

Hydrogenation of Ring Opening Metathesis Polymerization Polymers

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SYNOPSIS

Various methods of hydrogenating ring opening metathesis polymerization (ROMP) polymers were investigated as part of an effort to improve their stability and increase their usefulness as matrix materials for nanocluster synthesis. Hydrogenation with Pd/BaSO₄ catalyst in high-pressure hydrogen gas was only partly successful and limited to unfunctionalized polymers such as polymethyltetracyclododecene. Block copolymers containing phosphine or carboxylic acid functionalities were successfully hydrogenated by diimide generated in situ from *p*-toluenesulfonylhydrazide. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently we reported a method of synthesizing metal¹⁻³ and semiconductor⁴⁻¹⁰ nanoclusters within the microdomains of block copolymers prepared by ring opening metathesis polymerization (ROMP). Such clusters are expected to have interesting optical properties. A drawback of this route is that the resulting polymer contains carbon-carbon double bonds in the main chain (Scheme 1). These olefinic units react with H₂S during our process of making semiconductor nanoclusters (CdS,^{6,10} ZnS,^{6,8-10} PbS^{4,10}) and also undergo unwanted oxidation during heat treatment in the case of our metal (Ag,^{1,2} Au,¹ Pd,³ Pt³) nanocluster process. This makes it difficult to study the optical properties of nanoclusters because the transformed olefinic units absorb strongly in the same wavelength range as the clusters themselves.

To solve this problem, it is desirable to hydrogenate the polymers and thereby remove the unsaturation before generating any clusters. We first attempted to use Pd/BaSO₄ catalyst¹¹ to hydrogenate ROMP polymers, but we soon found that its success

was limited to simple homopolymers such, as poly(MTD) (MTD = methyltetracyclododecene). In this article we report the successful hydrogenation of ROMP block copolymers containing phosphine or carboxylic acid functionalities by diimide produced from *p*-toluenesulfonylhydrazide (TSH) precursor.

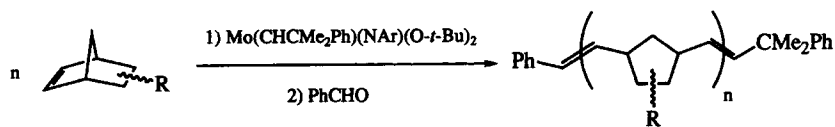
EXPERIMENTAL

Pd/BaSO₄ (Strem Chemicals) and *p*-toluenesulfonylhydrazide (TSH) (Aldrich Chemical Co.) were purchased and used as received.

All monomers were prepared as described in the literature.^{12,13} [NORPHOS]_{*n*}[MTD]₃₀₀ (*n* = 60, 30, 6) and [NORCOOH]₁₅[MTD]₃₀₀ (Fig. 1) were synthesized using the Schrock alkylidene initiator (Mo(CHCMe₂Ph)(NAr)(O-*t*-Bu)₂, (Ar = 2,6-diisopropylphenyl)), as described elsewhere.^{1,2,10,13} Homopolymer [MTD]₃₀₀ was prepared in the same way.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 300-MHz spectrometer and listed in parts per million (ppm) downfield from tetramethylsilane. Fourier transform infrared (FTIR) spectra were recorded from 4000 to 600 cm⁻¹ on a Nicolet model 510 infrared spectrometer.

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Scheme 1.

Catalytic Hydrogenation (Pd/BaSO₄)

Polymer (0.2 g) was dissolved in THF (30 mL), and Pd/BaSO₄ (0.2 g) was added to the solution. The resulting heterogeneous mixture was heated at 70°C under hydrogen gas (250 psi) for 48 h in a Parr Pressure Reaction Bomb. After reaction, the Pd/BaSO₄ catalyst was removed by either filtration or centrifugation. The polymer was then precipitated in methanol and dried under vacuum.

Stoichiometric Hydrogenation (*p*-Toluenesulfonylhydrazide)

Polymer (0.1 g) and TSH (ca. 1.0 g) were mixed in anhydrous *p*-xylene (10 mL) and heated for 1 h at 120°C under nitrogen.¹⁴ Complete solution was generally achieved by the time the temperature reached 100°C. The onset of the reaction was marked by the vigorous evolution of gas. After the reaction was finished, the mixture was allowed to cool and was poured into methanol. The hydrogenated polymer

was collected on a teflon filter, washed with methanol several times, and then dried under vacuum.

RESULTS AND DISCUSSION

Catalytic Hydrogenation (Pd/BaSO₄)

Initial attempts were made to hydrogenate homopolymer [MTD]₃₀₀ using Pd/BaSO₄. NMR spectra were taken in deuterated chloroform before and after hydrogenation. Before hydrogenation [Fig. 2(a)], there were strong olefinic resonances between 5.2 and 5.6 ppm. After hydrogenation, the olefinic signal was greatly reduced in intensity but not entirely eliminated, indicating partial but not complete hydrogenation [Fig. 2(b)].

Although the Pd/BaSO₄ catalyst did not fully hydrogenate the homopolymer, the results were encouraging enough for us to attempt the hydrogenation of more interesting functionalized block copolymers. The hydrogenation of [NORPHOS]₃₀[MTD]₃₀₀ by this method, however, was completely unsuccessful. The olefinic resonance after reaction was essentially undiminished (Fig. 3). One explanation for this result is that the phosphine functionalities of the NORPHOS block, which are known to coordinate to silver or gold complexes,^{1,2} somehow bind to the palladium of the Pd/BaSO₄ catalyst and deactivate its hydrogenating function. This hypothesis is consistent with the observed difficulty of separating the Pd/BaSO₄ catalyst from the polymer solution after reaction. Block copolymers having a shorter NORPHOS block, [NORPHOS]₆[MTD]₃₀₀, showed identical behavior. Hydrogenation of [NORCOOH]₁₅[MTD]₃₀₀ also failed, presumably for the same reason (i.e., binding of carboxylic acid groups to palladium).

In addition, we tried the soluble nickel catalyst,¹⁵ which has been used successfully to hydrogenate unsaturated polydienes. However, ROMP polymers could not be successfully hydrogenated with this catalyst.

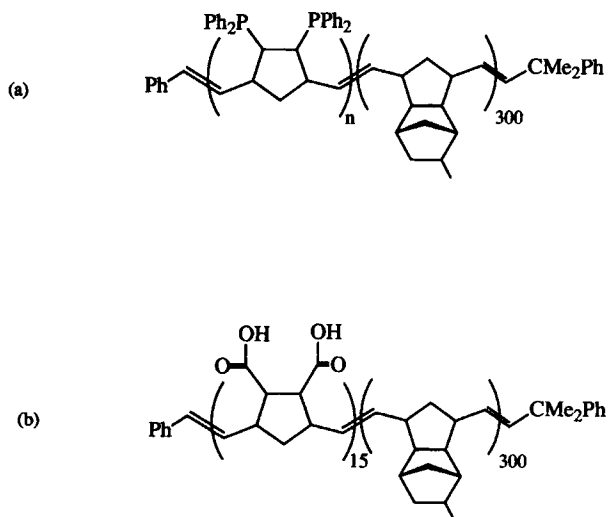


Figure 1 (a) [NORPHOS]_n[MTD]₃₀₀ ($n = 60, 30, 6$; NORPHOS = racemic 2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2,2,1]heptene; MTD = metyltetracyclododecene); (b) [NORCOOH]₁₅[MTD]₃₀₀ (NORCOOH = 2-norbornene-5,6-dicarboxylic acid).

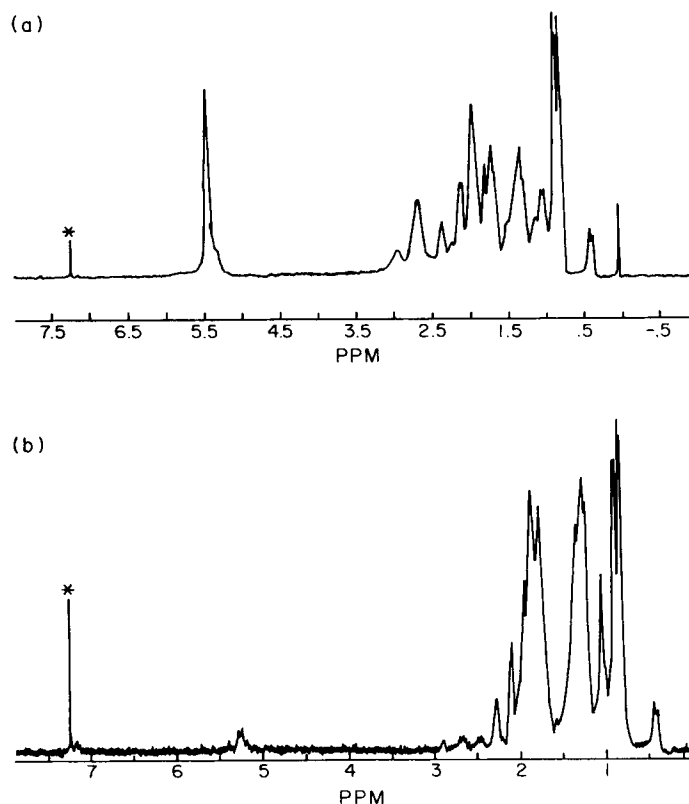


Figure 2 (a) ^1H -NMR spectrum of $[\text{MTD}]_{300}$ in chloroform- d_1 (*); (b) ^1H -NMR spectrum of $[\text{MTD}]_{300}$ in chloroform- d_1 (*) after hydrogenation with Pd/BaSO_4 .

Stoichiometric Hydrogenation (*p*-Toluenesulfonylhydrazide)

Diimide ($\text{NH}=\text{NH}$) has been used previously for the hydrogenation of olefinic compounds¹⁶ and unsaturated polymers.^{17,18} An important feature of diimide hydrogenation is its selectivity. Only non-polar double bonds are active; polar double bonds and aromatic ring systems are inert.¹⁶ Additionally, there are no metals present to which a functional group containing sharable lone pairs might coordinate. We thus expected that diimide would be compatible with polymers containing phosphine or carboxylic acid functionalities. TSH was used as a convenient precursor to generate diimide in situ. An excess amount of TSH (TSH/double bonds mole ratio > 10) was used since a large amount of the generated diimide is wasted by disproportionation.¹⁶

The NMR spectrum of hydrogenated $[\text{NORPHOS}]_{60}[\text{MTD}]_{300}$ was obtained in deuterated chloroform [Fig. 4(b)]. There was no olefinic resonance visible after hydrogenation. The broad phenyl proton resonances around 7.4 ppm were still present, which suggests that the phenyl rings of the

NORPHOS units remained essentially unchanged. This was also confirmed by the ^{13}C NMR spectrum of hydrogenated $[\text{NORPHOS}]_{60}[\text{MTD}]_{300}$, in which the phenyl carbon resonances remained between 126 and 130 ppm.

The hydrogenation of $[\text{NORCOOH}]_{15}[\text{MTD}]_{300}$ block copolymer with diimide was also successful. The hydrogenated polymer was insoluble in common organic solvents such as chloroform, toluene, and THF but was soluble in chlorobenzene, 1,2-dichlorobenzene, and bromobenzene. Deuterated THF and bromobenzene were chosen as respective NMR solvents for the unhydrogenated and hydrogenated polymers. Before hydrogenation [Fig. 5(a)], there were olefinic resonances between 5.2 and 5.7 ppm; after hydrogenation [Fig. 5(b)], the resonances completely disappeared. The carbonyl peak at 1703 cm^{-1} and the broad OH peak between 3600 and 2500 cm^{-1} in the IR spectrum remained after hydrogenation, which suggests that the carboxylic acid functionality remained unchanged.

To verify that the hydrogenation process led to improved stability and optical properties, thin films were cast and the hydrogenated polymers were

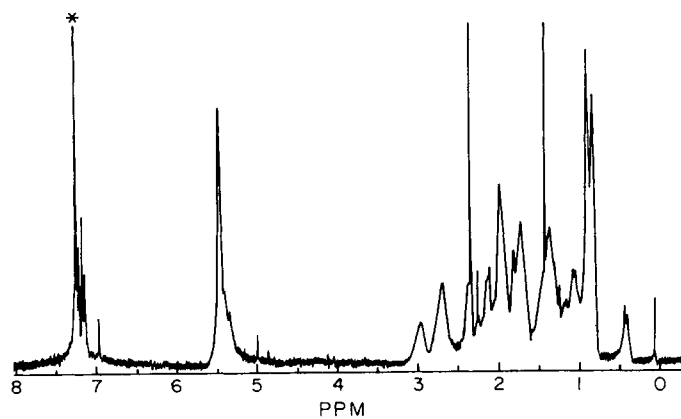


Figure 3 $^1\text{H-NMR}$ spectrum of $[\text{NORPHOS}]_{30}[\text{MTD}]_{300}$ in chloroform- d_1 (*) after reaction with Pd/BaSO_4 .

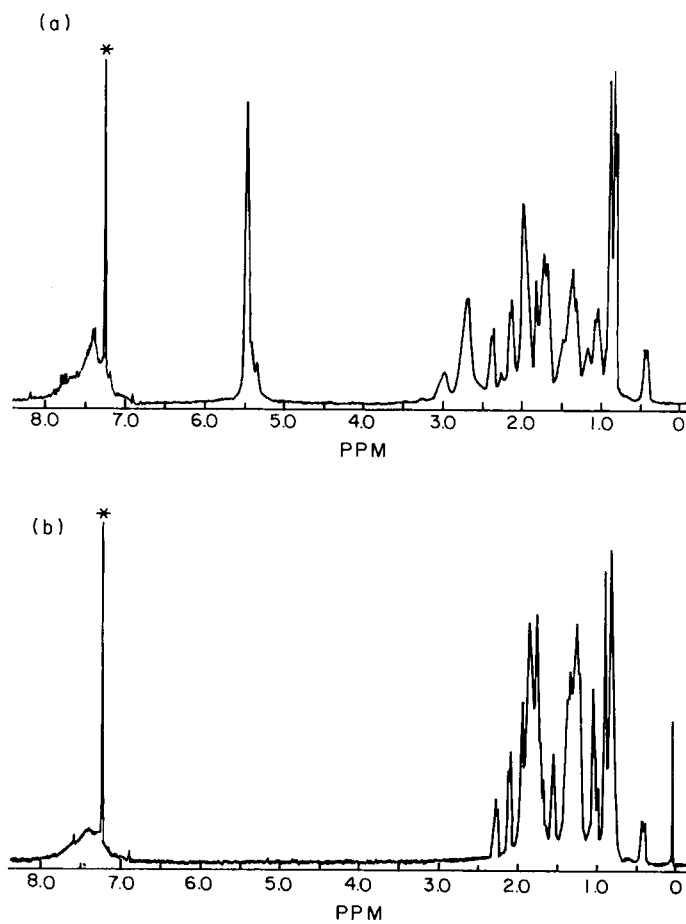


Figure 4 (a) $^1\text{H-NMR}$ spectrum of $[\text{NORPHOS}]_{60}[\text{MTD}]_{300}$ in chloroform- d_1 (*); (b) $^1\text{H-NMR}$ spectrum of $[\text{NORPHOS}]_{60}[\text{MTD}]_{300}$ in chloroform- d_1 (*) after hydrogenation with diimide.

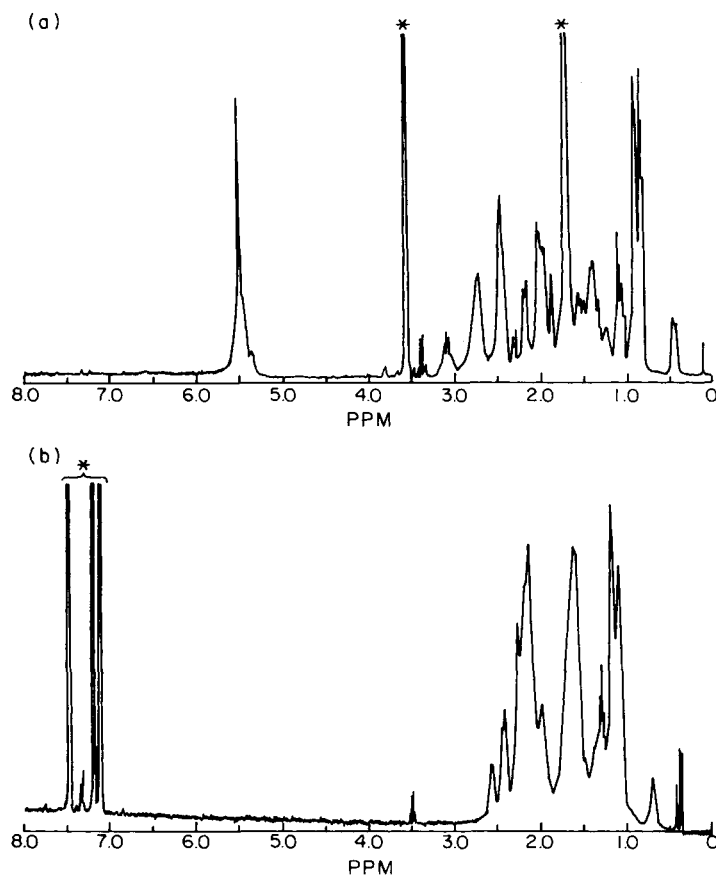


Figure 5 (a) $^1\text{H-NMR}$ spectrum of $[\text{NORCOOH}]_{15}[\text{MTD}]_{300}$ in $\text{THF-}d_8$ (*); (b) $^1\text{H-NMR}$ spectrum of $[\text{NORCOOH}]_{15}[\text{MTD}]_{300}$ in $\text{bromobenzene-}d_5$ (*) after hydrogenation with diimide.

heated in air at 135°C for 2 days alongside their corresponding unhydrogenated counterparts. Upon this heat treatment, the unhydrogenated polymers turned red, while the hydrogenated polymers remained colorless.

CONCLUSION

Pd/BaSO_4 is a somewhat effective hydrogenation catalyst for unfunctionalized ROMP polymers such as poly(MTD) but fails to hydrogenate ROMP block copolymers containing phosphine or carboxylic acid functionalities. These functionalized ROMP block copolymers can be hydrogenated successfully without loss of functionality by diimide generated in situ from *p*-toluenesulfonylhydrazide. Hydrogenated ROMP block copolymers are expected to provide stable materials in which metal or semiconductor nanoclusters can be grown without the degradative side reactions

that have been problematic; they should make it possible to study the optical properties of nanoclusters in greater detail. Further investigation of the morphology of hydrogenated ROMP block copolymers and optical properties of nanoclusters in their microdomains is in progress.

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