# Influence of Styrene Content on the Hydrogenation of Styrene–Butadiene Copolymer

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ABSTRACT: A hydrogenated styrene-butadiene copolymer (HSBR) was prepared by a diimide reduction of SBR in the latex stage. The influence of the styrene content on various reaction parameters, namely, time, temperature, and concentration of the reactants and the catalyst was studied. A comparatively lower temperature, longer time, lesser amount of hydrogen peroxide, and higher amount of the catalyst are required to optimize the hydrogenation reactions of SBR with a higher styrene content. The diimide reduction of SBR is first order with respect to the olefinic substrate and the apparent activation energy increases with increase in the styrene level. All the hydrogenated copolymers were characterized with the help of IR, NMR, and DSC. The TGA data indicate a higher thermal stability of HSBR as compared to SBR in nitrogen, although an anomalous behavior is observed in air due to crosslinking and oxidation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1581–1595, 1999

**Key words:** hydrogenation; styrene-butadiene rubber; rubber; thermoplastic elastomer; diimide reduction; modification; latex

### **INTRODUCTION**

Chemical modification of polymers is useful in altering the reactivity and/or stability of the polymer. Unsaturated polymers, especially the diene polymers, are a useful target for chemical modification, because of the technological importance associated with the parent materials and the reactivities of the double bonds in the polymer chains. Hydrogenation of diene polymers is an excellent example of chemical modification which improves both the chemical as well as the physical properties of the existing polymer. The hydrogenated acrylonitrile-butadiene copolymer has been shown to have superior physical properties to those of the parent copolymer.<sup>1</sup> Many hydrogenation methods have been used: Some require harsh conditions, for example, high temperature and/or high pressure,<sup>2-4</sup> which generally results in an appreciable degradation of the polymerchain backbone, while others are expensive.<sup>5</sup> The diimide-reduction technique is a mild method for hydrogenation, which relies on ambient pressure and moderately low temperature. This procedure has the advantage of minimizing side reactions and can be carried out without degradation of the backbone.<sup>6</sup>

Styrene-butadiene copolymers (SBR) have been successfully hydrogenated by a diimide-reduction technique into the latex stage.<sup>7,8</sup> It has also been claimed that newer thermoplastic elastomeric latexes could be obtained by this technique.<sup>9</sup> Scientifically, it is interesting to alter the properties of the butadiene units of SBR and to generate new polymers with controlled crystalline segments. Both the microstructure of butadiene units and the styrene level are expected to influence the hydrogenation reaction, although a

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literature search revealed that these have not been reported.

Since the styrene content is expected to play a dominant role in the hydrogenation of SBR, the present investigation was aimed at studying the effect of the styrene content on the hydrogenation of SBR latex. SBR lattices having 17, 23, 28, and 38% styrene content were used in this study. The variables chosen were time, temperature, and concentration of the reactants and the catalyst. The properties of the resultant hydrogenated copolymers are discussed in reference to the styrene content.

# **EXPERIMENTAL**

#### Materials

SBR lattices with a styrene content of 23, 28, and 38% used as a substrate for hydrogenation were obtained from Apcotex Lattices Ltd. (Mumbai, India). SBR latex with 17% styrene was procured from Nippon Zeon Co. Ltd. (Tokyo, Japan). Hydrazine hydrate, hydrogen peroxide, the cupric sulfate catalyst, the surfactant (sodium lauryl sulfate,  $C_{12}H_{25}OSO_3Na$ ), and methanol were received from the standard sources.

#### **Latex-Reduction Process**

SBR latex, 12.5 g, containing 28% of styrene (SBR-28), an aqueous solution of cupric sulfate, and the surfactant were taken in a 250-mL twonecked flask equipped with a dropping funnel and a reflux condenser. A specific volume of 80% aqueous hydrazine was added to the stirred solution dropwise before warming to a particular temperature. The solution was heated to and maintained at the desired temperature with the aid of a hotoil bath. A required volume of 30% hydrogen peroxide was introduced dropwise over a specific period of time using a dropping funnel. After the addition was completed, the latex was postreacted for several hours while cooling to room temperature. The hydrogenated polymer was coagulated into a saturated solution of NaCl, washed several times with methanol, and finally dried under a vacuum. The same procedure was followed for the SBR lattices with 17, 23, and 38% styrene content.

## **CHARACTERIZATION**

#### Infrared (IR) Spectroscopy

IR analyses were performed on a Perkin–Elmer 843 double-beam recording spectrophotometer.

The copolymers were analyzed as solution-cast films from a  $\rm CHCl_3$  solution on KBr plates. The spectra were taken with a 5.4 cm<sup>-1</sup> resolution in the range of wavenumbers from 4000 to 400 cm<sup>-1</sup> at a noise level of 0.1% transmittance.

#### Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded in a Brüker 200 MHz/52 MM spectrophotometer using TMS as the internal standard. Deuterated chloroform (CDCl<sub>3</sub>) was used as a solvent in all the cases. A minimum of 150 scans were collected for each spectrum.

#### **Differential Scanning Calorimetry (DSC) Studies**

DSC was carried out in a Stanton Red Croft thermogravimetric analyzer (Model No. STA 625) with the data analyzer version V-400. The glass transition temperature  $(T_g)$  was obtained from the DSC curves. The samples were initially cooled to  $-150^{\circ}\mathrm{C}$  and then heated to  $+150^{\circ}\mathrm{C}$  with a programmed heating rate of 10°C/min. Liquid nitrogen was used to achieve the subambient temperature. The  $T_g$  was taken as the midpoint of the step in the scan.

# Thermogravimetric Analysis (TGA) Studies

TGA was performed using a DuPont 9000 thermal analyzer (Model 910) in a nitrogen atmosphere and in air (flow rate 100 mL/min) at a heating rate of 10°C/min. Thermograms were recorded from room temperature (25°C) to 800°C. The temperature corresponding to 10% weight loss ( $T_{10}$ ) and the temperature corresponding to the maximum rate of decomposition ( $T_{\rm max}$ ) were estimated.

# **RESULTS AND DISCUSSION**

This section is divided into three parts. The first part contains the results of the characterization of the HSBR copolymer having a 28% styrene content. The second part describes the optimization of the reaction conditions for the same SBR. The influence of various parameters on the reaction yield and rate are clear from this part. The third part describes how the level of styrene would influence the reaction parameters and thermal properties.

#### Characterization of Hydrogenated SBR

#### IR Spectral Analysis

IR spectra of SBR and HSBR with a 28% styrene content are shown in Figure 1. The spectrum of



**Figure 1** Infrared spectra of (i) SBR and (ii,iii,iv) HSBR with 48, 62, and 92% hydrogenation, respectively.

the control SBR [Fig. 1(i)] indicates peaks at 699 cm<sup>-1</sup> due to the styrene unit, 757 cm<sup>-1</sup> due to 1,4-cis, 909 cm<sup>-1</sup> due to 1,2-vinyl, and 967 cm<sup>-1</sup> due to 1,4 trans-butadiene units. As the level of hydrogenation increases, the peaks due to butadiene units decrease and the peak at 1450 cm<sup>-1</sup> due to the —CH<sub>2</sub>— deformation vibration increases. A new peak at 723 cm<sup>-1</sup> due to the —CH<sub>2</sub>— rocking vibration [ (CH<sub>2</sub>)<sub>n>4</sub>] appears in the spectra of the hydrogenated SBR samples. A peak at 1374 cm<sup>-1</sup> due to the deformation vibration

tion of the —CH<sub>3</sub> group is also clear in the spectra of HSBR due to the reduction of the pendent vinyl group. Two peaks at 2852 and 2925 cm<sup>-1</sup> due to the C—H stretching vibration of the —CH<sub>2</sub> group increase with increase in the level of hydrogenation. The absorption peak at 699 cm<sup>-1</sup> shows no change in intensity, reflecting that the aromatic ring of the styrene unit is not reduced under the given hydrogenation conditions.

The possibility of kinetic selectivity of the diimide toward the *cis, trans,* or vinyl group present in butadiene segments is considered in a semiquantitative fashion by plotting the absorption factors

$$\left[1 - \frac{(\bar{A}_{967})_h}{(\bar{A}_{967})_0}\right], \left[1 - \frac{(\bar{A}_{909})_h}{(\bar{A}_{909})_0}\right], \text{ and } \left(1 - \frac{(\bar{A}_{757})_h}{(\bar{A}_{757})_0}\right)$$

against time, where

$$ar{A}_{967} = \! rac{A_{967}}{A_{699}}, \, ar{A}_{909} = \! rac{A_{909}}{A_{699}}, \, ext{and} \, ar{A}_{757} = \! rac{A_{757}}{A_{699}}$$

 $A_{967}$ ,  $A_{909}$ ,  $A_{757}$ , and  $A_{699}$  represent the absorbance values of *trans*, vinyl, *cis*, and styrene units at 967, 909, 757, and 699 cm<sup>-1</sup>, respectively. (As the aromatic ring of the styrene unit is unaffected during diimide reduction, the 699 cm<sup>-1</sup> peak serves here as the internal standard.) The subscripts 0 and *h* are used to indicate the absorbance values before and after hy-



Figure 2 Relative change of *cis, trans,* and vinyl double bonds for SBR-28 with reaction time.



**Figure 3** <sup>1</sup>H-NMR spectra of (i) SBR and (ii,iii,iv) HSBR with 48, 62, and 92% hydrogenation, respectively.

drogenation. These plots are shown in Figure 2. A rapid reduction of the vinyl units becomes readily apparent. At a particular reaction time (say 2 h), the values of the absorption factors corresponding to *cis*, *trans*, and vinyl butadiene units are 0.11, 0.34, and 0.40, respectively, reflecting the lowest reactivity of the *cis* unit toward hydrogenation. The highest reactivity observed for the vinyl group is in accord with the fact that this moiety contains the least amount of substitution on the olefinic group. Furthermore, as the vinyl double bonds occur in a pendent position of the polymer chain, it should be more accessible to the diimide reagent.<sup>10</sup> The order of the reactivity of the butadiene units is as follows: 1,2-vinyl > 1,4- trans > 1,4-cis. The diimide attacks trans double bonds more rapidly than it does *cis* double bonds.<sup>11</sup> The mechanism agrees with the observation that the rate of reduction decreases with increasing substitution about the multiple bond due to steric hindrance in the transition state. Furthermore, the transition-state complex should be more clustered for *cis*- rather than for *trans*-olefins, since, in the former case, the substituents are crowded more closely together<sup>12</sup> as shown below:



#### NMR Spectral Analysis

Figure 3 shows the representative <sup>1</sup>H-NMR spectra of the control and the partially hydrogenated SBRs. Major peaks are observed in the aliphatic (0.5-.2.8 ppm) and olefinic (4.6-5.8 ppm) regions. Aromatic protons show peaks in the region of 6.8-7.2 ppm. There is no change in intensity of the peaks due to styrene, reflecting the stability of the aromatic ring toward hydrogenation. With the progress of hydrogenation, the olefinic peak area decreases considerably. Concurrently, a peak at 1.25 ppm assigned to the methylene sequence increases with increase in the hydrogenation of the double bonds. The peak at 4.99 ppm



**Figure 4** Relationship of IR peak ratio  $[A_{967}/A_{699}]$  versus percent hydrogenation by <sup>1</sup>H-NMR.

due to the 1,2-butadiene unit is almost absent from the spectra of 62% hydrogenated SBR, indicating that 1,2-butadiene units are more rapidly hydrogenated than are 1,4 units. This is in accord with the IR results.

#### Determination of Degree of Hydrogenation

Calculation for the determination of the degree of hydrogenation is based on eq. (1), following that of Marshall et al. developed for the hydrogenated acrylonitrile-butadiene copolymer<sup>13</sup>:

Degree of hydrogenation (mol %)

$$= 100 - k[A_{967}/A_{699}] \quad (1)$$

where k is the calibration factor determined for HSBRs having a 28% styrene content and  $A_{967}$  and  $A_{699}$  are the absorbance values at 967 and 699 cm<sup>-1</sup> peaks, respectively.

Figure 4 shows the relationship between the degree of hydrogenation estimated from the <sup>1</sup>H-NMR spectra and based on the method reported in our earlier article<sup>8</sup> and from the absorbance ratio, which is proportional to the degree of hydrogenation. On the whole, there exists a fairly good linear correlation between them. The absorption at 967 cm<sup>-1</sup> becomes too weak at more than 90% hydrogenation to determine the degree of hydrogenation for SBR having 28% styrene can be de-

termined from the following equation with k [eq. (1)] equal to 47.24:

Degree of hydrogenation (mol %)

$$= 100 - 47.24(A_{967}/A_{699}) \quad (2)$$

In the subsequent discussion, the degree of hydrogenation in mol percent is reported.

#### **Optimization of Reaction Parameters**

#### Effect of Reaction Time

The effect of reaction time was studied at 318 K in the presence of 0.062 mol hydrazine, 0.067 mol hydrogen peroxide, and 0.008 mmol cupric sulfate as the catalyst. The results over a range of times from 1 to 8 h are plotted in Figure 5. With increase in the reaction time, the level of hydrogenation increases due to the reduction of a larger number of double bonds by diimide. The maximum level of hydrogenation is achieved at 4 h of reaction time.

#### Effect of Reaction Temperature

The hydrogenation reaction was studied from 298 to 328 K in the presence of 0.062 mol hydrazine, 0.067 mol hydrogen peroxide, and 0.008 mmol of the cupric sulfate catalyst for 4 h. The extent of hydrogenation increases with increase in the tem-



**Figure 5** Effect of reaction time and temperature on degree of hydrogenation. Hydrazine 0.062 mol; hydrogen peroxide 0.067 mol; catalyst 0.008 mmol.

perature to 308 K; at this temperature, maximum conversion is achieved (Fig. 5). After 308 K, the degree of hydrogenation decreases.

# Effect of Concentration of Hydrazine

The concentration of hydrazine was varied from 0.037 to 0.112 mol at 308 K in the presence of 0.067 mol hydrogen peroxide and 0.008 mmol of the cupric sulfate catalyst for 4 h of reaction time. The results are plotted in Figure 6. The conversion is maximum at 3.5 mL of 80% aqueous hydrazine (0.087 mol).

# Effect of Concentration of Hydrogen Peroxide

The effect of hydrogen peroxide concentration on the level of hydrogenation was studied in the presence of 0.087 mol hydrazine and 0.008 mmol of the cupric sulfate catalyst for a time period of 4 h at 308 K temperature. The addition of 0.084 mol hydrogen peroxide gives the maximum level of hydrogen peroxide gives the maximum level of hydrogen peroxide concentration, crosslinking reactions may take place which reduce the number of reaction sites, that is, the available double bonds and the mobility of rubber in the emulsion.

# Effect of Concentration of CuSO<sub>4</sub> 5H<sub>2</sub>O Catalyst

The effect of catalyst concentration on the percent hydrogenation was studied for a period of 4 h at

308 K in the presence of 0.087 mol hydrazine and 0.084 mol hydrogen peroxide. The concentration of the catalyst was varied from 0.004 to 0.020 mmol. The maximum level of hydrogenation was obtained at a catalyst concentration of 0.016 mmol (Fig. 6). At a high catalyst concentration (0.020 mmol), the extent of hydrogenation decreases.

# Influence of Styrene Content

# Dependence of Degree of Hydrogenation on Reaction Time and Influence of Styrene Content

The effect of the styrene content on the level of hydrogenation at various reaction times is displayed in Figure 7. The reaction times were varied from 1 to 8 h. It is observed that the percent hydrogenation of *trans* double bonds (equivalent to the degree of hydrogenation) is lowest in the case of SBR-38 for 1 h reaction time. The order is just the reverse when the reaction time is 6 h under similar conditions, the percent hydrogenation being the highest. At



Figure 6 Effect of hydrazine, hydrogen peroxide, and catalyst concentration on degree of hydrogenation. Temperature  $308 \pm 2$  K; time 4 h.



**Figure 7** Effect of reaction time and temperature on hydrogenation of *trans* double bonds for SBR with 17, 23, 28, and 38% styrene content.

an intermediate reaction time (4 h), the percent hydrogenation of trans bonds lies between 37 and 42%.

In an earlier section it was pointed out that the rate of hydrogenation of the vinyl double bond in the butadiene unit is the fastest. Figure 8 displays the plot of the percent hydrogenation of *cis*, trans, and vinyl units versus the reaction time of SBR lattices with styrene levels of 23, 28, and 38% (SBR-23, SBR-28, and SBR-38), respectively. For clarity, the results of only three samples were plotted. It is interesting to note that the optimum reaction time beyond which the level of hydrogenation decreases is the longest for SBR-38. For example, the optimum reaction times for the hydrogenation of vinyl units are 1 h for SBR-23, 4 h for SBR-28, and 6 h for SBR-38. The rate of the reduction of vinyl and *trans*-butadiene units is fastest with SBR-23 than with the other two systems (the amount of hydrogenation of vinyl bonds for lattices SBR-23, SBR-28, and SBR-38 are 58, 31, and 26% per hour, respectively. At a very long time beyond the optimum, the level of hydrogenation decreases.

The latex-reduction process involves in situ generation of the transitory species diimide  $(N_2H_2)$  within the latex by oxidation of hydrazine hydrate in the presence of the catalyst. The stereochemistry of the reduction of the double bond has been attributed to the formation of a cyclic transition state<sup>14</sup> (Scheme 1). As the styrene content increases, the steric hindrance between the aromatic ring of the styrene and incoming diimide  $(N_2H_2)$  increases and, hence, a longer period is required to achieve the maximum level of hydrogenation. Also, the  $T_g$  values, as reported later, increase with increasing styrene content and it seems likely that the diffusion rate of diimide through the matrix would be slower in higher styrene-containing systems, because they are more rigid.

# Dependence of Degree of Hydrogenation on Reaction Temperature and Influence of Styrene Content

The effect of the styrene content on the degree of hydrogenation of the SBR samples was car-



**Figure 8** Rates of hydrogenation of *cis, trans,* and vinyl units for SBR with 23, 28, and 38% styrene content.

ried out over the temperature range of 298–328 K. All the lattices containing styrene levels of 17, 23, 28, and 38% give a maximum level of hydrogenation within the temperature range of 308–318 K (Fig. 7). It is also seen that a comparatively lower reaction temperature is necessary to optimize the SBR latex with a higher styrene content.

## Dependence of Degree of Hydrogenation on the Concentration of Hydrazine Hydrate and Influence of Styrene Content

The degree of hydrogenation of SBR latex with a styrene content of 17 and 28% (SBR-17 and SBR-28) is plotted against the ratio of the moles of hydrazine to the moles of double bonds initially present (Fig. 9). It can be seen that the curves approach a limit only after a particular ratio of the concentrations. In both lattices, a maximum level of hydrogenation is achieved only when 1.6 mol of hydrazine per mole of butadiene units are used. After reaching a maxima, the degree of hydrogenation does not increase. This is probably due to the decreased availability of double bonds and increased probability of diimide disproportionation. The curve for SBR-28 lies below that of SBR-17 at all hydrazine concentrations, indicating a higher hydrogenation rate for SBR-17 due to larger number of double bonds present. The stoichiometry of the diimde reduction showed earlier<sup>15</sup> that a large excess (at least twofold) of diimide precursors with respect to the multiple bond to be reduced is necessarily required in order to compensate for the loss of anti (trans)-diimides which are inactive for reduction and also the concurrent disproportionation of diimide:

$$HN = NH \rightarrow N_2 + H_2$$
$$2HN = NH \rightarrow N_2 + NH_2NH_2$$

In Figure 9, it is observed that the degree of hydrogenation increases linearly with increase



Scheme 1



**Figure 9** Effect of hydrazine, hydrogen peroxide, and catalyst concentration on degree of hydrogenation for SBR-17 and SBR-28.

in the concentration of hydrazine even if the equivalent of the hydrazine used is less than/or equal to one.

# Dependence of Degree of Hydrogenation on Hydrogen Peroxide Concentration and the Influence of Styrene Content

The degree of hydrogenation is plotted against the ratio of the moles of hydrogen peroxide to the moles of the double bond initially present for SBR samples with 17 and 28% styrene levels (SBR-17 and SBR-28) in Figure 9. The results show that a lesser amount of hydrogen peroxide is needed to reduce the latex with a higher styrene content. In the latex reduction process, hydrogen peroxide acts as an oxidant.<sup>16</sup> The main function of hydrogen peroxide is to convert hydrazinium carboxylate (produced from the reaction of hydrazine with an ionic surfactant) to a transient intermediate diimide, which is capable of reducing the olefinic bonds. Hydrogen peroxide may promote the crosslinking reaction as well. Also, it may take part in the oxidation of double bonds. The chance of a crosslinking reaction increases with increase in the olefin content. Now, as the styrene content increases, the chance of peroxide crosslinking and an oxidation reaction decreases due to less availability of the double bonds. So, a comparatively lesser amount of hydrogen peroxide is needed for the diimide hydrogenation of SBR latex with a higher styrene content.

It is seen that for SBR-28 1.6 mol of hydrogen peroxide (per mole of the double bond) is needed to reduce 1.6 mol hydrazine (per mole of the double bond). On the other hand, in the case of SBR-17, a 2.1 mol equivalent of hydrogen peroxide is consumed for the oxidation of 1.6 mol equivalent of hydrazine. The stoichiometry of diimide reduction requires 1 mol of hydrogen peroxide per mole of hydrazine.

$$\begin{split} \mathrm{NH}_{2}\mathrm{NH}_{2} + \mathrm{H}_{2}\mathrm{O}_{2} + \mathbf{C} &= \mathbf{C} \longrightarrow \mathrm{N}_{2} \\ &+ 2\mathrm{H}_{2}\mathrm{O} + \mathrm{H}_{-}\mathbf{C}_{-}\mathbf{C} - \mathrm{H} \end{split}$$

A higher amount of hydrogen peroxide for SBR-17 may be due to the consumption of  $H_2O_2$  for the crosslinking or oxidation of the double bonds.

# Dependence of Degree of Hydrogenation on Catalyst Concentration and the Influence of Styrene Content

The degree of hydrogenation is plotted against the moles of the Cu(II) sulfate catalyst per mole of the double bonds initially present for SBR-17 and SBR-28 in Figure 9. As usual, the degree of hydrogenation initially increases with increase in the catalyst concentration, passes through a maxima, and then decreases. It is also seen from the figure that SBR latex with a higher styrene content requires a higher amount of the catalyst for optimization.

In latex, each polymer particle is surrounded and stablized by soap molecules<sup>7</sup> (anionic soaps of



Figure 10 Arrhenius plots of SBR-17 and SBR-28.

fatty acids are used as an emulsifier). It has been reported that when an aqueous solution of the Cu(II) sulfate catalyst is added to the latex the Cu(II) ion resides on the polymer particle/soap interface.<sup>7</sup> Diimides are generated rapidly at the interface. In the latex-reduction process, cupric ion [Cu(II)] appears to be an oxidant, and hydrogen peroxide which is present in the solution constantly regenerates it from the Cu(I) state. There was no evidence that it had any effect on the reactivity with the double bond.<sup>17</sup> The Cu(II) ion only accelerates the rate of oxidation of hydrazine, that is, it enhances the rate of the formation of diimide. Now, as the styrene content of the latex increases, the stabilization of Cu(II) on the polymer particle/soap interface decreases due to the steric hindrance and higher stiffness of the chain. Hence, a higher amount of the catalyst is required to optimize the latex with a higher styrene content.

# Kinetics of SBR Hydrogenation and Influence of Styrene Content

The kinetics of the diimide reduction of the SBR copolymer with 17 and 28% styrene content (SBR-17 and SBR-28, respectively) was studied. Assuming that the hydrogenation is a first-order

reaction in the olefinic substrate, the reaction rate can be represented according to the following equation:

$$\frac{-d[C=C]}{dt} = k'[C=C]$$
$$= k'[1 - x_{A}]$$

where  $x_A$  is the fraction of double bond hydrogenated and k' is the first-order rate constant. The values of k' at different temperatures ranging from 298 to 328 K are determined from the straight line plot of  $-\ln(1 - x_A)$  against the reaction times for SBR-17 and SBR-28. These reaction rates are then further plotted against 1/T on a semilogarithmic form for the determination of the activation energy. Figure 10 shows such an Arrhenius plot for SBR-17 and SBR-28. The values of the activation energy for the hydrogenation of SBR-17 and SBR-28 are found to be 9.5 and 29.0 kJ/mol, respectively. At room temperature (298 K), the apparent activation enthalpy is estimated to be 7.0 and 26.5 kJ/mol, respectively. The high activation energy for the SBR samples with a high styrene content is due to the difficulty in approaching the incoming diimides toward the



**Figure 11** Relationship between percent styrene content and  $T_g$  of SBR. Inset represents relationship between percent styrene content and  $T_g$  of HSBR.

double bond in the presence of the bulky aromatic ring of the styrene unit and the higher stiffness of the chain.

# Influence of Styrene Level on the Thermal Properties of SBR and HSBR: DSC Results

Figure 11 shows that a linear relationship exists between the  $T_g$  and the weight percent styrene content of SBR. Decreasing styrene levels of the polymer lowers the  $T_g$  value. As the styrene level increases, due to the bulk effect, the flexibil-

ity of the chain decreases, that is, the segmental mobility decreases.<sup>18</sup> Hence, with increase in the styrene level, the  $T_g$  value linearly increases. The linear relationship is predicted by the Gordon–Taylor equation<sup>19</sup>:

$$T_g = \sum (T_{g_i} W_i)$$

where  $T_g = T_g$  of the copolymer,  $T_{g_i} = T_g$  of the homopolymer, and  $W_i$  = weight fraction of monomer *i* present in the copolymer.

The experimental points are in accord with the theoretical prediction. It is apparent from the inset of Figure 11 that the  $T_g$  of the HSBR samples (80–85% hydrogenated) is higher than that of the parent SBRs at all styrene levels. The increase in the  $T_g$  value with saturation may be because the amorphous segments are gradually being replaced by crystalline segments in the HSBR. A similar observation was made by Parker.<sup>9</sup> It is also apparent from Figure 11 that the measured  $T_g$  values do not change with increase in the styrene content for the HSBR samples, although the Gordon–Taylor equation predicts a continual decrease in the  $T_g$  with a lower weight of styrene content. A similar observation was reported by Brown et al.<sup>20</sup> for HNBR with an ACN content below 40%.

#### TGA Results

Table I compares the TGA results of the SBR and HSBR samples with 17 and 28% styrene content. High  $T_{10}$  values of HSBRs in a nitrogen atmosphere are indicative of a higher thermal stability

Samples	Styrene Content (%)	Level of Hydrogenation (%)	$\begin{array}{c} T_{10} \\ (^{\circ}\mathrm{C}) \end{array}$	Maximum Decomposition Temperature $(T_{\text{max}} \circ C)$
Nitrogen atmosphere				
SBR-17	17	0	412	(i) 372, (ii) 450
HSBR-17	17	82	431	(i) 462
SBR-28	28	0	394	(i) 381, (ii) 449
HSBR-28	28	80	410	(i) 458
Air atmosphere				
SBR-17	17	0	427	(i) 427, (ii) 450
HSBR-17	17	82	404	(i) 461, (ii) 480, (iii) 540
SBR-28	28	0	404	(i) 400, (ii) 450, (iii) 477, (iv) 500
HSBR-28	28	80	383	(i) 323, (ii) 400, (iii) 450, (iv) 492

 Table I
 Parameters Evaluated from the Thermograms and Thermoderivatograms of HSBR and SBR

 in Nitrogen and Air

than that of the SBRs. It is also observed that the HSBR samples degrade in a single stage whereas two distinct stages of weight loss occur in the case of SBR. In the initial stage of degradation of SBR, the volatile products originate from the butadiene part only. Due to the unavailability of C—C bonds in the hydrogenated samples, the first step is absent. The single stage of degradation involves the scission of the main macromolecular chain. Now, on hydrogenated and —CH<sub>2</sub>—CH<sub>2</sub>— segments are generated. These —CH<sub>2</sub>—CH<sub>2</sub>— segments are relatively stable to heat due to the high bond energy of the C—C single bond.

In general, with diene-based elastomers, degradation resistance is related to the amount of allylic hydrogens present. Therefore, as the butadiene units in SBR become progressively more saturated, it would be expected that the thermal stability should increase. This happens in the low-temperature region only.9 Contrary to the expectation, the thermal stability of HSBR is less than that of SBR in the presence of air in the temperature range between 280 and 480°C and the thermal stability of SBR in air is higher than in nitrogen.<sup>21</sup> A similar observation was made here also. The  $T_{10}$  values for HSBRs are lower than those of SBRs. The double bonds are very susceptible to oxidation. As a result, the presence of oxygen causes chemical reactions to take place at higher temperatures, gen-

erating functional groups such as C=0 or -COOR on the main macromolecular chain. The bond energy of C=0 is considerably higher than that of the C—C or C—H bond (bond energy of C=0, C—H, and C—C are 724, 410, and 335 kJ/mol, respectively<sup>22</sup>). In addition to the sensitizing effect of unsaturated moieties toward oxidation, the ethylinic unsaturation may promote a crosslinking reaction. Crosslinks are mainly carbon–carbon bonds, but, admittedly, carbon–oxygen–carbon crosslinks have not been ruled out.<sup>23</sup> Crosslinking endows the polymer with diminished flexibility. This imparts to the crosslinked polymer a higher thermal stability.<sup>24</sup>

#### Isothermal Degradation of SBR Lattices at 593 K

Isothermal experiments were also carried out in order to investigate the effect of the styrene content on the degradation of SBR. It is found that the most suitable single temperature of degradation to compare the behavior of SBR lattices is



Figure 12 Infrared spectra of SBR degraded isothermally for (a) 0 h, (b) 1 h, (c) 2 h, (d) 4 h, and (e) 6 h.

593 K. Figure 12 displays the IR spectra of the SBR-28 sample degraded isothermally at 593 K. The peak values and their assignments from the polymer were reported in an earlier section. In the course of degradation, a new peak at  $807 \text{ cm}^{-1}$ 



**Figure 13** Relative change of absorbance factors accompanying loss of vinyl and 1,4-butadiene (*cis* + *trans*) units of SBR and relative change of *cis/trans* ratio at different times at a constant temperature of 593 K.

appeared which may be due to the formation of a cyclized ring. The absorption band at 909 cm<sup>-1</sup> disappears with increase in the degradation time. As the degradation time increases, the peak intensity at 967 cm<sup>-1</sup> gradually decreases, whereas the peak at 757 cm<sup>-1</sup> increases. This may be due to *trans*-to-*cis* isomerization.<sup>21</sup>

Figure 13 shows the loss of unsaturation as determined from the decrease of the absorbance ratios

$$\frac{[A_{757}\!/A_{699} + A_{967}\!/A_{699}]_a}{[A_{757}\!/A_{699} + A_{967}\!/A_{699}]_b} \text{ and } \frac{[A_{909}\!/A_{699}]_a}{[A_{909}\!/A_{699}]_b}$$

with the degradation time, where  $A_{967}$ ,  $A_{757}$ , and  $A_{699}$  are the absorbance values of the *trans*, cis, and styrene peaks, respectively. The subscripts b and a refer to solution-cast films of the copolymers before and after degradation. It is clearly seen from the figure that the unsaturation loss of both 1,2 and 1,4 units are more prominent with a lower styrene level. The thermal degradation of the butadiene parts of SBR occurs through a series of reactions, which start at a temperature lower than those when chain scission takes place and volatile products are formed. The reactions occurring at the initial stage of degradation involving double bonds proceed through an unsaturation loss and cistrans isomerization without depolymerization.<sup>25</sup> The disappearance of double bonds has been attributed to both crosslinking and the cyclization reaction. It is known that polymers containing both 1,2 and 1,4 units of double bonds that disappear with crosslinking are mainly those of vinyl groups $^{26}$ :



The corresponding hydrogen-transfer reaction between the 1,4 unsaturated structure and the tertiary C—H centers in the 1,2 structure would be sterically inhibited. Other types of reactions involving the pendent vinyl group account for the experimentally observed formation of methyl groups in the polymer<sup>27</sup>:



The cyclization reactions can be of different types depending on the units involved<sup>28,29</sup>:



As the styrene content increases, the polymerchain flexibility decreases and cyclization becomes difficult. Polymer chains with a high styrene level cannot come sufficiently closer together due to the steric hindrance of bulky aromatic rings and crosslinking is inhibited.

It has been reported in the case of 1,4-polybutadiene that thermal isomerization (*cis-trans* isomerization) reaches an equilibrium when the *cis* form amounts to 35% of its total weight.<sup>30</sup> In the case of SBR, with increase in the styrene level, the polymer chain becomes rigid and so isomerization is difficult. It is seen from Figure 13 that the polymer film thickness normalized *cis/trans* ratio  $[(A_{757}/A_{967})_{\rm a}]$   $[(A_{757}/A_{967})_{\rm b}]$  steeply increases for SBR with a 17% styrene content, whereas the increase is somewhat less in the case of SBRs with a high styrene level. The subscripts *b* and *a* refer to polymer films before and after degradation.

# **CONCLUSIONS**

The hydrogenation of SBR was carried out by a diimide-reduction technique. The influence of the styrene content on hydrogenation and the optimization of the reaction conditions were investigated in this article. With increase in the reaction time, temperature, and concentrations of hydrogen peroxide, hydrazine, and the copper (II) sulfate catalyst, the extent of hydrogenation of SBR-28 increases initially. The maximum level of hydrogenation (92%) of SBR is achieved at 308 ± 2 K, 0.087 mol hydrazine, 0.084 mol hydrogen peroxide, and 0.016 mmol copper(II) sulfate at a 4-h reaction time. The optimum reaction time increases with increase in the styrene content. It is observed that a comparatively lower reaction temperature is necessary to optimize the SBR with a higher styrene content. A lesser amount of hydrogen peroxide is required to reduce the latex with a higher styrene level. SBR latex with a higher styrene content requires a greater amount of a catalyst for optimization. The reaction kinetics studied for SBR-17 and SBR-28 exhibit an apparent first-order dependence with respect to the olefinic substrate. A higher activation energy was found for SBR with a higher styrene content. The  $T_g$  of the SBR samples increased with increase in the styrene content. There is an increase in the  $T_g$  associated with the reduction of double bonds by hydrogenation. For the HSBR samples, the  $T_{\sigma}$  value does not change with the styrene content. The thermal stability of HSBR in a nitrogen atmosphere is higher than that of SBR irrespective of the styrene content. The stability against oxidative degradation is markedly higher for SBR due to the formation of a stable species at high temperature.

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