Biodegradable Polycarbonate Synthesis by Copolymerization of Carbon Dioxide with Epoxides Using a Heterogeneous Zinc Complex

Il Kim, Min Ju Yi, Seung Hoon Byun, Dae Won Park, Bu Ung Kim, Chang Sik Ha*

Division of Chemical Engineering, Pusan National University, Jangjeon-dong,
Geumjeong-gu, Busan 609-735, Korea
E-mail: ilkim@pnu.edu

Summary: As a means for the chemical fixation of carbon dioxide and the synthesis of biodegradable polycarbonates, copolymerizations of carbon dioxide with various epoxides such as cyclohexene oxide (CHO), cyclopetene oxide, 4-vinyl-1-cyclohexene-1,2epoxide, phenyl glycidyl ether, allyl glycidyl ether, propylene oxide, butene oxide, hexene oxide, octene oxide, and 1-chloro-2,3-epoxypropane were investigated in the presence of a double metal cyanide catalyst (DMC). The DMC catalyst was prepared by reacting $K_3Co(CN)_6$ with $ZnCl_2$, together with tertiary butyl alcohol and poly(tetramethylene ether glycol) as complexing reagents and was characterized by various spectroscopic methods. The DMC catalyst showed high activity (526.2 g-polymer/g-Zn atom) for CHO/CO_2 (P_{CO2} = 140 psi) copolymerization at 80 °C, to yield biodegradable aliphatic polycarbonates of narrow polydispersity ($M_w/M_n = 1.67$) and moderate molecular weight (M_n = 8900). The DMC catalyst also showed high activities with different CO_2 reactivities for other epoxides to yield various aliphatic polycarbonates with narrow polydispersity.

Keywords: carbon dioxide; copolymerization; double metal cyanide catalyst; epoxides; polycarbonates

Introduction

Chemical fixation of CO_2 is a very attractive subject not only from the viewpoint of carbon resource utilization, but also because of increasing environmental concerns. As a kind of potential approach, one of the most promising areas of CO_2 utilization is its application as a direct material for polymer synthesis. The past three decades have witnessed great progress in the fixation of CO_2 into polycarbonates since the creative work of Inoue in 1969.[1,2] To date, many excellent reviews in different periods contributed by Kuran[3], Super[4,5], Darensbourg[6-10], Kim[11] and Ree[12-13] have made a good description of this topic, where the importance of the catalyst was never overestimated.

DOI: 10.1002/masy.200550616

Double metal cyanide complexes (DMC) are well-known catalysts for epoxide polymerization. Recent improvements have made DMC catalysts much more attractive for the commercial manufacture of polyoxypropylene polyols.[14–17] The catalysts are highly active and yield polyether polyols that have low unsaturation and narrow molecular weight distribution compared with similar polyols synthesized using conventional KOH catalysis.[18] While DMC catalysts offer significant advantages for the ring-opening polymerization of epoxides, few reports have been published on the copolymerization of epoxides with CO_2.[19]

In the present paper, the exploitation of double metal cyanide is investigated for the copolymerization of CO_2 and various epoxide compounds at both common and supercritical carbon dioxide conditions. The effects of copolymerization variables like operating temperature and pressure on the yield, the molecular weight and copolymer structure are discussed. The resultant copolymers are subjected to ^1H NMR spectroscopy, infrared spectroscopy and gel permeation chromatography analyses.

Experimental

Materials. All materials such as potassium hexacyanocobatate(III) ($K_3Co(CN)_6$), zinc chloride ($ZnCl_2$), and tertiary butyl alcohol (^tBuOH) were purchased from Aldrich and used without further purification. Cyclohexene oxide (CHO, 98%), cyclopetene oxide (CPO, 98%), 4-vinyl-1-cyclohexene-1,2epoxide (VCHO, 98%), phenyl glycidyl ether (PGE, 99%), allyl glycidyl ether (AGE, 99%), propylene oxide (PO, 99.5%), butene oxide (BO, 99%), hexene oxide (HO, 97%), octene oxide (OO, 96%), 1-chloro-2,3-epoxypropane (PO-Cl, 99%) were all purchased from Aldrich and refluxed over calcium hydride (CaH_2). They were then distilled and stored over a Linde type 4 Å molecular sieve. Carbon dioxide of 99.99% purity was used without further purification. A polymerization grade of poly(tetramethylene ether glycol) (PTMEG, molecular weight = 1800) was donated by BASF Korea, Ltd.

Preparation of catalyst. The DMC catalyst using PTMEG as a co-complexing agent has been prepared according to the following procedures.[19,20] $K_3Co(CN)_6$ (3.32 g, 0.01 mol) was dissolved in distilled water (40 mL) in a beaker (solution 1). $ZnCl_2$ (13.63 g, 0.1 mol) was dissolved in distilled water (100 mL) and ^tBuOH (20 mL) in a second beaker (solution 2). A third beaker contained solution 3: a mixture of distilled water (1 mL), ^tBuOH (20 mL) and PTMEG (3.5 g). Solution 2 was added to solution 1 over 60 min at 50 ℃ with mixing using a mechanical stirrer. Solution 3 was then added and the mixture was stirred for 3 min. The mixture was centrifuged. The resulting catalyst cake was dried at 60 ℃ under vacuum to a constant weight.

Copolymerizations of epoxides with CO_2. Copolymerization of epoxide compounds and CO_2 were carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. The dried catalyst (20 mg) was added into the reactor, followed by adding a desired amount of the purified epoxides (5 mL) using a syringe. Then the reactor was capped by the reactor head and the entire assembly was transferred to a pressure cell. The reactor was purged several times with CO_2. The reactor was then pressurized with CO_2 at 140 psi (9.6 atm) [1250 psi (85 atm) for copolymerizations at a supercritical condition] and the reaction started. Then the reactor was heated at the desired temperature with stirring. After a certain period of reaction time, the pressure was reduced to atmosphere to terminate the copolymerization. The polymer powder was separated by precipitation using excess methanol containing HCl (5 vol%), followed by filtration. The product solution was concentrated to proper volume using a rotary evaporator. The polymer precipitate was filtered off, followed by drying at room temperature in a vacuum oven. The solvents used were removed from the filtrate by distillation. The polymerization yield was determined by gravimetry.

Characterization. X-ray diffraction (XRD) patterns of the catalysts were obtained with a RINT2000 wide angle goniometer 185 using Cu Kα radiation at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on an ESCALAB 250 induced electron emission spectrometer with Al Kα (1486.6eV, 12mA, 20kV) X-ray sources. IR spectra of the catalysts were obtained in transmission mode using a React IR. ^1H NMR spectra of the polymers were performed on a Varian Gemini 2000 and HP5P $CDCl_3$ as a solvent. Molecular weight distributions (MWD) were measured using a Waters 150-C instrument, operated at 35℃, with a set at 103, 104 and 500 Å columns (dimethylformamide as a solvent).

Results and Discussion

Catalyst characterization. The DMC catalyst prepared by $ZnCl_2$ and $K_3Co(CN)_6$ in the presence of ^{t}BuOH as a complexing agent (CA) is expected to have a general formula:[19]

$Zn_3Co(CN)_6 \cdot xZnCl_2 \cdot yH_2O \cdot z\, CA$

The intrinsic insolubility of this complex makes it difficult to determine the structure; however, the surface formulation of the catalyst could be investigated by XPS. Atomic identification in an insoluble solid is possible using XPS to measure the energy required to create a role in a core electronic structure. The results of XPS analysis of the catalysts are summarized in Table 1. The binding energy (1023.7 eV) of the zinc atom of $ZnCl_2$ shifted towards a higher value by 3.7 eV for the DMC catalyst after complexation. The chemical shift results from the coordination of oxygen atoms in complexing agents to Zn by reacting $ZnCl_2$ with $K_3Co(CN)_6$ in the presence of ^{t}BuOH and PTMEG as complexing reagents. The Co 2P3 of $K_3Co(CN)_6$ shifts from 781 eV to 778 for DMC by forming complexes with oxygen coordinated zinc.

The infrared spectra of $K_3Co(CN)_6$ and the DMC catalyst (Fig. 1) show a shift of the ν(CN) band from 2133.4 cm^{-1} for $K_3Co(CN)_6$ to 2195.9 cm^{-1} for the DMC catalyst. The ν(CN) of free CN^- is 2080 cm^{-1}.[19,21] The ν(CN) shifts to higher frequencies demonstrate that the CN^- ion acts as not only a σ-donor by donating electrons to the cobalt, but also an electron donor by coordination to the zinc metal. In addition the band of 585.1 cm^{-1} assigned to the ν(Co-C) bond for $K_3Co(CN)_6$ shifts to the lower frequency of 472.6 cm^{-1} for the DMC catalyst.

Alteration of the crystal structure can be shown by X-ray diffraction patterns to be dependent on the different surfaces. The X-ray patterns for DMC prepared in the absence of the organic complexing agent resembled that for highly crystalline zinc hexacyanocobaltate hydrate. The X-ray patterns for DMC, which was synthesized in the presence of ^{t}BuOH and PTMEG, exhibit broad signals at *d*-spacing of 5.75, 5.07, 3.59,

Table 1. XPS analysis of DMC catalyst.

Compound	Zn 2p3		Co 2p3		O 1s		N 1s		C 1s		Cl 2p	
	B.E.[a] (eV)	[AT][b] %	B.E. (eV)	[AT] %	B.E. (eV)	[AT] %	B.E. (eV)	[AT] %	B.E. (eV)	[AT] %	B.E. (eV)	[AT] %
$ZnCl_2$	1023.7		-		-		-		-		-	
$K_3Co(CN)_6$	-		781		-		-		-		-	
DMC	1020	19.2	778	8.8	530	7.0	397	20.5	283	42.0	197	2.4

[a] Binding energy.

[b] Atomic ratio.

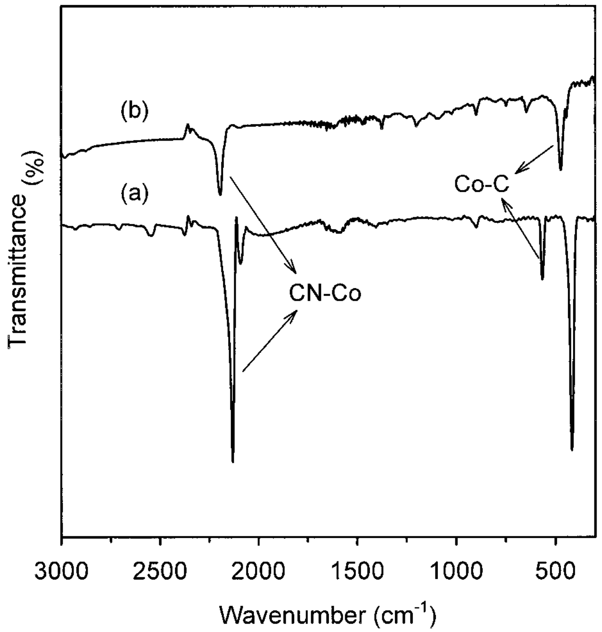
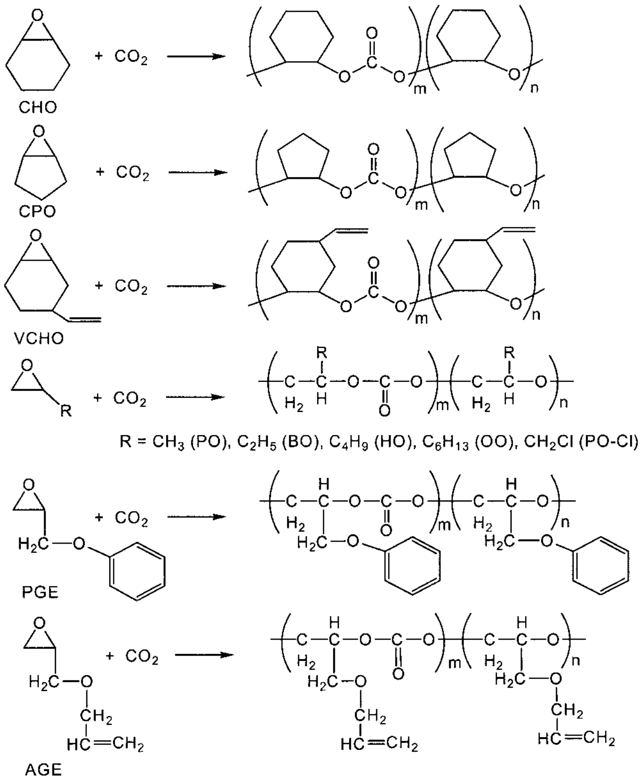


Figure 1. Infrared spectra of (a) $K_3Co(CN)_6$ and (b) DMC catalyst.

2.54, and 2.28 angstroms, ascribing to a cubic lattice structure of $Zn_3Co(CN)_6$.[14,19,22] This means that the catalysts are substantially amorphous. The crystallinity of the catalyst may strongly influence the catalytic activity.

Copolymerizations of epoxides and CO_2. The copolymerizations of epoxides and CO_2 using the DMC catalyst have been carried out at 50 °C and 80 °C with CO_2 at a desired pressure. The generalized scheme of the copolymerization and the proposed structure of the resulting copolymers were summarized in Scheme I. If the alternating copolymerization is perfect, only carbonate groups (-OC(O)O-) should be generated. However, kinetically controlled homopolymerization of CHO results in ether linkage (-COC-). The polymers were characterized by FT-IR and ^{1}H NMR spectroscopies utilizing the previously established methodology for similar copolymers produced from other zinc catalyst systems.[6,20] The isolated polycarbonates produced by using CHO, CPO, VCHO, PO, BO, HO, OO, PGE or AGE as a comonomer were analyzed by ^{1}H-NMR in $CDCl_3$,



Scheme I. Copolymerizations of epoxides and CO_2, and the expected structure of the resulting copolymers.

where the relative amount of ether linkages was determined by integrating the peaks corresponding to methane protons of the polyether units containing no CO_2 chain in its backbone and polycarbonate units formed by the addition of CO_2 in its backbone (Table 2). It is interesting to note that the copolymers

produced by epoxide monomers (VCHO and AGE) containing vinyl groups represent peaks attributed from CH of the vinyl group at $\delta = 5.6\text{-}6.9$ ppm.[23,24]

The IR spectra of the copolymers resulting from the copolymerization of CO_2 with epoxides are shown in Fig. 2. The existence of peaks around 1750 cm^{-1} corresponding to the carbonyl group ν(C=O), and around 1250 cm^{-1} assigned to the ether group ν(C-O), provide an evidence for the presence of a carbonate unit in the resultant copolymers. It can also be seen from Fig. 2 that characteristic peaks exist around 1645 cm^{-1} as well,

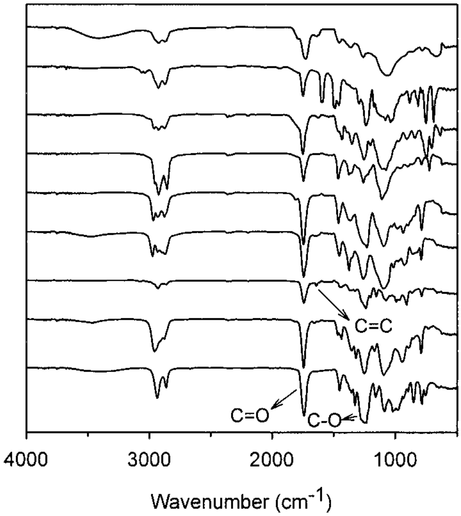


Figure 2. The IR spectrum of the synthesized polycarbonates at 50 ℃ and 140 psi (9.6 atm) CO_2 (a) CHO, (b)CPO, (c) VCHO,(d) PO, (e) BO, (f) OO, (g) PO-Cl, (h) PGE, and (i) AGE.

Table 2. ^{1}H-NMR characterization of polycarbonates produced by the copolymerization of CO_2 with various epoxide compounds.

Monomer	^{1}H-NMR (ppm, $CDCl_3$)		Carbonate content (f_{CO_2})
	polycarbonate	Polyether	
CHO	4.2-4.6	3.2-3.6	$A_{4.2\text{-}4.6}/(A_{4.2\text{-}4.6}+A_{3.2\text{-}3.6})$
CPO	4.8-5.2	3.6-4.0	$A_{4.8\text{-}5.2}/(A_{4.8\text{-}5.2}+A_{3.6\text{-}4.0})$
VCHO	4.5-4.9	3.4-3.8	$A_{4.5\text{-}4.9}/(A_{4.5\text{-}4.9}+A_{3.4\text{-}3.8})$
PO, BO, HO OO, PO-Cl	4.9-5.1 4.0-4.4	3.4-3.6	$(A_{4.9\text{-}5.1}+A_{4.0\text{-}4.4})/$ $(A_{4.9\text{-}5.1}+A_{4.0\text{-}4.4}+A_{3.4\text{-}3.6})$
PGE	4.9-5.2	3.6-3.8	$A_{4.9\text{-}5.2}/(A_{4.9\text{-}5.2}+A_{3.6\text{-}3.8})$
AGE	4.2-4.5	3.3-3.6	$A_{4.2\text{-}4.5}/(A_{4.2\text{-}5.5}+A_{3.3\text{-}3.6})$

indicating the presence of vinyl groups in the resultant copolymers produced by VCHO and AGE.

Table 3 summarizes the results of copolymerization. In general the DMC catalyst showed high copolymerization activities for all epoxide monomers. For CHO/CO_2

copolymerizations the DMC catalyst showed turnover frequencies (as g of polymer/g of Zn h) ranging from 126.54 at 50°C to 131.55 at 80°C. The copolymerization at a supercritical condition, in which CO_2 is used as both a solvent and a reactant, results in a much higher TOF value.

Table 3. Epoxides/CO_2 copolymerization results obtained by DMC catalyst.

Epoxides	T_p (°C)	Time (h)	TON[a)]	TOF[b)]	M_n[c)]	M_n/M_w	f_{CO_2}[d)]
CHO	50	4	506.14	126.54	6800	1.81	0.50
	80	4	526.15	131.55	8900	1.67	0.53
	SC-CO_2[e)]	2	712.38	356.19	10200	1.77	0.80
CPO	50	12	480.86	40.08	1900	1.83	0.32
	80	12	492.27	41.18	2300	1.55	0.36
VCHO	50	12	446.34	37.20	15500	2.66	0.63
	80	12	459.75	38.32	10100	2.22	0.73
PO	50	24	506.80	21.11	4400	3.92	0.22
	80	24	535.38	22.32	6500	1.98	0.13
	SC-CO_2	2	343.00	171.50	2600	1.39	0.39
BO	50	24	404.12	16.84	9000	3.79	0.28
	80	24	419.73	17.48	2800	1.44	0.12
HO	50	24	-[f)]	-	-	-	-
	80	24	413.14	17.22	6400	2.35	0
OO	50	24	397.09	16.49	9500	2.88	0
	80	24	404.56	16.86	12200	2.84	0
PO-Cl	50	24	520.87	21.70	2300	1.24	0.07
	80	24	545.94	22.76	3900	1.76	0
PGE	50	36	467.66	12.99	9300	3.60	0.10
AGE	50	36	448.31	12.44	6500	6.77	0.30

Polymerization conditions: catalyst = 0.02 g, CHO = 5 mL, P_{CO2} = 140 psi (9.6 atm)

[a)] Turnover number as g of polymer/g of zinc

[b)] Turnover frequency as g of polymer/g of zinc h

[c)] Data from GPC

[d)] [carbonate]/([carbonate]+[ether]) ratio determined by ^1H NMR spectra

[e)] Copolymerization at a supercritical CO_2 condition: 80 °C, 1250 psi (85 atm)

[f)] Negligible activity at this condition.

In addition the copolymerization at a supercritical condition is favorable in that it leads to an increase of the carbonate fraction indicating a level of CO_2 reactivity as a real monomer. The f_{CO2} value increases from 0.53 at $P_{CO2} = 140$ psi to 0.80 at $P_{CO2} = 1250$ psi. In addition a copolymer with a higher molecular weight was produced at a supercritical condition, remaining in polydispersity at a similar level. Similar increases of the yield and CO_2 reactivity were also observed for PO/CO_2 copolymerizations. Compared to the results obtained by using a homogeneous diethylzinc-based catalyst by Kuran[3] and Darensburg,[7,8] the DMC catalyst showed higher activities. Even though the activity of VCHO/CO_2 copolymerizations is lower than that of CHO/CO_2 copolymerizations, vinyl groups on CHO lead to an increase of molecular weight and CO_2 reactivity. Copolymerizations using a 5-membered ring CPO monomer result in lower polymer yield than those using the CHO monomer. In addition the CPO copolymers are characterized by lower molecular weight and lower carbonate composition than the CHO copolymer, indicating the CPO monomer has a stronger trend for homopolymerization and a much more enhanced inclination for chain termination than the CHO monomer. We carried out the similar copolymerizations of cyclooctene oxide with CO_2, resulting in negligible activities both at 140 psi and at supercritical conditions. These results demonstrate that the CHO monomer is the best raw material for the fixation of CO_2 into polycarbonates in the presence of a DMC catalyst.A series of alkylene oxides, PO, BO, HO, OO, and PO-Cl, were utilized for the copolymerizations with CO_2 (Scheme 1). As shown in Table 3, the polymer yield was higher at a higher temperature (80 °C). It is interesting to note that the carbonate contents are higher at higher polymerization temperatures for alicyclic CHO, CPO and VCHO monomers; however, PO, BO and PO-Cl ($f_{CO2} = 0.22$, 0.28 and 0.07 at 50 °C, respectively) monomers show lower carbonate content at a higher temperature ($f_{CO2} = 0.13$, 0.12 and 0 at 80 °C, respectively). As the size of the alkylene group in the epoxide ring increased, homopolymerization predominated over copolymerization. As shown in Table 3, for HO/CO_2 and OO/CO_2 copolymerizations, only polyether linkages were observed in the polymer backbone. These results indicate that long chain branching in polyether linkage disfavors an additional CO_2 forming carbonate linkage. However, the DMC catalyst was demonstrated to be an efficient catalyst for a ring-opening polymerization of various alkylene oxides. The decrease of a CO_2 fixation without losing polymerization activity was also recorded by substituting a hydride of the methyl group in PO for chlorine (see PO/CO_2 and PO-Cl/CO_2 copolymerizations in Table

3). The same type substitution with an allyloxy group (AGE) led to an increase of carbonate composition. The detailed studies on the structure of the DMC catalyst by changing the catalyst formulation are on–going, along with the investigation on the effect of the type of the active sites of the catalyst on the homo- and copolymerizations of epoxide monomers with CO_2.

Conclusion

The DMC catalyst prepared by reacting $ZnCl_2$ with $K_3Co(CN)_6$ in the presence of ^{t}BuOH and PTMEG as complexing reagents was very efficient for the copolymerization of various types of epoxide monomers with CO_2. The carbonate unit content indicating an efficiency of CO_2 fixation changed according to reaction parameters such as CO_2 pressure and temperature and especially according to the type of epoxide monomers. Copolymerizations of alicyclic oxides (CHO, CPO, VCHO) and CO_2 showed high activity (TON > 450 g/g-Zn) and carbonate content ($f_{CO2} > 0.36$) at 80 °C and $P_{CO2} = 9.6$ atm. The TON and f_{CO2} values for CHO/CO_2 copolymerization at supercritical conditions (80 °C, $P_{CO2} = 85$ atm) were 712.38 and 0.8, respectively. In the case of alkylene oxides/CO_2 copolymerizations, polymer yield was high, but carbonate content was relatively low. In general, the heterogeneous DMC catalysts showed higher activity and carbonate content for alicyclic oxides/CO_2 copolymerizations than alkylene oxides/CO_2 copolymerizations.

Acknowledgements

This work was supported by grant No. R01-2003-000-10020-0 from the *Basic Research Program of the Korea Science & Engineering Foundation*. The authors were also grateful for the *Brain Korea 21 Project*, the *Center for Ultramicrochemical Process Systems*, the *Pohang Accelerator Laboratory*, and the *NRL*.

[1] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Polym. Lett.* **1969**, *B7*, 287.
[2] S. Inoue, H. Koinuma, T. Tsuruta, *Makromol. Chem.* **1969**, *130*, 210.
[3] A. Rokicki, W. Kuran, *J. Macromol. Sci. Rev. Macromol. Chem.* **1981**, *C21*, 135.
[4] M. Super, E. Berluche, C. Costello, E.J. Beckman, *Macromolecules* **1997**, *30*, 368.
[5] M. Super, E.J. Beckman, *Macromol. Symp.* **1998**, *127*, 89.
[6] D.J. Darensbourg, M.W. Holtcamp, *Macromolecules* **1995**, *28*, 7577.
[7] D.J. Darensbourg, N. W. Stafford, T. Katsurao, *J. Mol. Catal. A: Chem.* **1995**, *104*, L1.
[8] D.J. Darensbourg, M.W. Holtcamp, G.E. Struck, M.S. Zimber, S.A. Niezgoda, P.Rainey, J.B. Robertson, J.D. Draper, J.H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*,107.
[9] D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, J.H. Reibenspies, *J. Am. Chem. Soc.* **2000**, *122*, 12487.
[10] D.J. Darensbourg, J.C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 6335.

[11] I. Kim, D..W. Park, C.S. Ha, *J. Korean Ind. Eng .Chem.* **2002**, *137*, 632.
[12] M. Ree, J.Y. Bae, J.H. Jung, and T.J. Shin, *J. Polym. Sci.: Part A: Polym.2 Chem.* **1999**, *37*, 1863
[13] M. Ree, J.Y. Bae, J.H. Jung, and T.J. Shin, *Korea Polymer J.* **1999**, *7*, 333
[14] B. Le-Khac, **1997**, EP 0755716.
[15] K.G. McDaniel, M.J. Perry, J.E. Hayes, **1999**, WO 9914258.
[16] J. Hofmann, P. Gupta, H. Pielartzic, **1999**, EP 0892002.
[17] R.M. Wehmeyer, **2001**, PCT Int. Appl. WO 0104177.
[18] I. Kim, S. Lee, **2004**, PCT Int. Appl. WO 04045764.
[19] I. Kim, J.T. Ahn, C.S. Ha, C.S. Yang, I. Park, *Polymer* **2003**, *44*, 3417.
[20] M.J. Lee, S.H. Lee, D.W. Park, C.S. Ha, I. Kim, *Solid State Ionics* **2004**, in press.
[21] K. Nakamoto, "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 3rd ed. Wiley, New York, 1978, p. 266.
[22] D.F. Mullica, G.W. Milligan, G.W. Beall, *Acta Cryst.* **1978**, *B34*, 3558.
[23] T.J. Hsu, C.S. Tan, *Polymer* **2002**, *43*, 4535.
[24] J. Lukaszczyk, K. Jaszcz, W. Kuran, T. Listos, *Macromol Rapid. Commun.* **2000**, *21*, 754.