

A phase separable polycarbonate polymerization catalyst†

Chayanant Hongfa, Jianhua Tian, Jeremy Andreatta, Donald J. Darensbourg* and David E. Bergbreiter*

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Polyisobutylene is shown to be a nonpolar phase tag that separates a highly colored salen Cr(III) complex from products but is otherwise kinetically similar to a low molecular weight salen Cr(III) complex in polycarbonate formation by Cr(III)-catalyzed copolymerization of CO₂ and cyclohexene oxide.

Polycarbonates are engineering polymers with outstanding properties that include high tensile strength, lightness, durability, high transparency, heat resistance, and useful electrical insulating ability.¹ However, the classical yet hazardous and expensive production process for synthesis of these polymers that involves the polycondensation of phosgene and diols is a textbook example of chemistry fraught with environmental problems.² In 1969, a Greener route to high molecular weight polycarbonates from carbon dioxide and epoxides was reported by Inoue and coworkers using heterogeneous zinc catalysts derived from diethylzinc and water.³ This discovery subsequently led to work in 2000 by Jacobsen and coworkers who patented the use of the (*R,R*)-enantiomer of salen Cr(III) complex **1** as a catalyst in a selective reaction of one atmosphere CO₂ with the (*S*)-enantiomer of racemic 1,2-epoxyhexane to afford a polycarbonate.⁴ (Fig. 1).

In 2004, Darensbourg described successfully using **2** as a catalyst for the copolymerization of CO₂ and cyclohexene oxide in the presence of *N*-MeIm as a cocatalyst.^{5a} Since that early report, anionic cocatalysts, such as PPN⁺Cl⁻ (PPN⁺ = bis(triphenylphosphorane)ammonium cation), have proven to be more effective.^{5b} However, while the polymerization is efficient, traces of the highly colored salen Cr(III) complex in the product polymer lead to undesired color in the product polycarbonate. Since polycarbonate is not colored, procedures that easily separate the catalyst complex from the product polymers are of interest. Here we describe preliminary work where we have explored the viability of liquid–liquid phase separation with a soluble polymer-bound catalyst as a way to address this issue. We believed this problem could be addressed by using a nonpolar polymer such as polyisobutylene (PIB) as a support for salen Cr(III) complexes. We show here that a phase selectively soluble PIB group bound to a salen complex can be used as a polymeric phase tag to prepare a catalyst that is like **2** but that separates from the polycarbo-

nate polymer that forms in reaction of cyclohexene oxide and CO₂ in CO₂.

While polymerization catalysts are not always separated from their product polymers, there are a number of reports where polymer-bound polymerization catalysts including soluble polymer bound catalysts have been designed to be separated from a product polymer. For example, we used a polyethylene-bound Nd carboxylate catalyst (PE_{olig}CO₂)₃Nd in the polymerization of butadiene.⁶ Polyethylene- and other soluble polymer-bound Cu(I) catalysts have also been used to separate Cu(I) from products in atom-transfer radical polymerization reactions.^{7–10} Another more recent example is described in a patent by Du Pont that details the use of various soluble polymer-tethered porphyrin-like metal complexes as chain transfer catalysts to produce polyacrylates that are separated from the catalyst by a filtration or centrifugation after a monophasic polymerization reaction.¹¹

Our synthesis of a PIB-supported salen Cr(III) complex started with commercially available vinyl-terminated polyisobutylene. This material is mostly vinyl terminated (*i.e.* it can be >90% =CH₂ terminated **3**). However all samples contain some of the structurally isomeric polyisobutylene oligomer with an internal double bond (**4**). However, both isomers yield the same 4-(polyisobutyl)-*tert*-butylphenol product **5** in an H₂SO₄-catalyzed Friedel–Crafts reaction with the activated arene 2-*tert*-butylphenol in dichloromethane.⁶ Further treatment of this oligomeric phenol using paraformaldehyde alkylates and then oxidizes the intermediate benzyl alcohol to in turn produce 3-*tert*-butyl-2-hydroxy-5-(polyisobutyl)benzaldehyde **6**. This product directly leads to the polyisobutylene supported salen ligand **7**. The salen ligand **7** was then metallated using CrCl₂ and oxidized to form the desired polyisobutylene salen Cr(III) complex **8** (Scheme 1).

The salen derivative **8** contains two polyisobutylated phenol groups and is phase selectively soluble in the heptane phase of a heptane/DMF, heptane/CH₃CN, or heptane/EtOH–H₂O biphasic mixture. This phase selective solubility was visibly high (Fig. 2) and was quantified by UV-visible spectroscopy ($\lambda_{\text{max}} = 350 \text{ nm}$, $\epsilon = 4514 \text{ M}^{-1} \text{ cm}^{-1}$). In a biphasic heptane/90% EtOH–H₂O mixture <0.001% of the starting complex **8** was in the polar phase.

The polymerization of CO₂ and cyclohexene oxide was carried out in CO₂ at 80 °C as shown in Scheme 2. The PIB–salen Cr(III) complex **8** (or **2**) and its cocatalyst PPN⁺Cl⁻ were dissolved in dichloromethane for 30 min, then the solvent was removed by vacuum. The catalyst and cocatalyst were then redissolved in cyclohexene oxide, loaded into a Parr

Chemistry Dept., Texas A&M Univ., College Station, TX 77842, USA. E-mail: bergbreiter@tamu.edu; Fax: 979-845-4719; Tel: 979-845-3437

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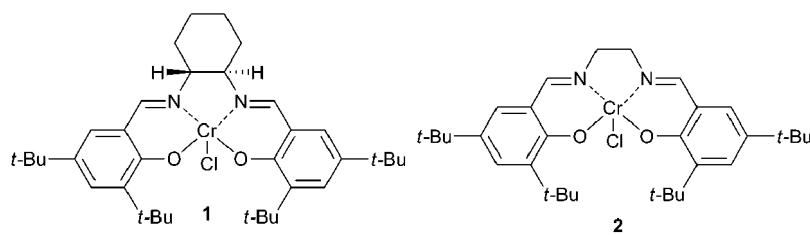
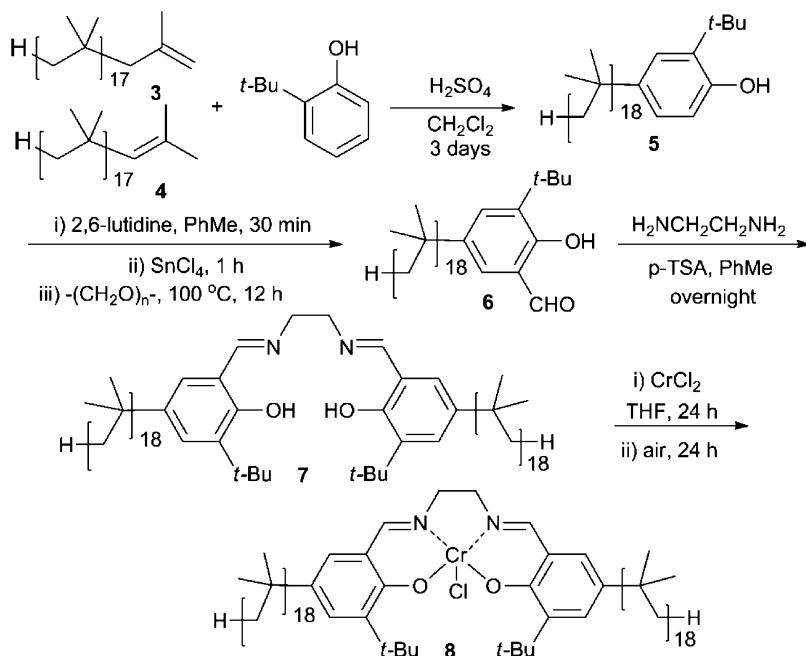
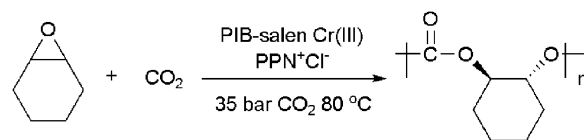


Fig. 1 Salen Cr(III) catalysts used for polycarbonate synthesis.



Scheme 1 Synthesis of polyisobutylene supported salen Cr(III) complex 8.

reactor, pressurized with 35 bar of CO₂, and heated to 80 °C. The reaction's progress was monitored using a ReactIR 1000 apparatus. Once the reaction was complete, the vessel was opened in air and allowed to cool. The product was dissolved in acetonitrile and acidified with conc. HCl. A heptane



Scheme 2 Polymerization of CO₂ and cyclohexane oxide by PIB-salen Cr(III) complexes.

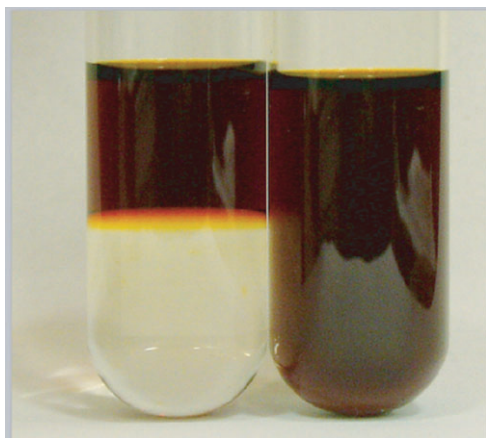


Fig. 2 A photograph showing the >99% phase selective solubility of 8 in a heptane/EtOH–H₂O biphasic mixture that was produced from a homogeneous equivolume heptane–EtOH solution of 8 by the addition of ca. 5 vol% H₂O.

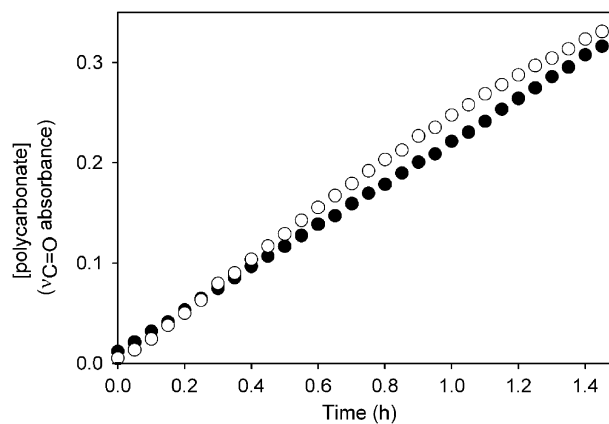


Fig. 3 Initial rates for polymerization of cyclohexane oxide and CO₂ using either the PIB-salen Cr(III) complex 8 (○) or a low molecular weight analogue 2 (●).

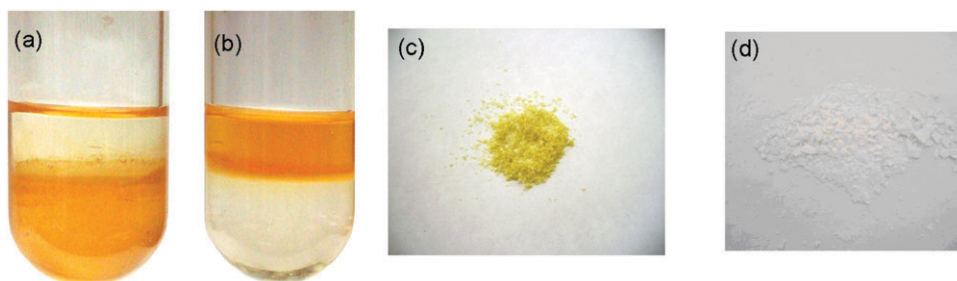


Fig. 4 Colorimetric comparisons of (a) a heptane/ CH_3CN biphasic mixture of **2** and the product polycarbonate; (b) a heptane/ CH_3CN biphasic mixture of **8** and polycarbonate product; (c) the polycarbonate formed using **2** isolated after one CH_3OH precipitation; and (d) the polycarbonate isolated using **8** after one heptane precipitation.

extraction removes most of the catalyst in the case of (**8**) (Fig. 4a vs. 4b). The typical isolation procedure for **2** involves precipitation in acidic methanol (**2**) to cleave the $\text{Cr}(\text{III})$ salen complex from the polycarbonate product. The slightly colored product (Fig. 4c) is colorimetrically different from the product (Fig. 4d) produced using catalyst **8** that is isolated by heptane precipitation of the polycarbonate/acetonitrile solution shown in Fig. 4b. Polycarbonate prepared using **2** can be isolated as an equally colorless solid but requires one or more reprecipitations.

The initial rate of polymerization by the the salen $\text{Cr}(\text{III})$ complexes **2** and **8** is shown in Fig. 3. These rates measured by *in situ* IR spectroscopy are very similar.

While **8** can be completely separated from the polymer, recycling **8** led to a *ca.* 20–30% lower polymerization rate. We believe this reflects the fact that the acidolysis step cleaves some $\text{Cr}(\text{III})$ from the PIB–salen complex **8**. Such Cr loss is seen both with **8** and with **2**. In the case of **8**, the loss is substantially less than with **2** and with **8** *ca.* 4% of the starting Cr is lost in the product polymer phase based on ICP-MS analysis of the polycarbonate.

In summary, the studies here show that a polyisobutylene oligomer is an excellent nonpolar phase tag for the chromophoric salen $\text{Cr}(\text{III})$ complex **8**. This phase tag facilitates separation of this catalyst from the polycarbonate products of a polymerization of cyclohexene oxide and CO_2 as seen by the difference in color for the product polymer or product polymer phase in Fig. 4. The synthesis of the a salen complex bound to a PIB oligomer is straightforward, and the intermediates can be readily analyzed spectroscopically. The activity of the PIB-supported catalyst is similar to that of a non-

supported catalyst, making it a useful but separable analog of these sorts of salen $\text{Cr}(\text{III})$ complexes.

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