High vinyl high styrene solution SBR

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Abstract

Objective: the objective of this study is to prepare high vinyl copolymers containing various levels of styrene and butadiene, and also to prepare random butadiene in high styrene content styrene–butadiene copolymers (SBR) while controlling the styrene block length. These materials could be used in race tread applications. *Summary*: This reports presents the synthesis and characterization of random, high vinyl copolymers containing styrene and butadiene (SBR's). The styrene content of these SBR's ranged from 10 to 80%. These SBR's were synthesized via anionic polymerization initiated by a catalyst system with a ratio of 1/0.4/5 of *n*-butyllithium (*n*-BuLi) to sodium dodecylbenzene sulfonate (SDBS) to N,N,N',N'-tetramethylethylenediamine (TMEDA). Kinetic data as well as NMR and ozonolysis techniques confirm that random SBR copolymers are being produced for low styrene content polymers. The glass transition temperature (T_g), increased dramatically as the styrene content was increased. The amount of vinyl based upon the polymer's total composition within the copolymer was found to decrease linearly as you increase the amount of styrene in the polymer. TGA results show that high styrene content polymers degrade at lower temperatures. The RPA confirms that as the styrene content increases, the elastic modulus decreases. As the frequency increased, the tan delta decreased for each polymer. Tan delta does not appear to be a function of styrene content. TEM results helped to describe polymer microstructure.
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1. Introduction

Currently, random solution SBR's (S-SBR's) with a composition of 20/80 SBR to 40/60 SBR are being used in tread applications. The preparation of random solution SBR is well known in the literature [1–6]. However the, high vinyl high styrene SBR's are difficult to make due to the fact that most polar modifiers appear to be limited in randomizing all the charged styrene. The most interesting example is found in the use of di-piperidine ethane, a powerful modifier for making 99.9% vinyl polybutadiene anionically. It failed to randomize SBR's of 20% styrene contents and higher [7]. We would like to report on a new modifier, dodecybenzenesulfonic acid sodium salt in combination with $N,N,N'N'$ Tetramethylene diamine (TMEDA) [8–10] in an anionic polymerization system for making high styrene high vinyl SBR. The glass transition temperature, T_g, determines the final tread properties. Low T_g SBR's are targeted for wear

and rolling resistance, whereas high T_g SBR's are used for their traction properties. High styrene content SBR's with a T_g above 0 °C have high tear strength. Yet, it is difficult to prepare high styrene content SBR's with the currently used modifier, because large styrene blocks occur at the end of the polymer chain.

A relatively new modifier, sodium dodecylbenzene sulfonate (SDBS), has been found to produce random low vinyl S-SBR's. High levels of SDBS were found to enhance the randomization of styrene into the polymer chain, but also greatly slowed reaction kinetics [1,2]. In this study, SDBS was used to modify *n*-butyllithium (*n*-BuLi) to synthesize random S-SBR's.

Another modifier, N,N,N',N'-tetramethylethylenediamine (TMEDA), is known to create higher vinyl content polymers. By using SDBS, TMEDA, and *n*-BuLi as a catalyst system, various styrene content random S-SBR's with varying vinyl content can be produced easily.

2. Preparation of sodium dodecylbenzene sulfate (SDBS)

A three-liter flask equipped with nitrogen inlet and a mechanical stirrer was charged with 2000 ml of anhydrous

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ethylbenzene and 0.50 mol of dodecylbenzenesulfonic acid. To this solution was added 0.50 mol of sodium hydroxide pellets. The heterogeneous mixture was stirred at room temperature for 1 h until all the sodium hydroxide was reacted. The soap like mixture is slowly heated and with care to avoid foaming until all the water was removed with a Dean Stark Trap via azeotroping with the ethylbenzene. The commercial SDBS contained flocculating agents that interfered with the polymerization in the absence of TMEDA. However, when polar modifiers were used in the polymerization, the commercial SDBS from Aldrich, Fluka, and Acros companies were used in the polymerization without any problem.

3. SBR synthesis

Styrene–butadiene copolymers were prepared via anionic polymerization [11]. In a one-gallon glass bowl reactor, under a blanket of nitrogen, equipped with a mechanical stirrer and temperature control via cooling water and low-pressure steam, polymerization of the styrene and butadiene monomers was carried out. Both butadiene and styrene premixes contained approximately 20% monomer dissolved in hexane or cyclohexane. The reactor was charged with amounts of styrene and butadiene to prepare an entire series of SBR's ranging from 10 to 80% styrene. A reactor held approximately 2000 g total of both premixes. A reaction temperature of 65 °C was used to synthesize these polymers. At reaction temperature, a catalyst system consisting of SDBS, TMEDA, and *n*-BuLi was added to the reactor to initiate polymerization. A ratio of 1/0.4/5, *n*-BuLi/SDBS/ TMEDA, was used for all polymerization runs. A molecular weight of 150,000 g/mol was targeted for all polymers, except where noted. Samples were taken over the course of the reaction to determine monomer conversion, which was presented as a function of time. At 100% conversion, SBR's with a styrene content of 30% and below were soluble in hexane, all others were soluble in cyclohexane. The reaction was short-stopped with denatured ethanol, and an antioxidant (2,6-ditertybuylphenol) was added to the polymer. The polymer was dried for several days in a hot oven to make sure all solvent had evaporated.

4. Results and discussion

Data is divided into two sections: S-SBR containing 10–30% styrene where styrene randomizes into butadiene and 40–80% styrene where butadiene randomizes into styrene.

4.1. Kinetic data: 10–30% styrene

Conversion versus time data shows that a 0.4/5/1 SDBS/TMEDA/*n*-BuLi catalyst system is randomizing the styrene into the polymer chain. Figs. 1 and 2 show
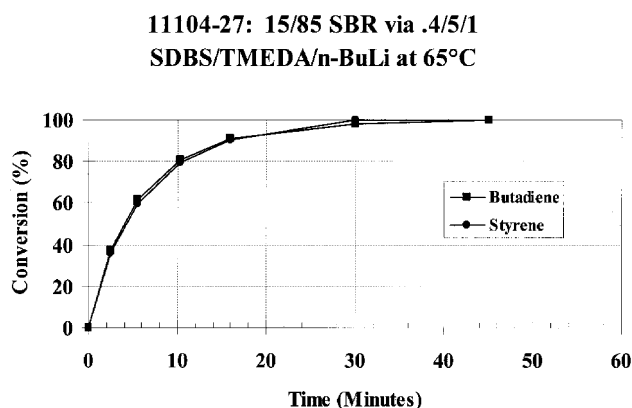

Fig. 1. Conversion versus time for a 15/85 SBR synthesized by 0.4/5/1 SDBS/TMEDA/*n*-BuLi at 65 °C.

conversions for a 15/85 and a 30/70 SBR, respectively. Each graph shows 100% conversion by 45 min.

Both Figs. 1 and 2 show that in the presence of SDBS, TMEDA, and *n*-BuLi butadiene and styrene have nearly identical reaction ratios. This indicates that a random SBR is being synthesized. Nuclear magnetic resonance (NMR) and ozonolysis results confirm this.

Figs. 3 and 4 illustrate the individual monomer conversion as a function of the total monomer conversion for the same two SBR's introduced above. Once again the graphs show that both monomers are being consumed at nearly the same rate.

Polymer composition stays nearly constant throughout the entire synthesis for these S-SBR's. Figs. 5 and 6 show that as the total conversion increases, the polymer composition remains the same. For example, the 30/70 SBR has 30% styrene in the polymer chain the entire run.

4.2. Polymer characterization: 10–30% styrene

Table 1 summarizes the polymer characteristics for 10–30% styrene S-SBR's. Polymer microstructure results were obtained by nuclear magnetic resonance (NMR) techniques, whereas T_g results were found through a differential
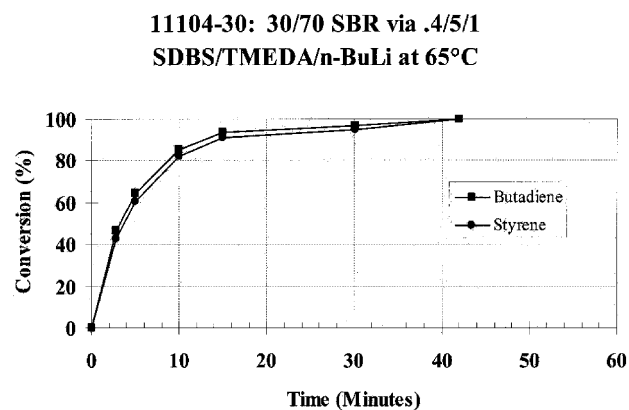

Fig. 2. Conversion versus time for a 30/70 SBR synthesized by 0.4/5/1 SDBS/TMEDA/*n*-BuLi at 65 °C.

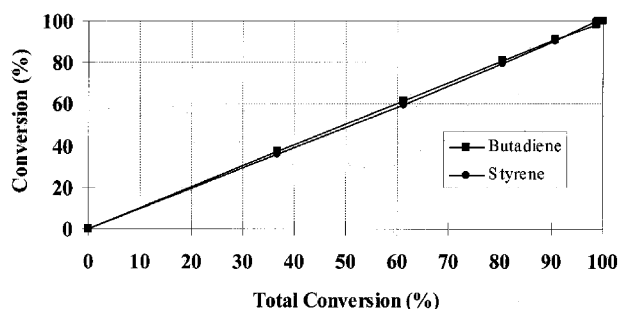**11104-27: 15/85 SBR via .4/5/1**
SDBS/TMEDA/n-BuLi at 65°C

Fig. 3. Monomer conversion versus total conversion for a 15/85 SBR.

11104-27: 15/85 SBR via .4/5/1
SDBS/TMEDA/n-BuLi at 65°C

Fig. 5. Polymer composition versus total conversion for a 15/85 S-SBR.

scanning calorimeter (DSC) and molecular weight (M_n) were obtained through gel permeation chromatography (GPC). The results illustrate that no block styrene is evident in these polymers. Also, as the amount of styrene incorporated into the polymer chain increases the T_g increases. Remember the target molecular weight was 150 K. The table shows M_n's nearly double this. This molecular weight fluctuation is being investigated.

4.3. Kinetic data: 40–80% styrene

For the higher styrene content S-SBR's no longer were the reaction ratios of styrene and butadiene identical. The conversion versus time curves for each were similar, but they did not fall right on top of each other. Also, these

higher styrene content polymers only took roughly 10 min to complete compared to 45 min for the lower styrene content ones. Figs. 7 and 8 illustrate conversion versus time curves for a 50/50 SBR and an 80/20 SBR made under identical conditions as mentioned before.

Monomer conversion versus total conversion graphs confirm that no longer are the polymers being evenly incorporated into the polymer chain. The 50/50 SBR certainly shows incorporation into the polymer chain is very close, but the 80/20 SBR starts to show a larger discrepancy. Figs. 9 and 10 illustrate this phenomenon in the monomer conversion as a function of total conversion.

For higher styrene content SBR's, the composition of the polymer is not constant across the total length of the run as it

11104-30: 30/70 SBR via .4/5/1
SDBS/TMEDA/n-BuLi at 65°C

Fig. 4. Monomer conversion versus total conversion for a 30/70 SBR.

11104-30: 30/70 SBR via .4/5/1
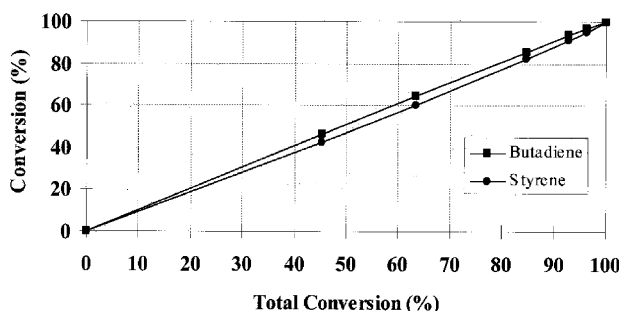**SDBS/TMEDA/n-BuLi at 65°C**

Fig. 6. Polymer composition versus total conversion for a 30/70 S-SBR.

Table 1
Polymer characterization of low styrene content S-SBR's

Polymer ID	Type	M_n	Vinyl	Cyclic W/vinyl	Block styrene	Random styrene	T_g
11104-26	10/90	427 K[a]	65.4	2.6?	0	10.5	−30.01
11104-27	15/85	288 K	60.9	2.6?	0	15.4	−24.26
11104-28	20/80	293 K	57.5	1.9?	0	20.3	−18.27
11104-29	25/75	292 K	53.9	1.3?	0	25.4	−14.42
11104-30	30/70	309 K	49.3	0	0	31.5	−11.28

[a] This sample's target molecular weight was 200 K instead of 150 K.
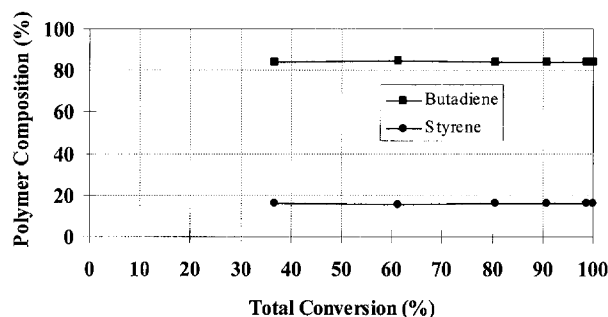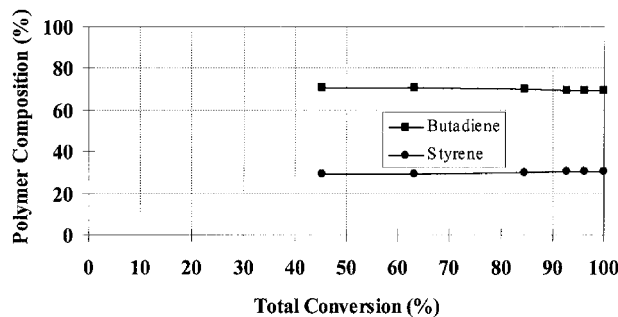
**11104-34: 50/50 SBR via .4/5/1
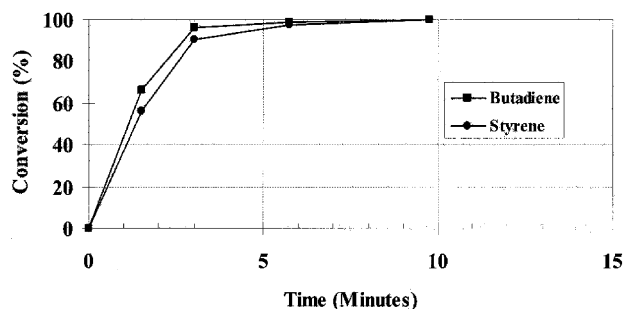SDBS/TMEDA/n-BuLi at 65°C**

Fig. 7. Conversion versus time for a 50/50 SBR.

**11104-34: 50/50 SBR via .4/5/1
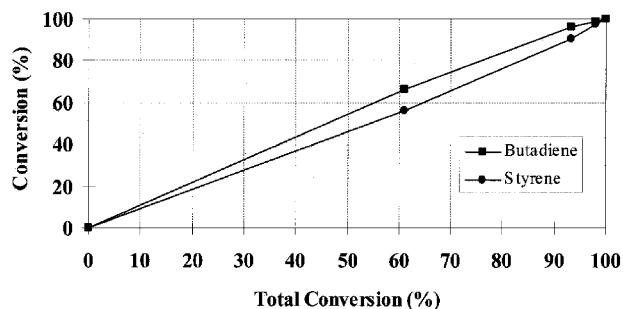SDBS/TMEDA/n-BuLi at 65°C**

Fig. 9. Monomer conversion versus total conversion for a 50/50 SBR.

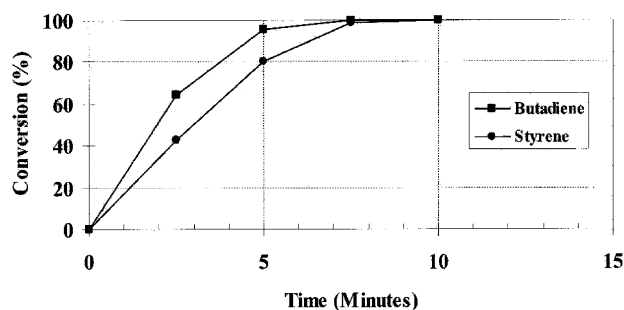**11104-38: 80/20 SBR via .4/5/1
SDBS/TMEDA/n-BuLi at 65°C**

Fig. 8. Conversion versus time for an 80/20 SBR.

**11104-38: 80/20 SBR via .4/5/1
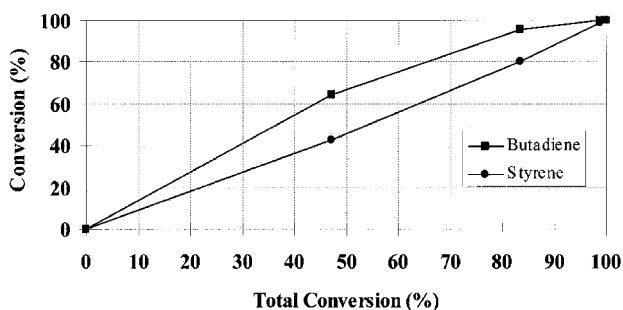SDBS/TMEDA/n-BuLi at 65°C**

Fig. 10. Monomer conversion versus total conversion for an 80/20 SBR.

was for the low styrene content polymers. For both the 50/50 and 80/20 SBR, the styrene content begins low and increases over the course of the synthesis. Figs. 11 and 12 illustrate this result.

4.4. Polymer characterization: 40–80% styrene

Table 2 summarizes the polymer characteristics for high styrene content S-SBR's. Once again polymer microstructure was determine by NMR techniques, T_g by DSC, and molecular weight by GPC. The results show that as the amount of styrene is increased, the block content also increases. SBR T_g's also dramatically increase as the styrene content is increased. Once again, twice the targeted molecular weight, 150 K, is observed in the final polymer product.

**11104-34: 50/50 SBR via .4/5/1
SDBS/TMEDA/n-BuLi at 65°C**

Fig. 11. Polymer composition versus total conversion for a 50/50 SBR.

Table 2
Polymer characterization of high styrene content S-SBR's

Polymer ID	Type	M_n	Vinyl	Block styrene	Random styrene	T_g
11104-31	40/60	263 K	39.2	1.8	40.9	−15.78
11104-34	50/50	287 K	29.1	6.6	48.4	−4.43
11104-36	60/40	290 K	21.8	19.3	45.4	9.66
11104-37	70/30	321 K	14.1	37.5	38.4	25.51
11104-38	80/20	306 K	6.8	59.2	26.7	41.8

**11104-38: 80/20 SBR via .4/5/1
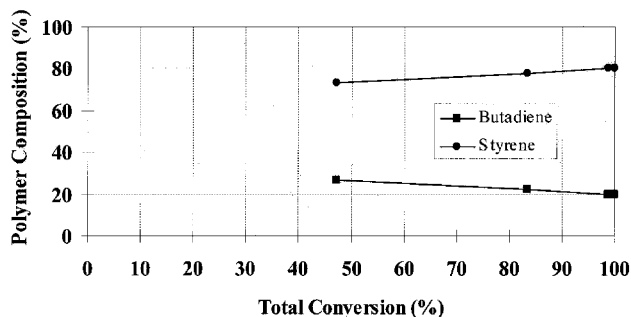SDBS/TMEDA/n-BuLi at 65°C**

Fig. 12. Polymer composition versus total conversion for an 80/20 SBR.

Cyclohexane is considered to have an effect on polymer microstructure; therefore, a 70/30 SBR was made with both cyclohexane and hexane as a solvent. The polymer phased out of solution when using hexane, but it was still able to be recovered from the reactor. The T_g's for both polymers were the same, which means similar microstructures resulted.

4.5. Vinyl content

The amount of vinyl synthesized within the polymer chain depends upon how much TMEDA and butadiene were added. The percentage of vinyl in the polymer backbone is presented in two ways. First, it is shown as a function of the styrene content based upon the total composition of the polymer. This gives a linear curve that decreases as the amount of styrene is increased. This is expected since the amount of butadiene decreases linearly. Fig. 13 shows these trends. Secondly, the amount of vinyl is plotted versus the styrene content based upon the amount of vinyl normalized by the amount of butadiene in the polymer. Using this method, the vinyl content stays constant up to a composition of 30% styrene in the polymer. Above 30% styrene, the vinyl content begins to decrease as the amount of styrene is increased. It is
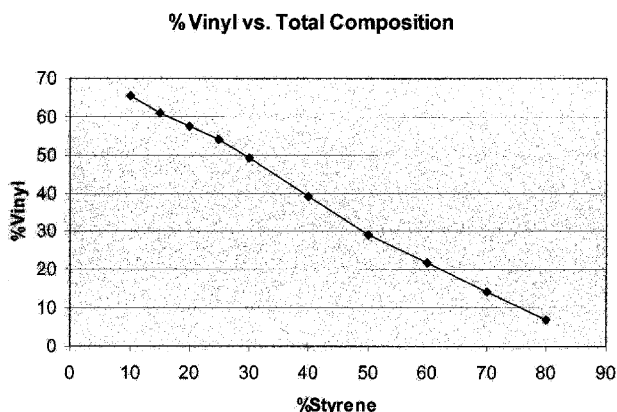

Fig. 13. %Vinyl based on total composition as a function of styrene content.
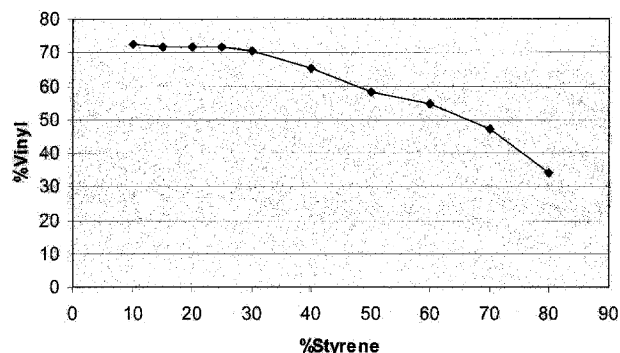
% Vinyl vs. Butadiene Composition

Fig. 14. %Vinyl normalized by butadiene content as a function of styrene composition.

interesting to note that the vinyl content in these high styrene SSBR's stayed constant up to 30% styrene in the polymer. In the high styrene SSBR it appears that the vinyl content is actually decreasing as seen in Fig. 13. The simple explanation is the chain ends being in the 1,4 structures does not allow isomerization to introduce the vinyl structures since the δ parameter of the styrene is much larger than the vinyl. In simple terms styrene does not want to be next to vinyl and forces the chain to be in the 1,4-structures to accommodate the randomization of the styrene. The SBR's containing 40% or more styrene exothermed during polymerization, and this increase in temperature may cause a drop in vinyl content in some cases but not in all. Fig. 14 illustrates these results.

4.6. TGA results

Thermal gravimetric analysis (TGA) is used to find the temperature where a polymer begins to degrade upon heating. Fig. 15 illustrates the degradation temperatures achieved for various content SBR's, from 10 to 80% styrene. As the amount of styrene is increased, the degradation temperature decreases. This suggests that styrene depolymerizes more easily than butadiene. Also, it
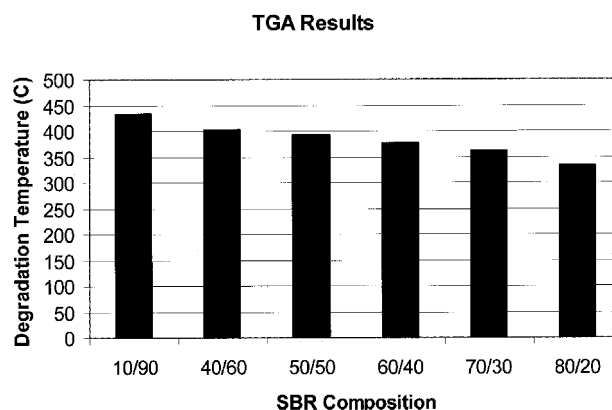
TGA Results

Fig. 15. TGA results for various composition S-SBR's.
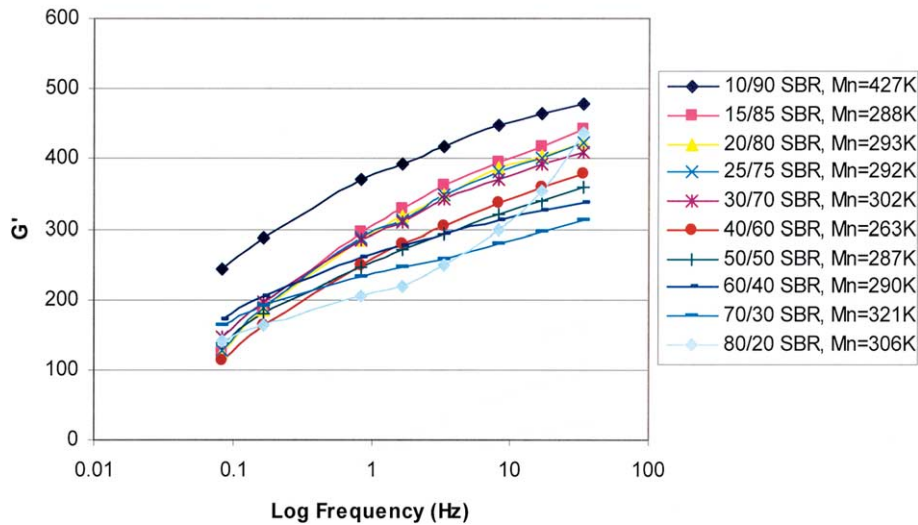
G' vs Frequency at 100C and 2% Strain

Fig. 16. Elastic modulus for various SBR's at 100 °C and 2% strain as determined by the RPA.

is believed that the butadiene polymers are crosslinked, causing them not to degrade as easily.

4.7. Rubber processing analyzer(RPA) analysis

Using the rubber process analyzer (RPA), the elastic and loss moduli and the tan delta of uncured polymers can be determined. These data from the RPA gives an insight into the dynamic and viscoelastic properties of the gum rubber for its potential application in tire performance. These characteristics give insight into the possible tire properties these SBR materials may exhibit [12]. The following figures show the results obtained by the RPA methods.

Figs. 16 and 17 show the elastic moduli for these SBR's at 100 and 150 °C and 2% strain, respectively. For both, as the amount of styrene increases, the elastic modulus decreases at a given frequency. This is attributed to the molecular entanglement in butadiene; more styrene means less molecular entanglement. The styrene chains are heavier; therefore, they are shorter than butadiene chains of similar molecular weights. Shorter chains mean less molecular entanglement and lower modulus. As the frequency is increased, the elastic modulus also increases. At 150 °C, it appears the elastic modulus is approaching a single value at low frequencies.

Higher styrene content polymers have higher T_g's and are

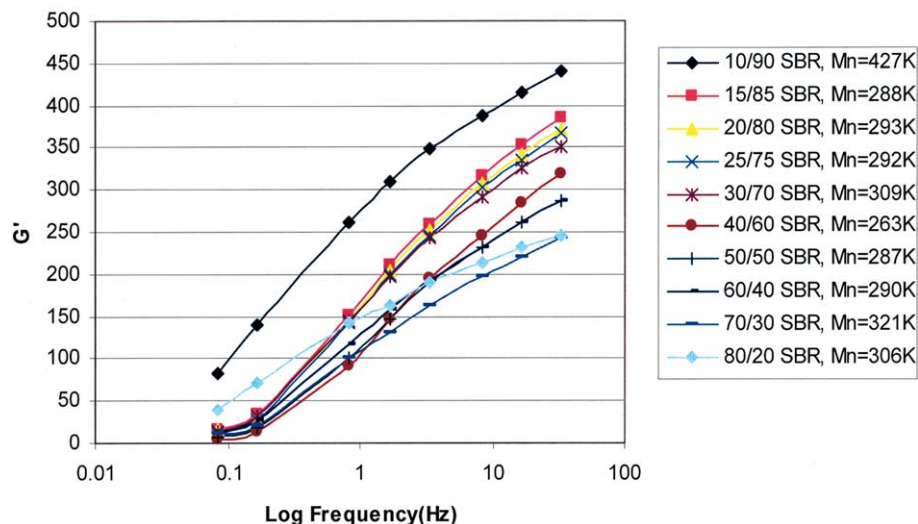## G' vs Frequency at 150C and 2% Strain

Fig. 17. Elastic modulus for various SBR's at 150 °C and 2% strain as determined by the RPA.

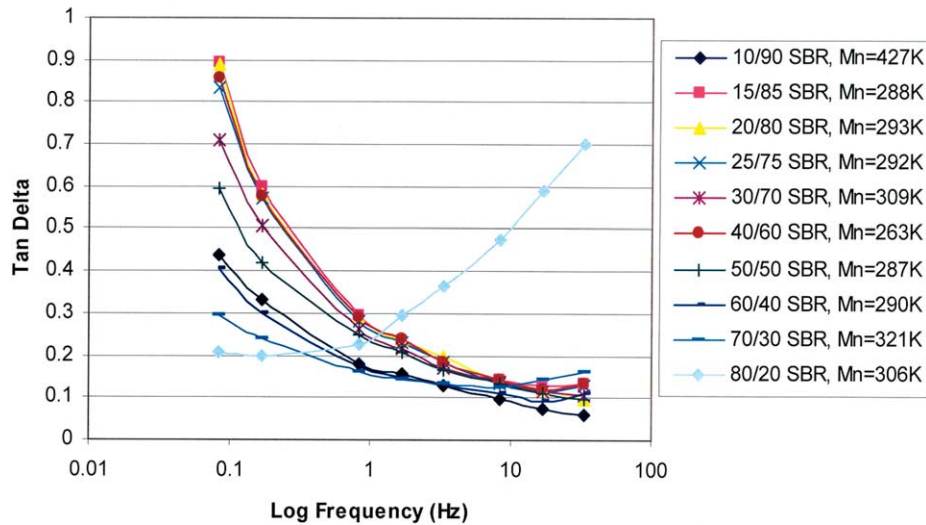## Tan Delta vs Frequency at 100C and 2% Strain

Fig. 18. Tan delta for various SBR's at 100 °C and 2% strain as determined by the RPA.

very plastic at room temperatures; therefore, their results in mechanical tests might not be accurate at lower temperatures. The 80/20 SBR shows interesting behavior at 100 °C in these RPA tests, and it is believed that the results are inaccurate.

Figs. 18 and 19 illustrate the tan delta for these SBR's at 100 °C and 150 °C and 2% strain, respectively. Tan delta decreased as the frequency increased is the general trend. At both temperatures, all polymers showed low tan delta at higher frequencies, which means low hysteresis or good rolling resistance. It is interesting to note that at high frequencies, all polymers approach the same tan delta value. At 100 °C, the 80/20 gave strange results which is attributed to the plastic nature of the polymer. High tan delta at lower frequencies indicates high hysteresis and better traction properties (note 40/60 and 50/50 SBR's).

4.8. Ozonolysis results

Samples were submitted for styrene sequence distribution by ozonolysis to determine the styrene blockiness within the polymer chain. Results confirm that for low

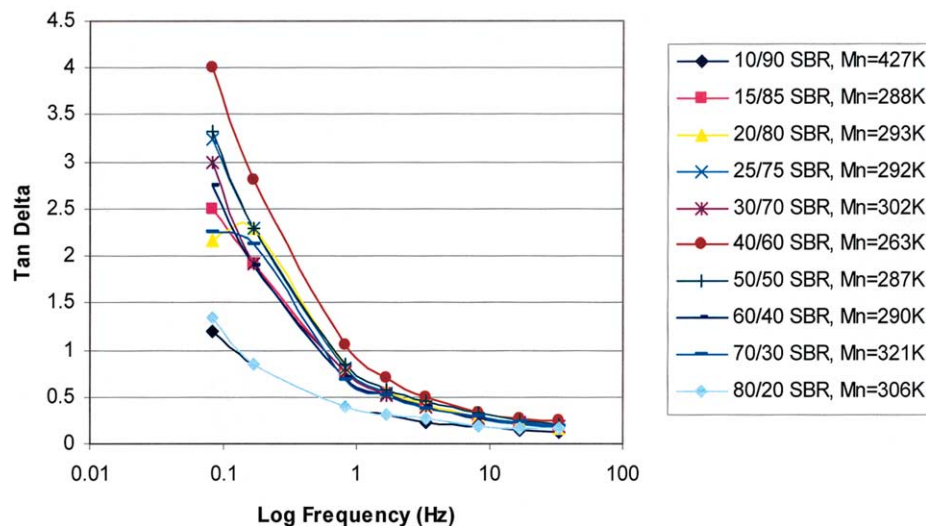## Tan Delta vs Frequency at 150C and 2% Strain

Fig. 19. Tan delta for various SBR's at 150 °C and 2% strain as determined by the RPA.

Table 3
Styrene sequence distribution by ozonolysis results for various composition SBR's

	10/90	15/85	20/80	25/75	30/70	40/60	50/50	60/40	70/30	80/20
IS×V	54.4	46.5	42.2	37.9	31.6	17.9	12.6	5.5	3.1	2
IS	36.6	35.6	32.3	30.1	25.9	18.4	14	7	5.1	1.9
2S×V	5.1	12.6	18.5	23.7	26.4	25.1	20.3	10.8	6	2
2Sr	2.5	3.4	4.6	5.3	6.5	9.9	9.9	6.1	4.6	2.2
2Sm	1.4	1.9	2.4	3	4.1	7.2	7.2	5.4	4.1	2.2
3S×V					4.3	16.3	18	15.1	95	35
3S					1.2	5.2	8.3	8.8	7.4	4
4S×V							6.6	10.1	8.3	4.1
4S							3.1	8.3	8.6	5.2
5S×V								5.1	5.6	3.7
5S								7.1	10	8
6S								4.9	8.3	7.7
7S								2.5	5.3	6.3
8S								1.4	3.7	5.3
9S								0.9	2.8	4.7
10S								0.6	2.1	4.2
11S								0.3	1.6	3.9
12S								0.1	0.8	2.3
13S									0.7	2.5
14S									0.6	2.3
15S									0.5	1.9
16S									0.3	1.6
17S									0.2	1.4
18S									0.2	1.2
19S									0.2	1.1
20S									0.1	1
21S									0.1	0.9
22S									0.1	0.8
23S									0.1	0.8
24S										0.7
Large block>24S										10.6

styrene content polymers, random SBR's were produced. Only SBR's containing 60% or more styrene began to have large styrene blocks within the polymer backbone. Even the 50/50 SBR contains high amounts of random styrene without large styrene blocks. Table 3 summarizes the results from ozonolysis.

In Table 3, 1*S* represents a 1,4 Bd-styrene-1,4Bd sequence. The *x* before a *V* indicates an unknown number of 1,2 Bd(vinyl) units. Parenthesis around a sequence indicates the exact order of units is unknown. Finally, *r* indicates the racemic form and m is the meso form.

4.9. Transition electron microscopy (TEM)

Transmission electron microscopy (TEM) pictures showed that for low styrene content SBR's (up to a 50/50 SBR) a homogenous, continuous singlephase resulted. This indicates that the polymer is totally random or has only small sequences of block styrene. The 60/40 SBR showed structures that were not well defined. Finally, the 70/30 and 80/20 SBR's showed laminar, two-phase morphology, indicating styrene blocks with large styrene sequences.

5. Conclusions

Random, high vinyl content S-SBR's can be produced via an SDBS/TMEDA/*n*-BuLi catalyst system at low styrene compositions (up to and including 50% styrene). As the styrene content increases, the amount of styrene blockiness also increases above 60% styrene. Kinetic data shows that at low styrene composition, styrene and butadiene have nearly identical reaction ratios. Vinyl content based on total polymer composition is a linear function of styrene content. Above 30% styrene, the reaction exotherm may have caused some drop in vinyl content; therefore, excellent temperature control is needed to produce accurate vinyl content to verify the non-isomerization mechanism that we proposed. RPA data illustrates that SBR's have low tan delta at higher frequencies, which means low hysteresis or good rolling resistance. RPA data also shows that as the styrene content is increased, the elastic modulus decreases. Overall, these random high glass-temperature high vinyl SBR's show good characteristics, and should be considered for tire applications in both traction and fuel economy (low hysteresis).

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