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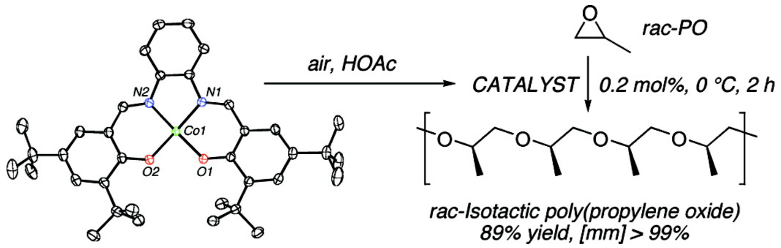
J. Am. Chem. Soc., **2005**, 127 (33), 11566-11567• DOI: 10.1021/ja053451y • Publication Date (Web): 26 July 2005



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A Highly Active, Isospecific Cobalt Catalyst for Propylene Oxide Polymerization

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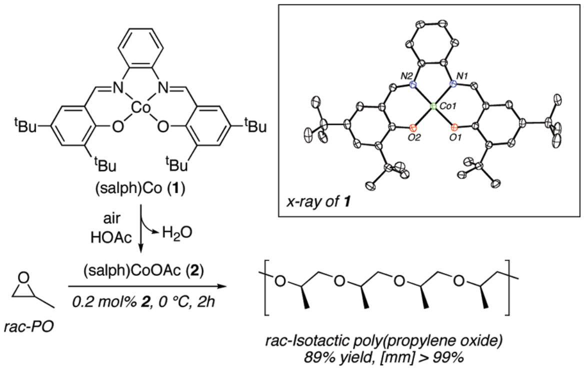
Over 57 million tons of propylene and 6.6 million tons of propylene oxide (PO) were produced in 2003. About 60% of each of these monomers are converted to their respective polymers annually.[1] Nearly all commercial polypropylenes are highly *isotactic*; interestingly all commercial poly(propylene oxide)s (PPO) are *atactic*. The lack of commercial isotactic PPO is due in part to the high expense of optically active PO and the lack of catalysts that can isospecifically polymerize *rac*-PO. Atactic PPO is readily synthesized by polymerizing PO in the presence of strongly basic initiators; metal-based catalysts are required to achieve high molecular weight (M_n), narrow molecular weight distribution (MWD), and the control of regio- and stereochemistry.[2] In general, catalyst systems that achieve high M_n PPO exhibit broad MWDs, while other systems can produce PPO with narrow MWDs but the molecular weights are typically low. Although some innovative catalysts polymerize PO with excellent regiocontrol,[3] the discovery of a catalyst for stereospecific *rac*-PO polymerization remains a challenge.

Pruitt and Baggett discovered a heterogeneous catalyst made from $FeCl_3$ and PO that produced a small amount of crystalline PPO,[4] which was later determined to have an isotactic microstructure.[5] This important finding stimulated further research concerning stereoselective PO polymerization, and since then a variety of heterogeneous catalysts have been used to afford mixtures of isotactic and amorphous PPO. Among these are multisited catalysts derived from AlR_3/H_2O/acetylacetone (R = alkyl)[6] and $Al(^iBu)_3/H_2O$.[7] Discrete aluminum porphyrin complexes[8] and chiral zinc alkoxides[9] have been developed that produce iso-enriched PPO as the sole product over a period of days, however *meso*-dyad contents are below 81%. To the best of our knowledge, no catalyst has been reported that exclusively produces highly isotactic PPO from *rac*-PO. Herein we report a highly active and stereoselective catalyst for *rac*-PO polymerization, generating regioregular, highly isotactic PPO. While developing cobalt catalysts for PO/CO_2 copolymerization,[10] we found that (salph)Co (**1**, salph = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidine-1,2-benzenediamine))[11] could be oxidized in the presence of acetic acid and air to yield a cobalt (III) complex, (salph)CoOAc (**2**). Under typical PO/CO_2 copolymerization conditions,[10] **2** produces a mixture of polyether and polycarbonate chains. To our surprise, the ^{13}C NMR spectrum of the reaction mixture revealed that the PPO component was highly isotactic with >99% *mm*-triads.[12] As this was the first example of isotactic PPO generation from *rac*-PO without concomitant atactic byproduct, we began to explore this catalyst system for isospecific PO polymerization.

Catalyst **2** was optimized for PO polymerization; conditions are summarized in Table 1. When the polymerization was run neat, it rapidly exothermed and solidified due to the high activity of the catalyst. Solvent was therefore utilized in all further studies. While the reaction did not take place in either THF (entry 1) or methylene chloride (entry 2), PPO was obtained in diethyl ether with a turnover frequency (TOF) of 60 h^{-1} (entry 3) and in toluene with a TOF of 220 h^{-1} (entry 4). We thus used toluene as the solvent for subsequent experiments in an effort to maximize catalyst activity. Both decreasing the PO concentration (while maintaining [PO]/[**2**] = 500) (entry 5) and reducing the catalyst concentration (entry 6), resulted in substantial slowing of the polymerization. This indicates that there is a reaction rate dependence on the concentration of both monomer and catalyst.

Scheme 1. Synthesis of Catalyst **2** and Isospecific Polymerization of *rac*-Propylene Oxide



To assess the effect of temperature on the polymerization, the reaction was conducted between −20 and 40 °C. Elevating the temperature from 0 to 25 °C decreased the catalyst TOF from 220 h^{-1} (entry 4) to 100 h^{-1} at 25 °C (entry 7). Additionally, the catalyst TOF dropped to 80 h^{-1} when the reaction was run at 40 °C (entry 8). We suspect the loss in activity is a result of the heat-promoted reduction of **2** to **1**, which is catalytically inactive for PO polymerization.[13] Finally, cooling the reaction mixture to −20 °C lowers catalyst activity significantly, yielding <1% conversion after 2 h.

The broad PPO MWDs (>2.0) we observe when reaction temperatures exceed 0 °C (entries 7 and 8) suggest that heat is detrimental to molecular weight control. In contrast, narrower MWDs (entries 3 and 4) were obtained for PPOs formed at 0 °C. Under all polymerization conditions, the product PPO generated by catalyst **2** is highly isotactic ([*mm*] > 99%) as determined by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of both crude and precipitated polymers reveal only three sharp peaks (Figure 1). These peaks correspond to the methyl, methylene, and methine carbons of isotactic PPO.[12] In addition, the peak melt transition temperatures (T_m) for all polymers (66−68 °C) are consistent with previous reports for highly isotactic PPO.[7]

Although we believe **2** is a square planar cobalt salen with an axial acetate (as proposed by Jacobsen for related cobalt salen complexes),[14] the complex is paramagnetic, which complicates analysis by NMR spectroscopy. Despite repeated attempts to

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Table 1. Isospecific Polymerization of *rac*-Propylene Oxide Catalyzed by **2**[a]

entry	solvent	[PO] (mol/L)	[PO]/[**2**]	T_{rxn} (°C)	yield[b] (%)	TOF[c] (h^{-1})	M_n[d] (kg/mol)	M_w/M_n[d]	*mm*-triads[e] (%)	T_m[f] (°C)
1	THF	1.0	500	0	<1	ND	ND	ND	ND	ND
2	CH_2Cl_2	1.0	500	0	<1	ND	ND	ND	ND	ND
3	Et_2O	1.0	500	0	23	60	168	1.45	>99	67
4	toluene	1.0	500	0	89	220	287	1.40	>99	66
5	toluene	0.5	500	0	1	3	ND	ND	ND	ND
6[g]	toluene	1.0	1000	0	6	30	52.1	1.62	>99	67
7	toluene	1.0	500	25	40	100	222	2.46	>99	68
8	toluene	1.0	500	40	32	80	209	2.11	>99	67
9	toluene	1.0	500	−20	<1	ND	ND	ND	ND	ND

[a] Polymerizations run with 0.5 mL of propylene oxide (PO) for 2 h unless otherwise indicated. [b] Based on crude polymer weight. [c] Turnover frequency = mol PO/(mol **2**·h). [d] Determined by size exclusion chromatography calibrated by polystyrene standards in 1,2,4-trichlorobenzene at 140 °C. [e] Determined by ^{13}C NMR spectroscopy ($CDCl_3$, 125 MHz). [f] Determined by differential scanning calorimetry, run from −90 to 90 °C at 1 °C/min. [g] 1.0 mL of PO.

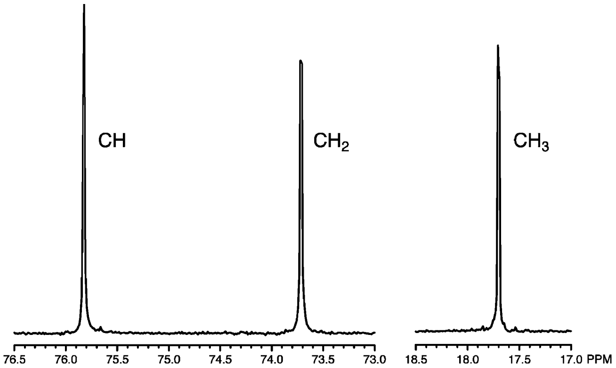

Figure 1. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of isotactic poly(propylene oxide) generated by catalyst **2** (Table 1, entry 4).

crystallize **2**, we can only produce a microcrystalline powder that we have not been able to successfully characterize by single crystal X-ray diffraction. Although the synthesis of isotactic PPO without measurable defects is a notable achievement, the lack of stereodefects unfortunately hampers our attempts to determine the mechanism of stereocontrol. The PPO M_n values are higher than predicted by the monomer/catalyst ratios, suggesting that only a fraction of the catalyst is active. It should be noted, though, that reproducible polymerization results were always obtained. Given the high degree of isotacticity of the polymer, we have not ruled out the possibility that the active catalyst has a cis-β ligand arrangement, or that it is a dimer of **2**.[15]

The scope of catalyst **2** was investigated by studying its polymerization behavior for 1-butene oxide (BO) and 1-hexene oxide (HO). Although BO and HO are structurally similar to PO, their propensities for polymerization by **2** were remarkably lower. The polymerization of BO is optimized at 25 °C with [BO] = 5M and [BO]/[**2**] = 500:1. The microstructure of the product poly(butene oxide) is highly isotactic ([*mm*] > 99%) as determined by ^{13}C NMR spectroscopy, consistent with our PO polymerization results. Under the same conditions, **2** was inactive for the polymerization of HO. Increasing the reaction time to 18 h at 25 °C and using neat HO afforded only a trace (∼3%) of poly(hexene oxide). Ethylene oxide is also polymerized by **2**.

In conclusion, we report **2** as a highly active catalyst for the isospecific polymerization of *rac*-PO, yielding isotactic PPO with [*mm*] > 99%. Isotactic PBO was also formed using this catalyst. To our knowledge, catalyst **2** exhibits the highest activity and greatest stereoselectivity for isospecific *rac*-PO polymerization to date. Further characterization of the catalyst and exploration of its use in epoxide polymerization is currently underway.

Acknowledgment. G.W.C. gratefully acknowledges funding from the NSF (CHE-0243605), the Cornell Center for Materials Research (supported through the NSF, DMR-0079992), the Cornell Nanobiotechnology Center (supported by the NSF, ECS-9876771), the Packard Foundation, and Sumitomo Chemicals. H.A. is grateful for a fellowship from the JSPS.

Supporting Information Available: Experimental procedures for catalyst synthesis and polymerizations, spectroscopic data of polymers, and X-ray data for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA053451Y