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SYNTHESIS OF GRAFT COPOLYMER OF SYNDIOTACTIC POLY(STYRENE-CO-4-METHYLSTYRENE) WITH POLYBUTADIENE VIA COPOLYMERIZATION BETWEEN (STYRENE AND 4-METHYLSTYRENE)

Miss Nathinee Srinate

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By	Miss Nathinee Srinate
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor ML. Supakanok Thongyai, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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ณฐินี ศรีเนตร : การสังเคราะห์พอลิเมอร์แบบกิ่งระหว่าง (ซินดิโอแทคติกพอลิสไตรีนและพอลิบิวตะไดอีน) โดยผ่านการของโคพอลิเมอไรเซชันระหว่าง (สไตรีนกับพาราเมทิลสไตรีน) (SYNTHESIS OF GRAFT COPOLYMER OF SYNDIOTACTIC POLY(STYRENE-CO-4-METHYLSTYREN) WITH POLYBUTADIENE VIA COPOLYMERIZATION BETWEEN (STYRENE AND 4-METHYL STYRENE)) อ.ที่ปรึกษา: รศ. ดร. มล. ศุภกนก ทองใหญ่, 99หน้า, ISBN 974-53-2951-7

งานวิจัยนี้ ได้ศึกษาและนำเสนอวิธีการสังเคราะห์โคพอลิเมอร์แบบกิ่งระหว่างซินดิโอแทคติกพอลิสไตรีนและพอลิบิวตะไดอีน โดยวิธีการสังเคราะห์ประกอบด้วย การสังเคราะห์โคพอลิเมอร์ระหว่างสไตรีนกับพาราเมทิลสไตรีน โดยใช้ระบบตัวเร่งปฏิกิริยาเมทัลโลซีน/เมทิลอะลูมินอกเซนแบบปรับปรุง โดยปฏิกิริยาที่เกิดจะดำเนินภายใต้บรรยากาศอาร์กอน ที่อุณหภูมิ 50 องศาเซลเซียส และกราฟท์พอลิบิวตะไดอีนบนสายโซ่หลักด้วยกระบวนการแอนไอออนิกพอลิเมอไรเซชั่น โคพอลิเมอร์แบบกิ่งที่ได้จะมีอุณหภูมิการหลอมเหลมสูง (240-250 องศาเซลเซียส) ซึ่งสูงกว่าโคพอลิเมอร์ระหว่างสไตรีนกับบิวตะไดอีนทั่วๆไป เนื่องจากโคพอลิเมอร์แบบกิ่งที่สังเคราะห์ได้จะมีส่วนของโครงร่างผลึกที่จัดเรียงตัวอย่างเป็นระเบียบอยู่ในโครงสร้าง โดยทั่วไป ซินดิโอแทคติกพอลิสไตรีนจะมีอุณหภูมิการเปลี่ยนช่วงสถานะคล้ายแก้วที่ 100 องศาเซลเซียส ซึ่งมีผลให้ซินดิโอแทคติกพอลิสไตรีนเปราะและแตกหักง่ายที่อุณหภูมิห้อง ดังนั้นโคพอลิเมอร์แบบกิ่งที่สังเคราะห์ได้จะถูกใช้เป็นสารควบคู่ในพอลิเมอร์ผสมของซินดิโอแทคติกพอลิสไตรีน เพื่อปรับปรุงคุณสมบัติเชิงกล และเสริมการรับแรงของซินดิโอแทคติกพอลิสไตรีนที่อุณหภูมิห้อง

ภาควิชา......วิศวกรรมเคมี......
สาขาวิชา......วิศวกรรมเคมี......
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ลายมือชื่อนิสิต......ณฐินี ศรีเนตร......
ลายมือชื่ออาจารย์ที่ปรึกษา......

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KEY WORD: SYNDIOTACTIC POLYSTYRENE / POLYMER BUTADIENE / GRAFT COPOLYMER

NATHINEE SRINATE: SYNTHESIS OF GRAFT COPOLYMER OF SYNDIOTACTIC POLY(STYRENE-CO-4-METHYLSTYREN) WITH POLYBUTADIENE VIA COPOLYMERIZATION BETWEEN (STYRENE AND 4-METHYLSTYRENE) THESIS ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 99 pp. ISBN 974-53-2951-7

The basic method for the synthesis of syndiotactic polystyrene-co-polybutadiene graft copolymers was investigated. Firstly, the syndiotactic polystyrene copolymer, poly(styrene-co-4-methylstyrene) (sPSMS), was prepared by the copolymerization between styrene and 4-methylstyrene monomer with $\mathrm{Cp^*TiCl_3}$/MMAO at 50°C. Polymerizations proceeded in argon atmosphere at ambient pressure. Secondly, the copolymer was grafted with polybutadiene (commercialized unsaturated elastomer) by anionic grafting polymerization with a metallation reagent. This graft copolymer showed high melting temperature (240-250°C) and was different from those of anionic styrene-butadiene copolymers due to the presence of crystalline syndiotactic polystyrene segments. Usually, highly syndiotactic polystyrene has the glass transition temperature at 100°C and behaves like glassy polymer (possessed brittle mechanical properties) at room temperature. Thus, the copolymer might be used as compatibilizer in syndiotactic polystyrene blends for modification of the mechanical properties to compensate the glassy properties of pure syndiotactic polystyrene at room temperature.

Department Chemical Engineering
Field of study Chemical Engineering
Academic Year 2005

Student's signature ณฐินี ศรีเนตร
Advisor's signature

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Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

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CHAPTER I

INTRODUCTION

Plastics have an influence on life at nearly every level in society today. Their resistance to corrosion and tremendous technological flexibility has enabled them even to supersede and replace metals in the construction of many household tools and creature comforts [1]

Polystyrene (PS), is a typical rigid plastic, has been known since the last century; it was commercialized by I.G. Farben in 1931 and it is now one of the most widespread polymeric material, appreciated for its excellent stiffness and transparency and its good processability. It is an amorphous polymer and has three forms that are atactic, isotactic and syndiotactic. Atactic polystyrene (aPS) is an amorphous (non-crystalline) polymer with a glass transition temperature (T_g) of 100 ºC. Its application at high temperature is limited and it has low solvent resistance. Syndiotactic polystyrene (sPS) is a semi-crystalline polymer with a T_g similar to aPS but it also has a melting temperature (T_m) of 270 ºC. sPS has excellent heat and solvent resistance. Isotactic polystyrene (iPS) is also classified as crystalline PS with a T_m of 240 ºC, but it has not been commercialized because of its very slower crystallization rate compared to sPS (roughly 100 times). [2]

High-impact polystyrenes, frequently referred to as HIPS, are an elastomer modified polystyrene thermoplastic. This two-phase system, consisting of a rubber phase and a continuous polystyrene phase, provides a polymer system that has grown into an importance world-scale commodity polymer. The addition of rubber increases impact strength considerably. This versatile product can be found in many compositions that offer an exceptional range of impact properties and processability for many applications. While HIPS products are also valued for their excellent dimensional stability and rigidity, they provide good impact strength and high rigidity that are not exhibited by general-purposed polystyrene. But relatively low ultraviolet light stability and lower chemical resistance, compared with crystalline materials.

The syndiotactic polystyrene was first synthesized by Ishihara et al. (Idemitsu Kosan Co., Ltd.) in 1985, followed by Zambelli et al. A variety of titanium compounds and some zirconium compounds, soluble in aromatic hydrocarbons, in the presence of methylaluminoxane (MAO) promote syndiotactic polymerization of styrene, with a tacticity even greater than 98%. This new isomer soon showed a much higher rate of crystallization, higher melting temperature, and the possibility of reaching high levels of crystallinity. Because of the crystals, the sPS displays entirely different properties to amorphous polystyrene such as high chemical resistance, excellent electrical properties, hydrolytic resistance, heat resistance and good moldability. However, the sPS does share one property with conventional polystyrene, namely inherent brittleness. [3]

The attempts have been made to characterize the new materials and improve the physical, mechanical properties and processability of sPS through several procedures. Firstly, addition of the olefin monomer, especially ethylene, during styrene polymerization procedure to achieve styrene/olefin copolymer with various microstructure, such as random, block, and alternating copolymers, by using metallocene catalyst at appropriate conditions.[4] Secondly, physical polymer blending also provides a feasible access to sPS modification. In addition, the synthesis of graft copolymer of sPS with macromonomers is of great interests.

Previously, sPS based graft copolymer had been prepared by copolymerization of styrene and small monomers. In this manner, metallocene copolymerization of styrene with monomer isoprene or atactic monomer styrene was performed to obtain Poly(sPS-g-isoprene)[5] or Poly(sPS-g-styrene)[6]. Thus the obtained copolymers were blend with pure sPS and their polymorphic behaviors were studied by x-ray diffraction. The two examples illustrated successful approaches for sPS modification.[5-6]

There are many reports about the techniques of sPS modification. For example, Xu and Chung introduced polar groups onto sPS to improve adhesion and compatibility.[7] Hydrogenation of the Poly(sPS-g-Butadiene) graft-like copolymer was studied by Shengsheng Liu.[4] Epoxy-containing sPS graft copolymer, effectively increased the thermal stability, was prepared via 4-methylstyrene with metallocene/MAO catalyst by Chi-Lan Li et al.[8] Recently, the achievements in the stereospecific copolymerization of styrene and butadiene monomer with transition metal has provide alternative ways to improve mechanical properties of these materials by controlling the cis selectivity of Butadiene segments.[9-12] The Poly(sPS-b-cis-Butadiene) was investigated and used as effective compatibilizer for immiscible syn-PS/cis-PB blends by Hoang The Ban et al.[13-14] However, their block copolymer, Poly(sPS-b-Butadiene), come from the reaction with butadiene monomer, dissimilar to copolymer this study, Poly(sPS-g-Polybutadiene).

This research reports the method for synthesis of graft copolymer between sPS and polybutadiene via n-Butyllithium polymerization. Many literatures reported about the production methods of the sPS copolymer, but they used butadiene monomer [13-15] or isoprene monomer [16] as a reactant. In this research, polybutadiene, ready made unsaturated polymer that composed of high cis-configuration were used as the reactant. The combination of metallocene copolymerization and anionic polymerization procedures will be used for the preparation of the copolymers with sPS segments. The resulted graft copolymers can be utilized as the toughness reinforcement of sPS.

1.1 Objectives of the Thesis

To synthesize graft copolymer of syndiotactic polystyrene and polybutadiene from syndiotactic poly(styrene-co-4-methylstyrene) to improve impact properties of the original syndiotactic polystyrene at room temperature.

1.2 Scope of the Thesis

1. Synthesize syndiotactic poly(styrene-co-4-methylstyrene) by using homogeneous half-metallocene catalytic system and characterize by ^{13}C-NMR
2. Synthesize graft copolymer between syndiotactic poly(styrene-co-4-methylstyrene) and polybutadiene by anionic polymerization
3. Blend the synthesized graft copolymer with syndiotactic polystyrene
4. Characterize properties of sPS-co-(p-methylstyrene) copolymer, graft copolymer of syndiotactic polystyrene and their blends by conventional techniques: DSC, NMR, SEM and Solution viscosity.

CHAPTER II

LITERATURE REVIEWS

1. Syndiotactic polystyrene

Ishihara N. *et al.* [17] succeeded in obtaining a new polystyrene which has a syndiotactic structure and a high degree of crystallinity. They described the determination of the stereoregularity and some other properties of the newly obtained polystyrene. They polymerized the styrene with their novel catalyst system, containing a titanium compound and an organoaluminum compound, for 2 h at 50 °C, and 20.3 g of polymer was obtained. The crude product was extracted with methyl ethyl ketone (MEK) under reflux for 4 h. A total of 98 wt % of the polymer was insoluble in MEK and its weight-average molecular weight was 82000.

N. Ishihara, M. Kuramoto and M. Uoi [18] found that a mixture of titanium compounds [$TiCl_4$, $Ti(OEt)_4$ or $(\eta\text{-}C_5H_5)TiCl_3$] with methylaluminoxane catalyzed the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which had a narrow molecular weight distribution (Mw/Mn = 2). Pure syndiotactic polymers were also obtained with ring-substituted styrenes. Monomer reactivity was enhanced by electron-releasing substituents on the aromatic ring.

W. Kaminsky, et al. [19] investigated fluorinated half-sandwich complexes catalysts in syndiospecific styrene polymerization. It was found that fluorinated half-sandwich complexes of titanium, such as $CpTiF_3$, showed an increase in activity of up to a factor of 50 compared to chlorinated compounds. In a temperature range of

10-70 °C, the methylaluminoxane could be reduced to an Al/Ti ratio of 300. If the cyclopentadienyl ligand in the metallocene catalyst was changed to a pentamethyl-cyclopentadienyl ligand (Cp*) that is a stronger electron donor and exerts a greater sterically hindrance, the polymerization activity was lower. But the pentamethyl-cyclopentadienyltitanium fluoride (Cp^*TiF_3) could be produced the polystyrene with highest melting point of 277 °C.

Kim Y. and Do Y. [20] prepared a new type of the half-metallocene catalysts for the syndiospecific polymerization of styrene by the reaction of various kinds of trialkanolamine with Cp^*TiCl_3 in the presence of triethylamine. All seven compounds have a highly thermal stability and they show fairly good activities in the presence of cocatalyst MMAO in styrene polymerization. Especially, highly bulky and electronically deficient modified catalyst system affords syndiotactic polystyrene with very high molecular weight.

2. Copolymerization of syndiotactic polystyrene

Carla Manfredi, Gaetano Guerra, Claudio De Rosa, Vincenzo Busico, and Paolo Corradini [21] investigated the change of the polymorphic behavior of syndiotactic polystyrene after introduction of different amounts (3-20 mol %) of p-methylstyrene comonomeric units. Variations of the polymorphic behavior have been observed for solvent extraction procedures, for annealing processes, and for solution and melt crystallizations. The behavior of samples subjected to extraction and annealing procedures indicates that the introduction of p-methylstyrene comonomeric units tends to destabilize the clathrate δ-form.

For the solution as well as for the melt crystallization, the increase of p-methylstyrene content favors obtaining the α-form over the β-form and, in particular, for the 20 mol % p-methylstyrene copolymer, the β-form is never obtained. The effect of the comonomeric units in favoring the α-form (with respect to the β-form) in melt crystallizations is mainly due to the reduction of the crystallization temperature. However, the melting temperatures of pure α- and β-form samples of the homopolymer and copolymers measured at different heating rates indicate that the introduction of the comonomeric units destabilizes the β-form more than the α-form.

Hisayuki Nakatani amd Koh-hei Nitta, et. al [22] examined the effects of the comonomer content on the glass transition point and melting temperatures as well as the crystallization behavior of syndiotactic polystyrene. Poly(styrene-co-4-methylstyrene) with a different content of comonomer units was prepared by using the typical syndiospecific homogeneous metallocene catalysts, i.e. η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$, combined with methylaluminoxane. The η-$C_5(CH_3)_5TiCl_3$ catalyst gave the polymers with higher syndiotacticity. The monomer reactivity ratios indicated that the copolymers obtained with η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ possessed random and slightly blocky structure, respectively.

When the 4-methylstyrene comonomer units increased, the glass transition temperature of the copolymer increased linearly and the crystallization temperature increased followed by a decrease in melting temperature since the incorporation of methyl group may prevent the syndiotactic polystyrene from crystallization.

Michela Caprio, Maria Cristina Serra, Daniel E. Bowen, and Alfonso Grassi [12] prepared samples of poly(syndiotactic styrene-co-butadiene) (sPS-B) by using methylalumoxane (MAO) activated $CpTiCl_3$ under a range of experimental conditions. Copolymerization activities were low and nearly constant over the range of polymerization temperatures investigated (25-70 °C). sPS-B samples were synthesized at 25 °C with styrene molar fractions (x_s) covering a full range of compositions (x_s : 0.15-0.92). The copolymer samples were characterized by solution and solid state ^{13}C NMR spectroscopy, X-ray powder diffraction analysis, and thermal (DSC) analysis. The ^{13}C NMR analysis of the copolymer microstructure suggests that the butadiene homosequences are primarily cis-1,4 and the styrene segments are syndiotactic. However, some 1,2- and trans-1,4-butadiene units are occasionally formed during the polymerization process. Copolymer samples in which nS > 9 are crystalline due to the syndiotactic polystyrene segments detected in the α-toluene clathrate form with melting points in the range 205-230 °C. Syndiotactic polystyrene segments with shorter styrene block lengths are amorphous and partially included in the poly(butadiene) rubber domains.

Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono [13] reported a practical method for preparing cis-polybutadiene-block-syn-polystyrene (cis-PB-b-syn-PS) copolymers with long crystallizable syndiotactic polystyrene (syn-PS) segments chemically bonded with high cis-1,4-polybutadiene segments through the addition of styrene (ST) to a cis-specific 1,3-butadiene (BD) living catalyst composed of cyclopentadienyl titanium trichloride (CpTiCl3) and modified methylaluminoxane (MMAO). The incorporation of ST into the living polybutadiene (PB) precursor remarkably depended on the polymerization temperature. A low temperature (-20 °C) suppressed the rate of ST incorporation, but a high temperature (50 °C) tended to decompose the livingness of the active species and enhance the rate of the aspecific

ST polymerization initiated by MMAO. Consequently, temperatures of 0–25 °C seemed to be best for this copolymerization system.

Because of the absence of ST livingness, the final products contained not only the block copolymer but also the homopolymers. Attempts to isolate the block copolymer were carried out with common solvent fractionation techniques, but the results were not sufficient. Cross-fractionation chromatography (CFC) was, therefore, used for the isolation of the cis-PB-b-syn-PS copolymer. The presence of long syn-PS segments was confirmed by the observation of a strong endothermic peak at 260 °C in the differential scanning calorimetry curve.

Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono [14] investigated and reported a new methodology for preparing highly stereoregular styrene (ST)/1,3-butadiene (BD) block copolymers, composed of syndiotactic polystyrene (syn-PS) segments chemically bonded with cis-polybutadiene (cis-PB) segments, through a stereospecific sequential block copolymerization of ST with BD in the presence of a $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$ catalyst. The first polymerization step, conducted in toluene at -25 °C, was attributed to the syndiospecific living polymerization of ST. The second step, conducted at -40 °C, was attributed to the cis-specific living polymerization of BD. The livingness of the whole polymerization system was confirmed through a linear increase in the weight-average molecular weights of the copolymers versus the polymer yields in both steps, whereas the molar mass distributions remained constant. The profound cross reactivity of the styrenic-end-group active species with BD toward ST led to the production of syn-PS-b-cis-PB copolymers with extremely high block efficiencies.

Because of the presence of crystallizable syn-PS segments, this copolymer exhibited high melting temperatures (up to 270 °C), which were remarkably different from those of the corresponding anionic ST–BD copolymers, for which no melting temperatures were observed. Scanning electron microscopy pictures of a binary syn-PS/cis-PB blend with or without the addition of the syn-PS-b-cis-PB copolymers proved that it could be used as an effective compatibilizer for syn-PS/cis-PB binary immiscible blends.

3. Graft copolymer of syndiotactic polystyrene

T. C. Chung, H. L. Lu, and R. D. Ding [16] provided a new method to prepare polyethylene graft copolymers, such as polyethylene-g-polystyrene and polyethylene-g-poly(p-methylstyrene), with a relatively well-controlled reaction mechanism. The chemistry involves a transformation process from the metallocene copolymerization of ethylene and p-methylstyrene to the anionic living polymerization of styrene or p-methylstyrene. The metallocene catalysis produces poly(ethylene-co-p-methylstyrene) random copolymers with molecular weight distribution (Mh w/Mh n) of about 2.5. The following selective metalation reaction of p-methylstyrene units in the copolymer and the subsequent anionic “living” graft-from polymerization were effective to produce polymeric side chains with well-defined structure. Both graft density and graft length can be controlled by p-methylstyrene content in the PE backbone, metalation reagent, and the quantity of monomer used in the graft-from reaction. In the bulk, the individual PE and PS segments in the graft copolymers are phases-seperated to form crystalline PE domains and amorphous PS domains.

The microscopy studies reveal the effectiveness of PE-g-PS in the polymer blends by reducing the phase sizes, improving the dispersion, and increasing interfacial interaction between domains.

Kiyoshi Endo, Kazunobu Senoo [5] synthesized copolymer of styrene with styrene terminated polyisoprene macromonomer (SIPM) by $CpTiCl_3$ and methylaluminoxane (MAO) catalyst (Cp: cyclopentadienyl). SIPM was prepared by reaction of living polyisoprene initiated with sec-butyllithium (s-BuLi) and p-chloromethylstyrene. The synthesized macromonomer has a high terminal degree of functionalization and a narrow molecular weight distribution. Graft copolymers of polystyrene-graft-polyisoprene have been synthesized with the $CpTiCl_3$-MAO catalyst. The synthesized graft copolymer was confirmed to have a highly syndiotactic sequence on the main chain. The melting point of the syndiotactic graft copolymer was 247°C, which is lower than that of sPS. This suggests that the long branch chains introduced by copolymerization with the macromonomer may disturb the crystallinity of the syndiotactic polystyrene.

Shengsheng Liu, Baotong Huang [4] provided a new method for the preparation of a novel graft-like copolymer of syndiotactic polystyrene (sPS) with polybutadiene (PB). The copolymerization of styrene in a toluene solution of PB using the cyclopentadiene titanium trichloride ($CpTiCl_3$)/methylaluminoxane (MAO) catalytic system was used. The effect of PB on the crystallization behavior of the copolymer was investigated by differential scanning calorimetry and wide angle X-ray diffraction. The melting points of the copolymers slightly decrease with increasing PB content in the copolymer, whereas the crystallinity was significantly decreased compared with that of pure sPS. Hydrogenation of the poly(sPS-g-Butadiene) copolymer with p-toluenesulfonyl hydrazine afforded a PE-like copolymer. These hydrogenated block copolymers can be used as compatibilizers for PS/PE blends. However, no syndiotactic polystyrene block copolymer was prepared with the same method because of the lack of stereospecific polymerization of styrene with an anionic initiator.

Kiyoshi Endo, Kazunobu Senoo [6] investigated the copolymerization of styrene (St) and styrene-terminated macromonomers with $CpTiCl_3$-MAO catalyst. The content of the macromonomer in the graft copolymer was found to depend on the miscibility of the macromonomer with the main chain polystyrene formed by copolymerization. Miscible system of the syndiotactic polystyrene in the main chain and atactic polystyrene in the side chain was favorable for the incorporation of the macromonomer into the graft copolymer as compared with immiscible system of syndiotactic polystyrene in the main chain and atactic polyisoprene in the side chain. The content of the SSTM in the graft copolymer was influenced by the MAO/Ti mole ratio and content of the SSTM in the comonomer feed.

Kazunobu Senoo, Kiyoshi Endo, Masatoshi Tosaka, Syozo Murakami, and Shinzo Kohjiya [23] investigated polymorphic behaviors of two types of syndiotactic graft copolymers (syndiotactic polystyrene ; SPS) having side chains of polyisoprene (PIP), namely SPS-graft-PIP, and SPS having side chains of atactic polystyrene (APS), namely (SPS-graft-APS). Though the as-prepared samples of the both types were in the δ form as well as the homopolymer, they showed different polymorphic behaviors. Furthermore, while SPS-graft-PIP and SPS-graft-APS with the lower contents of the

APS side chains could crystallize from the melt, SPS-graft-APS with the higher contents of APS was in an amorphous state. The effect of the graft chains on crystallinity was discussed in terms of the friction force for reptation and the cohesive power; the former may be increased by the side chains in both types of the graft copolymers, while the latter may be enhanced only in the case of SPS-graft-PIP, compensating the increment of the friction force.

I. Tausendfreund, F. Bandermann, H.W. Siesler, M. Kleimann [24] investigated the anionic dispersion copolymerization of styrene and butadiene. The suitability of the lower alkanes butane and pentane as dispersing media was tested. Only pentane turned out to be suited for the synthesis of non-aggregated polymer particles. Following block copolymerization experiments, the active chain ends were found to be homogeneously distributed over the whole particle volume by TEM analysis of OsO_4 treated polymer probes. This result contradicts the opinion of Kim et al. [Korea Polym J 7 (1999) 64] who suppose a location of the active centers only at the surface of the polymer particles. Polymer particle aggregation in the synthesis of poly(styrene-b-butadiene) and poly(styrene-b-butadiene-b-styrene) di- and triblock copolymers can be attributed during the early part of butadiene polymerization to the well known association of growing lithium chain ends from separated polymer. Later on, at higher butadiene conversions, an entanglement of longer polymer chains causes agglomeration, too. The most important parameter to obtain a stable poly(styrene-b-butadiene)lithium dispersion is the molecular mass of the poly(butadiene) block.

Chi-Lan Li, Shu-Hua Chan, Ching Ting and George J. Jiang [8] improved adhesion properties, compatibility with other materials and impact resistance of syndiotactic polystyrene by functionalization. The functionalized syndiotactic polystyrene copolymers were synthesized and characterized. Syndiotactic polystyrene copolymers, poly(styrene-co-4-methylstyrene) (sPSMS), were prepared by styrene and 4-methylstyrene with a metallocene/methylaluminoxane catalyst. In addition, grafted copolymers, chemically grafted with isoprene onto an sPSMS backbone [poly(styrene-co-4-methylstyrene)-g-polyisoprene (sPSMS-g-PIP)] were synthesized by anionic grafting polymerization with a metallation reagent. The degree of epoxidation of the sPSMS-g-PIP copolymer increased with increasing reaction time for all the solvent systems. The crystallinity of the sPSMS-g-PIP copolymer was lower than that of the ungrafted sPSMS copolymer. Moreover, the epoxy-containing sPSMS-g-PIP copolymer effectively increased the thermal stability more than did the sPSMS-g-PIP copolymer alone.

CHAPTER III

THEORIES

3.1 Catalytic system

3.1.1 Catalyst compounds

Metallocene [25] are a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π-bonded to the metal atom. Examples of metallocene compounds are shown in Figure 3.1.1.

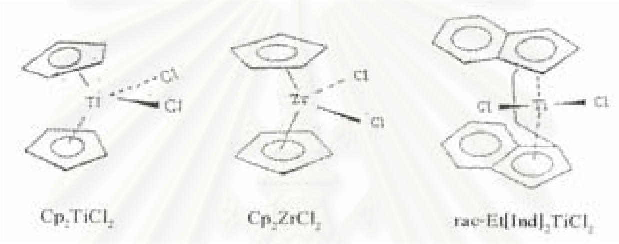
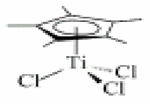


Figure 3.1.1 Metallocene Compounds [26]

These compounds are becoming an important class of catalyst for the synthesis of organic molecules and polymers. These compounds also have good potential to act as catalysts or catalysts precursors for a number of organic reactions. The discovery of Group 4 metallocene-aluminoxane systems as catalyst for polymerization reactions has opened up a new frontier in the area of organometallic chemistry and polymer synthesis.

Metallocene having a single Cp group include bridged and unbridged compounds. Two Cp groups are not required to generate chiral complexes. Monocyclopentadienyl titanium derivatives combined with MAO, afford very efficient catalysts which promote polymerization of styrene to highly syndiotactic polymers. The structures of half-metallocene compounds are shown in Figure 3.1.2.



Cp*TiCl$_3$

Figure 3.1.2 Half-metallocene compounds [27]

3.1.2 Aluminoxane

Aluminoxanes are synthesized by controlled hydrolysis of aluminium alkyls [28,29]. Simple synthetic routes to methylaluminoxane are not available due to the high reactivity of trimethylaluminum (TMA) with water. Many inorganic hydrated compounds are used as a source of water for preparing aluminoxane from alkyl aluminum. Hydrating compounds such as $CuSO_4.5H_2O$ and $Al_2(SO_4)_3.6H_2O$ are employed.

In metallocene based catalyst systems, the aluminoxanes appear to have a combination (depending on the nature of the catalyst and the polymerization conditions) of the following functions:

(1) Aluminoxane alkylates the metallocene compound and scavengers the impurity [103].

(2) Aluminoxane interacts with metallocene generate cationic metallocene alkyl species.

Aluminoxane alkylates the metallocene compound and scavenges the impurity. Aluminoxane interacts with metallocene to generate cationic metallocene alkyl species. The aluminoxane not only produces the cations but also stabilizes them.

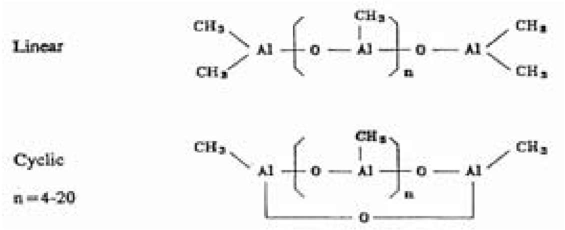


Figure 3.1.3 Plausible structure of methylaluminoxane [30]

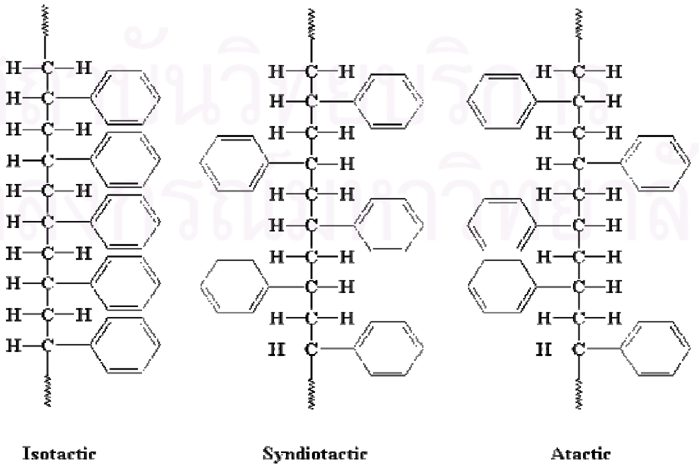
3.2 Polymer Tacticity

Stereoregularity arises because of order in the spatial structure of polymer chains. If the backbone of a polymer chain is drawn as a flat zigzag form in the plane of the paper, the patterns of molecule can be shown in Figure 3.1.4. They can be easily envisaged in the case of monosubstituted vinyl units. It should be noted that in

(a) All of the substituent R groups lie uniformly on the same side of the zigzag plane. Natta called this structure isotactic.

(b) The substituent R groups occupy positions alternatively above and below the backbone plane. Such a structure is termed syndiotactic.

(c) There is no regular arrangement of the substitutent R groups and this structure is called atactic.



(a) (b) (c)

Figure 3.1.4 Types of olefin polymer tacticity

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. Atactic polymers are amorphous (noncrystalline), soft (tacky) material with little or no physical strength. The corresponding isotactic and syndiotactic polymers are usually obtained as highly crystalline materials. Crystallinity leads to high physical strength and increased solvent and chemical resistance as well as differences in other properties that depend on crystallinity.

3.3 Syndiotactic polystyrene

Syndiotactic polystyrene (sPS) is a semicrystalline polymer synthesized from styrene monomer using a single-site catalyst, such as metallocene. First synthesized in 1985 by Idemitsu Kosan Co. Ltd. (Tokyo, Japan), the material has been under joint product and process development by Idemitsu and Dow Plastics (Midland, MI) since 1988.

Because of its semicrystalline nature, sPS products exhibit performance attributes that are significantly different from those of amorphous styrenic materials. These properties include a high melting point, good chemical and moisture resistance, and a high degree of dimensional stability.

sPS can be differentiated from conventional styrenic polymers on the basis of molecular structure. Atactic, or general-purpose, polystyrene is produced with random stereochemistry, resulting in nonspecific placement of the cyclic aromatic portion of the molecules. In contrast, isotactic and syndiotactic polystyrene are made using stereo-specific catalysis techniques that result in highly ordered molecular structures.

Some typical and mechanical properties of sPS are reported below; some reported values, e.g. the melting temperature, can slightly for polymers synthesized with different catalysts, owing to the different content of steric effect.[3]

Density	1050 kg/m^3
Glass transition temperature (T_g)	~100°C [31]
Melting temperature (T_m)	270°C [3]

Whereas atactic polystyrene is as amorphous polymer with a T_g of 100°C, syndiotactic polystyrene is semicrystalline with a T_g similar to atactic polystyrene and a T_m in the range 255-275°C. sPS exhibits a polymorphic crystalline behavior which is relevant for blend properties.

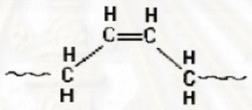
3.4 Polybutadiene

Polybutadiene (BR) is the second largest volume synthetic rubber produced, next to styrene-butadiene rubber (SBR). Consumption was about 1,953,000 metric tons worldwide in 1999. The major use of BR is in tires with over 70% of the polymer produced going into treads and sidewalls. Cured BR imparts excellent abrasion resistance (good tread wear), and low rolling resistance (good fuel economy) due to its low glass transition temperature (T_g). The low T_g , typically <–90°C, is a result of the low "vinyl" content of BR, which will be discussed below. However, low T_g also leads to poor wet traction properties, so BR is usually blended with other elastomers like natural rubber or SBR for tread compounds. BR also has a major application as an impact modifier for polystyrene. [32]

Polybutadiene is a homopolymer (only one monomer) of 1,3 butadiene, a monomer containing four carbon atoms, and six hydrogen atoms (C_4H_6). The four carbon atoms are in a straight chain containing two “double bonds” as follows: $CH_2=CH-CH=CH_2$

3.4.1 High Cis- Polybutadiene

The alkyllithium and transition metal catalysts make very different products. The transition metal, or so called Ziegler catalysts produce very “stereoregular” BRs with one type having the main polymer chain on the same side of the carbon-carbon double bond contained in the polybutadiene backbone. This is called the cis configuration.



cis-1,4

Figure 3.1.5 cis- configuration

High cis BR will usually have cis content >95% which gives rise to better “green strength” and increased cut growth resistance in the cured product. High cis BR also shows lower T_g compared to alkyllithium-based BR because it has almost no vinyl structure. As mentioned earlier, vinyl tends to increase the T_g of the polymer. The low vinyl content and low T_g makes high cis BR ideal for golf ball cores.

3.5 Common Types of Copolymers

Polymer made from only one kind of monomer, was normally considered. Copolymers can contain two kinds of monomers. These can be combined in various ways to obtain interesting and often highly useful materials. Some of the basic copolymer nomenclature is presented in Table 3.1.1. If three mers-A, B, and C- are considered, some of the possible copolymers are also named in Table 3.1.1. The connectives in copolymer nomenclature will be defined as below

Table 3.1.1 Some copolymer terminology

Type	Connective	Example
	Short Sequences	
Unspecified	-*co*-	poly(A-*co*-B)
Statistical	-*stat*-	poly(A-*stat*-B)
Random	-*ran*-	poly(A-*ran*-B)
Alternating	-*alt*-	poly(A-*alt*-B)
Periodic	-*per*-	poly(A-*per*-B-*per*-C)
	Long Sequences	
Block	-*block*-	poly A-*block*-poly B
Graft	-*graft*-	poly A-*graft*-poly B

3.5.1 Unspecified Copolymers

An unspecified sequence arrangement of different monomers in a polymer is represented by

poly(A-*co*-B)

Thus an unspecified copolymer of styrene and p-methylstyrene is named

Poly[styrene-*co*-(p-methylstyrene)]

In the old reference literature,-*co*- was used to indicate a random copolymer, where the mer were added in random order, or perhaps addition preference was dictated by thermo dynamic or spatial considerations. These are now distinguished from one another.

3.5.2 Statistical Copolymers

Statistical copolymers are copolymers in which the sequential distribution of the monomers obeys known statistical laws. The term **–*stat*-** embraces a large proportion of those copolymers that are prepared by simultaneous polymerization of two or more monomers in admixture. Thus the term **-*stat*-** is now preferred over –*co*- for most usage.

The arrangement of monomers in a statistical copolymer of A and B might appear as follows:

… -A-A-B-A-B-B-B-A-B-A-A-B-A- …

3.5.3 Random Copolymers

A random copolymer is a statistical copolymer in which the probability of finding a given monomeric unit at any given site in the chain is independent of the nature of the neighboring units at the position.

3.5.4 Alternating Copolymers

In the discussion above, various degrees of randomness were assumed. An alternating copolymer is just the opposite, comprising two species of monomeric units distributed in alternating sequence:

…-A-B-A-B-A-B-A-B-A-B-A-B-A-B-…

Alternating copolymerization is caused either by A or B being unable to add itself, or the rate of addition of the other monomer being much faster than the addition of itself.

3.5.5 Periodic Copolymers

The alternating copolymer is the simplest case of a periodic copolymer. For three monomers:

… A-B-C-A-B-C-A-B-C- ….

3.5.6 Block Copolymers

A block copolymer contains a linear arrangement of blocks, a block being defined as a portion of a polymer molecule in which the monomeric units have at least one constitutional or configurational feature absent from the adjacent portions. A block copolymer of A and B may be written

…-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-B-…

An especially important block copolymer is the triblock copolymer of styrene and butadiene

polystyrene-*block*-polybutadiene-*block*-polystyrene

In the older literature, -*b*- was used for -*block*-, and -*g*- was used for -*graft*- (below). Only the first poly was indicated. Structure was then written

polystyrene-*b*-polybutadiene-*b*-polystyrene

3.5.7 Graft Copolymers

A graft copolymer comprises a backbone species, poly A, and a side-Chain species, poly B. The side chain comprises units of monomer that differ from those comprising the backbone chain. If the two monomers are the same, the polymer is said to be branched. A graft copolymer structure of A and B may be written:

…-A-A-A-A-A-A-A-A-A-A-A-A-A-A-…
|
B-B-B-B-B-B-B-B-B-B-B-…

A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from the main chain, exclusive of branch points. In a graft copolymer, the distinguishing feature of the side chains is constitutional: the side chains comprise units derived from at least one species of monomer different from those that supply the units of the main chain. Graft polymerization is an attractive method for the modification of polymer properties [33]. Since the main chains and the branch are generally thermodynamically incompatible, most graft copolymers are polymer blends, block copolymers, and interpenetrating networks. Graft copolymers are also used as emulsifiers, surface-modifying agents, coating materials, adhesives and compatibilizing agents for polymer blends.

3.6 Anionic polymerization

Anionic polymerization is particularly suitable for the synthesis of graft copolymers with low degrees of compositional heterogeneity. The absence of termination and chain transfer reactions allows the preparation of polymers with narrow molecular weight distributions and predictable molecular weight. When applied to graft copolymer synthesis, anionic non-terminating systems have the advantage that branches with uniform length can be prepared. In principle, anionic system can provide graft polymers with well-defined structures delineate the relationships between structure, morphology, and properties. However, there is a major limitation for all of the available anionic methods for graft copolymer synthesis: there is generally a random distribution of branch points along the backbone chain since there is no control over the generation of the loci branch formation. [34]

General aspects of graft copolymer synthesis

There are three general methods for the synthesis of graft copolymers [26]:

(a) “grafting from” (Figure 3.1.6(a)), in which active sites are generated on a backbone polymer chain and are used to initiate the polymerization of a second monomer, M^2, to form a graft branch.

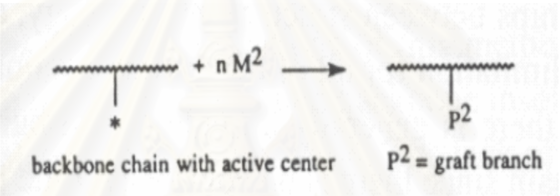


Figure 3.1.6(a) Grafting from

(b) “grafting onto” (Figure 3.1.6(b)), in which a backbone polymer chain contains randomly distributed reactive functional groups X, which can react with another macromolecular chain that carries antagonistic, reactive functional groups, Y, at the chain ends.

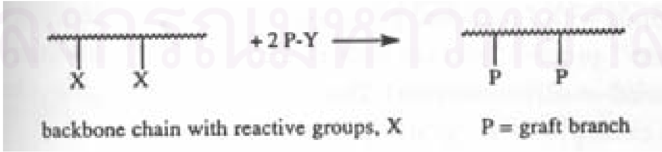


Figure 3.1.6(b) Grafting onto

(c) “grafting through” (Figure 3.1.6(c)), in which a growing polymer chain with reactive chain end sites incorporates a branch chain by addition to another polymer chain that processes reactive unsaturated groups and copolymerizes with the backbone-forming monomer (M^1).

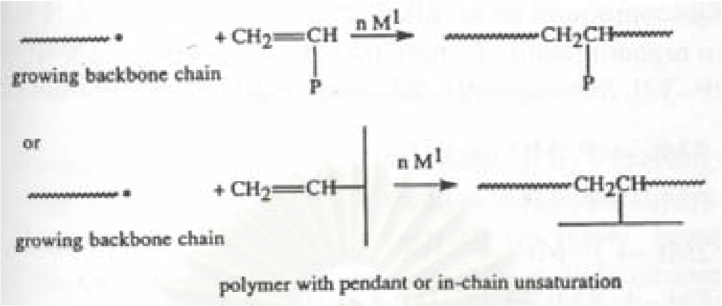


Figure 3.1.6(c) Grafting through

In this research, graft copolymer was prepared by metalation grafting.

3.7 Rubber Modification of Syndiotactic Polystyrene

Polystyrene (PS) in its atactic and syndiotactic forms is a brittle thermoplastic, even in an orientated state. To improve the toughness of aPS, impact modification has been practiced for a long time, either by polymerizing the styrene in the presence of a polybutadiene rubber leading to high impact polystyrene, commonly called HIPS, or by blending the polystyrene with multi-block copolymers, mainly of the styrene-butadiene-styrene (S-B-S) type.

In the case of sPS, the problem of its brittleness can be even more acute since it has to compete with engineering plastics which posses an inherent toughness superior to that of toughness of sPS. For this reason, a good impact modification of this product is of paramount importance and may even be essential for its survival as a commercial thermoplastic. Rubber modification plays an importance role for styrene polymers, whether atactic or syndiotactic.[3]

3.7.1 Energy dissipation in polystyrene

Polystyrene, in either atactic or syndiotactic form, is a polymer which shows no segmental mobility of chain segments below its glass transition temperature. Secondary relaxation processes which can be attributed to mobility in the main chain are missing. Therefore, these materials do not exhibit long-range energy dissipation deformation processes on impact below the glass transition temperature and thus the main method of energy dissipation is via craze formation. This has a consequence that PS polymers are very susceptible to brittle failure at these temperatures.

Above the glass transition, the whole polymer chain is mobile in the amorphous region and as a result stable energy-dissipating shear processes prevail. The prerequisite for this kind of deformation is high mobility of the molecules above their glass transition temperature in the amorphous region between crystalline lamellae. Crazes are not observed.

More importance is the use of sPS at lower temperatures is more importance. Below the glass transition temperature the dilatational strain within the bulk material in tension is released by the well known crazes. Crazes are crack-like structures bridged by highly oriented fibrils. These fibrils, after formation during tensile testing, are stress bearing and can therefore contribute to energy dissipation. A prerequisite for stress bearing is that the molecular weight of the sPS is high enough to form sufficient numbers of tie molecules between the crystalline phase and sufficiently strong entanglements between the individual polymer chains.

3.8 Polymer blend

Polymer blends are the mixtures of at least two or more polymers. The mixing of two or more existing polymers may obtain the new properties of the blend. By using these techniques the designed properties can be explored without synthesizing the new polymer which have the designed properties. The results of blending polymers have many advantages, for example, lower cost than synthesizing the desired properties of new polymer. The new properties can be under control.

3.8.1 Melt Mixing

Melt mixing of thermoplastics polymer is performed by mixing the polymers in the molten state under shear in various mixing equipment. This method is popular in preparation of polymer blends on the large commercial scale because of its simplicity, speed of mixing and the advantage of being free from foreign components (e.g. solvent) in the resulted blends. A number of devices are available for laboratory-scale mixing such as brabender mixer, electrically-heated two-roll mill, extruder, rotational rheometer.

The advantages of this method are the most similar to the industrial practice. The commercial compounding or adding additives into base polymers are applied by melt mixing. So the investigations of polymer blends by melt mixing method are the most practical methods in industrial applications.

3.8.2 Solvent Casting

This method group is performed by dissolving polymers in the same solvent. The solution is then cast on a glass plate into thin films and the removal of solvent from the films is performed by evaporating the solvent out at ambient or elevated temperature. Solvent casting is the simplest mixing method available and is widely practiced in academic studies, usually when the experiments need very small quantities of polymers.

The most severe problem with solvent casting is the influence of the solvent on the resulted product especially the shift of the phase diagram. In spite of the fact that the most of the solvent can be removed from a cast film, the nature of the film depends strongly on the types of solvents and casting condition.

To remove traces of solvents from the casting polymer films, the condition of high temperature is invariably needed, and protection of the polymer in case of degradation is essential. The inert gas or lower down the pressure (vacuum) typically used. In the vacuum conditions, the vapor pressure can be reduced and thus allows the solvents to evaporate more easily. However, too fast evaporation rate of solvent will result in the bubble in the final films produced.

3.8.3 Freeze Drying

In the freeze drying processes, the solution of the two polymers is quenched down immediately to a very low temperature and the solution is frozen. Solvent is then removed from the frozen solution by sublimation at a very low temperature. Dilute solutions must be used and the solution volume must have as large surface area as possible for good heat transfer.

3.8.4 Emulsions

The advantages of the emulsion polymer mixing are the easy handing and all the other advantages as the solvent casting. The mixing or casting of the film requires neither expensive equipment nor high temperature. However, emulsions of polymers are an advance technique and not always applicable to all monomers.

3.8.5 Reactive Blend

Co-crosslinking and interpenetrating polymer networks (IPN) formations are the special methods for forming blends. The idea of these methods is to enforce degree of miscibility by reactions between the polymer chains. Other methods involve the polymerization of a monomer in the presence of a polymer and the introduction of interface graft copolymer onto the polymer chains.

3.9 Dilute solution viscosity

Measurement of the dilute-solution viscosity of polymer solutions provides one of the most easily obtained and widely used items of information about the molecular structure of the samples. Since the dilute-solution viscosity of a given sample depends upon the type of solvent used and the temperature of the measurement, it is necessary that both these be specified (and the concentration also unless the intrinsic viscosity is calculated) for all measurements. Provided that it is known that the polymer is linear rather than branched, empirical correlations can be developed between the intrinsic viscosity and the molecular weight of the sample. The Ubbelodhe viscometer utilized in this experiment operates independent of the total volume of solution over a considerable range. It is therefore useful as a dilution viscometer, in which solutions having several different concentrations can be prepared and measured in situ. This facility results from its construction in which the solution emerging from the lower end of the capillary flows down the walls of bulb A in a manner which is independent of the liquid level in the main reservoir B. This mode of action is referred to as a suspended level.

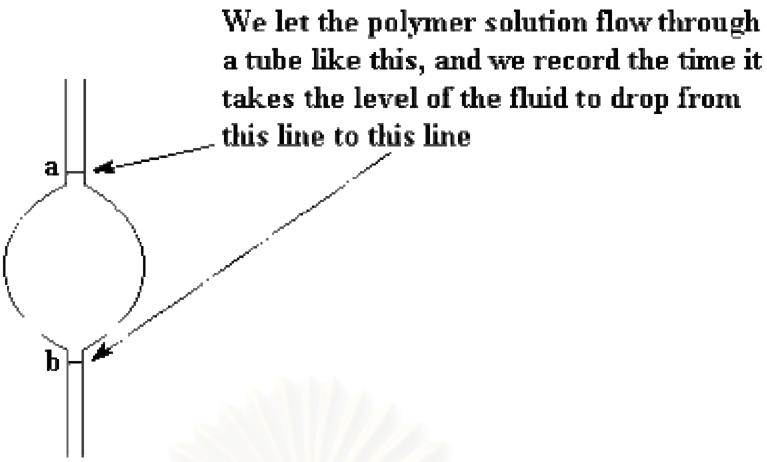


Figure 3.1.8 Measurement of efflux time of U-tube viscometer

The simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are so great. Several mathematical equations are available in the literature for determining the intrinsic viscosity [η] of a polymer solution, by graphical extrapolation. In this study, intrinsic viscosity was determined from Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad (1)$$

where k" is constant, ηr is relative viscosity, c is concentration in g/dl and [η] is determined from $[(\ln \eta r)/c]c=0$. According to the Mark-Houwink-Sakurada relation, the correlation between intrinsic viscosity and molecular weight, the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K' M^a \qquad (2)$$

where K´ and a are constants related to the stiffness of the chain and depend on the type of polymer, solvent and temperature.[35]

3.10 Dynamic Mechanical Analysis [36]

Dynamic mechanical analysis (DMA) is becoming more and more commonly seen in the analytical laboratory as a tool rather than a research curiosity. This technique is still treated with reluctance and unused, probably due its importation from the field of rheology. Rheology, the study of the deformation and flow of materials, has a reputation of requiring a fair degree of mathematical sophistication. Although many rheologists may disagree with this assessment, most chemists have neither the time nor the inclination to delve through enough literature to become fluent. Neither do they have an interest in developing the constituent equations that are a large part of the literature. However, DMA is a technique that does not require a lot of specialized training to use for material characterization. It supplies information about major transition as well as secondary and tertiary transitions not readily identifiable by other methods. It also allows characterization of bulk properties directly affecting material performance.

3.10.1 Basic principles

In DMA, a complex modulus (E^*), an elastic modulus (E'), and an imaginary loss modulus (E'') are calculated from the material response to the sine wave. These different moduli allow better characterization of the material, because we can now examine the ability of the material to return or store energy (E'), to its ability to lose energy (E''), and the ratio of these effects ($\tan \delta$), which is called damping.

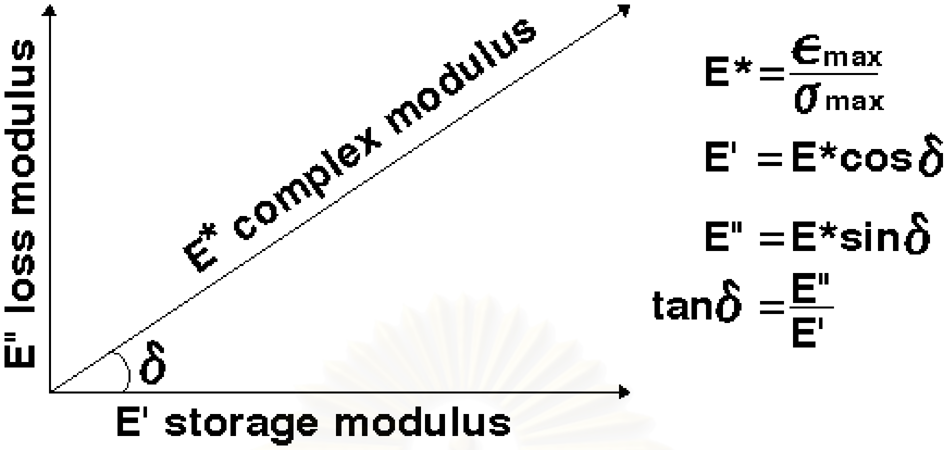
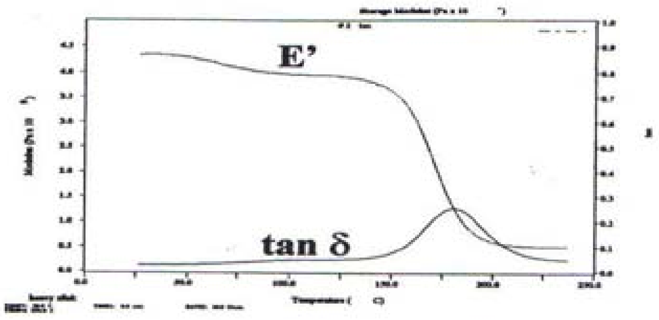


Figure 3.1.9 DMA relationships

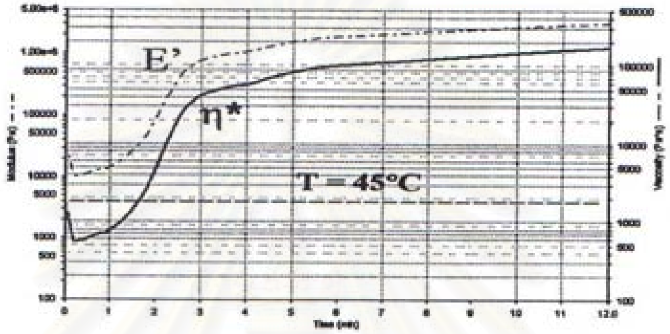
3.10.2 Time-Temperature Scans

One of most common uses of the DMA for users from a thermal analysis background is the measurement of the various transitions in a polymer. A lot of users exploit the greater sensitivity of the DMA to measure Tg’s undetectable by the differential scanning calorimeter (DSC) or the differential thermal analyzer (DTA). For more sophisticated users, DMA temperature scanning techniques let you investigate the relaxation processes of a polymer. In this topic, we will look at how time and temperature can be used to study the properties of polymers.

If we start with a polymer at very low temperature and oscillate it at a set frequency while increasing the temperature, we are performing a temperature scan (Figure 3.1.10). This is what most thermal analysis thinks of as a DMA run. Similarly, we could also hold the material at a set temperature and see how its properties change over time (Figure 3.1.10b).



(a) Temperature Scan



(b) Time Scan

Figure 3.1.10 Time-temperature studies in the DMA (a) Vary temperature (b) Hold temperature constant

CHAPTER IV

EXPERIMENT

In the present study of the influence of homogeneous half-metallocene catalyst system with modified methyl aluminoxane as cocatalyst on copolymerization of styrene and 4-methylstyrene. Then high cis-polybutadiene was grafted onto the syndiotactic poly(styrene-co-4-methylstyrene) backbone and the mechanical properties of graft copolymers and their blends was investigated. The experiments were divided into four parts.

(i) Preparation of styrene and 4-methylstyrene monomer

(ii) Polymerization procedure

(iii) Blend polymer between synthesized graft copolymer and syndiotactic polystyrene

(iv) Characterization of all syndiotactic polystyrene copolymer products

The details of the experiment were explained in the following.

4.1 Materials and Chemical

The chemicals used in these experiments were analytical grade, but only critical materials were specified as followed:

1. Styrene monomer purchased from Fluka Chemie A.G., Switzerland was distilled from sodium under vacuum just before use.
2. p-Methylstyrene purchased from Aldrich chemical Company, Inc. was distilled from sodium under vacuum just before use.
3. Polybutadiene donated from BST Elastomers Co., Ltd.

4. Trichloro(pentamethyl cyclopentadienyl) titanium (IV) (Cp*$TiCl_3$, 97.0%) was purchased from Aldrich chemical Company, Inc.
5. Modified methyaluminoxane (MMAO) 1.831 M in toluene was donated from Tosoh Akso, Japan.
6. n-Butyl Lithium 2.0 M in cyclohexane was purchased from Aldrich chemical Company, Inc.
7. tert-Potassium Butoxide was purchased from Aldrich chemical Company, Inc.
8. Cyclohexane was purchased from Aldrich chemical Company, Inc.
9. Toluene commercial grade was donated from Exxon Chemical Ltd.,Thailand. This solvent was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone under argon atmosphere before use.
10. Argon gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG) and further purified by passing through columns packed with copper catalyst, NaOH, P_2O_5 and molecular sieve 4A to remove traces of oxygen and moisture.
11. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
12. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.
13. Methanol (Commercial grade) was purchased from SR lab.
14. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.
15. Methyl ethyl ketone (MEK) purchased form Carlo Erba, Italy was used without further treatment.

4.2 Equipments

All equipments used in the catalyst preparation, and polymerization of the polymer is listed as below:

4.2.1 Equipment for handling air-sensitive compounds

Since the most of reagents and catalysts were very sensitive to the oxygen and moisture therefore special techniques were taken in the handling of reagents and for loading the catalyst into the reactor. Such equipments utilized for this purpose are as follows:

(a) **Glove box** (Vacuum Atmospheres) with oxygen and moisture analyzer for transferring solid reagents under inert atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box. The glove box is shown in Figure 4.2.1(a).

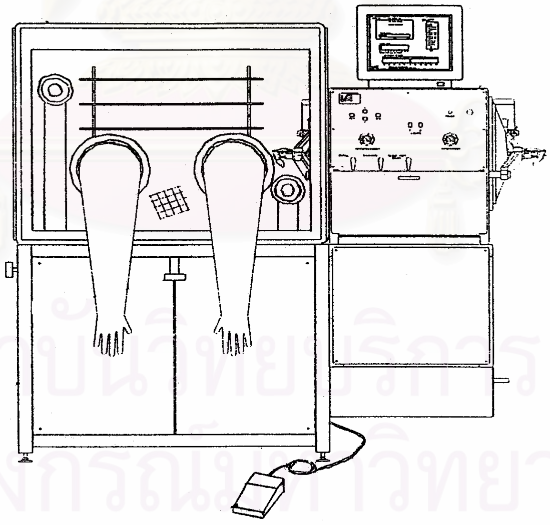


Figure 4.2.1(a) Glove box

(b) **Schlenk line** included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 4.2.1(b).

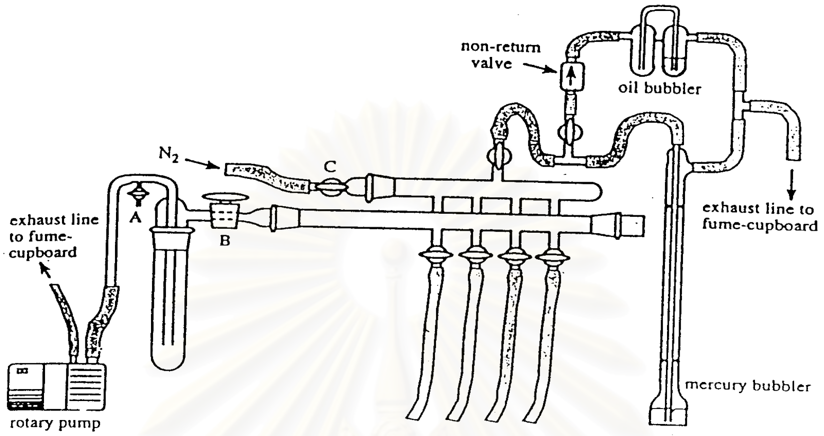


Figure 4.2.1(b) Schlenk line

(c) **Schlenk tube** for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is a tube with a ground joint and side arm which was three way glass valve as shown in Figure 4.2.1(c).

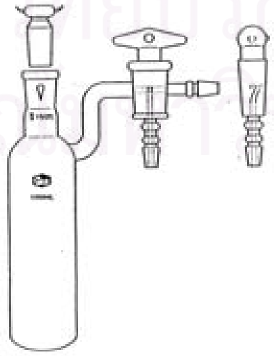


Figure 4.2.1(c) Schlenk tube

(d) **The inert gas** (argon) was pass through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) for purifying ultra high purity argon before use in Schlenk line and solvent distillation column. The inert gas supply system is shown in Figure 4.2.1(d).

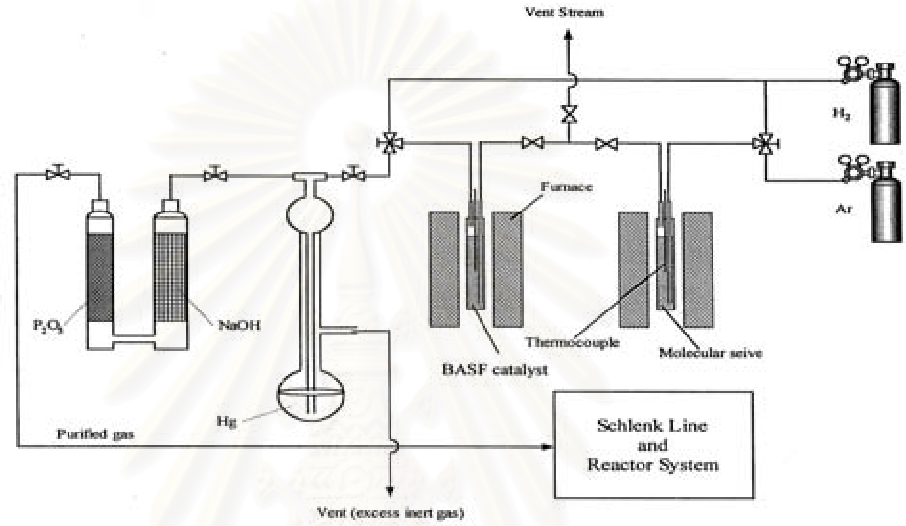


Figure 4.2.1(d) Inert gas supply system

(e) **The vacuum pump** model 195 from Labconco Coporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line. The vacuum pump is shown in Figure 4.2.1(e).

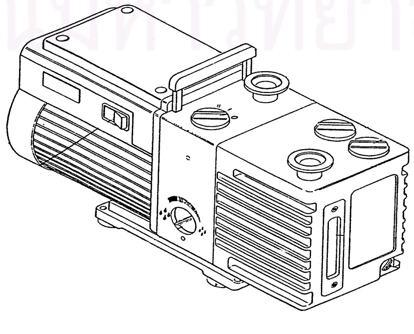


Figure 4.2.1(e) Vacuum pump

4.2.2 Glass Reactor

The polymerization reactor was a 250 ml. three-neck flask. The reactor was equipped with several fittings for injecting the chemicals and purging with argon gas. The Glass Reactor is shown in Figure 4.2.2.

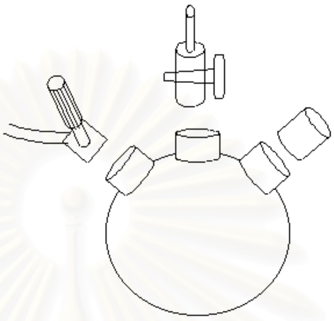


Figure 4.2.2 Glass Reactor

4.2.3 Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

4.2.4 Digital Hot Plate Stirrer

A Cole-Parmer digital hot plate stirrer was used for blending the polymers. The hot plate stirrer is programmable. All functions can be set from digital panel and display their status on LCD. The plate temperature, stirrer speed and time are controllable.

4.2.5 Cooling System

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

4.2.6 Syringe, Needle and Septum

The syringe was used in the experiment had a volume of 50 and 10 ml and the needle were No. 17 and 20, respectively. The septum was a silicone rod. It was used to prevent the surrounding air from entering into glass bottle by blocking at the needle end. The solvent, catalyst, cocatalyst and monomer were transferred to a glass reactor by using needles.

4.3 Polymerization procedures

All operations were performed under argon atmosphere by using Schlenk line and glove box.

4.3.1 Preparation of Catalyst Precursor

Approximately 5.8 mg of Cp*$TiCl_3$ was dissolved in 10 ml toluene under argon atmosphere in glove box. The catalyst solution was stirred until the catalyst was completely soluble. The solution was used as a catalyst for copolymerization styrene and p-methylstyrene with MMAO. ([Al]/[Ti]=200)

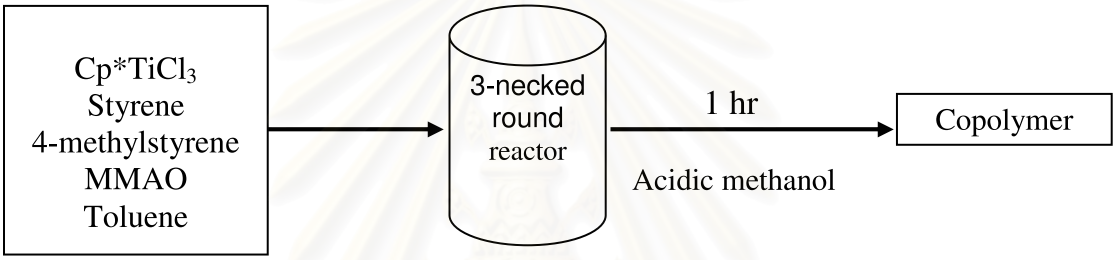
4.3.2 Purification of Styrene and p-Methylstyrene Monomer

Styrene and p-Methylstyrene monomer (chemical reagent grade) was washed with 5% aqueous sodium hydroxide (NaOH) solution and distilled water, then distilled under reduced pressure.

4.3.3 Synthesis of syndiotactic poly(styrene-co-4-methylstyrene)

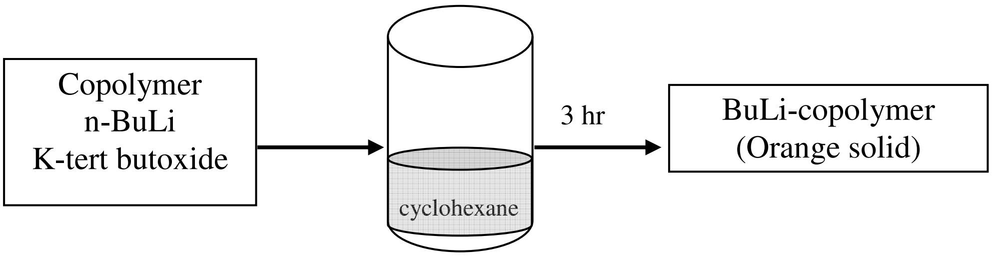
Copolymerization of styrene and p-methylstyrene was carried out in a 250 cm^3 glass reactor equipped with a magnetic stirring by introducing prepared Cp*$TiCl_3$

precursor (from 4.3.1), 9 ml of styrene, 1.2 ml of p-methylstyrene, MMAO, ([Al]/[Ti]=200), and 46 ml of tolueneat the desired temperature of 25 °C under argon atmosphere. The total volume of the polymerization mixture was 120 ml. After the desired reaction time was passed, reaction was terminated by addition acidic methanol. The resulting precipitated polymer was washed several times with methanol and dried in vacuum oven at 60°C. The polymer was extracted with refluxing methyl ethyl ketone (MEK) for 12 h in order to determine the SPS portion of the polymer obtained.



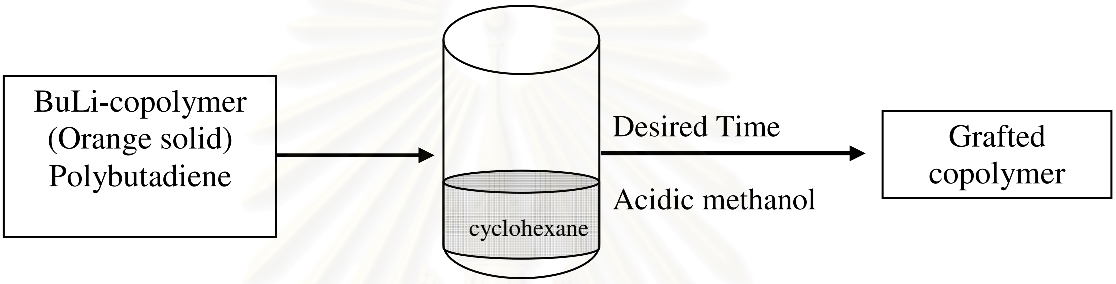
4.3.4 Deprotonation of syndiotactic poly(styrene-co-4-methylstyrene)

The syndiotatic poly(styrene-co-4-methylstyrene) was prepared as the described method. Deprotonation of the copolymers were conducted as the following procedure: The 1 g of syndiotatic poly(styrene-co-4-methylstyrene) containing 25 mole % of p-methylstyrene with a crystalline melting point of 246°C. was suspended in a cyclohexane solution. Then 1 mmole of n-Buli and 0.1 mole of potassium tertbutoxide were added. The solution was allowed to react at room temperature for 3 hr to provide the deprotonated polymer as an orange solid. The deprotonated polymer was isolated after filtration, washed with cyclohexane and dried under vacuum.



4.3.5 Synthesis of graft copolymer between syndiotactic poly(styrene-co-4-methylstyrene) and polybutadiene

The 0.5 g of the deprotonated copolymer prepared from described method was allowed to suspend in cyclohexane before 1 g of polybutadiene was added. The anionic polymerization took place at room temperature. The reaction continued for 1 hour before it was terminated by the addition of methanol. The resulting polymer was isolated by filtration and dried under vacuum.



4.4 Blend Preparation

The blends of syndiotactic polystyrene and grafted copolymers were prepared by using melt mixing method. The blends were made at 300°C by hand on the digital controllable hot plate with 0.25% of graft copolymers.

4.5 Characterization

4.5.1 Stereospecificity

The syndiotacticity of polystyrene can be determined in a number of ways. The most widely used method involved extracting the polymer in a Soxhlet extraction with a boiling solvent. For syndiotactic polystyrene, boiling methyl ethyl ketone (MEK) was commonly used. A % syndiotactic index (% S.I.) is computed from

% S.I. = (Insoluble Weight of PS/Total Weight of PS) x 100

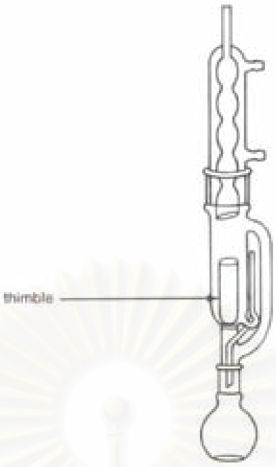


Figure 4.5.1 Soxhlet Extractor

4.5.2 Thermal properties

The melting temperature (Tm) crystalline temperature (Tc) and glass transition temperature (Tg) of the polymer was determined with differential scanning calorimetry (DSC) which an instrument designed to measure the thermal properties. The melting temperature of polymers was determined from the critical point of DSC curve.

Perkin-Elmer Diamond DSC at Center of excellent on Catalytic and Catalytic reaction Engineering, Chulalongkorn University, was used in this research. The analyses were performed at heating rate 20 ºC/min in the temperature range -60 to 300 ºC. The heating cycle was run twice. The first scan, samples were heated and then cooled to start temperature. The second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan were influenced by the mechanical and thermal history of samples.

Figure 4.5.2 Perkin-Elmer Diamond DSC

4.5.3 Comonomer incorporation and Polymer structure

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful tools available to the chemists and biochemist for elucidating the structure of both organic and inorganic species. For polymer, ^{13}C-NMR spectroscopy was widely used methods for determination of comonomer incorporation and polymer structure.

^{13}C NMR spectra were records on Avance DPX-400 spectrometer at Chemical department, Faculty of science, Chulalongkorn University.

4.5.4 Average Molecular Weight

One of the most widely used methods for the routine determination of molecular weight (Mw) was solution viscosity. Samples were dissolved in *o*-Xylene at initial concentration of approximately 0.2g/dl and measured at 90 °C by U-tube viscometer. The effux time was recorded. The data used for viscosity calculations and converted to average molecular weight.

4.5.5 Morphology

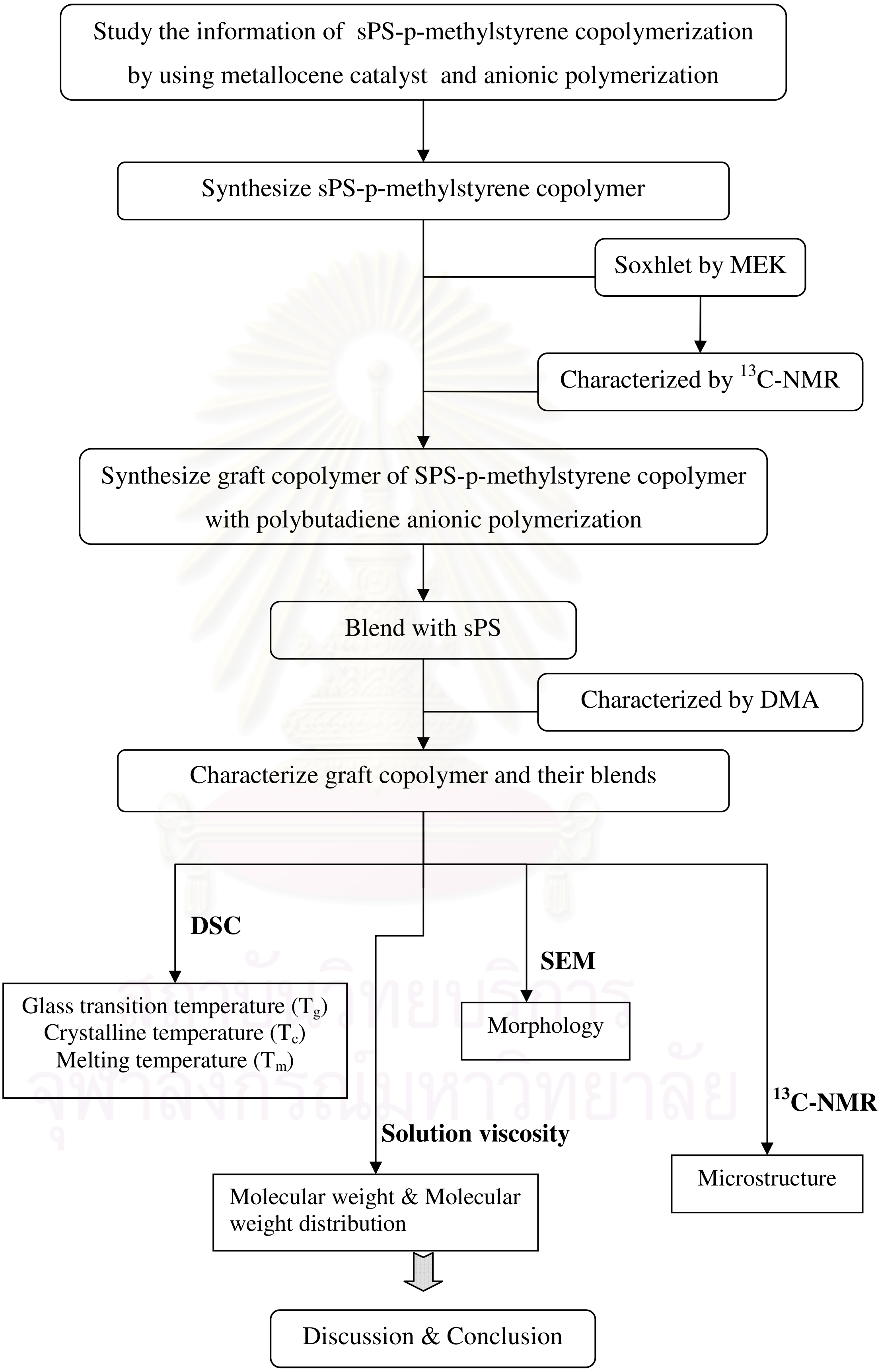
Scanning electron microscopic (SEM) technique was the effective method to investigate catalyst precursor morphologies. The term of morphology was referred to shape, texture or form of polymer, and all distribution on the polymer particles.

SEM observation with a JSM-5410LV Scanning Microscope at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University was employed to investigate the morphology of all syndiotactic polystyrene derivatives. The samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

4.6 Research Methodology

Research Methodology of flow diagram is shown in Figure 4.6

Figure 4.6 Flow diagram of research methodology



CHAPTER V

Results and Discussion

In this research, the graft copolymers of grafted syndiotactic polystyrene (sPS) with polybutadiene were synthesized by combination of metallocene catalyst system and anionic polymerization system. Then the graft copolymers may be used as compatibilizer in the blend of syndiotactic polystyrene to modify mechanical properties in order to compensate the glassy properties of pure syndiotactic polystyrene at room temperature. This chapter provides information about the copolymerization of styrene and 4-methylstyrene, the properties of syndiotactic polystyrene graft copolymers and their blends.

5.1 Copolymerization of Styrene and 4-Methylstyrene

The process conditions and polymer properties from the copolymerization of styrene and 4-methylstyrene using Pentamethylcyclopentadienyl titanium trichloride ($\mathrm{Cp^*TiCl_3}$)/modified methylaluminoxane (MMAO) system are given in Table 5.1.

Table 5.1 Copolymerization of Styrene and 4-methylstyrene using $\mathrm{Cp^*TiCl_3}$ with MMAO[a]

% Yield[b]	86.61 wt %
Catalytic Activity	5,302.2 g copolymer/mole Ti·hr
% Syndiotactic Index	96.85 %
T_g[c]	100 °C
T_m[c]	247 °C

[a] Conditions: $[\mathrm{Cp^*TiCl_3}] = 0.15$mmol, [MMAO] = 1.83 M, [Styrene] = 2.06, Al/Ti = 200, 25 °C

[b] Calculated from (weight of synthesized polymer/weight of monomer)×100, [c] Obtained from DSC

The sPSMS random copolymer was synthesized by the copolymerization of styrene and 4-methylstyrene with Cp*$TiCl_3$/MMAO catalyst. The chemical structures of this copolymer were confirmed by ^{1}H-NMR analysis as shown in Figure 5.1. The peaks appearing at 2.26 ppm confirmed the presence of methyl protons from 4-methylstyrene units. From the ^{1}H-spectra of sPSMS, the ratio of integral peak intensity at 2.26 ppm (-CH_3) to integral peak intensity at 1.8 ppm (-CH of the main chain) showed that the synthesized sPSMS copolymer has 25 mol% of 4-methylstyrene.

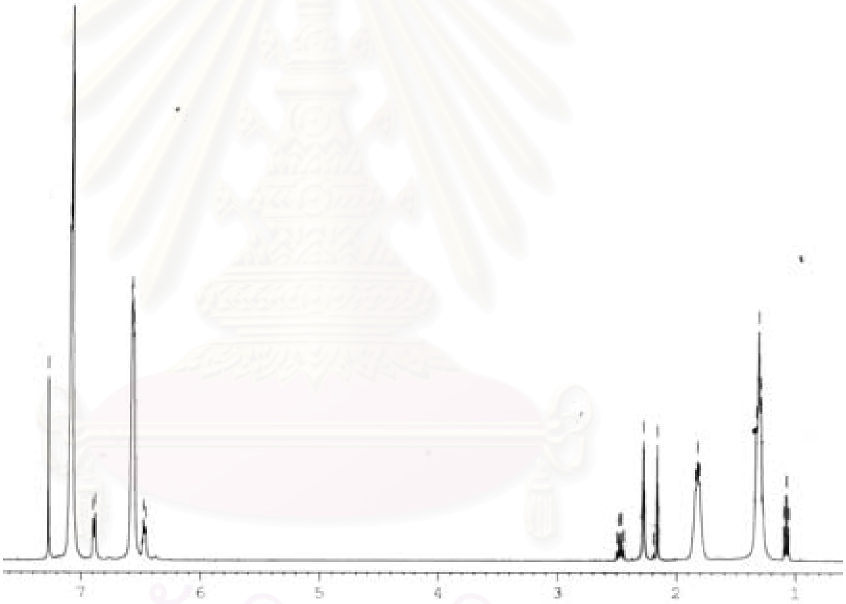


Figure 5.1 ^{1}H-NMR spectra of sPSMS copolymers in $CDCl_3$ solvent

5.2 Grafting of Syndiotactic poly(styrene-co-4-methylstyrene) with polybutadiene

In this study, we attempted to prepare graft copolymer of sPS by alternative pathway and to introduce polybutadiene graft to sPS. Here, there are three-stages in this method. The first stage is to introduce the CH_3 substituted, which serves as further metalation site for grafting polybutadiene, into sPS backbone (see in 5.1). The second stage is to use *n*-BuLi in strong base condition to generate metalated anionic sites from the copolymer (sPSMS). The resulting anionic sites served as initiators and the addition of polybutadiene to the sites in the last stage yielded the poly(sPS-g-polybutadiene). To obtain polymer with different polybutadiene content, three different reaction times were performed in the last stage. The reaction products identification and their properties were given in this report.

5.2.1 Effect of reaction time on copolymerization system

Polybutadiene is one of the well known commercialized elastomer and usually produced with high cis-configuration. The polymerization experiments were conducted by the same excess amount of polybutadiene to sPSMS content at all reaction conditions. Even if ungrafted sPSMS may exist, the amounts of polybutadiene were added in excess in all the reaction. Moreover the addition of excess amounts of polybutadiene led to the poly(sPS-g-PB) copolymers in good yields without any difficulty. Results of grafting conditions with various reaction times are shown in Table 5.2.

Table 5.2 Results of copolymeriztion of styrene with polybutadiene[a]

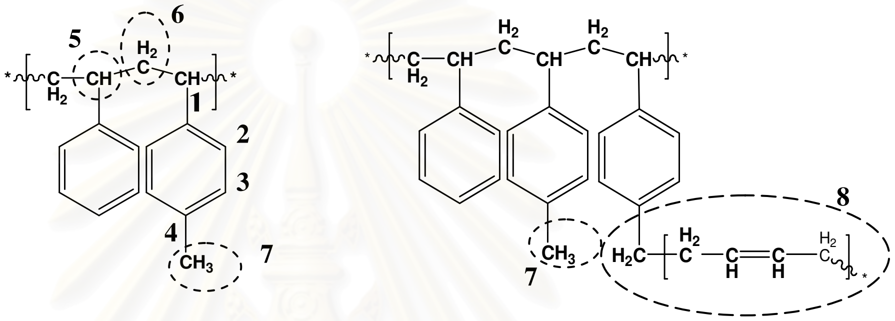
Sample	sPSMS (g)	PB (g)	Reaction time (hr)	Yield (g copolymer)	Content of PB in %wt
PS-1	0.5	1	0.5	0.85	3.94
PS-2	0.5	1	1	1.26	11.50
PS-3	0.5	1	2	1.38	34.47

[a] copolymerization conditions: 2 mmol *n*-BuLi, 0.01 mol K-tertbutoxide and 25°C

From Table 5.2, the polymerization activities, based on polymer yield, and polybutadiene contents in the products varied proportional to the reaction times.

5.2.2 Characterization of copolymers

The copolymer structures and each carbon positions which represented by ^{13}C-NMR are defined in Figure 5.2. The characteristics of ^{13}C-NMR spectra for all mentioned copolymers were shown in Figure 5.3. The strong and sharp peak appearing at 145.9 ppm confirmed that the graft copolymers were highly syndiotactic.[13,14]



(A) (B)

Figure 5.2 Structure of the synthesized copolymers: (A) sPSMS and (B) sPSMS-g-PB

Figure 5.3(A) shows the peaks at 21.4 ppm derived from methylene carbon in 4-methylstyrene. During the anionic graft polymerization, Figure 5.3(B), 5.3(C) and 5.3(D) reveals a decrease in the peak intensity at 21.4 ppm and is corresponded to a increase in the peak intensity of the PB units at 27.5 ppm. This peak also proved that polybutadiene was highly cis-1,4.[13,14] In addition, when compared the peak intensity at 21.4 and 27.5 ppm of each graft copolymers, we found that the peak intensity at 27.5 ppm increase with increasing of reaction time while the peak intensity at 21.4 ppm remains constant. This showed that the number of metalated anionic sites were approximately unchanged when the reaction time of grafting increases. Thus the molecular weight increases because the grafted polybutadiene side chain grows continuously without more active sites.

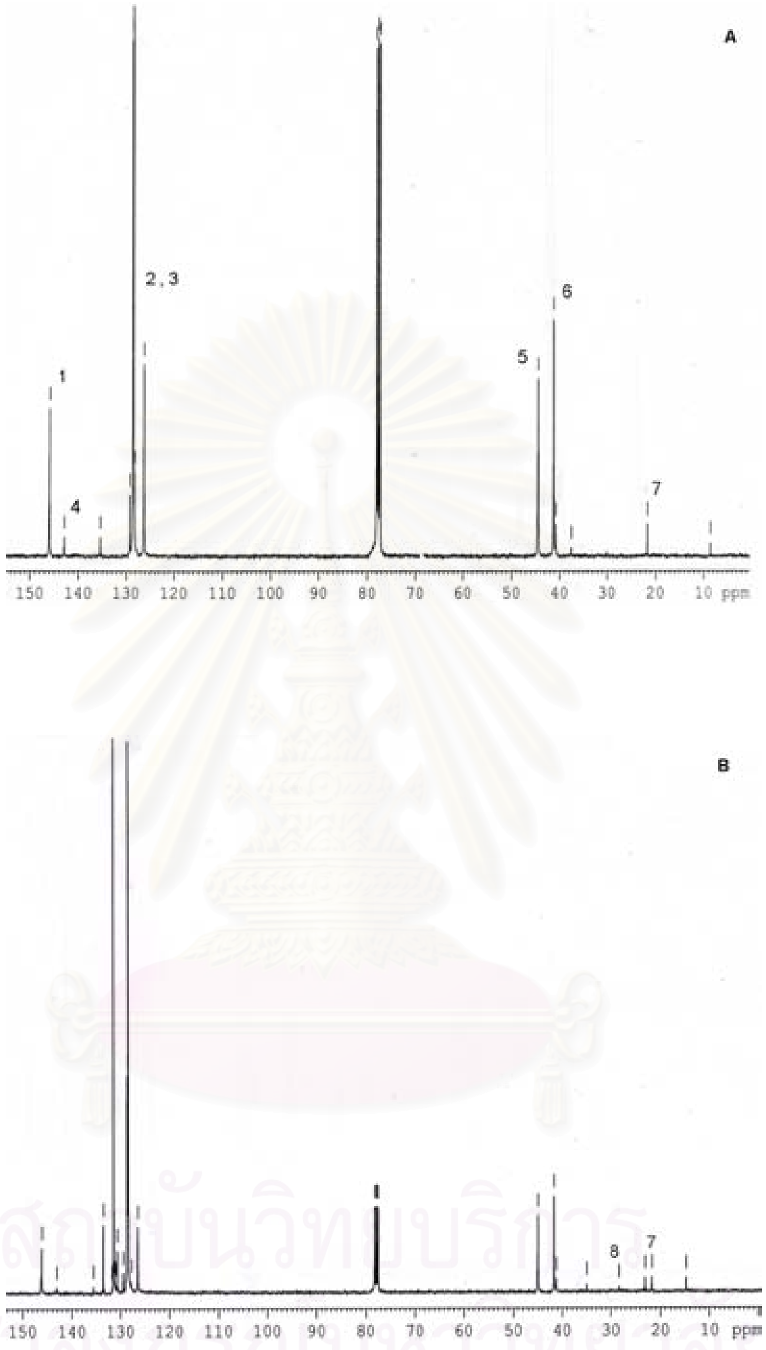


Figure 5.3 ^{13}C-NMR spectra of sPS copolymers in $CDCl_3$/o-dichlorobenzene: (A) PS-0[a], (B) PS-1, (C) PS-2 and (D) PS-3

[a] Dissloved in $CDCl_3$ only

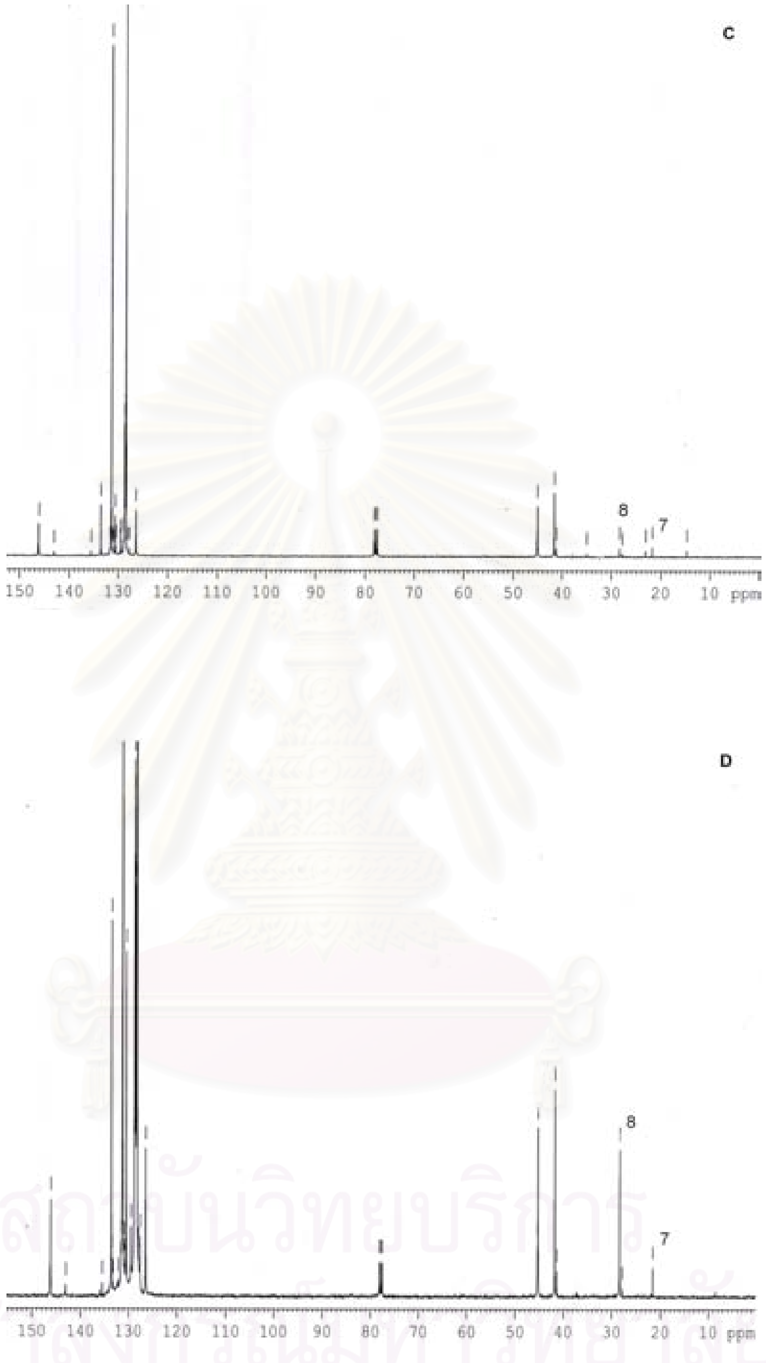


Figure 5.3 ^{13}C-NMR spectra of sPS copolymers in $CDCl_3$/o-dichlorobenzene: (A) PS-0[a], (B) PS-1, (C) PS-2 and (D) PS-3 (continued)

[a] Dissloved in $CDCl_3$ only

If the CH_3 of 4-methylstyrene are all consumed in the graft polymerization, the ^{13}C-NMR spectra peak at 21.4 ppm should disappear completely and the intensity of the peak at 27.5 ppm should reach its maximum. Unfortunately, there are the peak at 21.4 ppm remained which showed the incomplete depletion of CH_3 in all reaction condition. Due to the relatively high Mw of these graft copolymers, it can only be dissolved in dichlorobenzene but not in chloroform d1 solvent, so the mix solvents of dichlorobenzene and chloroform d1 were used for NMR measurements. The polybutadiene peak at 133 ppm are interfered with the peak of dichlorobenzene, thus the only peak at 27.5 ppm of polybutadiene can only be verified.

5.2.3 Solution viscosity of copolymers

Livingness of these polymerization systems can be confirmed by the increasing molecular weights of these copolymers. Molecular weights of copolymers were determined by solution viscosity instead of GPC (Gel Permeation Chromatography) because of the difficulty in dissolving these high molecular weight grafted copolymers. We obtained the viscosity by using U-tube viscometer and interpreted intrinsic viscosity data to obtain the average-molecular weight (M_w).

Solution viscosity is the basically properties that represented the size of polymer molecules and is empirically related to molecular weight for linear polymers. Several mathematical equations are available in the literature for determining the intrinsic viscosity [η] of a polymer solution, by graphical extrapolation. In this study, intrinsic viscosity was determined from Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad (1)$$

where k" is constant, η_r is relative viscosity, c is concentration in g/dl and [η] is determined from the extrapolation of $[(\ln \eta_r)/c]_{c=0}$ at zero concentration. According to the Mark-Houwink-Sakurada relation, the correlation between intrinsic viscosity and molecular weight, the correlation of the value of intrinsic viscosity with the molecular weight of the polymer in a solvent can be represented as:

$$[\eta] = K'M^{a} \tag{2}$$

where K´ and a are constants related to the stiffness of the chain and depend on the type of polymer, solvent and temperature.[35] From both equations, we can relate the molecular weight of these copolymers from their relative viscosity by extrapolation $(\ln \eta_r)/c$ at c = 0. The intrinsic viscosity [η] and molecular weight (M_w) of copolymer were also summarized in Table 5.3.

Table 5.3 Intrinsic viscosity[a] and Average molecular weight of resulting copolymers

Sample	Reaction time (hr)	[η]	M_w (×10^4)
PB[*]	-	0.24	35.35
PS-0[**]	-	0.07	0.48
PS-1	0.5	0.11	2.17
PS-2	1	0.19	17.28
PS-3	2	0.28	66.31

[a]Measured at 90°C in *o*-Xylene solvent
[*]cis-polybutadiene(commercial), [**]sPSMS : non-graft copolymer

It observed that the copolymer molecular weights increase when the reaction time increases, due to the increase of cooperated polybutadiene. Furthermore, when compared the results between PS-1 – PS-2 and PS-2 – PS-3, it was obvious that Mw increase more than twice when the reaction time increase. We suspected that this system might have the living behavior since molecular weight and PB content increase more than double corresponding to the increase of reaction time, while metalated anionic site (CH_3) of the main chain measured by NMR remains constant.

From the acquired M_w in Table 5.3, we found that PS-3 exhibited the highest M_w and even has higher M_w than that of PB. On the other hand, M_w of PS-1 and PS-2 were lower than M_w of PB. This was probably because of the effects of solvent cage and the initial anionic graft polymerization initiated firstly by small-chain polybutadiene which can be observed in 0.5 hr and 1 hr respectively and the longer-chain of polybutadiene grafted onto the backbone when the reaction time was increased to 2 hr. Due to the high molecular weight of PB molecules, the diffusion rate of the larger molecules are slower than the smaller molecules in liquids.[37] Thus reactions of large polymers molecules are much lower than reactions of small molecules, so the increase of M_w was clearly observed in longer reaction time.

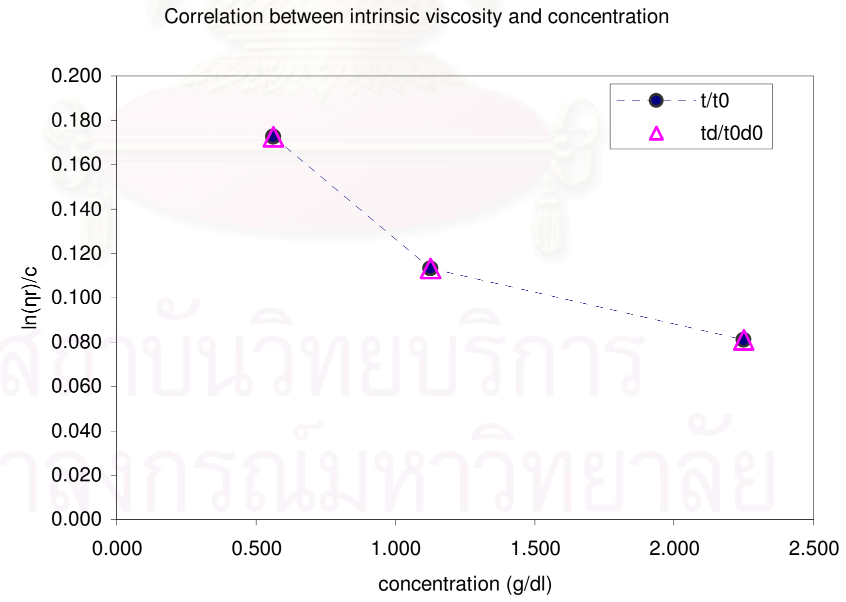


Figure 5.4 Plotting between intrinsic viscosity and concentration of PS-3 in *o*-Xylene at 90°C

Furthermore, we cannot observe any solutions' density effect in this concentration range (0.5-2.5 g/dl). These results can be shown in Figure 5.4, the triangular points represented the correction of the eluted times according to the different density (d) of polymer solution from the pure solvent (d0) at different concentrations. From Figure 5.4, the differences of the triangular points to the bold points can be neglect. Since we are dealing with the dilute solutions, it can be common to assume no difference in the density of polymer solution and pure solvent. [35]

5.2.4 Thermal properties of copolymers

Table 5.4 showed the thermal properties of sPS copolymers. Generally, sPS is a semicrystalline materials and usually displayed very high melting temperatures, up to 270°C.[18] From Table 5.4, T_m value of PS-0 was lower than 270°C because when 4-methylstyrene units is cooperated into the sPS backbone, the crystallinity of sPS decreases from the pure sPS due to the steric hindrance of the methyl group. The bulkiness or the electron donating effect of the CH_3 group may subpress the sPS from crystallization.[22] Moreover, after polybutadiene was grafted onto the sPSMS backbone, T_m values of PS-1, PS-2 and PS-3 approximately remain the same as PS-0. It can be inferred that grafted polybutadiene doesn't interfere with T_m of sPSMS backbones. On the other hand, when compared the result of ΔH value, it was obviously showed that grafted polybutadiene effects to ΔH value of copolymers. The ΔH value of copolymer continuously decreases while larger amount of polybutadiene was grafted onto the sPSMS backbone. This implied that incorporation of the grafted polybutadiene tends to interrupt the crystallization contents of sPSMS in the main chain due to a bulky group of polybutadiene which could have resulted in steric hindrance.

Table 5.4. Thermal properties of syndiotactic polystyrene copolymers obtained with $C_p^*TiCl_3$/ MMAO catalyst[a]

Sample	Heat 1*					Cool*		Heat 2*				
	T_g (°C)	T_{m11}^a (°C)	ΔH_{11} (J/kg)	T_{m21}^b (°C)	ΔH_{21} (J/kg)	T_c (°C)	ΔH_C (J/kg)	T_g (°C)	T_{m12}^a (°C)	ΔH_{12} (J/kg)	T_{m22}^b (°C)	ΔH_{22} (J/kg)
PS-0	na	Na	na	247	22	205	22	100	na	na	247	22
PS-1	na	na	na	246	15	196	14	99	na	na	246	15
PS-2	na	-13	1	246	14	196	14	99	-20	1	245	14
PS-3	na	-12	6	247	7	197	7	99	-20	4	246	7

*Determined by DSC with rate 20°C/min

[a]T_m of polybutadiene, [b]T_m of sPSMS copolymer, na : not available

Thus the packing density of polymer backbone chains decreased, resulting in the decreased crystallinity of the sPSMS-g-PB.[8] Moreover, the grafted copolymers have two T_m, which the first T_m represented polybutadiene and the second T_m represented sPSMS copolymer. Comparing among three graft copolymers samples, the value of T_g and both T_m is mostly constant but the peak area (ΔH) of T_{m1} in PS-3 is higher than PS-2 which correspond to the increase of grafted polybutadiene content when reaction time increases. Moreover the decreases of ΔH of T_{m2} also correspond to the increase polybutadiene content in the copolymer both in the first heating and the second heating. The more polybutadiene added, the less percent of crystallinity observed.

5.2.5 Phase morphology of copolymers

To confirm these results, the surface morphologies of sPS copolymers were investigated by SEM and shown in Figure 5.5.

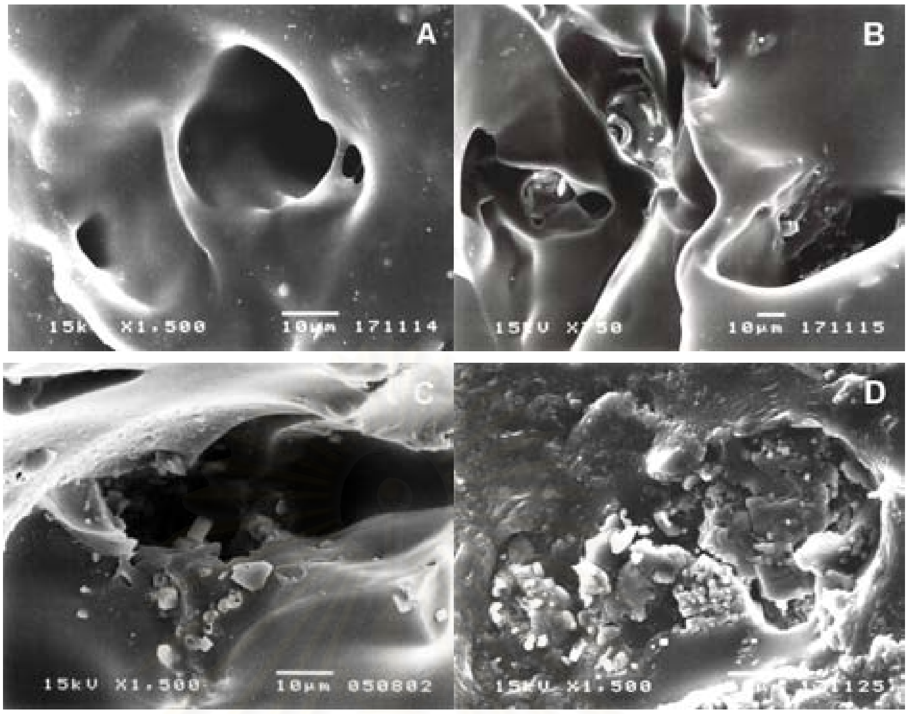


Figure 5.5 SEM micrographs of sPS copolymers: (A) PS-0, (B) PS-1, (C) PS-2 and (D) PS-3

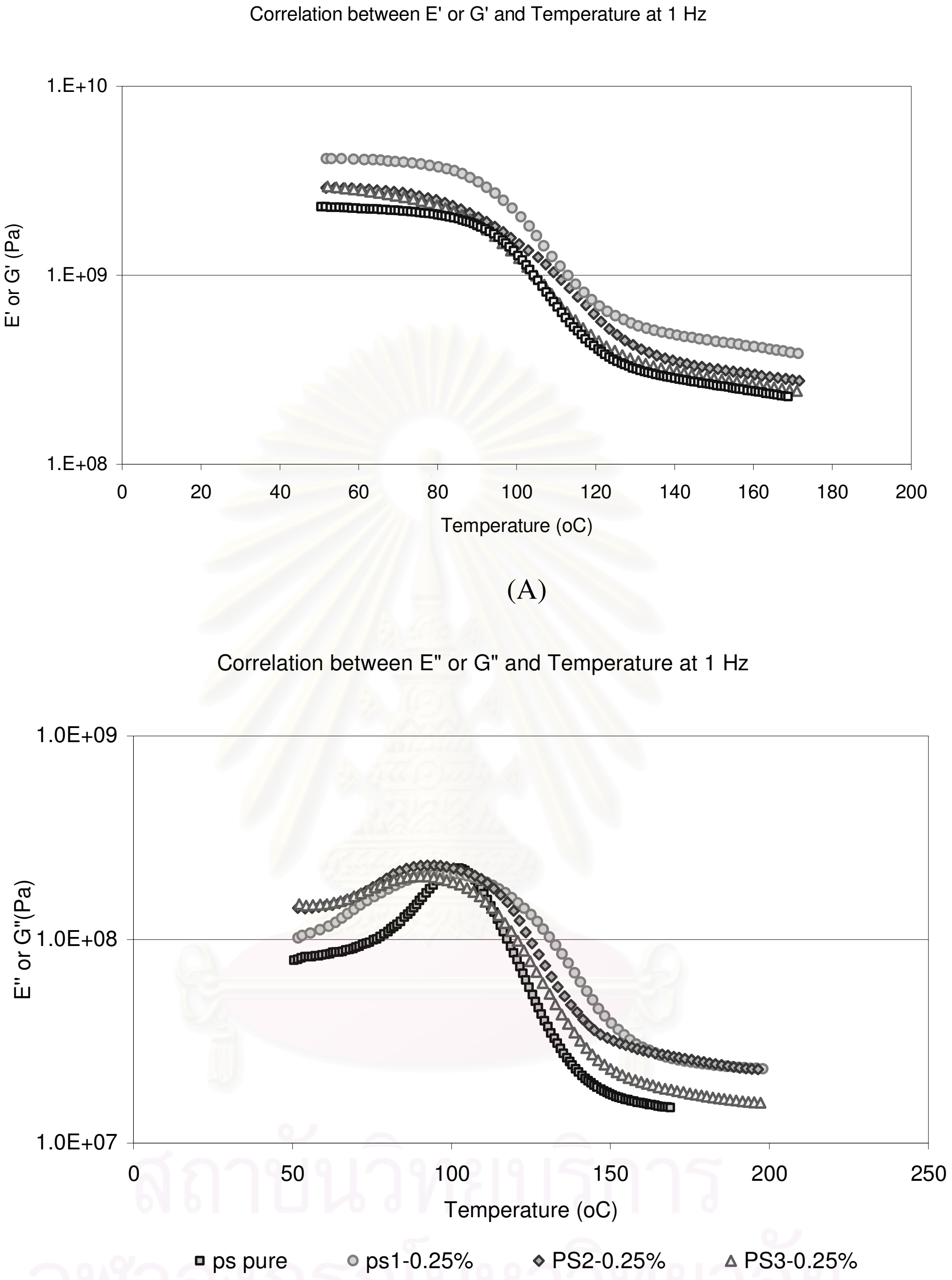
The grafted sPS changed both the thermal properties together with the surface morphologies from the pure sPS. It can be seen that grafted copolymers consisted of 2 phases. Figure 5.5 exhibited the distribution of cis-PB (rubber particles) into sPSMS (dark phase). When compared Figure 5.5(A) and the others, we found that when polybutadiene grafted to the backbone, the rubber particles appeared as separated phases from the dark phase. It should be noted that the rubber particles are not in simple form of rubber spheres. Furthermore, it was found that the contents and distributions of cis-PB increases with increasing of reaction time which is corresponding to these mentioned results.

5.3 Blending of poly(sPS-g-PB)

There are many attempts to improve the impact resistance of original syndiotactic polystyrene. Rubber toughening of syndiotactic polystyrene and poly (styrene/diphenyl- ethylene) [38] and blending of sPS with poly(*p*-phenylene sulfide) [39] was studied and aimed to improve these properties. It is well known that block and graft copolymer was effective compatibilizer in immiscible blend. To investigate the effectiveness of the synthesized graft copolymer, poly(sPS-g-PB), in this research and to compare the different mechanical properties when PB was added, the pure sPS and poly(sPS-g-PB)/pure sPS blends were conducted and verified.

5.3.1 Mechanical properties

In this research, the blended sample was prepared by melt mixing. Both polymers were blended at 300°C on hot plate and pressed to obtain film samples, which molded on the hot plate about 2 times. The blends mechanical properties were measured by DMA. Firstly, we obtained the suitable condition for sample molding by varying molding temperature from 260 to 300°C and poly(sPS-g-PB) content in blends, 10, 5, 1 and 0.25% respectively. However there are difficulties in sample preparation due to its inferior brittle properties of the pressed blends. The best molding condition was 0.25% poly(sPS-g-PB) at 280°C. Furthermore it was found that blend samples shouldn't be grinded before molding on the hot press. If blend sample was powdered, it couldn't be formed again to the film shapes which needed in the measurement by DMA. Since film sample crackles which caused these samples rupture during the DMA measurement were occurred, the DMA measurements cannot be performed.



(A)

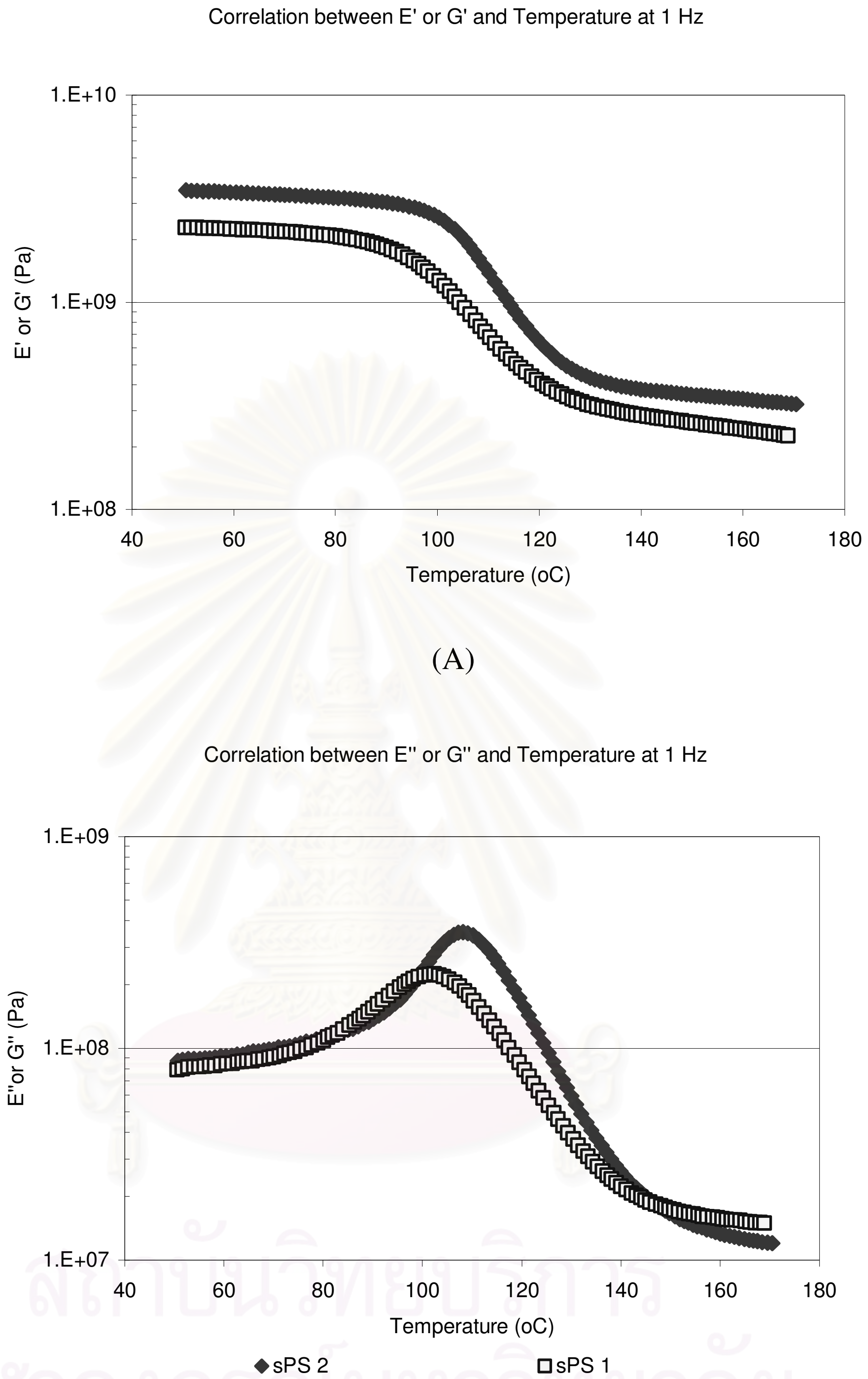
(B)

Figure 5.6 DMA results of pure sPS and poly(sPS-g-PB)/pure sPS blends

The mechanical properties of pure-sPS and the poly(sPS-g-PB)/pure-sPS blend are shown in Figure 5.6. As Shown in Figure 5.6(A), the storage modulus (E′ or G′) of blends are higher than pure-sPS, thus poly(sPS-g-PB) can improve the toughness strength of original pure sPS. Moreover, comparison among graft copolymers, it was found that PS-1 which has the least polybutadiene content exhibited the highest E′. On the other hand, the storage modulus decreased with increasing of polybutadiene content. These results can be happened because the original polybutadiene burnt at molding temperature (280°C). Thus the impact strength of sPS blends also decreased with increase the amount of polybutadiene content.

Considering Figure 5.6(B), the loss modulus (E′′ or G′′) of the blends are also higher than pure-sPS, which indicated that the blend with poly(sPS-g-PB) can adsorb energy more than the pure-sPS. Because sPS is a polymer which shows no segmental mobility of chain segments below its glass transition temperature and doesn’t exhibit long-range energy dissipation deformation processes on impact below the glass transition temperature.[3] This is a reason that sPS are very brittle at room temperature.

The addition of poly(sPS-g-PB) will increase the present of rubbery phase in sPS matrix according to the added PB, thus the blends can well absorb and dissipate energy when the forces or loads interact with samples than the pure sPS. According to E′′ profile as shown in Figure 5.6(B) it indicated that PS-1 showed the highest E′′ as well. The loss modulus decreased with increasing of polybutadiene content. Thus energy absorption of sPS blends decreased with increase of polybutadiene content. These results were similar to what we have found in E′ results. It can be concluded that the poly(sPS-g-PB)/pure-sPS blend has better mechanical strength and less brittle than pure-sPS but these properties were deteriorate by the inappropriate increase of polybutadiene content.



(A)

(B)

Figure 5.7 DMA results of pure sPS samples which have different cycles of molding

Furthermore we found that the impact strength and energy absorption of pure sPS decreased if the cycles of molding increased. The DMA results of pure-sPS which had different cycles of molding were exhibited in Figure 5.7. From Figure 5.7 the E´ and E´´ of sPS 2, which molded 2 times, were less than sPS 1, which molded 1 time. It indicated that sPS 2 was more brittle than sPS 1 and the cycles of molding effected to the impact strength and energy absorption of polymers. Due to the destroyed molecular chains during melting step, the strength of the samples, that subjected to many cycle of hearing or molding, decreased.

5.3.2 Fracture surface

The surfaces morphology of pure sPS and their blends were investigated by SEM and shown in Figure 5.8.

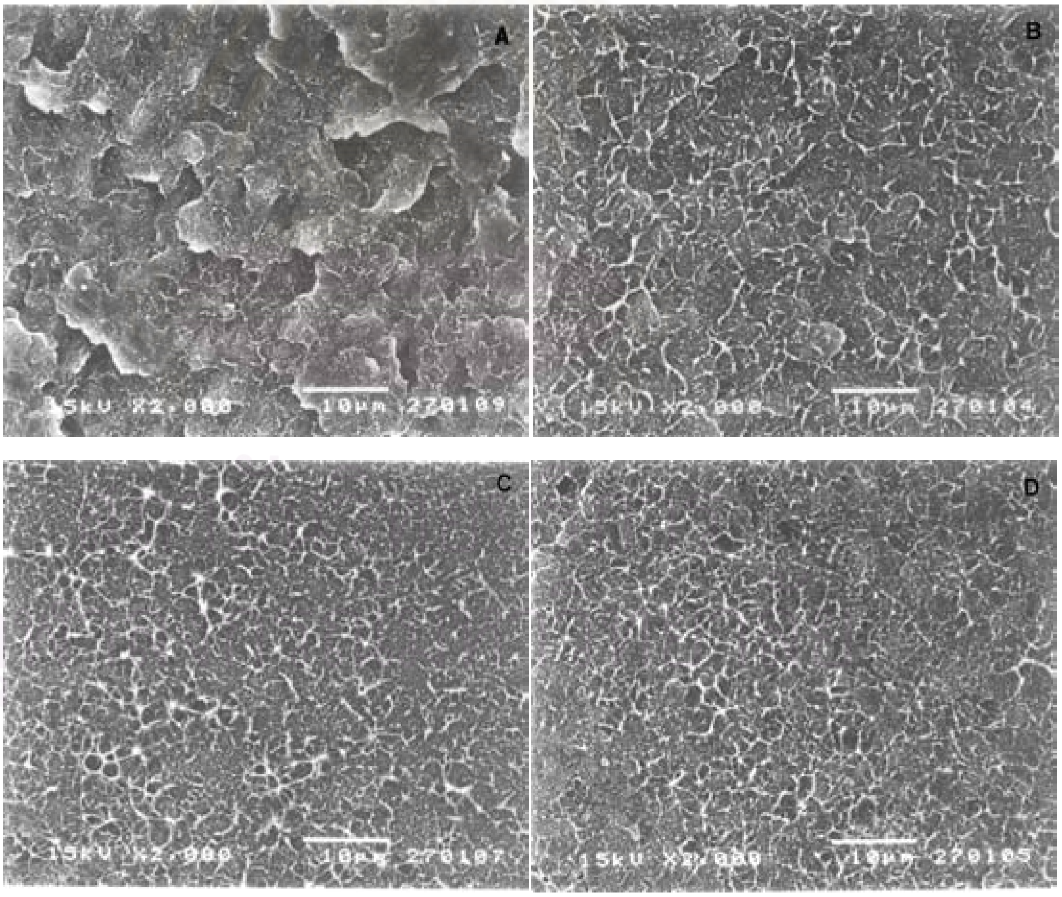


Figure 5.8 SEM micrograph of pure sPS and poly(sPS-g-PB)/pure sPS blends: (A) pure-sPS, (B) 0.25% PS-1, (C) 0.25% PS-2 and (D) 0.25% PS-3

As shown in Figure 5.8, the fracture surfaces of poly(sPS-g-PB)/sPS blends were tougher than pure sPS, because they had rubbery networks on the fracture surfaces. The rubbery phases are smaller when blended with poly(sPS-g-PB) with the increase grafted reaction time. Thus it can be said that poly(sPS-g-PB)/sPS blends has better toughness than pure-sPS. These conclusions also corresponded to the DMA results of the blends.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS

6.1 Conclusions

In this research, the method for synthesis of graft copolymer between syndiotactic polystyrene and polybutadiene were proposed. The graft copolymers of syndiotactic polystyrene (sPS) were synthesized by combination of metallocene catalyst and anionic polymerization system. Moreover, the mechanical properties of their blends were also studied. The conclusion of this research can be summarized as follows:

1. Grafted syndiotactic copolymer composed of high sPS segments in backbone and cis-polybutadiene side chains was prepared by combination of metallocene and anionic polymerization technique. It is possible to corporate the large molecule of unsaturated elastomer polybutadiene onto the backbone of sPSMS chains.

2. From ^{13}C-NMR the microstructures of ST units were proved to be highly syndiotactic and polybutadiene segments were proved to be high cis-configuration.

3. The resulting graft copolymers showed high melting temperature (240-250°C) and were different from those of anionic styrene-butadiene copolymers due to the presence of crystalline sPS segments.

4. The grafted polybutadiene content increased with increasing the reaction time.

5. From DSC result it was found that the crystallinity of sPSMS backbone decreased when polybutadiene was grafted onto the sPSMS backbone since bulky group of polybutadiene which could have resulted in steric hindrance. Thus the packing density of polymer chains decreased resulting in the decreased crystallinity of the sPSMS-g-PB.

6. These copolymerization systems exhibit the effect from solvent cage since reactions of large molecules in polymers being much lower than small molecules, so M_w results were clearly observed in long reaction time.

7. sPS-g-PB/pure-sPS blend has higher strength and toughness than pure-sPS which confirmed by DMA result.

6.2 Suggestions

The recommendations for further research may be given as follows:

1. This research can be extended to the study of the living nature on this graft polymerization condition.

2. It should be interesting to find the most suitable % graft copolymer in sPS blends.

REFERENCES

1. Aldo Guiducci, Chemistry and Industry, 464-465 (1996)
2. Guodong Zheng and Harald D.H. StÖver, Macromolecules 35(2002), 6828-6834
3. J. Scheirs and D.B Priddy, Modern Styrenic Polymers: Polystyrene and Styrenic Copolymers, John Wiley & Son, England (2003).
4. Shengsheng Liu, Baotong Huang, Macromol. Rapid Commun. 20(1999), 484-486
5. Kiyoshi Endo, Kazunobu Senoo, Macromol. Rapid Commun. 19(1998), 536-566
6. Kiyoshi Endo, Kazunobu Senoo, Polymer Bulletin 44(2000), 25-30
7. Xu, T.C. Chung, Macromolecules, 32(1999), 8689
8. Chi-Lan Li, Shu-Hua Chan, Ching Ting and George J. Jiang, Journal of Applied Polymer Science, 86(2002), 1038-1045
9. Kobayashi E., Kaita S., Aoshima S. Furakawa J., J. Polym. Sci., Part A: Polymer chem., 33(1994), 2175
10. Kobayashi E., Hayashi N., Aoshima S. Furakawa J., J. Polym. Sci., Part A: Polymer chem., 36(1998), 1707
11. Endo K., Matsuda Y., J. Polym. Sci., Part A:Polymer chem. 37(1999), 3838
12. Michela Caprio, Maria Cristina Serra, Daniel E. Bowen, and Alfonso Grassi, Macromolecules, 35(2002), 9315-9322
13. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Polymer chem., 42(2004), 2698-2704
14. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Polymer chem., 43(2005), 1188-1195
15. Guodong Zheng and Harald D.H. StÖver, Macromolecules, 35(2002), 6828-6834
16. T.C.Chung, H. L. Lu, and R. D. Ding, Macromolecules, 30(1997), 1272-1278

17. Ishihara N, Seimiya T, Kuramoto M and Uoi M. Macromolecules, 19(1986), 2464.

18. Ishihara N, Kuramoto M, Uoi M. Macromolecules, 21(1988), 3356.

19. Kaminsky W. Macromolecules, 30(1997), 7647.

20. Y. Kim, B. H. Koo, and Y. Do, J. Organomet. Chem.,527 (1997), 155-161.

21. Carla Manfredi, Gaetano Guerra, Claudio De Rosa, Vincenzo Busico, and Paolo Corradini, Macromolecules, 28(1995), 6508-6515

22. Hisayuki Nakatani and Koh-hei Nitta, et al., Polymer, 38(1997), 4751-4756

23. Kazunobu Senoo, Kiyoshi Endo, Masatoshi Tosaka, Syozo Murakami, and Shinzo Kohjiya, Macromolecules, 34(2001), 1267-1273

24. I. Tausendfreund, F. Bandermann, H.W. Siesler, M. Kleimann, Polymer, 43 (2002), 7085-7091

25. Pinrat Pinweha. Titanocene Catalysts with Boron Cocatalyst for Syndiotactic Polymerization of Styrene Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 2000

26. Wild F.R.W.P., Wasincioneck M., Hunttner G. and Brintzinger H.H. J. Organomet. Chem., 63(1985), 288.

27. Schellenberg J. and Tomotsu N. ,Prog. Polym. Sci., 27(2002), 1925.

28. Boleslawaski M and Pasynkiewiez S., J. Organomet. Chem., 43(1972), 81.

29. Ueyama N, Araki T and Tani H., Inorg. Chem., 12(1973), 2218.

30. Huang J and Rampel G.L., Prog. Polym. Sci., 20(1995), 459

31. Yee AF., Polym. Eng. Sci., 17(1977), 213

32. www.iisrp.com/WebPolymers/01FinalPolybutadieneVer2.pdf

33. R.J.Ceresa, Ed., Block and Graft copolymerization, Vol.1 and 2, Wiley Interscience, New York (1973)

34. Henry L. Hsieh, Roderic P. Quirk, Anionic polymerization : Principles and Practical Applications, Marcel Dekker, Inc., Newyork (1996)

35. Fred W. Billmeyer, JR, Textbook of polymer science, Third Edition, John Wiley & Son, Singapore (1984)

36. Kevin P. Manard, Dynamic Mechanical Analysis. Florida: CRC Press LLC, 1999.

37. E.T. Denisova, T.G. Denisova and T.S. Pokidova, Handbook of free radical initiators, John Wiley & Son, New Jersy (2003)

38. F. Ramsteiner, G.E. McKee et al., Polymer, 41(2000), 6635-6645

39. Seok-Ho Hwang, Myeong-Jun Kim and Jae-Chang Jung, European Polymer J., 38(2002), 1881-1885

APPENDICES

Appendix A

The Data of DSC Characterization

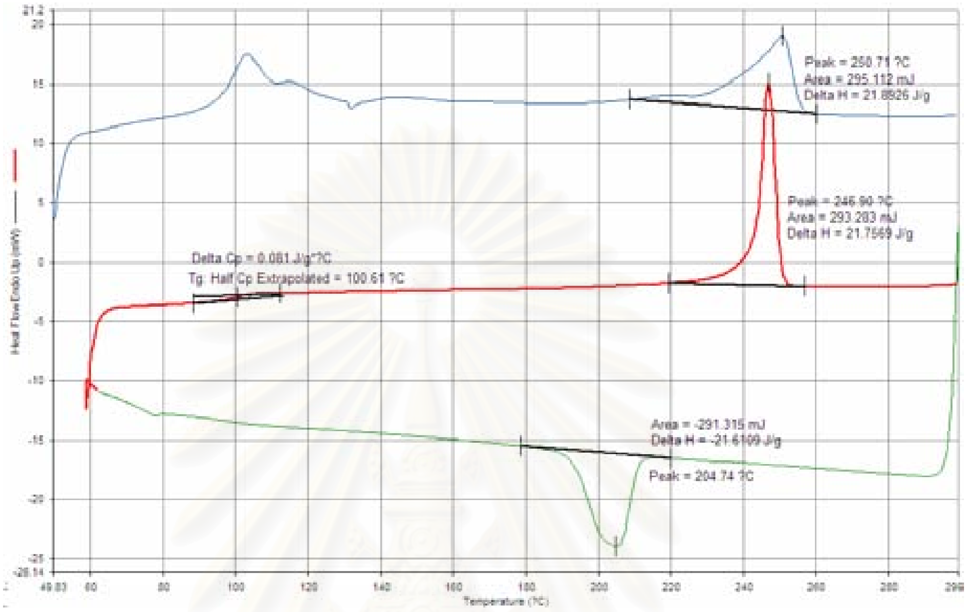


Figure A.1 DSC curve of sPSMS, PS-0

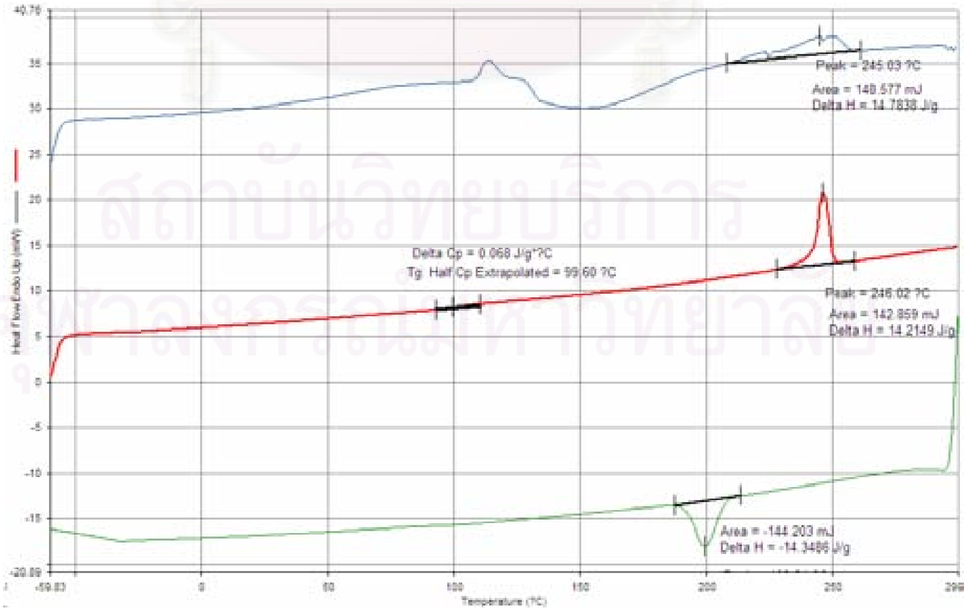


Figure A.2 DSC curve of poly(sPS-g-PB),PS-1 (0.5 hr)

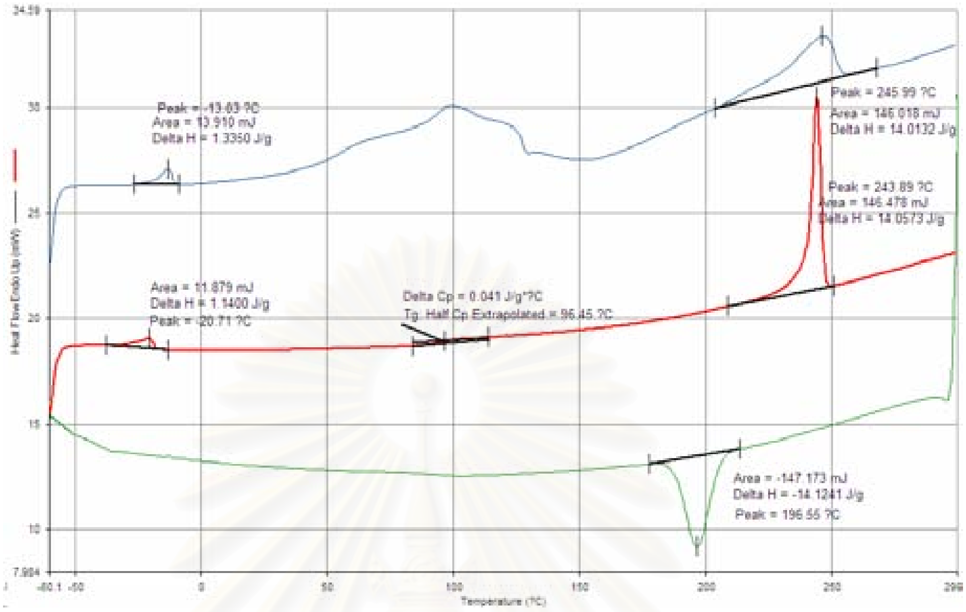


Figure A.3 DSC curve of poly(sPS-g-PB), PS-2 (1 hr)

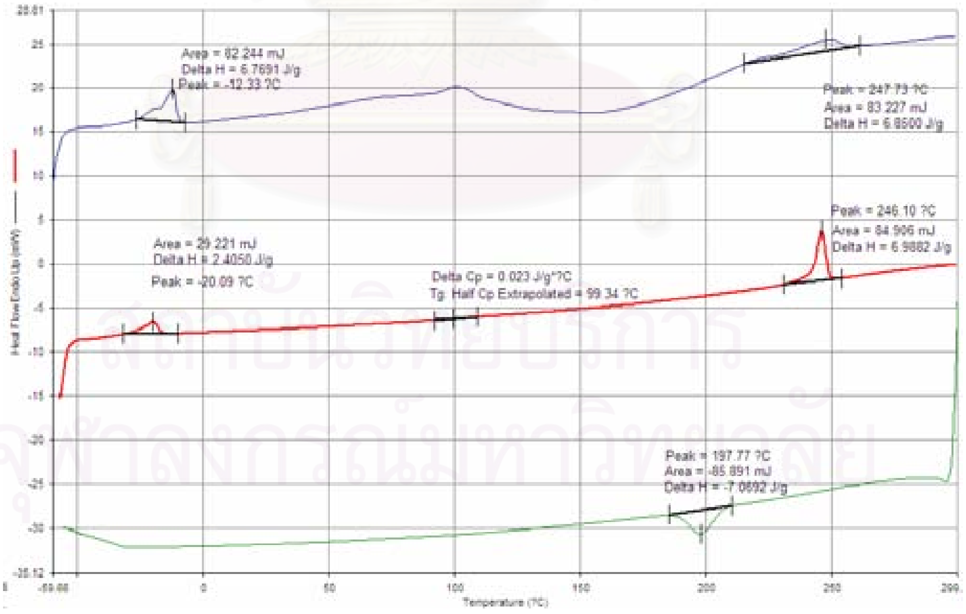


Figure A.4 DSC curve of poly(sPS-g-PB),PS-3 (2 hr)

Appendix B

The Data of NMR Characterization

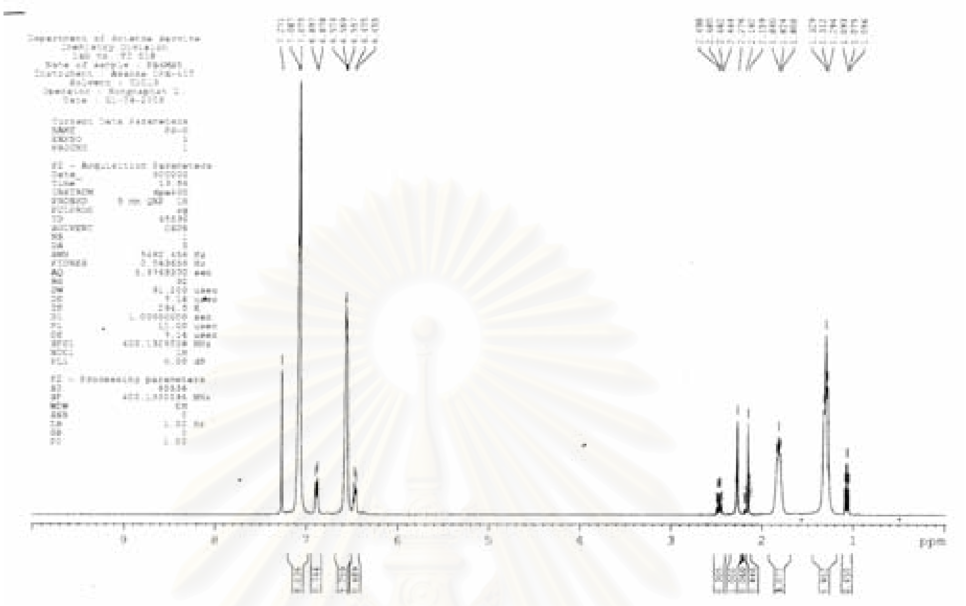


Figure B.1 ^{1}H-spectra of sPSMS, PS-0

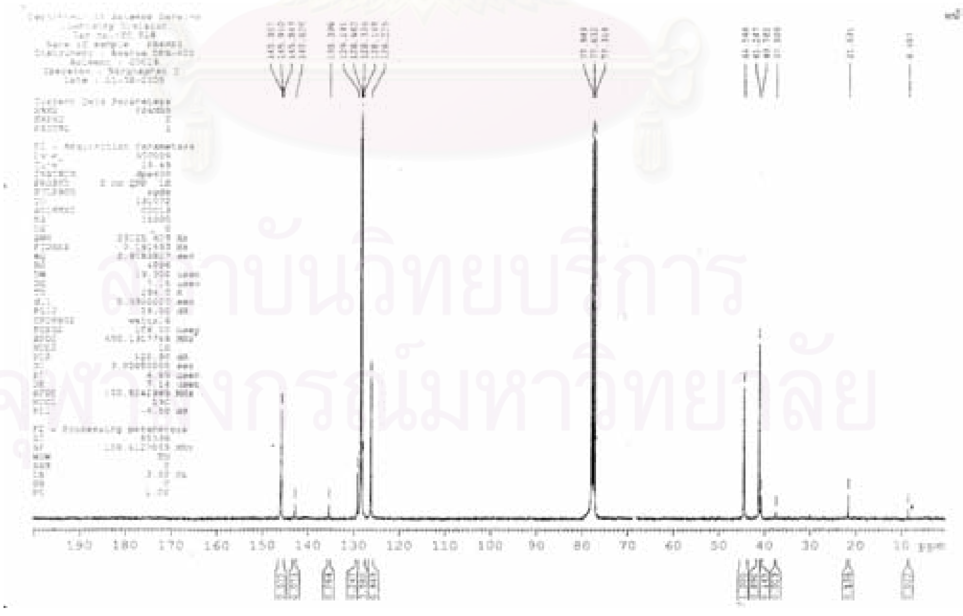


Figure B.2 ^{13}C-spectra of sPSMS, PS-0

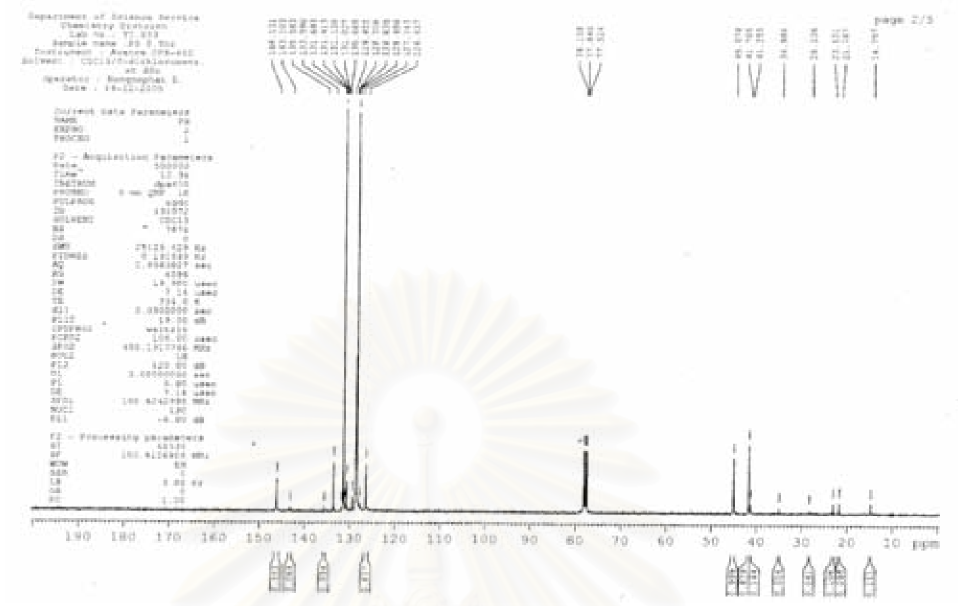


Figure B.3 ^{13}C-spectra of poly(sPS-g-PB),PS-1 (0.5 hr)

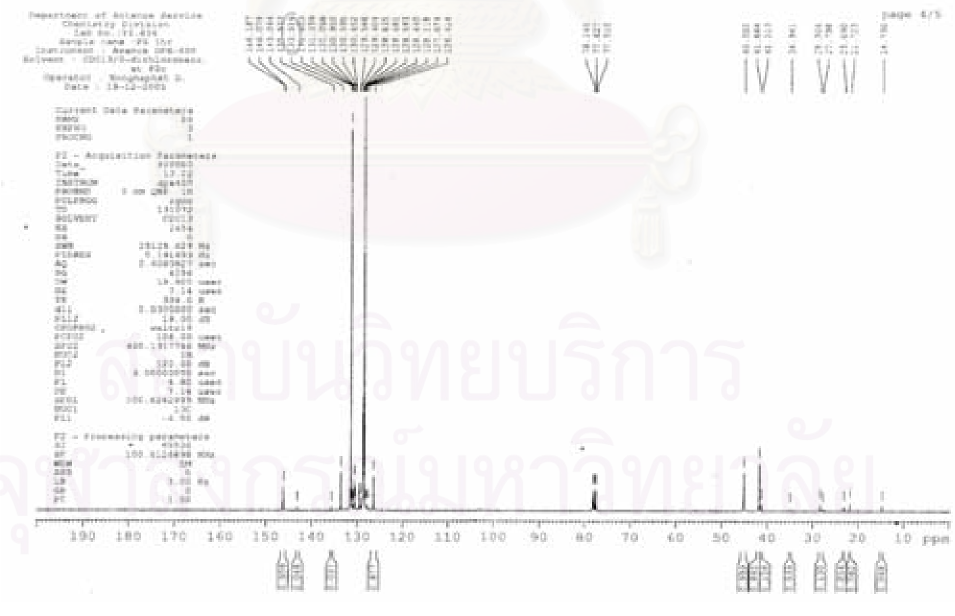


Figure B.4 ^{13}C-spectra of poly(sPS-g-PB),PS-2 (1 hr)

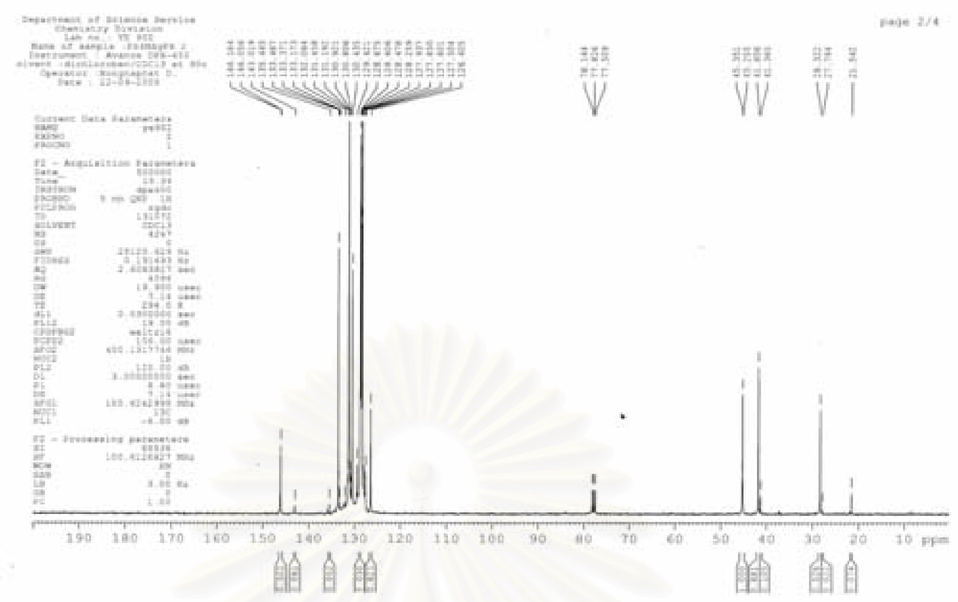
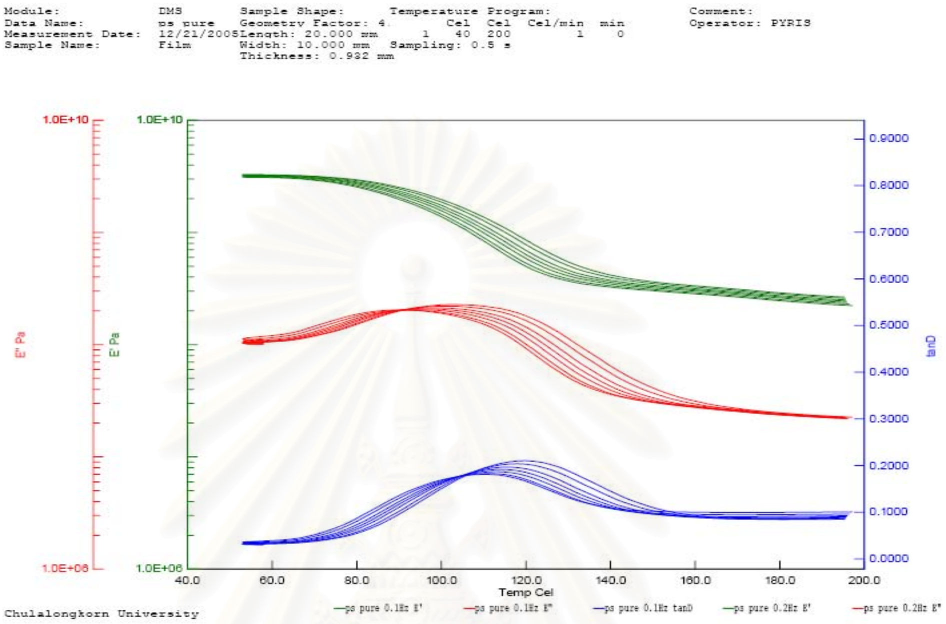


Figure B.5 ^{13}C-spectra of poly(sPS-g-PB),PS-3 (2 hr)

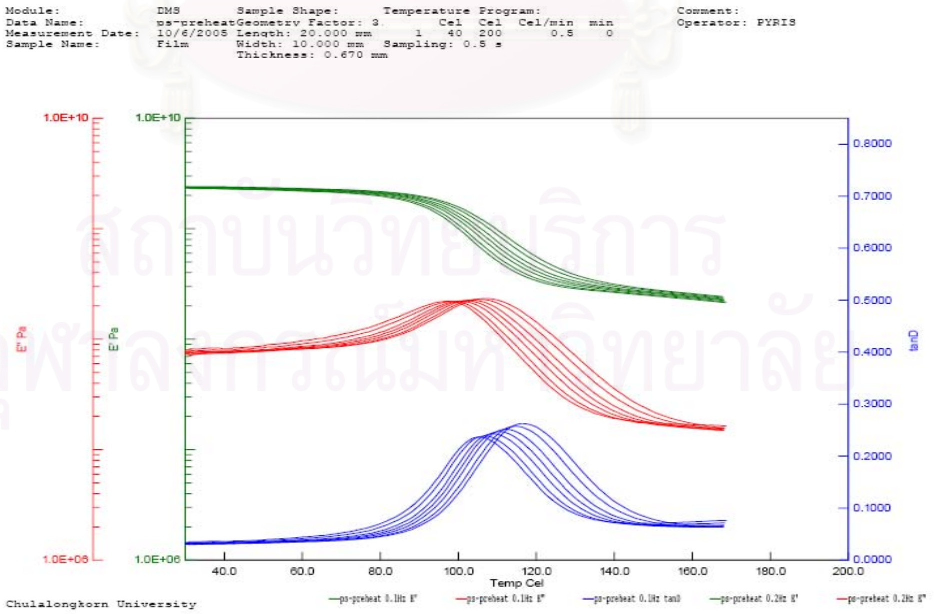
Appendix C

The Data of DMA Characterization



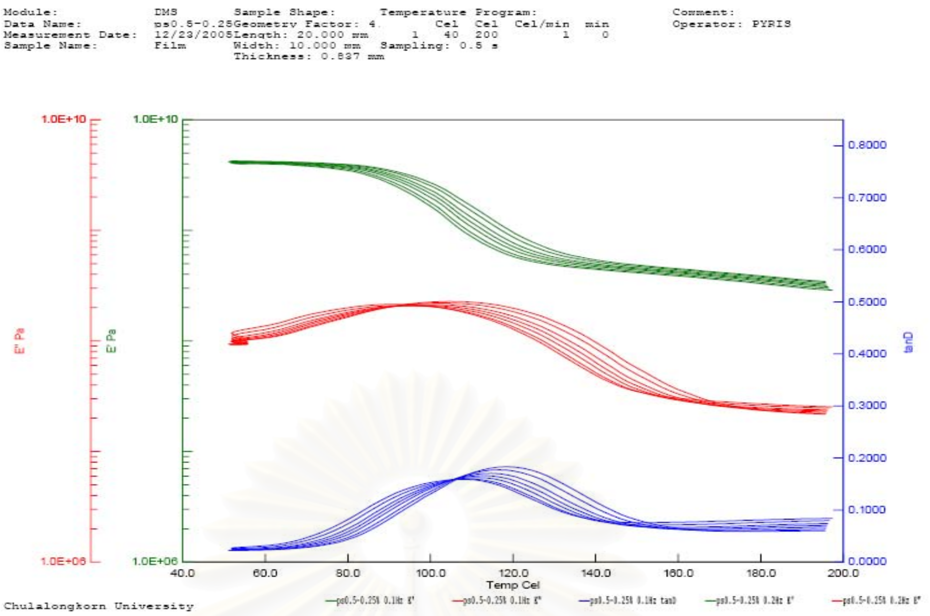
```
Module:             DMS        Sample Shape:      Temperature Program:              Comment:
Data Name:          ps pure    Geometry Factor: 4       Cel  Cel  Cel/min  min      Operator: PYRIS
Measurement Date:   12/21/2005Length: 20.000 mm     1   40  200        1    0
Sample Name:        Film       Width: 10.000 mm   Sampling: 0.5 s
                               Thickness: 0.932 mm
```

Figure C.1 DMA curve of pure sPS1



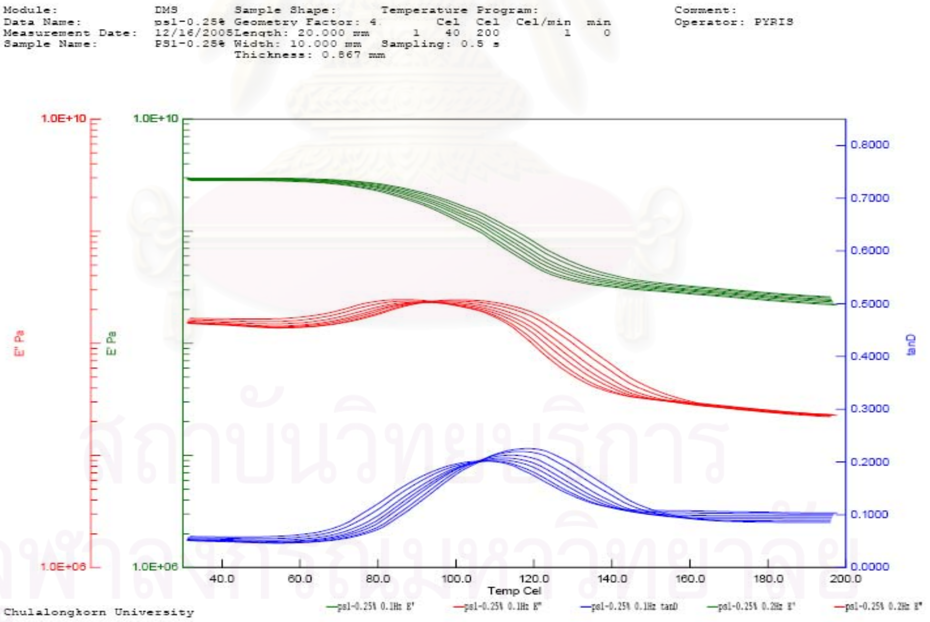
```
Module:             DMS        Sample Shape:      Temperature Program:              Comment:
Data Name:          ps-preheatGeometry Factor: 3       Cel  Cel  Cel/min  min       Operator: PYRIS
Measurement Date:   10/6/2005 Length: 20.000 mm     1   40  200      0.5    0
Sample Name:        Film       Width: 10.000 mm   Sampling: 0.5 s
                               Thickness: 0.670 mm
```

Figure C.2 DMA curve of pure sPS2



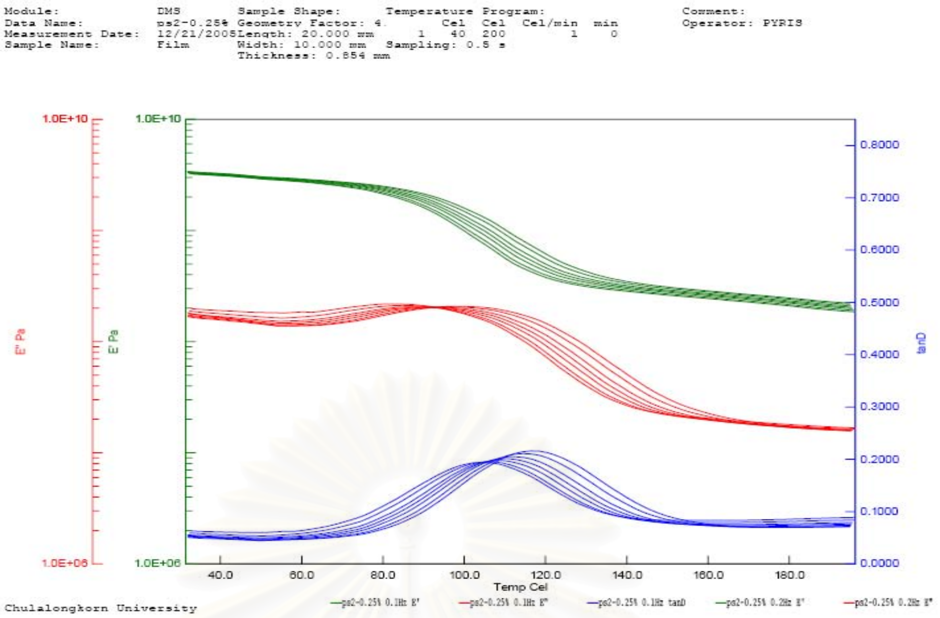
```
Module:              DMS       Sample Shape:      Temperature Program:             Comment:
Data Name:           ps0.5-0.25Geometry Factor: 4.       Cel  Cel  Cel/min  min    Operator: PYRIS
Measurement Date:    12/23/2005Length: 20.000 mm     1   40  200        1    0
Sample Name:         Film      Width: 10.000 mm   Sampling: 0.5 s
                               Thickness: 0.837 mm
```

Figure C.3 DMA curve of 0.25% PS-1(0.5 hr)/pure sPS blends



```
Module:              DMS       Sample Shape:      Temperature Program:             Comment:
Data Name:           ps1-0.25% Geometry Factor: 4.       Cel  Cel  Cel/min  min    Operator: PYRIS
Measurement Date:    12/16/2005Length: 20.000 mm     1   40  200        1    0
Sample Name:         PS1-0.25% Width: 10.000 mm   Sampling: 0.5 s
                               Thickness: 0.867 mm
```

Figure C.4 DMA curve of 0.25% PS-2(1 hr)/pure sPS blends



```
Module:             DMS       Sample Shape:      Temperature Program:              Comment:
Data Name:          ps2-0.25% Geometry Factor: 4.       Cel  Cel  Cel/min  min     Operator: PYRIS
Measurement Date:   12/21/2005Length: 20.000 mm      1   40  200        1    0
Sample Name:        Film      Width: 10.000 mm  Sampling: 0.5 s
                              Thickness: 0.854 mm
```

Figure C.5 DMA curve of 0.25% PS-2(2 hr)/pure sPS blends

Appendix D

The Data of Solution Viscosity

Sample : **sPSMS, PS-0**
Initial
Conc. : 0.2 g/50 ml = 4 g/dl
Solvent : o-Xylene η_0 = 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.49	54.61	54.44	54.513
1	0.250	55.35	55.37	55.25	55.323
2	0.500	56.12	56.04	56.23	56.130
3	1.000	56.75	56.83	56.87	56.817
4	2.000	58.82	58.94	58.96	58.907
5	4.000	60.12	60.21	60.16	60.163

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	ln η_r	ln(η_r)/c	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.250	1.015	0.373	0.015	0.015	0.059	0.059
2	0.500	1.030	0.379	0.030	0.029	0.058	0.059
3	1.000	1.042	0.384	0.042	0.041	0.041	0.042
4	2.000	1.081	0.398	0.081	0.078	0.039	0.040
5	4.000	1.104	0.406	0.104	0.099	0.025	0.026

Sample : **graft 0.5 hr**
Initial
Conc. : 0.1 g/50 ml 0.2 g/dl
Solvent : o-Xylene η_0 = 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.95	54.92	54.96	54.943
1	0.013	55.77	55.89	55.87	55.843
2	0.025	56.36	56.31	56.35	56.340
3	0.050	57	57.05	57.02	57.023
4	0.100	58.7	58.62	58.65	58.657
5	0.200	61.4	61.42	61.41	61.410

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	ln η_r	ln(η_r)/c	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.125	1.016	0.374	0.016	0.016	0.130	0.131
2	0.250	1.025	0.377	0.025	0.025	0.100	0.102
3	0.500	1.038	0.382	0.038	0.037	0.074	0.076
4	1.000	1.068	0.393	0.068	0.065	0.065	0.068
5	2.000	1.118	0.411	0.118	0.111	0.056	0.059

Sample : **graft 1 hr**
Initial
Conc. : 0.1 g/50 ml 0.2 g/dl
Solvent : o-Xylene η_0 = 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.94	54.92	54.97	54.943
1	0.013	56.01	56.05	56.03	56.030
2	0.025	57.35	57.31	57.38	57.347
3	0.050	58.59	58.52	58.45	58.520
4	0.100	60.11	60.06	60.12	60.097
5	0.200	62.1	62.09	62.12	62.103

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	ln η_r	ln(η_r)/c	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.125	1.020	0.375	0.020	0.020	0.157	0.158
2	0.250	1.044	0.384	0.044	0.043	0.171	0.175
3	0.500	1.065	0.392	0.065	0.063	0.126	0.130
4	1.000	1.094	0.403	0.094	0.090	0.090	0.094
5	2.000	1.130	0.416	0.130	0.122	0.061	0.065

Sample : **graft 2 hr**
Initial
Conc. : 0.225 g/50 ml 0.45 g/dl
Solvent : o-Xylene η_0 = 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.64	54.55	54.67	54.620
1	0.281	58.44	58.34	58.32	58.367
2	0.563	59.74	59.16	59.27	59.390
3	1.125	61.04	61.03	61.13	61.067
4	2.250	64.02	64.85	64.49	64.453
5	4.500	65.33	65.17	65.73	65.410

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	ln η_r	ln(η_r)/c	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.281	1.069	0.393	0.069	0.066	0.236	0.244
2	0.563	1.087	0.400	0.087	0.084	0.149	0.155
3	1.125	1.118	0.411	0.118	0.112	0.099	0.105
4	2.250	1.180	0.434	0.180	0.166	0.074	0.080
5	4.500	1.198	0.441	0.198	0.180	0.040	0.044

Sample : **PB high cis-**
Initial
Conc. : 0.1 g/50 ml 2 g/dl
Solvent : o-Xylene $\eta_0 =$ 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.94	54.97	54.96	54.957
1	0.125	56.54	56.64	56.71	56.630
2	0.250	57.89	57.85	58.65	58.130
3	0.500	60.87	60.85	60.72	60.813
4	1.000	66.5	66.77	66.62	66.630
5	2.000	72.45	72.53	72.38	72.453

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln(\eta_r)/c$	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.125	1.030	0.379	0.030	0.030	0.240	0.244
2	0.250	1.058	0.389	0.058	0.056	0.225	0.231
3	0.500	1.107	0.407	0.107	0.101	0.203	0.213
4	1.000	1.212	0.446	0.212	0.193	0.193	0.212
5	2.000	1.318	0.485	0.318	0.276	0.138	0.159

Sample : **PS-100,000**
Initial
Conc. : 0.1 g/50 ml 2 g/dl
Solvent : o-Xylene $\eta_0 =$ 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.64	54.55	54.67	54.620
1	0.125	55.65	55.56	55.21	55.473
2	0.250	56.78	56.82	56.64	56.747
3	0.500	58.38	58.76	58.72	58.620
4	1.000	60.15	60.21	60.08	60.147
5	2.000	61.05	61.12	61.08	61.083

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln(\eta_r)/c$	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.125	1.016	0.374	0.016	0.016	0.124	0.125
2	0.250	1.039	0.382	0.039	0.038	0.153	0.156
3	0.500	1.073	0.395	0.073	0.071	0.141	0.146
4	1.000	1.101	0.405	0.101	0.096	0.096	0.101
5	2.000	1.118	0.412	0.118	0.112	0.056	0.059

Sample : **PS-1,000,000**
Initial
Conc. : 0.1 g/50 ml 2 g/dl
Solvent : o-Xylene $\eta_0 =$ 0.368 cP
Temp : 95°C

No.	Conc.(g/1000ml)	Time (sec)			
		1	2	3	average
0*	-	54.64	54.55	54.67	54.620
1	0.125	58.23	58.37	58.42	58.340
2	0.250	59.14	59.12	59.18	59.147
3	0.500	63.12	63.24	63.09	63.150
4	1.000	71.13	71.1	71.26	71.163
5	2.000	84.37	84.49	84.36	84.407

No.	Conc.(g/1000ml)	$\eta_r = t/t_o$	η	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln(\eta_r)/c$	η_{sp}/c
0*	-	1.000	0.368	0.000	0.000	-	-
1	0.125	1.068	0.393	0.068	0.066	0.527	0.545
2	0.250	1.083	0.398	0.083	0.080	0.318	0.332
3	0.500	1.156	0.425	0.156	0.145	0.290	0.312
4	1.000	1.303	0.479	0.303	0.265	0.265	0.303
5	2.000	1.545	0.569	0.545	0.435	0.218	0.273

Appendix E

The Data Calculations

D.1. Calculation of % 4-methylstyrene in sPSMS copolymer

sample	intensity at		%4-methylstyrene
	1.8 ppm	2.26 ppm	
PS-1	1	3.077	0.75

We obtained the percentage of 4-methylstyrene from ^{1}H-spectra of PS-0

$$\% \text{ 4-methylstyrene} = \frac{\text{Peak intensity at 1.8 ppm}}{\text{Peak intensity at 2.26ppm + Peak intensity at 1.8 ppm}}$$

$$= 1/4.077$$

$$= 0.245$$

The synthesized sPSMS copolymer has 25 mol% of 4-methylstyrene.

D.2. Calculation of % cis-PB in graft copolymer

sample	intensity at		%cis-PB
	28 ppm	45.3 ppm	
PS-1	0.041	1	3.94
PS-2	0.130	1	11.50
PS-3	0.526	1	34.47

Example of PS-1

We obtained the percentage of cis-PB from ^{13}C-spectra of PS-1

$$\% \text{ cis-PB} = \frac{\text{Peak intensity at 27.5 ppm}}{\text{Peak intensity at 45.3 ppm + Peak intensity at 27.5 ppm}}$$

$$= 0.041/(1+0.041)$$

$$= 0.394$$

The synthesized PS-1 copolymer has 3.94 mol% of cis-PB.

D.3. Calculation of M_w of copolymer

In this study, intrinsic viscosity was determined from Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c$$

where k" is constant

η_r is relative viscosity

c is concentration in g/dl and

$[\eta]$ is determined from the extrapolation of $[(\ln \eta_r)/c]_{c=0}$ at zero concentration.

From plotting between $[(\ln \eta_r)/c]$ and c, the $[\eta]$ value was determined and shown below:

sample	[η]	Mw
ps100000	0.1645	100,017
ps1000000	0.3239	1,000,173
PB	0.2385	353,455
PS-0	0.0675	4,845
PS-1	0.1049	21,679
PS-2	0.1932	172,756
PS-3	0.287	663,061

According to the Mark-Houwink-Sakurada relation, the correlation between intrinsic viscosity and molecular weight, the correlation of the value of intrinsic viscosity with the molecular weight of the polymer in a solvent can be represented as:

$$[\eta] = K'M^a$$

We can determine the K′ and a value from data of both PS-standard samples.

Find a

$0.3239 = K'(1{,}000{,}000)^a$ 1
$0.1645 = K'(100{,}000)^a$ 2

from 1/2 $1.96899696 = (10)^a$
$\log(1.969) = a \log(10)$
$0.294245046 = a$

Find K'

$(100,000)^{0.294245046} = 29.59547$

$K' = 0.005558283$

$(1,000,000)^{0.294245046}$ 58.27339

$K' = 0.005558283$

$[\eta] = 0.005558M^{0.294245046}$

Thus $K' = 0.005558$

$a = 0.294245046$

<u>Example of PS-1</u>

From data of PS-1 we can determine the molecular weight.

$$0.1049 = 0.005558(M_w)^{0.294245046}$$

$$M_w = 21,679$$

Thus the molecular weight of PS-1 is 21,679.

Appendix F

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Synthesis of Graft Copolymer of Syndiotactic Polystyrene with Polybutadiene by Way of 4-Methyl styrene

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Abstract

The basic method to synthesize syndiotactic polystyrene-g-polybutadiene graft copolymers was investigated. Firstly, the syndiotactic polystyrene copolymer, poly(styrene-co-4-methylstyrene) (sPSMS), was prepared by the copolymerization between styrene and 4-methylstyrene monomer with Cp*$TiCl_3$/MMAO at 50°C. Polymerizations proceeded in argon atmosphere at ambient pressure. Secondly, the copolymer was grafted with polybutadiene (ready made commercialized unsaturated elastomer) by anionic grafting polymerization with a metallation reagent. This graft copolymer showed high melting temperature (240-250°C) and was different from those of anionic styrene-butadiene copolymers due to the presence of crystalline syndiotactic polystyrene segments. Usually, highly syndiotactic polystyrene has the glass transition temperature at 100°C and behaves like glassy polymer (possessed brittle mechanical properties) at room temperature. Thus the copolymer may be used as a compatibilizer in syndiotactic polystyrene blends to modify its mechanical properties in order to compensate the glassy properties of pure syndiotactic polystyrene at room temperature.

Keywords: Syndiotactic Polystyrene, Polybutadiene, graft-copolymer

1. Introduction

Syndiotactic polystyrene (sPS) is an important engineering plastic and has excellent physical properties such as low dielectric constant, high chemical resistance, hydrolytic resistance, heat resistance and good dimensional stability.[1,2] However, sPS limited its applications at room temperature because of its inferior compatibility and low impact resistance.

The attempts have been made to characterize the new materials and improve the physical, mechanical properties and processability of sPS through several procedures. Firstly, addition of the olefin monomer, especially ethylene, during styrene polymerization procedure to achieve styrene/olefin copolymer with various microstructure, such as random, block, and alternating copolymers, by using metallocene catalyst at appropriate conditions.[3] Secondly, physical polymer blending also provides a feasible access to sPS modification.[4] In addition, the synthesis of graft copolymer of sPS with macromonomers is of great interests.

Previously, sPS based graft copolymer had been prepared by copolymerization of styrene and small monomers. In this manner, metallocene copolymerization of styrene with monomer isoprene or atactic monomer styrene was performed to obtain Poly(sPS-g-styrene)[4,5] or Poly(sPS-g-isoprene)[5,6]. Thus the obtained copolymers were blend with pure sPS and their polymorphic behaviors were studied by x-ray diffraction. The two examples illustrated successful approaches for sPS modification.[4-6]

There are many reports about the techniques of sPS modification. For example, Xu and Chung introduced polar groups onto sPS to improve adhesion and compatibility.[7] Hydrogenation of the Poly(sPS-g-Butadiene) graft-like copolymer was studied by Shengsheng Liu.[3] Epoxy-containing sPS graft copolymer, effectively increased the thermal stability, was prepared via 4-methylstyrene with metallocene/MAO catalyst by Chi-Lan Li et al.[1] Recently, the achievements in the stereospecific copolymerization of styrene and butadiene monomer with transition metal has provide alternative ways to improve mechanical properties of these materials by controlling the cis selectivity of Butadiene segments.[8-11] The Poly(sPS-b-cis-Butadiene) was investigated and used as effective compatibilizer for immiscible syn-PS/cis-PB blends by Hoang The Ban et al.[12,13] However, their block copolymer, Poly(sPS-b-Butadiene), come from the reaction with butadiene monomer, dissimilar to copolymer this study, Poly(sPS-g-Polybutadiene).

This research reports the method for synthesis of graft copolymer between sPS and polybutadiene (ready made elastomer) via n-Butyllithium polymerization. Many literatures reported about the production methods of the sPS copolymer, but they used butadiene monomer [12-14] or isoprene monomer [4-6,15] as a reactant. In this research, polybutadiene, ready made unsaturated polymer that composed of high cis-configuration were used as the reactant. The combination of metallocene copolymerization and anionic polymerization procedures will be used for the preparation of the copolymers with sPS segments. The resulted graft copolymers can be utilized as the toughness reinforcement of sPS.

2. Experimental

2.1 Materials

Cp*TiCl3 (Aldrich) and MMAO (1.83 M in toluene), donated from Tosho Finechem Co, were used without further treatment. Polybutadiene (PB), donated by BST Elastomers Co., Ltd. (Thailand, high cis- grade), was used without purification. Styrene and 4-methyl styrene (MS) monomer (Aldrich) were distilled under reduced pressure before use. n-Butyllithium (Aldrich), Potassium tert-butoxide (Fluka), and cyclohexane (Fluka) were used without purified. Toluene was refluxed over sodium metal and distilled before used. *o*-Xylene (Aldrich) was also used without purification and PS standard which have the molecular weight of 10,000 and 100,000 (Fluka) were used for determining molecular weight (M_v or M_w) of copolymers.

2.2 Synthesis of sPSMS (PS-0)

The copolymerization between sPS and 4-methyl styrene (MS) was carried out as following: Styrene (78.3 mmol) and 4-methyl styrene monomer (8.7 mmol), MMAO (0.03 mol) and Cp*$TiCl_3$ (0.15 mmol) were injected into a 250 ml glass reactor with a magnetic stirring and using toluene as the solvent. The reaction conducted at 50°C under argon atmosphere for 1 hr and terminated by adding acidic methanol. The precipitated polymer was washed with acidic methanol, followed by drying in vacuum at 60°C. The copolymer was purified by soxhlet extraction with methyl ethyl ketone for 24 hr.

2.3 Synthesis of sPSMS-g-PB

Under argon atmosphere, the sPSMS copolymer (1 g) was suspended in 20 ml of cyclohexane in a 250-mL round flask with magnetic stirring. Then 2 mmol of n-BuLi and 0.01 mole of potassium tertbutoxide were added. The solution reacted at room temperature for 3 hr to provide the deprotonated sPSMS powder. Then unreacted reagents were removed by filtration and washing a few times with cyclohexane.

The deprotonated sPSMS powder (0.5 g) was suspended in 20 ml cyclohexane before 1 g of polybutadiene was added. The polymerization took place at room temperature for desired reaction time (0.5, 1 and 2 hr is represented by PS-1, PS-2 and PS-3 respectively) before it was terminated by adding acidic methanol. The grafted copolymer was purified by soxhlet extraction with pentane for 24 hr to remove any unreacted homo polybutadiene.

2.4 Polymer characterization

The weight average molecular weights (M_v or M_w) of the polymers were determined with solution viscosity by using ubbelohde tube. The ^{13}C NMR spectra were recorded on a Avance DPX-400 spectrometer. The sPS copolymers were dissolved in o-dichlorobenzene and chloroform-d_1 at an elevated temperature. The thermal properties were measured by Perkin-Elmer Diamond DSC at heating rate 20 ºC/min in the temperature range -60 to 300 °C. The heating cycle was run twice. The morphology of all sPS copolymers were investigated by JSM-5410LV Scanning Microscope. The samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

3. Results and Discussion

3.1 Synthesis of the Poly(sPS-g-PB) copolymer

The present study showed method for synthesis of graft copolymer between syndiotactic polystyrene and polybutadiene by reaction of the CH_3 group of MS with n-BuLi. The grafting of the sPSMS with the reaction of polybutadiene at the CH_3 will be accomplished. The sPSMS random copolymer (PS-0) which synthesized by the copolymerization of styrene and 4-methylstyrene with Cp*$TiCl_3$/MMAO catalyst, has 25 mol% of 4-methylstyrene which obtained from the ^1H-spectra of sPSMS (not shown in this report) by the ratio of peak intensity at 2.26 ppm (-CH_3) to peak intensity at 1.8 ppm (-CH). Then the sPSMS copolymer was metallated by n-BuLi in strong base condition. When polybutadiene was added, the anionic graft polymerization of polybutadiene to sPSMS chains started to form a graft copolymer with well-defined side chains [sPSMS-g-PB] from the methyl group of MS. Polybutadiene is a commercialized elastomer and has high cis-configuration. The polymerization experiments were conducted by the same amount of polybutadiene and sPSMS content at all reaction conditions. Even if ungrafted sPSMS may exist, the amounts of polybutadiene were added in excess in all the reaction. Moreover the addition of excess amounts of polybutadiene led to the Poly(sPS-g-PB) copolymers in good yields without any difficulty. Results of graft copolymer with various reaction times are shown in Table 1.

Table 1. Results of copolymeriztion of styrene with polybutadiene[a]

Sample	sPSMS (g)	PB (g)	Reaction time (hr)	Yield (g copolymer)	Content of PB in %wt	[η]	M_w ($\times 10^4$)
PB**	-	-	-	-	-	0.24	35.35
PS-0*	-	-	-	-	-	0.07	0.48
PS-1	0.5	1	0.5	0.85	3.94	0.11	2.17
PS-2	0.5	1	1	1.26	11.50	0.19	17.28
PS-3	0.5	1	2	1.38	34.47	0.28	66.31

[a] copolymerization conditions: 2 mmol *n*-BuLi, 0.01 mol K-tertbutoxide and 25°C
*sPSMS : non-graft copolymer, ** cis-polybutadiene(commercial)

From Table 1, the polymerization activities, based on polymer yield, increased with increasing of reaction time. Livingness of these polymerization systems can be checked by molecular weights of these copolymers. Molecular weights of copolymers were determined by solution viscosity because of the difficulty in dissolving these high molecular weight grafted copolymers.

Solution viscosity is basically a measurement of the size of polymer molecules. It is empirical related to molecular weight for linear polymers. Several mathematical equations are available in the literature for determining the intrinsic viscosity [η] of a polymer solution, by graphical extrapolation. In this study, intrinsic viscosity was determined from Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \quad (1)$$

where k" is constant, η_r is relative viscosity, c is concentration in g/dl and [η] is determined from $[(\ln \eta_r)/c]_{c=0}$. According to the Mark-Houwink-Sakurada relation, the correlation between intrinsic viscosity and molecular weight, the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K'M^a \quad (2)$$

where K´ and a are constants related to the stiffness of the chain and depend on the type of polymer, solvent and temperature.[16] From both equations, we can estimate the molecular weight of these copolymers from the extrapolation at c = 0. The intrinsic viscosity [η] and molecular weight (M_w) of copolymer were also summarized in Table 1. It observed that the polybutadiene content increases when the reaction time increases. Furthermore, when compared the results between PS-1 – PS-2 and PS-2 – PS-3, it was obvious that M_w increase more than twice when the reaction time increase. We suspected that this system might have the living behavior since molecular weight and PB content increase corresponding to the increase of reaction time, while metalated anionic site remains constant.

From M_w results in Table 1, we found that PS-3 exhibited the highest M_w and higher than M_w of PB. On the other hand, M_w of PS-1 and PS-2 were lower than PB. This was probably because of the effect of solvent cage and the anionic graft polymerization initiated by small-chain polybutadiene which observed in 0.5 hr and 1 hr respectively and long-chain polybutadiene grafted onto the backbone when the reaction time increased to 2 hr. Due to the high molecular weight of macromolecules, the rate of their diffusion is lower than small molecules in liquids.[17] Thus reactions of large molecules in polymers being much lower than small molecules so M_w results were clearly observed in long reaction time.

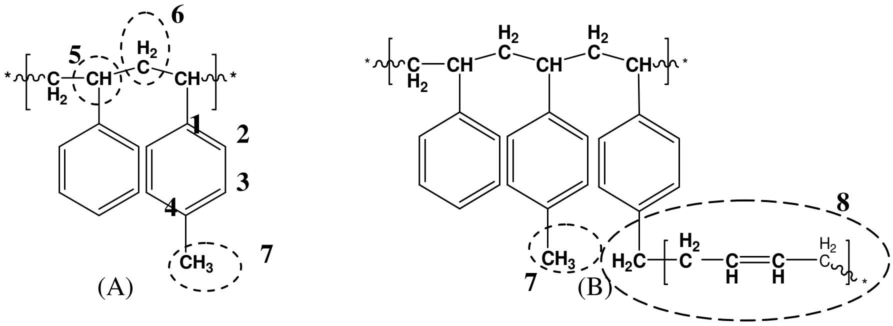


Figure 1. Structure of the synthesized copolymers: (A) sPSMS and (B) sPSMS-g-PB

The copolymer structures and positions of each carbon which obtained by ^{13}C-NMR are defined in Figure 1. The characteristics of ^{13}C-NMR spectra for all mentioned copolymers were shown in Figure 2. The strong and sharp peak appearing at 145.9 ppm confirmed that the graft copolymers were highly syndiotactic.[12,13] Figure 2(A) shows the peaks at 21.4 ppm derived from methylene carbon in 4-methylstyrene. During the anionic graft polymerization, Figure 2(B), 2(C) and 2(D) reveals a decrease in the peak intensity at 21.4 ppm and corresponding increase in the peak intensity of the PB units at 27.5 ppm. This peak proved that polybutadiene was highly cis-1,4.[12,13] In addition, when compared the peak intensity at 21.4 and 27.5 ppm of each graft copolymers, we found that the peak intensity at 27.5 ppm increase with increasing of reaction time while the peak intensity at 21.4 ppm remains constant. This showed that the number of metalated anionic sites were approximately unchanged when the reaction time increases. Thus the molecular weight increases because the grafted polybutadiene side chain grows continuously. If the graft polymerization was complete, the ^{13}C-NMR spectra peak at 21.4 ppm should disappear completely and the intensity of the peak at 27.5 ppm should reach its maximum. Unfortunately, there are the peak at 21.4 ppm remained which showed the incomplete depletion of CH_3 in all reaction condition. Due to the relatively high Mw of these graft copolymers, it can be dissolved in dichlorobenzene. The polymers cannot dissolve in chloroform d1 solvent, so the mix solvents of dichlorobenzene and chloroform d1 were used. The polybutadiene peak at 133 ppm will be interfered with the peak of dichlorobenzene, thus the only peak at 27.5 ppm of polybutadiene will only be verified.

Table 2 shows the thermal properties of sPS copolymers. Generally, sPS is semicrystalline materials and displayed very high melting temperatures up to 270°C.[18] From Table 2, T_m value of PS-0 was lower than 270°C because when 4-methylstyrene units is introduced to the sPS backbone, the crystallinity of sPS decreases. Since the bulkiness or the electron donating effect of the CH_3 group may prevent the sPS from crystallization.[19] Although, after polybutadiene was grafted onto the sPSMS backbone, T_m values of PS-1, PS-2 and PS-3 approximately remain the same. It can be implied that grafted polybutadiene doesn't further interfere with T_m of sPSMS.

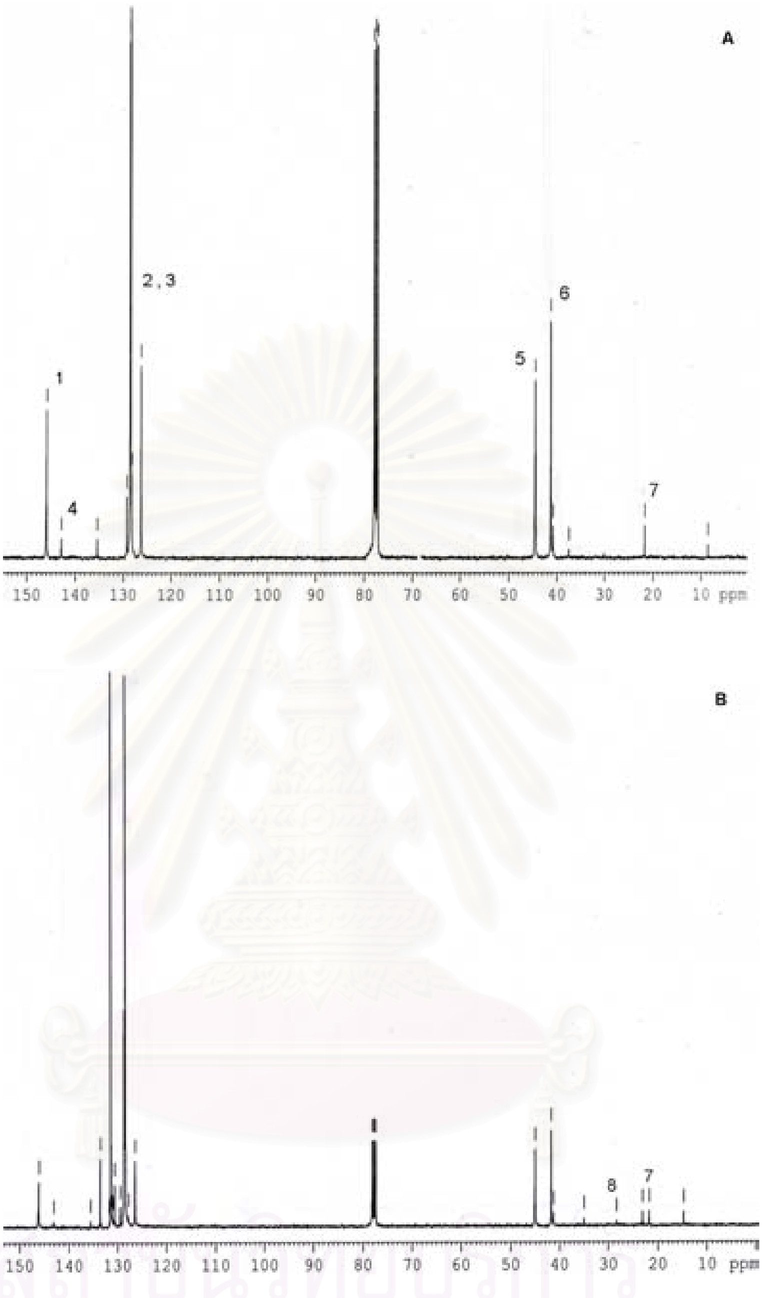


Figure 2. ^{13}C-NMR spectra of sPS copolymers in $CDCl_3$/o-dichlorobenzene: (A) PS-0[a], (B) PS-1, (C) PS-2 and (D) PS-3

[a] Dissloved in $CDCl_3$ only

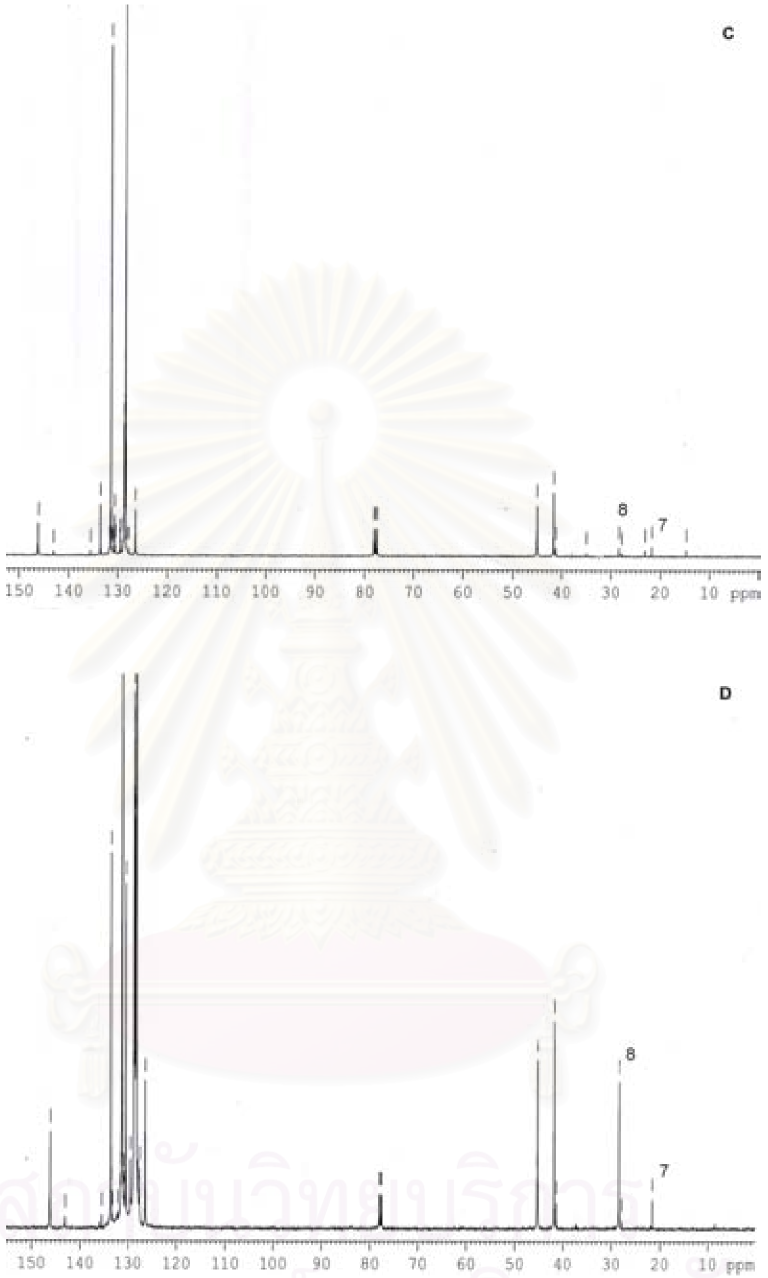


Figure 2. ^{13}C-NMR spectra of sPS copolymers in $CDCl_3$/o-dichlorobenzene: (A) PS-0[a], (B) PS-1, (C) PS-2 and (D) PS-3 (continued)

[a] Dissloved in $CDCl_3$ only

Table 2. Thermal properties of syndiotactic polystyrene copolymers obtained with $C_p^*TiCl_3$/ MMAO catalyst[a]

Sample	Heat 1*					Cool*		Heat 2*				
	T_g (°C)	T_{m11}^a (°C)	ΔH_{11} (J/kg)	T_{m21}^b (°C)	ΔH_{21} (J/kg)	T_c (°C)	ΔH_C (J/kg)	T_g (°C)	T_{m12}^a (°C)	ΔH_{12} (J/kg)	T_{m22}^b (°C)	ΔH_{22} (J/kg)
PS-0	na	na	na	247	22	205	22	100	na	na	247	22
PS-1	na	na	na	246	15	196	14	99	na	na	246	15
PS-2	na	-13	1	246	14	196	14	99	-20	1	245	14
PS-3	na	-12	6	247	7	197	7	99	-20	4	246	7

*Determined by DSC with rate 20°C/min

[a]T_m of polybutadiene, [b]T_m of sPSMS copolymer, na : not available

On the other hand, when compared the result of ΔH value, it was obviously showed that grafted polybutadiene affects ΔH value of copolymers. The ΔH value of copolymer continuously decreases when more polybutadiene was grafted onto the sPSMS backbone, implying that incorporation of the grafted polybutadiene tends to interrupt the crystallization contents of sPSMS main chain. It is probable due to a bulky group of polybutadiene which could have resulted in steric hindrance. Thus the packing density of polymer chains decreased, resulting in the decreased crystallinity of the sPSMS-g-PB.[1] Moreover, the grafted copolymers have two T_m, which the first T_m represented polybutadiene and the second T_m represented sPSMS copolymer. Comparing among three graft copolymers samples, the value of T_g and both T_m is mostly constant but the peak area (ΔH) of T_{m1} in PS-3 is higher than PS-2 which correspond to the increase grafted polybutadiene content when reaction time increases. Moreover the decreases of ΔH of T_{m2} also correspond to the increase polybutadiene content in the copolymer both in the first heating and the second heating. The more polybutadiene added, the less crystallinity observed.

To confirm these results, the surfaces morphology of sPS copolymers were investigated by SEM and shown in Figure 3.

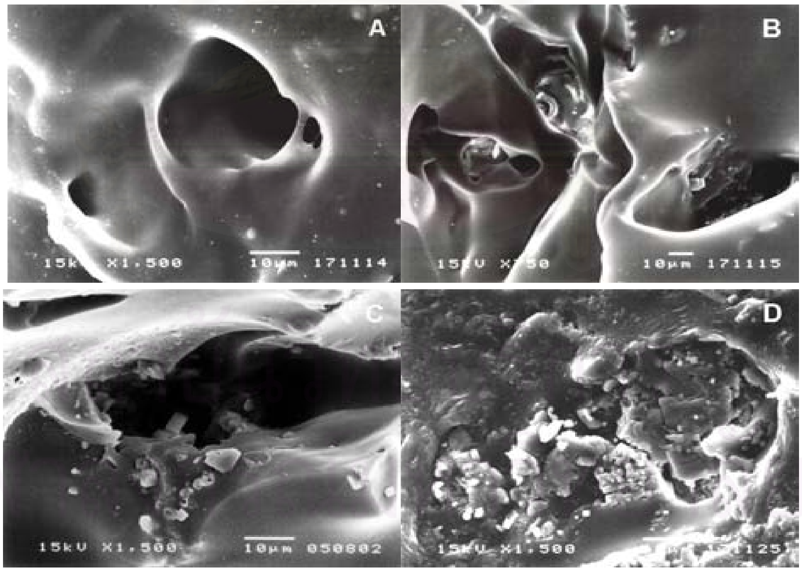
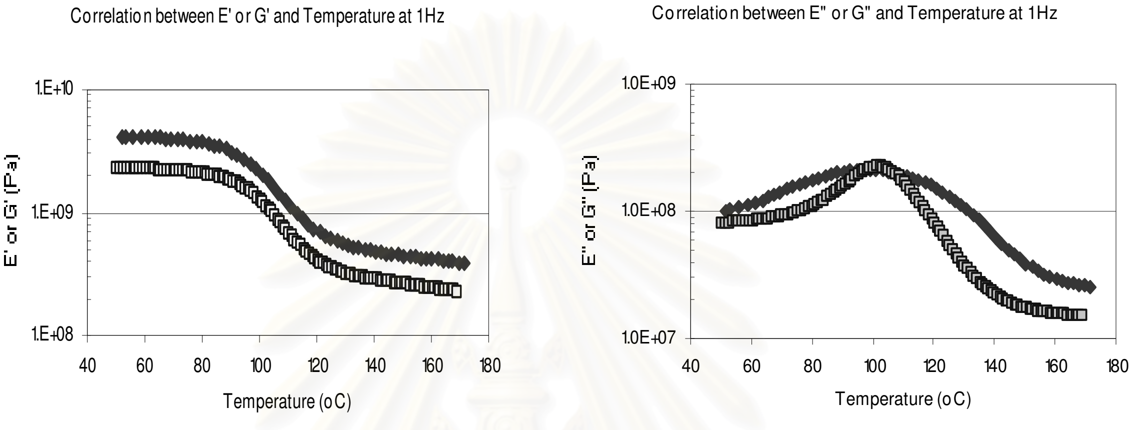


Figure 3. SEM micrographs of sPS copolymers: (A) PS-0, (B) PS-1, (C) PS-2 and (D) PS-3

The grafted sPS changed both the thermal properties and the surface morphology. It can be seen that grafted copolymers consisted of 2 phase. Figure 3 exhibited the distribution of cis-PB (rubber particles) into sPSMS (dark phase). When compared Figure 3(A) and the others, we found that when polybutadiene grafted to the backbone, rubber particles appeared as separated phases from the dark phase. It should be noted that the rubber particles are not simple rubber spheres. Furthermore, it was found that the content and distribution of cis-PB increases with increasing of reaction time which is corresponding to these mentioned results.

3.2 Blending of sPSMS-g-PB

There are many attempts to improve impact resistance of original syndiotactic polystyrene. Rubber toughening of syndiotactic polystyrene and poly (styrene/diphenyl- ethylene) [20] and blending of sPS with poly(*p*-phenylene sulfide) [21] was studied and aimed to improve these properties. It is well known that block and graft copolymer was effective compatibilizer in immiscible blend. To investigate the effective of the synthesized graft copolymer, Poly(sPS-g-PB), and this research compared the impact strength between pure sPS and Poly(sPS-g-PB)/pure sPS blends. Blend sample was prepared by melt mixing and composed of 0.25% Poly(sPS-g-PB). Both polymers were blended at 300°C on hot plate and film samples, which molded on the hot plate about 2 times, were measured by DMA. The mechanical properties of pure-sPS and the Poly(sPS-g-PB)/pure-sPS blend are shown in Figure 4.



(A) (B)

Figure 4. DMA result of commercial sPS and Poly(sPS-g-PB)/pure sPS blend
◆ Poly(sPS-g-PB)/pure-sPS ■ pure-sPS

As Shown in Figure 4(A), the storage modulus (E′ or G′) of blends are higher than pure-sPS thus Poly(sPS-g-PB) can improve toughness strength of original sPS. Considering Figure 4(B), the loss modulus (E′′ or G′′) of blends also higher than pure-sPS, which indicated that the blend of Poly(sPS-g-PB) can adsorb energy more than pure-sPS. Because sPS is a polymer which shows no segmental mobility of chain segments below its glass transition temperature and doesn't exhibit long-range energy dissipation deformation processes on impact below the glass transition temperature.[2] This is a reason that sPS are very brittle at this temperature. Thus the addition of Poly(sPS-g-PB) represents to the presence of rubbery phase in sPS matrix and polybutadiene particles can absorb and dissipate energy when the forces or loads interact with sample. It can be concluded that the Poly(sPS-g-PB)/pure-sPS blend has better mechanical strength and less brittle than pure-sPS.

4. Conclusions

Grafted syndiotactic copolymer composed of high sPS segments in backbone and cis-polybutadiene side chains was prepared by combination of metallocene and anionic polymerization technique. It's possible to corporate the large molecule of unsaturated elastomer polybutadiene onto the backbone of sPSMS chains. The microstructures of the BD and ST units were proved to be highly syndiotactic. It showed high melting temperature (240-250°C) and was different from those of anionic styrene-butadiene copolymers due to the presence of crystalline sPS segments. The grafted polybutadiene content increased with increasing of reaction time but these copolymerization systems present the effect from solvent cage. The crystallinity decreased when polybutadiene was grafted onto the sPSMS backbone. Poly(sPS-g-PB)/pure-sPS blend has higher strength and toughness than pure-sPS which confirmed by DMA result..

Acknowledgement

The author would like to thank BST Elastomers Co., Ltd. for supplying the polybutadiene. Furthermore we would also like to thank MEKTEC manufacturing corporation (Thailand) Ltd. for supporting the characterized equipments.

References

1. Chi-Lan Li, Shu-Hua Chan, Ching Ting and George J. Jiang, Journal of Applied Polymer Science, Vol. 86, 1038-1045 (2002)
2. J. Scheirs and D.B Priddy, Modern Styrenic Polymers: Polystyrene and Styrenic Copolymers, John Wiley & Son, England (2003).
3. Shengsheng Liu, Baotong Huang, Macromol. Rapid Commun. 20, 484-486 (1999)
4. Kiyoshi Endo, Kazunobu Senoo, Polymer Bulletin 44, 25-30 (2000)
5. Kazunobu Senoo, Kiyoshi Endo, Masatoshi Tosaka, Syozo Murakami, and Shinzo Kohjiya, Macromolecules, 34, 1267-1273 (2001)
6. Kiyoshi Endo, Kazunobu Senoo, Macromol. Rapid Commun. 19, 536-566 (1998)
7. Xu, T.C. Chung, Macromolecules, 32,8689 (1999)
8. Kobayashi E., Kaita S., Aoshima S. Furakawa J., J. Polym. Sci., Part A:Polymer chem. 33, 2175 (1994)
9. Kobayashi E., Hayashi N., Aoshima S. Furakawa J., J. Polym. Sci., Part A:Polymer chem. 36, 1707 (1998)
10. Endo K., Matsuda Y., J. Polym. Sci., Part A:Polymer chem. 37, 3838 (1999)
11. Michela Caprio, Maria Cristina Serra, Daniel E. Bowen, and Alfonso Grassi, Macromolecules, 35, 9315-9322 (2002)
12. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Vol. 42, 2698-2704 (2004)
13. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Vol. 43, 1188-1195 (2005)
14. Guodong Zheng and Harald D.H. StÖver, Macromolecules, 35, 6828-6834 (2002)
15. T.C.Chung, H. L. Lu, and R. D. Ding, Macromolecules, 30, 1272-1278 (1997)
16. Fred W. Billmeyer, JR, Textbook of polymer science, Third Edition, John Wiley & Son, Singapore (1984)
17. E.T. Denisova, T.G. Denisova and T.S. Pokidova, Handbook of free radical initiators, John Wiley & Son, New Jersy, p.29 (2003)
18. N. Ishihara, M. Kuramoto, and M. Uoi, Macromolecules. 21, 3356-3360. (1988)
19. Hisayuki Nakatani and Koh-hei Nitta, et al., Polymer, Vol. 38, pp. 4751-4756 (1997)
20. F. Ramsteiner, G.E. McKee et al., Polymer, Vol. 41, 6635-6645 (2000)
21. Seok-Ho Hwang, Myeong-Jun Kim and Jae-Chang Jung, European Polymer J., Vol. 38, 1881-1885 (2002)

Appendix G

The proposed paper to Technology and Innovation for sustainable Development Conference (TISD2006)

Technology and Innovation for sustainable Development Conference (TISD2006)
Faculty of Engineering, Khon Kaen University, Thailand
25-27 January 2006

Synthesis of graft copolymer of Syndiotactic polystyrene with polybutadiene by way of 4-methyl styrene

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Abstract

The basic method for the synthesis of syndiotactic polystyrene graft copolymers was investigated. The syndiotactic polystyrene copolymer, poly(styrene-co-4-methylstyrene) (sPSMS), was prepared by the copolymerization between styrene and 4-methyl- styrene monomer with Cp*$TiCl_3$/MMAO at 50°C. Polymerizations proceeded in argon atmospheric pressure. After that, the copolymer was grafted with polybutadiene by anionic grafting polymerization with a metallation reagent. This graft copolymer showed high melting temperature (240-250°C) and was different from those of anionic styrene-butadiene copolymers due to the presence of crystalline syndiotactic polystyrene segments. ^{13}C-NMR was used to investigate the polymer microstucture and also the percent insertion of each comonomer. Graft copolymer was expected to improve impact properties of the original syndiotactic polystyrene at room temperature, thus it will be used as compatibilizer in syndiotactic polystyrene blends for modifies its properties and its miscibility with other polymers.

Keywords: Syndiotactic Polystyrene, Butadiene, graft-copolymer

1. Introduction

Syndiotactic polystyrene (sPS) is an important engineering plastic and has excellent physical properties such as a low dielectric constant, high chemical resistance, hydrolytic resistance, heat resistance and good dimensional stability.[10] However, sPS is limited its applications at room temperature because of its inferior compatibility and low impact resistance.

The attempts have been made to characteristics of the new materials and improve the physical, mechanical properties and processability of sPS through several procedures. First, Addition of the olefin monomer, especially ethylene, during styrene polymerization procedure to achieve styrene/olefin copolymer with various microstructure, such as random, block, and alternating copolymers, by using metallocene catalyst at appropriate conditions. Second, physical polymer blending also provides a feasible access to sPS modification.[6] In addition, the synthesis of graft copolymer of sPS with macro- monomers is of great interests.

There are many reports about the techniques of sPS modification. For example, Xu and Chung introduced polar groups onto sPS to improve adhesion and compatibility. [11]Hydrogenation of the sPS/PB graft-like copolymer was studied by Shengsheng Liu.[6] Epoxy-containing sPS graft copolymer, effectively increased the thermal stability, was prepared via 4-methylstyrene with metallocene/MAO catalyst by Chi-Lan Li et al.[10] Recently, the sPS-block-cis-PB (polybutadiene) was investigated and used as effective compatibilizer for immiscible syn-PS/cis-PB blends by Hoang The Ban et al.[15,16]

This research reports the basic method for the synthesis of graft copolymer between sPS and polybutadiene via n-Butyllithium polymerization.

The combination of metallocene copolymerization and anionic polymerization procedures will be used for the preparation of polymers with sPS segments. The resulting graft copolymers will expand the scope of their utilizations in the field of polymer blend or polymer composite and increase the impact resistance and elongation of the polymer blend.

2. Experimental

2.1 Materials

Cp^*TiCl3 (Aldrich) and MMAO (1.83 M in toluene), donated from Tosho Finechem Co, were used without further treatment. Polybutadiene (PB), donated by BST Elastomers Co., Ltd. (Thailand, high cis- grade), was used without purification. Styrene and 4-methyl styrene monomer was distilled under reduced pressure before use. n-Butyllithium (Aldrich), Potassium tert-butoxide (Fluka), and cyclohexane (Fluka) were used without treatment. Toluene was refluxed over sodium metal and distilled before used.

2.2 Synthesis of sPSMS (PS-1)

The copolymerization was carried out as following:

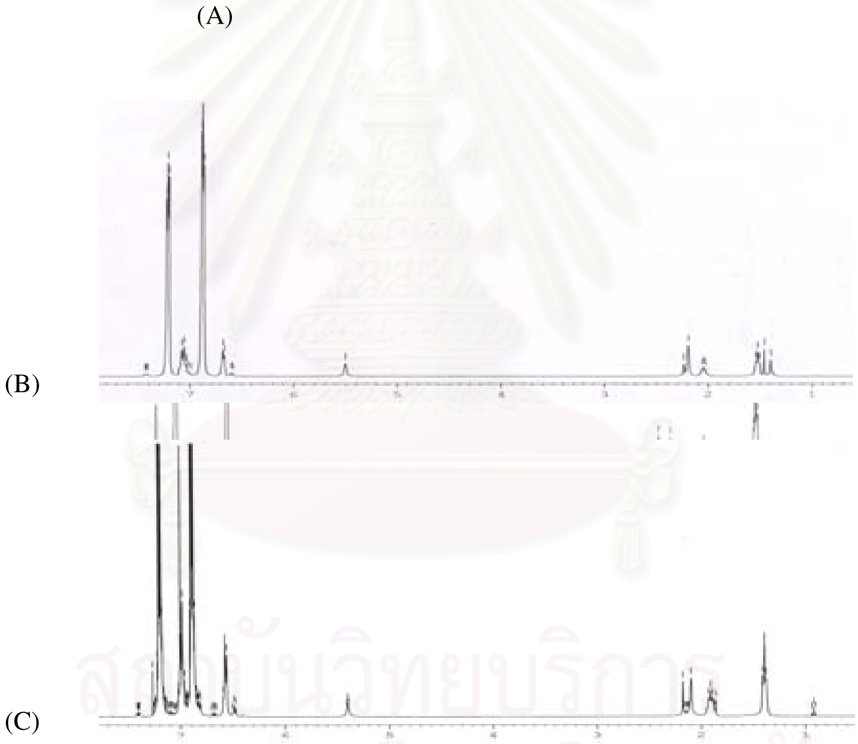


Figure 1. ^{1}H spectra of syndiotactic polystyrene copolymers: (A) PS-1, (B) PS-2, (C) PS-3

Styrene and 4-methylstyrene monomer (87 mmol), MMAO (0.03 mol) and $C_p^*TiCl_3$ (0.15 mmol) were injected into a 250 ml glass reactor with a magnetic stirring using toluene as the solvent. The reaction conducted at 50°C under argon atmosphere for 1 hr and terminated by adding acidic methanol. The precipitated polymer was wash with acidic methanol, followed by drying in vacuum at 60°C. The copolymer was purified by soxhlet extraction with methyl ether ketone for 24 hr.

2.3 Synthesis of sPSMS-g-PB

Under argon atmosphere, the sPSMS copolymer was

suspended in cyclohexane in a 250-mL round flask with magnetic stirring. Then 2 mmol of n-BuLi and 0.01mole of potassium tertbutoxide were added. The solution reacted at room temperature for 3 hr to provide the deprotonated sPSMS powder. Then unreacted reagents were removed by filtration and washing with cyclohexane a few times.

The deprotonated sPSMS powder was suspended in cyclohexane before polybutadiene was added. The polymerization took place at room temperature for desired reaction time (1 and 2 hr is represented by PS-2, PS-3, respectively) before it was terminated by adding acidic methanol. The grafted copolymer was purified by soxhlet extraction with pentane for 24 h to remove any homopolybutadiene.

2.4 Polymer characterization

The ^{1}H and ^{13}C NMR spectra were recorded on a Avance DPX-400 spectrometer. The sPS copolymers were dissolved in o-dichlorobenzene and chloroform-d_1 at an elevated temperature. The thermal properties were measured by Perkin-Elmer Diamond DSC at heating rate 20 ºC/min in the temperature range -60 to 300 ºC. The heating cycle was run twice. The morphology of all sPS copolymers were investigated by JSM-5410LV Scanning Microscope. The samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

3. Results and Discussion

3.1 Characterization of sPS copolymers

The sPSMS random copolymer which synthesized by the copolymerization of styrene and 4-methylstyrene with $C_p^*TiCl_3$/MAO catalyst, has 25 mol% 4-methyl- styrene. Then the sPSMS copolymer was metallated by n-BuLi in super base condition. When polybutadiene was added, the anionic graft from polymerization started to form a graft copolymer with well-defined side chains [sPSMS-g-PB].

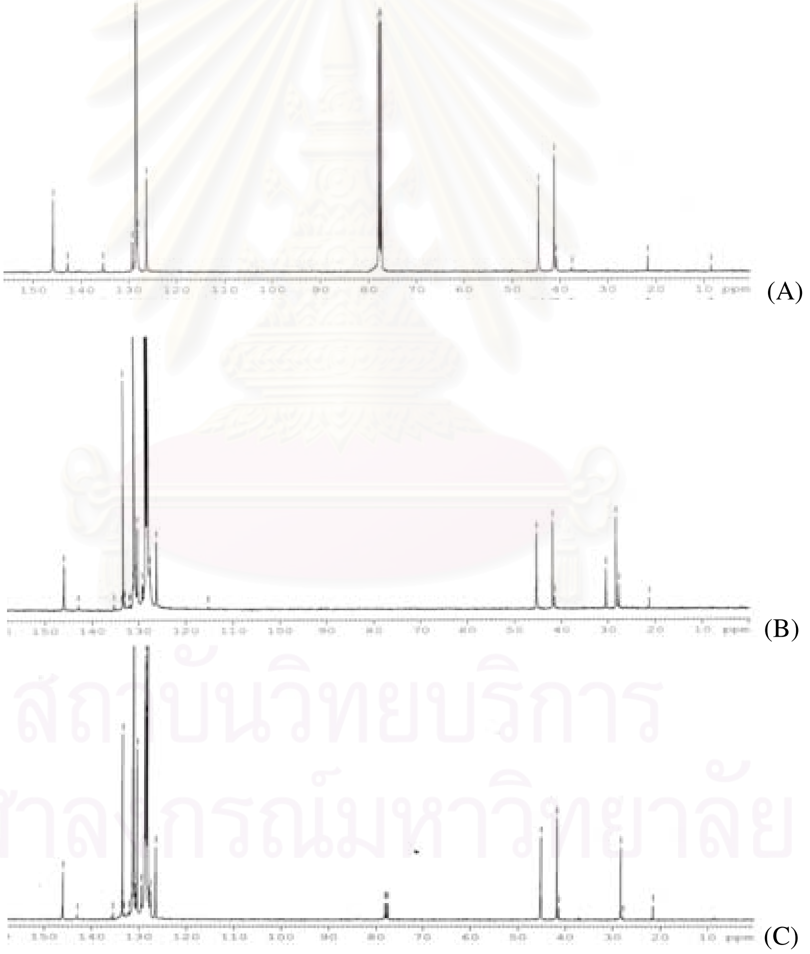


Figure 2. ^{13}C spectra of syndiotactic polystyrene copolymers: (A) PS-1, (B) PS-2, (C) PS-3

The microstructures of graft copolymer were determined by ^{13}C-NMR. As shown in Figure 2(B), the sharp peaks appearing at 145.9 ppm confirmed that the ST units were highly syndiotactic. Figure 2(A) shows the peaks at 21.4

ppm which derived from methylene carbon in 4-methylstyrene. During the anionic graft polymerization, Figure 2(B) reveals a decrease in the peak intensity at 21.4 ppm and corresponding increase in the peak intensity of the BD units at 27.5-30.4 ppm. Unfortunately, Because of the relatively high Mw of the PS-3 sample (Fiure 1(c) and 2(C)), such a ^{1}H and ^{13}C signal could not be observed. It was also difficult to exactly determine the content of ST and BD unit in this copolymerization system.

The chemical composition of these mentioned polymers was confirmed by ^{1}H-NMR and ^{13}C-NMR analysis. Figure 1 shows the ^{1}H-NMR spectra of the (A) sPSMS copolymer, (B) sPSMS-g-PB copolymer. Figure 1(A), the peaks appearing at 2.3-2.5 ppm proved the presence of methyl protons in the 4-methylstyrene units. Figure 1(B), the peaks appearing at 6.5-7.2 ppm indicated the presence of phenyl protons in the ST units and the peak at 5.3-5.7 ppm derived from olefinic protons in the BD units.[15,16] The contents of each unit can be estimated from calculating of intensity ratio between the phenyl and olefinic protons. The graft copolymer contained about 85 mol% ST units and 15 mol% BD units.

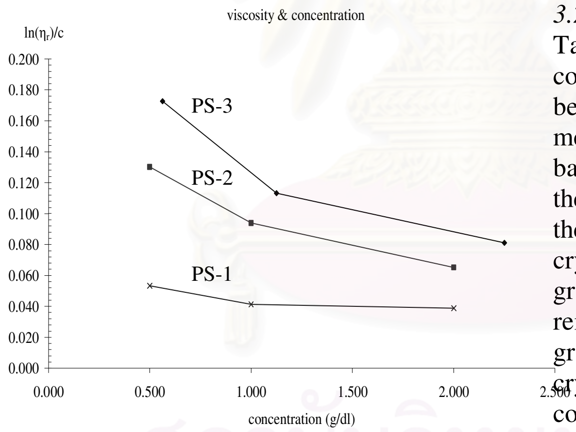


Figure 3. Inherent viscosity-concentration curves for sPS copolymers in o-Xylene

The molecular weights of these copolymers were determined by solution viscosity. Solution viscosity is basically a measure of the size of polymer molecules. It is empirical related to molecular weight for linear polymers. From Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad (1)$$

where k” is constant, η_r is relative viscosity, c is concentration in g/dl and [η] is intrinsic viscosity determined from $[(\ln \eta_r)/c]_{c=0}$. Moreover, the correlation between intrinsic viscosity and molecular weight is expressed in the equation (2)

$$[\eta] = K'M^a \qquad (2)$$

where K’ and a are constants [20]. From both equations, we can estimate the molecular weight of these copolymers from the extrapolation at c = 0. For these systems, we observed that viscosity of PS-3 is the highest and twice of PS-2 in Figure5. Therefore the molecular weight of PS-3 was expected to twice of PS-2. It could be said that the molecular weight of copolymers and the grafted polybutadiene contents increase when the reaction time increases.

3.2 Thermal properties

Table 1 shows thermal properties of sPS copolymers. The T_m value of PS-1 was found to be lower as compared with PS-0. When 4-methylstyrene units is introduced to the sPS backbone, the crystallinity of sPS decreases since the bulkiness or the electron donating effect of the CH_3 group may prevent the sPS from crystallization.[3] Although, polybutadiene was grafted onto the sPSMS backbone, PS-2 and PS-3 remain the same T_m value. It can be implied that grafted polybutadiene doesn’t disturb the crystallinity of sPSMS. Moreover, the grafted copolymers have two T_g, the first is T_g of polybutadiene and the second is T_g of sPSMS copolymer. Comparison of PS-2 and PS-3, the value of T_m and both T_g is mostly constant

Table 1. Thermal properties of syndiotactic polystyrene copolymers obtained with $C_p^*TiCl_3$/MMAO catalyst^a

Sample	Heat 1 (°C)*			Heat 2 (°C)*		
	T_{g1}^a	T_{g2}^b	T_m	T_{g1}^a	T_{g2}^b	T_m
PS-0**	na	na	270.67	na	99.78	271.36
PS-1	na	na	247.24	na	100.55	246.90
PS-2	-13.03	na	245.99	-20.71	98.73	244.89
PS-3	-12.33	na	248.25	-20.09	99.59	246.10

*Determined by DSC with rate 20°C/min, **PS-0 : sPS

$^a T_g$ of polybutadiene, $^b T_g$ of sPSMS copolymer, na : not available but the peak area of T_{g1} in PS-3 is approximately twice of PS-2. There are many reasons for explaining and one of those reasons is the grafted polybutadiene content may be increase.

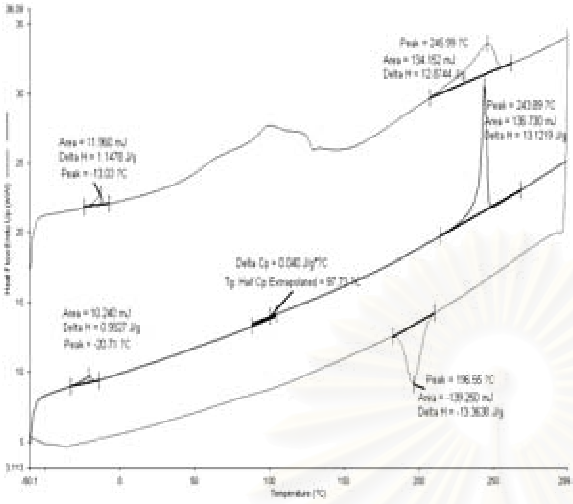


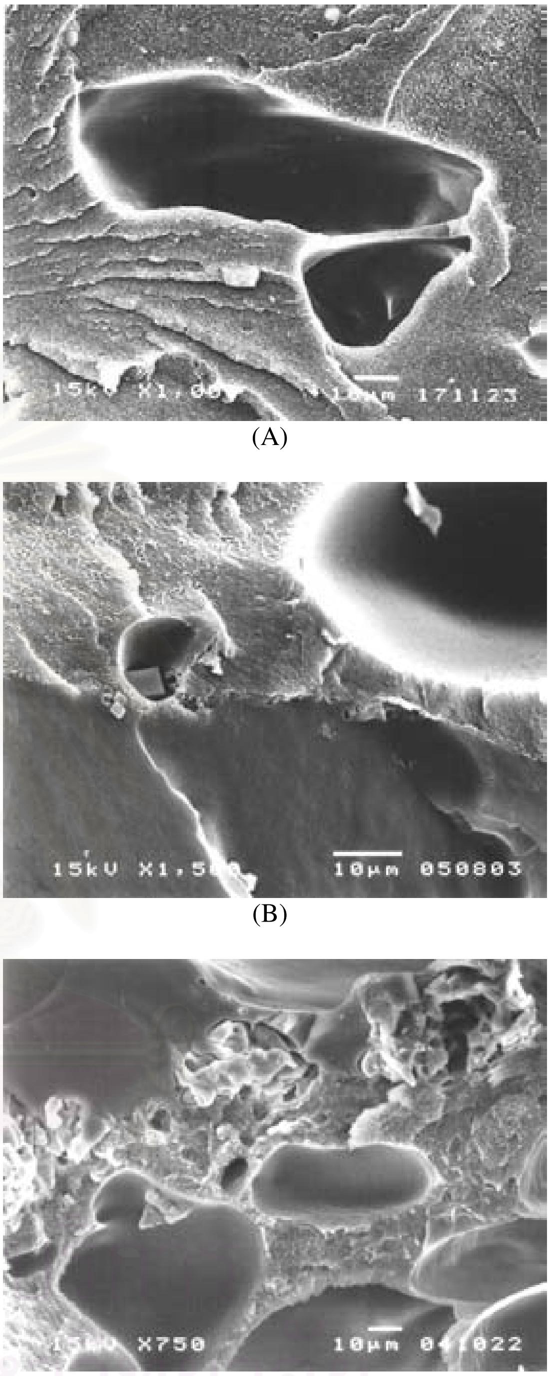
Figure 4. DSC curves of sPSMS-g-PB copolymers, PS-3* (*reaction time: 2hr)

3.3 Phase morphology

The grafted sPS changed both the thermal properties and the surface morphology. The fracture surfaces of sPS copolymers were shown in Figure 4. Grafted copolymers consisted of cavities and particles which represented to sPS and polybutadiene, respectively. When polybutadiene grafted onto the backbone, particles appeared in the cavities. Comparison Figure 4(B) and 4(C), they obviously differ. The content and distribution of particles in the cavities in Figure 4(B) is less than 4(C). It indicated that grafted polybutadiene contents increase when the reaction time increases which is corresponding to the DSC and solution viscosity results so these reactions were expected to living polymerization.

4. Conclusions

Grafted syndiotactic copolymer composed of high sPS segments in backbone and cis-polybutadiene side chains was prepared by combination of metallocene and anionic polymerization technique. This graft copolymer contained about 85 mol % ST units and 15mol % BD units. The microstructures of the BD and ST units were proved to be highly syndiotactic. It showed high melting temperature (240-250°C) and was different from those of anionic styrene-butadiene copolymers due to the presence of crystalline sPS segments. It was expected to improve impact properties of the original syndiotactic polystyrene at room temperature, thus it will be used as compatibilizer in sPS blends.



(A)

(B)

(C)

Figure 5. SEM micrographs of sPS copolymers: (A) surface of PS-1, (B) surface of PS-2, and (C) surface of PS-3

Acknowledgement

The author would like to thank BST Elastomers Co., Ltd. for supplying the polybutadiene. Further- more we would also like to thank MEKTEC manufacturing corporation (Thailand) Ltd. for supporting the characterized equipments.

References

1. N. Ishihara, M. Kuramoto, and M. Uoi, Macro- molecules. 21 (1988) 3356-3360.
2. Carla Manfredi, Gaetano Guerra, Claudio De Rosa, Vincenzo Busico, and Paolo Corradini, Macro- molecules (1995), 28, 6508-6515
3. Hisayuki Nakatani amd Koh-hei Nitta, et al., Polymer, Vol. 38, pp. 4751-4756 (1997)
4. Kiyoshi Endo, Kazunobu Senoo, Macromol. Rapid Commun. 19, 536-566 (1998)
5. Kiyoshi Endo, Kazunobu Senoo, Polymer Bulletin 44, 25-30 (2000)
6. Shengsheng Liu, Baotong Huang, Macromol. Rapid Commun. 20, 484-486 (1999)
7. F. Ramsteiner, G.E. McKee et al., Polymer, Vol. 41 (2000), 6635-6645
8. Kazunobu Senoo, Kiyoshi Endo, Masatoshi Tosaka, Syozo Murakami, and Shinzo Kohjiya, Macromolecules (2001), 34, 1267-1273
9. I. Tausendfreund, F. Bandermann, H.W. Siesler, M. Kleimann, Polymer, Vol. 43 (2002) 7085-7091
10. Chi-Lan Li, Shu-Hua Chan, Ching Ting and George J. Jiang, Journal of Applied Polymer Science, Vol. 86, 1038-1045 (2002)
11. Xu, T.C. Chung, Macromolecules (1999), 32,8689
12. Michela Caprio, Maria Cristina Serra, Daniel E. Bowen, and Alfonso Grassi, Macromolecules (2002), 35, 9315-9322
13. Guodong Zheng and Harald D.H. StÖver, Macro- molecules (2002), 35, 6828-6834
14. T.C.Chung, H. L. Lu, and R. D. Ding, Macromolecules (1997), 30, 1272-1278
15. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Vol. 42 (2004),2698-2704
16. Hoang The Ban, Yasuo Tsunogae, Takeshi Shiono, J. of polymer science: Part A, Vol. 43 (2005),1188-1195
17. J. Scheirs and D.B Priddy, Modern Styrenic Polymers: Polystyrene and Styrenic Copolymers, John Wiley & Son, England (2003).
18. Sperling, L.H., Introduction to Physical Polymer Science 3rd ed., John Wiley & Son, New York (2001).
19. R.J.Ceresa, Ed., Block and Graft copolymerization, Vol.1 and 2, Wiley Interscience, New York (1973)
20. Fred W. Billmeyer, JR, Textbook of polymer science, Third Edition, John Wiley & Son, Singapore (1984)

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