Formation of SBS Triblock Copolymers Using Waste Soybean Oil as Coupling Agent

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ABSTRACT: Triglyceride in the waste soybean oil (WSO) was used as coupling agent to synthesize a linear styrene-butadiene-styrene (SBS) triblock copolymer. The reaction occurred via a living anionic polymerization of styrene-butadiene block copolymer (SB) using n-butyllithium as initiator and cyclohexane as solvent and followed by the coupling reaction with the added WSO. Gel permeation chromatography (GPC) showed that for all SB-Li precursors except the one with the M_n of 1000 g/mol, the resultant products consisted of two different sizes, one with the nearly comparable size with the precursor, the other with a M_n two-fold higher than the precursor. On the other hand, the reaction of the SB-Li precursor with the M_n of 1000 g/mol and the WSO only resulted in forming the molecule with a M_n two-fold higher than the precursor. The results from the GPC and spectral analysis supported that upon the nucleophilic attack the ester group of the triglyceride in the WSO was broken, giving the SB-C(O)-fatty acid susceptible to the second the nucleophilic attack, thus forming the coupled product. The size of the SB-Li precursor, the SB-Li : WSO molar ratio, the S:B weight ratio and the coupling time were found to influence on the coupling efficiency. However, the size of the SB-Li precursor showed highest impact on the coupling efficiency at which the larger the SB-Li precursor, the lower the coupling efficiency. Regardless of the low coupling efficiency of the WSO, the WSO was found to be a potential coupling agent for the formation of the linear triblock copolymer. This was because the SBS triblock copolymer containing high SB diblock copolymers and prepared by the WSO showed slightly higher tensile strength than the one with less SB diblock copolymers prepared by a traditional coupling agent. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40684.
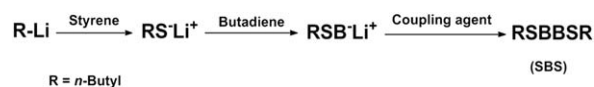
INTRODUCTION

Styrene-butadiene-styrene triblock copolymers (SBS) constitute an important class of thermoplastic elastomers whose elastic and thermoplastic behaviors are joined together in the same material. A variety of SBS triblock copolymers are manufactured commercially in large volumes with a high degree of control over the block length, molecular weight, and microstructure.[1–3] They often have been produced via a well-understood living anionic polymerization technology initiated by organolithium compound such as n-butyllithium and sec-butyllithium in cyclo-aliphatic media as solvent.[4–6] The key feature of living reaction is the ability of polymeric chain ends to survive even when monomer is completely consumed and to reinitiate the reaction again when monomer is newly added.

In general, to obtain a linear SBS triblock copolymer from an anionic polymerization, the living styrene-butadiene diblock copolymer (SB) will be prepared first as a precursor. Then, a linear SBS triblock copolymer can traditionally be obtained by either a coupling or sequential method. For a coupling method, the triblock copolymer is formed via the coupling reaction of two living SB chains with a difunctional coupling agent such as organic chlorides (as shown in Scheme 1). Instead of the addition of a coupling agent, the sequential addition of the styrene monomer also leads to the formation of a linear SBS triblock copolymer. This is called as a sequential method. Finally a terminating agent such as methanol must be added in order to terminate the active chain-ends. Huang[7] synthesized a linear SBS triblock copolymer using both sequential and coupling methods. N-butyllithium and 1,2-dibromoethane were used as initiator and coupling agent, respectively. By comparing the results from these two methods, it was reported that the coupling process produces more symmetrical end blocks and highly monodisperse block copolymers. Although organic chlorides are

R-Li $\xrightarrow{\text{Styrene}}$ RS⁻Li⁺ $\xrightarrow{\text{Butadiene}}$ RSB⁻Li⁺ $\xrightarrow{\text{Coupling agent}}$ RSBBSR

(SBS)

R = n-Butyl

Scheme 1. Coupling polymerization process of SBS.

commonly used as coupling agent and show better coupling performance, they are expensive and high toxicity. Therefore, the search for a cheaper and environmentally friendly coupling agent is a new research field.

Soybean oil (SO) is one of the most widely used edible vegetable oil. Large amount of waste soybean oil was produced from catering establishments and food industries every year. There are lots of researches focusing on the reusing of waste soybean oil (WSO),[8] such as the production of biodiesel fuel for diesel engines by transesterification of WSO with alcohol;[9] or the production of biosurfactant from WSO using some bacteria.[10]

Generally, the SO consists of complex multicomponent mixtures of different triglycerols which are esters of glycerol with both saturated and unsaturated long fatty acid chains.[11] Because of the presence of the unsaturated carbons, consequently it is possible to polymerize or copolymerize these natural oils into useful new materials.[12] The SO has been used to prepare polyols for general polyurethane manufacture.[13,14] Boron trifluoride[15] and boron trifluoride ether complexes[16] have been used to initiate polymerization of the methyl esters of the fatty acids of the SO. Typical thermosets were produced by the cationic copolymerization of regular or low saturation SO with divinylbenzene.[16] The SO itself also can be directly used in some industrial manufacture. It has been used as an adhesive in the manufacture of pressboard.[17] Researchers from the Goodyear Tire and Rubber Company have discovered that the SO can help reduce the amount of petroleum used in tires, while also extending the tread life of those tires. Accordingly, the SO can be used as intermediate chemicals to form polymers and may be a well substitute of extending oil for modified properties of elastomers.

Recently, our research group found that the reaction of the poly(butadienyl)lithium with the methyl oleate (MO) resulted in the formation of the mixed products with the one- and two-fold M_n higher than that of the original polybutadiene.[18] The changes in the size, as evaluated by GPC chromatograms, and the FTIR and NMR spectral analysis, support that the reaction between these two molecules had taken place via cleaving of the ester bond (nucleophilic substitution and then nucleophilic addition). It cleanly proved that the cleaving of the ester bond had been able to take place under anionic polymerization condition. The result showed that the 75% of the product were the molecule with the M_n two-fold higher than the original one. This evidence strongly supported the nucleophilic attack to the C=O ester was possible with a result of the coupled chain.

From the above result, it can be seen that the C=O ester can act as coupling agent for the anionic species. From the structure of vegetable oil consisting of a triglyceride of three various fatty acids, it was expected that vegetable oil may act as a potential coupling agent for the formation of the linear SBS triblock copolymers from the SB precursors. With regard to the price,

abundance, and commercial availability, the soybean oil is potential candidate amongst other vegetable oils. Moreover, instead of using virgin soybean oil, this study was interested in using waste soybean oil considerably obtained every day from the food catering. The use of waste cooking oil instead of virgin oil is an effective way to reduce the raw material cost. In this study, the possibility of the use of the WSO as coupling agent for the formation of the linear SBS triblock copolymer was investigated. The factors affecting the coupling efficiency were evaluated. And the coupling efficiency of the WSO was comparatively studied with that of a general coupling agent, dimethyldichlorosilane (DMDCS). Finally, the potential of the WSO as coupling agent was determined by considering both the coupling efficiency and the mechanical properties of the product.

EXPERIMENTAL

Materials

1,3-Butadiene gas (purity > 99%) was kindly supplied from Kumho Petrochemical. The styrene monomer (purity > 99.5%), dimethyldichlorosilane and n-butyllithium at $2M$ concentration in cyclylohexane were purchased from Aldrich and used as received. Waste soybean oil (WSO) used in this study was obtained from the local food catering. The origin WSO clearly consisted of two phases including the upper portion of clear and brownish oily liquid and the lower portion of opaque yellowish oily liquid. Only clear and brownish oily liquid was used here, and it was treated under vacuum at 60°C for 24 h and then purged with nitrogen gas for 10 min. Tetrahydrofuran (purity > 99.5%; THF) purchased from Daejung Chemical was treated with molecular sieve 4A (8–12 mesh) to remove the moisture before use. Cyclohexane, methanol, and acetone were extra pure grade, and the first two were purged with nitrogen gas before use.

Polymerization Procedures

Solution polymerization of the SBS triblock copolymer was carried out in a 1000 mL glass reactor equipped with a high speed stirrer under nitrogen atmosphere at 40°C. Cyclohexane was put into the reactor and followed by the addition of THF. The reactor was then completely closed. Nitrogen gas was thoroughly purged into the reactor. The certain amount of styrene monomer was then injected to the reactor. Once the temperature of the solution reached 40°C, n-butyllithium was charged into the reactor. The formation of the poly(styryl)lithium was indicated by the increase in temperature and the rapid color change from colorless to reddish solution. After the temperature of the solution reached the maximum, the solution was allowed to naturally cool down for 5 min, and then a certain amount of butadiene monomer was charged into the reactor to continue the polymerization. The solution color immediately changed from red to yellow color indicative of the crossover polymerization to form the living anionic polystyrene-polybutadiene diblock copolymer with lithium ion (SB-Li). The small amount of SB-Li was sampled for molecular weight and chemical composition analysis. After a certain copolymerization time, the temperature of the solution was held at 50°C, and then the WSO was charged into the reactor. Finally, the reaction was terminated by the addition of methanol. Then the product was

precipitated into methanol and washed with acetone and methanol in turn to remove the rest of the WSO, unreacted reagents, and by product. The final product was obtained after dried at 50°C in a vacuum oven. The effect of the size of the SB-Li, the amount of the WSO, the coupling time and the S : B weight ratio on the coupling efficiency were investigated here.

Characterization Techniques

Nuclear Magnetic Resonance Spectroscopy (NMR). Nuclear magnetic resonance (NMR) spectroscopy was performed on a 500 MHz Avance Bruker NMR spectrometers equipped with Ultrashield magnets. $CDCl_3$ was used as the NMR solvent, whereas calibration was performed using the signal from residual protonated ($CHCl_3$) solvent (peak at 7.26 ppm). The composition of copolymer was determined from the ^{1}H-NMR spectra.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) spectroscopy analyses were performed in a Nicolet iS5 FTIR spectrometer. The samples were prepared by casting films on KBr disks from dissolved sample solutions with subsequent drying to remove the solvent.

Gel Permeation Chromatography. Samples of the WSO, the SB diblock copolymers and the resultant products obtained after adding the WSO were characterized in terms of their molecular weights and molecular weight distributions using gel permeation chromatography (GPC). The sample was dissolved in THF to prepare the sample solution with a concentration of 3 wt %. The GPC chromatogram was calibrated using monodisperse polystyrene standards. And the GPC instrument was equipped with 515 HPLC pump, 717 autosampler, and 2410 refractive index detector. It was working at room temperature with tetrahydrofuran (THF) as eluent and a flow rate of 1 mL/min.

Transmission Electron Microscopy (TEM). The microphase-separated morphology of the samples was investigated by means of a transmission electron microscope (TEM, 120 kV, Leo 912, Germany). Ultrathin sections of the samples were microtomed from a bulk specimen and were stained by osmium tetroxide. As a result, the butadiene-rich (soft) and styrene-rich (hard) phases appear dark and bright respectively in the TEM micrographs.

Tensile and Hardness Testing

The resultant products were compression molded at 160°C for 6 min. Dumbbell-shaped samples were punched from compression-molded sheets with dimensions of 75 × 5 × 2 mm and a parallel specimen length of 20 mm. Tensile strength, modulus, and elongation at break of the samples were measured using a universal testing machine (Instron series IX Automated Materials Testing System 7.25). The testing was performed at room temperature with a constant crosshead speed of 500 mm/min. All samples were tested at least in five-fold. The hardness of the resultant products compression molded into sheets was measured using a Shore A durometer.

RESULTS AND DISCUSSION

Analysis of Waste Soybean Oil

The clear liquid obtained from the waste soybean oil used in this research is analyzed by FTIR, GPC, and ^{1}H-NMR. Figure 1

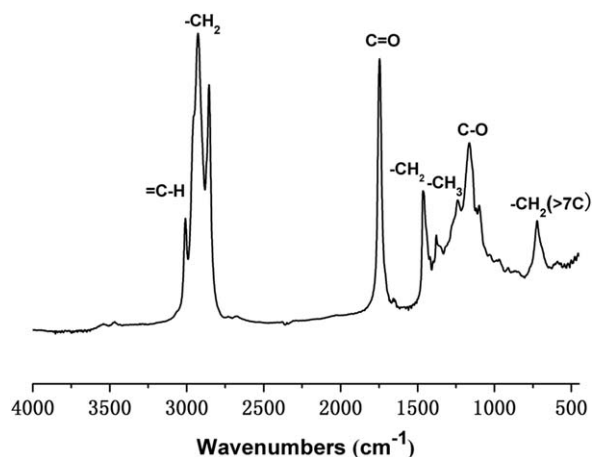**Figure 1.** FTIR spectra of WSO.

shows the FTIR spectra of the WSO at region of 4000–500 cm^{-1}. The assignment of functional groups responsible for IR absorption is as follows: =C—H stretching vibration (3009 cm^{-1}), C—H stretching vibration (2853 cm^{-1} and 2926 cm^{-1}), C=O stretching vibration (1746 cm^{-1}), C—H flexural vibration (1465 cm^{-1}, 1150–1350 cm^{-1}, and 720 cm^{-1}) and C—O stretching vibration (1160 cm^{-1}). In comparison to the FTIR spectra of the soybean oil reported in the past,[19] it can be deduced that all of the above IR absorption peaks of the WSO are in agreement with the structure of a typical triglyceride structure of soybean oil, which consists of both unsaturated and saturated fatty acids esterified to a glycerol backbone.

Figure 2 shows the ^{1}H-NMR spectra of the WSO used in this study. ^{1}H-NMR spectra of the WSO with that of the virgin soybean oil reported in many literatures[16] are comparing with each other, and the peak positions and their corresponding assignment are listed in Table I.[20–22] It was found that they are comparable except the diglyceride which only existing in the waste soybean oil. And according to the weak peaks ($\delta = 3.72$, 4.13ppm) in ^{1}H-NMR spectra, the number of diglyceride in WSO is very small.

The GPC chromatogram of the WSO is shown in Figure 3. Generally, soybean oil is a triglyceride with both unsaturated
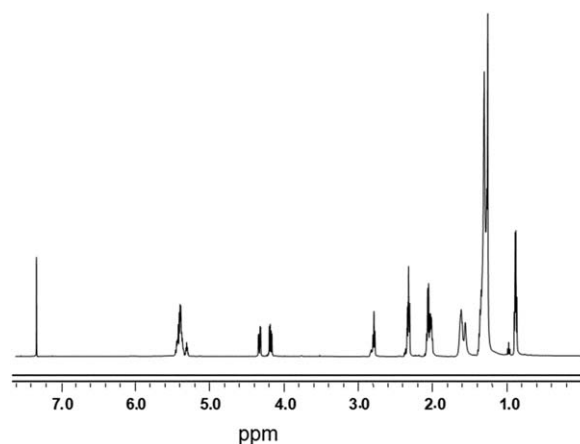

Figure 2. ^{1}H-NMR spectra of WSO.

Table I. Comparison of the Chemical Shift of the ^{1}H-NMR Spectra Between the Virgin Soybean Oil and the WSO

Assignment	Chemical surroundings	Chemical shift (δ, ppm)	
		Virgin soybean oil	Waste soybean oil
—CH=CH—CH$_2$—CH$_3$	All acyl chains, except for linolenic	0.85	0.88
—CH=CH—CH$_2$—CH$_3$	Linolenic acid	0.95	0.94
—(CH$_2$)$_n$—	All acyl chains	1.2	1.3
—CH$_2$CH$_2$—COO—	All acyl chains	1.6	1.6
—CH$_2$CH=CH—	Allylic protons	2.02	2.05
—CH$_2$CH$_2$-COO—	All acyl chains	2.2	2.3
—CH=CHCH$_2$CH=CH—	Bis-allylic protons (linoleic acid and linolenic acid)	2.76	2.79
—CH$_2$OCOR	Diacylglycerol	N/A	3.75
—CH$_2$OCOR	Glycerol (a-position)	4.19, 4.3	4.17, 4.3
—CHOCOR	Glycerol (b- position)	5.15	5.28
—CH=CH—	All unsaturated fatty acids	5.29	5.37

and saturated long fatty acid chains. The unsaturated fatty acids are oleic (C18 with one C=C bond), linoleic (C18 with two C=C bond) and linolenic (C18 with three C=C bond). The saturated fatty acids are palmitic (C16) and stearic (C18). The major components are oleic (23–25%) and linoleic acids (50–55%). Because of the presence of many different fatty acids at various contents, based on the existing molecular formulas, the average calculated molecular weight of soybean oil can range from 860 to 920 g/mol. By GPC analysis as shown in Figure 3, it was shown that the average molecular weight of the WSO is 980 g/mol. The determined molecular weight is higher than the calculated molecular weight. An aberration in molecular weight may be due to the use of linear polystyrenes as standard, whereas the triglyceride soybean oil sample is star shaped. From the GPC chromatogram of the WSO, other components with M_n of 1735 g/mol (6.58%), 244 g/mol (2.94%), and 31 g/mol (1.57%) also existed in the WSO. As mentioned earlier, the WSO used here was obtained from the food catering. Once the oil is exposed to high temperature, the oil rapidly deteriorated and undergoes three chemical reactions including hydrolysis,
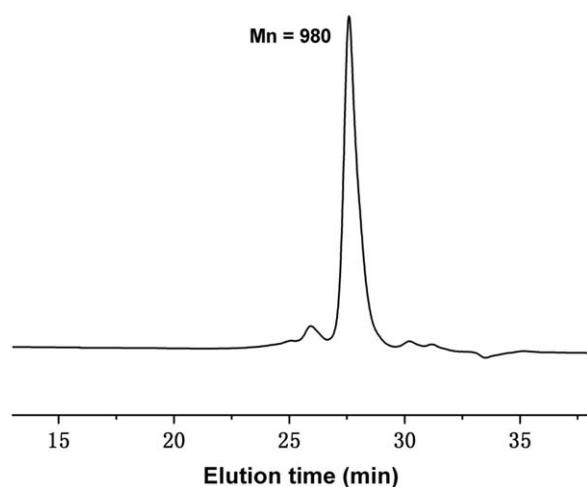
thermal oxidation, and polymerization.[23] There are new substances formed during heating, such as free fatty acids, momoacylglycerols, hydrogenperoxides, alkalides, ketones, dimers, trimers, and polymers. The molecule with the M_n of 1735 g/mol might be the dimer of triglycerides. Due to the low content of the other components in the WSO, therefore they were neglected in this study, and the WSO was used without the removal of those other components.

Synthesis and Characterization of the SBS Triblock Copolymers

The styrene-butadiene-styrene (SBS) triblock copolymers were prepared via the coupling reaction between the living anionic polystyrene-polybutadiene diblock copolymer with lithium ion (SB-Li) and a novel coupling agent: WSO.

Figure 4 shows the GPC chromatograms of the SB diblock copolymers (S: B = 3 : 7) with the calculated M_n of 1000, 5000, 10,000, and 15,000 g/mol before and after reacting with WSO at a SB-Li : WSO molar ratio of 2 : 1. Because of the large viscosity of the solution and the solution cannot contact with air, it is difficult to get the sample of the SB-Li precursors with the calculated M_n higher than 5000 g/mol before added WSO. So the SB diblock copolymers with the calculated M_n higher than 5000 g/mol are obtained by the parallel experiment of the polymerization of the SB at the same condition. However, for the SB-Li precursors with the calculated M_n of 1000 and 5000 g/mol are directly obtained before added WSO.

The M_n values of SB precursors and the resultant products after reacting with WSO are listed in Table II. From the GPC analysis, it can be observed that the reaction between SB-Li and WSO for all SB-Li precursors except the one with the calculated M_n of 1000 g/mol gave the products with two different chain lengths. As in Table II, it can be clearly seen that after reacting with WSO, the obtained products had roughly two and one times higher M_n than the original molecule. For SB-Li with the calculated M_n of 1000 g/mol, the molecular weight of the polymer before and after reacted with WSO are 1081 g/mol and 2515 g/mol, respectively. It can be inferred that the obtained

Figure 3. GPC chromatogram of WSO.
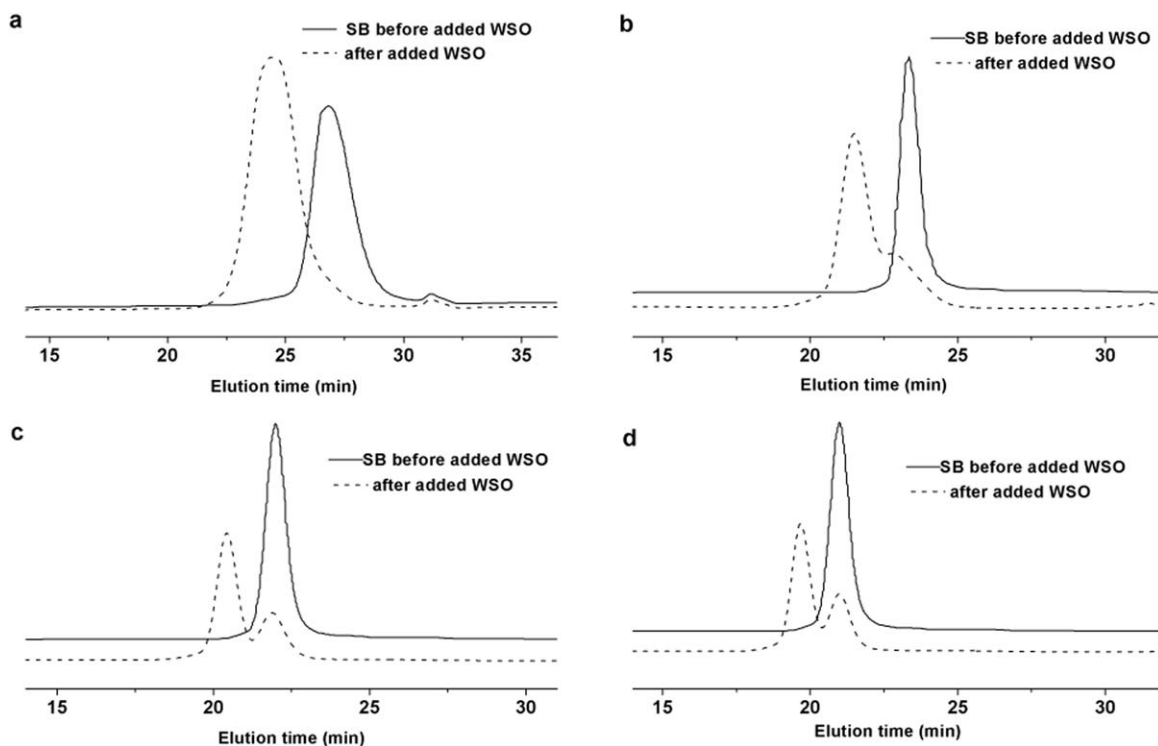
Figure 4. GPC chromatograms of SB with the calculated M_n of (a) 1000 g/mol, (b) 5000 g/mol, (c) 10,000 g/mol, (d) 15,000 g/mol, before (——) and after (- - - -) reacting with WSO at the SB-Li/WSO molar ratio of 2 : 1 and the S : B weight ratio of 3 : 7.

product which had a two-fold higher M_n than the original SB is formed by two SB molecules and one fatty acid molecule ($2M_{nSB} + M_{nfatty} = 2359$ g/mol, $M_{nSBS} = 2515$ g/mol). Therefore, the occurrence of the polymer with a two-fold higher M_n than the original polymer can imply that during reaction the WSO acted as coupling agent towards the anionic species. The cou-

pling mechanism of the anionic species with the WSO is to be discussed next.

Soybean oil consists of three ester functional groups and roughly 4.6 double bonds. Usually, reaction of triglyceride with nucleophile under suitable condition leads to the cleaving of the ester bond, thus breaking the integrity of the triglyceride.

**Table II.** The Calculated M_n, the GPC-Derived M_n and the Coupling Efficiency

No.	S:B[a]	M_n of SB (g/mol)[b]	SB-Li:WSO (molar ratio)	Before adding WSO M_n (g/mol)[c]	After adding WSO M_n (g/mol)[c]	M_n (g/mol)[c]	Coupling efficiency (%)
1	3:7	1,000	2:1	1,081	N/A	2,551	100
2	3:7	5,000	2:1	5,309	5,640	10,740	82.63
3	3:7	10,000	2:1	N/A	10,085	20,086	69.68
4	3:7	15,000	2:1	N/A	15,324	30,395	66.58
5	3:7	20,000	2:1	N/A	21,806	41,354	61.99
6	3:7	25,000	2:1	N/A	25,872	50,422	56.58
7	3:7	25,000	1:1	N/A	24,957	50,193	52.55
8	5:5	25,000	1:1	N/A	24,653	49,463	56.20
9	3:7	25,000	1:2	N/A	25,796	50,893	50.04
10	5:5	25,000	1:2	N/A	25,556	50,060	56.20
11[d]	3:7	25,000	N/A	N/A	25,088	49,955	83.72
12[d]	5:5	25,000	N/A	N/A	24,228	48,481	87.85

[a] Weight ratio of styrene to butadiene monomer added to the reaction.
[b] The calculated M_n of the SB precursor by dividing the weight of monomer in gram with the initiator concentration in mole.
[c] The GPC-derived M_n values.
[d] SBS synthesized by using DMDCS as coupling agent.

Formation of polystyrene-polybutadiene-Li :
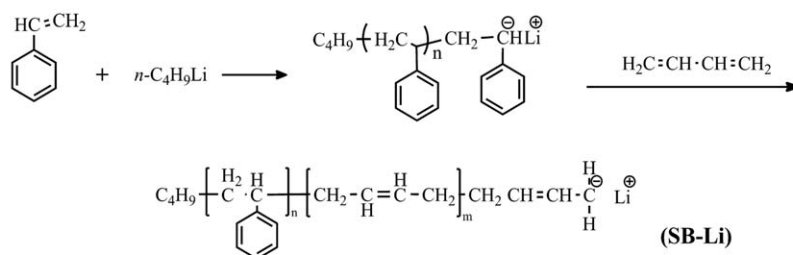
**Coupling process :**
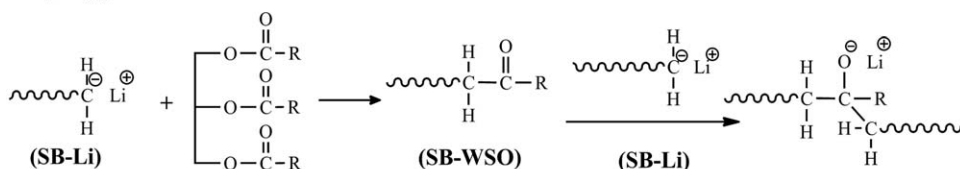
Termination :
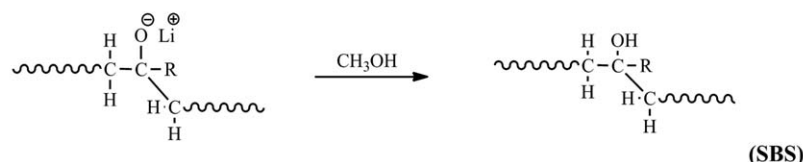
Scheme 2. A proposed reaction mechanism of the SB-Li precursor with the WSO.

The well-known example of above reaction is transesterification of vegetable oil with methanol/ethanol. The overall mechanism is a sequence of three consecutive transesterification, in which diglyceride, monoglyceride, and glycerol are formed, respectively. The resultant products are methyl/ethyl esters of fatty acids also known as biodiesel. From above example, it was proposed here that the formation of the SBS triblock copolymer when using the WSO as coupling agent starts from the nucleophilic attack of the SB-Li at the electrophilic C in the carbonyl group of the triglyceride. Electrons from the C═O move to the electronegative O, generating a tetrahedral intermediate. The intermediate then collapses and displaces the alcohol portion of the ester as a leaving group, thus leading to the formation of the corresponding anion of the diglyceride and the ketone of fatty acid consisting of one SB diblock copolymer (SB-C(O)-fatty acid). Because of the superior reactivity of ketone compared to that of ester,[18] another SB-Li strongly attacks to this newly formed ketone, yielding an alcoholate anion of fatty acid. Finally, the alcoholate anion of fatty acid consisting of two SB diblock copolymers is protonated with methanol added to the reaction later, creating the alcohol of fatty acid bonding with two SB diblock copolymers ((SB)$_2$-C(OH)-fatty acid). The structure of the resultant product can be depicted as a three armed star molecule at which two arms are contributed by two SB diblock copolymers and the other is contributed by an alkyl of the fatty acid. When the length of the SB diblock copolymer is much longer than that of the

alkyl of the fatty acid, the presence of the alkyl of the fatty acid can be neglected. Therefore, the structure of the resultant product can be described as a SBBS or SBS triblock copolymer. A proposed mechanism for the formation of the SBS triblock copolymer when using the WSO as coupling agent is outlined in Scheme 2.

FTIR and NMR Analysis

To further prove the reaction mechanism, SB with molecular weight of 1000 g/mol is selected as a typical copolymer. Figures 5 and 6 show the FTIR and ^{1}H-NMR spectra of the SB diblock copolymer with the M_n of 1000 g/mol and the resultant product at the SB-Li/WSO molar ratio of 2 : 1. After reacting with the WSO, there was only the product with the M_n two-fold higher than that of the SB-Li precursor as shown earlier in Figure 4. Therefore, it can be implied that all obtained products were the SBBS or SBS copolymers hold together by an alcohol of the fatty acid. As seen in Figure 5, IR absorption peaks shown in the spectrum of the resultant product were comparable to those of the SB precursor except the presence of one small broad peak at ~3580 cm^{-1}. Structurally, the new peak roughly locating at the above wavenumber can be corresponding to the absorption of the OH group in the product. The key absorption peaks indicating the butadiene segment are ═C—H stretching vibration (3005 cm^{-1}), C—H asymmetric and symmetric stretching vibration (2916 and 2844 cm^{-1}), —C═C— stretching vibration (1655, 1650, and 1636 cm^{-1} for 1,4-trans; 1,4-cis and 1,2 vinyl,
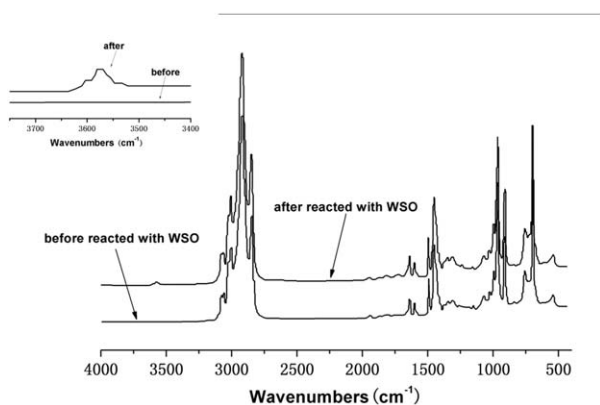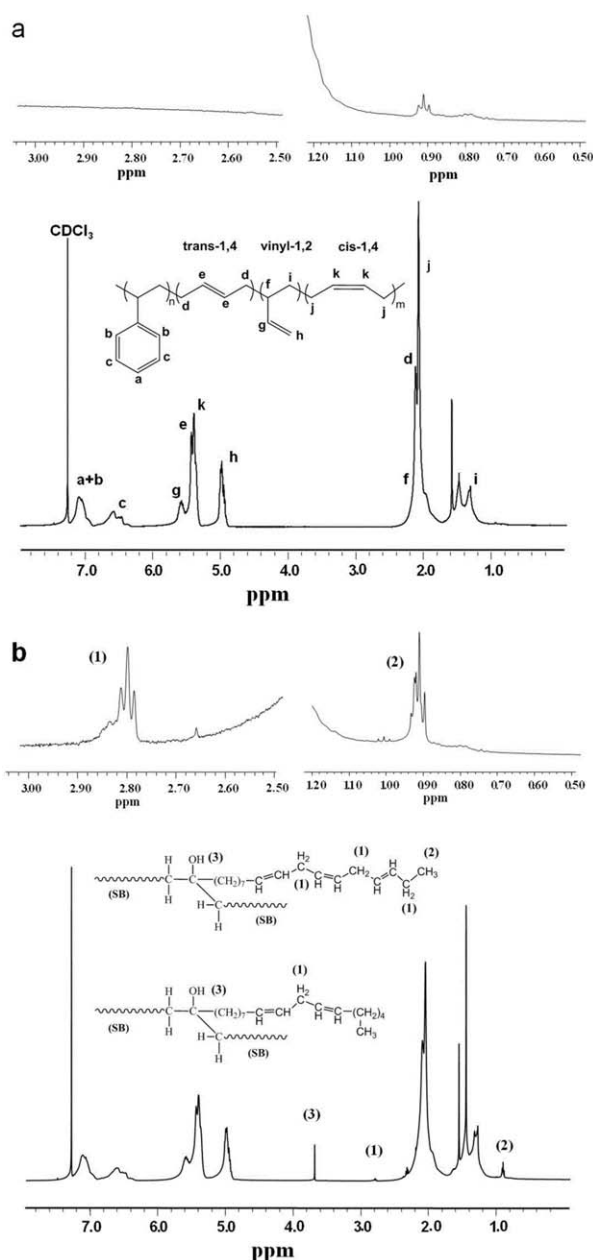
Figure 5. FTIR spectra of SB with the calculated M_n of 1000 g/mol before and after reacting with WSO at the SB-Li/WSO molar ratio of 2 : 1 and the S : B weight ratio of 3 : 7.

respectively), CH$_2$ deformation vibration (1449 cm^{-1} for 1,4-trans and 1,4-cis). Taking into account of the styrene segment, C—H out of plane deformation vibration occurs at 3061 cm^{-1}, polystyrene unit absorption occurs at 1940 cm^{-1} and aromatic C—C stretching vibration occurs at 1602 cm^{-1}.

The ^{1}H-NMR spectra of the resultant product was compared with that of the SB precursor in Figure 6. The assignment of the protons responsible to the butadiene unit and styrene unit in the SB diblock copolymer is given in the figure.[24–26] The protons of CH$_2$ and CH for 1,4-cis/trans butadiene unit reveal at 1.8–2.2 and 5.2–5.8 ppm, respectively. While the protons of CH$_2$ and CH for 1,2-vinyl butadiene unit show at 1.2, 5.0 ppm (for 1,2-methylene, 1,2-terminated) and 5.6 ppm (for 1,2-nonterminated), respectively. For the styrene unit, the protons of aromatic ring respond around 7.2–6.2 ppm. As seen, the ^{1}H-NMR spectrum of the SB precursor and its corresponding product were nearly the same. However, the additional small peaks were observed in the spectrum of the product. The new two peaks locating at 0.9 and 2.7 ppm are associated with the CH$_3$ and bis-allylic protons of the fatty acid (as indicated in Table I and Figure 6). The new peak at 3.7 ppm not observed in the spectrum of the WSO and the precursor SB diblock polymer is responsible to the proton of OH functional group.[27]

Moreover, for the precursor with the M_n higher than 1000 g/mol, besides the product with the M_n two-fold higher than the precursor, GPC analysis revealed that reacting with the WSO also gave the product with the M_n comparable with the precursor. Evidently, it was found that for the SB precursor with a calculated M_n of 5,000 g/mol, the difference in the GPC-derived M_n between the SB precursor and its corresponding product was 331 g/mol. This additional molecular weight is very close to the molecular weight of one fatty acid (278 g/mol). Therefore, it can be implied that the structure of product with an M_n comparable to the precursor is the SB-C(O)-fatty acid. It was believed this resultant product is formed by the necleophilic attack and then followed by the breakage of triglyceride without the further coupling reaction with other SB-Li precursor as shown in Scheme 2. According this the C=O ketone was expected to form. Therefore, the products prepared from the SB-Li precursor with the M_n 25,000 g/mol was analyzed by ^{13}C-

Figure 6. ^{1}H-NMR spectra of SB with the calculated M_n of 1000 g/mol (a) before and (b) after reacting with WSO at the SB-Li/WSO molar ratio of 2 : 1 and the S : B weight ratio of 3 : 7.

NMR (Figure 7) and FTIR (Figure 8) spectroscopy. As shown in Figure 8, the different of IR absorption peaks between the resultant product and the SB precursor is a small new peak at ~1743 cm^{-1} which is corresponding to the absorption of the C=O group in the product. However, in Figure 7, peak of the C=O ketone in ^{13}C-NMR spectrum was not observed. This might be due to the hindrance effect caused by the long polymeric chain.

In conclusion, these results from FTIR and NMR analysis supported the formation of the SBS triblock copolymer by the reaction between the SB-Li precursor and WSO via the proposed reaction mechanism as shown in Scheme 2.
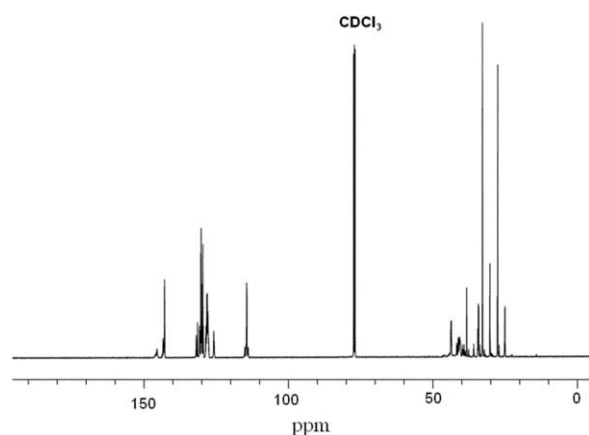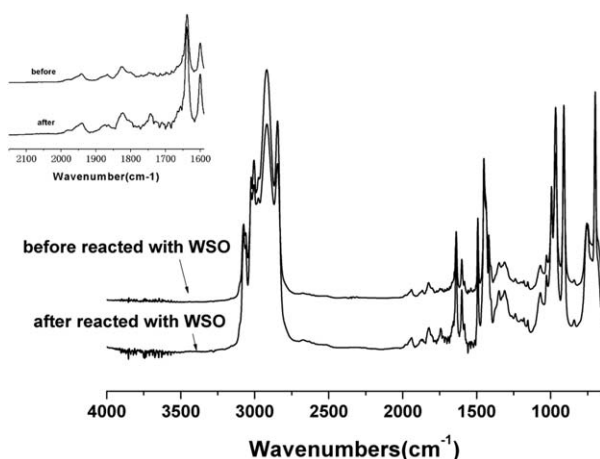
Figure 7. ^{13}C-NMR spectra of the resultant product after SB with the calculated M_n of 25,000 g/mol reacting with WSO at the SB-Li/WSO molar ratio of 2 : 1 and the S : B weight ratio of 3 : 7.

According to the reaction mechanism as predicted in Scheme 2, the nucleophilic attack to the ester C=O of triglyceride gave the SB-C(O)-fatty acid molecule and the anion of the diglyceride still containing two more ester groups. If there is the nucleophilic attack to one of these remaining ester groups, the di-anion of the monoglyceride will be formed. Moreover, if the di-anion of the monoglyceride is attacked by the other nucleophile, the tri-anion of the glyceride will be formed in the reaction, respectively. Due to the loss of fatty acid, it can be seen that the ester group contained less steric hindrance in each step. Therefore, it was expected here that if the system had di-anion of the monoglyceride, the anion of the diglyceride, and triglyceride, the nucleophile preferably attacks the di-anion of the monoglyceride first, the anion of the diglyceride later, and triglyceride last.

The Coupling Efficiency of the WSO

The formation of the product with the M_n two-fold higher than that of the SB precursor indicated that the WSO can act as coupling agent. The factors affecting the coupling efficiency of WSO were discussed here. The coupling efficiency is defined as the fraction of the product that is di-functionally coupled with

Figure 8. FTIR spectra of SB with the calculated M_n of 25,000 g/mol before and after reacting with WSO at the SB-Li/WSO molar ratio of 2 : 1 and the S : B weight ratio of 3 : 7.

a bi-functionally coupling agent. The coupled product is a SBS triblock copolymer while the uncoupled product is a SB diblock copolymer. The coupling efficiency is one of the important factors controlling the properties of the thermoplastic elastomer. For this study, the calculation of the coupling efficiency is taken from the GPC chromatograms as shown in the following equation.

Coupling efficiency (%)

$$= (\text{peak area of SBS/peak area of SBS and SB})100$$

Effect of the Size of the SB Diblock Copolymer

A series of the SB precursor with different molecular weights (M_n of 1000, 5000, 10,000, 15,000, 20,000, and 25,000 g/mol) was prepared. Then certain amount of the WSO at a constant SB-Li : WSO molar ratio of 2 : 1 was added into the reactor in order to form the SBS triblock copolymer with the S : B weight ratio of 3 : 7. The effect of the size of the SB precursor on the coupling efficiency of the WSO is shown in Table II (No.1–6). As seen in Table II, the coupling efficiency of the WSO was strongly dependent of the size of the precursor polymer. The larger the size of the precursor polymer, the lower the coupling efficiency of the WSO. By increasing the size of the SB precursor from M_n of 1000 g/mol (Sample no. 1) to M_n of 25,000 g/mol (Sample no. 6), the coupling efficiency of the WSO significantly decreased from 100 to 56.58%. The reduction of the coupling efficiency of the WSO when increasing the size of the SB precursor might be due to the steric hindrance effect and the increase in viscosity significantly reducing the mobility of the polymeric chain.
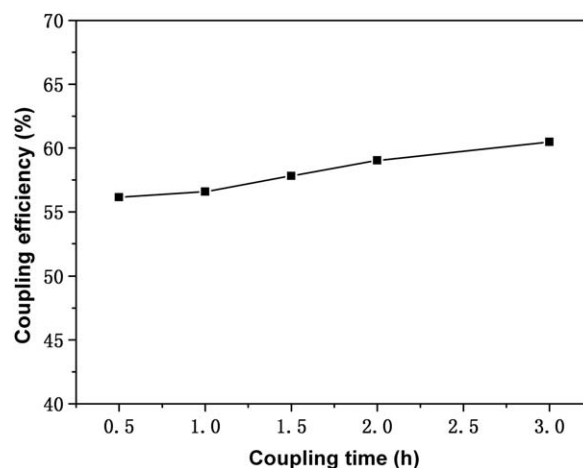
Effect of the SB-Li : WSO Molar Ratio

To study the effect of the SB-Li : WSO molar ratio on the coupling efficiency, a SB precursor with an M_n of 25,000 g/mol was synthesized and then reacted with WSO at varying SB-Li : WSO molar ratios in the range of 0.5 : 1 to 6 : 1 to form the SBS triblock copolymer with the S:B weight ratio of 3 : 7. The effect of the SB-Li : WSO molar ratio on the coupling efficiency is shown in Figure 9. As the SB-Li:WSO molar ratio was increased in the range of 0.5 : 1 to 2 : 1, the coupling efficiency increased. However, when the SB-Li : WSO molar ratio was further increased from 2 : 1 up to 6 : 1, the coupling efficiency slightly decreased and then leveled off. The highest fraction of the SBS triblock copolymer was obtained at the SB-Li : WSO molar ratio of 2 : 1. From the chemical structure of the WSO and the reaction mechanism described in Scheme 2, it can be seen that one single triglyceride molecule can react with six nucleophiles. Therefore, to completely form all coupled products, ideally a SB-Li : WSO molar ratio of 6 : 1 is required. As seen in Figure 9, when increasing the SB-Li : WSO molar ratio from 0.5 : 1 to 2 : 1, the coupling efficiency was increased as a result of the reduction of the C=O ester available for the initial nucleophilic attack to form the newly formed ketone functionality. However, the decrease of the coupling efficiency was observed with the further increase of the SB-Li : WSO molar ratio. This might possibly be due to the dilution effect. It is worth to note here that for the SB-Li with an M_n of 1000 g/mol, even though the reaction was carried out at the SB-Li : WSO molar ratio of 2 : 1, only the SBS triblock copolymer was formed. This indicated
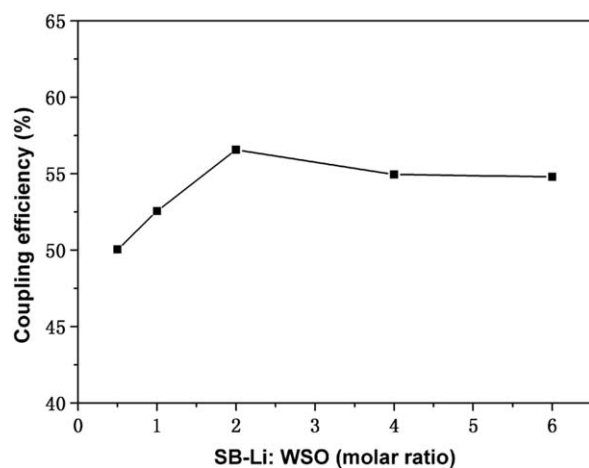
Figure 9. Effect of the SB-Li:WSO molar ratio on the coupling efficiency (SB-Li with the calculated M_n of 25,000 g/mol; the S : B weight ratio of 3 : 7; the coupling time of 1 h).

Figure 10. Effect of the coupling time on the coupling efficiency (SB-Li with the calculated M_n of 25,000 g/mol; the S : B weight ratio of 3 : 7; the SB-Li : WSO molar ratio of 2 : 1).

that the newly formed C=O ketone is much more active than that of the C=O ester.

Effect of the Coupling Time

The influence of coupling time between the SB precursor and WSO on the coupling efficiency was shown in Figure 10. It can be seen that the increase in the coupling time from 0.5 to 3 h only increased the coupling efficiency about 3%. During reaction, it was observed that the reaction temperature immediately increased about 2–3°C after adding the WSO. This indicated that the reaction between the SB-Li and WSO took placed very fast. The coupling reaction results in the formation of double size molecule, thus rapidly increasing the reaction viscosity. Possibly, there are still a few SB precursors trapped in the viscous solution. The longer reaction time will give these molecules more chance to couple. Therefore, the slightly increase in the coupling efficiency was observed during increasing reaction time from 0.5 to 3 h.

Effect of the Styrene to Butadiene Weight Ratio

To study the effect of the chemical composition on the coupling efficiency, two SB-Li precursors with the weight ratio of styrene monomer to butadiene monomer of 3 : 7 and 5 : 5 were prepared. From Table II (sample No. 7–10), it is clearly seen that the SB-Li precursors with the S : B weight ratio of 5 : 5 gave higher coupling efficiency than those with the S : B weight ratio of 3 : 7. As known, the molecular weight of styrene monomer is almost twice as much as that of butadiene monomer. However, only two carbons are contributed the backbone chain. So the increase in weight fraction of styrene decreases the chain length of the SB precursor. Usually, the molecule with shorter chain length has higher mobility than the one with longer chain length. Therefore, the SB precursor with the higher S : B weight ratio possessing higher mobility can undergo coupling reaction easier.

Mechanical Properties of the SBS Triblock Copolymer

From above result, it can be seen that the WSO can act as coupling agent to form the SBS triblock copolymer. However, under certain conditions used in this study, the coupling effi-

ciency of the WSO for the high molecular weight precursor was no more than 60%. There have been some studies on the properties of the SBS triblock copolymers containing SB diblock molecules. Adhikari[28] showed that the tensile strength of the SBS/SB blends decreased rapidly when the SB concentration was larger than 30%. Therefore, to study the possibility of the use of the WSO as coupling agent for the forming the SBS triblock copolymer, the mechanical properties of the SBS triblock copolymer prepared by the WSO were investigated and compared with that of the SBS triblock copolymer synthesized by the traditional coupling agent, DMDCS. The experimental results of the SBS synthesized by DMDCS were obtained from GPC data and list in Table II (No. 11, 12). These SBS obtained from two different coupling agents have similar molecular weights of both the triblock and diblock copolymers. In addition, SBS with similar molecular weight was synthesized by sequential method via living anionic polymerization. The mechanical testing results of these SBS synthesized by coupling method (using WSO and DMDCS, respectively) and by sequential method are shown in Table III. It has been known the chemical composition and chain architecture of polymer play important role on the properties. So the composition of the triblock copolymer and the coupling efficiency were first studied using ¹H-NMR spectroscopy and GPC chromatography, respectively. From Table III, the composition of styrene in SBS triblock copolymers prepared by two different coupling agents and the sequential method was comparable and agreed well with the relative amounts charged to the reaction. However, these two coupling agents showed much different in the coupling ability. The WSO had coupling efficiency much less than the DMDCS. Therefore, the mechanical behaviors of these three different kinds of SBS with similar molecular weights and copolymer compositions were compared with each other.

It has been known that the elastomeric properties of the thermoplastic elastomer such as SBS triblock copolymer arise from the phase separation between the rigid polystyrene domains and the soft polybutadiene domains, and the mechanical behavior of SBS was found to deteriorate with the increase of SB concentration in

Table III. Comparison of the Mechanical Properties of SBS

| No. | wt % S | | Coupling agent | Coupling efficiency[b] (%) | Tensile strength (MPa) | Elongation at break (%) | Modulus at 300% (MPa) | Hardness shore A |
	Nominal[a]	^{1}H-NMR						
1	30	31.2	DMDCS	83.72	6.9	1130	1.5	48
2	50	48.3	DMDCS	87.85	12.7	649	5.2	83
3	30	30.7	WSO	56.58	8.3	999	3.2	49
4	50	47.8	WSO	57.39	13.4	761	7.3	85
5[c]	30	30.1	N/A	N/A	9.9	1071	3.3	51
6[c]	50	48.8	N/A	N/A	14.5	684	7.4	87

[a] Nominal: the weight ratio of styrene monomer added in the reaction; NMR: the weight ratio of styrene in SBS calculated by ^{1}H-NMR data.
[b] Coupling efficiency of the SB-Li precursor with an M_n of 25,000 g/mol for coupling time of 1 h.
[c] SBS synthesized by sequential method with an M_n of 50,000 g/mol.

the system.[28] Consistent with this, SBS synthesized by sequential method display higher tensile strength and elongation at break than that synthesized by coupling method, as shown in Table III. As mentioned earlier, the SBS triblock copolymer prepared by WSO contained much more SB diblock copolymers than that prepared by the DMDCS. However, in Table III, the tensile testing showed that the SBS triblock copolymers prepared by the WSO had higher modulus and slightly higher tensile strength than those prepared by the DMDCS. For a pure triblock, all endblocks are anchored in polystyrene domains and all entanglements are physically trapped. But the SB diblock has butadiene block on one side and styrene block on the other. For the presence of diblock in the triblock, it was said that the glassy PS chains of the
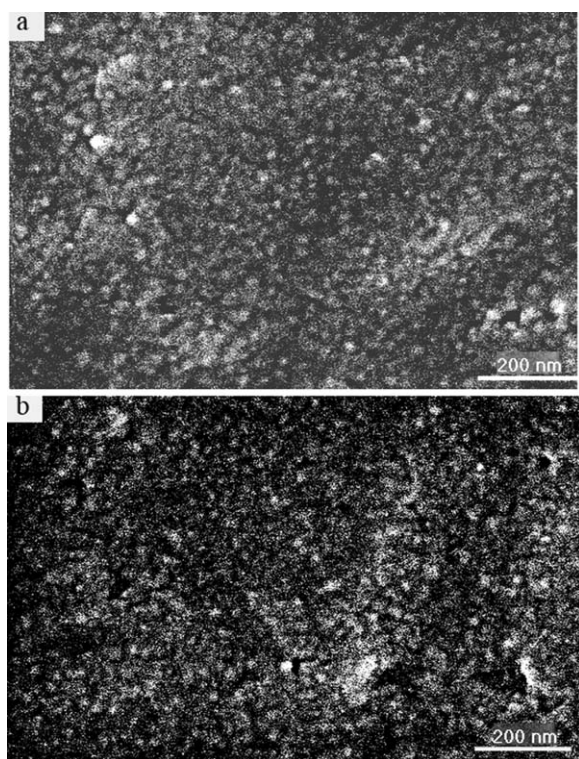
diblock are coupled with other PS block of the SBS triblock copolymer while its highly flexible PB blocks remain dangled and uncoupled.[28] Hence, the untrapped polybutadiene endblocks are able to relax stress by chain reptation through the rubbery polybutadiene matrix, which lead to the lower strength and the microphase separation temperature of the diblock-containing SBS triblock systems.[29] As seen in Scheme 2, the SBS triblock copolymer prepared by the WSO consists of one fatty acid and OH functional group at the middle of the chain and the SB diblock copolymer consists of one fatty acid functional group at the end of the chain, PB is no longer the endblock, which are different from the traditional copolymer. The presence of this fatty acid consisting of 16–18 carbons in the chain may enhance the phase separation. Therefore, TEM was used to analysis the morphological characterization representative triblock copolymers produced by using WSO and DMDCS as coupling agent respectively.

Figure 11 shows the TEM images of these copolymers. As expected from the polystyrene weight ratio (PS content 30 wt%), the block copolymer possesses cylindrical morphology comprising polystyrene cylinders (bright domains in the TEM image) dispersed in the matrix of polybutadiene (dark areas in the TEM image). As shown in the Figure 11, although the SBS triblock copolymer prepared by WSO contained much more SB diblock copolymers than that prepared by the DMDCS, these two different polymers have similar phase separation with each other. Therefore, the presence of the fatty acid enhance the phase separation, due to their compatibility can help the dangled and uncoupled PB blocks coupled with other PB block of the SBS triblock copolymer and trapped the PB blocks, thus resulting in the increase of the strength.

In addition, it was found that the hardness of the SBS triblock copolymers was independent of the amount of the diblock polymer in the sample. This possibly was because the SBS triblock copolymers prepared by two different coupling agents contained the similar styrene contents in the net composition.

Figure 11. TEM images of SBS using (a) WSO and (b) DMDCS as coupling agent, respectively.

CONCLUSIONS

The SBS triblock copolymer was successfully synthesized by coupling reaction of the SB-Li precursor and the WSO. It was proposed here that the coupling reaction had taken place by

two step reactions: the cleaving of the ester bond by the nucleophilic substitution giving the SB-C(O)-fatty acid and then followed by the nucleophilic addition to the SB-C(O)-fatty acid at the carbon of the newly formed ketone. After terminating with methanol, the (SB)$_2$-C(OH)-fatty acid equivalent to the SBS triblock copolymer was obtained. Even though the coupling reaction was carried out with an excess of WSO, the formation of only SBS triblock copolymer from the SB precursor with an M_n of 1000 g/mol indicated that the newly formed ketone was much more active than the C=O ester of the triglyceride. However, the coupling efficiency significantly dropped with the increase in the size of the SB precursor. For the SB precursor with an M_n of 25,000 g/mol, it was found the highest coupling efficiency was observed at the SB-Li : WSO molar ratio of 2 : 1 and the increase in the weight fraction of styrene monomer in the SB precursor further enhanced the coupling efficiency. Although the WSO had much lower coupling efficiency compared with the traditional coupling agent DMDCS, the resultant product prepared by the WSO showed higher tensile strength.

The results from this study showed that the WSO can be used as coupling agent in the synthesis of triblock copolymer. The WSO from the food catering can be directly used without any complicated purifying process. Moreover, the WSO offered not only a reaction with lower cost, more environmentally friendly chemistry, and less toxicity but also a resultant product with desired mechanical properties.

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