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Catalytic Hydrogenation of Polymers in the Bulk

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ABSTRACT: Although research on the catalytic hydrogenation of polymers historically has focused on solution studies,[1,2] the *bulk* hydrogenation of polymers using molecular catalysts is reported here. In spite of slow reaction rates, high conversions (>90%) can be obtained at moderate temperatures and pressures. Samples were prepared by evaporating solutions containing the catalyst ($Rh(PPh_3)_3Cl$, $[Ir(COD)(PMePh_2)_2]PF_6$) and a reducible hydrocarbon polymer. The initial hydrogen uptake rates are shown to be sensitive to catalyst loading and the resulting distribution of catalyst in the polymer. The implications of the results with respect to catalyst mobility are discussed.

Introduction

One advantage of homogeneous catalysis over heterogeneous catalysis is its greater ability to effectively catalyze reactions on polymeric substrates.[3,4] The slow rates and low yields observed when heterogeneous catalysts are used in such reactions are generally ascribed to the difficulty of orienting the long polymer chain on the immobile active site.[3] In contrast, homogeneous catalysis offers catalytic mobility and circumvents such orientational problems. Catalytic hydrogenation has been one proving ground for these ideas. While hydrogenations of olefin-containing polymers and solvent-swelled networks were slow and did not go to completion when catalysts such as Pd/C or Rh/Al_2O_3 were used, the hydrogenations proceeded well with homogeneous catalysts.[5]

During a search for a material effective at irreversibly gettering hydrogen gas,[6,7] we became interested in learning whether the mobility of homogeneous catalysts was sufficient to permit effective hydrogenation of polymers in the *absence of solvent*. The synthesis of polymers within a bulk polymer matrix using Zeigler catalysts has been reported by others.[8] This paper describes the bulk hydrogenation of olefinic polymers using molecular catalysts.

Two catalysts were selected for this study from the large number of known homogeneous hydrogenation catalysts. Wilkinson's catalyst,[9] $Rh(PPh_3)_3Cl$, is the best understood of all such catalysts. Each step of its catalytic cycle has been elucidated by painstaking studies.[10] Most relevant to this work is the unambiguously homogeneous nature of the catalyst[11] and its previous use in solution hydrogenations of polymers.[12] Additionally, its low sensitivity to air simplified sample preparation and manipulation. In contrast, the mechanism of the relatively new series of hydrogenation catalysts $[Ir(COD)(L)_2]PF_6$ (COD = 1,5-cyclooctadiene; L = PR_3, R = alkyl, aryl), developed by Crabtree et al.,[13] is less definitive. These catalysts are notable for their great reactivity in hydrogenations even with highly substituted olefins. They differ from all other known hydrogenation catalysts in that their activity is unaffected by the presence of oxygen. For these reasons, and because of evidence supporting the homogeneous nature of its chemistry,[12] the Crabtree catalyst $[Ir(COD)(PMePh_2)_2]PF_6$ was chosen for this study.

Several factors contributed to the selection of olefinic polymers as substrates. Double bonds with low steric hindrance and a low number of substituents were required to enhance reactivity toward catalytic hydrogenation. Only thermoplastic polymers were considered because of their structural integrity and processibility. The polybutadiene polymers readily satisfy the first two requirements. Obtaining the desired material characteristics limited the available choices. Polystyrene-*block*-polybutadiene-*block*-polystyrene (PS–PB–PS) is a thermoplastic rubber. The low T_g of its polybutadiene continuous phase provides elasticity while the phase-separated polystyrene domains afford physical cross-linking. A related nonchemical cross-linking scheme is found in the partially crystalline polymer syndiotactic 1,2-polybutadiene (1,2-PB). In this case, crystalline domains cohere the amorphous regions of the polymer.

Experimental Section

Materials and Sample Preparation. The syndiotactic 1,2-polybutadiene was purchased from Polysciences, Inc. Nuclear magnetic resonance (NMR) analysis indicates an olefinic to aliphatic proton ratio of 0.9:1.0. Shell Chemical Co. supplied the butadiene–styrene triblock copolymer (Kraton D1102) with a 72% by weight butadiene center block. The proton NMR spectrum confirms the specified styrene:butadiene ratio. Based on carbon NMR analysis, the butadiene center block contains a mixture of 1,4-cis, 1,4-trans, and 1,2-vinyl additional units in the approximate ratio of 40:45:15, respectively. $Rh(PPh_3)_3Cl$ was obtained from Aldrich Chemical Co. Research grade chemicals, polymers, and solvents were used without further purification. $[Ir(COD)(PMePh_2)_2]PF_6$ was prepared by literature methods.[15]

Samples for hydrogenation studies were cast from solution. For example, 1.0 g of the triblock copolymer was dissolved in 50 mL of toluene. The solution was degassed, 0.1 g of $Rh(PPh_3)_3Cl$ was added, and the solvent was then removed under vacuum. The resulting polymer/catalyst mixture (9.1% by wt catalyst) was analyzed by capillary gas chromatography to confirm that there is less than 0.1% residual solvent. Samples containing Wilkinson's catalyst were cast from toluene while those containing $[Ir(COD)(PMePh_2)_2]PF_6$ were cast from dichloromethane.

Hydrogenations. Hydrogenations were performed in a pressure reaction apparatus purchased from Lab Glass Inc. and modified to include a pressure guage (0–100 psig) and gas inlet ports. The total volume of the system was 120 mL. For those experiments requiring low hydrogen pressures, an absolute

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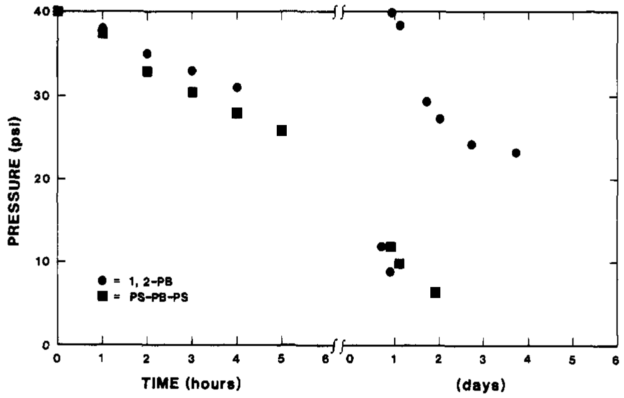

Figure 1. Hydrogen uptake data obtained by using Wilkinson's catalyst, 9.1 wt % loading, at 60 °C.

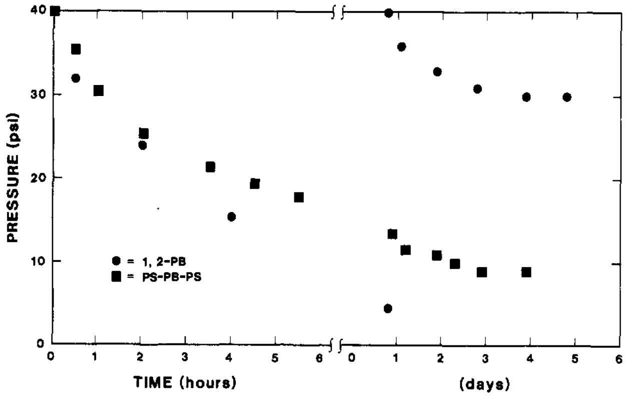

Figure 2. Hydrogen uptake data obtained by using Crabtree catalyst, 9.1 wt % loading, at 60 °C.

pressure gauge, MKS Baratron type 222B with a PDR-C-2C power supply and readout, was attached to the system. This increased the total volume to 180 mL.

For each experiment, 1 g of the polymer/catalyst sample was accurately weighed and placed in the reaction vessel. The vessel was evacuated and hydrogen was admitted at ambient temperature. The temperature was then raised to and maintained at 60 + 1 °C by immersing the glass pressure vessel in a regulated oil bath.

Analysis. Solution NMR samples were prepared by dissolving product polymer in $CDCl_3$ with heating, when necessary. Spectra were obtained by using an IBM NR/AF 200 with TMS as an internal standard. The ratio of polymer peaks in the olefinic (δ 5.5–4.5) and in the aliphatic (δ 2.5–0.5) regions was used to calculate percent hydrogenation in the soluble fraction. Infrared spectra of the soluble product were obtained from films on NaCl plates. A Perkin-Elmer 1750 Fourier transform spectrometer interfaced with a Perkin-Elmer Model 7730 computer was used. In all cases the disappearance of the ν(C=C) near 1629 cm^{-1} was monitored. Scanning electron micrographs were obtained on a Hatachi S-500 microscope. Gas chromatographic analyses utilized a 25 m × 0.33 mm DB1 capillary column in a Hewlett-Packard Model 5890 chromatograph (HP 3392A integrator) with helium carrier. A Perkin-Elmer DSC-4 calorimeter calibrated with indium was used for calorimetric measurements.

Results

The catalyst/polymer samples were fabricated and hydrogenated as described in the Experimental Sections. Figures 1 and 2 include the raw data obtained by monitoring hydrogen pressure versus time for each mixture. In every case the hydrogenations proceeded well under the moderate conditions used. Those runs containing 1,2-polybutadiene required a second charge of hydrogen, as shown in the right halves of Figures 1 and 2. Although there were no dramatic differences in initial reaction rates with changes in either catalyst or polymer, care must be taken to avoid overinterpreting the data. Since no special fabrication techniques were used to ensure uniformity of surface area, density, or thickness, local concentrations of hydrogen and its permeation through the material probably vary from sample to sample and within individual samples. Certain conclusions can be drawn from Figure 3 in which the butadiene–styrene copolymer data for both catalysts are compiled. The Crabtree catalyst showed faster initial hydrogen uptake; however, the reaction went nearest to completion when Wilkinson's catalyst was used. In both cases, the reactions reached greater than 80% of theoretical capacity within 70 h.

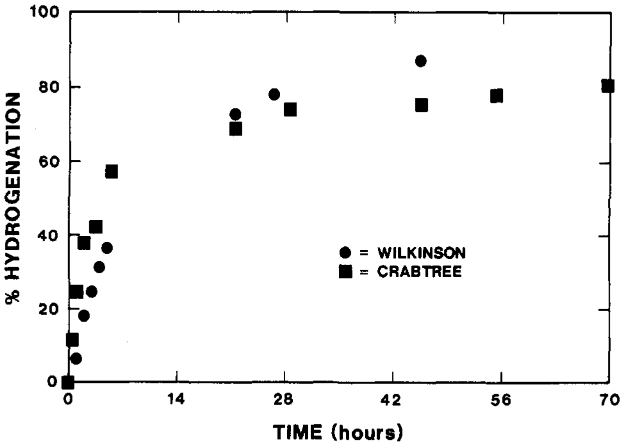

Figure 3. Percent hydrogenation versus time for the reaction of PS–PB–PS using the indicated catalysts.

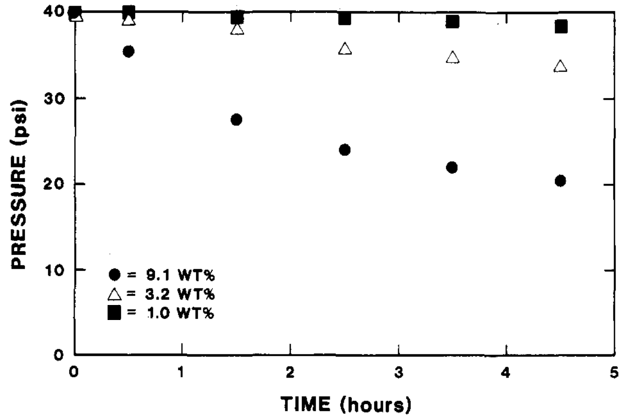

Figure 4. Initial hydrogen uptake data obtained by using Crabtree's catalyst at the indicated loadings and 60 °C.

The data summarized in Figures 1–3 were based exclusively on pressure measurements. The total hydrogen uptake was confirmed at the end of each experiment by accurate weighing of the product. Spectroscopic analysis of the hydrogenated triblock copolymer was complicated by the presence of crystalline polymer. The proton NMR spectrum of the product was obtained at 50 °C and showed near-complete reduction of peaks attributable to olefinic protons. Infrared spectra of the bulk product also indicated substantial hydrogenation of the polymer. The bulk hydrogenation products from 1,2-polybutadiene were much more readily soluble (less crystalline) than those from the copolymer. Again, the spectroscopic data substantiated the incorporation of hydrogen into the polymer.

In those experiments discussed above, the weight percent catalyst was arbitrarily selected at 9.1%. Since hydrogen could well be the limiting reagent, reactivities at lower loadings of catalyst were investigated. The initial hydrogen uptake data for Crabtree/PS–PB–PS at 9.1, 3.3, and 1.1 wt % loadings are plotted in Figure 4. An approximately first-order rate dependence in catalyst was observed. Surprisingly, the data for Wilkinson/PS–PB–

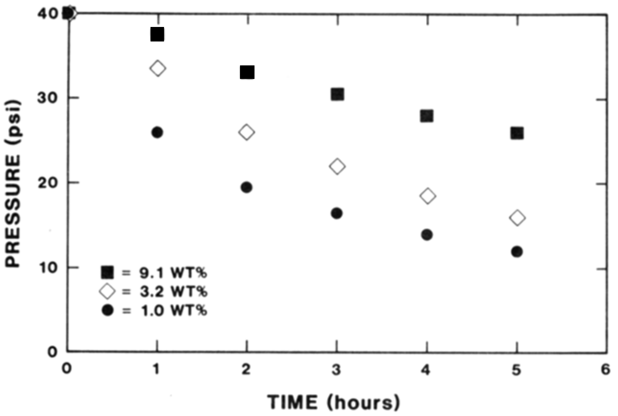

Figure 5. Initial hydrogen uptake data obtained by using Wilkinson's catalyst at the indicated loadings and 60 °C.

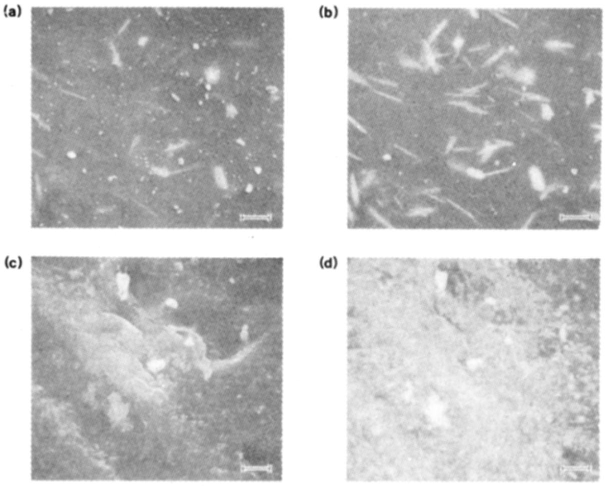

Figure 6. Scanning electron and backscattered electron micrographs of the polymer/catalyst mixture: (a, b) Wilk/PS–PB–PS, 9.1 wt % (bar = 10 μm); (c, d), Crab/PS–PB–PS, 9.1 wt % (bar = 5 μm). The backscatter technique enhances high Z elements.

PS, shown in Figure 5, indicate an inverse dependence of rate on catalyst concentration. The reaction rate actually increases as the loading is decreased. One explanation for this result is that early crystallization of Wilkinson's catalyst from the casting solution results in poor catalyst distributions at high loading. The formation of large crystallites would limit the area of exposed catalyst surface. This explanation is consistent with the known solubilities of the two catalysts. Wilkinson's catalyst is only "slightly soluble" in toluene[9] while the Crabtree catalyst is "readily soluble" in a variety of organic solvents.[13]

Scanning electron microscopy (SEM) also provides evidence for early crystallization at high loadings of Wilkinson's catalyst. Both SEM and backscatter micrographs of samples with 9.1 wt % loadings of the two catalysts are shown in Figure 6. Numerous crystallites approximately 10 μm long are apparent in the top half. Crystallites of the Crabtree catalyst are also apparent; however, they are 2 orders of magnitude smaller and more uniformly dispersed throughout the polymer. Clearly in neither case is a molecular-level homogeneous distribution attained on solvent casting. Presumably an equilibrium fraction of catalyst is in solution in the hydrocarbon polymer and is responsible for the catalysis.

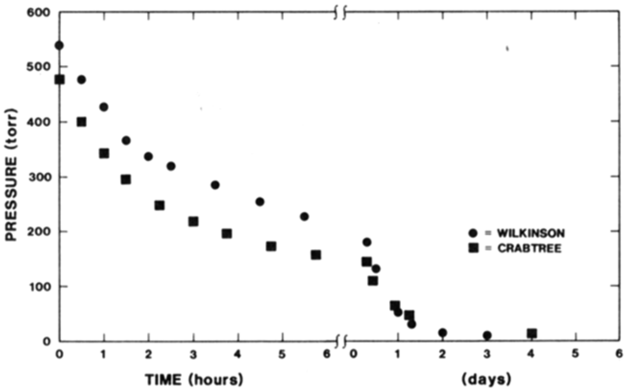

Figure 7. Low-pressure hydrogenation of PS–PB–PS at 60 °C with Wilkinson's catalyst at 1.1 wt % loading and Crabtree's catalyst at 9.1 wt % loading.

Table I
Hydrogen Uptake Analysis

sample[a]	wt % cat.	capacity[b] theory	capacity[b] achieved	% completn	turnovers[c]
Wilk/PS–PB–PS	9.1	274	246	90	110
Wilk/PS–PB–PS	1.1	300	263	88	1140
Wilk/1,2-PB	9.1	381	358	94	160
Crab/PS–PB–PS	9.1	274	232	85	100
Crab/1,2-PB	9.1	381	337	88	150

[a] Abbreviations are as follows: $Rh(PPh_3)_3Cl$ = Wilk; $[Ir(COD)(PMePh_2)_2]PF_6$ = Crab; PS–PB–PS = styrene–butadiene–styrene triblock copolymer; 1,2-PB = syndiotactic 1,2-polybutadiene. [b] Milliliters of H_2 at STP per gram of polymer/catalyst material. [c] Moles of double bonds hydrogenated per moles of catalyst.

Since the bulk hydrogenation of the triblock copolymer went well at moderate pressures and temperature, it seemed reasonable to study the reaction under even milder conditions. Figure 7 shows a subatmospheric pressure hydrogenation run at 60 °C. The sample size was chosen so that complete consumption of hydrogen in the reactor would reduce about 40% of the available double bonds. Within days both catalysts had lowered the pressure to under 10 Torr. Final pressures under 1 Torr have been attained at longer reaction times.

Attempts to study the reaction at room temperature and low pressure were unsuccessful. Rate reductions considerably greater than typical Arrhenius behavior were observed. This may be due to lowered mobility of the polymer or to decreased solubility/mobility of the catalyst within the polymer matrix at low temperatures.

Discussion

Numerical data on the overall hydrogen uptakes, compiled from the graphical data in Figures 1 and 2, are presented in Table I along with the results obtained by using 1.1% loading of Wilkinson's catalyst in the triblock copolymer. The primary intent of these experiments was to demonstrate that catalytic reactions on bulk polymers are possible. The fact that hydrogenations do occur under these conditions is best illustrated by the percent completion column. High conversions are most apparent for Wilkinson's catalyst and for 1,2-polybutadiene. In every case the hydrogenation reached 80% completion within days. The observed number of turnovers has particularly interesting implications at the molecular level. Assuming each molecule of catalyst was equally involved in the reaction, obtaining greater than 1000 turnovers (Wilk/PS–PB–PS, 1.1 wt % loading) requires sufficient mobility in the system for the catalyst to encounter more than 1000 double bonds.

The glass transition temperature of the polybutadiene center block of PS–PB–PS is low—approximately −96 °C.

On hydrogenation this polymer phase becomes similar to low-density polyethylene, with a T_g estimated[16] around −70 °C. Since all hydrogenations were performed at 60 °C, all reducible polymer domains would remain mobile on the molecular level throughout the reactions.[17] The amorphous regions of syndiotactic 1,2-polybutadiene also have a low T_g, −10 °C, and as a result have localized chain mobility. In contrast, the high order in its crystalline domains excludes catalyst and prevents segmental motion. Because of this polymer's crystallinity, the observation in these experiments that catalytic hydrogenation goes to high conversion is remarkable. Analysis of the polymer/catalyst mixture by X-ray crystallography confirms the presence of significant polymer crystallinity after catalyst loading. Work continues to quantify the crystallinity before and after hydrogenation and to assess the probability of localized melting due to the reaction exotherm.

An additional source of mobility is provided by the movement of solvated catalyst molecules in the polymer. As discussed in the Introduction, homogeneous catalysts were selected for this study specifically because of their potential for diffusion in the polymer. Whether their behavior would be truly homogeneous in bulk hydrogenations was not clear at the outset. Although their solution chemistry is homogeneous, reduction might occur yielding metal particles under the conditions used in this work. Collman's solution studies[5] on catalytic reactions of both polymer- and network-supported olefins showed that polymers discriminate between homogeneous and heterogeneous catalysts. Although the potential involvement of small metal colloids (<80 Å) could not be ruled out, effective hydrogenation of polymers required a soluble catalyst. The selectivity observed by Collman should be magnified in more concentrated solutions. The fact that hydrogenations of double bonds in polymers do go to high conversion in the absence of solvent provides strong evidence that the catalytically active species is homogenous.

Conclusions

1. Catalytic hydrogenation of polymers in the bulk is possible using traditional organometallic hydrogenation catalysts. While other workers[8] have demonstrated the feasibility of performing catalytic reactions in a polymer matrix, this is the first example of the bulk catalytic modification of the polymer matrix. Investigation of the morphological implications of this hydrogenation is in progress.

2. High conversions of unsaturated polymer to hydrogenated polymer were obtained at moderate temperatures and pressures.

3. The observed reactivity coupled with Collman's polymer-based test for homogeneity provides strong evidence for the homogeneous nature of the catalysis. While the micrographs shown in Figure 6 show that much of the organometallic is in the crystalline form, some partial solubility in the polymer is expected. Presumably the solvated molecules are responsible for the catalysis.

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Registry No. Wilkinson's catalyst, 14694-95-2; Crabtree catalyst, 38465-86-0; syndiotactic 1,2-polybutadiene, 36522-63-1.

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