

The Synthesis of Biodegradable Polycarbonates and Polyesters from Renewable Resources Using Highly Active (Porphyrin)Cr(III) Chloride Catalysts

Chandrani Chatterjee¹

Department of Chemistry,

The Ohio State University,

100 W 18th Ave,

Columbus, OH 43210, USA

Abstract

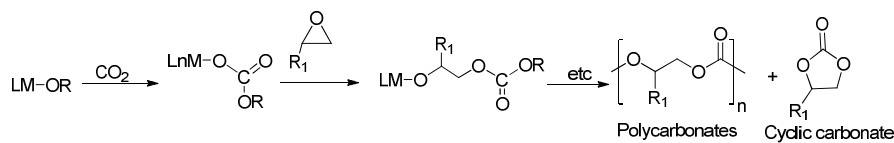
A series of porphyrin metal(III) compounds of general formula LMX (where L = tetraphenylporphyrin, tetrakis(pentafluorophenyl)porphyrin and octaethylporphyrin, M = Al, Cr, Co, and X = Cl⁻ and OEt) has been synthesized and studied as catalysts for the ring opening polymerization of propylene oxide (PO) as well as copolymerization of PO with CO₂ to produce polypropylene oxide (PPO), polypropylene carbonate (PPC) and propylene carbonate (PC), respectively. The electronic nature of the porphyrin ligand and the addition of Lewis basic cocatalysts *e.g.* DMAP and PPN⁺Cl⁻ showed a dramatic influence on the catalytic TOF, product selectivity and polymeric microstructure. The origin of these effects was attributed to the electronic factors associated with the individual reaction steps and equilibria.

Introduction

Recently the copolymerization of aliphatic epoxides and CO₂ by metal coordinate catalysis has received significant attention^{1,2} as an environmentally benign synthetic route to the

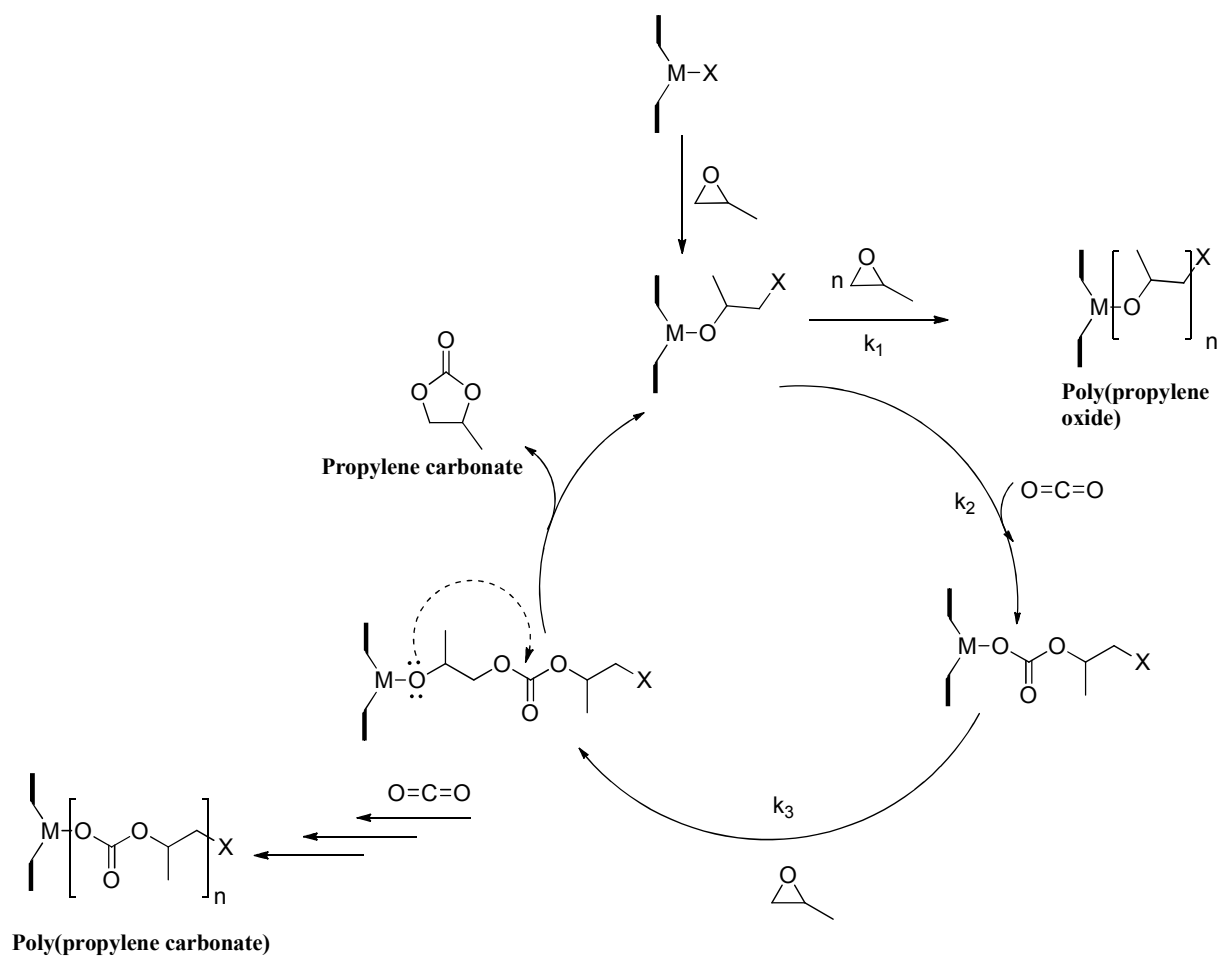
¹With sincere thanks to my Advisor Prof. Malcolm H. Chisholm for his guidance and support.

production of polycarbonates (Scheme 1). This copolymerization process is often associated with a competing reaction, which produces the cyclic carbonate.



Scheme 1. Copolymerization of epoxide and CO₂ by metal catalyst of general formula LM-OR, where L is the ancillary ligand and M is the Lewis acidic metal center.

This atom efficient process utilizes CO₂ as an inexpensive, sustainable, nontoxic C₁ feedstock and is an attractive alternative to the conventional synthesis, which utilizes petrochemical feedstocks and toxic phosgene derivatives. Following the pioneering work of Inoue³, there has been an explosion of interest in this copolymerization reaction, however, the aliphatic polycarbonates are still mainly used as sacrificial binders in ceramic industry.⁴ More widespread application of these materials requires low cost production and improved physical and mechanical properties, which in turn need higher catalytic turnover and control in the polymerization process. Hence matters pertaining to the catalytic process become crucial, see Scheme 2. The ring opening of the epoxide, namely propylene oxide by the metal catalyst produces the metal alkoxide intermediate which subsequently reacts with CO₂ to produce the metal carbonate species. The relative reactivity of these two competing intermediates determine the fate of the reaction and polypropylene carbonate is formed as the major product when $k_2 > k_3 > k_1$. Additionally, nucleophilic attack of the metal alkoxide group on adjacent carbonate functionality forms the cyclic propylene carbonate. Thus a better understanding of the individual reaction steps and equilibria involved in the polymerization process will be useful to improve catalytic activity and selectivity.



Scheme 2. Fundamental reactions involved in the polymerization process.

In this work a series of porphyrin metal(III) complexes with electron donating and electron withdrawing substituents on the porphyrin ligand frame (Figure 1) are employed to study the electronic effect on the copolymerization of propylene oxide (PO) and CO₂. The electronic environments of the metal centers are further tuned by the addition of Lewis base cocatalyst (DMAP or PPNCI). The square pyramidal geometry of the porphyrin complexes offer mechanistic simplicity as ligand dissociation or adaptation of any other geometry is impossible. Again the magnetic anisotropy of the porphyrin ligand frame and the choice of diamagnetic

aluminum metal center enable the use of NMR spectroscopy as an unambiguous tool to elucidate the nature of species bound to the metal center.⁵

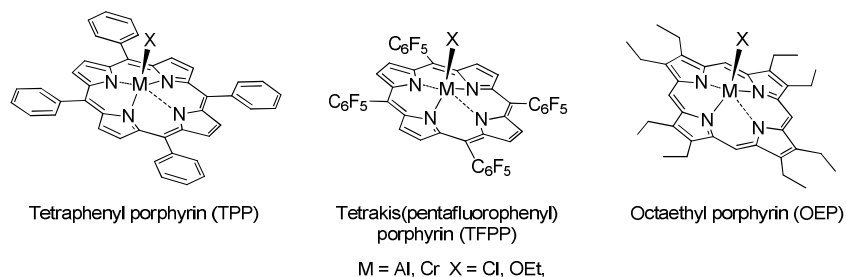


Figure 1. Structures of the porphyrin metal chloride catalysts.

Experimental Section

Methods. All porphyrin aluminum(III) and Chromium (III) complexes were prepared according to slight modifications of previously published procedures.^{5,6}

Instrumentation. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were carried out with a Bruker DPX-400 and a Bruker DRX-500 spectrometer. All chemical shifts are in ppm relative to the solvent chloroform-*d* at 7.24 ppm for ^1H NMR and 77.23 ppm for $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

FT-IR spectra were recorded in dichloromethane solution using a Perkin-Elmer Spectrum GX spectrometer at room temperature.

Gel permeation chromatographic (GPC) analyses were carried out at 40°C using a Waters Breeze system equipped with a Waters 2415 Refractive index detector and Waters styragel HR-2 and HR-4 (7.8 x 300 mm) columns. CHCl_3 was used as the mobile phase at 1.0 mL/min. The calibration curve was made with polystyrene standards.

Matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) was performed on a Bruker Microflex mass spectrometer, operated in a linear, positive ion mode with N_2 laser. The accelerating voltage was 28 kV. Electrospray ionization mass

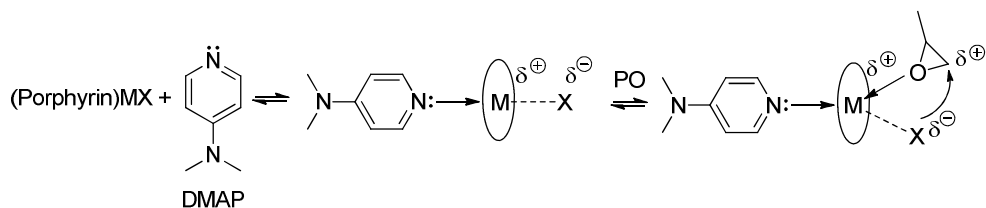
spectroscopy (ESI MS) was carried out in positive ion mode on a Bruker MicroTOF mass spectrometer.

Polymerizations In a typical reaction, 0.04 mmol of (porphyrin)AlX, 0.02 mmols of DMAP or PPN⁺X⁻ (wherever used as additives) were dissolved in PO (ranging from 0.8 to 2 ml) and was pressurized in a stainless steel reaction vessel (Parr) with CO₂ (50 Bar) at room temperature. After the reaction time (ranging from 2 h to 48 h) an aliquote was taken for ¹H NMR analysis and rest of the polymer was precipitated from a concentrated dichloromethane solution, by the addition of 1N HCl/Methanol. The polymer samples were further characterized by NMR, MS and GPC analysis.

Results and Discussion

In the absence of cocatalysts, the (porphyrin)M(III) chlorides are relatively slow catalysts for either homopolymerization of PO or its copolymerization with CO₂. In the copolymerization reaction, these catalysts yield ether rich copolymers with carbonate junctions, instead of the alternating copolymer. Moreover the TFPP complexes with Al(III) or Cr(III) centers are reminiscent of acid catalysis, producing region-irregular low molecular weight oligomers by carbonium ion mediated epoxide ring opening. In contrast, regio-regular and predominantly isotactic polypropylene oxides (PPO) are obtained from OEP or TPP catalyst, following interchange associative substitution (Scheme 3).

Scheme 3. Ring opening of propylene oxide in the presence of Lewis base cocatalyst



The remarkable influence of added DMAP or PPN⁺Cl⁻ (0.5 or 1.0 equiv) cocatalyst are manifested in higher TOFs and the order of reactivity of these complexes are TPP > TFPP >> OEP for PO homopolymerization and TFPP > TPP > OEP for PO/CO₂ copolymerization (Table 1). The addition of a cocatalyst enhances both consumption of PO as well as the incorporation of CO₂ in case of copolymerization, see Figure 2. The TFPP now selectively produces regioregular polypropylene carbonate (PPC) with essentially alternating PO and CO₂ units. In PO homopolymerization, it produces region-regular and predominantly isotactic polypropylene oxide (PPO) when a cocatalyst is used. In contrast, the OEP complex is now less reactive and also produces propylene carbonate (PC) as the major product in the copolymerization reaction. Hence, the electronic effect of the porphyrin ligand frame has a predominant influence on the reactivity of various metal-oxygenate species, determining the overall outcome of the polymerization processes.⁵

Table 1. Turn Over Frequency (TOF) Values Observed With (porphyrin)M(III) Chloride Catalysts Using PPN⁺Cl⁻ Cocatalyst.

Catalyst	TOF (h⁻¹) for PPO	TOF (h⁻¹) for PPC
TPPAI ₂ Cl	27	73
TFPPAI ₂ Cl	25	120
OEPAl ₂ Cl	3	20
TPPCrCl	~2000	~2000
TFPPCrCl	7.2	9
OEPCrCl	21	60

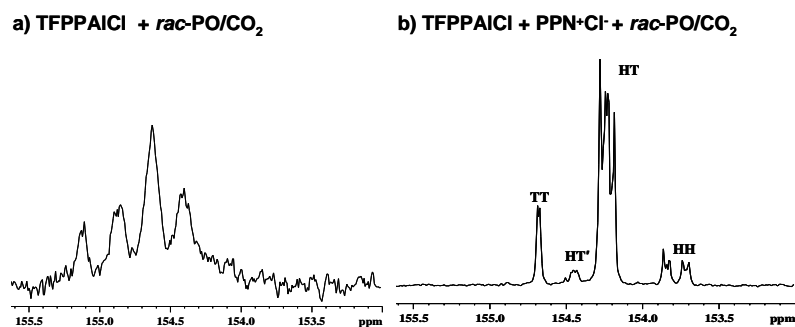
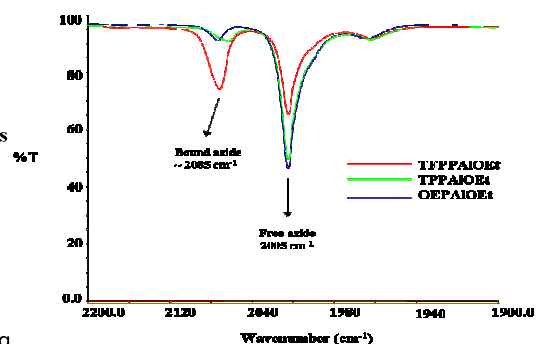
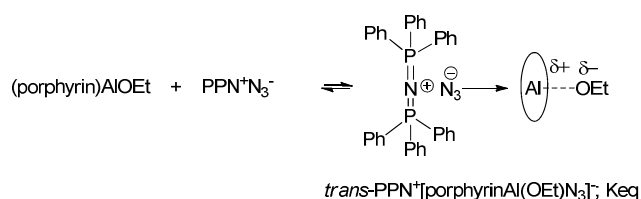


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ (125.73 MHz, CDCl_3) NMR spectra of the PPC produced using TFPPAICI a) ether rich copolymer in the absence of cocatalyst, b) alternating PPC in the presence of PPN^+Cl^- cocatalyst.

Lewis base binding to porphyrin AlX compounds: The affinity of the five coordinate

Al(III) centers towards Lewis bases is explored by FT IR spectroscopy, using the IR active N_3^- functionality, see Scheme 4. The extent of binding between the catalysts and PPN^+N_3^- is greatly influenced by the electronic nature of porphyrins and allows a comparison of the Lewis acidity of the Al(III) centers. The Al(III) center is most Lewis acidic with the fluorinated porphyrin, which showed maximum amount of N_3^- binding.

Scheme 4. The Binding of the N_3^- to the Al center in (porphyrin)AlOEt catalysts



Polymerization Activities of Chromium(III) Catalysts

In the absence of cocatalysts, porphyrin chromium(III) catalysts were only moderately active and produced mainly ether rich copolymers with low CO_2 incorporation.

The TPPCrCl catalyst is highly active in the presence of PPN⁺Cl⁻ (0.5 equiv) and in comparison with TPPAlCl under identical condition, the chromium catalyst is 2 orders of magnitude more active in either PO homopolymerization, and produced region-regular PPO (Figure 3). Mass spectroscopic analysis of the resulting polymer showed the presence of chloride end groups in the predominant series OH-(C₃H₆O)-Cl.Na⁺.

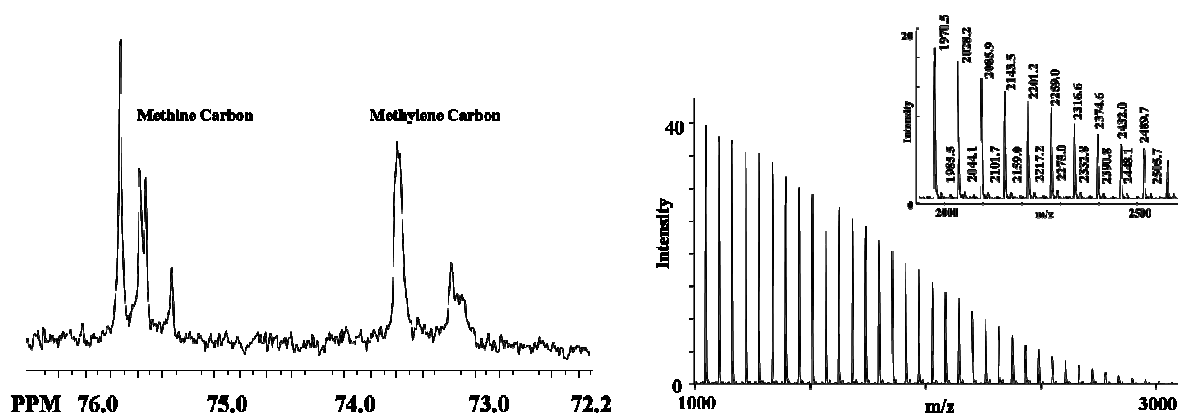


Figure 3. ¹³C{¹H} (125.73 MHz, CDCl₃) NMR and MALDI TOF analysis of the regioregular PPO obtained by TPPCrCl using 0.5 equiv PPN⁺Cl⁻.

The observed order of reactivity is now TPP > OEP >> TFPP and the OEPCrCl catalyst shows higher reactivity towards PO homopolymerization as well as PO/CO₂ copolymerization than its aluminum analog (Table 1). In case of OEPCrCl and TFPPCrCl catalysts, the addition of PPN⁺Cl⁻ also enhanced the incorporation of CO₂ into the polymer backbone, producing carbonate rich, mostly region-regular PPC, even at 10 Bar CO₂ pressure, see Figure 4. The ring opening of PO at the methylene carbon produces region-regular HT junctions whereas the PO ring opening at the sterically more hindered methane carbon produces region-irregular TT and HH junctions, see Scheme 4. Mass spectroscopic analysis showed the alternative enchainment of PO and CO₂ in these copolymers. In contrast, the TPPCrCl, still produced ether rich copolymer, even in the presence of 0.5 equiv PPN⁺Cl⁻, possibly due to its very high activity

towards PO ring opening.⁷ Careful modification of the reaction conditions, *e.g.* 1.0 equiv cocatalyst instead of 0.5 equiv, addition of a solvent, allowed the incorporation of more carbonate junctions into the ether rich copolymer, thereby modifying its resulting physical properties.

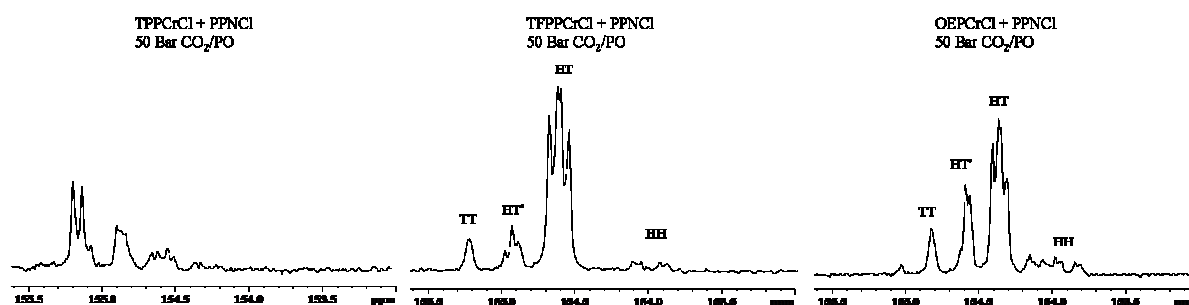
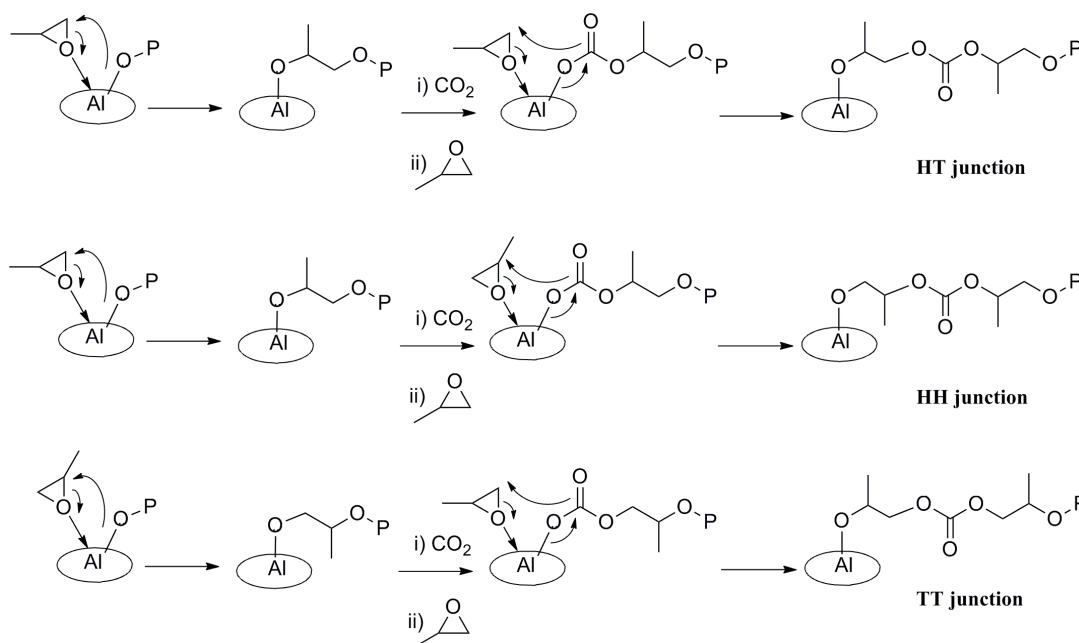


Figure 4. ^{13}C NMR spectra obtained from the porphyrin Cr(III)Cl catalysts and 0.5 equiv PPn^+Cl^- .



Scheme 3. Regio-consequences of PO ring opening in the copolymerization process.

The higher reactivity of the chromium catalysts compared to their aluminum analogs, is ascribed to the higher Lewis acidity of the five coordinate d^3 chromium centers and their preference for six coordination. Further kinetic studies are in progress to investigate the possibility of a bimolecular PO ring opening by the metal catalyst, when only 0.5 equiv cocatalyst is employed. The TFPPCrCl catalyst, however, due to insolubility in PO, resulted in low TOFs. GPC analysis of all PPC samples showed moderately high molecular weight polymers with narrow polydispersity (Table 2).

Table 2. GPC analysis of PPC Produced Using Porphyrin Metal(III) Chloride Catalysts and PPN^+Cl^- Cocatalyst.

Catalyst	Reaction time	M_n	M_w	PDI
TPPAIcI	6 h	11500	14800	1.29
TFPPAIcI	6 h	29700	37000	1.24
TPPCrCl	2 h	19100	23500	1.23
OEPCrCl	20 h	9300	13000	1.41

Conclusion

This comparative study of the porphyrin metal(III) catalysts shows a remarkable influence of the porphyrin in the polymerization activities, in the binding of Lewis bases and in the position of the equilibrium involving the insertion of CO_2 into the Al-OR bond. We also observed a rate enhancement of > 2 orders of magnitude compared to that originally observed by Inoue employing TPPAIcI as initiator⁸. The detailed ^1H NMR spectroscopic analysis showed 1st order

dependence in metal, similar to Darensbourg's pioneering study of salen CrX complexes². The more detailed studies of the epoxides and CO₂ copolymerization, with chromium and cobalt metals is, currently in progress and will be reported shortly.

Acknowledgements

We thank the Department of Energy, Basic Chemical Sciences Division for financial support.

References

1. Kember M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2011**, 47, 141.
2. Darensbourg, D. J. *Chem. Rev.* **2007**, 107, 2388.
3. Inoue, S.; Koinuma, H.; Koinuma, T. *Makromol. Chem.* **1969**, 130, 210
4. <http://www.empowermaterials.com/> and <http://www.novomer.com/>, accessed 20 February 2011.
5. Chatterjee, C.; Chisholm, M. H. Manuscript accepted for publication in *Inorganic Chemistry*.
6. Chen, P.; Chisholm, M. H.; Gallucci, J. C.; Zhang, X.; Zhou, Z. *Inorganic Chemistry*. **2005**, 44(8), 2588.
7. Chatterjee, C.; Chisholm, M. H. Manuscript to be submitted soon
8. Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, 51, 3564.