Synthesis and Distribution of Structural Units–Thermal Property Relationship of Random and Block Butadiene-Styrene Copolymers with High Trans 1,4 Units Content Produced Using an Initiator Composed of Alkyl Aluminum, *n*-Butyl Lithium, and Barium Alkoxide

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ABSTRACT: Random, diblock, and triblock copolymers of butadiene and styrene, with a well-defined, high number of 1,4-trans units (c.a. 80%), were synthesized by anionic living polymerization using an initiator system composed of alkyl aluminum, *n*-butyl lithium, and barium alkoxide. The thermal properties of the block copolymers obtained by sequential addition of monomers were basically determined by the 1,4-trans units of the polybutadiene block. Kinetic data and [1]H-nuclear magnetic resonance analyses showed that simultaneous polymerization of butadiene and styrene provided copolymers with a predominantly random distribution. By increasing the styrene content, the thermal properties of these copolymers were modified; polymers with 80% content of 1,4-trans units and 5% of styrene presented an endothermic transition at or slightly below room temperature (20°C), corresponding to the crystalline monoclinic form of high 1,4-trans polybutadiene, whereas copolymers with 25–50% styrene content were amorphous. The glass transition temperature of these copolymers increased significantly as the styrene content was increased. Both the block and random copolymers have a sufficient number of 1,4-trans units to display a regular distribution of structural units that makes them susceptible to strain-induced crystallization, which is important for the manufacture of products such as high-performance tires. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3103–3110, 2010

Key words: anionic polymerization; distribution of structural units; thermal properties; copolymerization; high trans 1,4 polybutadiene

INTRODUCTION

Anionic living polymerizations make it possible to produce tailor-made polymers with well-defined distribution of structural units and low degrees of compositional heterogeneity. This synthetic approach facilitates varying and controlling the desired properties of the polymers by regulating important parameters, such as molecular weight, molecular weight distribution, copolymer composition, distribution of structural units, branching, and chain-end functionality.

Anionically synthesized random and block butadiene-styrene copolymers are widely used in different industries, such as that of tires,[1–3] engineering plastics,[4] and modified asphalts.[5]

In particular, the polybutadiene structural units distribution (i.e., the relative number of its isomers: 1,4-cis, 1,4-trans, and 1,2-vinyl) has an important role in affecting the behavior of these copolymers.[6–8] It has been shown[9–12] that polybutadienes with a high content of 1,4-trans units (more than 70% of the 1,4-trans isomer) have superior dynamic mechanical properties. These properties include low rolling resistance, good green strength, and improved tensile strength, tear strength, and flex fatigue, which are important in the manufacture of products such as high-performance tires. These advantages explain the production of polybutadiene with a well-defined distribution of structural units, such as those with a relatively high content of 1,4-trans units (TPBD).[1–3,13–24]

Ziegler-Natta[25] and rare earth-based catalysts[20,22] allow for the synthesis of polybutadiene with a high specificity of monomer insertion (>90% of 1,4-trans

units). However, they also have certain disadvantages. For instance, these catalysts usually are insoluble; the resultant polymers have a wide molecular weight distribution, and a low yield is obtained (40–50%).[20] Both Ziegler-Natta and rare earth-based catalytic systems are inferior to anionic polymerization for synthesizing copolymers, as the polymer composition includes a significant amount of homopolymers due to the strong selectivity of these catalysts towards specific monomers.[25,26]

There have been reports on the synthesis of butadiene-styrene copolymers with a relatively high content of 1,4-trans units by anionic solution polymerization using organometallic compounds based on groups IA, IIA, and IIIA of the periodic table.[13–19,27,28] However, these compounds present a low activity for diene polymerization. In particular, the initiators from group IIA metals[16] or barium-based complexes face poor solubility in nonpolar hydrocarbon solvents, low activity, and relatively complicated preparation procedures.[14,16,17] An important advantage of a system based on alkaline earth metals, such as barium, lies in their ability to form organometallic electron-accepting complexing species, thus increasing the possibilities for controlling the activity and the mode of diene insertion into the polymer.

It is interesting to note that most of the work on the synthesis of butadiene-styrene copolymers with a relatively high content of 1,4-trans units via anionic solution is reported in patent literature, with few or no systematic studies on the distribution of structural units/property relationship for copolymers with a relatively high content of 1,4-trans units prepared using barium-based initiators. Therefore, this system was considered an ideal subject for this report.

A series of random, diblock, and triblock copolymers of butadiene and styrene with a high number of 1,4-trans units (referred to in this article as HT-SBR, HT-SB, and HT-SBS, respectively) was obtained by examining the polymerization of 1,3-butadiene and styrene using cyclohexane solutions of trioctyl aluminum, n-butyl lithium, and barium 2-ethyl-hexoxide. The initiator system was chosen for its solubility in nonpolar hydrocarbon solvents, reproducibility, and commercial availability; barium 2-ethylhexoxide, combined with n-butyl lithium and trioctyl aluminum, fits all these requirements. The influence of the distribution of structural units, composition, and monomeric distribution of the polymeric chains on the thermal characteristics of the copolymers obtained has been studied.

EXPERIMENTAL

In the following paragraphs, a brief description of the materials, the polymerization process, and the characterization of polymers are given.

Cyclohexane, styrene, and butadiene monomers were purified by the following process. First, they were passed through a series of two-packed columns, one with activated γ-alumina and the other with molecular sieves of 3 Å, to reduce the inhibitor (tert-butyl cathecol) and humidity. They were then stored in separated stainless steel tanks under an ultra-high nitrogen atmosphere until use. The initiator components: n-butyl lithium (Lithco), alkyl aluminum (Aldrich), and barium alkoxide (Strem Chemicals) were used as received.

Polymerization procedure

Polymerization reactions of the styrene and butadiene monomers were carried out in a 1 liter glass-jacketed reactor equipped with an internal stainless steel coil for heat exchange. To have precise control over copolymer composition and molecular weight, we used the following procedure to diminish the amount of catalyst scavenger substances. First, the reactor was twice purged with ultra-high-purity nitrogen to lower the in-gas initiator deactivating substances and to maintain an inert gas atmosphere. Next, the desired amount of solvent was fed into the reactor and treated with n-butyl lithium, based on a colorimetric titration process,[29] to minimize residues of initiator scavengers. Afterwards, the desired amount of monomer(s) was fed into the reactor, and the titration procedure was then applied again to eliminate the remains of initiator scavengers. Finally, the components of the catalytic system were added in the following order: alkyl aluminum, n-butyl lithium, and barium alkoxide.

The reactor was charged with appropriate amounts of styrene and butadiene to prepare an entire series of copolymers ranging from 10–30% w/w of styrene content. Block copolymers with high trans 1,4 units content were obtained by sequential addition of monomers. Polymerizations were carried out at a temperature of 70°C using a 10/1 v/v solvent/monomer ratio, which enabled control of polymerization temperature. A molecular weight of 150,000–170,000 g/mol was targeted for all polymers. Samples were taken at different reaction times and were deactivated using a 2 M methanol/cyclohexane solution. These samples were protected from thermal degradation with 2–6-di-tert-buthyl-p-cresol (BHT). Finally, the samples were dried in a vacuum oven 40°C overnight for further characterization.

Characterization

The [1]H-nuclear magnetic resonance (NMR) spectra were obtained with a Varian 300 MHz spectrometer at room temperature. Samples were dissolved in deuterated chloroform (CDCl$_3$) with an approximate
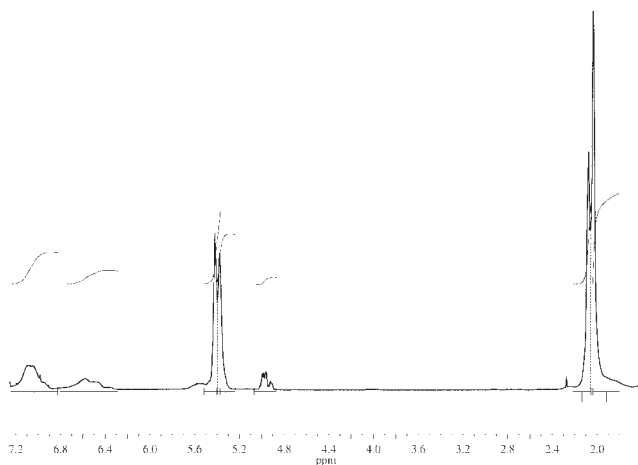
Figure 1 Signals of the ^{1}H-NMR spectra used to calculate the composition and structural units distribution of block copolymers of butadiene and styrene. ^{1}H-NMR spectra corresponds to a copolymer (SBS-Li) with a block of low number of 1,4-trans units (50%) synthesized with *n*-BuLi in cyclohexane solution at 70°C.

concentration of 10% w/v, and the resonant frequencies were referenced to tetramethylsilane as an internal standard. Monomer composition and distribution of structural units of the copolymers was determined from ^{1}H-NMR characteristic signals, applying previously reported equations.[30]

Molecular weights of the polymers were obtained from gel permeation chromatography (GPC) using tetrahydrofuran solutions of the polymer samples. The molecular weights reported here are polystyrene-equivalent molecular weights as polystyrene standards (c.a. 0.012 g/mL) were used. A HP 1100 liquid chromatograph, equipped with a high-resolution PLgel 5μ mixed-C column and differential refractive index detector, was used for polymer analysis. The tests were operated under isothermal conditions (35°C) using THF as carrier (1.0 mL/min).

Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo 2000 differential scanning calorimeter, in the temperature range −130 to 130°C with a rate of 10°C/min. A heating–cooling–heating thermal cycle was used to determine the thermal transition of the constituent components. The heat flow and the second derivative of the heating scans were used for the analysis of the glass transition temperature.

RESULTS AND DISCUSSION

The results of the copolymerization of butadiene and styrene in $R_1Al/R_2Li/R_3OBa$ cyclohexane solutions are presented and discussed here. The data are divided into two sections: block copolymerization and copolymerization of reaction mixtures.

Block copolymerization

Polymer distribution of structural units and chemical compositions

Figure 2 shows the typical ^{1}H-NMR spectra of a styrene-butadiene-styrene triblock copolymer (HT-SBS) obtained by adjusting the molar composition of a ternary initiator prepared with alkyl aluminum, *n*-butyl lithium, and barium alkoxide (Al : Li : Ba 1 : 1 : 0.25 molar ratio). For comparison, Figure 1 shows the ^{1}H-NMR spectra of an ordinary styrene-butadiene-styrene triblock copolymer (SBS-Li) with medium content of 1,4-trans units (c.a. 50%), synthesized through the standard procedure using a cyclohexane/*n*-butyl lithium solution.[6]

As shown in Figure 2, the peaks appearing at 6.5–7.1 ppm indicate the presence of phenyl protons in the styrene units. The peaks at 4.9–5.6 ppm confirm the presence of olefinic protons in the butadiene units. Based on the intensity ratio of the phenyl group and the oleofinic protons, the total amount of styrene content in the copolymers was 5–21% (Table I).

^{1}H-NMR analyses of the copolymers indicated the presence of a butadiene block with high 1,4-trans unit content (TPBD). The distribution of structural units of the butadiene portion of these block copolymers was determined from the ^{1}H-NMR characteristic signals. The signals obtained were 77–79% 1,4-trans units, 16–15% 1,4-cis units, and 7–6% 1,2-vinyl units (Table I).

All samples have unimodal molar mass distribution curves (Fig. 3), and no shoulder peak or low molecular weight tail was detected during the
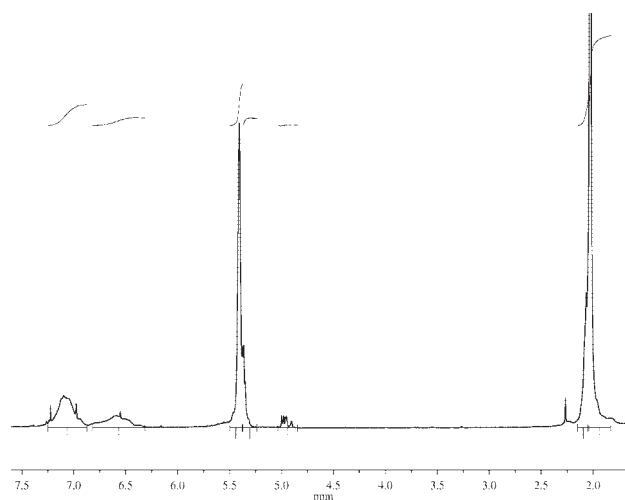

Figure 2 Typical ^{1}H-NMR spectra of block copolymers of butadiene and styrene HT-SB_1 (Table I), with a block of polybutadiene with high number of 1,4-trans units (78%), synthesized with an initiator with Al/Li/Ba/ molar ratio of 1 : 1 : 0.25, [Ba] = 0.3510 mmol at 70°C in cyclohexane solution.

TABLE I
Compositions, Number Average Molecular weight, polydispersity, and Structural Units Distribution of Block Copolymers of Styrene and Butadiene with High Number of 1,4-Trans units Synthesized with Al/Li/Ba Initiator

Copolymer	Type	F_{ST} mol/L	F_{BD} mol/L	Polymerization time (h)	[a]Total styrene (wt%)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	Polybutadiene structural units (%)		
								1,4-trans	1,2-vinyl	1,4-cis
HT-S_1	First Block	0.06355	–	2	100	18	1.20	–	–	–
HT-SB_1	Diblock	–	0.9794	4	10	137	1.21	78	6	16
HT-SBS_1	Triblock	0.06355	–	2	21	154	1.32	77	7	16
HT-S_2	First Block	0.0307	–	2	100	10	1.21	–	–	–
HT-SB_2	Diblock	–	1.0655	4	5	152	1.24	79	6	15
HT-SBS_2	Triblock	0.0307	–	2	9	161	1.30	78	7	16

[a] Obtained by ^{1}H-NMR.

F_{ST} = styrene content in feed, F_{BD} = butadiene content in feed. Composition % feed HT-SBS_1: ST-BD-ST = 10 : 80 : 10, HT-SBS_2:ST-BD-ST = 5 : 90 : 5. Feed ratio in weight %.

Copolymerization conditions: Al : Li : Ba molar ratio = 1 : 1 : 0.25, [Ba] = 0.3510 mmol, T = 70°C and 10/1 v/v solvent (cyclohexane)/monomer ratio.

course of the polymerization. These results show the homogeneity of the copolymers synthesized.

Additionally, the sequential triblock copolymerization of styrene with butadiene proceeded with high block efficiencies under living polymerization conditions.

The molecular weight distribution of the first styrene block was observed to be narrow (1.17); however, the distribution slightly broadened when the following blocks were formed: 1.21 and 1.32 for HT-SB and HT-SBS blocks, respectively (Table I). That broadening can be attributed to the monomers acting as active-site scavengers to deactivate some of the "living polymer chains."

Regardless of this observation, we previously reported[23] the polymerization reaction of high 1,4-trans polybutadiene with the Al/BA/Li initiator ternary system, and we observed an inverse relat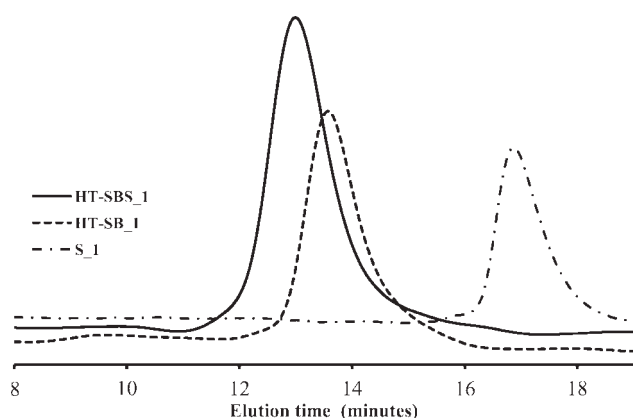ionship between the initiator system concentration and the polymer's average molecular weight; such an observation is consistent with the preparation of this polymer type using with n-buthyl lithium solutions.[6,7]

Thermal analysis of block copolymers

The results of the DSC analysis of the polymers are summarized in Figure 4 and Table II. As expected, the block copolymer synthesized with just n-butyl lithium (SBS-Li) displayed a thermogram (T_g = −90°C) typical of an amorphous styrene-butadiene copolymer.

The T_g values for the polybutadiene segments of the HT-SB and HT-SBS correlated with the high 1,4-trans content obtained using the Al/Li/Ba initiator. The T_g of the polybutadiene block (−68 to −70°C) varied slightly from the value for butadiene

Figure 3 Representative molar mass distribution curves of the copolymers obtained in the first, second, and third polymerization steps (Table I), by sequential copolymerization of butadiene and styrene using a ternary initiators containing 1 : 1 : 0.25 Al : Li : Ba molar ratio, [Ba] = 0.3510 mmol at 70°C in cyclohexane solution.
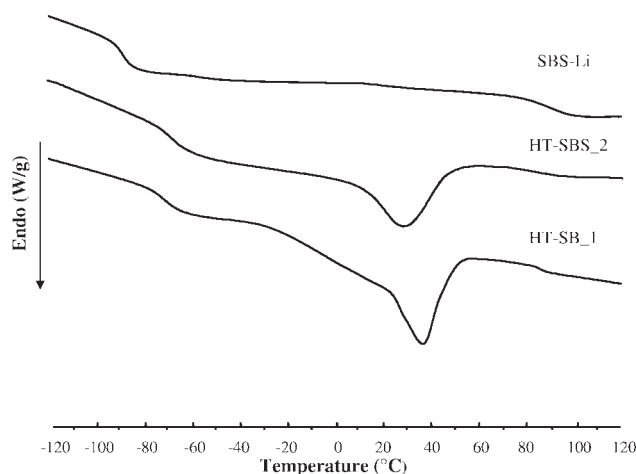

Figure 4 Thermograms of block copolymers of butadiene and styrene: SBS-Li, corresponds to a copolymer with a block of low number of 1,4-trans units (50%) synthesized with n-BuLi. HT-SB_1 and HT-SBS_1 to a block copolymers with high number of 1,4-trans units (78%), produced with ternary initiators containing 1 : 1 : 0.25 Al : Li : Ba molar ratio.

TABLE II
Glass Transition T_g Temperatures, Fusion T_m Temperatures, Enthalpy ΔH, and Degree of Crystallinity X_w as Determined by Differential Scanning Calorimetry of Copolymers of Styrene and Butadiene with High Number of 1,4-Trans Units Produced with Al/Ba/Li Initiator System

Copolymer	T_g (°C)	T_m (°C)	ΔH (J/g)	X_w (%)
HT-SB_1	−70	25	17.71	12.3
HT-SBS_1	−68	14	13.64	9.5
HT-SB_2	−71	36	32.50	22.5
HT-SBS_2	−70	30	27.19	18.8

homopolymers (−72°C), with comparable high trans 1,4 unit content (c.a 80%).[23] This observation can be explained by the thermodynamic incompatibility of the copolymers. For completely incompatible systems, the thermal properties of the copolymer are determined by the properties of each phase and are independent of each other. However, if the system is not completely incompatible, some interactions can occur between these two phases that can result in a displacement of T_g.

On other hand, the T_g of the styrene block, which should occur at around 100°C,[31] was not observed. This result was due to the relatively low polystyrene quantity as well as having a molecular weight that is below the level of detection.

The block copolymers with high 1,4-trans unit content showed a melting endotherm at around 35–40°C, which corresponded to the crystalline monoclinic form of trans-1,4 polybutadiene. As typical for semicrystalline polymers, these endotherms are wide and flattened. The broad endotherm is due to a large distribution of lamellar crystalline sizes that develop as a result of the formation of defects during the phase transition of the noncrystalline fractions to prevent regular crystalline packing.

Compared with high 1,4-trans diblock copolymers, the triblock copolymers displayed lower melting temperatures (36 versus 31°C) and enthalpies of fusion as well. This difference could be a consequence of the homopolymer distribution of the crystalline block; for the triblock, the high 1,4-trans polybutadiene block is in the middle of two polystyrene portions, which prevents the chains from packing into a regular arrangement.

The overall crystallinity of copolymers can be simply assessed from heats of fusion. Specifically, the degree of crystallinity (X_w) was calculated from the experimentally determined enthalpies of the copolymers (ΔH_f) and the characteristic enthalpies for a 100% crystalline 1,4 trans polybutadiene ($\Delta H_f^\circ = 144$ J/g).[32]

The results showed that block copolymers prepared with the Al/Li/Ba initiator system are semicrystalline materials whose percentage of crystallin-

ity is a function of the 1,4-trans units and the styrene content (Table II). The triblock possessed a lower crystallinity with respect to the diblock copolymer (22.5 versus 18.8 %). This difference is likely due both to the different styrene content and polymer distribution.

For the triblock, the block that crystallizes is situated between the two styrene blocks, which makes it difficult for the polymeric chains to have a regular ordering. It is important to mention that the trans 1,4-configuration in the polybutadiene chains can easily form crystals even for relatively short butadiene blocks in the copolymers. These crystalline regions can act as entanglements that lead to the development of a more mechanically resistant material; however, this mechanical enhancement also leads to processing difficulty.[11]

X-ray analyses

Analyses by diffraction of wide-angle x-rays showed that block copolymers prepared with Al/Li/Ba initiator system are semicrystalline materials, which is consistent with the DSC results. Figure 5 presents the X-ray diffraction patterns of the reference SBS-Li, TPBD with 85% of 1,4-trans unit[23] and those of HT-SBS_1 with 78% of 1,4-trans units. The diffraction pattern of the SBS-Li displays only the amorphous halo, which indicates that such polymers do not have the ability to crystallize, while those of the TPBD and HT-SBS_1 exhibit one intense main diffraction peak at 22.47° that have been related to the crystalline reflections (200),[32,33] along with an amorphous halo at 20.80°, that belongs to their noncrystalline part.
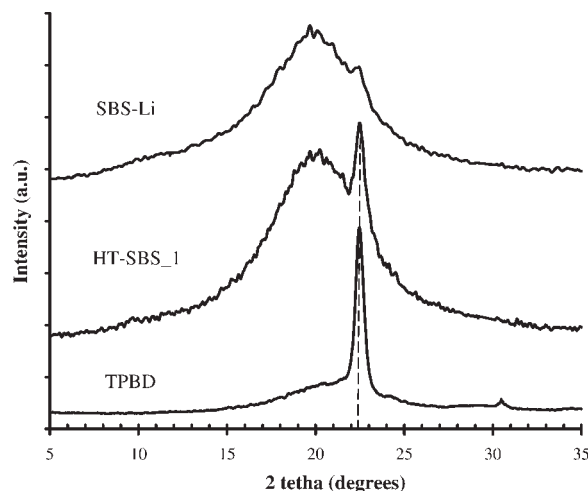

Figure 5 X-ray diffraction patterns recorded at room temperature of conventional SBS, TPBD with 90% of 1,4 trans units and HT-SBS_1 (Table I), having a high number of 1,4-trans units (76%), synthesized with an initiator with Al/Li/Ba/ molar ratio of 1 : 1 : 0.25, [Ba] = 0.3510 mmol at 70°C in cyclohexane solution.
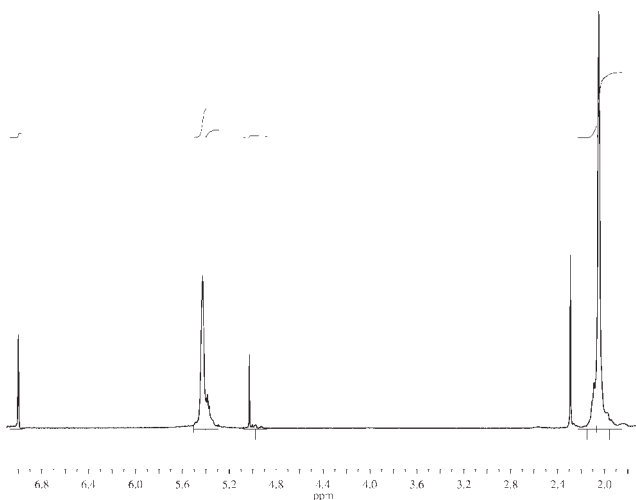
Figure 6 Typical ^{1}H-NMR spectra of a random copolymer of butadiene and styrene with high number of 1,4-trans units (80%, HT-SBR_1, Table III) synthesized with an initiator with Al/Li/Ba/ molar ratio of 1 : 1 : 0.25, [Ba] = 0.3510 mmol at 70°C.

Random copolymers

Polymer distribution of structural units and chemical compositions

Figure 6 shows the ^{1}H-NMR spectra of the copolymers obtained by the simultaneous copolymerization of a mixture of butadiene and styrene with a cyclohexane solution having 1 : 1 : 0.25 Al : Li : Ba molar ratio (referred to as HT-SBR).

The total amount of styrene quantified by ^{1}H-NMR was consistent with the added amount of monomers in the initial feed. The distribution of structural units of the butadiene portion of the copolymers determined by ^{1}H-NMR was 78–80% 1,4-trans units, 14–13% 1,4-cis units, and 8–6% 1,2-vinyl units.

In the ^{1}H-NMR of the butadiene-styrene block copolymer, a displacement of the orto protons towards a high field is observed, which is due to the phenyl ring of the neighboring styrenics units.[30,34] In statistically random copolymers, this chemical shift in the signals of orto protons are not observed as all the phenyl groups are equivalent and resonate around 7 ppm.

From the ^{1}H-NMR spectra of the HT-SBR copolymers (Fig. 6), the resonant frequencies at 6.65 and 7 ppm suggest that the composition of these copolymers is largely random compared to the copolymers synthesized by anionic polymerization with n-BuLi (SBR-Li).

For the alkyllithium-initiated anionic copolymerization polymerized in hydrocarbon solution, it is observed that butadiene incorporated more rapidly into the copolymer compared to styrene. Only after 70–80% butadiene conversion does the styrene incorporate into the macromolecular chain. This incorpo-
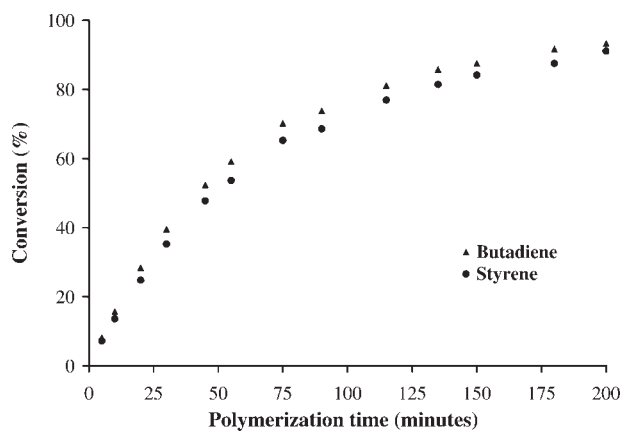

Figure 7 Monomer conversion (X) as function of reaction time for the copolymerization of butadiene and styrene (75/25 wt %, HT-SBR_4, Table III) with cyclohexane solution having 1 : 1 : 0.25 Al : Li : Ba molar ratio, [Ba] = 0.3510 mmol at 70°C in cyclohexane solution.

ration process produces a tapered copolymer or graded block copolymer structure due to the disparity in the copolymerization parameters of styrene.[35,36] Adding a small amount of a Lewis base in the alkyl lithium system polymerization may result in a random copolymer; however, the amount of 1,2 vinyl units will also increase.[37,38]

Thus, the copolymers synthesized using the Al : Li : Ba initiator system are particularly different from the copolymers synthesized with n-BuLi because they display a predominantly random distribution of monomeric units in the chain having a high 1,4-trans unit content.

Kinetic data

Figure 7 shows the conversion data of a butadiene-styrene copolymer (75/25 wt %) synthesized using the 1 : 1 : 0.25 Al : Li : Ba molar ratio initiator system. Figure 8 shows that, as the total conversion
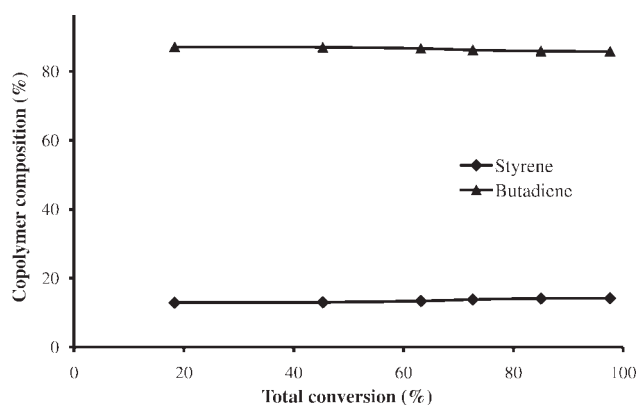

Figure 8 Polymer composition versus total conversion for the copolymerization of butadiene and styrene (75/25 wt %, HT-SBR_4, Table III) with cyclohexane solution having 1 : 1 : 0.25 Al : Li : Ba molar ratio, [Ba] = 0.3510 mmol at 70°C.
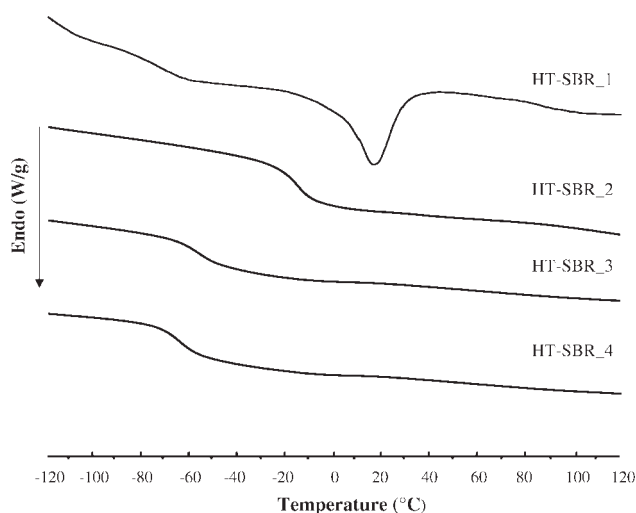
Figure 9 Thermograms of random copolymers of butadiene and styrene with high number of 1,4-trans units, produced with ternary initiators containing 1 : 1 : 0.25 Al : Li : Ba molar ratio, [Ba] = 0.3510 mmol at 70°C.

increases, the polymer composition stays nearly constant throughout the entire copolymerization reaction.

These results suggest that the butadiene and styrene have nearly identical reaction ratios, and indicate that the synthesis of a random SBR, which is consistent with the ^{1}H-NMR results.

Thermal analysis of random copolymers

Figure 9 shows the DSC data for the random copolymers. It was observed that HT-SBR containing about 5% styrene (HT-SBR_1, Fig. 9) showed crystalline melting temperatures at or slightly below room temperature (20°C). It has been reported that melting temperatures just below room temperature are desirable because, upon extension, stress-induced crystallization takes place as the melting temperature of the crystallites is increased. The crystalline melting

temperature of the copolymer with high 1–4 trans unit content decreases with increasing comonomer content according to Flory's equation for melting point depression.[39]

Also, as more styrene was incorporated into the polymer chain, the T_g shifted to higher values, and the melting temperature decreased until the 25% level of styrene (HT-SBR_3, Fig. 9) was reached. According to this point, an endotherm transition was not observed by DSC. This observation can be explained by the randomness of the polymerization, as the butadiene and styrene units are chemically joined in a statistical fashion.

Numerous attempts have been made to relate the glass transition temperature of a miscible mixture to their compositions. In the case of random copolymers, several expressions that take into account the weight fraction or the molar fraction of each monomer and the T_g of the homopolymer are used to evaluate their T_g. In this case, the equation proposed by Fox[40] was used.

$$Tg_{SB} = \frac{1}{\sum_i w_i/T_{gi}}$$

$T_{g,i}$ represents the glass transition temperatures of the constituent homopolymers (T_g of polystyrene = 100°C and T_g of 1,4-trans polybutadiene = −80°C) [33], and w_i corresponds to the weight fractions of the constituent homopolymers. It was observed that the Fox equation works reasonably well at low styrene content.

T_g values calculated using the equation of Fox for copolymers with styrene contents higher than 40% showed considerable differences. It has been considered that systems following Fox's equation have a more random distribution, whereas the systems that deviate from the equation have blocky sequences. In this case, due to the presence of a high 1,4-trans

TABLE III
Composition, Number Average Molecular Weight, Polydispersity, and Distribution of Structural Units of Random Copolymers of Styrene and Butadiene with High Number of 1,4-Trans Units, Synthesized with Al/Li/Ba Initiator System

Copolymer	F_{ST} mol/L	F_{BD} mol/L	[a]Total styrene (wt %)	[a]Block styrene (wt %)	[a]Random styrene (wt %)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	Polybutadiene structural units (%)		
								1,4-trans	1,2-vinyl	1,4-cis
HT-SBR_1	1.1065	0.03024	5	0.5	4.5	150	1.23	80	7	13
HT-SBR_2	0.6817	0.3540	52	7.8	44.2	167	1.41	79	8	13
HT-SBR_3	0.8871	0.1974	28	5.6	22.4	160	1.34	78	8	14
HT-SBR_4	0.934	0.1617	24	3.75	21.25	160	1.32	80	6	14

[a] Obtained by ^{1}H-NMR.
F_{ST} = styrene content in feed, F_{BD} = butadiene content in feed. Composition % feed HT-SBR_1: ST-BD 5 : 95, HT-SBR_2: ST-BD 50 : 50, HT-SBR_3: ST-BD 30 : 70, and HT-SBR_4: ST-BD 25 : 75. Feed ratio in weight %.
Copolymerization conditions: Al : Li : Ba molar ratio = 1 : 1 : 0.25, [Ba] = 0.3510 mmol, T = 70°C, reaction time 4 h and 10/1 v/v solvent (cyclohexane)/monomer ratio.

 3. Lynch, T. U.S. Pat. 6,184,168 (2000).

TABLE IV
Glass Transition Temperatures T_g as Determined by Differential Scanning Calorimetry and T_g Values Calculated Using the Equation of Fox, of Random Copolymers of Styrene and Butadiene with High Number of 1,4-Trans Produced with Al/Ba/Li Initiator System

Copolymer	T_g (°C)	T_gFOX (°C)
HT-SBR_2	−15	−25
HT-SBR_3	−55	−54
HT-SBR_4	−60	−58

polybutadiene crystallizable block, a greater difference in the results was observed by the equation of Fox.

CONCLUSIONS

Random, diblock, and triblock copolymers of butadiene and styrene, with a well-known, high number of 1,4-trans units and well-defined distribution, were obtained by anionic polymerization using a ternary initiator system of trioctyl aluminum, *n*-butyl lithium, and barium 2-ethyl-hexoxide. The sequential block copolymerization of these copolymers proceeded with high block efficiencies under a living polymerization condition. Their thermal properties were similar to those of the 1,4-trans polybutadiene, which exhibited a T_g and degree of crystallinity that were determined primarily by structural units distribution of the polybutadiene block. Kinetic data and ^{1}H-NMR showed that copolymerization of butadiene and styrene by a barium-based initiation system provided copolymers with a high 1,4-trans unit content and predominantly random distribution of the monomers. Thermal analysis of these random copolymers indicated that the number of 1,4-trans units, monomer distribution, and quantity of styrene along the backbone determined their thermal behavior.

Both the block and random copolymers have a sufficient amount of 1,4-trans units to display a regular structure. This distribution of structural units makes them susceptible to strain-induced crystallization, which provides superior dynamic properties that may well be profitable in the manufacture of composites.

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