

New "Green" Route for Catalytic Latex Hydrogenation

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Abstract

Nowadays, catalytic latex hydrogenation appears to be the pursuit of industry. A catalyst predispersion method was employed to improve the hydrogenation rate. The mechanism of the ligand Triphenylphosphine (TPP) in the delivery of the catalyst molecules into the polymer particles was explored. ¹H NMR was used to monitor the hydrogenation conversion versus reaction time. The spectroscopic analysis suggests that a higher conversion of more than 95 mol% can be reached. It was found that this predispersion technique was able to remarkably increase the catalysis efficiency during the course of hydrogenation.

Keywords: Predispersion, Latex Hydrogenation, Catalysis, Triphenylphosphine, Reaction Rate.

Introduction

The selective hydrogenation of the C=C in poly(acrylonitrile-co-butadiene) (NBR) is an important commercial process because of the great resistance of the hydrogenated NBR (HNBR) towards oxidative and thermal degradation while maintaining its elastomeric properties in chemically aggressive environments [1]. The commercial process for HNBR production involves a number of cumbersome steps, including isolating and purifying NBR solids from the latex, dissolving the NBR in large amounts of organic solvent, and recovering this solvent after the completion of hydrogenation [2]. With increasing attention to sustainable development, it is very desirable to develop a "Green" technology, which would eliminate the need for a large amount of organic solvent and minimize the negative impact on the environment. Direct hydrogenation of NBR in latex/bulk form in the absence of any organic solvent is such an excellent success, which is of prime importance when HNBR in latex form is the desired end-use product or only surface/gradient hydrogenation of the product is required [3]. However, while considerable efforts have been made, the hydrogenation rate is still very slow even under a high catalyst loading and elevated reaction conditions [4]. The reason is rationalized to be due to the lipophilic property of Wilkinson's catalyst which limits its dispersion rate in an aqueous system, which therefore greatly slows down the rate of the hydrogenation reaction. It can be inferred that in order to accelerate the reaction rate of the latex hydrogenation, the central challenge is to shorten the dispersion time of the catalysts in water (hydrophilic) and to enhance diffusion into the latex particles. This paper reports

on our new approaches for successful organic solvent-free NBR hydrogenation.

Methods

Materials

Commercial NBR latex was provided by LANXESS Inc. Ultra-pure H₂ and N₂ were O₂-free being of ultra high purity (99.999%) provided by Praxair Inc. Triphenylphosphine (TPP) was obtained from Sigma-Aldrich and recrystallized using ethanol before use. RhCl(PPh₃)₃ was prepared according to standard literature procedures [5].

Procedure

The direct hydrogenation of NBR in latex form was carried out in a 300 mL Parr reactor. A *catalyst pre-dispersion approach* was employed in the present latex hydrogenation [6]. It is called the catalyst pre-dispersion method since there is an introduction period allowing for the mass transfer of catalyst into the latex particles before the initiation of hydrogenation. In a typical run, a measured volume of NBR latex with a certain amount of additional water, catalyst and TPP were added into the reactor, and then the reactor was sealed. The latex was sufficiently degassed and the temperature was raised to the reaction temperature. The latex system was then left to mature for a certain period of time under the reaction temperature before charging the H₂ and initiating the reaction. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Sampling of the reaction as a function of time was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to collect the final product and clean the reactor.

LEO 912 AB 100 kV Energy Filtered Transmission Electron Microscopy (EFTEM) (Carl Zeiss Inc. Germany) was used to observe the size and morphology of the latex particles. Proton nuclear magnetic resonance (¹H NMR) spectra, recorded on a Bruker 300 MHz Spectrometer (Bruker BioSpin Corp. Massachusetts, US), were used to measure the degree of hydrogenation. The degree of hydrogenation can be calculated using the following equation [7]:

$$\text{Hydrogenation Degree (mol\%)} = \left(1 - \frac{(8-5C(\text{AN})) / (2+4(A/B))}{(1-C(\text{AN}))} \times \frac{A}{B} \right) \times 100\%$$

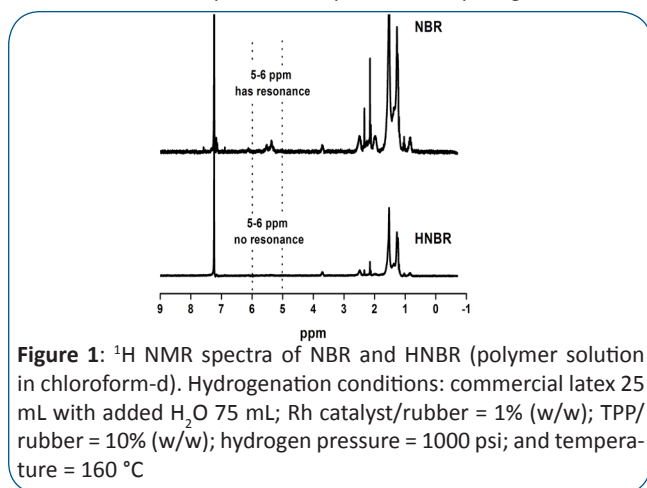
where C(AN) = the mole fraction of AN in HNBR, A is the

integral of the peaks representing protons of the residual olefinic units in HNBR, and B is the integral of peaks of protons in the methylene chains in NBR.

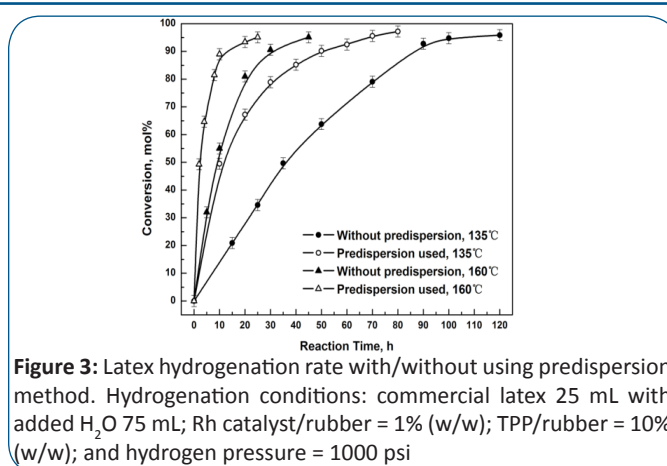
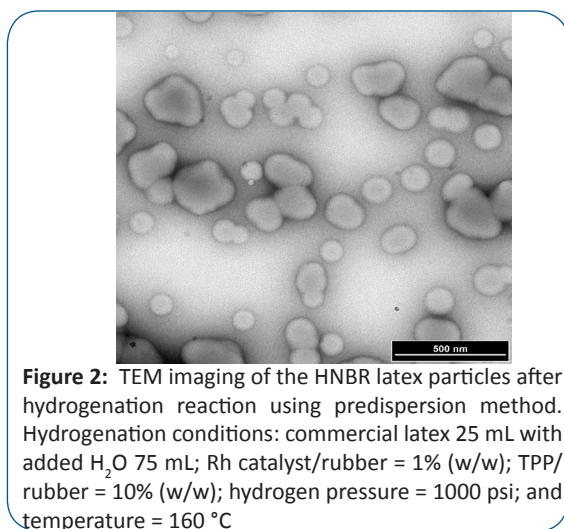
Crosslinking was estimated by the amount of the resultant HNBR which is insoluble in acetone at room temperature [8].

Results

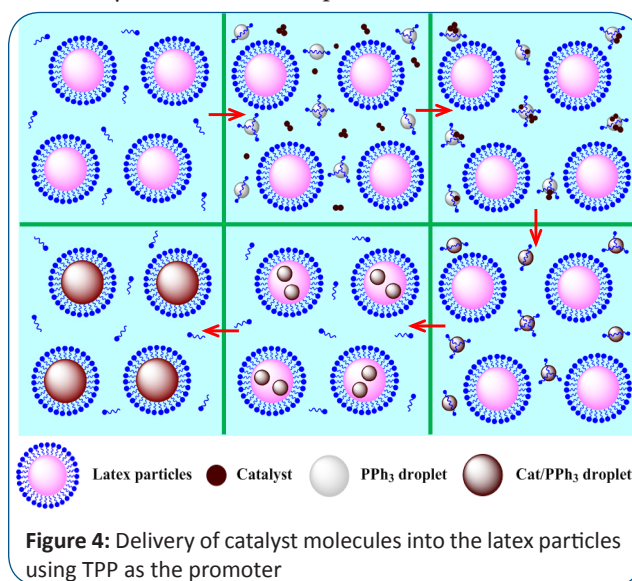
A series of latex hydrogenation reactions were carried out as described in the Experimental Sections. Figure 1 shows a typical proton NMR spectrum of NBR and HNBR. The spectroscopic analysis showed near-complete reduction of the double peaks attributable to olefinic protons ($\delta=5-6$ ppm) and that hydrogen has been incorporated into the polymer. To detect whether any cross-linking occurred in the resultant HNBR, the hydrogenated latex product was first isolated and then re-dissolved in acetone. It was found that all HNBR products were completely soluble in acetone and no visible gel was observed, even with a conversion higher than 95 mol%. Therefore, the processibility of the HNBR will not be adversely affected by the latex hydrogenation.



The morphology and particle size of the HNBR latex particles are presented in Figure 2. As can be seen from Figure 2, the distributions of the size and shape of the HNBR latex particles are polydispersed. One can easily see that some particles aggregated together and formed larger particles of more than 200 nm, while the other particles show a spherical morphology and the particle size is very small, ranging from 50-100 nm. These small nanoparticles accounts for the major parts of overall particles.



As shown in Figure 3, the hydrogenation rate increased greatly when the predispersion method was employed, compared to the hydrogenation rate under the same conditions but without using predispersion of the catalyst. This confirms that catalyst transport is the limiting step for the latex hydrogenation as mentioned in the introduction section. The predispersion process provided a higher concentration of $\text{RhCl}(\text{TPP})_3$ inside the polymer particles before the hydrogenation was initiated and thus avoiding the mass transfer step of catalyst. In addition, $\text{RhCl}(\text{TPP})_3$ has higher mobility in the polymer chains at elevated temperature, which is evidenced by the considerably shorter time required to reach a hydrogenation degree of 95 mol% at 160 $^\circ\text{C}$ than at 135 $^\circ\text{C}$. The principal reason that catalyst molecules can diffuse into the particle-swollen micelles while no alien solvent is used, lies in the great promotion role derived from the co-catalyst (TPP) which can help deliver the principal catalyst (Wilkinson's catalyst) into NBR phase, as shown in Figure 4. The melting point of TPP purchased from Sigma-Aldrich is within 79-81 $^\circ\text{C}$, which will be melted and form liquid droplets at the reaction temperatures of 135 and 160 $^\circ\text{C}$. The TPP entered into the latex system will be encapsulated and stabilized by the moving surfactant molecules. The dissolved catalyst will form a homogenous solution with the TPP. By taking advantage of the active equilibrium between the micelles and surfactant molecules, the surfactant molecules attached with newly formed TPP-Catalyst droplets would statistically assemble into the particle-swollen micelles.



Conclusion

A catalyst predispersion technique was designed and targeted to a “green” hydrogenation technology, which showed great advantages with respect to the reaction rate over the normal latex hydrogenation without using the predispersion technique. The ¹H NMR analysis showed that a high hydrogenation conversion of more than 95 mol% can be reached using 1wt% catalyst loading after around 20 h at 160 °C under 1000 psi hydrogen. The mechanism involved in the catalyst delivery was illustrated and as an alternative to an alien solvent, TPP played a crucial role in the delivery of the catalyst molecules into the particles. This improvement has made the latex hydrogenation process more economical and practical.

Acknowledgements

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References

1. Rempel GL, Pan Q, Wu J. In: G de V Johannes, Cornelis JE, editors. *Handbook of Homogeneous Hydrogenation*. Germany: Wiley-VCH; 2006. p. 547-584.
2. Wang H, Yang L, Rempel GL. Homogeneous Hydrogenation Art of Nitrile Butadiene Rubber: A Review. *Polym Rev*. 2013; 53(2):192-239. doi:10.1080/15583724.2013.776586.
3. Wang H, Yang L, Scott S, Rempel GL. Organic Solvent-Free Catalytic Hydrogenation of Diene Polymer Nanoparticles in Latex Form: Part II. Kinetic Analysis and Mechanistic Study. *J Polym Sci Part A Polym Chem*. 2012; 50(22):4612-4627. doi: 10.1002/pola.26276.
4. Rempel GL, Pan Q, Wu J. Hydrogenation of diene-based polymer latex. US Patent 7,385,010 B2. 2006.
5. Osborn JA, Jardine FH, Young JF, Wilkinson G. The Preparation and Properties of Tris(Triphenylphosphine)Halogenorhodium(I) and Some Reactions thereof Including Catalytic Homogeneous Hydrogenation of Olefins and Acetylenes and Their Derivatives. *J Chem Soc A*. 1966; 12:1711-1732. doi: 10.1039/J19660001711.
6. Wei Z. Direct Catalytic Hydrogenation of Unsaturated Diene-Based Polymers in Latex Form. Ph.D. Thesis, University of Waterloo, Canada, January 2007.
7. Singha NK, Bhattacharjee S, Sivaram S. Hydrogenation of Diene Elastomers, Their Properties and Applications: A Critical Review. *Rubber Chem Technol*. 1997; 70(3):309-367. doi: <http://dx.doi.org/10.5254/1.3538435>.
8. Wang H, Pan Q, Rempel GL. Diene-Based Polymer Nanoparticles: Preparation and Direct Catalytic Latex Hydrogenation. *J Polym Sci Part A Polym Chem*. 2012; 50:2098-2110.