Determination of the Stereochemistry of Poly(1,3-cyclohexadiene) via End Group Functionalization

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Received February 22, 2001
Revised Manuscript Received June 11, 2001

Introduction

The polymerization of cyclic dienes, such as 1,3-cyclohexadiene, received minor attention during the late 1970s,[1−5] but interest dwindled due to a number of deleterious side reactions that limited the attainable molecular weights.[6,7] In 1997, Natori reported the first example of a living anionic polymerization of 1,3-cyclohexadiene.[8] The polymerization was reported to proceed in a living fashion in the presence of the additive tetramethylethylenediamine (TMEDA) with the initiator *n*-butyllithium (*n*-BuLi). The regiochemistry was determined using ^{1}H NMR at elevated temperatures (160 °C) in dichlorobenzene.[9] The homopolymer was reported to contain approximately 50% 1,2 and 50% 1,4 repeating units. More recent studies have reported the regiochemistry to be approximately 70% 1,2-addition and 30% 1,4-addition.[10] The degree of 1,2-addition vs 1,4-addition is a critical factor that dictates the mechanical and thermal properties of diene-based polymers.[11] Typically, poly(dienes) containing high degrees of 1,2-addition exhibit higher glass transition temperatures and higher moduli as compared to those of polymers containing high degrees of 1,4-addition.[11]

In light of conflicting results and the critical role of 1,2-addition vs 1,4-addition on polymer properties, poly(1,3-cyclohexadiene) homopolymers were prepared in the presence of the ligating agent TMEDA and the initiator *n*-BuLi at 40 °C. The regiochemistry and stereochemistry of the resulting polymers were determined via complementary NMR techniques. The living nature of the 1,3-cyclohexadiene polymerization also ensured a novel quantitative end-capping reaction with chlorotrimethylsilane (TMSCl). Thus, a terminal spectroscopic tag suitable for ^{1}H, ^{13}C, and ^{29}Si NMR studies was quantitatively introduced. These end group studies were also corroborated with ^{1}H NMR studies examining the regiochemistry of the polymer repeating unit.

Experimental Section

Materials. 1,3-Cyclohexadiene (Aldrich) was degassed several times and vacuum-distilled (0.13−0.16 mmHg, 10 °C) from dibutylmagnesium (DBM). *n*-Butyllithium (FMC Corporation Lithium Division, 1.35 M in *n*-hexane) was used without further purification. TMEDA (Aldrich) and chlorotrimethylsilane (Aldrich, 98%) were vacuum-distilled (0.13−0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at −25 °C. Cyclohexane was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7−10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Polymer Synthesis. A 100 mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol), 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), and TMEDA (0.094 mL, 0.625 mmol) was heated to 40 °C. The initiator *n*-BuLi (0.31 mL, 0.5 mmol) was added by syringe, and the solution was heated at 40 °C for 25 min. Upon completion of the 1,3-cyclohexadiene polymerization, excess chlorotrimethylsilane (0.5 mL, 2.5 mmol) was added by syringe to ensure quantitative capping of the living polymer chain ends with trimethylsilyl (TMS) end groups. The resulting end-capped polymer was precipitated into 2-propanol (600 mL), filtered, and dried at 50 °C in vacuo for 12−18 h. Precipitation ensured complete removal of excess TMSCl and hydrolyzed products, and ^{1}H and ^{29}Si NMR confirmed the absence of appreciable TMSCl. An antioxidant such as Irganox 1010 (0.10 wt % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage. To control the product molecular weight, both TMEDA and *n*-BuLi concentrations were varied. However, the ratio of TMEDA/*n*-Buli was maintained at 5/4, and the monomer concentration was maintained at 10 wt %.

Polymer Characterization. Molecular weights were determined using a Waters Alliance size exclusion chromatography (SEC) system equipped with a Viscotek 150R viscosity detector. The determinations of molecular weights using universal calibration based on polystyrene standards is well established.[12] SEC measurements were performed at 25 °C in chloroform at a flow rate of 1.0 mL/min.

NMR Measurements. ^{1}H and ^{13}C NMR high-resolution NMR spectra were obtained at 400 and 100 MHz, respectively, using a Varian NMR spectrometer equipped with a 10 and 5 mm broad-band probe and standard pulse decoupling. ^{1}H NMR samples were referenced to the residual signal of the deuterated solvent. The samples were dissolved in dichlorobenzene, and chromium(III) acetylacetonate was added to reduce the relaxation time for the ^{13}C and ^{29}Si NMR studies. The ^{13}C and ^{29}Si spectra were obtained at 80 °C using an inverse gated, double filtered, broad-band decoupling sequence. Our earlier studies involving the oxidation of poly(1,3-cyclohexadiene)s demonstrated that oxidative degradation did not occur under these conditions.[13] The error associated with the NMR measurements was determined as outlined earlier.[14]

Results and Discussion

The trimethylsilyl-terminated poly(1,3-cyclohexadiene)s were synthesized as depicted in Scheme 1. To examine the effect of chain length on the stereochemistry, TMS end-capped poly(1,3-cyclohexadiene) homopolymers were synthesized with calculated number-average molecular weights of 10 000 and 5000. The resulting polymers exhibited narrow molecular weight distributions ($M_w/M_n = 1.01-1.06$) and controlled number-average molecular weights (9980 and 6000, respectively). In addition, the number-average molecular weight, as determined via ^{1}H NMR analysis of the trimethylsilyl end group, agreed well (6200) with the GPC value (6000). This indicated quantitative end-capping and the absence of significant protonation via acidic impurities in the chlorosilane reagent. The polymers were spectroscopically characterized using both the polymer repeating unit and the TMS end group. Two different ^{1}H NMR methods were utilized to determine the polymer regiochemistry.

The first method (method A) compared the olefinic integration with the allylic integration, and the second method (method B) compared the allylic integration with the aliphatic integration. Both of the methods have been widely employed throughout the literature.[9,10,15−17] These assignments are based on a previous study by Natori et al., which describes the deconvolution of the

10.1021/ma0103167 CCC: $20.00
Published on Web 07/20/2001

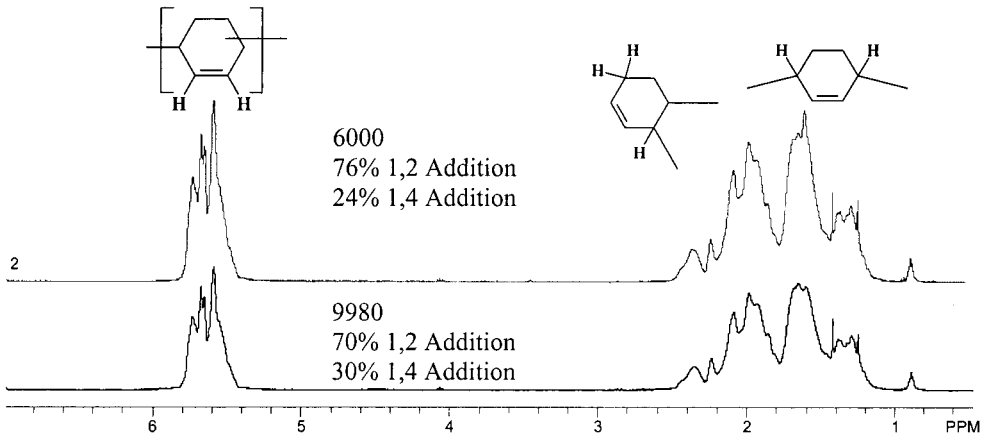
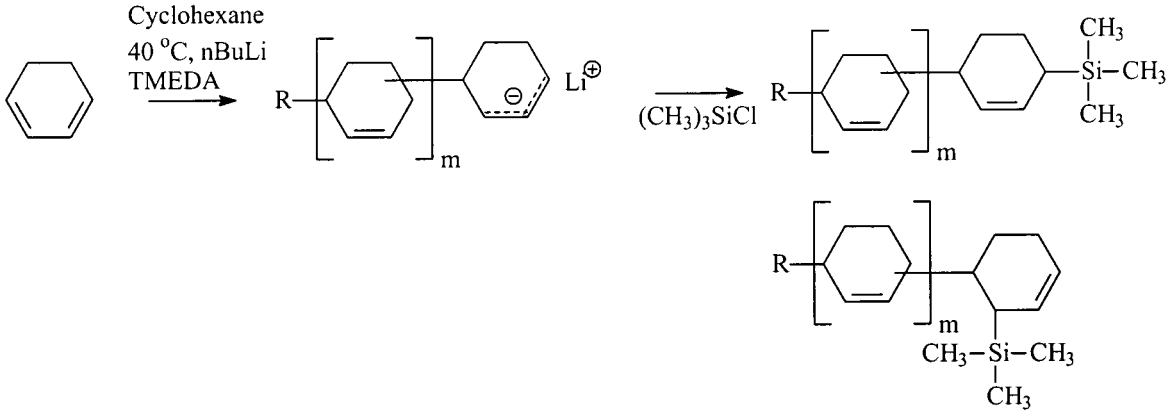


Figure 1. ^{1}H NMR spectra of the 9980 (bottom spectrum) and the 6000 (top spectrum) homopolymer.

Scheme 1. Synthetic Methodology for the Preparation of Trimethylsilyl-Terminated Poly(1,3-cyclohexadiene) Homopolymers



allylic from the aliphatic region at 1.8 ppm.[15] The approximation of the chemical shift by deconvolution was determined using 2D-NMR spectroscopy.[9] The following set of linear equations was utilized to determine the regiochemistry using method A, which compares the allylic integration with the olefin integration.

$$\text{area}_{\text{olefinic}} = 2x + 2y$$

x = relative amount of 1,2-addition

$$\text{area}_{\text{allylic}} = 3x + 2y$$

y = relative amount of 1,4-addition

Using method A, the percentage of 1,2 vs 1,4 was reproducibly determined to be 70% 1,2 and 30% 1,4 for the 9980 homopolymer and 76% 1,2 and 24% 1,4 for the 6000 homopolymer (Figure 1). Method B, which utilizes the aliphatic and allylic proton integrations, was also used to determine the stereochemistry of poly(1,3-cyclohexadiene) homopolymers. Characterization of the homopolymer using method B to determine the regiochemistry resulted in 52% 1,2-addition and 48% 1,4-addition. These values agreed well with previous literature references.[9,15–18] The lack of agreement between these two apparently complementary methods has resulted in some confusion in determining the correct stereochemistry of poly(1,3-cyclohexadiene). In addition, poor polymer solubility in common solvents renders ^{13}C NMR more complicated due to the poor spectral resolution and spectral complexity.

To ascertain the correct regio- and stereochemistry, a trimethylsilyl end group was introduced as a spectroscopic tag for both ^{1}H and quantitative ^{29}Si NMR studies. The NMR end groups were used to determine the regiochemical and stereochemical structure of the polymer chain end. Because of the reactivity difference between addition of the living poly(1,3-cyclohexadienyllithium) anion to 1,3-cyclohexadiene vs chlorotrimethylsilane, the regiochemistry adjacent to the trimethylsilyl end group does not necessarily need to agree with the regiochemistry of the repeating unit. ^{1}H NMR analysis of the TMS end groups on the 9980 polymer (Figure 2) indicated a ratio of 73% 1,2-addition and 27% 1,4-addition. A similar ^{1}H NMR analysis of the 6000

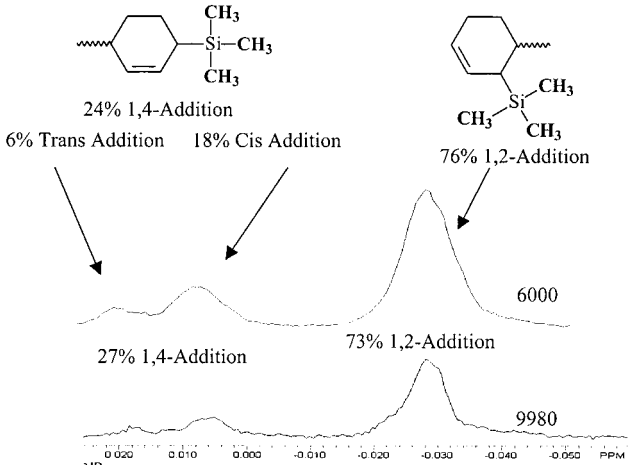


Figure 2. ^{1}H NMR spectra of the trimethylsilyl end group on the 9980 and 6000 homopolymer.

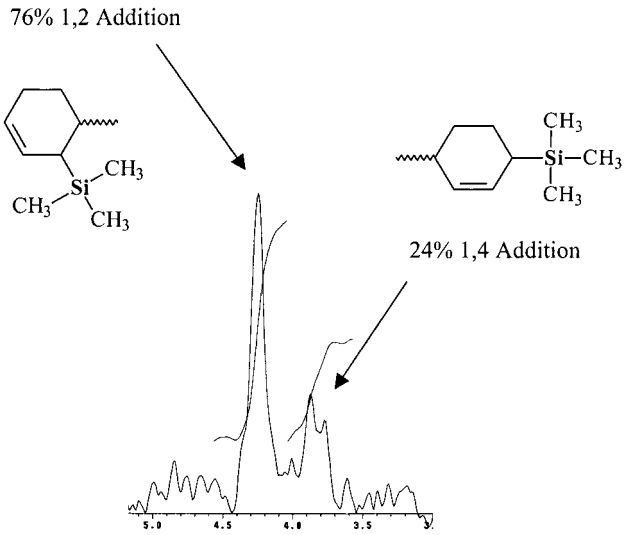


Figure 3. ^{29}Si NMR spectrum of the 6000 homopolymer

polymer (Figure 2) resulted in a ratio of 76% 1,2-addition and 24% 1,4-addition. The TMS groups resulting from 1,4-addition are expected to be in a less shielded environment and occur further downfield of the shielded TMS groups arising from a 1,2-addition. The cis-1,4 TMS peak from 0.018 to 0.003 ppm and the trans-1,4 TMS peak at 0.031 to 0.019 ppm were assigned (Figure 2). On the basis of these assignments, the 6000 polymer is proposed to contain 6% trans and 18% cis-1,4 units. To further support the ^{1}H NMR determined 1,2-addition vs 1,4-addition ratio, the silicon methyl chain ends were also characterized using ^{29}Si NMR (Figure 3). Analysis of the ^{29}Si NMR spectrum indicated a ratio of 76% 1,2-addition and 24% 1,4-addition. These values, determined by examining the TMS end groups, corroborated with the percentage of 1,2- vs 1,4-addition as determined by the examination of the ratio of the allylic and olefinic peaks in the ^{1}H NMR spectrum. This excellent agreement between regiochemistry of the polymer backbone and the silicon chain ends suggested that the reactivity of the polymer chain end toward the monomer or the end-capping reagent was similar. Furthermore, these complementary spectroscopic techniques suggested that the regiochemistry of poly(1,3-cyclohexadiene) as prepared using the above reaction conditions was 76% 1,2-addition and 24% 1,4-addition.

Conclusions

The stereochemistry of poly(1,3-cyclohexadiene) was examined through end group functionalization with chlorotrimethylsilane. The end group studies were compared with a more conventional study of the backbone of the polymer chain. The polymer backbone contained 70% 1,2-addition and 30% 1,4-addition. The regiochemistry of the 6000 trimethylsilyl end-capped chain ends was examined via both ^{1}H and ^{29}Si NMR. Using end group analysis, the homopolymer was found to exhibit 76% 1,2-addition and 24% 1,4-addition. The ratio of the cis vs trans was determined upon ^{1}H NMR examination of the TMS end groups and found to be 6% trans and 18% cis of the total 24% 1,4-addition. In addition, these studies demonstrated that comparing the allylic to the aliphatic peaks to determine the polymer regiochemistry leads to erroneous results. Studies examining the nature of the difference between the two apparently complementary methods are currently being performed. This is the first reported determination of the cis vs trans ratio for the polymerization of 1,3-cyclohexadiene and the use of an end-capping approach to study the stereochemistry of the cyclohexene containing poly(1,3-cyclohexadiene) backbone. These complementary methods represent a significant improvement over the previously reported methods used to study the stereochemistry of poly(1,3-cyclohexadiene).

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MA0103167