

## **Homogeneous Catalytic Hydrogenation of Polypentenamer**

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### SUMMARY

A high degree of hydrogenation of a polypentenamer was achieved with a homogeneous catalyst based on a metal alkyl-transition metal complex. Essentially complete saturation of the polymer was achieved without significant changes in molecular weight or molecular weight distribution.

### INTRODUCTION

Hydrogenation of a polypentenamer and its sulfonated derivatives has been previously reported from this laboratory<sup>1,2</sup>. The reagent used was p-toluenesulfonyl hydrazide, which decomposes in solution to yield the hydrogenation agent, diimide<sup>3</sup>. The purpose of the current work was to develop a catalytic method for the complete hydrogenation of the same polymers with hydrogen without altering the molecular weight or polymer structure. If successful, a procedure would then be available to deuterate identical polymers with deuterium for use in neutron scattering studies.

A homogeneous catalyst complex, made by the reaction of n-butyllithium with cobalt(II) 2-ethylhexanoate<sup>4,5</sup>, was investigated. Infrared spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) were used in the characterization of the hydrogenated products.

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## EXPERIMENTAL

For purification, the polypentenamer sample (82 % trans) was dissolved in chloroform, the solution was filtered, and the polymer was reprecipitated in methanol and dried. Dimethylformamide was vacuum distilled over calcium hydride and stored over molecular sieves (3 Å pore pellets). Cyclohexane was dried by storage over molecular sieves.

Hydrogenations were carried out in a 300 ml, high-pressure reactor (Parr Instrument Co.). Catalyst solutions (0.06 M based on cobalt) were prepared by slowly adding a solution of cobalt(II) 2-ethylhexanoate in cyclohexane to a solution of n-butyllithium in cyclohexane under a dry nitrogen atmosphere. Approximately one gram of polymer was added to 100 ml of the reaction solvent, and the solution was stirred under a nitrogen atmosphere until the polymer was completely dissolved. This polymer solution and a specific amount of the catalyst solution were placed in the reactor inside a glove bag under a nitrogen atmosphere, and the reactor was closed. The reactor was purged with hydrogen, brought to the reaction temperature, and pressurized with hydrogen. After the reaction, the insoluble product was filtered and washed with a solution of 10 % hydrogen chloride in methanol to decompose the catalyst and filtered. The polymer was redissolved in a suitable solvent, reprecipitated in methanol, filtered, and dried.

Infrared spectra of solvent-cast films on NaCl plates were obtained on a Perkin-Elmer Model 283 grating infrared spectrophotometer. The molecular weight distributions for both the starting polypentenamer and the product polymers were obtained in o-dichlorobenzene at 135°C on a Waters Model 200 GPC equipped with a differential refractometer. The polymer melting temperatures were measured on a Perkin-Elmer Model DSC-1B differential scanning calorimeter.

## RESULTS and DISCUSSION

Table 1 summarizes the various conditions used in the catalytic hydrogenation of polypentenamer with the n-butyllithium-cobalt(II) 2-ethylhexanoate catalyst. A lithium to cobalt molar ratio of 3.5 to 4.0 was used at various catalyst loading levels, hydrogen pressures, and reaction times. Only the conditions for Reaction C of Table 1 led to a high degree of hydrogenation. Contrary to previous results using organolithium (or aluminum) - transition metal complex catalysts on both low molecular weight and polymeric unsaturated hydrocarbon systems <sup>4,5,6</sup>, longer reaction times and higher

pressure were found necessary in order to achieve this high degree of hydrogenation. Similar requirements of high catalyst loading levels for complete hydrogenation have been reported <sup>6</sup>.

The degree of hydrogenation was qualitatively determined from the infrared spectra (see Figure 1) by monitoring the  $965\text{ cm}^{-1}$  absorption band of the trans vinylene unsaturation <sup>7</sup>. A sharp DSC melt transition, which peaked at  $124^{\circ}\text{C}$  and returned to the base line at  $128^{\circ}\text{C}$ , was observed for the highly hydrogenated sample of Reaction C <sup>7</sup>. Although a long reaction time (19.5 hours) and a high hydrogen pressure (400 psi) was used, the GPC results indicated that no major structural changes had occurred in the product from Reaction C. The molecular weight distributions ( $M_w/M_n$ ) for the polypentenamer and this hydrogenated polymer were closely equivalent as seen in Figure 2 and Table 2. The difference in the molecular weight averages observed for the two samples (based on polystyrene standards) can probably be attributed to differences in the effective volumes of the two types of polymers at a given molecular weight rather than to backbone modification.

The absence of extensive structural changes in the hydrogenated polymer from Reaction C is different from the results observed by other workers using closely related homogeneous catalysts and reactions temperatures but at a much lower hydrogenation pressure <sup>5</sup>. It was reported in that work, in which the base polymer was polybutadiene, that the molecular weight distributions of the hydrogenated products were much different from those of the starting polymers, particularly if the molecular weights of the latter were greater than 100,000. Both the GPC and melt viscosity results in that work indicated that extensive scission and cross-linking reactions had occurred during the hydrogenation <sup>5</sup>.

An attempt was also made to catalytically hydrogenate sulfonated polypentenamer samples by the same procedure <sup>2</sup>, but a satisfactory reaction solvent could not be found. Diglyme, tetrahydrofuran, and mixed solvent systems of diglyme or tetrahydrofuran with toluene or xylene would not dissolve the polymer. Water was known to affect catalyst activity <sup>4</sup>, and mixed systems of alcohols with toluene or xylene were not good solvents for these polymers <sup>2</sup>. Dimethylformamide would dissolve a 10 % sulfonated polypentenamer (based on polypentenamer repeat unit) with heating, but attempted hydrogenations on 1.0 % solutions of 10 % sulfonated polypentenamer in dimethylformamide at various catalyst loading levels, hydrogen pressures, and reaction times were unsuccessful. Every combination of conditions

**Table 1** Reaction Conditions for the Hydrogenation of Polypentenamer

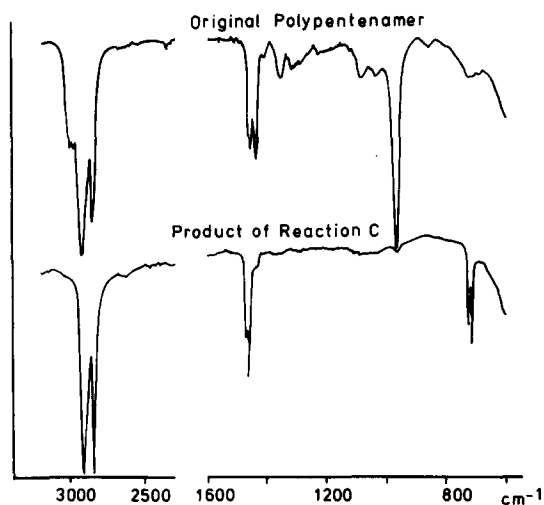
Reaction	Catalyst, Mole% <sup>a</sup>	Reaction Time, hr.	Temp. °C	Pressure psi	Li/Co Mole Ratio
A	5.0	3.5	80	125	3.5
B	10.4	12.0	80	200	3.5
C	31.2	19.5	85	400	4.0

a. Moles C<sub>o</sub> per mole of double bonds x 100

**Table 2** Properties of Starting and Hydrogenated Polymers

Sample	GPC Analysis <sup>a</sup>		Elemental Analysis			
	10 <sup>-5</sup> $\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Calcd.		Obsvd.	
			C	H	C	H
Poly-pentenamer	3.2	2.2	88.2	11.8	88.15 88.39	11.65 11.85
Reaction C	4.1	2.1	85.7	14.3	85.58 85.53	14.61 14.54

a. Based on polystyrene standards

**Figure 1:** Infrared spectra of polymers before and after hydrogenation

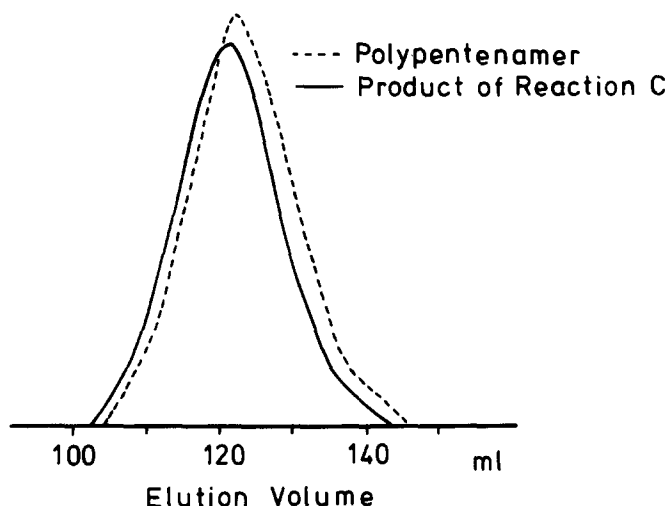


Figure 2: GPC distribution plots of polymers before and after hydrogenation

yielded insoluble, black products. Previous studies with the diimide reagent had yielded soluble hydrogenated products from sulfonated polypentenamers<sup>2</sup> indicating that the present catalytic hydrogenation reactions were causing crosslinking to occur in these polymers.

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