

HIGHLY ACTIVE SALEN-SUPPORTED, COBALT-BASED CATALYSTS FOR
THE SYNTHESIS OF REGIO- AND STEREOREGULAR POLYCARBONATES

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HIGHLY ACTIVE SALEN-SUPPORTED, COBALT-BASED CATALYSTS FOR THE SYNTHESIS OF REGIO- AND STEREOREGULAR POLYCARBONATES

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Synthetic routes to new (salen)CoX (salen = *N,N'*-bis(salicylidene)-1,2-diaminoalkane; X = halide or carboxylate) epoxide/CO₂ copolymerization catalysts are described, and the X-ray crystal structures of (*R,R*)-(salen-**1**)CoCl (**2.4**) and *rac*-(salen-**1**)CoI are presented. The (salen)CoX series are highly active catalysts for the alternating copolymerization of propylene oxide (PO) and CO₂, yielding poly(propylene carbonate) (PPC) with no detectable propylene carbonate byproduct. The PPC generated using these catalyst systems is highly regioregular with 92 – 99% carbonate linkages and a narrow molecular weight distribution. Inclusion of organic-based, ionic or Lewis basic cocatalysts with (salen)CoX catalysts results in a remarkable activity enhancement for the copolymerization. In the case of (*R,R*)-(salen-**1**)CoOBzF₅ (**2.3**) with [PPN][OBzF₅] (**3.1**), an unprecedented catalytic activity exceeding 700 turnovers per hour is achieved for the copolymerization of *rac*-PO and CO₂, yielding iso-enriched, regioregular PPC. When the *rac*-PO/CO₂ copolymerization is carried out with catalyst system **2.3**/[PPN]Cl at -20 °C, a *k*_{rel} of 9.7 for (*S*)- over (*R*)-PO is observed. The stereochemistry of the monomer and catalyst used in the copolymerization has dramatic effects on catalytic activity and the PPC microstructure. Using catalyst (*R,R*)-(salen-**1**)CoBr (**2.5**) with (*S*)-PO/CO₂ generates highly regioregular, isotactic PPC, whereas using (*R*)-PO/CO₂ with the same catalyst gives an almost completely regiorandom copolymer. The *rac*-PO/CO₂

copolymerization catalyzed by *rac*-(salen-1)CoBr (**2.30**) yields syndio-enriched PPC, a novel PPC microstructure.

The (salen)CoX systems are also successful catalysts for the alternating copolymerization of cyclohexene oxide (CHO) and CO₂, yielding syndiotactic poly(cyclohexene carbonate) (PCHC), a previously unreported PCHC microstructure. Variation of the salen ligand and reaction conditions, as well as the inclusion of organic-based, ionic cocatalysts, has dramatic effects on the polymerization rate and the resultant PCHC tacticity. Catalyst *rac*-(salen-2)CoBr (**4.6**) has the highest activity for CHO/CO₂ copolymerization, yielding syndiotactic PCHCs with 81% *r*-centered tetrads. Using Bernoullian statistical methods, PCHC tetrad and triad sequences were assigned in the ¹³C{¹H} NMR spectra of these polymers in the carbonyl and methylene regions, respectively.

BIOGRAPHICAL SKETCH

Claire Tova Cohen was born and raised in West Hartford, CT. She graduated from Hall High School in 1997 and continued her education at The University of Massachusetts, Amherst. Although initially an exercise science major, she changed her major to chemistry after an inspiring freshman chemistry course taught by Professor R. Metz. In her sophomore year, Claire was an undergraduate researcher for Professor Vincent Rotello and then in the following summer, began research with Professor D. Venkataraman towards the synthesis of robust, metal-organic crystalline networks. Claire worked in the Venkataraman lab for her remaining undergraduate years and also spent a summer at Colorado State University on an NSF REU fellowship working for Professor Bruce Parkinson. While pursuing her degree in chemistry, Claire also played on the UMass women's ice hockey team. In 2001, Claire graduated from UMass *magna cum laude* with a B.S. in chemistry and in the fall, entered the Ph.D. program at Cornell University. At Cornell, her graduate research focused on catalyst development for the stereo- and regioselective synthesis of polycarbonates under the direction of Professor Geoffrey Coates.

In the spring of 2006, Claire started as a Visiting Assistant Professor of Chemistry at the University of Toledo where she is currently teaching general chemistry. On June 12th, 2006, Claire married former Coates group post-doc Joe Schmidt, and has since changed her name to Claire Tova Cohen Schmidt.

Dedicated to
my brother
Jeffrey S. Cohen
in loving memory
(1976 – 2004)

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