

Stereospecific Polymerization of Propylene Oxide on Thermally Activated Synthetic Hydrotalcite

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The stereodirecting influence of a thermally activated synthetic hydrotalcite material on the polymerization of propylene oxide has been demonstrated. Racemic propylene oxide can be polymerized to yield a crystalline, isotactic polymer fraction and a liquid, atactic fraction. (*S*)-(–)-propylene oxide, under similar conditions, yields an optically active crystalline fraction and a liquid fraction of considerably reduced optical activity. Both liquid fractions exhibit a high degree of regioirregularity in the polymer chain. © 1991 Academic Press, Inc.

INTRODUCTION

The synthesis and physical properties of the clay mineral hydrotalcite (ideal formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$), have been reviewed by Miyata (1). Thermal decomposition of this layered anionic clay yields a product of approximate composition, $\text{Mg}_6\text{Al}_2\text{O}_8(\text{OH}^-)_2$ or $(\text{MgO})_6 \cdot \text{Al}_2\text{O}_3$ having a high surface basicity ($\text{p}K_a = 35$) (2). The catalytic properties of calcined hydrotalcite (CHT) in a number of organic reactions have been discussed by Kohjiya and co-workers (3). These authors later reported the polymerization of propylene oxide (PO) on CHT catalyst (4), demonstrating that high molecular weight poly(propyleneoxide) (PPO) could be obtained, leading them to conclude the involvement of a coordinate, anionic mechanism.

Our interest in CHT and related materials as polyalkoxylation catalysts (5) led to an examination of the selectivity of CHT and the extent to which it might resemble other inorganic and organometallic complexes identified as "coordination" initiators or catalysts. In this study, polymer samples from the CHT-catalyzed polymerization of racemic and optically active PO were examined. Potassium hydroxide (KOH), a typical

anionic catalyst (6), was used to prepare isotactic PPO from optically active PO, and regioregular atactic PPO from racemic PO, for comparison purposes.

Experimental

Quantitative ($\pm 5\%$) ^{13}C NMR spectra were recorded at the University of Waterloo on a Bruker AM250 spectrometer at 62.9 MHz, in acetone- d_6 solvent, in inverse gated decoupling mode. The Bruker J-MOD technique was employed to identify CH and CH_2 carbons; one delay time was used with $J_{\text{C-H}}$ assumed equal to 125. Optical rotations were measured on a Perkin-Elmer 141 polarimeter in benzene at 26°C. DSC measurements were carried out on polymer samples using a DuPont 9900 thermal analysis system; temperature calibration was performed using indium and water standards. All samples were normalized to ensure uniform thermal history; samples were cooled to -120°C , then scanned at $10^\circ/\text{min}$. Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with a 401 differential refractometer and five micro-styragel columns ($100\text{--}10^5 \text{ \AA}$); all samples were run in tetrahydrofuran at ambient temperature at 1.2 ml min^{-1} . BET surface measurements

were obtained by the continuous flow method with a N₂/He mixture on a Perkin-Elmer vapor sorptometer (Surface Science Western, London Canada); each sample was outgassed for 3 hr at 250°C in a 28 ml min⁻¹ He flow. XPS data was collected using a McPherson ESCA-36 photoelectron spectrometer (Surface Science Western); measurements were recorded relative to C(1s) at 284.9 eV. Powder XRD data were recorded using a Rigaku Dmax II powder diffractometer (CuK α radiation) at 0.5° min⁻¹ (University of Western Ontario).

PO (Dow Chemical Canada Inc.) was distilled over KOH pellets before use. (S)-(-)-PO (99%, $[\alpha]_D^{26} = -10.6^\circ$) was used as received from Aldrich Chemical Co. Synthetic hydrotalcite was obtained gratis from Mitsui & Co. (Canada) Ltd. The material received had a specific surface area of 10 m² g⁻¹, a mean particle size of 0.4 μ m, pH 9.0 (measured as 1 g ml⁻¹ ethanol suspension), and a reported composition of Mg_{4.5}Al₂(OH)₁₃CO₃ · 3.5H₂O. This material (CHT) was calcined at 500°C in air for 1 hr, then cooled in a vacuum desiccator.

PO samples (2.0 g) were polymerized on CHT or KOH (0.2 g) under nitrogen, in sealed vials at room temperature. KOH-catalyzed products were extracted with methylene chloride (10 ml); the extracts were passed through magnesium silicate to remove the catalyst, then concentrated *in vacuo* to yield polymer A from (S)-(-)-PO (waxy powder, 1.8 g, 90% of starting material), and polymer B from (\pm)-PO (liquid, 1.8 g, 90%). Acetone solutions (1% w/w) of CHT-catalyzed products (polymers C and D from (S)-(-)- and (\pm)-PO resp.) were filtered to remove residual catalyst particles, then fractionated at -20°C to give polymers CS (0.2 g, 8% of whole polymer), DS (0.7 g, 12%) as waxy solids, and acetone soluble liquid fractions CL (0.6 g, 80%) and DL (0.7 g, 87%).

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD powder pattern for synthetic hydrotalcite shows a high degree of crys-

tallinity with relatively sharp symmetrical peaks and a broadband at 15–40° 2 θ , consistent with patterns reported for synthetic hydrotalcite (1); *d*-spacings of 7.63 Å (at 11.7° 2 θ), 3.83 (at 23.3), 2.58 (at 34.95), and 2.30 (at 39.1) were observed for *hkl* reflections 003, 006, 102, and 105 respectively). The calcined material (CHT) showed a poorly crystalline nature with broad diffraction lines but the hydrotalcite structure is still recognizable. There is some degradation in both the commercial material and the thermally activated sample, possibly due to stacking disorder. Surface area (BET) increased from 10 m² g⁻¹ in hydrotalcite to 191 m² g⁻¹ in CHT and a substantial increase in basicity was evident (pH > 11, for 1 g ml⁻¹ ethanol suspension). Wide range XPS scans using Mg(2s) and Al(2s) photoelectron line intensities, revealed a Mg/Al surface ratio of 2.3 ($\pm 10\%$) for the hydrotalcite precursor and 3.0 ($\pm 10\%$) for CHT; the increase in Mg/Al ratio for CHT is likely due to a relative restructuring of Mg and Al surface atoms, as described elsewhere (7). In addition, the O/Al and O/Mg has increased compared with hydrotalcite, suggesting an elevated level of OH groups near the surface, suppressing the intensities of the Mg and Al lines. Hence, in contrast with the precursor material, where Al and Mg lie in the same plane (1), it is evident that in CHT, the first row of Al atoms now lies further from the outer surface relative to the Mg atoms. There was also detected a substantial amount of Cl⁻ on the CHT surface, a possible exchange contaminant (Cl⁻ for CO₃²⁻ ion), and/or due to the method of hydrotalcite preparation (from Cl⁻ salts). Detailed spectra of the C(1s) and O(1s) peaks indicate a well-defined single peak at a binding energy of 284.8 eV attributable to hydrocarbon; CHT showed a particularly "clean" peak. A high binding energy trail (290 eV) on this peak in the hydrotalcite specimen, and essentially absent for CHT, probably results from carbonate ion. The contribution from the carbonate ion is very likely masked to some extent by the layers of magnesium/aluminum and hydroxyl ions close to the

surface. The peak in the O(1s) region at 532 eV in the hydrotalcite spectrum is indicative of oxygen in CO_3^{2-} while a broad peak at 531 eV noted for the CHT sample may include contributions from OH^- and O^{2-} oxygen; there is no other direct evidence for the presence of the strongly basic O^{2-} sites but these have certainly been invoked as possible contributors to the basicity of this type of material (3).

Magnesium oxide is thought to contain at least two types of basic sites, OH^- and O^{2-} (8), while alumina may have as many as five types of OH^- site, having from zero to four adjacent O^{2-} species (9). The activity observed in CHT, depending upon calcination temperature, may result from a composite of contributions from MgO and Al_2O_3 , neither of which alone exhibits appreciable basicity of PO polymerization activity.

Polymer Characterization

M_w for liquid polymers B, CL, and DL were 0.35, 0.53, 0.59×10^4 ; M_n were 0.30, 0.43, 0.53×10^4 , respectively. Polymers A, CS, and DS were obtained as relatively high molecular weight, crystalline products ($M_w = 2.79, 19.35, 3.71 \times 10^4$; $M_n = 1.38, 10.06, 1.76 \times 10^4$, respectively); the melting temperature (T_m) and heat of fusion (ΔH_f) indicate a much higher relative crystallinity in the case of KOH-catalyzed PPO (polymer A, $T_m = 59^\circ\text{C}$, $\Delta H_f = 86 \text{ J g}^{-1}$). An experimental literature value could not be found for ΔH_f , but T_m for crystalline PPO ranges from 58 to 75°C (10). For polymers CS and DS ($T_m(\Delta H_f) = 47(36)$ and $54(28)$ respectively), small shoulders were evident on the T_m peaks at 37°C for CS and 33°C for DS. Glass transition temperatures ($T_g = -72, -72,$ and -70°C for polymers A, CS, and DS, respectively) are consistent with reported literature values (-67 to -75°C) (11). Optical activities were significantly higher in the case of polymers A ($[\alpha]_D = 38^\circ$) and CS ($[\alpha]_D = 49^\circ$) compared with that measured for the liquid polymer CL ($[\alpha]_D = 16^\circ$). Polymers B, DS, and DL were optically inactive.

It is known that the direction of ring open-

ing of asymmetrically substituted oxiranes is dependent upon catalyst type and the substituent on the oxirane ring (6, 11, 12). Anionic polymerization of PO typically involves ring opening almost exclusively in the β sense ($\text{CH}_2\text{-O}$ cleavage) (11), giving rise to regioregular (but stereorandom) head-to-tail (H-T) linkages. In contrast, cationic and coordination catalysts promote PO ring opening in both β and α directions ($\text{CH}_3\text{CH-O}$ cleavage) (1, 12), resulting in irregular head-to-head (H-H) and tail-to-tail (T-T) in addition to H-T sequences. Shilling and Tonelli have recently reported an exhaustive ^{13}C NMR study of PPO microstructure (13).

The ^{13}C NMR spectrum of polymer A, as expected, clearly shows it to be regioregular and isotactic while that of polymer B is entirely typical of base-catalyzed atactic PPO (13). In Fig. 1, the methine (75.99 ppm) and methylene (73.89 ppm) regions of the spectra of the crystalline polymer fractions CS and DS from CHT-catalyzed polymers, are closely similar to those of polymer A. The whole spectra of polymers A, CS, and DS (not shown) consist of three additional lines; terminal CH (66.15 ppm), terminal CH_3 (19.70 ppm), and internal CH_3 (17.85 ppm).

The ^{13}C NMR assignments for the amorphous polymers CL and DL (labeled in Fig. 1) are based on J -modulated sequencing techniques (not shown) and by reference to assignments made previously for atactic PPO (13). Both polymers show appreciable regioirregularity as a result of PO ring opening in both directions; the calculated amount of reverse addition (H-H:T-T) is 35 and 41% for CL and DL, respectively, compared with 6% for polymer B. The presence of defect structures may, in part, account for the secondary melting transitions observed in the DSC thermograms of polymers CL and DL above (14).

It is likely that the lower optical rotation for the CL polymer is due largely to the presence of regioirregularity in this fraction; the ^{13}C NMR spectrum for polymer CL provides strong evidence in favor of this conclusion. This spectrum is distinguished from

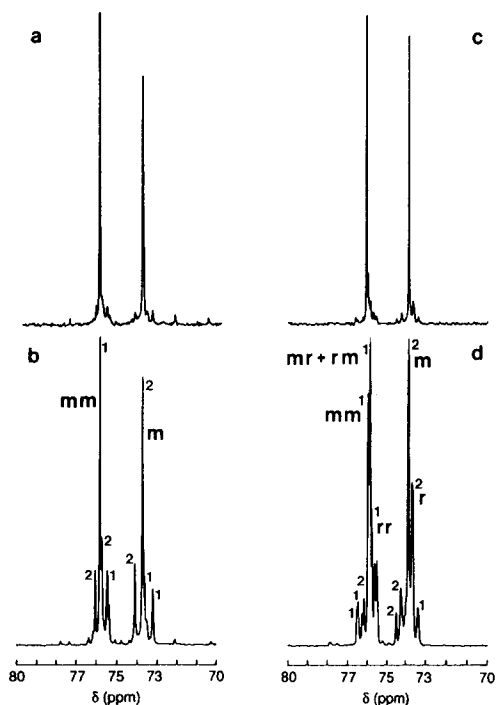


FIG. 1. ^{13}C NMR spectra for CH and CH_2 regions of (a) polymer CS, (b) CL, (c) DS, and (d) DL. Peak assignments for meso (m), and racemic (r) diads and triads, are indicated; CH and CH_2 carbons resulting from H-H: T-T placements are indicated by 1 and 2, respectively.

that of polymer DL in that it reveals an essentially isotactic structure while possessing considerable regioirregularity. As shown in Fig. 1b, the heterotactic (mr + rm) and syndiotactic (mr) triad and the syndiotactic (r) diad are essentially absent from polymer CL, while there are clearly peaks assignable to CH and CH_2 from defect chain units. The syndiotactic terminal CH carbon peak (67.0 ppm (13)) was also absent in the spectrum of polymer CL. In addition, the absence of one peak in each of the three methyl multiplets (terminal, H-H: T-T defect and internal CH_3) (not shown) in the spectrum of polymer CL distinguishes this fraction from typical atactic PPO (polymer B) and polymer DL.

In contrast with the KOH-catalyzed process, CHT produces PPO, having apparently catalyzed the opening of the optically

active PO ring in the α sense, thus creating the observed regioirregular linkages, while producing largely stereoregular, but amorphous, PPO by the normal, β ring opening of the monomer. Since both ring opening modes would be expected to occur with inversion of the carbon center (15), the "reduced" optical activity of the product is largely proportional to the relative amount of α ring opening.

In summary, the CHT-catalyzed polymers appear to be the products of ring opening of a coordinated PO monomer on a heterogeneous surface. The existence of discrete, sterically hindered catalytic sites, upon which (*S*)-(–)-PO and (\pm)-PO can open in a specific configurational sense, is implied by the formation of isotactic polymers CS and DS. Other, geometrically random centers may be responsible for the less regioselective ring opening observed in the formation of polymers CL and DL; it is highly likely that these also originate from coordinated monomer since both display a preponderance of the stereoregular isotactic placement. The reverse (or α) addition process, resulting in formation of H-H: T-T placement, implies ring activation, through coordination to a metal atom, generating substantially electron deficient centers at both primary and secondary carbons of PO, a cationic-like process similar to that invoked for other coordination catalysts (15).

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