

Thermoplastic Elastomeric Hydrogenated Styrene–Butadiene Elastomer: Optimization of Reaction Conditions, Thermodynamics, and Kinetics

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ABSTRACT: Thermoplastic elastomeric hydrogenated styrene–butadiene (HSBR) elastomer was prepared by diimide reduction of styrene–butadiene rubber in the latex stage. The products were characterized by infrared, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy, and differential scanning calorimetry (DSC). The standard free energy change, ΔG^0 at 298°K is -44.7×10^4 kJ/mol, indicating that the formation of HSBR is thermodynamically feasible. The value of heat change of the reaction at constant volume, ΔU_T is -41.6×10^4 kJ/mol. The effect of different reaction parameters on the level of hydrogenation, calculated from nuclear magnetic resonance spectroscopy, was also investigated. The degree of hydrogenation increases with the increase in reaction time, temperature, the concentration of reactants and catalyst. A maximum of 94% hydrogenation was obtained under the following conditions: time, 4 h; temperature, $45 \pm 2^\circ\text{C}$; pH, 9.36; cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) catalyst concentration, 0.0064 mmol; hydrazine concentration, 0.20 mol; and hydrogen peroxide concentration, 0.26 mol. The diimide reduction of SBR is first-order with respect to olefinic substrate, and the apparent activation energy is 9.5 kJ/mol. The glass transition temperature increases with the increase in saturation level due to development of crystalline segments. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1151–1162, 1997

Key words: hydrogenation; styrene–butadiene rubber; thermoplastic elastomer; rubber; chemical modification; diimide

INTRODUCTION

Thermoplastic elastomers are a relatively new class of polymeric materials. Their properties are similar to those of vulcanized elastomers, though they do not need any vulcanizing agent. In addition, they can be processed like thermoplastics. The typical processing and performance properties are derived from their multiphase structure.¹ Development of thermoplastic elastomers from the existing polymers by physical and chemical modification is gaining attention recently, because of ease of manufacturing, superior pro-

cessing, improved mechanical properties, low cost, etc. We have reported a few interesting thermoplastic elastomers from the blends of rubber and plastic by phase modification.^{2,3}

A new direction in this area is to obtain thermoplastic elastomers in the latex form. They have advantages over conventional rubber latex; for example, a large number of additives used here may be avoided, and the subsequent processing steps may be shortened. Potential applications of such lattices may include gloves, thin walled tubings, paints, adhesives, rust proof coatings, fabric treatments, etc. Wideman⁴ discovered that an elastomer in latex form can be converted directly into its saturated analogue when treated with hydrazine hydrate, an oxidant, and a metal ion initiator without any requirement of pressure vessel, suit-

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able solvent, or hydrogen gas. Parker et al.⁵ later prepared hydrogenated styrene-butadiene rubber (SBR) latex by the diimide reduction technique and claimed that the material is a thermoplastic elastomer in nature. A part of the butadiene units of SBR is converted into crystalline polyethylene segments by hydrogenation. These units may crystallize even in the unstretched state under ambient conditions. However, more work is needed for understanding, as optimization of various reaction parameters and detailed properties of the modified rubber have not been dealt with. In the present work, we report on thermodynamics of the diimide reduction of the SBR latex; optimization of the process parameters by varying reaction time and temperature; pH of the latex; concentration of the catalyst, hydrogen peroxide, and hydrazine; type of catalyst under normal atmospheric condition; and, finally, kinetics of the reaction. Such studies on the high-pressure hydrogenation of nitrile rubber and carboxylated nitrile rubber have been reported earlier by us.^{6,7} It has been demonstrated that the chemical modification of nitrile rubber can yield new rubbers with improved physical and mechanical properties.⁸

EXPERIMENTAL

Materials

SBR latex, LX-110, was obtained from Nippon Zeon Co. Ltd., Japan. The styrene content was determined to be 17% by infrared (IR) spectroscopy. Hydrazine, hydrogen peroxide, catalysts (cupric sulphate, cupric acetate, cupric chloride, ferric chloride), surfactant (sodium lauryl sulphate), methanol, sodium chloride, and antifoam (silicone) were received from the standard sources. Reagent-grade chemicals and solvents were used throughout the experiments.

Latex Reduction Process

A 25.0 g quantity of SBR latex containing 83 mol % butadiene, a few drops of silicone antifoam agent, and an aqueous solution of cupric sulphate and surfactant (sodium lauryl sulphate; $C_{12}H_{25}O-SO_3Na$) were added to a 250-mL three-necked flask. A particular volume of 80% aqueous hydrazine was added to the stirred solution dropwise before warming to a specific temperature. The volume of hydrazine was varied from 2 to 12 mL (0.05 to 0.30 mol), and the temperature was varied from 25 to 55°C. At a particular temperature,

30% hydrogen peroxide was added dropwise over the specific period of time with the help of a dropping funnel. The volume of H_2O_2 was varied from 10 to 40 mL (0.09 to 0.35 mol). Antifoam agent was added periodically during the reaction as required.

The hydrogenated polymer was coagulated into a saturated solution of NaCl, washed with methanol several times, and finally dried under vacuum.

Characterization

IR Spectroscopy

Studies on IR spectroscopy were carried out by using Perkin Elmer 843 spectrophotometer by casting thin films of the reprecipitated polymer on KBr plates. The spectra were taken with 5.4 cm^{-1} resolution in the range of wave numbers from 4000 to 400 cm^{-1} at a noise level of 0.1% transmittance.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded in a Brüker 200 MHz/52 MM (coil No. 120 20 67 F) spectrophotometer using TMS as the internal standard. Deuterated chloroform was used as solvent in all the cases. A minimum of 150 scans were collected for each 1H -NMR spectrum. The degree of hydrogenation was calculated according to the procedure similar to that reported by Marshall et al.,⁹ as given below:

Degree of hydrogenation (mol %):

$$100 - \frac{[8 - 5C_S][A]/[2 + 4(A/B)][B]}{[1 - C_S]} \times 100 \quad (1)$$

where C_S is the mole fraction of styrene in HSBR; A is the integral of peaks representing protons of the residual olefinic bonds in HSBR (range: 4.6–5.8 ppm); and B is the integral of peaks representing protons of methylene chains (range: 0.25–2.8 ppm).

Derivation of Equation (1)

The proton signals observed in the 1H -NMR spectrum of HSBR due to each of the microstructures are given in Table I. Since only butadiene and styrene are assumed to be present, it can be represented as

$$1 - S = H + C \quad (2)$$

Table I Proton Signals Present in the ¹H-NMR Spectrum of Hydrogenated SBR

| Microstructure | Olefinic Area (4.6–5.8 ppm) | Aliphatic Area (0.25–2.8 ppm) |
|---------------------------------|-----------------------------|-------------------------------|
| <i>cis/trans</i> -Butadiene (C) | Two protons | Four protons |
| Hydrogenated butadiene (H) | Zero protons | Eight protons |
| Styrene (S) | Zero protons | Three protons |

where *S* is the total number of protons in styrene unit; *H* is the total number of protons in the hydrogenated butadiene part; and *C* is the total number of protons in the butadiene unit.

Hence, the level of hydrogenation can be represented as

$$1 - \frac{(\text{mol fraction of } C)}{\text{mol fraction of } (C + H)} \times 100$$

The value of *C* can be obtained by using the ratio of the olefinic to aliphatic area of the ¹H-NMR spectrum, as follows:

$$\frac{\text{olefinic area } (A)}{\text{aliphatic area } (B)} = \frac{2(C)}{8(H) + 4(C) + 3(S)} = R \text{ (say)} \quad (3)$$

However, $H = 1 - S - C$ from eq. (2).

$$R = \frac{2C}{8(1 - S - C) + 4C + 3(S)} \quad (4)$$

$$C = \frac{[8 - 5(S)]R}{2 + 4(R)} \quad (5)$$

after substituting the values of *H* and *C* in eq. (3).

Degree of hydrogenation (mol %):

$$100 - \frac{8 - 5(C_S) \cdot A}{2 + 4(A/B) \cdot B} \times 100 \quad (6)$$

Differential Scanning Calorimetry

The glass transition temperature was obtained from differential scanning calorimetry (DSC) using a Dupont 9000 thermal analyzer (Model 910). The samples were initially cooled to -100°C and then heated to 150°C with a heating rate of $20^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. Liquid nitrogen was used to achieve the subambient temperature. The thermograms were recorded during the second heating. The glass transition temperature (T_g) was taken as the midpoint of the step in the scan.

Thermodynamics

The equilibrium conversion of the reaction and the standard free energy change (ΔG^0) at 298°K and a higher reaction temperatures are evaluated theoretically. The calculations are based on the following reaction scheme.

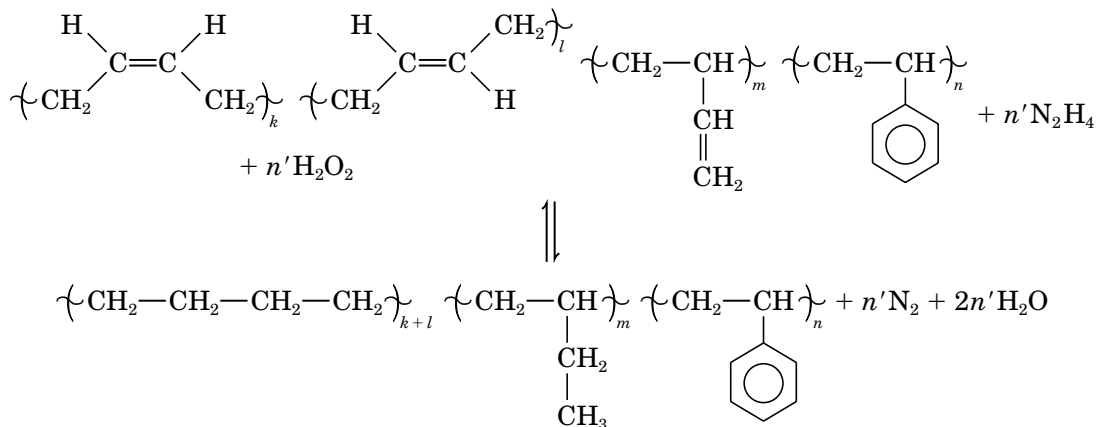


Table II Thermodynamic Parameters at Room Temperature (298 K)

| Sample | ΔH° , 298 K (kJ/mol) | ΔS° (kJ/mol K) | a | $b \times 10^2$ | $c \times 10^4$ |
|-----------------------------------|--------------------------------------|--------------------------------|---------|-----------------|-------------------------|
| SBR (17 mol % styrene) | -53183.09 | 325.98 | -689.02 | 7253.41 | -441.59 |
| N ₂ H ₄ (l) | 50.82 | 121.67 × 10 ⁻³ | 8.36 | 1.47 | 0.13 |
| H ₂ O ₂ (l) | -188.50 | 110.04 × 10 ⁻³ | 13.02 | -0.27 | 0.08 |
| H ₂ O (l) | -285.83 | 69.95 × 10 ⁻³ | 11.20 | 0.72 | — |
| N ₂ (g) | 0 | 191.50 × 10 ⁻³ | 6.76 | 0.06 | 0.13 × 10 ⁻² |
| HSBR | -143393.92 | 311.30 | -328.74 | 8095.56 | -477.86 |

where k is the number of 1,4 cis units of SBR; l , the number of 1,4 trans units of SBR; m , the number of 1,2 olefinic groups in SBR; n , the number of styrene units in SBR; and

$$n' = k + l + m \quad (7)$$

In the present study, the number of k , l , m , and n for SBR containing 17 mol % styrene, as calculated from IR spectra, are 83, 526, 157, and 81, respectively.

The relationship used for calculation of ΔG^0 at room temperature (298 K) is given by

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

where ΔH^0 and ΔS^0 are the standard enthalpy change and standard entropy change of the reaction, respectively.

ΔH^0 and ΔS^0 values of N₂H₄, H₂O₂, H₂O, and N₂ are available from the literature.¹⁰ ΔH^0 and ΔS^0 of SBR and hydrogenated SBR were calculated from group contribution.¹¹ ΔG^0 values at higher reaction temperatures have been calculated according to the following relationship:

$$\Delta G^0 = \Delta H_0 - \Delta aT \ln T - \left(\frac{1}{2}\right)\Delta bT^2 - \left(\frac{1}{6}\right)\Delta cT^3 + IT \quad (9)$$

and

$$\Delta H^0 = \Delta H_0 + \Delta aT + \left(\frac{1}{2}\right)\Delta bT^2 + \left(\frac{1}{3}\right)\Delta cT^3 \quad (10)$$

The coefficients a , b , and c for N₂ and water were obtained from the literature,¹² and those for hydrazine, hydrogen peroxide, SBR, and HSBR were calculated by a group contribution method reported by Rihani and Doraiswami.¹³ All necessary data are listed in Table II. The integration constant I and ΔH_0 have been calculated by incorpo-

rating the values of ΔG^0 and ΔH^0 at 298 K in eqs. (9) and (10).

The equilibrium constant (expressed in terms of molar units of concentration of components, assuming the system behaves almost ideally) at various temperatures has been calculated according to the following relationship:

$$\Delta G^0 = -RT \ln K_c \quad (11)$$

The values of ΔG^0 at various reaction temperatures and the corresponding K_c values are reported in Table III. It can be observed from Table III that the formation of hydrogenated SBR is thermodynamically feasible.

The integration of Vant Hoff equation gives

$$\ln K_c = -\Delta U_T/R \cdot 1/T + \text{constant} \quad (12)$$

A plot of $\ln K_c$ against $1/T$ gives a straight line with a positive slope (Fig. 1). The nature of the plot is indicative of the fact that the reaction is exothermic, and the slope of the line gives the value of heat change of the reaction at constant volume $\Delta U_T = -41.6 \times 10^4$ kJ/mol.

RESULTS AND DISCUSSION

¹H-NMR spectroscopy has been used here as a primary method for determination of the degree

Table III Thermodynamics of Diimide Reduction of SBR

| | Temperature (K) | | | |
|----------------------------------------|-----------------|-------|-------|-------|
| | 298 | 308 | 318 | 328 |
| $\Delta G^\circ \times 10^{-4}$ kJ/mol | -44.7 | -44.8 | -44.8 | -44.9 |
| $\Delta H^\circ \times 10^{-4}$ kJ/mol | -42.3 | -42.2 | -42.2 | -42.1 |
| $\ln K_c \times 10^{-4}$ | 18.0 | 17.5 | 16.9 | 16.5 |

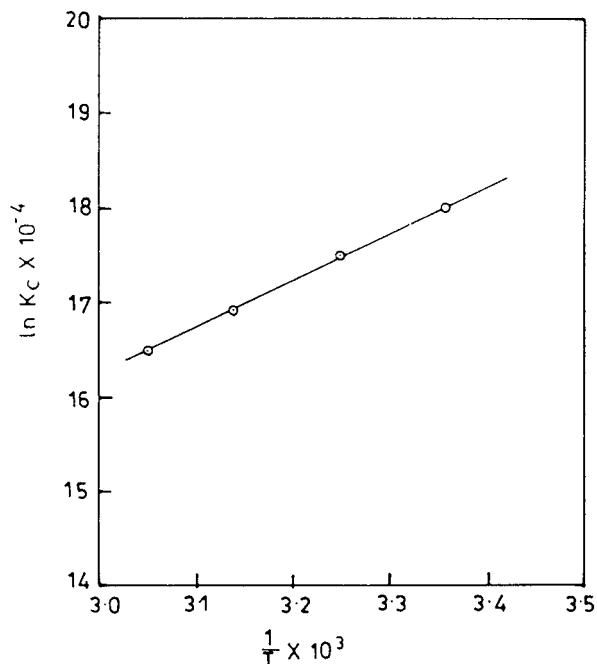


Figure 1 Plot of $\ln K_c$ versus $(1/T)$ for hydrogenation of SBR.

of hydrogenation since the identification of signals due to protons of aliphatic and residual olefinic group is unambiguous. Figure 2 shows the representative $^1\text{H-NMR}$ spectra of the control and the hydrogenated SBRs. The olefinic protons appear as a broad peak in the region of 4.6–5.8 ppm.

With the increase in the degree of hydrogenation, the peak in the olefinic region disappears gradually. Since the styrene content of the polymer is known, the degree of hydrogenation is calculated using eq. (1). For example, the degree of hydrogenation of HSBR obtained under conditions of 1 h, $45 \pm 2^\circ\text{C}$, 9.36 pH, 0.20 mol hydrazine, 0.26 mol hydrogen peroxide, and 0.015 mmol cupric sulphate catalyst is 80% [Fig. 2(b)]; and that obtained under conditions of 4 h, $45 \pm 2^\circ\text{C}$, 9.36 pH, 0.20 mol hydrazine, 0.26 mol hydrogen peroxide, and 0.0064 mmol cupric sulphate catalyst is 94% [Fig. 2(c)]. $^{13}\text{C-NMR}$ spectra corroborate the results of hydrogenation (Fig. 3). The assignment of all peaks is recorded in Table IV. With the progress of hydrogenation, the peaks in the range of 114–142 ppm gradually disappear.

The IR spectra shown in Figure 4 indicate peaks at 699 cm^{-1} due to styrene unit, 767 cm^{-1} due to 1,4 *cis*, 909 cm^{-1} due to 1,2 vinyl, and 967 cm^{-1} due to 1,4 the *trans*-butadiene unit. As the reaction time or hydrogenation level increases, the peaks due to butadiene units decrease. The aromatic ring of the styrene unit remains unaffected (there is no change in the intensity of the peak). After 1 h of hydrogenation, the absorption band at 909 cm^{-1} disappears (Fig. 4). The reactivity of 1,2-vinyl, 1,4-butadiene units are as follows: 1,2-vinyl > 1,4-butadiene. Figure 5 shows the IR spectra of the pure and the hydrogenated polymers at 70 and 94% hydrogenation level over the

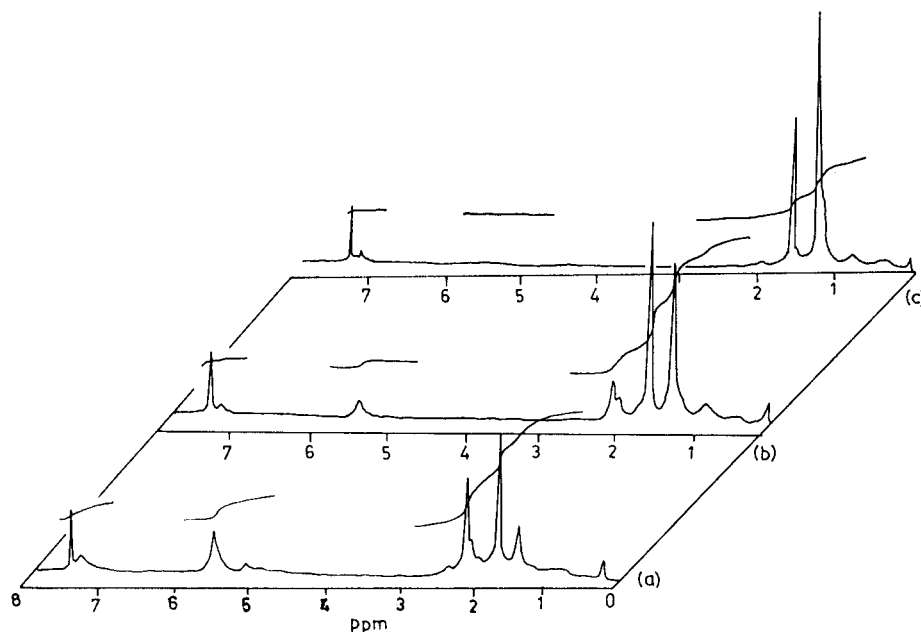


Figure 2 $^1\text{H-NMR}$ spectra of (a) SBR, (b) HSBR with 80% hydrogenation, and (c) HSBR with 94% hydrogenation.

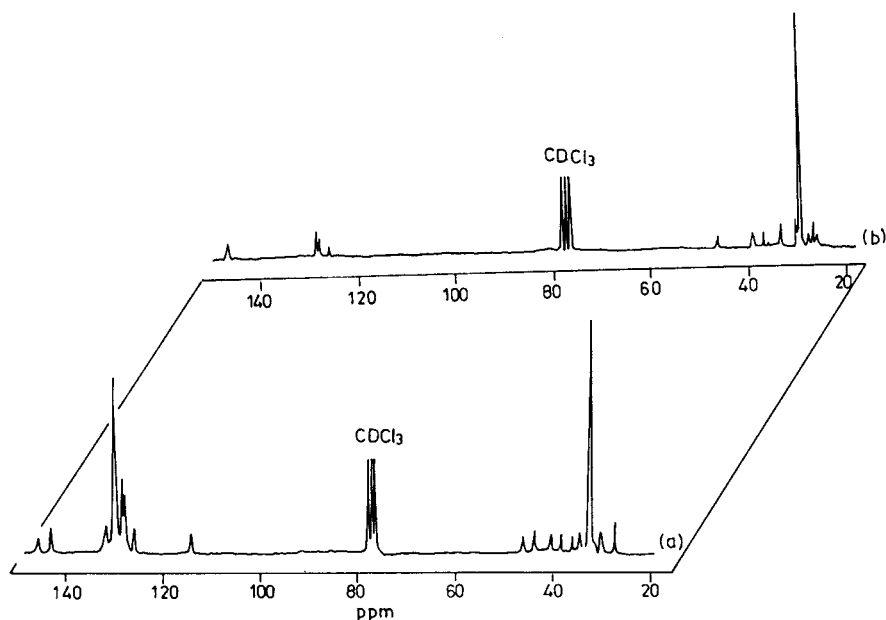


Figure 3 ^{13}C -NMR spectra of (a) SBR and (b) HSBR with 94% hydrogenation.

whole region. The peak due to $\text{C}=\text{C}$ (1,4-trans) at around 967 cm^{-1} is successively replaced by a new peak at 723 cm^{-1} due to CH_2 rocking vibration [$w(\text{CH}_2)_{n>4}$] in the polymethylene segment.

The glass transition temperature (T_g) of the pure and the hydrogenated samples have been determined. These are reported in Table V. With an increase in the level of hydrogenation, the glass transition temperature (T_g) of the amorphous rubber phase increases gradually. There is an increase of T_g by 13°C at 94% hydrogenation, as compared to the control sample. This may be due to the fact that the amorphous segments are gradually being replaced by the crystalline units in the HSBR. A similar observation was made by Parker et al.⁵

Optimization of Reaction Conditions

The hydrogenation reaction has been carried out by varying different parameters, such as time, temperature, pH of the latex, reactants and catalyst concentrations, and types of catalyst. The effect of these parameters on the level of hydrogenation has been studied.

Effect of Reaction Time

The effect of reaction time has been studied at $45 \pm 2^\circ\text{C}$ in the presence of 0.2 mol hydrazine, 0.26 mol hydrogen peroxide, and 0.015 mmol cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) as catalyst, and at a pH

of 9.36. The results over a range of times from 0 to 360 min are plotted in Figure 6. With the increase in reaction time, the percent of conversion increases. Maximum conversion of 80% is attained after 1 h. The extent of hydrogenation is not increased further with an increase in reaction time. Parker et al.¹⁵ reported the maximum level of hydrogenation of 96% at $45\text{--}50^\circ\text{C}$ after 7 h using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a catalyst. The increased level of hydrogenation at longer time is due to the reaction of larger number of double bonds with diimide. The concentration of the double bonds gradually reduces with time, as shown in Figure 4. After 1 h, all the double bonds are exhausted for reaction.

Effect of Reaction Temperature

The hydrogenation reaction has been studied from 25 ± 2 to $55 \pm 2^\circ\text{C}$ in the presence of 0.20 mol hydrazine; 0.26 mol hydrogen peroxide; a pH of 9.36; and 0.015 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst for 1 h. The extent of hydrogenation increases with the increase in temperature up to $45 \pm 2^\circ\text{C}$ (Fig. 7). A maximum conversion of 80% is achieved at that temperature. After that, the degree of hydrogenation decreases slightly. This may be due possibly to the crosslinking at higher temperatures which reduces the number of reaction sites, that is, available double bonds and the mobility of the rubber in the emulsion.

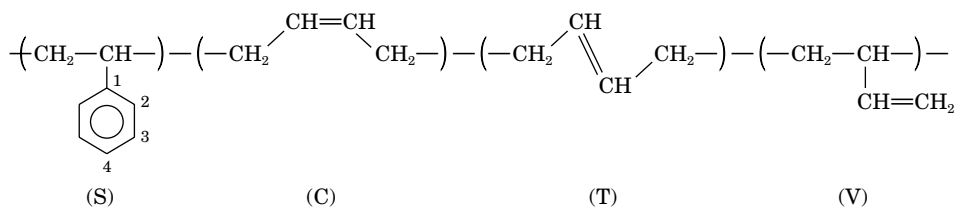
Table IV ^{13}C -NMR Assignments for SBR Polymer¹⁴

| Peak Chemical Shift (in ppm) | Polymer ^a | Carbon Type ^b | Sequence ^c |
|------------------------------------|----------------------|-----------------------------------|-------------------------------------------------------------|
| Saturated Carbon Region | | | |
| 27.4 | BD | C _{CH₂} | CC, CT |
| 30.1 | BD | T _{CH₂} | TV _{CH₂} |
| 30.4 | BD | T _{CH₂} | TS _{CH₂} |
| 32.7 | BD | T _{CH₂} | TT, TC |
| 34.0 | BD | V _{CH₂} | V (T or C) |
| 35.7 | S | S _{CH₂} | SBD _{1,4} |
| 38.1 | BD | T _{CH₂} | TV _{CH} |
| 39.3 | BD | V _{CH} | VVV |
| 40.1 | BD | T _{CH₂} | TS _{CH} |
| 42.7 | S | S _{CH₂} | SSS |
| 43.5 | BD | V _{CH} | V (T or C) |
| 45.7 | S | S _{CH} | SBD _{1,4} |
| Unsaturated Carbon Region | | | |
| 114.2 | BD | V _{CH₂} | All |
| 125.8 | S | C ₄ | All |
| 127.8 | BD | T _{CH} , C _{CH} | TS _{CH₂} , CS _{CH₂} |
| 128.1 | S | C ₃ , C ₅ | All |
| 128.3 | S | C ₂ , C ₆ | All |
| 128.5 | BD | T _{CH} , C _{CH} | TV _{CH₂} , CV _{CH₂} |
| 129.4 | BD | C | CCT, TCT |
| 130.0 | BD | T | TTT, TTC |
| 131.4 | BD | C, T | CV _{CH} , TV _{CH} |
| | BD | C, T | CS _{CH} , TS _{CH} |
| 142.7 | BD | V _{CH} | All |
| 145.4 | S | C ₁ | All |

^a BD, butadiene; S, styrene.

^b T, *trans*; C, *cis*; V, vinyl; S, styrene; C₁, carbon 1 on a styrene ring.

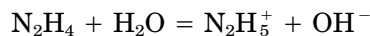
^c C, *cis*; T, *trans*; V, vinyl, and S, styrene, in the following.



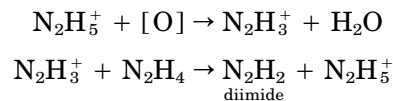
Effect of pH of the Latex

The effect of pH of the latex on the extent of hydrogenation was studied in the presence of 0.20 mol hydrazine; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at a temperature of $45 \pm 2^\circ\text{C}$ for a time period of 1 h. A maximum level of hydrogenation of 80% is observed at a pH of 9.36 (Fig. 8).

The solution of hydrazine in water is basic in nature. The reaction between hydrazine and water is represented by the following equilibrium:



Aylward and Sawistowska¹⁶ proposed the mechanism of formation of diimide by oxidation of hydrazonium ion, as follows.



The rate of hydrogenation decreases with an in-

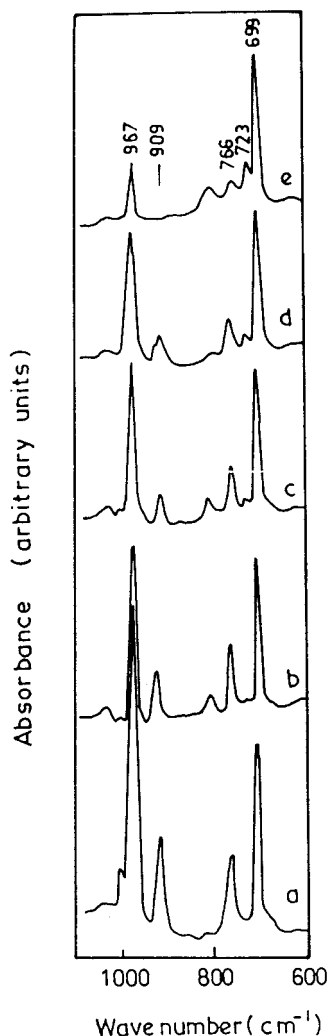


Figure 4 IR spectra of SBR samples taken at different times: (a) 0, (b) 10, (c) 20, (d) 30, and (e) 60 min of hydrogenation at a temperature of $45 \pm 2^\circ\text{C}$, a pH of 9.36, 0.2 mol hydrazine, 0.26 mol hydrogen peroxide, and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst.

crease with pH ($\text{pH} > 9.36$), owing to the decrease in the concentration of hydrazonium ion at higher pH. Also, at a higher pH, decomposition of hydrogen peroxide (the oxidant) may take place.

Effect of Concentration of Hydrazine

The concentration of hydrazine has been varied from 0.05 to 0.3 mol at $45 \pm 2^\circ\text{C}$ temperature in the presence of 0.26 mol hydrogen peroxide and 0.015 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst, at a pH of 9.36 for 1 h reaction time. The results are plotted in Figure 9. The conversion is maximum (80%) at 8 ml 80% hydrazine (0.20 mol). After that, the

degree of hydrogenation remains almost constant. Parker et al.¹⁵ reported that the addition of excess hydrazine with respect to surfactant concentration results in no visible effect in the appearance or stability of the latex. However, an exothermic heat of mixing is observed.

Effect of Concentration of Hydrogen Peroxide

The effect of hydrogen peroxide concentration on the degree of hydrogenation has been studied in the presence of 0.20 mol hydrazine, 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst for a time period of 1 h, at a pH of 9.36 and at $45 \pm 2^\circ\text{C}$ temperature. The addition of 0.26 mol hydrogen peroxide gives a maximum level of hydrogenation (80%), as shown in Figure 10. At a higher hydrogen peroxide concentration, there is possibly a crosslinking reaction taking place, which reduces the number of double bonds available for diimide reduction.

Effect of Concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Catalyst

The effect of catalyst concentration on the percentage of hydrogenation has been studied for the time period of 4 h at $45 \pm 2^\circ\text{C}$ in the presence of 0.20 mol hydrazine and 0.26 mol hydrogen peroxide and at a pH of 9.36. The concentration of the catalyst has been varied from 0.0024 to 0.028 mmol. Here, we have initially started with a very low concentration of catalyst ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Hence, the reaction has been studied for longer period of time (4 h). Maximum hydrogenation of 94% is obtained at a catalyst concentration of 0.0064 mmol (Fig. 11). At a higher concentration of the catalyst, the extent of hydrogenation is lower, which may be due to the fact that Cu(II) gets reduced to form a brown insoluble precipitate of cuprous oxide (Cu_2O) with the addition of a mild reducing agent, hydrazine; and, thus, the catalytic activity of Cu(II) decreases.

Effect of Different Catalysts

The effect of different types of catalysts on the degree of hydrogenation was also studied. All other reaction parameters, as described in the earlier section, have been kept constant. In all the cases, 0.015 mmol of the catalysts have been taken. The results are shown in the form of a bar graph [Fig. 12(a,b)]. These also indicate the effect of the cation and the anion on the degree of hydrogenation. The degree of hydrogenation is found to be maximum with cupric acetate as a catalyst.

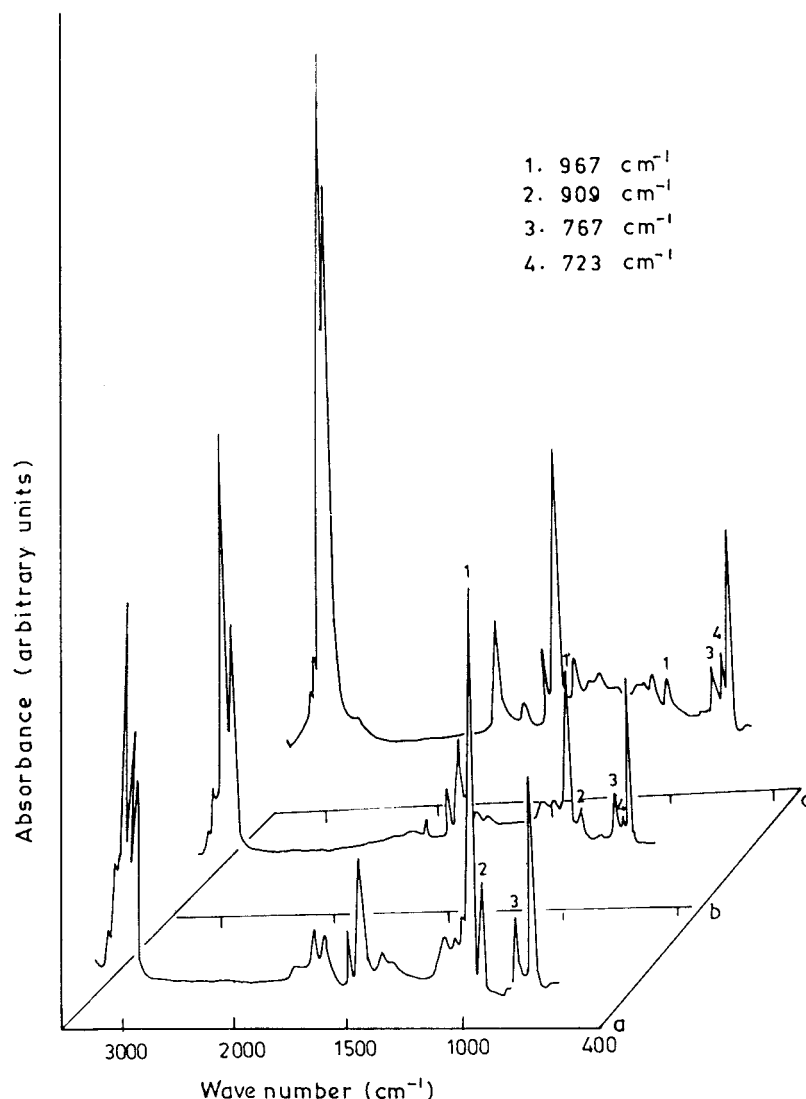


Figure 5 IR spectra of (a) SBR, (b) HSBR with 70% hydrogenation, and (c) HSBR with 94% hydrogenation.

The catalytic activity of cupric complexes is expected to depend upon two properties of the complex: (1) the basicity of the ligand, and (2) the

Table V Degree of Hydrogenation and Corresponding Glass Transition Temperature of SBR and HSBR (Containing 17 mol % Styrene)

| Sample | Degree of Hydrogenation (mol %) | T_g (°C) |
|--------|---------------------------------|------------|
| SBR | 0 | -48 |
| HSBR | 40 | -47 |
| HSBR | 66 | -42 |
| HSBR | 70 | -42 |
| HSBR | 80 | -37 |
| HSBR | 94 | -35 |

metal ligand bond strength. The catalytic activity of the complexes increases in the same order as the basicity of the ligand: $\text{Cl}^- < \text{SO}_4^{2-} < \text{CH}_3\text{-COO}^-$. On the other hand, removal of the ligand becomes increasingly difficult with the increasing strength of the metal–ligand bonding reflected in the magnitude of the formation constant (Table VI). Hence, low catalytic activity would be expected for very stable complex.¹⁷

Kinetics of SBR Hydrogenation

The kinetics of hydrogenation of SBR copolymer (17 mol % styrene content) in the presence of $\text{Cu-SO}_4 \cdot 5\text{H}_2\text{O}$ as catalyst was studied at different

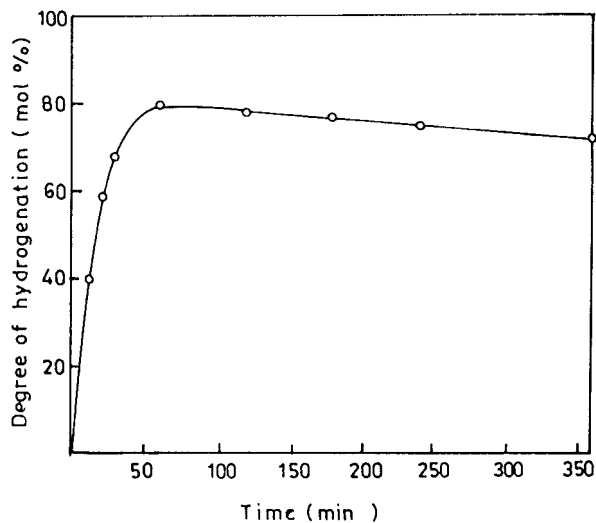


Figure 6 Effect of reaction time on degree of hydrogenation of SBR (temperature, $45 \pm 2^\circ\text{C}$; pH 9.36; 0.2 mol hydrazine; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

temperatures. Figure 6 represents the plot of the percentage of conversion with the time of hydrogenation at $45 \pm 2^\circ\text{C}$. Such a plot indicates that the reaction is apparently first-order in an olefin

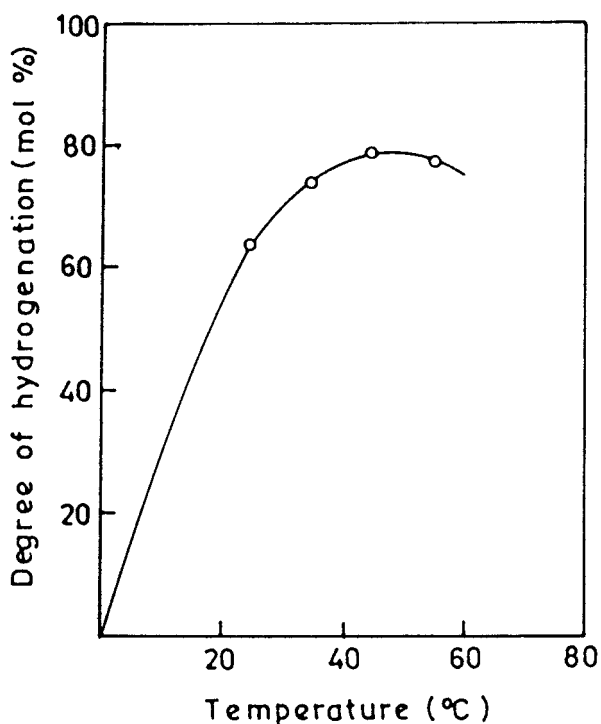


Figure 7 Effect of reaction temperature on the degree of hydrogenation of SBR (time, 1 h; pH 9.36; 0.20 mol hydrazine; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

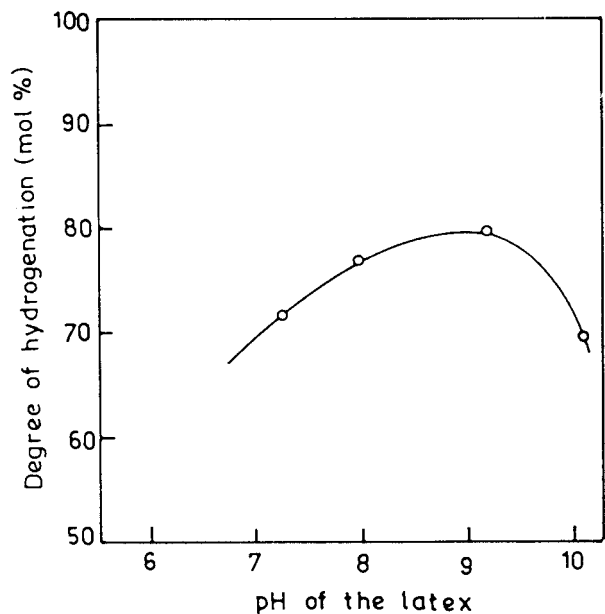


Figure 8 Effect of pH of the SBR latex on the degree of hydrogenation (time, 1 h; temperature, $45 \pm 2^\circ\text{C}$; 0.2 mol hydrazine; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

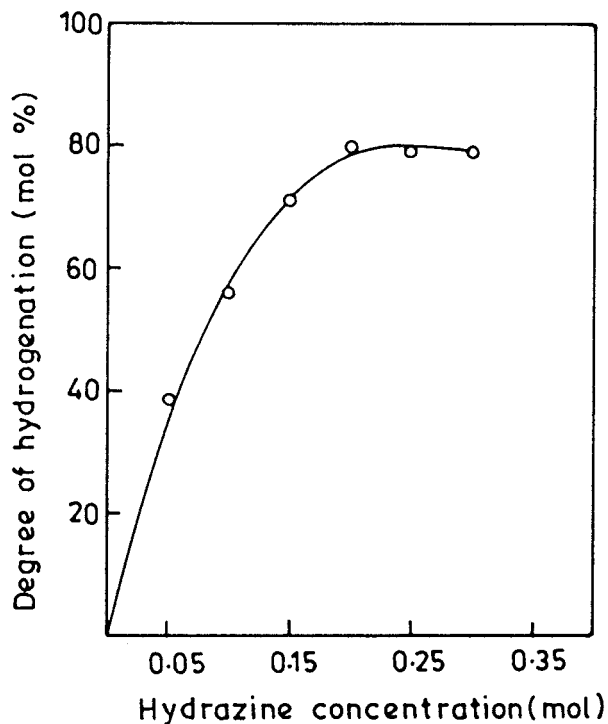


Figure 9 Effect of hydrazine concentration on the degree of hydrogenation of SBR (time, 1 h; temperature, $45 \pm 2^\circ\text{C}$; pH 9.36; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

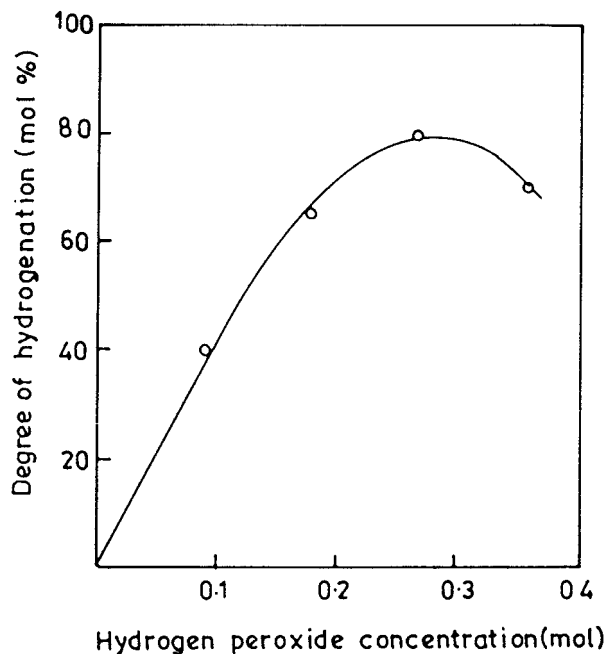


Figure 10 Effect of hydrogen peroxide concentration on the degree of hydrogenation of SBR (time, 1 h; temperature, $45 \pm 2^\circ\text{C}$; pH 9.36; 0.2 mol hydrazine; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

substrate. The first-order dependence was also reported by us for hydrogenation of nitrile rubber.⁸ The effect of temperature on the reaction rate

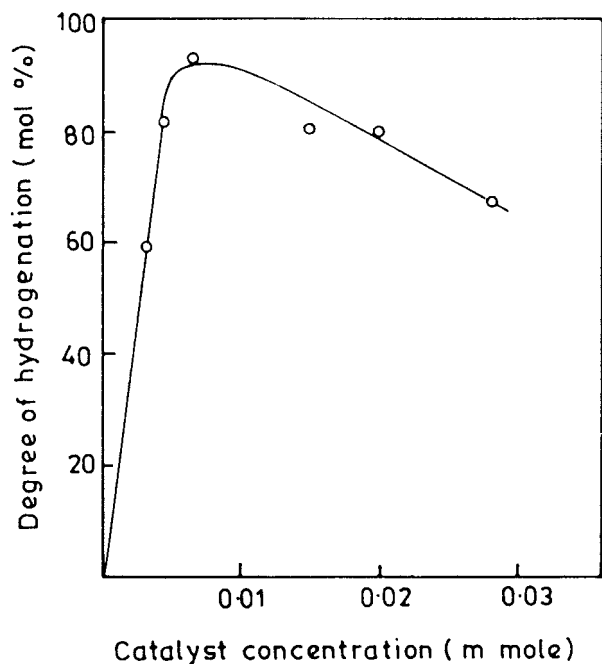


Figure 11 Effect of catalyst concentration on the degree of hydrogenation of SBR (time, 4 h; temperature, $45 \pm 2^\circ\text{C}$; pH 9.36; 0.2 mol hydrazine; and 0.26 mol hydrogen peroxide).

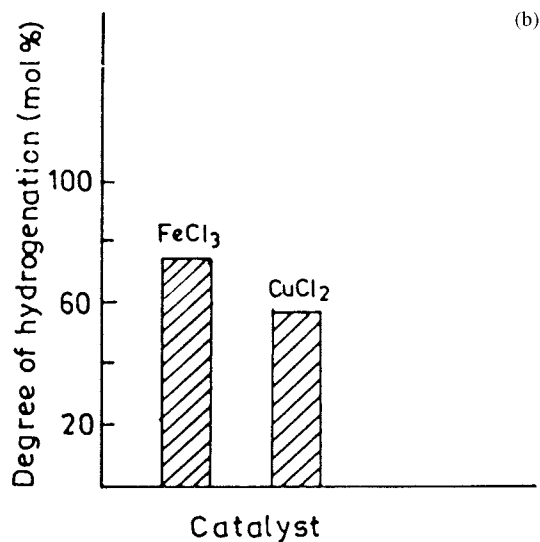
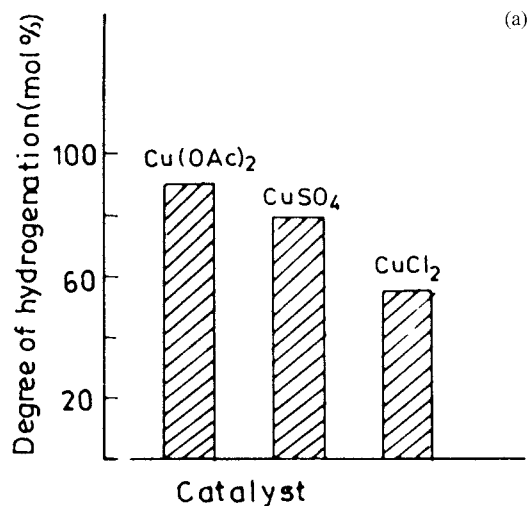


Figure 12 (a) Effect of catalyst having different types of ligands on the degree of hydrogenation. (b) Effect of catalyst with the same type of ligand but different types of metal ions. (time, 1 h; temperature, $45 \pm 2^\circ\text{C}$; pH 9.36; 0.2 mol hydrazine; 0.26 mol hydrogen peroxide; and 0.015 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst).

has also been studied. Rate constants (k_1) have been calculated from the slope of the linear plot of $-\ln(1 - X_A)$ versus time according to

$$-\frac{d(\text{H}_2)}{dt} = \frac{d(\text{C}=\text{C})}{dt} = k_1(\text{C}=\text{C}) = k_1(1 - X_A) \quad (13)$$

where X_A is the fraction of double bonds hydrogenated. A plot of $\ln k_1$ versus $1/T$ shows that the activation energy of hydrogenation is 9.5 kJ/mol.

Table VI Mean Formation Constants of Various Copper(II) Catalysts

| Complexes | Mean Formation Constant | Relative Catalytic Activity |
|----------------------|-------------------------|-----------------------------|
| Cu(OAC) ₂ | 30 | 120 |
| CuSO ₄ | 1 × 10 ² | 6.5 |
| CuCl ₂ | 5 × 10 ⁷ | < 0.5 |

At 45°C, the apparent activation enthalpy is estimated to be 6.9 kJ/mol.

CONCLUSIONS

Selective catalytic hydrogenation of SBR by the diimide reduction technique has been investigated in this article. The following conclusions have been reached.

1. The reaction is thermodynamically feasible with a value of $\Delta G^0 = -44.7 \times 10^4$ kJ/mol at 298°K. ΔG^0 values have also been calculated at 308, 318, and 328°K. The enthalpy change, ΔH^0 , is -42.3×10^4 kJ/mol.
2. The hydrogenated products have been characterized by IR, ¹H-NMR, ¹³C-NMR, and DSC. IR spectra indicate the disappearance of peaks at 909 cm⁻¹ due to complete hydrogenation of 1,2-vinyl units. Gradual reduction of the ¹H-NMR peaks in the range of 4.6–5.8 ppm and ¹³C-NMR peaks in the range of 114–142 ppm confirm the hydrogenation reaction. The degree of hydrogenation has been calculated from the ¹H-NMR spectroscopy. There is an increase of the glass transition temperature associated with the reduction of the double bonds by hydrogenation.
3. The reaction conditions have been optimized. With an increase of reaction time and temperature, concentrations of hydrogen peroxide, hydrazine, and CuSO₄ · 5H₂O catalyst, the extent of hydrogenation increases in the initial stages. 80% hydrogenation of SBR is obtained at 45 ± 2°C, 9.36 pH, 0.20 mol hydrazine, 0.26 mol hydrogen peroxide, and 0.015 mmol copper(II) sulfate for 1 h reaction time.
4. The reaction kinetics exhibit an apparent first-order dependence with respect to the olefinic

substrate. The activation energy of the hydrogenation reaction is 9.5 kJ/mol.

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