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Homogeneous catalytic hydrogenation of poly(styrene-*co*-butadiene) using a ruthenium based Wilkinson catalyst*

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Summary

Poly(Styrene-*co*-butadiene) can be quantitatively hydrogenated using tris(triphenyl phosphine) ruthenium(II) chloride, $RuCl_2(PPh_3)_3$ as catalyst. The effect of temperature, pressure and catalyst concentration on both the rate and degree of hydrogenation have been studied. The hydrogenated elastomers have been characterized by IR, ^1H NMR and TGA.

Introduction

Hydrogenation is an important method for chemical modification of polymers(2). It offers a convenient route to novel polymers with desirable physical properties which are otherwise inaccessible or difficult to prepare by conventional polymerization method. For example a strictly alternating copolymer of ethylene and propylene can be prepared by the hydrogenation of synthetic cis-1,4 polyisoprene (3,4) or natural rubber (5). Hydrogenation of diene elastomers also improves the thermal, oxidative, and ozonolytic stability as well as imparts excellent resistance to oil and fluids, especially, at high temperature (6-8).

Random and block copolymers of styrene-butadiene and styrene-isoprene are useful elastomers and thermoplastic elastomers (9,10). The presence of unsaturation in these elastomers leads to poor ageing properties of the unsaturated soft phase, poor long term elastic properties at temperature as low as 20°C and rapidly decreasing tensile properties as a function of temperature (11,12). Styrene-butadiene (11,13,14) and styrene-isoprene (15,16) copolymers have been hydrogenated using Ziegler-Natta type catalysts comprising of nickel and cobalt carboxylates with alkylaluminum or alkyllithium as reducing agents. Catalysts based on metallocene-alkyl lithium (17-20) have also been used to hydrogenate these copolymers. Recently noble metal catalysts based on Rh complexes (21,22) have been explored for hydrogenation of poly(styrene-*b*-butadiene) copolymers. There is no report of hydrogenation of styrene-butadiene copolymers using Ru based catalysts which are preferable because of its significantly lower cost than Rh based catalysts. We have, therefore, explored the utility of $RuCl_2(PPh_3)_3$ as homogeneous hydrogenation catalyst for poly(styrene-*co*-butadiene) (SBR). The present paper reports the result of this study.

Experimental

All operations were conducted under dry nitrogen using standard benchtop inert atmosphere techniques.

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* Ref. 1

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Materials

Tris(triphenylphosphine) ruthenium (II) chloride (Aldrich, U.S.A), and triphenylphosphine (TPP) (E.Merck, Germany) were used as received. Poly(styrene -*co*-butadiene) (SBR) (Synaprene-1502, ML_{1+4} at 100°C = 50, Styrene = 13 mol%) was procured from Synthetic and Chemicals, Barielly, India. Toluene (AR grade, Loba) was purified by distillation under nitrogen from sodium-benzophenone ketyl.

Hydrogenation procedure

Hydrogenation reactions were carried out using a 300 mL Paar reactor. The pressure drop due to the consumption of hydrogen was followed using digital pressure transducer connected to the Paar reactor. In a typical hydrogenation procedure, SBR (0.5 g) was dissolved in 50 mL toluene. $RuCl_2(PPh_3)_3$ (0.04 g) and triphenylphosphine (0.010 g) were introduced into the reactor. The reaction was carried out at a hydrogen pressure of 30 kg/cm^2 and at 100°C for 12 h. After the reaction the product was precipitated by addition of methanol, filtered and dried in vacuo at 50°C. ^{1}H NMR ($CDCl_3$, δ, ppm) 0.84 ($-C\underline{H}_3$), 1.23 ($-C\underline{H}_2-$),

Analysis

^{1}H NMR spectra of polymers were recorded using Bruker 90 MHz NMR spectrophotometer. IR spectra were recorded on PC-16 Perkin-Elmer FT-IR spetrophotometer. Thermal analysis was performed on a Perkin-Elmer TGA-7 thermal analyzer under nitrogen atmosphere at the heating rate of 10 °C/min.

Results and Discussion

SBR was hydrogenated using $RuCl_2(PPh_3)_3$ as catalyst in the temperature range 40-100°C and 10-50 kg/cm^2 hydrogen pressure. Complete hydrogenation was achieved using 0.7 mole % catalyst at 100°C and 40 kg/cm^2 hydrogen pressure. ^{1}H NMR and IR spectra showed that SBR had three different microstructures: trans (65 mol%), vinyl (15 mol%) and cis (20 mol%). Upon hydrogenation the characteristic peaks for all types of unsaturation, 966 cm^{-1} (C-H bending for trans content), 911 cm^{-1} (C-H wagging for vinyl group) and 736 cm^{-1} (C-H wagging for cis content) (Figure-1) disappear confirming near quantitative hydrogenation. In the ^{1}H NMR spectrum of hydrogenated (Figure-2) the peaks at 5.40 ppm (for olefinic protons of 1,4 polybutadiene content) and 4.90 ppm (for olefinic protons of 1,2 polybutadiene content) are not present. New peaks appeared at δ = 0.80-1.30 ppm for saturated aliphatic protons.

Hydrogenation of SBR was carried out under a range of experimental conditions. There are reports (23,24) that in the absence of added triphenylphosphine the Wilkinson type

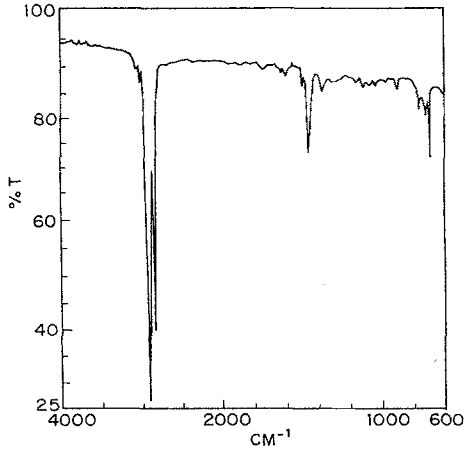


Fig.1. IR spectrum of Hydrogenated Styrene-butadiene copolymer (HSBR)

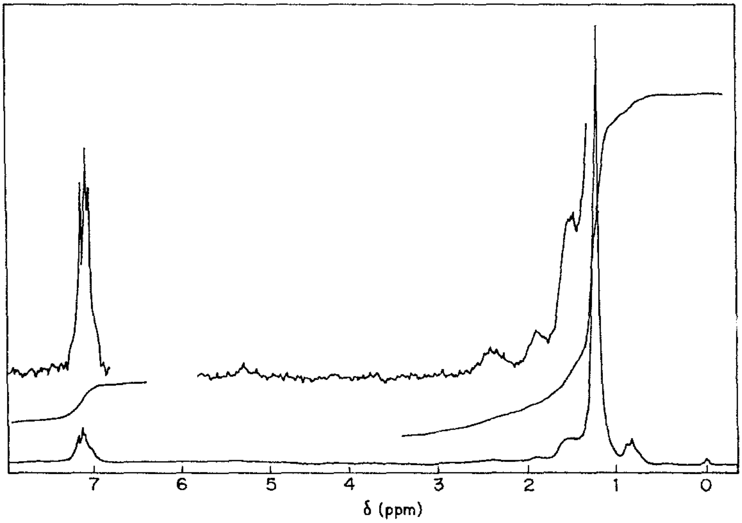


Fig.2. ^{1}HNMR spectrum of HSBR

catalysts form dimers which complicate the nature of reactions mechanisms. Therefore, all the experiments were carried out in presence of added triphenylphosphine. A representative plot of hydrogen consumption (Figure-3) indicates that the reaction is first order with respect to the concentration of the double bond. The apparent first order reactions rates (*k*) were calculated from the slope of the plot of ln[C=C] vs time (Figure-4). The apparent activation energy of hydrogenation reactions was calculated as 41.1 Kj/mole. The apparent activation enthalpy and entropy were estimated as 37.90 Kj/mol and -158.0 J.mol^{-1}K^{-1} respectively. These values have been compared with those reported for other unsaturated polymers (Table-1). The higher negative value for activation entropy ($\Delta S^\dagger$) of SBR can be explained as due to steric effects caused by the pendant aromatic group present in the polymer chains. Figure-5 shows that the rate of hydrogenation is first order with respect to catalyst concentration. The degree of hydrogenation increased with increasing temperature (Figure-6) and pressure (Figure-7). But the rate of hydrogenation decreases with increasing concentration of triphenylphosphine (Figure-8).

Table-1. Thermodynamic parameters for the hydrogenation of unsaturated polymers

Sr. No.	Polymers	E_{act} (Kj/mol)	$\Delta H^\dagger$ (Kj/mol)	$\Delta S^\dagger$ (J.mol^{-1}K^{-1})	Temp (at which$\Delta S^\dagger$ was calculated) (°C)
1[a].	SBR	41.1	37.90	-158.0	100
2[b,c].	St-BD block copolymer	60.8	72.3	-88.5	51
3[b,c].	St-BD-St block copolymer	78.8	79.2	-79.8	65
4[b,c].	Cis 1,4-PBD	98.5	95.7	-26.0	65
5[b,c].	1,2-PBD	102.1	99.4	-10.5	50

[a]Catalyst used $RuCl_2(PPh_3)_3$, [b]Catalyst used $RhCl(PPh_3)_3$, [c]Ref. 21

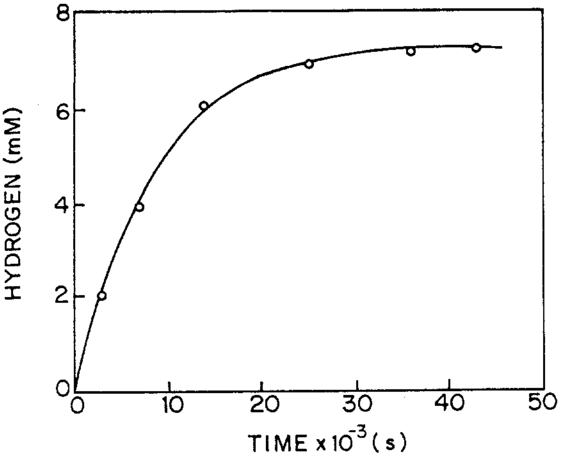


Fig.3. Plot of hydrogen consumption *vs* reaction time: [C=C] = 0.144 M, $[RuCl_2(PPh_3)_3]$ = 8.34x10^{-4} M, Temperature = 100°C, Pressure = 30 Kg/cm^2, $[PPh_3]$ = 7.63x10^{-4} M, Toluene = 50 mL

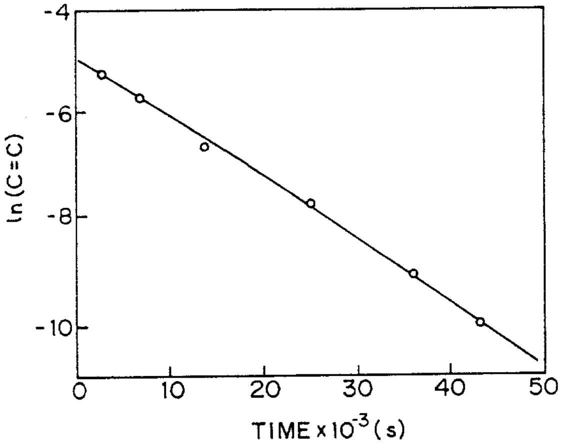


Fig.4. Plot of ln(C=C) *vs* reaction time: [C=C] = 0.144 M, $[RuCl_2(PPh_3)_3]$ = 8.34x10^{-4} M, Temperature = 100°C, Pressure = 30 Kg/cm^2, $[PPh_3]$ = 7.63x10^{-4} M, Toluene = 50 mL

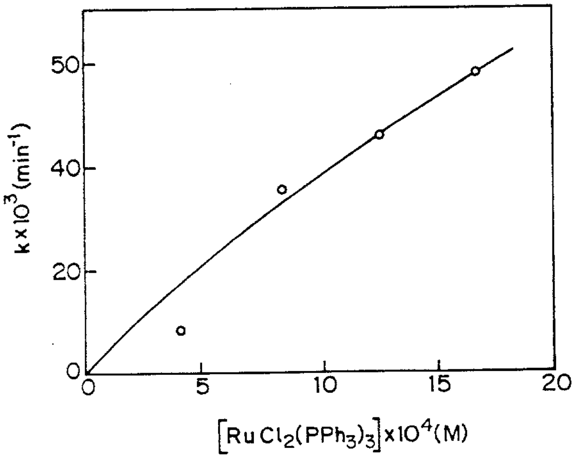


Fig.5. Effect of concentration of $RuCl_2(PPh_3)_3$ on the rate of hydrogenation of SBR: [C=C] = 0.144 M, Pressure = 30 Kg/cm^2, Temperature = 100°C, Time = 12 h, $[PPh_3]$ = 7.63x10^{-4} M, Toluene = 50 mL

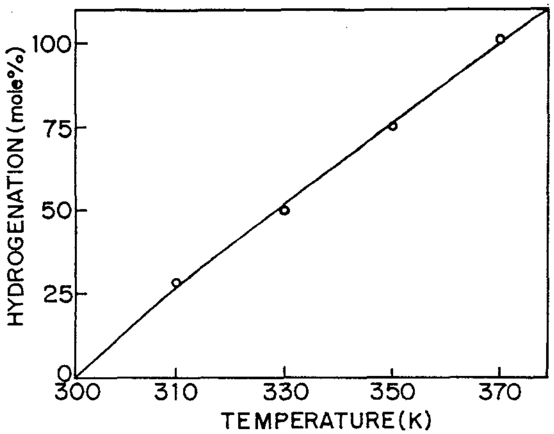


Fig.6. Effect of reaction temperature on the hydrogenation of SBR: [C=C] = 0.144 M, [$RuCl_2(PPh_3)_3$] = 8.34×10^{-4} M, Pressure = 30 Kg/cm^2, Time = 12 h, [PPh_3] = 7.63×10^{-4} M, Toluene = 50 mL

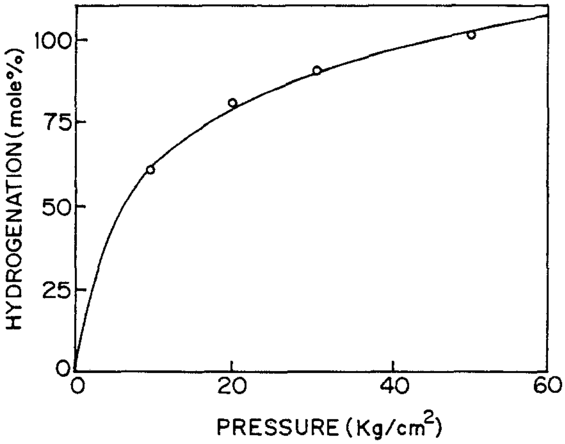


Fig.7. Effect of hydrogenation pressure on the hydrogenation of SBR: [C=C] = 0.144 M, [$RuCl_2(PPh_3)_3$] = 8.34×10^{-4} M, Temperature = 100°C, Time = 12 h, [PPh_3] = 7.63×10^{-4} M, Toluene = 50 mL

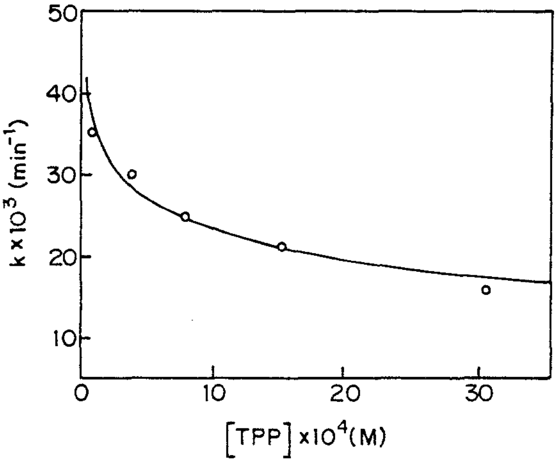


Fig.8. Effect of concentration of PPh_3 on the rate of hydrogenation of SBR: [C=C] = 0.144 M, [$RuCl_2(PPh_3)_3$] = 8.34×10^{-4} M, Temperature = 100°C Pressure = 30 Kg/cm^2, Time = 12 h, Toluene = 50 mL

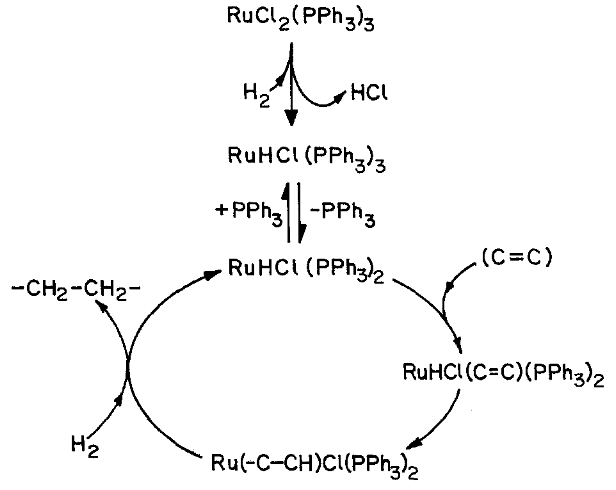
Table-2. Comparative Data of Hydrogenation of styrene-butadiene copolymers using $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$

Sr. No.	Polymer	[C=C] (mM)	[Catalyst] (mM)	mole % catalyst	Temp. (°C)	T.O. No.	Rate Const. (*k*) x 10^3 (min^{-1})
1[a,c,e]	St-BD-St block copolymer	272	1.99	0.73	75	136	37.2
2[a,d,e]	St-BD block copolymer	445	2.05	0.46	60	217	38.5
3[b,d]	SBR	144	0.83	0.58	100	160	35.2

[a] Catalyst used $RhCl(PPh_3)_3$; Pressure = 1 atm. [b] Catalyst used $RuCl_2(PPh_3)_3$; Pressure = 30 Kg/cm^2 [c] Solvent = *o*-dichlorobenzene; [d] Solvent = toluene [e] Ref. 21

The reaction rates (*k*) and turn over number of Rh and Ru catalysts for the hydrogenation of styrene-butadiene copolymers are compared in Table-2. It can be inferred that the Rh based catalysts have slightly higher catalytic activity than the Ru analog.

The hydrogenation of SBR proceeds via the metal hydride path way as reported for natural rubber (NR), polybutadiene and styrene-butadiene copolymers using $RhCl(PPh_3)_3$ as catalyst (5,21,25). In case of Ru based Wilkinson catalyst it reacts with hydrogen gas to form hydridotris(triphenylphosphine) ruthenium(II) chloride (26), $RuHCl(PPh_3)_3$. This is the reactive species in the hydrogenation of SBR. Based on the observed kinetics and the known mechanism of hydrogenation of olefins (26,27)with $RuCl_2(PPh_3)_3$, a mechanistic pathway for the hydrogenation of SBR is shown in Scheme-1.



Scheme-1. Catalytic cycle of hydrogenation of SBR using $RuCl_2(PPh_3)_3$

Table-3. Thermogravimetric Analysis (TGA) of SBR and HSBRs

Sr. No	Polymer	Hydrogenation (mole%)	IDT (^oC)
1	SBR	-	397
2	SBR-1	60	419
3	SBR-2	100	430

The TGA data (Table-3) shows that the completely hydrogenated SBR (HSBR) has higher IDT (Initial Decomposition Temperature) than the unhydrogenated SBR or partially hydrogenated SBR. The IDT of the elastomer increases as the degree of hydrogenation increases.

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