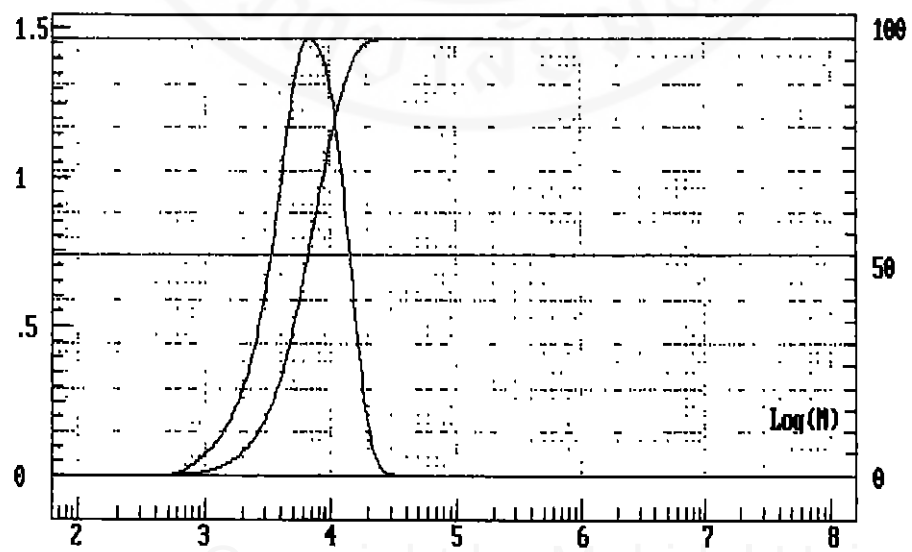

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Figure 2B-2 GPC chromatograms IS2(1)

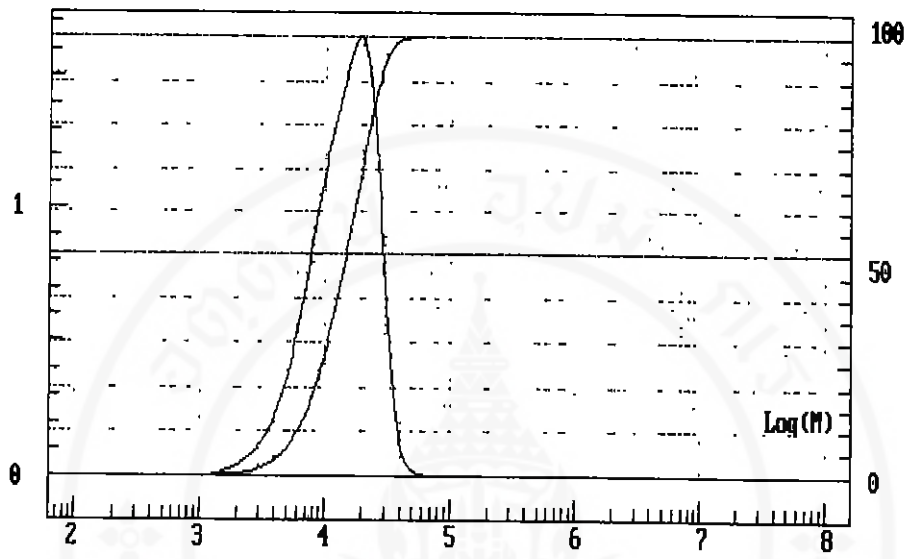

Figure 2B-3 GPC chromatograms IS3(2)

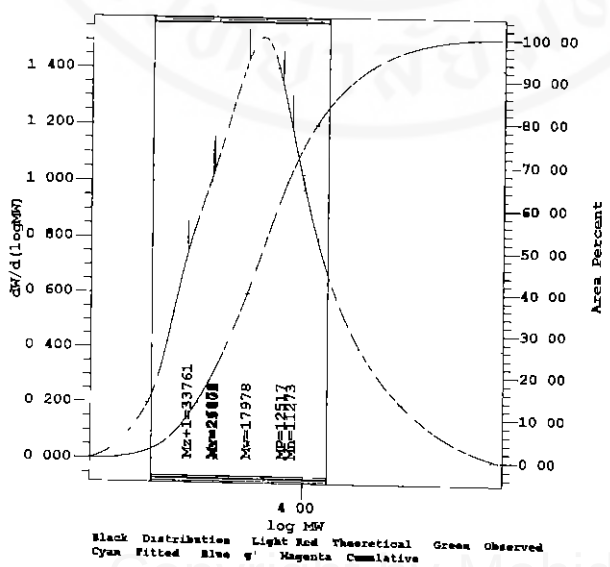

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Figure 2B-4 GPC chromatograms IS4(2)

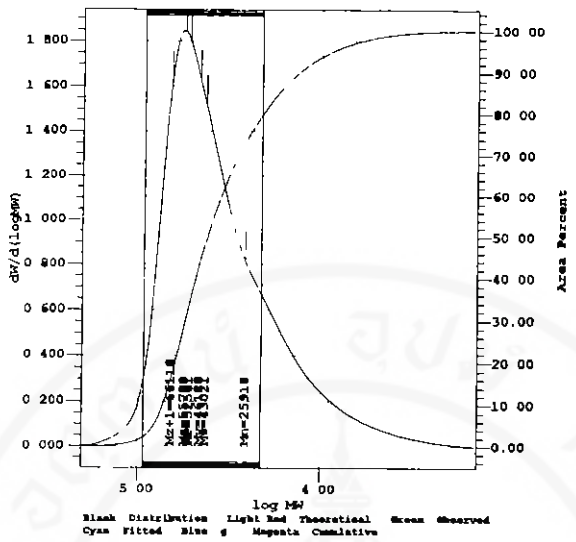

Figure 2B-1 GPC chromatograms IS5(2)

Appendix 3B : GPC chromatograms of mixed isoprene styrene block copolymer(MIS)

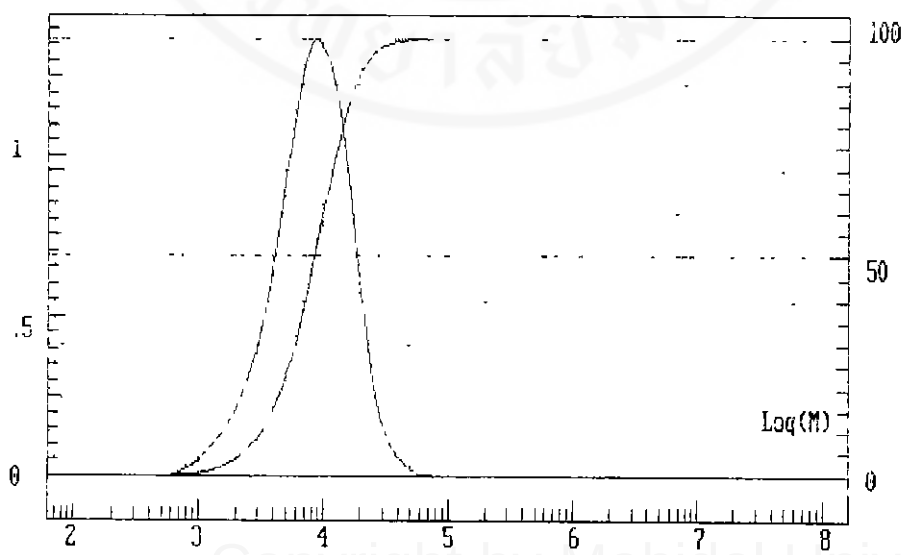

Figure 3B-1 GPC chromatograms MIS1

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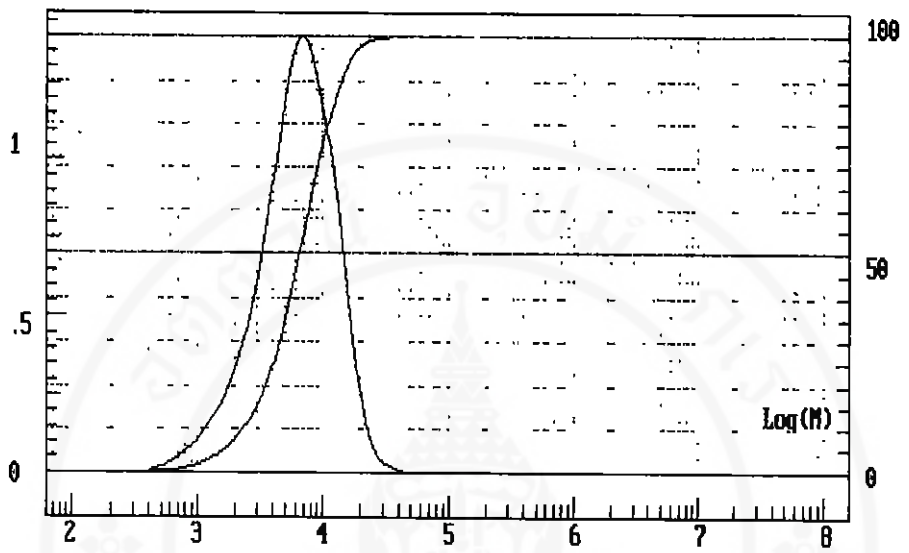

Figure 3B-2 GPC chromatograms MIS2

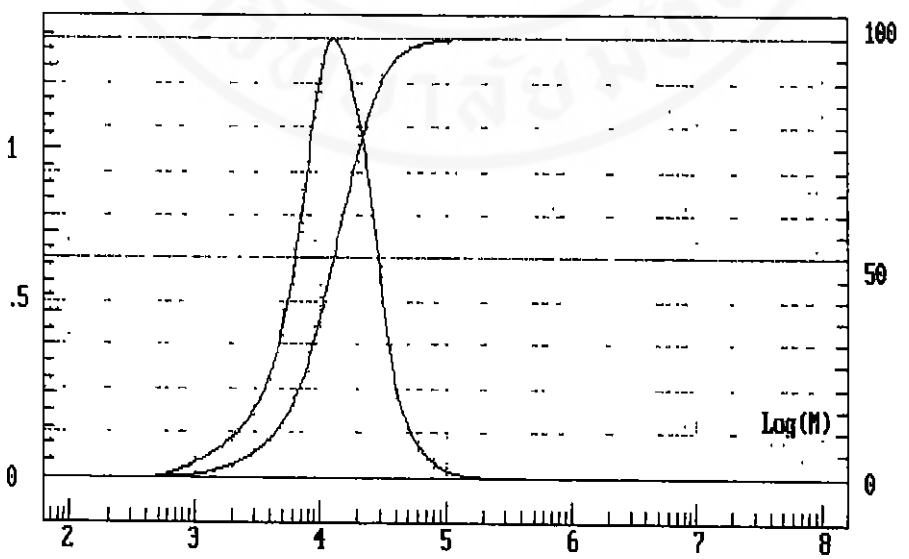

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Figure 3B-3 GPC chromatograms MIS3

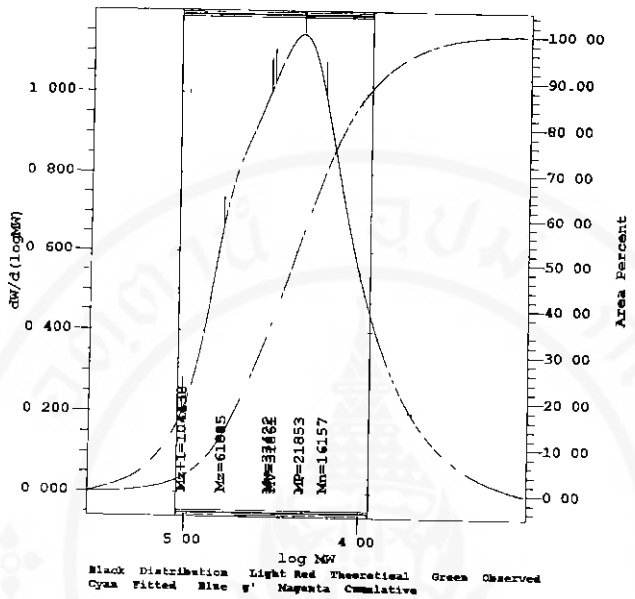

Figure 3B-4 GPC chromatograms MIS4

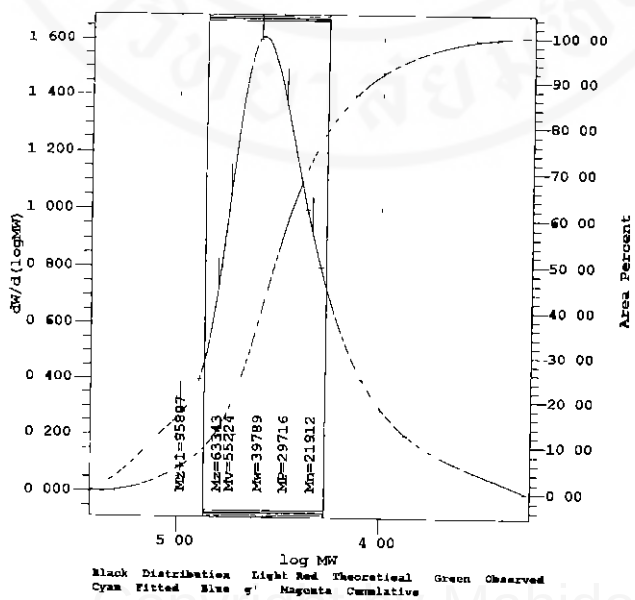

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Figure 3B-5 GPC chromatograms MIS5

APPENDIX C : IR and ^{1}H-NMR spectra of hydrogenated polyisoprene (HPI)

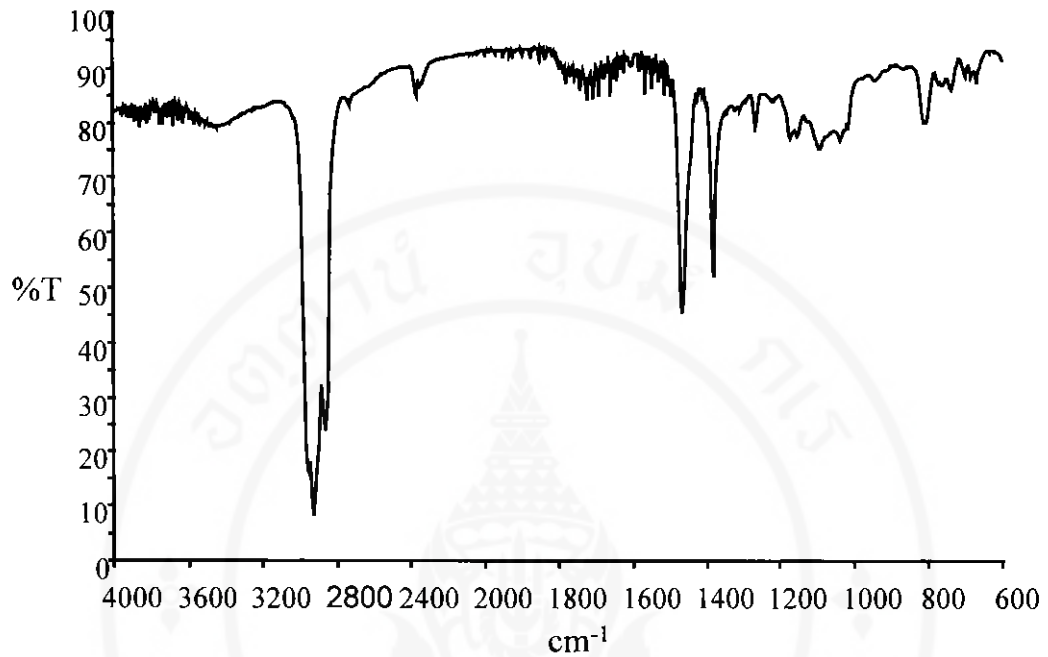

Figure C-1 IR spectrum of hydrogenated polyisoprene (HPI)

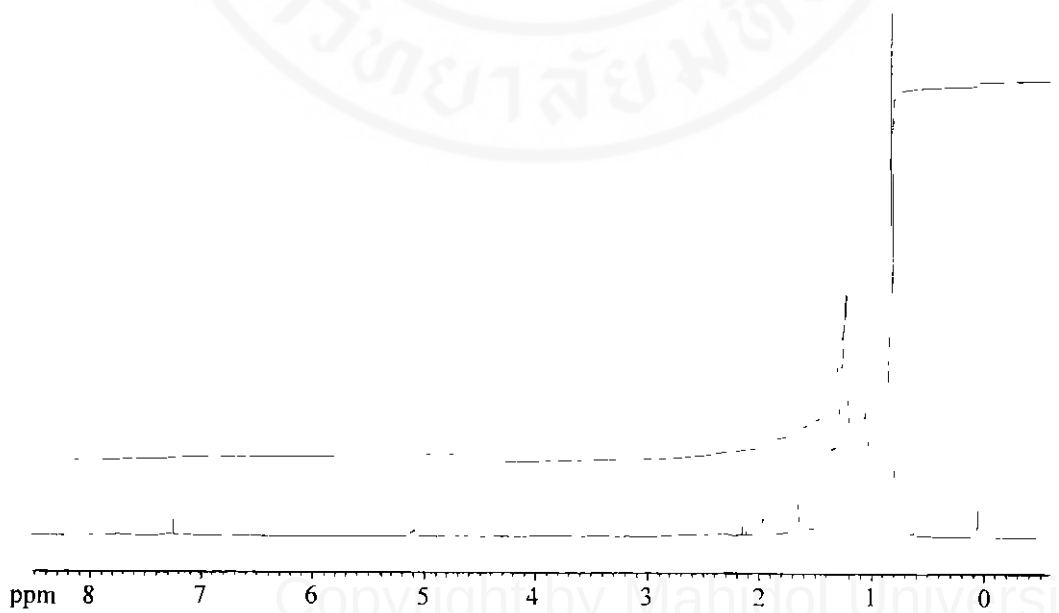

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Figure C-2 ^{1}H-NMR spectrum of hydrogenated polyisoprene (HPI)

APPENDIX D : The experimental data for calculation of %hydrogenation

Appendix 1D : Percentage of isoprene : styrene composition using ^{1}H-NMR in calculation of %hydrogenation from equation 11 in section 2.8.1

Sample	% I:S[b]	%I:S[a]	%H
HMIS1(1)	54.95 : 45.05	15.50 : 84.50	84.96
HMIS1(2)	54.95 : 45.05	16.65 : 83.35	83.62
HMIS2	44.00 · 56.00	8.83 : 91 17	87.65
HMIS3	51.03 : 48.97	8.84 : 91.16	85.33
HMIS4(1)	42.61 : 57 39	19 53 : 80.47	67.31
HMIS4(2)	42.61 : 57.39	13.54 : 86 46	77 34

[a] . after hydrogenation, [b] : before hydrogenation

Appendix 2D : Percentage of isoprene : styrene composition using absorption band of IR spectra for calculation of %hydrogenation from equation 13 in section 2.8.3

Sample	I_B	S_B	I_B/S_B	I_A	S_A	I_A/S_A	%H
HMIS1(1)	2 7571	1 7298	1 5939	0 1521	1 2467	0.0765	92 3456
HMIS1(2)	2.7571	1.7298	1.5939	0.2161	1.5535	0 0873	91 2726
HMIS2	4 265	2 5988	1 6411	0.1581	1.0099	0.0954	90.4609
HMIS3	1.5649	1.2484	1.2535	0 2880	1 5827	0.1452	85 4835
HMIS4(1)	1 4749	1 3609	1.0838	0.1211	1.1010	0 1015	89 8511
HMIS4(2)	1 4749	1 3609	1.0838	0 0789	0.9249	0.0788	92 1287

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Appendix 3D : Percentage of isoprene : styrene composition using I.V. in calculation of %hydrogenation from equation 12 in section 2.8.2

Sample	% I:S[b]	%I:S[a]	%H
HMIS1(1)	178 ± 1	43.5 ± 0 5	75.56
HMIS1(2)	178 ± 1	45.5 ± 0.5	74 44
HMIS2	161 ± 2	53.1 ± 0.5	67.02
HMIS3	175 ± 2	45.0 ± 1	74.29
HMIS4(1)	151 ± 1	42.4 ± 0.5	71.92
HMIS4(2)	151 ± 1	42.0 ± 1	72.19

[a] : after hydrogenation, [b] : before hydrogenation

Appendix 3D : Comparison of % isoprene:styrene (w/w) used in polymerisation [a] with %I:S(w/w) calculated from I.V.[b]

sample	% I:S[a]	% I S[b]
IS1(1)	49 : 51	47 : 53
IS1(2)	49 : 51	49 : 51
IS1(3)	49 : 51	47 · 53
IS1(4)	49 · 51	48 . 52
MIS1	49 : 51	48 . 52
IS2(2)	43 : 57	44 56
IS2(3)	43 57	44 : 56
MIS2	43 : 57	43 : 57
IS3(1)	43 : 57	50 : 50
IS3(2)	43 · 57	45 : 55
IS3(3)	43 : 57	47 : 53
IS3(4)	43 · 57	46 : 54
MIS3	43 : 57	47 : 53
IS4(1)	49 : 51	46 · 54
IS4(2)	49 : 51	46 : 54
IS4(3)	49 : 51	41 : 59
IS4(4)	49 : 51	45 : 55
MIS4	49 : 51	40 . 60
IS5(1)	49 : 51	45 : 55
IS5(2)	49 · 51	44 : 56
MIS5	49 · 51	45 : 55

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APPENDIX E : DSC and TGA thermograms

Appendix 1E : DSC thermograms of mixed isoprene-styrene block copolymer(MIS)

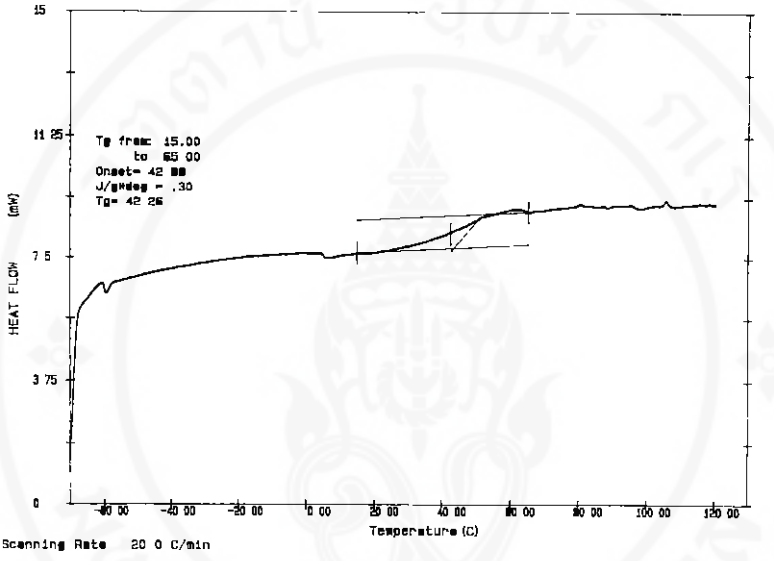

Figure 1E-1 DSC thermograms of MIS1

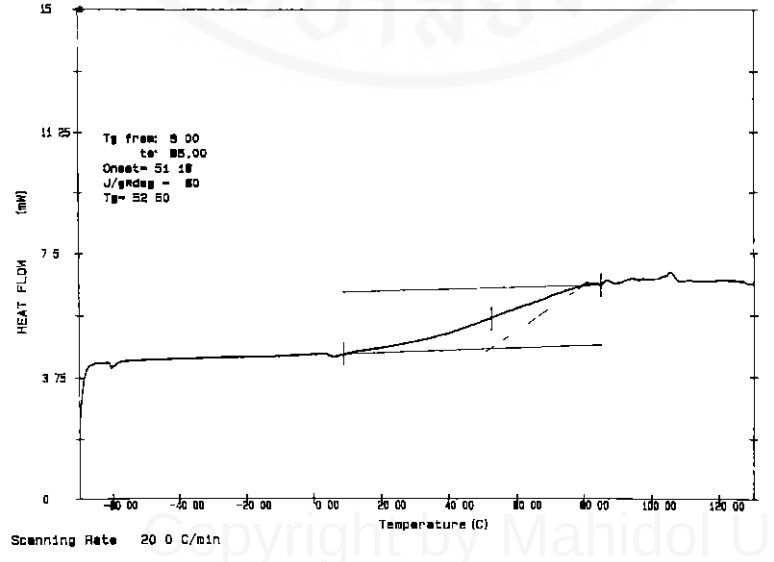

Figure 1E-2 DSC thermograms of MIS2

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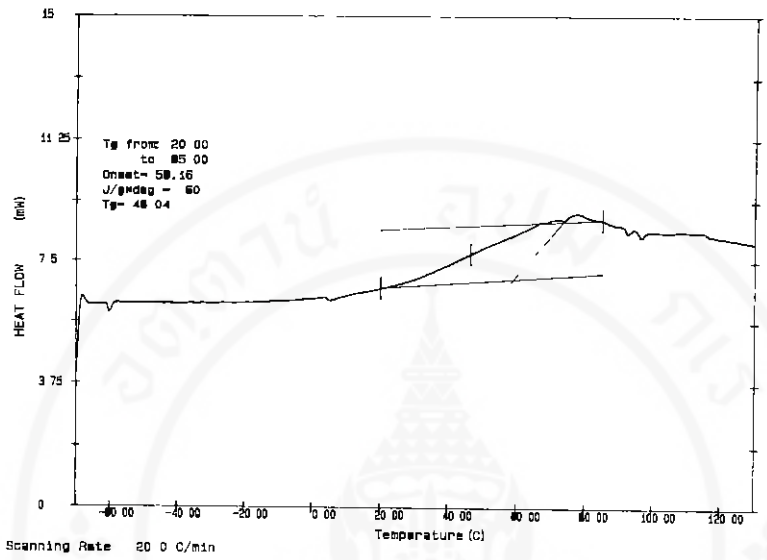

Figure 1E-3 DSC thermograms of MIS3

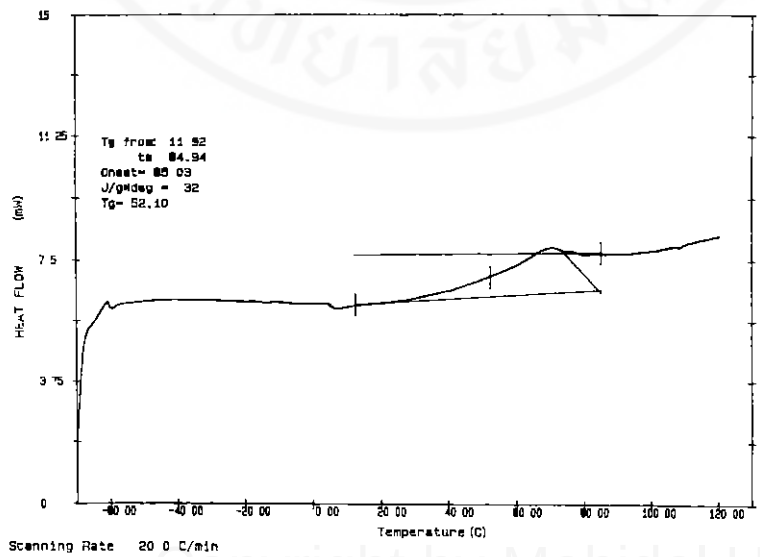

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Figure 1E-4 DSC thermograms of MIS4

Appendix 2E : DSC thermograms of hydrogenated mixed isoprene styrene block copolymer(HMIS)

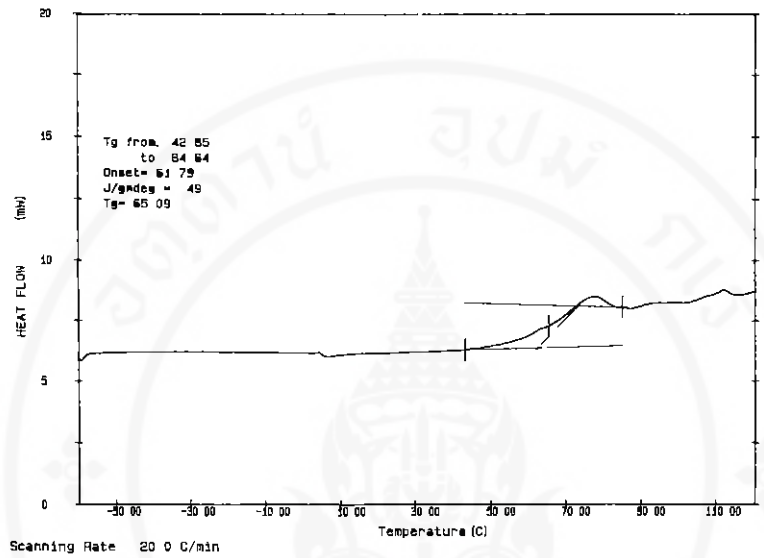

Figure 2E-1 DSC thermograms of HMIS1(1)

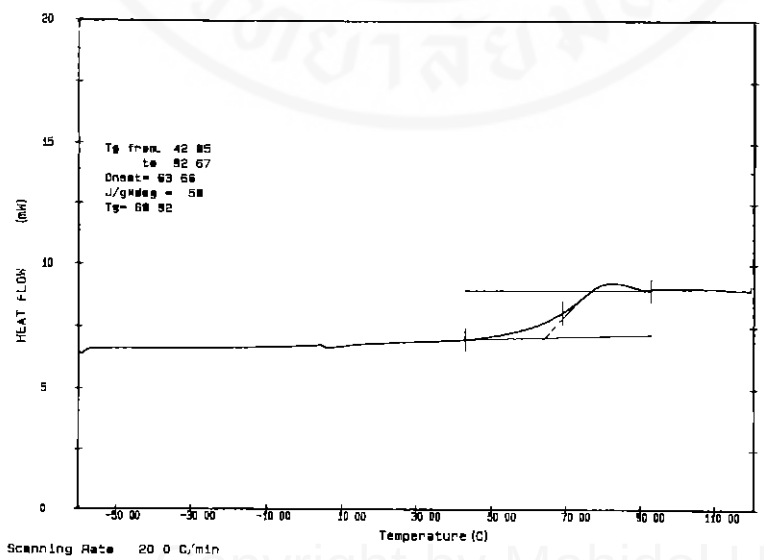

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Figure 2E-2 DSC thermograms of HMIS1(2)

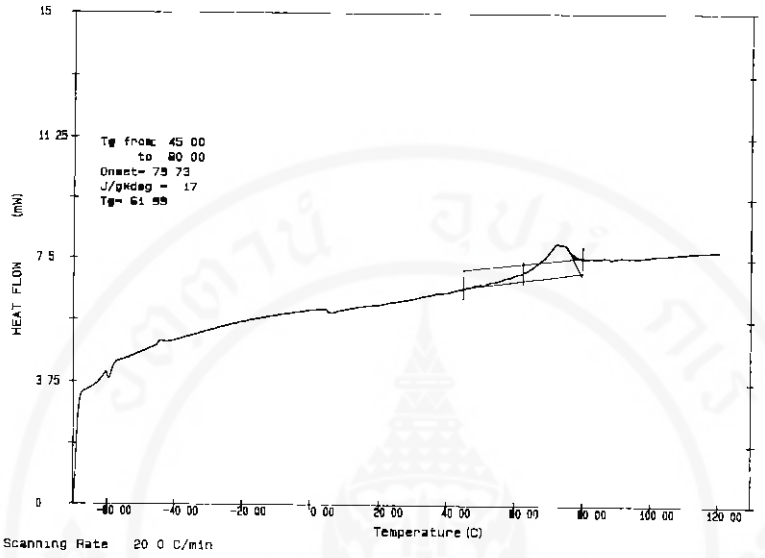

Figure 2E-3 DSC thermograms of HMIS2

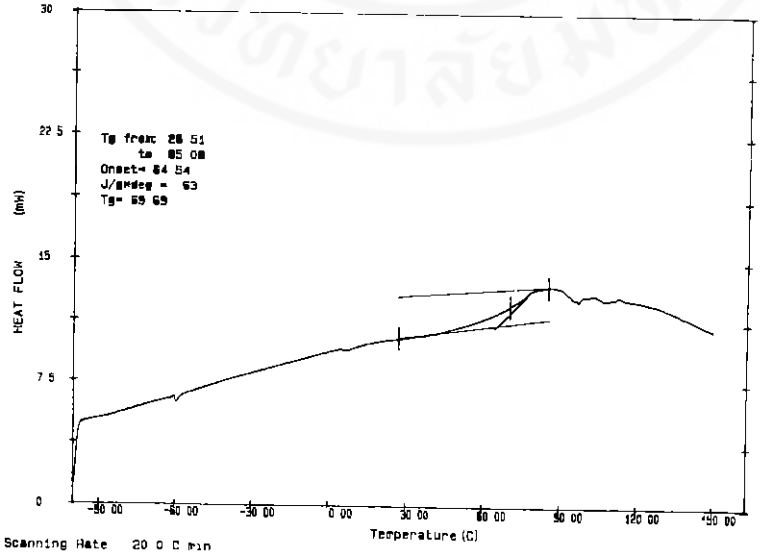

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Figure 2E-4 DSC thermograms of HMIS3

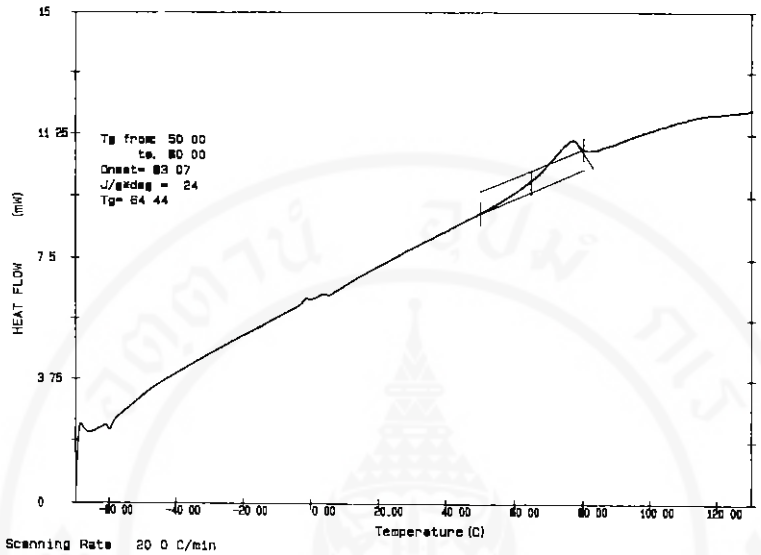

Figure 2E-5 DSC thermograms of HMIS4(1)

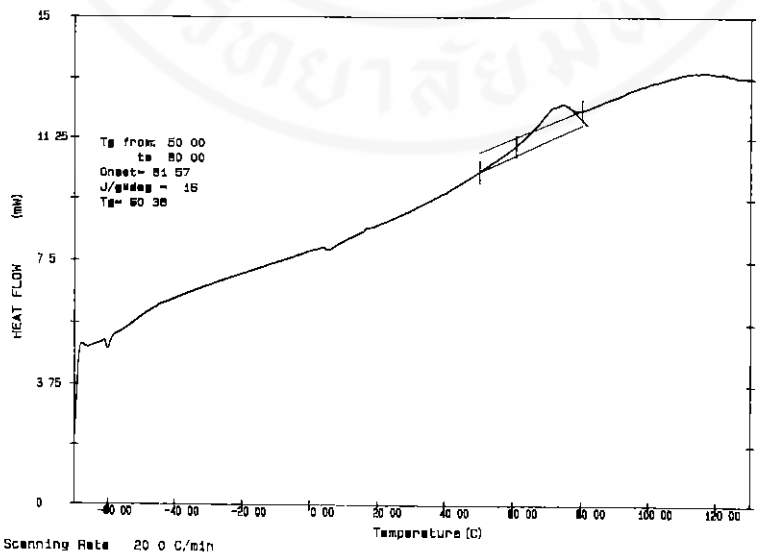

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Figure 2E-6 DSC thermograms of HMIS4(2)

Appendix 3E : TGA thermograms of hydrogenated mixed isoprene-styrene block copolymers (HMIS) compared with mixed copolymers (MIS)

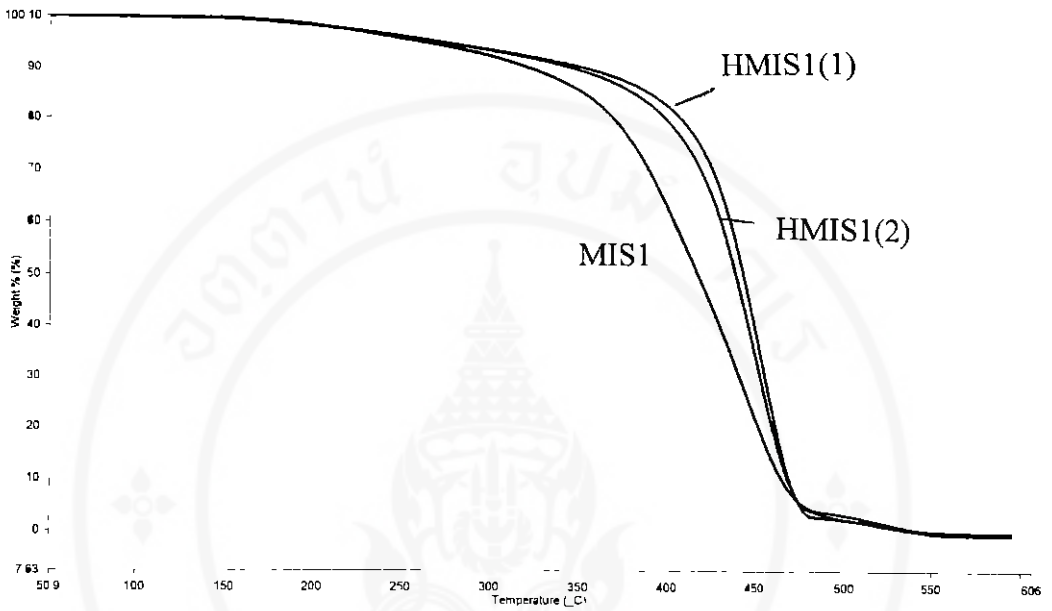

Figure 3E-1 TGA thermograms of MIS1, HMIS1(1) and HMIS1(2)

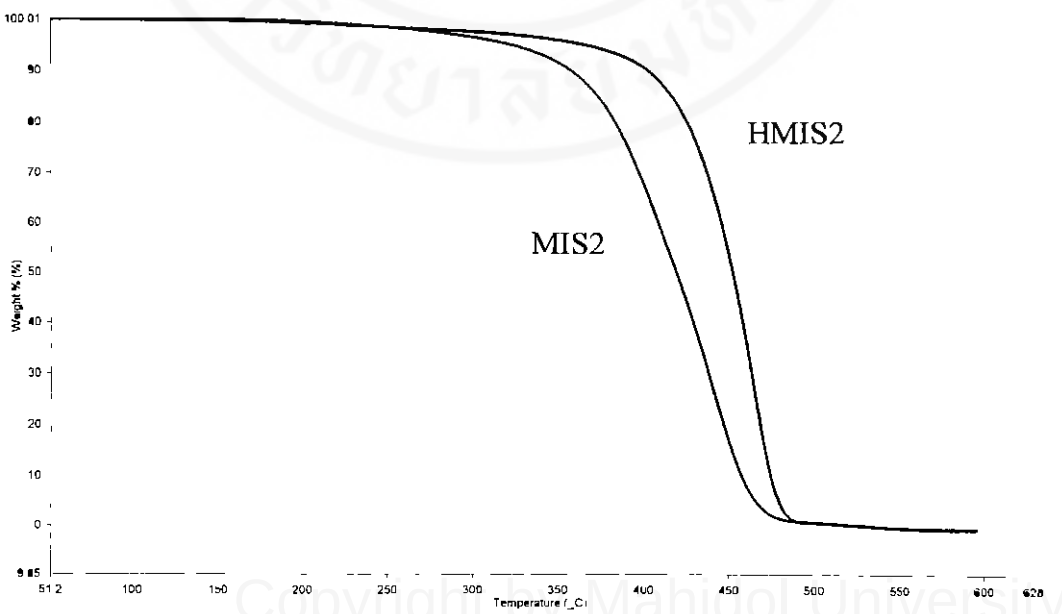

Figure 3E-2 TGA thermograms of MIS2 and HMIS2

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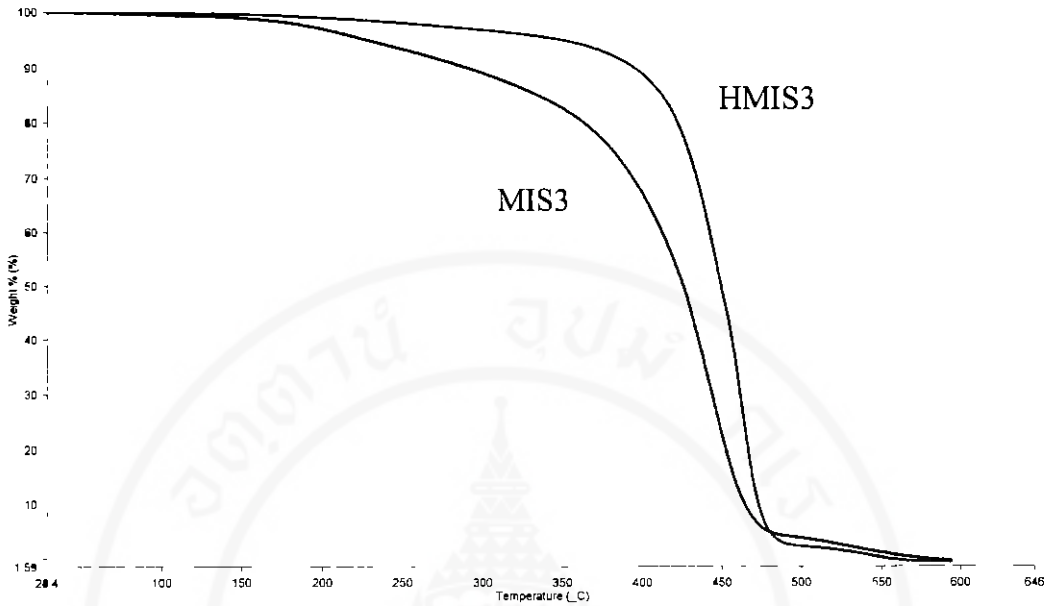

Figure 3E-3 TGA thermograms of MIS3 and HMIS3

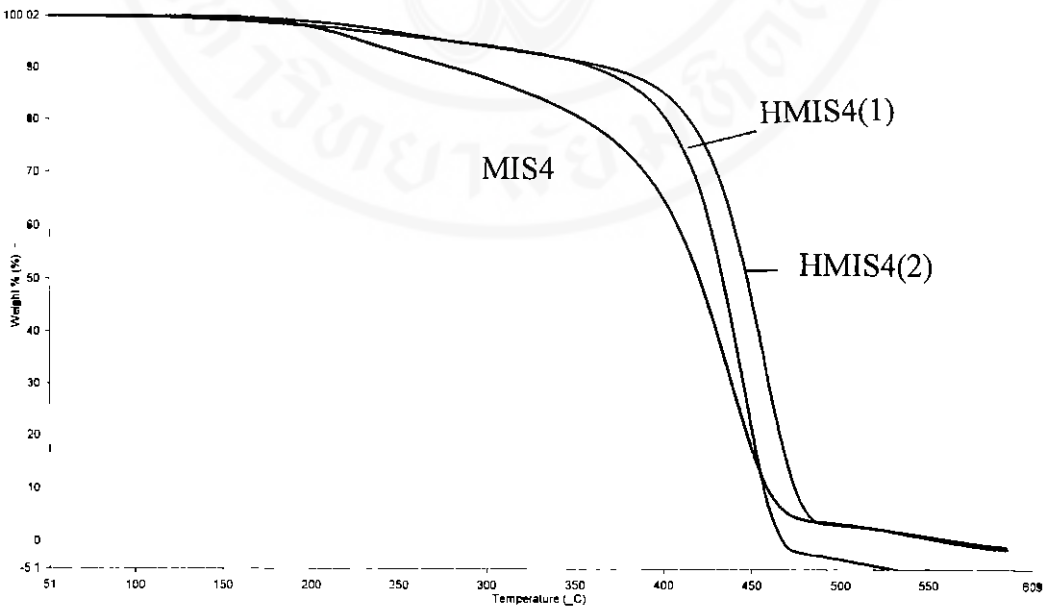

Figure 32E-4 TGA thermograms of MIS4, HMIS4(1) and HMIS4(2)

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