Synthesis of Novel Triblock Copolymers Containing Hydrogen-Bond Interaction Groups via Chemical Modification of Hydrogenated Poly(styrene-*block*-butadiene-*block*-styrene)

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Introduction. The triblock copolymer of hydrogenated poly(styrene-*block*-butadiene-*block*-styrene) (SEBS) is widely used as a thermoplastic elastomer.[1] Increasing interest in the block copolymer in both theory and application is connected with the following well-known facts. First, SEBS possesses a well-defined triblock structure and a narrow molecular weight distribution. Second, it is able to serve as both a compatibilizer and a toughening agent[2] because of its excellent mechanical properties and because the two kinds of blocks, i.e., polystyrene (PS) and poly(ethylene-*co*-butylene) (EB), are compatible with PS homopolymers and polyolefins, respectively. However, the nonpolar nature of both kinds of blocks limits its application in polar systems such as blends containing engineering plastics. Therefore, great efforts have been made to modify SEBS by introducing functional groups. Besides chloromethylation[3] and sulfonation,[4] functionalized SEBS with short maleic anhydride grafts has been commercialized by Shell Co. and used in blending with nylon.[5] Considering the plentiful reactivity of the phenyl rings in the PS block, we think that a wide research field of SEBS functionalization is still open.

The project of functionalization of SEBS being carried out in this laboratory is part of our program exploring miscibility and complexation between polymer pairs due to hydrogen bonding. For some polymer pairs of poly(alkyl acrylate) and modified PS with introduced hydroxyl groups, a miscibility−complexation transition has been found as hydrogen bonding is intensified.[6] However, in solution the complexation usually leads to precipitation, and this makes full characterization of the complex difficult. As the first stage of extension of the research to complexation between a block polymer and homopolymer, this communication reports on the preparation and characterization of functionalized SEBS with hydrogen-bond interaction groups. Obviously, these well-defined block copolymers may also serve as objects in the research of phase morphology, solution behavior, compatibilization, surface and interface, etc.

We chose Friedel−Crafts acetylation of the PS blocks of SEBS as the initial step and then transformed the acetyl groups to carboxyl via oxidation and hydroxyl via reduction. There have been no reports on the Friedel−Crafts acylation of SEBS since this polymer was introduced in the 1970s. This may be associated with the following two problems. First, the Lewis acid catalysts used in Friedel−Crafts acylation often led to cross-linking or degradation of the PS chain and frequently yielded colored products indicative of undesirable side reactions.[7] Fortunately, a novel method using a mild catalyst was developed recently to overcome this problem.[8,9] Second, the hydrogenated midblock of SEBS inevitably has residual double bonds in the backbone instead of the side chain. Although the content of the double bonds is usually small, less than 1 mol %, they may lead to cross-linking even at the mild conditions. Therefore, the key points here are to ensure complete saturation of SEBS and to use mild acetylation conditions.

Experimental Section. Materials. The hydrogenated poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (Kraton G1652, from Shell Co.) had M_n = 52500, $M_w/M_n \leq 1.06$, and contained 28.6 wt % styrene units. The content of the residual double bonds was 0.8 mol % as measured by ^{1}H-NMR.[10] Before use, nitrobenzene was dried over calcium chloride and then distilled under reduced pressure. Anhydrous aluminum trichloride was sublimated twice and dissolved in nitrobenzene (1 g into 5 mL). Other chemicals were purified by general methods.

Characterization. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker MSL300 NMR spectrometer using carbon disulfide (CS_2) as solvent. IR spectra of thin polymer films on potassium bromide plates were obtained using a Perkin-Elmer 983G spectrophotometer. Size exclusion chromatography (SEC) was performed using a Waters 510 pump, an ERMA refractive index detector, and a set of Polymer Standards Service columns with tetrahydrofuran (THF) as the solvent at a 1 mL/min flow rate. For measuring the degree of substitution, the carboxylated SEBS was dissolved in THF and titrated with a 0.015 N standard solution of sodium methoxide in a toluene/methanol mixture (19/1 v/v) under the protection of a nitrogen atmosphere to a phenolphthalein end point.

Bromination and Hydrogenolysis. A mixture of 0.50 mL of bromine and 50 mL of toluene was added to a solution of 40 g of SEBS in 500 mL of toluene at 0 °C. The solution was stirred in the dark for 0.5 h and then washed with 1% aqueous bisulfite solution and water successively. Finally, the brominated SEBS was precipitated from ethanol and dried thoroughly.

Fifty milliliters of 1 M lithium aluminum hydride ($LiAlH_4$)/THF clear solution was added to a solution of 40 g of brominated SEBS in 500 mL of dry THF. The mixture was stirred at room temperature overnight and then refluxed vigorously for 3 h. The product was precipitated in 5 vol % of hydrochloric acid. The yield of completely saturated SEBS (CS-SEBS) was almost 100%.

Acetylation. The Perrier procedure[11] was used here. The acetylating agents composed of nitrobenzene/aluminum trichloride ($PhNO_2/AlCl_3$) complex and acetyl chloride with CS_2 as diluent were added to the polymer solution (1.5 g/dL in CS_2) at room temperature, and then the mixture was refluxed gently for 2 h. The reactions were quenched by the addition of hydrochloric acid and ice. The white products were obtained by precipitation in ethanol, and the yields were near 100%.

Oxidation. The procedure was described in ref 8. The concentration of the acetylated CS-SEBS in toluene was 1.3 g/dL. Aqueous 5% sodium hypochlorite solution and cetyltrimethylammonium bromide (CTAB) were used as oxidizing agent and phase transfer catalyst, respectively. The yields were about 80%.[12]

Reduction. A similar procedure had been described in ref 13, except that a clear $LiAlH_4$/THF solution was used here as the reducing agent. The yields were near 100%.

Results and Discussion. In the Friedel−Crafts reaction employed in this study, the residual unsaturation in the SEBS polymer led to formation of a microgel

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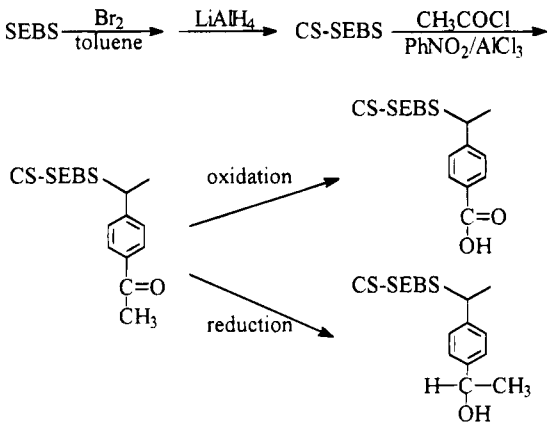
Scheme 1



which would not go through a 0.2 μm filter. Alkylation of the aromatic rings of the PS blocks with the residual double bonds in the rubber block under acetylation conditions is probably responsible for the gelation.[14] It is well known that bromine is very reactive with materials containing double bonds and that the addition proceeds quantitatively.[15] In this study, an excess of bromine and long reaction time were adopted to ensure that all the residual double bonds were changed to *sec*-alkyl bromides. The hydrogenolysis of *sec*-alkyl bromide by a clear $LiAlH_4$/THF solution is also quantitative, and the corresponding alkane can be obtained free from side products.[16] Thus it was believed that the brominated SEBS was transformed to the CS-SEBS in such a condition. The SEC result demonstrated that the molecular weight and monodispersity were unchanged after undergoing these procedures. In the ^{1}H-NMR spectrum the triplet absorption peak at $\delta = 5.0-5.4$ ppm disappeared completely.[10] The final product of the Friedel–Crafts reaction using CS-SEBS as the reactant could pass through a 0.2 μm filter easily in contrast to untreated SEBS. This result can be regarded as evidence of the complete saturation of the starting CS-SEBS.

In the Friedel–Crafts reaction of this study, nitrobenzene/aluminum trichloride ($PhNO_2/AlCl_3$) complex was used as the catalyst and CS_2 as the solvent. This complex is a quite different from and is generally a more selective catalyst than the uncomplexed $AlCl_3$.[17] In addition, it is soluble in CS_2 and allows a more homogeneous reaction. It was demonstrated that the complex led to neither cross-linking nor degradation of PS homopolymer and introduced no unwanted moieties into the polymer chain. Furthermore, the bulky complex formed by the catalyst, nitrobenzene and acetyl chloride, tends to acylate only the more accessible (i.e., less sterically hindered) positions on the styrene ring.[8,18] Thus acylation occurred exclusively in the para position of the styrene unit using this technique. Because of the homogeneity of the reaction, the distribution of the acyl groups is believed to be random along the polymer chain. Due to the advantage of excluding undesirable side reactions such as cracking, rearrangement, and isomerization, the $PhNO_2/AlCl_3$ complex was used in organic synthesis as a selective catalyst for alkylation[17] so that the EB block of CS-SEBS would not be influenced by the complex. The characterization data of the acetylated SEBS prove that the advantages of the mild catalyst were maintained in the reactions of CS-SEBS.

The samples of acetylated SEBS were fully characterized. The IR spectra exhibited a sharp absorption band at 1685 cm^{-1} attributed to carbonyl stretching. The ^{1}H-NMR spectra showed an absorption at $\delta = 2.55$ ppm and the ^{13}C-NMR spectra showed an absorption at $\delta = 195.2$ ppm attributed to the methyl and carbonyl of the acetyl group, respectively. The SEC analyses indicated that the molecular weights and monodispersity of the acetylated products were unchanged. See Table 1 for details.

Table 1. Acetylation of CS-SEBS

	reaction conditions			characterization		
run	CS-SEBS (g)	acetyl chloride (mL)	$PhNO_2/AlCl_3$ (mL)	DS[a] (%)	M_w/M_n	retention time[b] (min)
1	5.00	0.20	2.3	2	1.06	38.9
2	5.00	0.29	3.4	8	1.06	38.9
3	5.00	0.49	5.7	12	1.06	38.9
4[c]	3.78	0.74	8.6	35	1.08	38.9

[a] Degrees of substitution determined by ^{1}H-NMR. [b] The retention time of untreated SEBS is 38.9 min. [c] This product was slightly yellow.

Table 2. Oxidation of the Acetylated CS-SEBS (ACS-SEBS)

	reaction conditions			characterization		
run	ACS-SEBS (g)[a]	CTAB (g)	oxidizing agent (mL)	DS[b] (%)	M_w/M_n	retention time (min)
1	3.00	0.30	30	3.2	1.07	38.9
2	2.00	0.20	30	8.3	1.08	39.0
3	3.00	0.30	50	10.2	1.08	39.0
4	3.00	0.30	150	36.4	1.10	38.9

[a] The products of the acetylations listed in Table 1 in sequence. [b] Degrees of substitution determined by titration.

Furthermore, the acetyl groups introduced in the SEBS chains were transformed to carboxyl groups using the procedure of the phase-transfer-catalyzed chloroform oxidation.[8] The IR spectra of the products exhibited the characteristic bands of the acid at 1685 and 1726 cm^{-1}.[19] In the ^{1}H-NMR spectra the absorption at $\delta = 2.55$ ppm disappeared, and in the ^{13}C-NMR spectra the absorption at $\delta = 195.2$ ppm transferred to $\delta = 169.9$ ppm. The changes manifested the complete elimination of the methyl and the formation of the carboxyl. The SEC analyses showed no changes in molecular weight and monodispersity of the products. These demonstrated that both the PS and EB blocks of CS-SEBS were not broken by the strong oxidizing agent at elevated temperature. The degree of substitution determined by titration was in accordance with that of ^{1}H-NMR within the experimental errors. See Table 2 for details.

The acetyl groups introduced in the SEBS chain were easily reduced to a secondary alcohol by $LiAlH_4$.[20] In the IR spectra, the disappearance of the absorption band of carbonyl at 1685 cm^{-1} and the appearance of a wide band at 3400 cm^{-1} associated with the hydroxyl groups indicated a complete reduction. The SEC analyses showed no change in molecular weight and monodispersity.

It is interesting to notice that all the reactions, i.e., saturation, acetylation, oxidation, and reduction, studied here did not change the retention time of the block copolymers compared to the starting material SEBS. This was not expected since a polymer with different substituted functional groups should show some difference in the hydrodynamic radius even when the degree of polymerization is kept constant. However, since the PS block accounts for only 28.6 wt % (17.8 mol %) and

the maximum functionality is only 36 mol %, perhaps this change is not large enough to alter the hydrodynamic volume substantially. Another explanation is that THF, used as the eluant in SEC, is a good solvent for the modified PS blocks and may mask the effects due to the functional centers.

Anionic polymerization is the only viable way for preparing block copolymers with controlled architecture and a narrow molecular weight distribution. The monomer containing hydroxyl or carboxyl groups cannot be polymerized anionically. The chemical modification of block copolymers thereby incorporating these hydrogen-bonding groups is now possible. The method is also suitable for chemical modification of other block copolymers composed of polystyrene block and saturated hydrocarbon blocks.

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