

Synthesis of Random or Tapered Solution Styrene–Butadiene Copolymers in the Presence of Sodium Dodecylbenzene Sulfonate as a Polar Modifier

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ABSTRACT: Random or tapered solution styrene–butadiene copolymer (SSBR) is very difficult to prepare in an isothermal batch process without the use of polar modifiers because of the diverse reactivity ratios of the styrene and the butadiene in hydrocarbon solvents. In the presence of polar modifiers, the random SSBR can be synthesized by anionic living polymerization with the variety of microstructures, which results in the change of glass transition temperature (T_g). This article will discuss the use of sodium dodecylbenzene sulfonate as a polar modifier in isothermal batch process that controls the microstructure of the SSBR resulting in a random as well as tapered SSBR with low T_g (-67°C to -80°C). The T_g of SSBR was controlled by the styrene content rather than the microstructure of polybutadiene. Physical properties of SSBR compounding were discussed for tire tread applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: styrene–butadiene copolymer; polar modifier; sodium dodecylbenzene sulfonate; *n*-BuLi; anionic polymerization

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INTRODUCTION

We have previously shown that a random styrene–isoprene copolymer has been made with low 3,4-microstructure and its glass transition temperature (T_g) was controlled by the styrene content of the copolymer using anionic polymerization procedures of conjugated dienes and vinyl aromatics in the presence of the sodium dodecylbenzene sulfonate (SDBS) as a new modifier.¹ In this article, we are reporting on the preparation of random or tapered solution styrene–butadiene copolymer (SSBR) by an isothermal batch process using traditional organolithium chemistry in the presence of SDBS in hexane.

The literatures^{2–6} contain several reports on the preparation of random and tapered SSBR using polar modifiers that increase the vinyl microstructures with an increase T_g of such copolymers. In these reports, the authors have used polar modifiers such as ethers, glymes, tetrahydrofurfuryl compounds, and *N*-*N*-*N*'-*N*'-tetramethylethylenediamine.^{2,7–11} These polar modifiers usually randomize the styrene but also increase the vinyl structure units in the 1,3-butadiene position resulting in high T_g of SSBR copolymers and a high degree of branching via chain metallation.^{12–15}

High T_g polymers that have an increase in short-chain branching are used to improve processes and filler distributions with

an enhancement of traction tire tread properties with a sacrifice in the tread wear properties, due to the higher vinyl structure units in the polybutadiene portion of the SSBR. It is desirable to have SSBR composition having the major contributor to T_g from the styrene composition for improving traction and the low vinyl microstructure for better tread wear in tire tread in high performance tires. It is highly desirable to have one anionic polymerization modifier that can be used in a chemical plant which is environmentally friendly and can be used to synthesize low vinyl, low T_g SSBR, whereas all the styrene is incorporated randomly or tapered with styrene sequences of less than 10 units in a row. Early on, in our investigation, we have found that commercially available SDBS from chemical suppliers used in our studies gave extremely high molecular weights and copious amounts of insoluble gel when used as a modifier in one gallon batch reactors to prepare SSBR. However, a laboratory prepared sample of SDBS, which was made by heating dodecyl benzene sulfonic acid dissolved in ethyl benzene and aqueous sodium hydroxide, following the azeotropic distillation of the resultant water using a Dean-Stark trap to yield a highly purified SDBS, was used in all subsequent reactions in this article.

In this article, a combination of organolithium initiator with SDBS, which is soluble in hydrocarbon solvent, is able to

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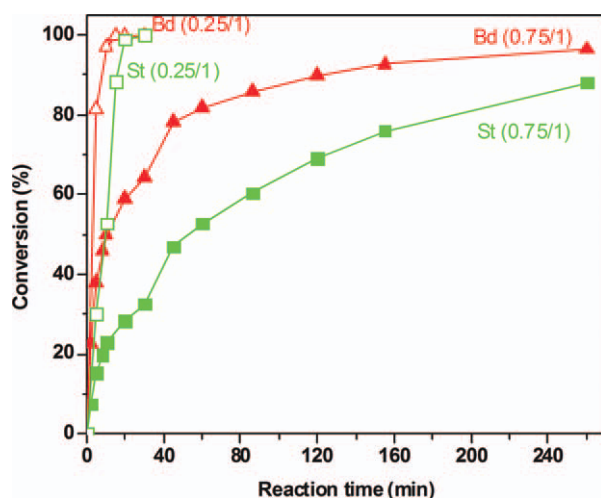


Figure 1. Comparing reaction kinetics of 40/60 SSBR made at different SDBS to *n*-BuLi ratios, 0.25/1 and 0.75/1; hollow triangle (butadiene, 0.25/1), filled triangle (Butadiene, 0.75/1), hollow square (styrene, 0.25/1), and filled square (styrene, 0.75/1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

randomly copolymerize styrene/butadiene that yield SSBR with low vinyl structures and low T_g without metallation or chain branching.

EXPERIMENTAL PROCEDURES

SSBR Synthesis

Styrene–butadiene copolymers were prepared via an anionic polymerization. A one-gallon glass bowl reactor was equipped with a mechanical stirrer and temperature control via cooling water and low pressure steam under nitrogen atmosphere.

n-Butyllithium (*n*-BuLi, 1.6M in hexane, Chemetall, Germany) was diluted to 1.0 concentration using hexane before use. Different composition of styrene and butadiene was premixed in hexane with 20% of monomer content. The monomer solution was circulated through the desiccants composed of 3 Å molecular sieves, silica, and aluminum oxide. The reactor was charged the premixed monomer under nitrogen at low temperature. The reactor was charged with amounts of styrene and butadiene to prepare an entire series of styrene-butadiene rubber (SBRs) ranging from 10% to 80% styrene at low temperature. A reactor held ~ 2000 g total of both premixes. A catalyst system consisting of SDBS and *n*-BuLi was added to the reactor to initiate the polymerization at 90°C. Different ratios of *n*-BuLi/SDBS were used for all polymerization runs with 100,000 g/mol of targeted molecular weight. The progress of reaction was monitored by gas chromatography (GC) analysis taking samples at intermedi-

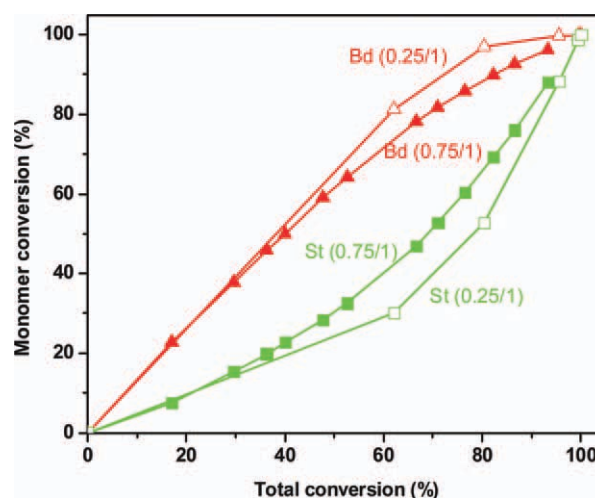


Figure 2. Total monomer conversion compared with individual monomer conversions for various SDBS to *n*-BuLi ratios; hollow triangle (butadiene, 0.25/1), filled triangle (Butadiene, 0.75/1), hollow square (styrene, 0.25/1), and filled square (styrene, 0.75/1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ate time to determine monomer conversion. During the reaction, the samples were taken and mixed with ethanol and hexane solution containing dodecane as a standard. The mixture was injected to the GC to measure the remaining monomers. At 100% conversion, SBRs with a styrene content of 30% and below were soluble in hexane and all others were soluble in cyclohexane. The reaction was terminated by adding denatured ethanol, and 2,6-di-*tert*-butylphenol (1.0 wt %) as an antioxidant was added to the solution. The polymer was dried for several days in a hot oven for further analysis.

Preparation of SDBS

A total of 2000 mL of anhydrous ethylbenzene and 0.50 mol of dodecylbenzenesulfonic acid were added into a 3-L flask equipped with nitrogen inlet and a mechanical stirrer. Sodium hydroxide pellets (0.50 mol) were added into this solution. The heterogeneous mixture was stirred at room temperature for an hour until sodium hydroxide was completely reacted. The soap like mixture was slowly heated with care to avoid foaming until all the water was removed with a Dean-Stark trap via azeotropic distillation in the presence of ethylbenzene.

Characterization

The molecular weight and molecular weight distribution of the products were measured by size exclusion chromatography. The system consisted of a Wyatt MiniDawn TREOS three angle laser light scattering detector with a Wyatt Optilab rex RI Detector, 2

Table I. NMR Data Showing Microstructure and Block Styrene for a 40/60 SSBR Made via Different SDBS to *n*-BuLi Ratios

| SDBS/ <i>n</i> -BuLi ratio | Styrene (block) | 1,2-PBd | 1,4-PBd | Normalized 1,2 Bd | Reaction time (min) |
|----------------------------|-----------------|---------|---------|-------------------|---------------------|
| 0.25/1 | 37.1 (15.0) | 7.9 | 55 | 12.6% | 30 |
| 0.35/1 | 35.3 (13.5) | 8.1 | 54.6 | 12.9% | 45 |
| 0.5/1 | 37.2 (8.3) | 8.7 | 54.1 | 13.9% | 60 |
| 0.75/1 | 35.7 (4.4) | 10.7 | 53.6 | 16.6% | 260 |

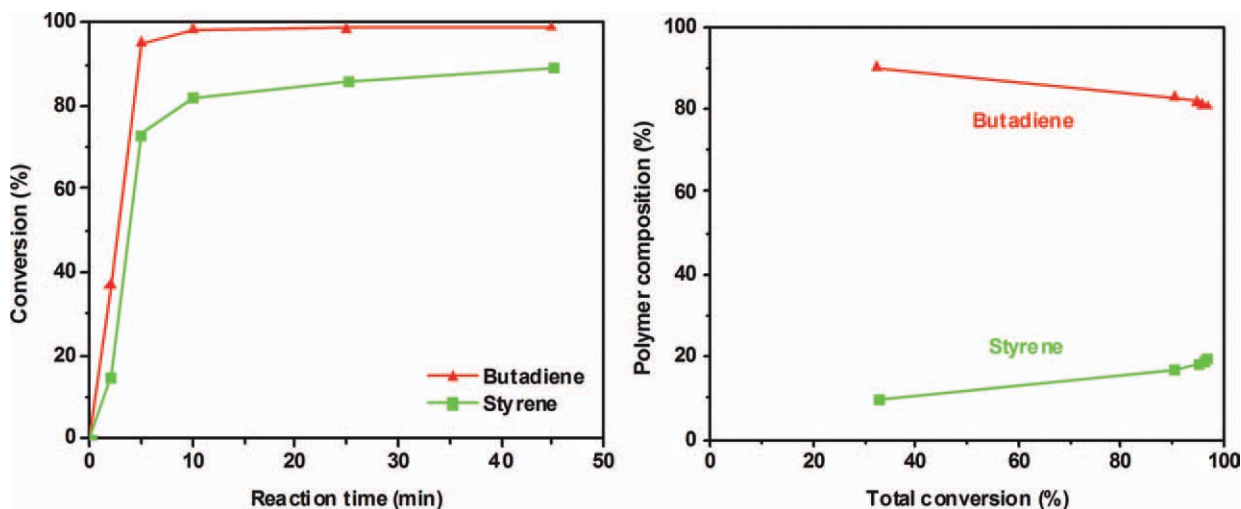


Figure 3. Monomer conversion versus reaction time (left) and composition versus total conversion (right) for an 18/82 SSBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

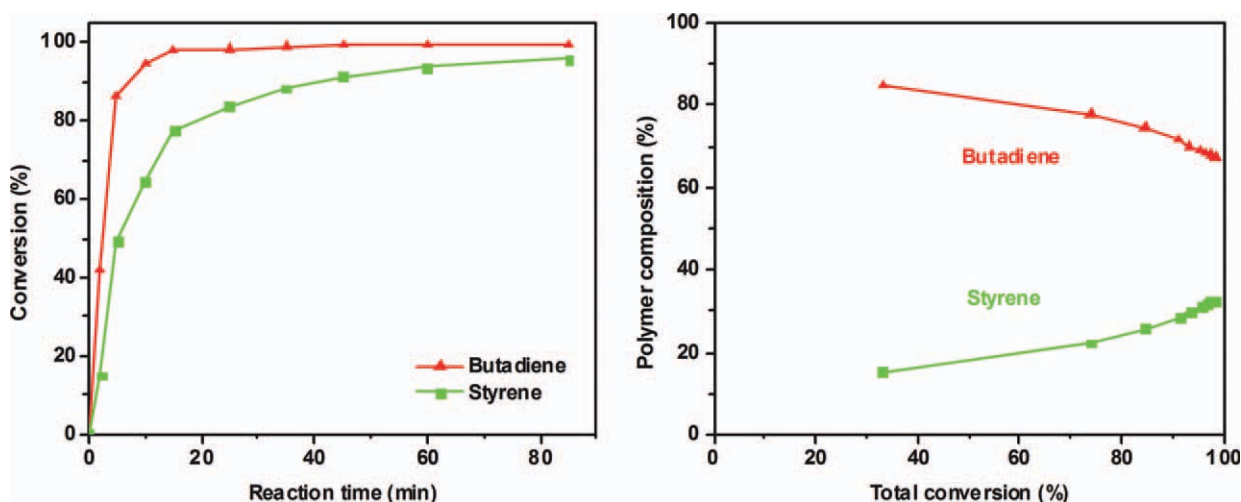


Figure 4. Monomer conversion versus reaction time (left) and polymer composition versus total conversion (right) for a 30/70 SSBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Agilent Mixed C 5 μm PLgel size exclusion columns with guard column, and Agilent 1200 with solvent degassing. The results were analyzed using the ASTRA software. Tetrahydrofuran was used as the mobile phase at a flow rate of 1 mL/min. ^1H NMR analysis was processed on a Varian Inova NMR at 400 MHz. The sample was prepared in 5 wt % with 2 : 1 ratio of CS_2 : tetrachloroethane- d_2 , with the internal reference of $\delta = 5.97$ ppm. The blocky styrene contents were determined based on the integrations of aromatic regions with $\delta = 7.60\text{--}7.07$ ppm [A], $\delta =$

$7.07\text{--}6.75$ ppm [B], and $\delta = 6.75\text{--}5.30$ ppm [C].¹ The blackness of styrene in the polymer was calculated by following equation with the normalization of the total wt % in styrene content.

$$1\text{S} = [\text{A}] - (0.55 \times [\text{C}]) - [\text{B}]$$

$$2\text{-}4\text{S} = 2 \times [\text{B}] - (0.95 \times [\text{C}])$$

$$\geq 5\text{S} = 2.5 \times [\text{C}]$$

Table II. NMR Results for a Series of SSBR Made via 0.5/1 SDBS to *n*-BuLi

| SBR ratio | Styrene (block) | 1,2-PBd | 1,4-PBd | T_g ($^{\circ}\text{C}$) |
|-----------|-----------------|---------|---------|------------------------------|
| 40/60 | 37.2 (8.3) | 8.7 | 54.1 | -67 |
| 30/70 | 29.3 (4.2) | 9.6 | 61.1 | -72 |
| 18/82 | 18.3 (2.4) | 11.5 | 70.2 | -80 |

Table III. Reactivity of Butadiene and Styrene Monomers Made via 0.5/1 SDBS to *n*-BuLi Compared with Unmodified Kinetics

| SBR ratio | Styrene (block) | r_{Bd} | r_{St} |
|-----------|-----------------|-----------------|-----------------|
| 40/60 | 0.5/1 | 3.28 | 0.41 |
| 40/60 | Unmodified | 11.8 | 0.04 |
| 30/70 | 0.5/1 | 3.95 | 0.95 |
| 18/82 | 0.5/1 | 3.08 | 1.07 |

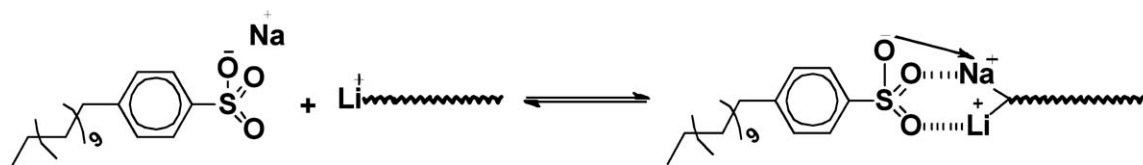


Figure 5. Intermediate bimetallic complex of SSBR copolymerization.

The further specific sequential distributions of styrene were analyzed by ozonolysis-GPC method¹⁶ (the data are not shown in this article). The viscoelastic and rheological properties of SSBR compounds were analyzed by a rubber process analyzer (RPA2000).¹ The reactivity ratios were calculated based on Mayo-Lewis equation.

RESULTS AND DISCUSSION

Preparation of a SSBR with *n*-butyllithium (*n*-BuLi) and SDBS was carried out in one gallon batch reactors with a polymerization temperature of 90°C. Samples were taken during polymerization to determine the monomer conversion (Figure 1) and study the effect of SDBS to *n*-BuLi ratios on the polymerization rates and styrene incorporation (random vs. blocky). The data in Table I give a good indication into the styrene randomization, especially as to how it relates to the amount of SDBS used. The results confirmed that as the SDBS to *n*-BuLi ratio increased from 0.25/1 to 0.75/1 the block styrene in the solution SBR decreased. Moreover, the vinyl content of the solution SBR normalized on the polybutadiene (PBd) portion was always very low, typically less than 17%.

If the plot of the individual monomer conversion versus the total conversion is examined, as shown is Figure 2, one would observe the uniformity throughout the polymer chain of a SSBR made in the presence of SDBS. When total conversion was 61% for 0.25/1 ratio of SDBS and *n*-BuLi, 22% of styrene and 80% of butadiene were incorporated in the polymer chain.

Table IV. Compounding Recipe Using SSBR (30/70) for Tire Tread Application

| Materials | Sample 1 | Sample 2 |
|----------------------------------|----------|----------|
| Nonproductive mix stages | | |
| Styrene/butadiene rubber (30/70) | 30 | 30 |
| Natural rubber | 55 | 0 |
| 3,4-Polyisoprene rubber | 15 | 0 |
| Cis 1,4-polybutadiene rubber | 0 | 70 |
| Carbon black | 38 | 38 |
| Silica | 10 | 10 |
| Coupling agent | 2 | 2 |
| Stearic acid | 2 | 2 |
| Antidegradants | 3 | 3 |
| Processing aids | 6 | 6 |
| Productive mix stage | | |
| Sulfur | 1.5 | 1.5 |
| Zinc oxide | 2.5 | 2.5 |
| Accelerators | 1.1 | 1.1 |

In contrast to 0.25/1 ratio of SDBS and *n*-BuLi, the copolymerization with 0.72/1 ratio of SBDS/*n*-BuLi showed higher amounts incorporation for styrene at similar total conversion (%). This indeed helps to confirm that SDBS can be used at either 0.25/1 or 0.75/1 to prepare a solution SBR where the styrene is uniform and random throughout the polymer backbone. In addition to the monomer conversion versus total conversion, styrene blockiness observed through NMR techniques can also help to determine which ratio is preferred. Several SDBS to *n*-BuLi ratios were investigated and given to NMR for block styrene analysis.

This study was extended to varying the styrene to 1,3 butadiene ratios as well, from 10/90 up to 40/60 SSBR, using only one ratio of SDBS to *n*-BuLi of 0.5/1. Using styrene to butadiene ratios of 18/82 and 30/70, the effects that different ratios of styrene and butadiene had on conversion were investigated. Conversion versus time graphs indicate that for each ratio the styrene incorporation was quite similar to the butadiene incorporation. Also, the plots of composition versus conversion suggest that the polymers are uniform and not heterogeneous. These results of the 0.5/1 SDBS to *n*-BuLi ratio are shown in Figures 3 and 4.

The amount of styrene in the SSBR can be correlated to the block styrene seen from NMR results. More blocky styrenes were observed with higher styrene (40%) composition in SSBR copolymerization. Table II illustrates NMR results obtained for this series of SSBR. These data indicate that the 40/60 SBR has the highest amount of block styrene with the lowest amount of vinyl in the PBd portion.

Table V. Comparison of Physical Properties of SBR (30/70)

| Properties | Sample 1 | Sample 2 |
|---------------------------|----------|----------|
| Stress/strain | | |
| 300% modulus (MPa) | 10.2 | 8.7 |
| Tensile strength (MPa) | 18.5 | 13.7 |
| Ultimate elongation (%) | 485 | 430 |
| Hardness | | |
| 23°C | 63 | 64.4 |
| 100°C | 57.4 | 60 |
| Rebound (traction) | | |
| 23°C | 46.8 | 56.3 |
| 100°C | 66.1 | 64.3 |
| DIN abrasion | | |
| Relative volume loss (cc) | 146 | 57 |
| Tan delta | | |
| 0°C (Traction) | 0.2 | 0.12 |
| 60°C (fuel economy) | 0.085 | 0.092 |

The reactivity ratios of styrene and butadiene were also determined at a ratio of 0.5/1 SDBS to *n*-BuLi. These results are shown in Table III. These data show that the butadiene monomer appears to be more reactive to both butadiene and styryl lithium chain ends. However, in the absence of SDBS, the butadiene monomer is reactive toward the butadienyl lithium but not to the styryl lithium. This indicates that SDBS does indeed alter polymerization kinetics.

The bimetallic complex of propagating species in the presence of SDBS was shown in Figure 5. The Li^+ at the propagating chain-end complexes with sodium sulfonate group of SDBS. This complexation is able to achieve the identical rate constant of styrene and butadiene, which can randomize the polymerization with low vinyl contents. The reactivity ratios for unmodified (no SDBS use) SB (40/60) were $r_{\text{BD}} = 11.8$ and $r_{\text{St}} = 0.04$, described in Table III. For SB (40/60) with 0.5/1 SDBS/*n*-BuLi, the reactivity ratios were $r_{\text{BD}} = 3.28$ and $r_{\text{St}} = 0.41$, which means improve the randomization process in the presence of SDBS.

To compare physical properties of SSBR in tire tread application, two compounding recipes were prepared using SSBR (30/70) with natural rubber, 3,4-polyisoprene and cis-1,4-polybutadiene (Table IV) using ASTM D3192 method. Based on the physical properties of two compounding samples (Table V), there were no significant differences for stress/strain, hardness, and rebound behavior. However, Sample 1 prepared by SSBR with natural rubber and 3,4-polyisoprene rubber showed significant improvement for wear properties as well as traction fuel economy. Thus, randomized or tapered SSBR can be used to improve wear resistances without the change of other properties.

CONCLUSIONS

By using SDBS as a polar modifier to *n*-BuLi, random, low vinyl SSBR copolymers could be synthesized at the proper SDBS to *n*-BuLi ratios. From kinetics, at SDBS/*n*-BuLi ratios of less than or equal to 0.5/1, very fast rates were observed. The data from polymer composition versus monomer conversion gave an indication that homogeneous polymers were synthesized. NMR results confirmed that as the SDBS to *n*-BuLi ratio increased less styrene blocks were observed. Also NMR showed that the normalized vinyl content on the Bd portion of the polymer was typically less than 17% no matter the SDBS to *n*-BuLi ratio.

Finally, from a reactivity investigation, it was shown that unmodified *n*-BuLi prefers the butadiene monomer, whereas modified with SDBS shows an affinity to both styrene and butadiene.

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