Selective Hydrogenation of Olefinic Bonds in Styrene–Isoprene–Styrene Triblock Copolymer by Palladium Acetate Catalyst

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SYNOPSIS

Homogeneous catalytic hydrogenation of styrene–isoprene–styrene triblock copolymer (SIS) has been carried out selectively at the carbon–carbon double bond in the presence of palladium acetate catalyst under mild conditions. Degree of hydrogenation has been calculated with the help of infrared and nuclear magnetic resonance spectroscopic techniques. Almost 90 mol % complete hydrogenation has been achieved at 60°C under 1.4 MPa hydrogen pressure, 40 mg catalyst (for 2 g of polymer) in chloroform–acetone solution for 1 h. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogenation of diene elastomers is an excellent example of chemical modification which improves both chemical as well as physical properties of an existing elastomer. The double bond present in the diene part of the elastomer is more susceptible to thermal and oxidative degradation. On saturating the polymer backbones, significant improvement in resistance to degradation has been obtained.[1] It has been observed that the hydrogenation extends the performance range of diene–diene and diene–aromatic block copolymers.[2] When poly(styrene–butadiene–styrene) block thermoplastic elastomer is hydrogenated, the product is poly[styrene-b-(ethylene-co-butylene)-b-styrene]. The hydrogenated product is a thermally and oxidatively more stable thermoplastic elastomer with improved tensile strength and elongation. Similarly, hydrogenation of styrene–isoprene block copolymers gives a polystyrene(ethylene-co-propylene) block thermoplastic elastomer, which can be used as a viscosity index improver for lubricating oils.[3]

Several novel methods have been developed for selective hydrogenation of olefinic unsaturation in diene polymers.[4–10] Both homogeneous and heterogeneous catalysts can be used for conversion of unsaturated polymers to saturated ones. Shahab and Basheer[11] used palladium on calcium carbonate and tris(triphenylphosphine)chlororhodium (I) for hydrogenation of natural rubber, gutta percha, and cis-1,4-polybutadiene. Polyisoprene could also be hydrogenated in heterogeneous phase by using palladium on calcium carbonate.[12] Bates and co-workers[13] synthesized a model-saturated diblock copolymer of cis-1,4-polyisoprene–1,2-polybutadiene in presence of a heterogeneous palladium catalyst. Recently, Takenaka et al.[14] used palladium on carbon and tris(triphenylphosphine)chlororhodium (I) for hydrogenation of block copolymers of styrene–butadiene and styrene–isoprene. The available literature suggests that homogeneous catalysts are preferred over heterogeneous ones because of their better selectivity. Velichkova et al.[15] developed a homogeneous catalyst based on nickel complex for hydrogenation of styrene–isoprene block copolymers. Hence, for promoting the homogeneous catalytic hydrogenation, various catalyst systems may be developed, which would facilitate better conversion to the desired products under milder reaction conditions.

Most of the effective homogeneous catalyst systems, particularly those based on transition metal complexes, are poisoned by carbonyl and other ox-

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ygen- or nitrogen-containing groups. Palladium acetate similar to the Wilkinson's catalyst is not and is much cheaper at the same time. In our earlier communication,[8] we reported that palladium acetate offers good selectivity for homogeneous catalytic hydrogenation of carbon–carbon double bonds in acrylonitrile–butadiene copolymer under a very mild reaction condition. In the present work, we report on the catalytic activity of palladium acetate for hydrogenation of styrene–isoprene–styrene triblock copolymer (SIS). The characterization of the product by infrared and nuclear magnetic resonance spectroscopies is presented here. Also, the reaction condition has been optimized by variation of reaction time, catalyst concentration, temperature, hydrogen pressure, and solvent. A possible reaction mechanism has been proposed for the hydrogenation process.

EXPERIMENTAL

Commercial sample of palladium acetate was obtained from Arora-Matthey Ltd., India. The compound was recrystallized by dissolving it in worm benzene, mixing the solution with half its volume of glacial acetic acid, and allowing the mixture to evaporate slowly at room temperature. The decomposition temperature of the recrystallized sample was 200°C. The structure of the complex is shown in Scheme 1:
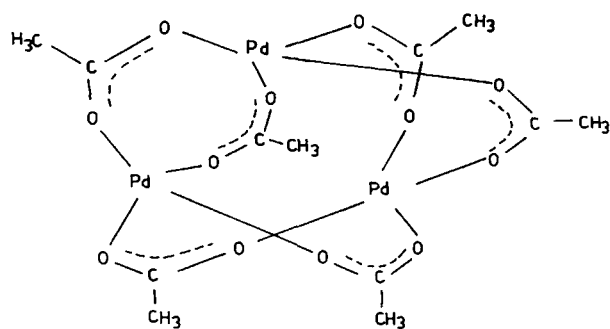
Scheme 1

Benzene, acetic acid, chloroform, ethyl acetate, ethyl methyl ketone, acetone, and methanol were used as received from commercial sources [E. Merck (India) Ltd.] with purities in excess of 99 mol %.

Styrene–isoprene–styrene triblock copolymer (Kraton D-1107) was procured from Shell Chemical Co. (USA). The styrene to isoprene ratio of the polymer is 14 : 86. Commercially available hydrogen gas (purity 99.9%) supplied by M/s. Indian Oxygen Ltd., Calcutta, was used directly.

High Pressure Autoclave[6–18]

A high pressure rocking autoclave (High Pressure Equipment Co., USA) of 300 mL capacity, having an angular play of 15° with 30 oscillations/min was used. The autoclave was electrically heated, and the temperature was controlled by a temperature controller.

Hydrogenation Procedure

The polymer sample (2 g) was dissolved in organic solvent (100 mL), and a weighed amount of the catalyst was added to the solution. The mixer was introduced into a glass liner in order to minimize the corrosion inside the autoclave. The liner was placed into the autoclave, and hydrogen gas was passed through it up to the required pressure. For reactions done at room temperature, the autoclave was kept rocking for a specific time period, and the reaction mixture was taken out. When the reactions were carried out at higher temperature, the autoclave was heated slowly to the desired temperature, and the temperature was kept constant for a definite time period with continuous rocking. The autoclave was allowed to cool down to room temperature, and the polymer was coagulated into methanol. The polymer was washed with methanol and hexane and finally dried in vacuum.

Temperature, pressure, time, and catalyst concentration were varied subsequently to study the effect of these parameters on the extent of hydrogenation.

Characterization

Studies of the samples by infrared (IR) spectroscopy were carried out using a Perkin-Elmer 843 Spectrophotometer by casting thin films of the polymer on KBr plates.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 spectrophotometer operating at 90 MHz. Deuterated chloroform was used as the solvent in all cases.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum of the SIS copolymer. The aliphatic C—H stretching appears between 2960 and 2850 cm^{-1}. The —CH$_2$— deformation vibrations absorb in the region of 1448 cm^{-1}. A sharp peak is observed at 1376 cm^{-1}, which is due
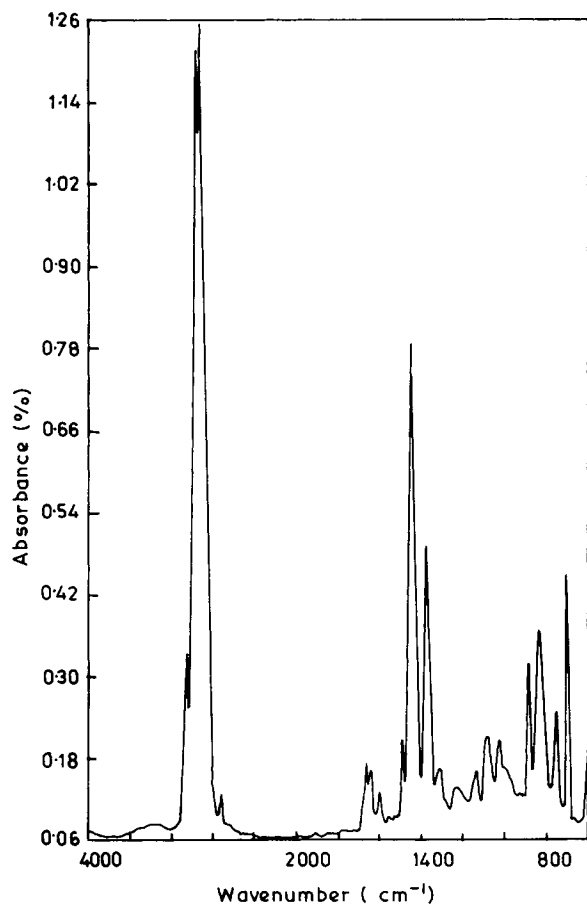
Figure 1   Infrared spectrum of SIS.

to deformation vibration of the —CH_3 group. The principal absorbance peak of SIS appears due to styrene. The characteristic absorbance band for styrene is observed at around 700 cm^{-1}. The out-of-plane deformation vibration of 3,4- and 1,4-cis double bonds is observed as sharp peaks at 889 and 837 cm^{-1}, respectively. Figure 2 represents the IR spectrum of hydrogenated SIS (HSIS). It is observed that there is no change in the styrene moiety of the polymer after hydrogenation, as no additional absorbance band appears on the spectrum. With increase in the level of hydrogenation, the peaks at 889 and 837 cm^{-1} decrease gradually. The reduction in above two peaks gives a measure of extent of hydrogenation in the product.

Nuclear magnetic resonance spectroscopy provides insight into the microstructure of the hydrogenated and nonhydrogenated block copolymers. The ^{1}H-NMR spectrum of SIS is presented in Figure 3. The signals due to protons on saturated carbon, in —CH_3 and >CH_2 microstructure appear in between 1.6 and 2.5 ppm. The aromatic protons are

observed in between 6.5 and 7.2 ppm. The signals of olefinic protons due to 1,4-unsaturation is centered at 5.1 ppm, while the 3,4-unsaturation is centered at around 4.9 ppm. Figure 4 illustrates the ^{1}H-NMR spectra of hydrogenated block copolymer. The relative integration of olefinic proton signals is reduced significantly on hydrogenation. This confirms the saturation of carbon–carbon double bonds of the isoprene unit of the polymer chain. The proton NMR spectrum also supports that the styrene unit in the polymer is not affected during hydrogenation reaction. It is evident from Figure 4 that the 3,4-unsaturation is hydrogenated faster than 1,4-unsaturation.

The method developed by Bruck[16,17] and Marshall et al.,[18] and reported by us in earlier communications,[7,8] is followed to estimate the extent of hydrogenation. Both infrared and nuclear magnetic resonance spectroscopies have been used for calculating the degree of conversion. The absorbance ratios of the peaks at 889 and 837 cm^{-1} are evaluated with
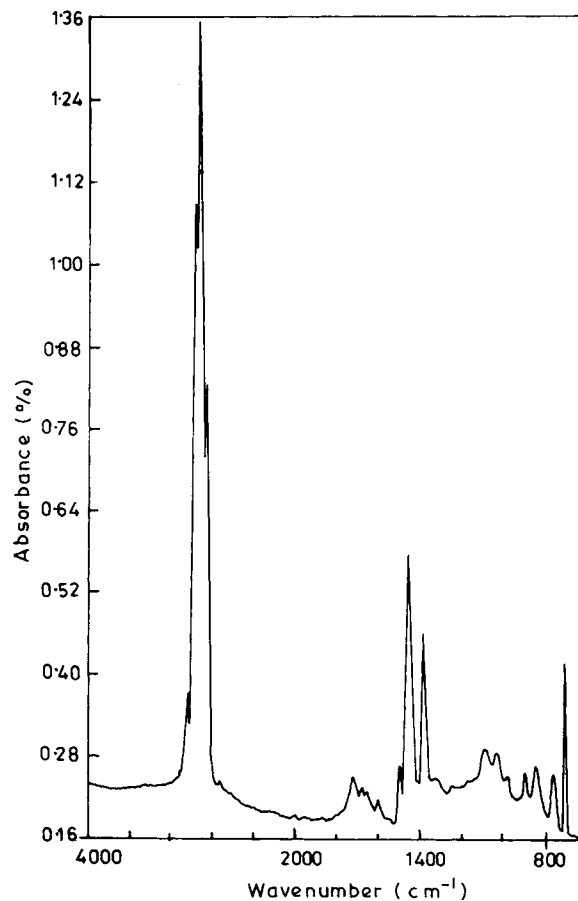

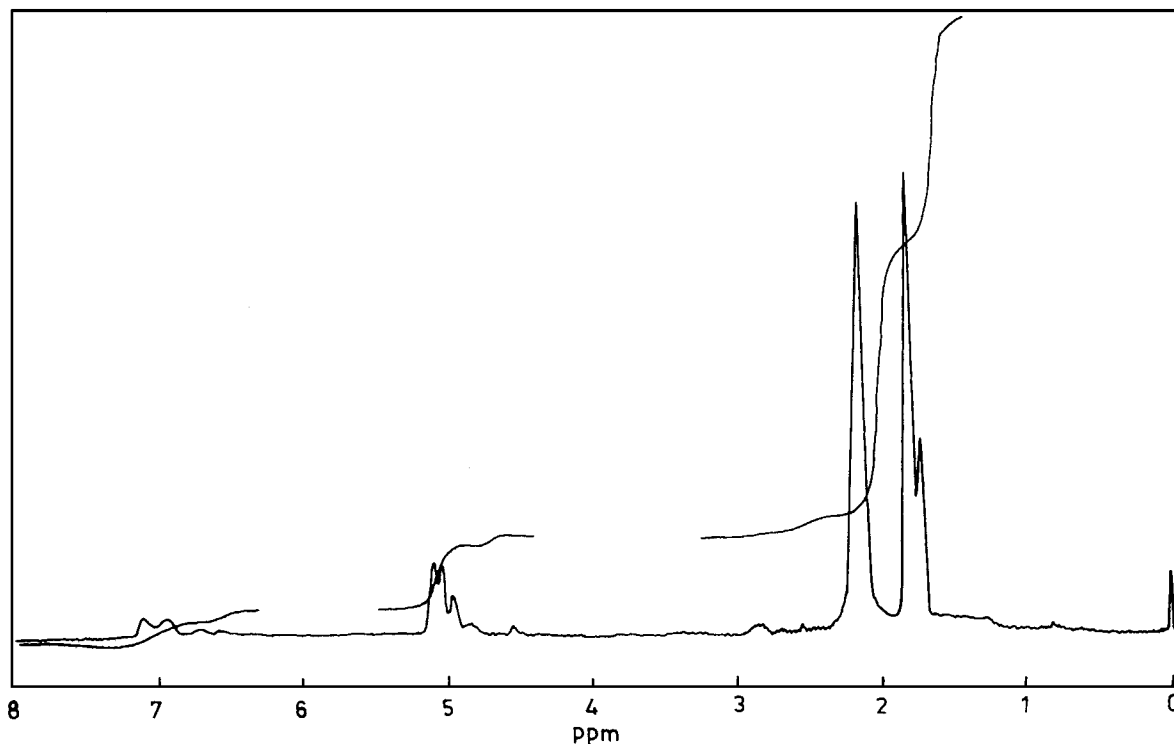**Figure 2**   Infrared spectrum of hydrogenated SIS (70 mol % hydrogenation).

Figure 3 ¹H-NMR spectrum of SIS.

respect to that of 700 cm⁻¹ due to styrene, which is taken as the internal standard. Figure 5 lists a few spectra of hydrogenated polymer, which indicates how the absorbance ratio is decreasing gradually with the progress of the reaction. The degree of hydrogenation has been calculated from ¹H-NMR spectra from the relative decrease in the integral of the peak representing protons of the residual olefinic
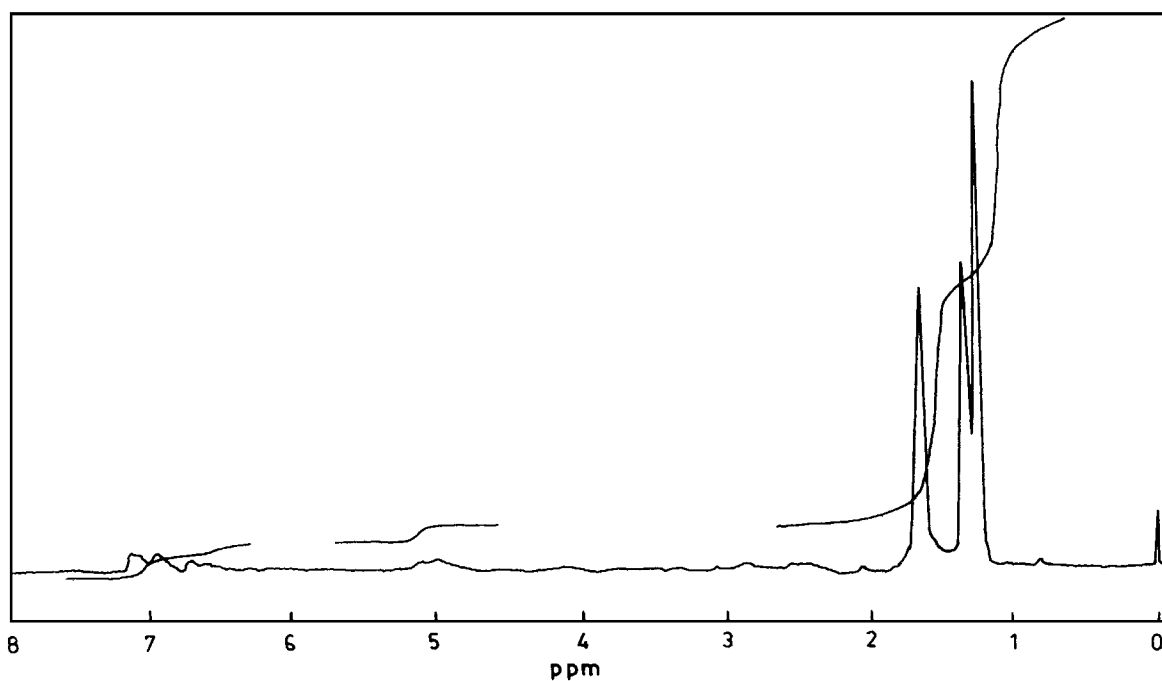

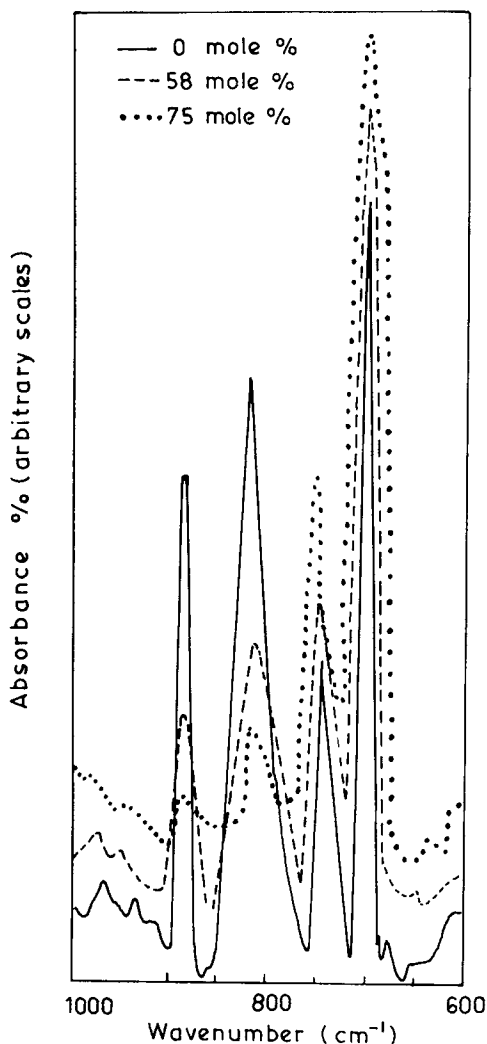**Figure 4** ¹H-NMR spectrum of hydrogenated SIS (75 mol % hydrogenation).

Figure 5 Infrared spectrum of HSIS with various degrees of hydrogenation.

drogenation has been studied. Table I describes the reaction conditions adopted for optimizing the hydrogenation process. With increase in the reaction time, the degree of hydrogenation increases. Maximum conversion takes place in 1 h reaction time. Reactions were carried out at various temperatures for 1 h. Twenty-four mole percent hydrogenation is obtained at room temperature (34°C). In an earlier communication,[8] we have reported room temperature hydrogenation of acrylonitrile–butadiene copolymer. A maximum hydrogenation of 66 mol % is achieved when the temperature is 60°C.

The optimized reaction time and temperature are preferable when compared with earlier systems requiring 90 h at 100–110°C[14] and 80–100°C for 16 h.[15] Hydrogen pressure was varied from 0.35 MPa to 1.5 MPa (Table I, reactions 3 and 7–10). A reaction pressure of 1.4 MPa is optimum for 66 mol % hydrogenation. With decrease in the catalyst concentration, the overall conversion decreases. When 40 mg of catalyst is used, the extent of reduction is maximum. The effect of solvent on the degree of hydrogenation of SIS has also been studied. It is observed that solvent plays a major role in determining the amount of conversion in the product. When chloroform is used as solvent, only 23 mol % hydrogenation takes place, whereas, in ethyl acetate and ethyl methyl ketone solution, the degree of hydrogenation is 66 and 72 mol %, respectively. A remarkable change in the product formation is observed when 1 : 1 (50 + 50 mL) chloroform and acetone is used as the solvent. Almost 90 mol % saturation is obtained. This may be explained with the help of proposed mechanism discussed later.
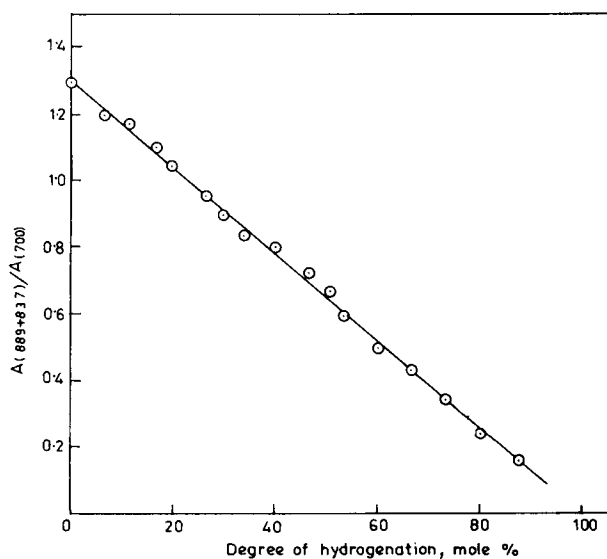
bonds with respect to the increase in the integral of aliphatic protons. Figure 6 shows a plot of absorbance ratio of 889 and 837 cm^{-1} to 700 cm^{-1} against degree of hydrogenation calculated from NMR studies. Hence, it is clearly observed that palladium acetate has a potential to be a catalyst for the hydrogenation of styrene–isoprene–styrene block copolymer. We have shown earlier from gel permeation chromatography studies that the molecular weight of the modified polymer does not change and hence there is no degradation with the use of this catalyst.[8]

Optimization of the Reaction Condition

The hydrogenation reaction has been carried out by varying different parameters such as time, temperature, pressure, catalyst concentration, and solvent. The effect of these parameters on the level of hy-


Figure 6 Infrared calibration curve for calculating degree of hydrogenation.

Table I Reaction Conditions for Hydrogenation of SIS

Sample No.	Catalyst Used for 2 g of Polymer (mg)	Hydrogen Pressure (MPa)	Temperature (°C)	Time (min)	Solvent (100 mL used)	Degree of Hydrogenation (mol %)
1	40	1.4	60	15	Ethylacetate	31
2	40	1.4	60	30	Ethylacetate	55
3	40	1.4	60	60	Ethylacetate	66
4	40	1.4	60	90	Ethylacetate	66
5	40	1.4	50	60	Ethylacetate	38
6	40	1.4	40	60	Ethylacetate	30
7	40	1.4	34	60	Ethylacetate	24
8	40	1.05	60	60	Ethylacetate	59
9	40	0.7	60	60	Ethylacetate	48
10	40	0.35	60	60	Ethylacetate	35
11	20	1.4	60	60	Ethylacetate	47
12	10	1.4	60	60	Ethylacetate	26
13	40	1.4	60	60	Chloroform	23
14	40	1.4	60	60	Ethylmethyl ketone	72
15	40	1.4	60	60	Chloroform + acetone (50 + 50 mL)	90

Hence, the optimum reaction condition for 90 mol % hydrogenation is 1.4 MPa hydrogen pressure, 40 mg catalyst (for 2 g of polymer), 60°C temperature, 1-h reaction, and 1 : 1 chloroform–acetone mixture as solvent.

The mechanism of hydrogenation using palladium acetate may be proposed in line with earlier work.[19] It is known that the palladium (II) acetate has an unusual structure comprising three metal atoms in a triangle held together by six bridging acetate groups.[20] When the complex is dissolved in a solvent, it is dissociated to form monomeric species. If the solvent contains donor atoms, the dissociation is facilitated, and the solvent occupies the vacant coordination sites of the metal atom. This active catalyst species reacts with hydrogen to form metal hydride complex. There is successive (or possibly simultaneous) coordination of olefinic bonds to the metal center and hydride transfer to the double bond site to give the saturated product (Scheme 2):
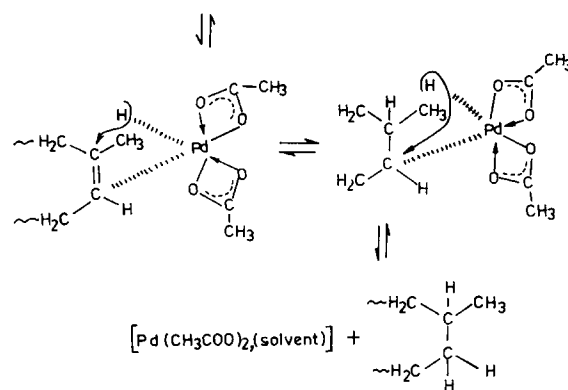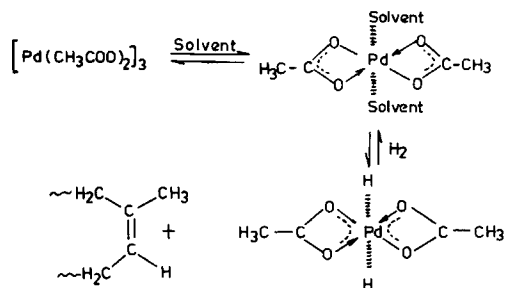
Scheme 2

Since dissociation of the complex is an important step in the process, the solvent plays the deciding role. Acetone is a better donor solvent than ethyl acetate. Hence, the degree of hydrogenation is much higher in acetone solution. It may be mentioned that hydrogenation of acrylonitrile–butadiene elastomer has been carried out in acetone solution.[8] Since SIS does not dissolve in acetone, a chloroform–acetone mixture has been used. As there is a competition between 1,4- and 3,4- double bonds for coordination with the metal center, it may be assumed that the pendent double bonds being unhindered are more easily coordinated. Hence, the 3,4- segments are hydrogenated faster than the 1,4 segments (Fig. 4).

CONCLUSIONS

The olefinic unsaturation of styrene–isoprene–styrene copolymer can be selectively hydrogenated under mild condition by using palladium acetate as a homogeneous catalyst. During the hydrogenation process, the styrene unit does not undergo any reaction. The degree of hydrogenation has been calculated from spectroscopic studies. Almost 90 mol % hydrogenation is obtained at 60°C, under 1.4 MPa hydrogen pressure, 40 mg catalyst (for 2 g polymer) in chloroform–acetone solution for a time period of 1 h.

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