Macromolecules **1999,** *32,* 5744−5746

Concerning the Mechanism of Ring-Opening Polymerization by Coordinate Catalysts: The 2D Homonuclear *J*-Resolved Spectrum of Poly(cyclohexene oxide)

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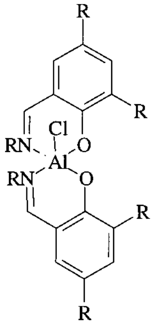
Received February 8, 1999; Revised Manuscript Received June 29, 1999

ABSTRACT: The use of 2D homonuclear *J*-resolved ^{1}H NMR spectroscopy in the examination of the methine region of poly(cyclohexene oxide) formed by polymerization of cyclohexene oxide employing the Union Carbide calcium−amide−alkoxide catalyst reveals that the majority of the ring opening occurs by backside attack.

In contrast to the notable advances in the development of homogeneous catalysts for poly(α-olefin) syntheses,[1] the chemistry of polyoxygenates derived from ring-opening polymerization, ROP, of 1,2-epoxides and other cyclic ethers has progressed much more slowly. Commercially viable catalysts are limited to heterogeneous coordinate catalysts, such a the Union Carbide patented calcium−amide/alkoxide,[2] whose mechanisms and structure are relatively ambiguous. To date, the only class of single-site catalysts known to polymerize epoxides is Al and Zn porphyrin species **1**, developed by Inoue,[3] and related Schiff base complexes of putative structure **2**, which have been reported by LeBorgne, Spassky, and co-workers.[4] None of these systems exhibit high catalytic activity in the absence of cocatalysts, and studies of kinetics implicate a mechanism that is bimolecular in metal complex.



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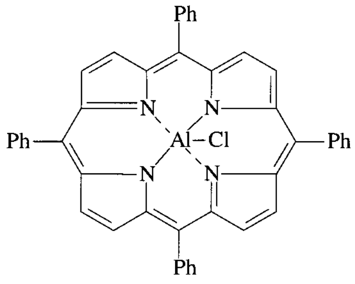

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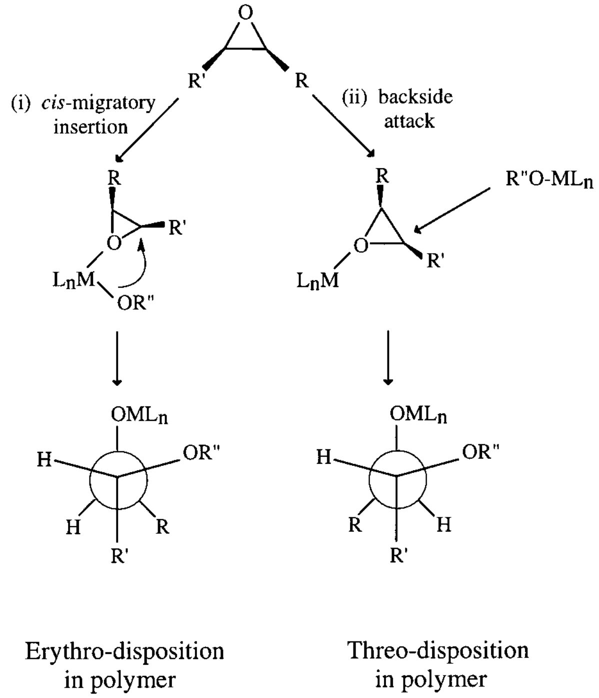
Scheme 1



In principle, a coordinate catalyst can operate by two fundamental mechanisms as illustrated in Scheme 1 for a disubstituted epoxide. Pathway i illustrates a cis-migratory insertion at a single-metal site. It is akin to alkyl migration to a coordinated carbonyl or olefin ligand in organometallic chemistry[5] and would be expected to proceed with retention of stereochemistry during the O−C bond-forming step. In pathway ii the substrate and nucleophile are bound to different metal centers. The reaction proceeds via backside attack leading to inversion of stereochemistry as is most often seen in the chemistry of epoxides[6] and as is consistent with the kinetic data for the homogeneous systems noted above.[7] Moreover, Vandenberg,[8] some 30 years ago in studying the polymerization of R,R-*trans*-dimethylethylene oxide by a ^{i}Bu$_3$Al/H$_2$O catalyst system determined that the resultant crystalline polymer showed no optical purity and that polymer degradation gave only meso-diols. From these elegant studies he concluded that ROP of the D-(+)-2,3-epoxybutane proceeded by inversion. Other researchers have attempted to extend this conclusion to the polymerization of other disubstituted,[9] monosubstituted,[10] and unsubstituted[11] epoxides with considerably less success. We describe here our studies of homonuclear *J*-resolved spectroscopy[12] to poly(cyclohexene oxides), PCO, formed from the reaction between cyclohexene oxide, CO, and the Union Carbide catalyst. If we assume that the ring-opening event occurs with inversion, the resultant polymer should contain a repeat unit wherein the ether linkages are trans as shown in **3a** and **3b**. Of these, **3a** should be favored considerably by both steric and electronic factors,[13] and thus **3b** should contribute negligibly to the physical properties of the polymer.

10.1021/ma9901745 CCC: $18.00

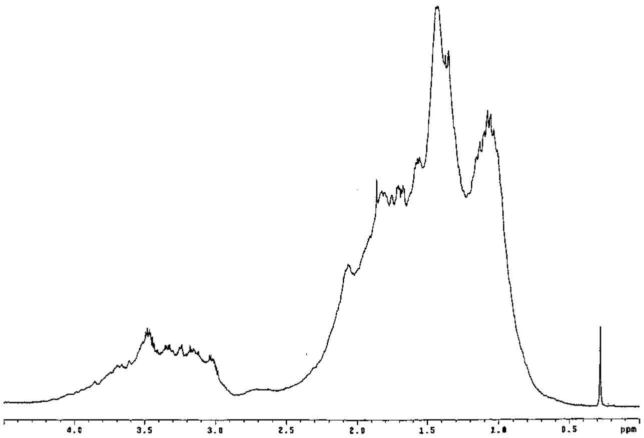
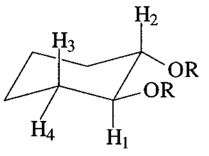
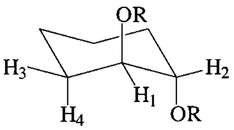


Figure 1. The 400 MHz ^{1}H spectrum of poly(cyclohexene oxide) in C_6D_6 solution.

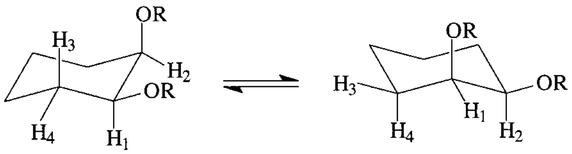


3a



3b

If ring-opening proceeded with retention, the polymer chain would contain a repeat unit with cis-ether linkages, and the two relevant conformations are shown in **4a** and **4b**. These are energetically degenerate and would be expected to interconvert rapidly. The coupling constants for the methine protons of **3a** and **4a/4b** would be expected to be markedly different.



4a **4b**

The ^{1}H NMR spectrum of the purified PCO in C_6D_6 is shown in Figure 1. The methine protons appear as a cluster of resonances of high multiplicity in the range δ 3.0−4.0 while the methylene protons are upfield δ 2.5−0.7. The methine cluster resonances approximate a linear combination of the spectra of racemic and meso-diols prepared by Tsuruta, but little more can be gleaned from the ^{1}H NMR spectrum shown in Figure 1.

The 2D homonuclear *J*-resolved spectrum of the PCO sample in C_6D_6 is shown in Figure 2. The dominant features of the spectrum are the two ridges of eight spots at 3.01 and 3.46 on the F_2 axis. An expanded view of the lower ridge and a COSY spectrum, showing the cross-peaks for the 3.01 and 3.46 resonances, are shown in the Supporting Information. The ridge represents an eight-line ddd resonance of the type expected for a polymer bearing a repeat unit with trans disposed ether linkages. The major coupling constants contributing to this multiplet are 11.0, 8.5, and 4.5 Hz. Very similar coupling constants (10.1, 8.5, and 4.3 Hz) were observed for the multiplet at δ 3.01.

Trimer molecular models were constructed using PC-MODEL (Serena Software, Bloomington, IN) with hydroxyl group chain termini in the equatorial positions. The two oxide links were set to axial or equatorial positions, generating a total of 16 different models. After energy minimization of each molecular model, vicinal coupling constants were calculated. These are listed in Table 1. These results clearly show that only **3a** can account for the observed spin system. Furthermore, the calculated coupling constants for **3a** agree extremely well with the experimentally observed coupling constants at δ 3.01 and 3.46. This supports the assignment of these resonances to **3a** and indicates that the predominant mechanism of ROP by the Union Carbide catalyst for cyclohexene oxide proceeds with inversion.

Comparison of the calculated and experimental coupling constants strongly suggests that the resonances at 3.01 and 3.46 ppm arise from the two methine hydrogens within the same repeat unit. Therefore, the two methine hydrogens of each repeat unit must be in a different chemical shift environment, and there are no more than two major chemical shift environments for all methine hydrogens in the polymer. The alternate hypothesis that the different signals arise from chemically equivalent tertiary hydrogens in the monomer units but that these are in two different monomer

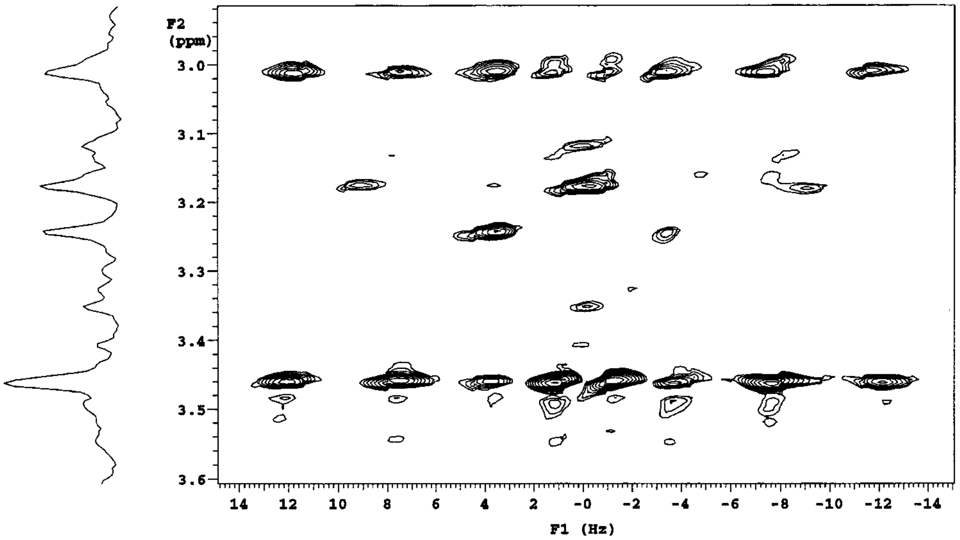


Figure 2. The 400 MHz 2D homonuclear *J*-resolved spectrum of the methine region of poly(cyclohexene oxide) in C_6D_6 solution.

Table 1. Calculated Coupling Constants for PCO Trimer Molecular Models

1	**3a**[a]	**3b**[a]	**4a**[a]	**4b**[a]	**4a** + **4b**[b]	expt[c]
H_1-H_3	11.3 ± 0.1	2.6 ± 0.1	11.4 ± 0.1	2.5 ± 0.1	5.2 ± 3.8	11.0, 10.1
H_1-H_2	8.5 ± 0.2	3.1 ± 0.3	2.2 ± 0.3	2.5 ± 0.1	2.3 ± 0.3	8.5, 8.5
H_1-H_4	4.3 ± 0.3	3.6 ± 0.1	3.9 ± 0.4	3.7 ± 0.1	5.2 ± 3.8	4.5, 4.3

[a] The oxide stereocenter of the PCO trimer end residues were set to equatorial or axial orientations, creating four molecular models for each of **3a**, **3b**, **4a**, and **4b**. Each coupling constant is listed as the average and standard deviation of the calculated coupling constants from each of these four models. [b] The **4a** + **4b** H_1-H_2 coupling constant is the average of the H_1 and H_2 coupling constants for the eight **4a** and **4b** models; the **4a** + **4b** H_1-H_3 and **4a** + **4b** H_1-H_4 coupling constants are the averages of the H_1-H_3 and H_1-H_4 coupling constants of the eight **4a** and **4b** models, respectively. [c] The experimentally determined coupling constants for the multiplets at 3.46 and 3.01 ppm from the 2D *J*-resolved NMR spectrum, respectively.

environments is not consistent with the observed signal shape. In this case, the chemically equivalent hydrogens in question would be magnetically nonequivalent, and a non-first-order signal would be expected. Calculation of the signal shape for the tertiary hydrogens in these two situations verifies that the observed signal is not consistent with the alternate hypothesis. Several types of PCO molecular models with isotactic and/or heterotactic stereochemistries can be constructed that comply with these requirements. While additional experiments are required to determine which model or models represent the product of this polymerization, the mere existence of these plausible models supports the spectral interpretation and confirmation that polymerization of CHO by the Union Carbide coordinate catalyst proceeds with inversion of stereochemistry.

Acknowledgment. We thank the Petroleum Research Fund for support of this work.

Supporting Information Available: Experimental section, COSY, and additional *J*-resolved spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA9901745