Macromolecules **1994,** *27,* 6985–6987 **6985**

Notes

Solution Hydrogenation of Chloroprene Rubber Using a Wilkinson Catalyst[†]

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Received April 23, 1994

Introduction

Hydrogenation of elastomers bearing unsaturation is of both fundamental and practical interest.[1,2] It offers a unique method for the synthesis of polymers with unusual monomer sequences, which are otherwise difficult to prepare by direct polymerization. Examples are strictly alternating ethylene–propylene copolymers[3,4] formed by hydrogenation of *cis*-1,4-polyisoprene, random copolymers of styrene and ethylene formed by hydrogenation of styrene–butadiene rubber[5] (SBR), and random copolymers of acrylonitrile and ethylene formed by hydrogenation of acrylonitrile-*co*-butadiene rubber[6] (NBR). From a practical viewpoint, hydrogenation also improves elastomer properties such as resistance to oxidative thermal degradation and resistance to oils and fluids, especially at high temperatures.[7–9]

Elastomers can be hydrogenated using stoichiometric reagents[3,10,11] (for example, *p*-toluenesulfonyl hydrazide, diimides) or catalytically using transition metal compounds. Both heterogeneous and homogeneous catalyst have been reported for the hydrogenation of poly(butadiene)s[12,13] and NBR.[14] However, there is no prior report on the hydrogenation of chloroprene rubber (CR). Our interest in the hydrogenation of CR was kindled by the fact that it should afford an interesting and presently unknown sequence of an alternating ethylene-*co*-vinyl chloride copolymer. We therefore studied the solution hydrogenation of CR using $Rh(PPh_3)_3$. This paper reports the results of this study.

Experimental Section

Materials. $RhCl_3 \cdot 3H_2O$ (Arora-Matthey Ltd, Calcutta, India) and triphenylphosphine (E. Merck) were used as received. Toluene was refluxed over sodium and distilled prior to use, Skyprene B-30 (Toyosoda Mfg. Co. Ltd.) was purified by dissolving in toluene and precipitation using methanol. $RhCl(PPh_3)_3$[15] and 1-chlorocyclohexene[16] were prepared using reported procedures.

Hydrogenation. CR (0.50 g) was dissolved in toluene (50 mL) in a 300 mL agitated Parr reactor under N_2 atmosphere. $RhCl(PPh_3)_3$ (0.010 g, 1.08×10^{-5} mol) was introduced into the reactor. Hydrogenation reaction was carried out for 12 h at 100 °C and 50 kg/cm^2 hydrogen pressure. Subsequently, the polymer solution was precipitated using methanol, filtered, and dried in vacuo at 50 °C.

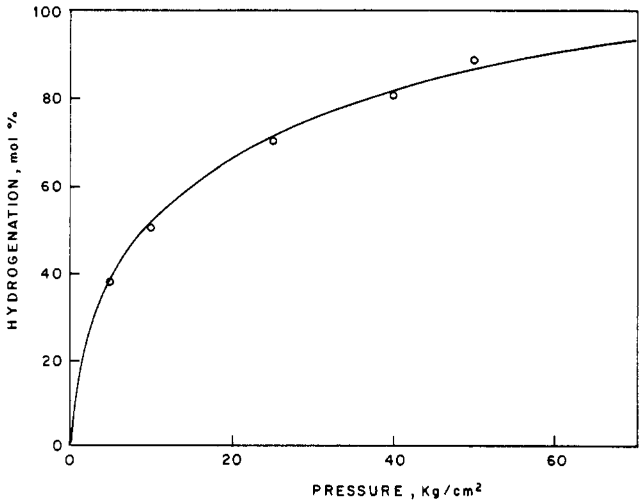

Figure 1. Effect of pressure on the hydrogenation of chloroprene rubber. [C═C] = 113 mM, [$RhCl(PPh_3)_3$] = 0.226 mM, temperature = 100 °C time = 12 h, toluene = 50 mL.

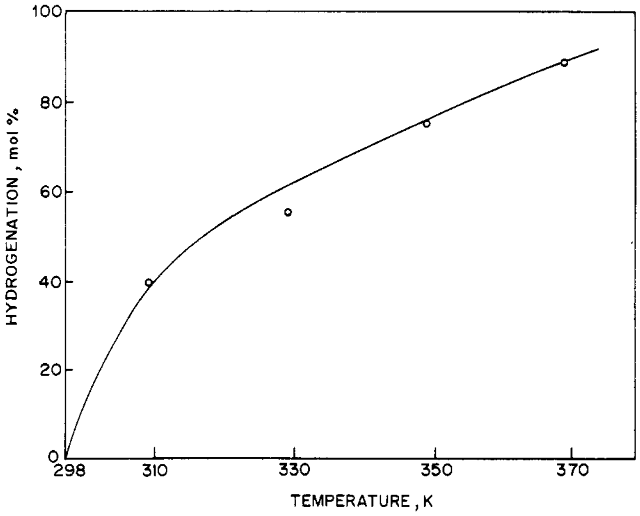

Figure 2. Effect of temperature on the hydrogenation of chloroprene rubber. [C═C] = 113 mM, [$RhCl(PPh_3)_3$] = 0.226 mM, pressure = 50 kg/cm^2, time = 12 h, toluene = 50 mL.

^{1}H NMR ($CDCl_3$, δ, ppm) 5.5 (—C(Cl)═C*H*— of CR), 4.0 (—C(Cl)*H*— of HCR), 2.4 (—C(Cl)═CHCH_2— of unhydrogenated CR) 1.3 (—CH_2— of polyethylene unit); IR (film NaCl) 725 cm^{-1} due to CH_2 rocking; Cl: 14.0% (by ^{1}H NMR) and 14.5% (by elemental analysis).

Analysis. ^{1}H NMR of polymers were recorded on a 200 MHz Bruker spectrometer using $CDCl_3$ or *o*-dichlorobenzene (d_4) as solvent. The IR spectrum was recorded using a PC-16 Perkin-Elmer FT-IR spectrometer. GC analysis was performed on Hewlett-Packard Model GC analyzer using a capillary column (tetramethylsilicone, 50 m × 0.53 μm) and helium as carrier gas (flow rate = 1 mL/min). The injection, oven, and detector temperatures were 275, 60, and 300 °C respectively. Thermal analysis was performed on a Perkin-Elmer TGA-7 thermal analyzer. T_g was determined using a Mettler DSC-30 thermal analyzer.

Results and Discussion

Hydrogenation of CR in toluene solution was performed using $RhCl(PPh_3)_3$ as a catalyst in the temperature range

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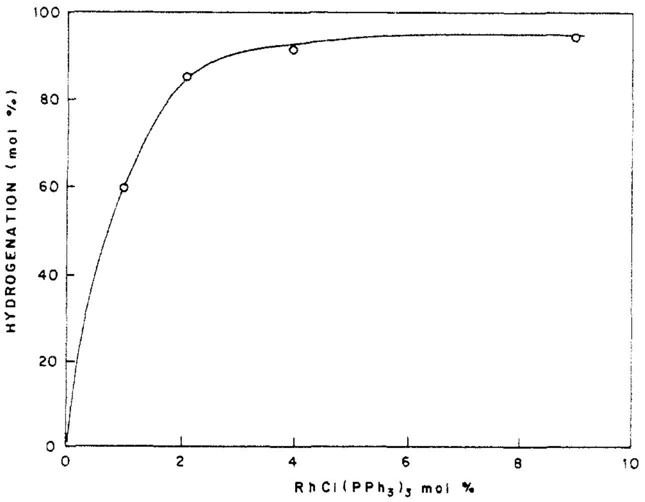

Figure 3. Effect of mole % of $RhCl(PPh_3)_3$ on the hydrogenation of chloroprene rubber. [C═C] = 113 mM, temperature = 110 °C, pressure = 50 kg/cm^2, time = 12 h, toluene = 50 mL.

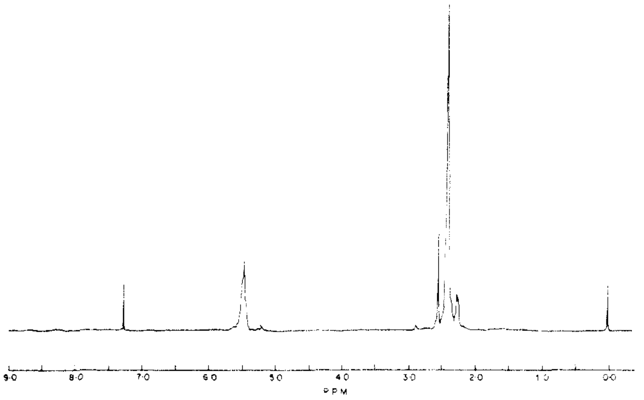

Figure 4. ^1H NMR of chloroprene rubber.

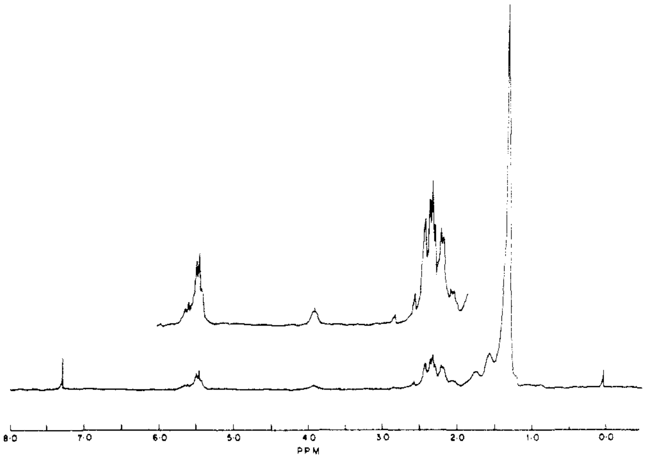

Figure 5. ^1H NMR of hydrogenated chloroprene rubber (HCR).

40–100 °C and 10–50 kg/cm^2 H_2 pressure. Greater than 85 mol % hydrogenation could be achieved in 12 h using 0.2 mol % catalyst at 100 °C and 50 kg/cm^2 H_2 pressure (Figures 1–3). The structure of products derived from hydrogenation was established by ^1H NMR (Figures 4 and 5). It was observed that the products comprise of three structural types, namely, —C(Cl)═CH—(CR), —CH_2CH(Cl)— [ethylene–vinyl chloride copolymer (EVC)] and —$(CH_2)_n$(PE). The relative proportions of the three components could be varied by changing the reaction time (Figure 6).

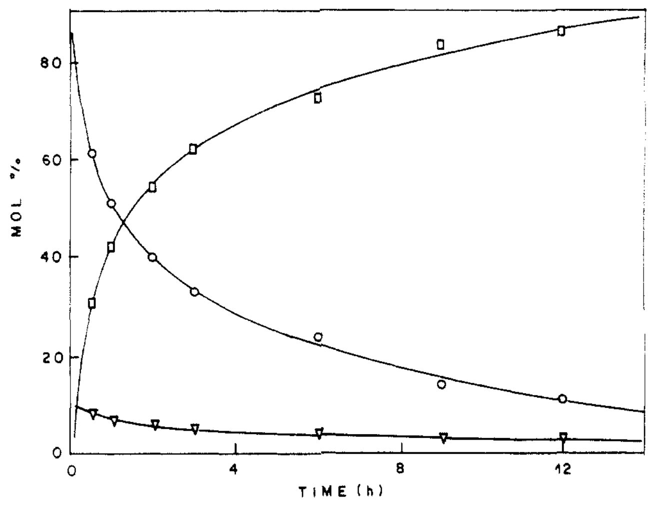

Figure 6. Plots of different components (mole %) in the reaction mixture *vs* reaction time. [C═C] = 113 mM, temperature = 100 °C, pressure = 50 kg/cm^2, time = 12 h, toluene = 50 mL. Key: (○) [—$CH_2C(Cl)$═CH_2CH_2—] (CR), (□) (—CH_2CH_2—) (PE), (▽) [—$CH_2CH(Cl)CH_2CH_2$—] (EVC).

Scheme 1. Catalytic Cycle of Hydrogenation of Chloroprene Rubber using $RhCl(PPh_3)_3$

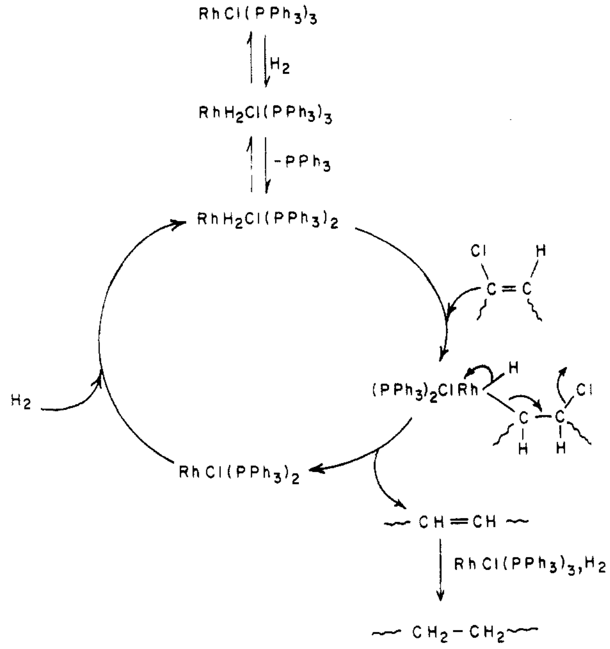

Table 1. Thermal Properties of CR and Hydrogenated Chloroprene Rubbers (HCRs)

polymer	CR (mol %)	EVC (mol %)	PE (mol %)	T_g (°C)	T_m (°C)	IDT (°C)
CR	-	-	-	-35	-	226
HCR-1	41	4	55	-20	-	273
HCR-2	11	3	86	-21	-	286
HCR-3	4	3	93	-24	100	336

The appearance of a polethylene sequence in the hydrogenated product was surprising and unexpected. This indicates that the hydrogenation reaction is accompanied by dehydrochlorination. It was confirmed by the evolution of HCl gas as a byproduct during hydrogenation. Under similar reaction conditions, poly(vinyl chloride) was recovered unchanged, indicating that a saturated poly(ethylene-*co*-vinyl chloride) was not a precursor to poly(ethylene). Since dehydrochlorination was not anticipated from the known hydrogenation chemistry using Wilkinson catalysts, we undertook a brief study of the hydrogenation of 1-chlorocyclohexene and 1-chlorocyclohexane as model compounds using $RhCl(CPPh_3)_3$ (a 0.24 M solution of substrate in toluene, 0.45 mol % catalyst, 90 °C, 30 kg/cm^2 H_2 pressure). Hydrogenation of 1-chlorocyclohexene yielded after 12 h, cyclohexane as the major product (90 mol % hydrogenation). Under similar conditions 1-chlorocyclohexane was recovered unchanged.

These results are best explained by the catalytic cycle shown in Scheme 1.

The thermal properties and T_g of hydrogenated CR are shown in Table 1. The results indicate that the initial decomposition temperature increases as the degree of hydrogenation increases. The hydrogenated chloroprene rubbers have slightly higher T_g than CR.

In conclusion, catalytic hydrogenation of CR yields a product with a predominantly linear polyethylene sequence with minor proportions of *alt*(ethylene-*co*-vinyl chloride) copolymer.

Acknowledgment. Nikhil K. Singha is thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the research fellowship.

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