Selectivity of the $OsHCl(CO)(O_2)(PCy_3)_2$ Catalyzed Hydrogenation of Nitrile–Butadiene Rubber

J. SCOTT PARENT, NEIL T. MCMANUS, AND GARRY L. REMPEL

Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada, N2L 3G1

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ABSTRACT: A new homogeneous catalyst precursor has been discovered for the hydrogenation of carbon–carbon unsaturation resident within acrylonitrile–butadiene copolymers. The hydrido-phosphine complex $OsHCl(CO)(O_2)(PCy_3)_2$ (**1**) selectively and quantitatively saturates olefin, leaving the copolymer's nitrile functionality intact. However, the process suffers from an undesirable crosslinking reaction that is not demonstrated by the established rhodium technology. The extent of this crosslinking is dependent on the process conditions and can be minimized by operating with a low catalyst concentration and high H_2 pressure. Kinetic studies have identified a previously unknown unexpected influence of olefin on the polymer crosslinking process. In light of this new information, the prevailing mechanism for this class of reactions has been reconsidered. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1618–1626, 2001

Key words: hydrogenation; catalytic; nitrile rubber; crosslinking

INTRODUCTION

Due to its resistance to apolar solvents, acrylonitrile–butadiene rubber (NBR) is well suited for use in oil and gas production equipment and engine fluid delivery systems.[1] However, residual carbon–carbon unsaturation in the polymer backbone makes the material susceptible to degradation when exposed to oxygen and ozone, especially at high temperatures.[2] This deficiency can be alleviated by selectively hydrogenating the copolymer to yield HNBR; an apparent ethylene–acrylonitrile copolymer (Fig. 1). Given that this chemical structure cannot be synthesized by conventional polymerization techniques, the modification of the butadiene-based elastomer remains the only synthetic route for HNBR production.[3]

To retain the oil resistance of the material, an HNBR process must hydrogenate the olefin while leaving the nitrile unsaturation intact. Nitrile hydrogenation is also suspected to compromise the mechanical and processing qualities of the rubber.[4] To date, the only catalyst technologies to be commercialized appear to be homogeneous rhodium complexes[5] such as $RhCl(PPh_3)_3$ and palladium colloids derived from $Pd(acetate)_2$ complexes.[6,7] We recently demonstrated the remarkable selectivity of the Rh(I) phosphine systems for the hydrogenation of carbon–carbon unsaturation over the RCN functionality of NBR.[8] Irrespective of the hydrogenation conditions employed, these catalysts generate a product of uniform quality.

Two of the more promising alternative catalysts are the hydrido-phosphine complexes of osmium and ruthenium, $MXCl(CO)(L)(PCy_3)_2$ (**1**: M = Os, X = H, L = O_2; **2**: M = Ru, X = styryl, L = no ligand).[9,10] Both of these systems are less expensive and more robust than their rhodium counterparts. The osmium analogue offers the further advantage of superior catalytic activity at the hydrogenation conditions used industrially.[9,11]

Correspondence to: G. L. Rempel.

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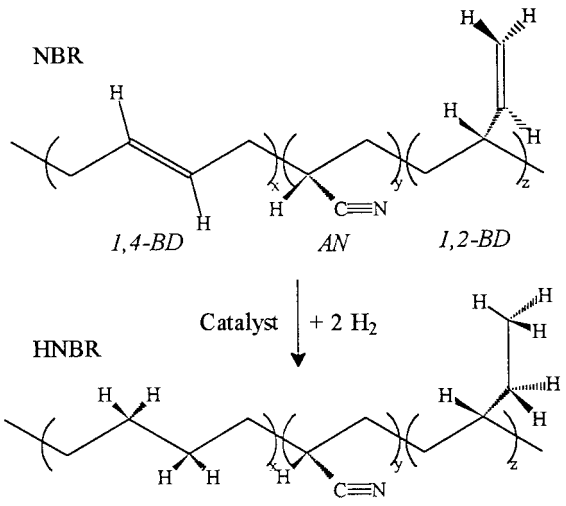


Figure 1 Hydrogenation of NBR to HNBR.

Nevertheless, neither of these alternatives has displaced the existing rhodium technology, partly due to the prevalence of an undesirable crosslinking reaction. Although HNBR derived from complexes **1** and **2** shows no evidence of nitrile reduction,[12] the polymer products have inordinately high intrinsic and Mooney viscosities. By adversely affecting the processibility of the rubber, this rise in molecular weight has impeded the widespread adoption of the technology.

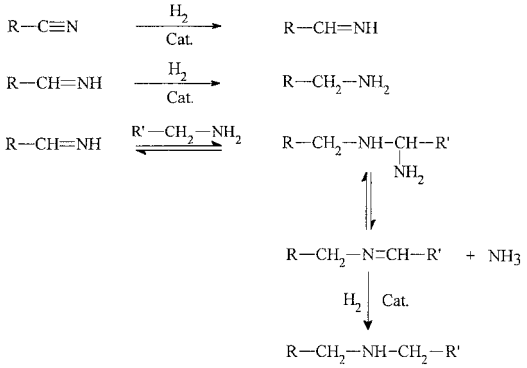
The performance of the ruthenium-based catalysts can be improved by using additives developed to reduce the extent of crosslinking.[13,14,15] However, for reasons that are presently unknown, these viscosity modifiers have yet to produce a commercially acceptable material. To date, only McManus and Rempel have speculated on the reaction pathway (**Scheme I**).[4] This mechanism was originally developed to account for secondary amine formation during the hydrogenation of heptylcyanide by nickel salts.[16] When applied to NBR hydrogenation, this reaction sequence envisages crosslinks as secondary amines that are produced by an addition of fully hydrogenated nitrile to an imine intermediate. Although this mechanism can explain the efficacy of viscosity modifying additives, it has yet to be substantiated by definitive experimental results.

Previous work examining NBR hydrogenation catalyzed by Os catalysts has looked at the effects of various reaction parameters with respect to the kinetics of hydrogenation. This article details a careful examination of the crosslinking process which operates in parallel with the hydrogenation reaction and compromises the quality of HNBR produced by $OsHCl(CO)(O_2)(PCy_3)_2$. An appropriate measure of selectivity is defined and applied toward understanding the influence of process factors such as the concentrations of catalyst, hydrogen, and polymer. Independent studies of the kinetics of HNBR crosslinking seek to provide the mechanistic understanding of the process required for making the osmium technology a commercially viable process.

EXPERIMENTAL

$OsHCl(CO)(PCy_3)_2$ was prepared from $OsCl_3$-$0.3H_2O$ and PCy_3 (all from Strem Chemical Newburyport, MA) by the method of Esteruelas et al.[17] Its dioxygen adduct (complex **1**) was synthesized by exposing a hexane slurry to pure O_2 for 10 min, then isolating the complex according to the previously cited technique. $RuCl(CO)(Sty)(PCy_3)_2$ was synthesized by using the method of Martin et al.[18] Reagent grade monochlorobenzene (MCB) and 2-butanone were used as received from Fischer Chemical Co. Nepean, Canada. Oxygen-free hydrogen with a purity of 99.99% was purchased from Linde-Union Carbide Canada Ltd. Toronto, Ontario. The nitrile–butadiene rubber provided by Bayer Inc. Sarnia, Ontario, Canada (Krynac 38.50) contained 62 wt % butadiene (80% *trans*, 15% *cis*, 5% *vinyl* isomerization) and possessed an M_n = 70,000 and a polydispersity of 3.6.

The apparatus and procedures used to hydrogenate monochlorobenzene solutions of NBR have been detailed elsewhere. Samples of fully saturated HNBR were prepared by monitoring the amount of H_2 consumed by the reaction until 99% conversion was attained, after which the reactor was cooled rapidly. The HNBR product was iso-



Scheme I von Braun mechanism for nitrile hydrogenation leading to NBR crosslinking.

lated by precipitation with ethanol and dried under an aspirator vacuum at 60°C for 72 h. A second sample collection technique was developed to monitor the evolution of crosslinking with time. Rather than isolating fully hydrogenated HNBR, these samples were collected at regular intervals during the reaction. From the initial 150 cm^3 charged to the autoclave, 16 cm^3 were withdrawn for each sample and immediately coagulated with 100 cm^3 of ethanol to avoid exposing the hot solution to air. This polymer was pressed to remove entrained fluid, washed with a further 10 cm^3 of ethanol, and dried at room temperature under high vacuum for 72 h.

The degree of hydrogenation for samples containing $< 10\%$ residual olefin was determined by using a Nicolet 520 FTIR spectrophotometer according to the method of Marshall et al.[19] The conversion of all other samples was measured by ^{1}H-NMR in $CDCl_3$ by using a Bruker AC-300 NMR spectrometer. The viscosity of dilute, 2-butanone solutions (0.25000 ± 0.00015 g of HNBR/25 cm^3) was measured at 35°C by using an Ibellohde capillary viscometer. Sample filtration through a coarse, sintered-glass filter provided a means of detecting insoluble gel. Gelled HNBR products, which could not be analyzed by viscometry, are noted in the text. Relative viscosity data (η_{rel}) are reported as the ratio of the polymer solution viscosity to that of 2-butanone at 35°C.

RESULTS

HNBR Product Analysis

HNBR produced by using complex **1** showed no evidence of nitrile hydrogenation in its infrared (IR), ^{1}H-NMR, or ^{13}C{^{1}H}-NMR spectra. The spectra were consistent with those previously reported for a $RhCl(PPh_3)_3$-catalyzed HNBR product.[20,21] Typically, residual C═C is of the *trans* conformation, as the *cis* and *vinyl* moieties are preferentially hydrogenated in the early stages of the reaction.[11] The nitrile resonance in the ^{13}C-NMR and υCN in the IR spectra were easily resolved, whereas the characteristic signals for primary or secondary amines were lacking in both spectra. This suggests that the oil resistance of the material would not be compromised following hydrogenation.

Crosslinking Determinations

Given that $OsHCl(CO)(O_2)(PCy_3)_2$ does not hydrogenate nitrile to a measurable extent, it remains to assess the catalyst's propensity to crosslink the material. However, this product assessment is not straightforward. Although IR or NMR spectroscopy can be used to determine the degree of hydrogenation, these techniques lack the sensitivity required to detect the amount of polymer crosslinks in a manageable HNBR sample. We have found dilute solution viscosity to be an efficient method for this determination. Although not a direct measure of crosslink density, this technique reflects the quality of an HNBR sample by responding to changes in molecular weight.

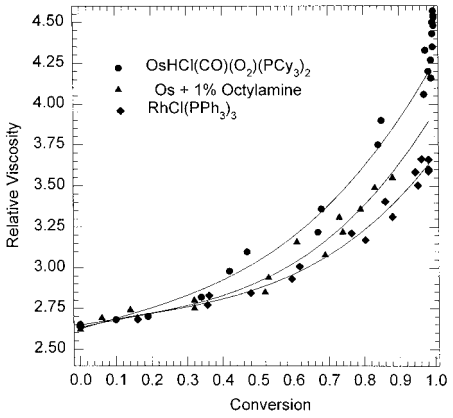


Figure 2 η_{rel} versus conversion produced by $RhCl(PPh_3)_3$ and **1** with octylamine.

Although viscometry is a comparatively simple technique for making inferences on molecular weight, the data must be collected and interpreted carefully. To draw meaningful comparisons between the relative viscosities of various HNBR products, the polymers must share a common structure and composition. The extent of hydrogenation is of particular importance, for as the backbone is saturated, the material's composition approaches that of an ethylene–acrylonitrile copolymer. The conformation of the molecule in solution is thereby altered, resulting in a change in η_{rel} with conversion that is independent of polymer crosslinking. The relationship between viscosity and composition for three HNBR processes is illustrated in Figure 2 for three different hydrogenation systems.

The η_{rel} versus conversion profile of $RhCl(PPh_3)_3$ represents the innate response of the polymer toward hydrogenation. Because it has been assumed that this catalyst system does not crosslink HNBR,[8] the rhodium data (derived from two experiments at [Rh] = 95 μM, P_{H2} = 83 bar, [RCN] = 917 mM, T = 140°C) depicts the lower

Table I Operating Conditions for the Selectivity Studies

[Catalyst]: 20–155 μM
H_2 Pressure: 4.5–42 bar
[Nitrile]: 46–255 mM
Temperature
Osmium study: 130°C
Rhodium study: 145°C

limit of η_{rel} for a given degree of hydrogenation. In comparison, complex **1** yields an inferior product, as the viscosity at all conversions is greater than that afforded by the rhodium technology. This is expected to make the material tougher and more difficult to process by extrusion, calendaring, and injection molding.

It is also evident from Figure 2 that the performance of the osmium system can be improved by the presence of specific additives. Rempel and coworkers have established the efficacy of C_1–C_{20} amines, and inorganic and organic acids to affect the performance of the ruthenium analogue of complex **1**, [$RuHCl(CO)(PCy_3)_2$].[13–15] The effect of 1% octylamine relative to nitrile has on the osmium systems in relation to product viscosity is substantial, but inadequate when compared to the quality of HNBR derived from $RhCl(PPh_3)_3$. Furthermore, the primary amine reduced the reaction rate by nearly 50%. The compound must be present during hydrogenation, as octylamine that was added following hydrogenation had no effect on η_{rel}. Therefore, the potential gains in product quality are necessarily offset by a loss in catalyst activity.

Crosslinking Selectivity

For the purpose of this work, a selective catalyst is defined as one that hydrogenates olefin without crosslinking the polymer. We believe that an appropriate measure of catalyst selectivity is the relative viscosity of 99% hydrogenated HNBR. This viscosity (denoted η_{rel}^*) quantifies the amount of crosslinking produced over the time taken to complete the hydrogenation process. Valid comparisons between samples may be drawn due to the common backbone structure of the saturated products. Although a measurement has little meaning in isolation, it will be shown that η_{rel}^* measured over the range of conditions listed in Table I provide valuable insight into the overall crosslinking process.

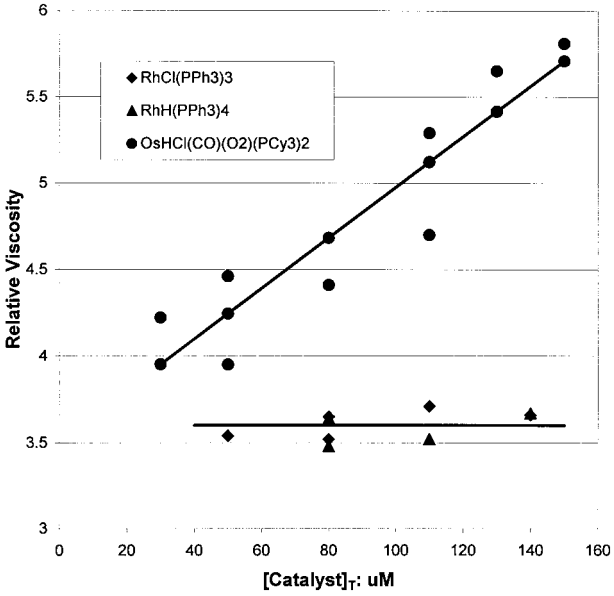


Figure 3 Selectivity as a function of total metal loading; [CN] = 172 mM, P_{H2} = 24 bar.

By definition, η_{rel}^* measures the relative rates of hydrogenation and crosslinking. The kinetics of the former reaction have been studied extensively. Over the range of conditions explored in this work, the rate of NBR hydrogenation by complex **1** is known to be first-order with respect to [osmium], second-order with respect to [H_2], and inversely proportional to the amount of nitrile charged to the system. Figures 3-5 illustrate the effect of these factors on the selectivity of **1,** as well as the established rhodium catalysts. Be-

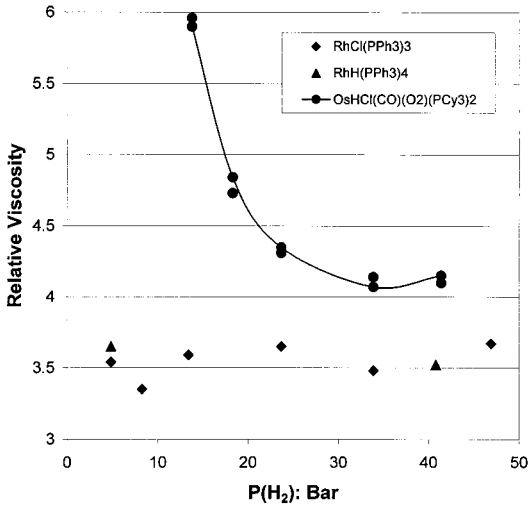


Figure 4 Influence of pressure on selectivity; [metal] = 80 μM, [CN] = 172 mM.

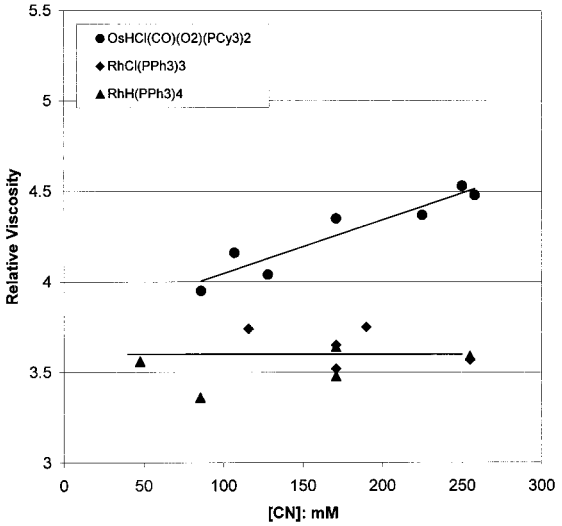


Figure 5 Selectivity as a function of NBR loading; [metal] = 80 μM, P_{H2} = 24 bar.

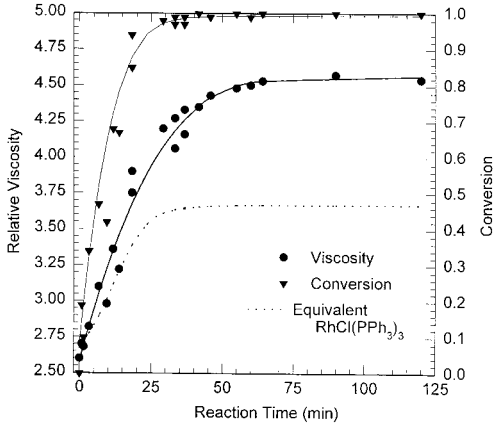


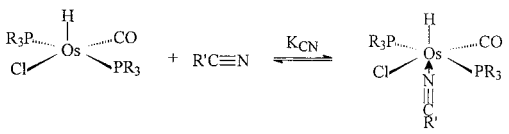
Figure 6 Conversion, η_{rel} versus time; [**1**] = 80 μM, P_{H2} = 23.7 bar, [CN] = 249 mM, T =130°C.

cause the rhodium systems represent the standard for HNBR selectivity, the previously reported $RhCl(PPh_3)_3$ and $RhH(PPh_3)_4$ data are included for comparison.[8]

The influence of catalyst concentration on selectivity is shown in Figure 3. Although η_{rel}^* of the rhodium products is constant, the selectivity of the osmium system is compromised by increased amounts of catalyst. If the crosslinking reaction was noncatalytic, selectivity could be improved by any means of enhancing the hydrogenation rate, including the addition of more osmium to the system. The observed increase of η_{rel}^* with increasing [Os] therefore proves that crosslinking is, in fact, a metal-mediated reaction. Barring any influence of the PPh_3 added to stabilize the rhodium catalysts, the consistency of the rhodium viscosity data provides further evidence. If crosslinking was not a catalytic process, the η_{rel}^* of these samples should have fallen as the amount of rhodium was increased.

Given the strong dependence of the hydrogenation rate on the concentration of H_2 that the relative rates of crosslinking and hydrogenation are influenced disproportionately by pressure is not surprising. The selectivity data presented in Figure 4 show a substantial improvement in the performance of complex **1** as the reaction pressure is raised. Note that the HNBR produced at pressures below 13 bar contained insoluble gel that precluded analysis by viscometry. Although the trend toward lower η_{rel}^* is encouraging, higher pressure cannot persuade complex **1** to render the selectivity of the rhodium technology. At 69 bar H_2, [Os] = 45 μM, [RCN] = 950 mM, and T = 140°C, Rempel et al.[9] report an intrinsic viscosity of 1.56 dL/g compared to the standard rhodium value of 1.53 dL/g. Even under severe reaction conditions, an inferior product is created by the osmium system.

From a commercial standpoint, it is desirable to maximize reactor productivity by operating with high polymer concentrations. However, Figure 6 shows the selectivity of the osmium process is adversely affected by this practice. A linear relationship between η_{rel}^* and [RCN] is evident, but given the narrow range of conditions studied and the variability in the data, this linearity is unlikely to hold over a wider domain. This rise of η_{rel}^* with increasing [RCN] could result from the influence of nitrile on the hydrogenation rate. Coordination of nitrile to the activated form of complex **1** (**Scheme II**) is known to reduce hydrogenation activity. Although this catalyst inhibition can account for the observed loss of selectivity, the possibility that nitrile coordination is directly involved in HNBR crosslinking cannot be excluded. The prospect of nitrile involvement in the process is considered in an investigation of the reaction kinetics.



Scheme II Nitrile coordination to the activated form of complex **1**.

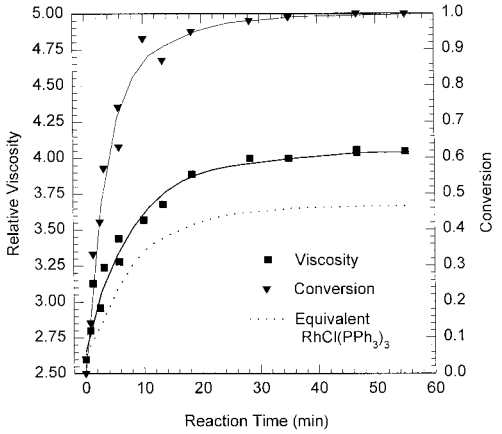


Figure 7 Conversion, η_{rel} versus time; [**2**] = 80 μM, P_{H2} = 41 bar, [CN] = 249 mM, T = 160°C.

Crosslinking Kinetics

Understanding how crosslinking develops with time requires knowledge of the product viscosity both during and after the completion of the hydrogenation process. However, interpreting the viscosity of unsaturated HNBR is not straightforward. We have overcome this difficulty, at least qualitatively, by applying the $RhCl(PPh_3)_3$ viscosity-conversion, illustrated in Figure 2. Using the rhodium data as a baseline, the influence of composition can be decoupled from η_{rel} data to provide a meaningful indication of crosslink density. The von Braun mechanism (**Scheme I**) suggests that nitrile, hydrogen, and active catalyst are the only components required to crosslink HNBR. The viscosity is therefore expected to rise sharply during the reaction as a result of the conversion effect and continue to increase beyond 100% olefin hydrogenation. The η_{rel} versus time data of Figure 7, comprising four independent experiments, is therefore remarkable.

Together with measurements of conversion and viscosity data produced by complex **1**, Figure 6 illustrates a calculated η_{rel} versus time profile for the $RhCl(PPh_3)_3$ system. This dashed curve is the viscosity that HNBR would possess if prepared by a rhodium complex. It has been generated by applying the η_{rel}-conversion relationship of Figure 2 to the observed conversion profile. By comparing the osmium η_{rel} data to these rhodium projections, it is clear that crosslinking occurs during all stages of the hydrogenation. However, beyond 99.5% conversion, the viscosity approaches an asymptotic limit. This unexpected plateau is evidence relating η_{rel} to conversion, a strong indication that crosslinking involves residual C═C reactivity.

Two investigations have confirmed this result. In the first trial, fully saturated HNBR from a previous osmium experiment was redissolved in chlorobenzene and exposed to standard hydrogenation conditions ([Os] = 80 μM, P_{H2} = 23 bar, T = 130°C) for 1 h. Our selectivity data suggest that this treatment raises the viscosity of NBR substantially during an NBR hydrogenation. In this case, only a trace amount of residual olefin existed in the material. That no significant change of viscosity was detected supports the assertion that olefin is required by the crosslinking process. Further confirmation of the olefin dependence is provided from hydrogenations carried out with the ruthenium analogue, $Ru(Sty)Cl(CO)(PCy_3)_2$. Consistent with the osmium result, the η_{rel} data presented in Figure 8 approached a limiting value once hydrogenation was complete. It may therefore be suggested that complexes **1** and **2** crosslink by a similar mechanism. Note that a reaction temperature of 160°C was used to compensate for the disparity between the hydrogenation activities of the ruthenium and osmium analogues.

In light of this new information, the applicability of the von Braun mechanism (**Scheme I**) to HNBR crosslinking needs to be reconsidered. Both complex **1** and **2** are stable for indefinite periods under the reaction conditions studied. Therefore, were the von Braun reaction sequence operative, crosslinking should proceed in the absence of olefin, a fact that is not supported by the kinetic data. Note that a free-radical process is

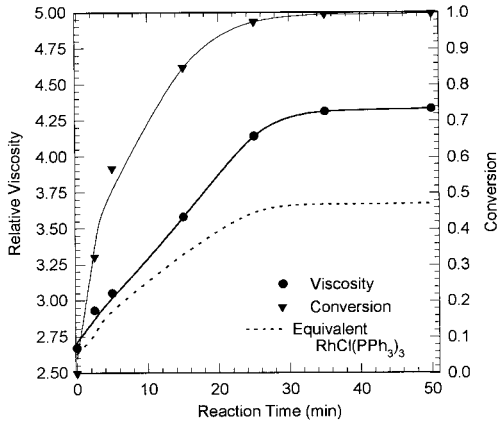
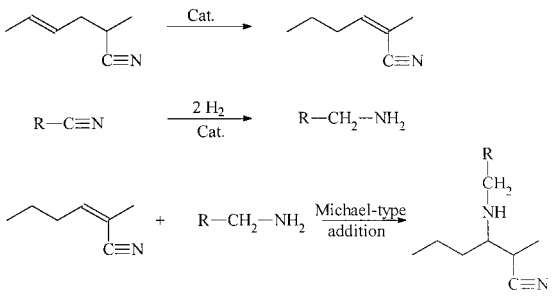


Figure 8 Conversion, η_{rel} versus time with added Tempo; [**1**] = 80 μM, P_{H2} = 23.7 bar, [CN] = 249 mM, T = 130°C.



Scheme III Michael-type addition mechanism for NBR crosslinking.

also unlikely, given that a temperature-stable radical trap failed to alter the performance of complex **1**. Figure 8 presents viscosity and conversion profiles for hydrogenation performed with 1 wt % relative to olefin of 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (TEMPO). The data are comparable to those derived in the absence of the radical trap, indicating that although TEMPO does not diminish the hydrogenation activity of complex 1, it does not improve the process selectivity.

One alternate mechanism that could rationalize the kinetic data is illustrated by **Scheme III**. By this reaction sequence, crosslinking results from a Michael-type addition of a primary amine to an activated olefin. The olefin, by nature of its adjacent nitrile group, would be relatively electron deficient and therefore susceptible to nucleophilic attack by amine. Accordingly, the metal-mediated components of the crosslinking process would be the reduction of nitrile and the migration of olefin. Although there is no evidence of large-scale reduction of nitrile to amine, there is a precedent for positional isomerization of olefins by $OsHCl(CO)(PiPr_3)_2$. Esteruelas et al. have reported the migration of olefin within 1,4-cyclohexadiene to the 1,3 position under either an N_2 or an H_2 atmosphere.[22] For NBR applications, the distinctive IR stretch at 2214 cm^{-1} of conjugated olefin–nitrile system provides a means of monitoring positional isomerization development over the course of hydrogenation. Figure 9 illustrates this migration process for complex **2** operating at low hydrogen pressure. The IR spectra clearly demonstrate the ability of this class of catalysts to produce precursors for Michael-type crosslinking. Under more severe reaction conditions, the conjugated system is not produced in sufficient quantities to be detected by IR spectroscopy.

Octylamine could obviate crosslinking by competing with reduced nitrile for conjugated olefin sites on the polymer. Other viscosity modifiers, such as ammonium sulfate, could promote the hydrolysis of the imine intermediate produced during RCN hydrogenation or by protonating amine to an inert ammonium salt. Therefore, a Michael-type addition mechanism can explain the efficacy of modifying additives. However, model verification requires a demonstration of the ability of a primary amine to add to the activated olefin created within HNBR. Two approaches were taken to explore this possibility. In the first trial, the conditions used to produce Figure 9 were repeated in the presence of 1% octylamine. Although the rate of hydrogenation was diminished, IR spectra showed no significant loss of conjugated olefin. In the second attempt, a large excess of amine was charged after all inactivated olefin had been hydrogenated. Once again, no evidence to support the addition of amine to the activated olefin was observed by IR spectroscopy. As a result, no confirmation of a Michael-type addition mechanism can be put forth at this time.

Other possible mechanisms can be postulated on the basis of reported catalytic chemistry of Pt group metal complexes and salts. Reports have shown that $RuCl_3$.aq and selected Ru–phosphine complexes catalyze the dimerization of acrylonitrile to adiponitrile in the presence of hydrogen.[23,24] James and Markham[25] have shown that $RuHCl(CO)(PPh_3)_3$ is an active catalyst for the polymerization of ethylene or butadiene. Further studies have shown that Rh and Ru trichlorides are effective catalysts for the coupling of various

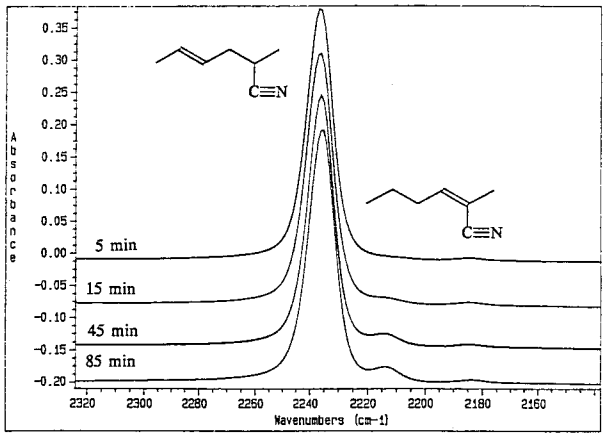
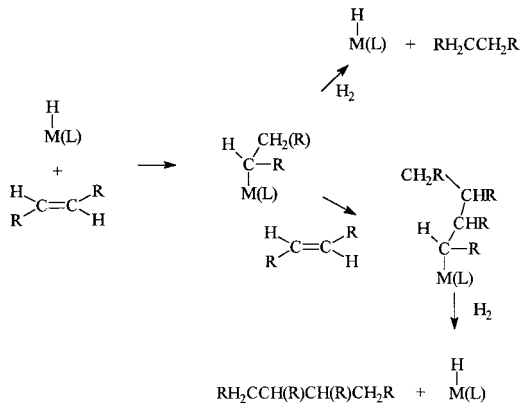


Figure 9 IR evidence for olefin migration within NBR; [**2**] = 200 μM, P_{H2} = 7 bar, [CN] = 172 mM, T = 160°C.



Scheme IV Olefin coupling mechanism for NBR crosslinking.

olefinic substrates in the absence of H_2 by a mechanism that is similar to the textbook Alder-ene reaction.[26] More recent studies have shown that Ru–phosphine complexes are effective catalysts for the coupling of acetylene with acrylonitrile[27] and vinylsilanes to cyclopentene derivatives.[28] It is feasible that such olefin-coupling reactions could be occurring to a small extent as shown in Scheme IV in parallel to hydrogenation reactions and if so could lead to the molecular weight increases indicated by our results. Given the low level of coupling necessary to cause significant crosslinking, it is difficult to pinpoint the products of such reactions within the polymer matrix. Thus the actual definition of the crosslinking reaction cannot be put forward at the present time.

CONCLUSION

The complex $OsHCl(CO)(O_2)(PCy_3)_2$ is an efficient catalyst precursor for the hydrogenation of olefin within nitrile–butadiene rubber. The copolymer's nitrile unsaturation is preserved in the process, suggesting that the oil resistance of the material is not compromised. However, this new technology catalyzes an undesirable crosslinking reaction, which is not produced by the commercial rhodium-based systems.

The quality of HNBR produced using $OsHCl(CO)(O_2)(PCy_3)_2$ is enhanced by low catalyst concentrations and high H_2 pressure. Although a viscosity-modifying additive such as octylamine reduces the extent of crosslinking, it cannot render HNBR equivalent to a rhodium product and its presence has a detrimental effect on the hydrogenation rate. Kinetic studies of the crosslinking process have revealed an influence of residual olefin that cannot be rationalized by the prevailing crosslinking mechanism purely on the basis of hydrogenation of CN groups.

A Michael-type addition sequence, although accounting for the observed behavior, could not be substantiated. Other possible reactions involving metal-catalyzed olefin coupling reactions must therefore be considered the most likely mechanisms for the observed crosslinking. However, further research is required to confirm the reaction mechanism and improve the performance of the new technology.

This paper is dedicated to Professor Brian R. James on the occasion of his 65th birthday for his many outstanding contributions to homogenous catalysis.

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