The Palladium(II)-Catalyzed Polymerization of Functionalized Norbornenes.

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Introduction

The metal-catalyzed addition polymerization of norbornene derivatives is of great interest from both academic and industrial standpoints. Polynorbornenes have useful properties such as high thermal stability and glass transition temperature, as well as optical transparency [1]. Functionalized polynorbornenes also exhibit superior etch resistance and are expected to find application in deep UV photolithography [1]. However, the presence of functionalities, most often in the 5-position opposite the C=C bond, has been found to significantly attenuate the activity of the catalyst [2]. Below we discuss our results pertaining to the homo and copolymerization of functional norbornenes.

Results and Discussion

The determination of reactivity ratios allows the quantitative assessment of the effect of functionality on the ability of the monomer to undergo copolymerization. The traditional method of reactivity ratio determination involves the use of linear equations applied to copolymerizations where the conversion is kept below 10% [3]. However, this has been shown to be an inaccurate method for reactivity ratio determination [4]. A non-linear method of reactivity ratio determination, sum of space squares method (*SSS method*), has been applied for the first time to a metal-catalyzed norbornene addition polymerization system [5-8]. Figure 1 is the result of the SSS method and shows a 95% joint confidence interval plot for the copolymerization of butyl-norbornene and norbornene methyl acetate using the combination of (π-allyl)Pd(PCy_3)(CF_3CO_2) and dimethylanilinium tetraperfluorophenylborate. A direct comparison between non-linear reactivity ratio determination and linear reactivity ratio determination was also carried out.

The SSS method of reactivity ratio determination requires following the disappearance of each monomer over the course of the reaction. This technique of tracking reactions made it possible to follow the relative uptake of the endo and exo isomers for each monomer. Generally, the uptake of the exo isomer was significantly faster than the endo isomer. The relative preference for the two is influenced by the ligand on the metal. The formation of chelates, both upon the coordination of the endo-fuctionalized nobornene and in the endo-inserted product, is thought to be responsible for the observed decrease in polymerization rate for functionalized norbornene derivatives where the endo isomer predominated [2]. However, the preference for exo over endo isomer is also observed for butyl-norbornene which lacks a coordinationg functionality (e.g., Figure 2).

Fig. 1. Sum of Squares Reactivity Ratio Plot

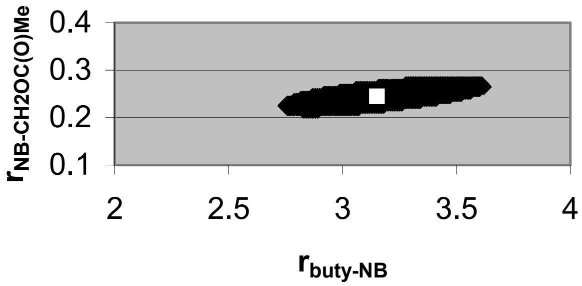
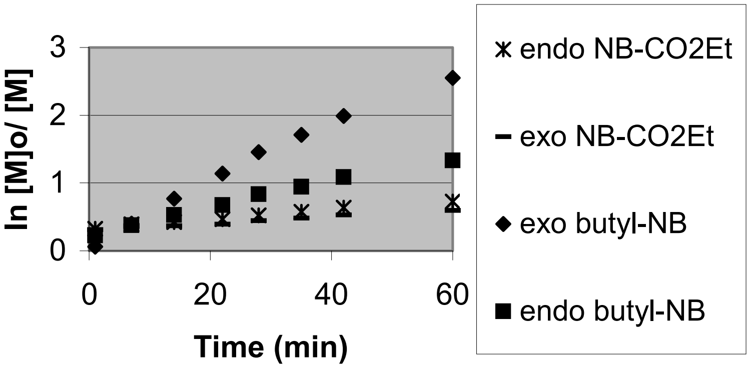


Figure 2. Conversion of Each Monomer by Isomer



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