Copolymerization of Carbon Dioxide and Propylene Oxide with Zinc Glutarate as Catalyst in the Presence of Compounds Containing Active Hydrogen

L. J. Gao, M. Xiao, S. J. Wang, F. G. Du, Y. Z. Meng

State Key Laboratory of Optoelectronic Materials and Technologies, Institute of Optoelectronic and Functional Composite Materials, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

ABSTRACT: To enhance the catalytic copolymerization of CO_2 and propylene oxide catalyzed by zinc glutarate, the influence of trace of water, ethanol, and propanal on the catalytic activity, the resulted copolymer structure, and the molecular weight and molecular weight distribution of the copolymer were investigated extensively. The experimental results showed that the catalytic activity decreased remarkably in the presence of either trace of ethanol or water, but increased in the presence of trace of propanal. Both ^{1}H-NMR and ^{13}C-NMR spectra suggested that the content of carbonate linkages of resulted copolymer was not effected obviously in the presence of above-mentioned impurities, giving completely alternating poly(propylene carbonate) (PPC). GPC results indicated that these impurities reduced the molecular weights but broadened the molecular weight distributions of resulted copolymers. Finally, the byproduct contents including both propylene carbonate determined by GC and polyether increased with the increase of three impurity concentrations. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 104: 15–20, 2007

Key words: carbon dioxide; propylene oxide; copolymerization; compounds containing active hydrogen

INTRODUCTION

Chemical fixation of CO_2 is a very attractive subject not only from viewpoint of carbon resource utilization, but also from increasing environmental concerns. One of the most promising means to effectively utilize CO_2 is its application as a direct starting material for polymer synthesis. Since the first discovery in 1969 that organometal-catalyzed coupling reaction of CO_2 with propylene oxide gave poly(propylene carbonate) (PPC) copolymer with an alternating structure,[1] there has been a longstanding interest in this process. A wide variety of catalytic systems, including both heterogeneous catalyst mixtures and homogeneous discrete metal complex catalysts, such as ZnEt$_2$-protic compounds,[2–4] zinc dicarboxylates,[5] metal porphyrin derivatives,[6,7] zinc phenoxide derivatives,[8] salen chromium chlorides,[9,10] zinc bis(β-diiminates),[11] rare earth catalysts,[12,13] and double metal cyanide complex,[14] have been developed over the past decades to improve catalytic activity and selectivity for the copolymerization of epoxide and CO_2 to afford aliphatic polycarbonate. Bechman and Coates reviewed the reaction of CO_2 and epoxides.[15,16] Up to now, zinc dicarboxylates, especially zinc glutarate, are considered to be the most commercial suitable catalysts for production of PPC with reasonably high molecular weights.[17] It is well known that the copolymerization of epoxide and CO_2 is often accompanied by the formation of polyether and cyclic carbonate as byproduct. Higher temperature always results in increased cyclic carbonate yields; therefore, cyclization has been proposed to be preferred rather than polymer formation, owing to the thermodynamic stability of five-membered cyclic carbonate.[18] So it is inevitable for the majority of catalysts to give more or less cyclic carbonate byproducts in PPC production. However, it could be controlled not to produce byproduct polyether for some catalytic systems. In addition, the obtained PPCs from the copolymerization of CO_2 with epoxides sometimes contain polyether units in the main chains. The PPC with high concentration of carbonate linkages in the main chains is considered to be the most commercial available thermoplastic.[19]

It is noticeable that the copolymerization is carried out free of water and suchlike impurities in both

starting materials and reaction system. For example, in the preparation of zinc dicarboxylate catalysts, unreacted dicarboxylic acid should be removed completely, otherwise, it could depress catalytic activity of catalysts.[20] Although it is well known that this reaction is sensitive to water and other proton donors, there are little information available on this characteristic in literatures. Furthermore, the influence of these impurities on the selectivity for PPC and the molecular weight of PPC remain unclear. Recently, the copolymerization of CO_2 and propylene oxide in the presence of compounds containing active proton has been investigated.[21] In addition, the enhancement of water content on the reaction rate in cycloaddition of CO_2 to propylene oxide with Engelhard titanosilicate-10 molecular sieve catalysts was observed.[22]

Herewith, in this article, the influences of water, ethanol, and propanal on the coupling reactions of CO_2 and propylene oxide with zinc glutarate catalysts were extensively investigated. The related reaction mechanism was proposed accordingly.

EXPERIMENTAL

Materials

Carbon dioxide (purity more than 99.00%) was commercially obtained without further purification. Propylene oxide (PO) of 95.0% purity was pretreated by potassium hydroxide and refluxed over calcium hydride for 24 h, and then distilled. Ethanol with a purity of above 99.7% was refluxed over sodium pieces and was distilled. Propanal (chemical purity) was dried over anhydrous magnesium sulfate and then distilled. Above three regents were stored over 4 Å molecular sieves prior to use. Glutaric acid (GA) of 98.0% purity, zinc oxide of 99.0% purity, and solvents, such as toluene, methanol, acetone, chloroform, were of analytical reagent grade and used as received.

Preparation of catalyst

Zinc glutarate (ZnGA) was synthesized from zinc oxide and GA under magnetic stirring as described in previous work.[23] GA (98 mmol) was dissolved in 150 mL toluene in a 250 mL round-bottom flask equipped with mechanical stirrer, a Dean-Stark trap and a reflux condenser with a drying tube. Then, to the GA/toluene solution was slowly added 100 mmol ZnO, and the resulting slurry mixture was stirred vigorously at 55°C for 4 h. Upon cooling, the reaction mixture was filtered off and washed with acetone several times, followed by drying overnight in a vacuum oven at 80°C, giving zinc glutarate in white powder, which was stored in a drier prior to use.

Copolymerization of CO_2 and PO

The copolymerization of CO_2 and PO in the presence of water, ethanol, or propanal was carried out in a 500 mL autoclave equipped with a mechanical stirrer using PO as both reactant and solvent. The number of active sites of ZnGA as a heterogeneous catalyst may vary with different batches of the catalysts prepared. To minimize these effects in this work, same batch of ZnGA was used in all runs. Dry ZnGA was introduced into the autoclave as quickly as possible. The autoclave was capped with its head and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with catalyst inside was further dried for 24 h under vacuum at 100°C. Subsequently, the autoclave was purged carefully with carbon dioxide and evacuated alternatively for three times, followed by adding purified quantitative PO together with other impurity like water, ethanol, or propanal using a large syringe. The autoclave was then pressurized to 5.2 MPa via a CO_2 cylinder. The copolymerization was performed at 60°C under stirring for 40 h and afterwards the autoclave was cooled to room temperature and the pressure was released. The resulting viscous mixture was removed, dissolved in a proper volume of chloroform, and filtered off with G4 sand-core funnel to remove the catalyst residual. The filtrate was concentrated by using a rotary evaporator to give a proper concentration. Finally, the copolymer was precipitated out by pouring the concentrated solution into vigorously stirred methanol and was washed with methanol several times. This copolymer was dried for 2 days at 80°C under vacuum and was weighed to calculate the yield of copolymer. Meanwhile, all methanol solution was combined together and sampling for GC to determine the content of byproduct propylene carbonate. The remaining solution was distilled with a rotary evaporator to remove methanol and chloroform to yield a methanol soluble product, which was weighed to estimate the content of byproduct polyether.

Measurements

^{1}H-NMR and ^{13}C-NMR spectrum were recorded on Bruker NMR spectrometer (Model: DRX 400 MHz) using tetramethylsilane as the standard and chloroform-d$_1$ ($CDCl_3$) as the solvent. The molar fraction of CO_2 in main chain was calculated by integrating area (A). Molecular weight distributions (M_w and M_n) of a polymer product were measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500 Å, 10,000 Å, and 100,000 Å). The GPC system was calibrated by a series of polystyrene standards with poly-
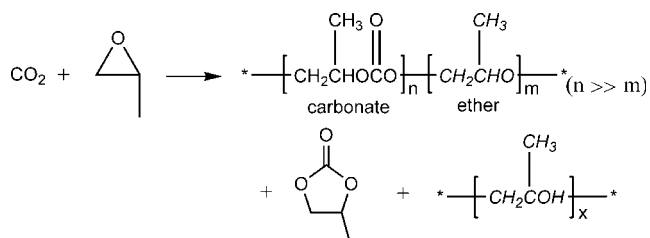
Scheme 1 Coupling reactions between carbon dioxide and propylene oxide.

dispersities of 1.02, which were supplied from Shodex (Tokyo, Japan). THF (HPLC grade) was used as an eluent. In addition, the combined methanol solution was analyzed by Varian CP3800 gas chromatography (Palo Alto, CA), equipped with a flame-ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 μm) to estimate the content of byproduct PC.

RESULTS AND DISCUSSION

Characterization of the copolymer

As depicted as Scheme 1, the copolymerization of CO_2 and PO with ZnGA as catalyst resulted in the main product poly(propylene carbonate) (PPC), with concomitances of byproducts propylene carbonate and polyether. Figure 1 showed both ^{1}H-NMR and ^{13}C-NMR spectra for the methanol insoluble polymer from the copolymerization of CO_2 and PO: ^{1}H-NMR (δ, $CDCl_3$), 1.3(3H; CH_3), 4.2(2H;CH_2CH), 5.0(1H; CH_2CH), 1.16(CH_3), 3.4–3.9(CH_3CH_2). ^{13}C-NMR (δ, $CDCl_3$), 16.4 (CH_3), 69.2 (CH_2CH), 72.8(CH_2CH), 154.7 (OCOO). Compared to the results in literature,[24,25] the ^{1}H-NMR data confirmed the existence of carbonate linkages and small fraction of random incorporated ether units in PPC's backbone. The carbonate content was determined via ^{1}H-NMR by integrating the peaks corresponding to the protons of the PPC copolymer. The calculation was conducted using the following equation

$$f_C(\text{mol}\%) = (I_{5.0} + I_{4.2})/[2(I_{5.0} + I_{4.2}) + I_{3.4-3.9}] \times 100\%$$

Where I indicates the integration of correlated proton signals in ^{1}H-NMR, which is the ratio of carbonate units to all units in the main chain. f_C has the maximum value of 50%, which denotes completely alternating copolymerization of CO_2 and PO. As listed in Table I, the concentration of carbonate linkages in the methanol insoluble polymer is of above 49% by molar fraction, showing the almost alternating PPC.

Effect of water on the coupling reactions of CO_2 and PO

The coupling reaction of CO_2 and PO are very sensitive to active proton donors due to a chain transfer

mechanism. The accepted mechanism for the production of PPC involves epoxide addition to a metal carbonate with subsequent CO_2 addition to a metal alkoxide alternatively.[26] The coordination of PO to metal in active site is necessary prior to insertion into metal–oxygen bond, but CO_2 insertion does not necessitate prior metal coordination. As shown in Table I, the yields of PPC copolymer varied significantly with water content. The PPC yield showed almost a half reduction with the increase of water content in PO from 5.6 parts of million to 25.4 parts of million. Moreover, the contents of byproduct PC and polyether increased with increasing water content. It can also be seen that the propylene carbonate formation was favorable over polyether formation. However, for all cases, three impurities did not greatly affect the concentration of carbonate linkages in PPC's backbone with a carbonate linkage molar fraction of above 0.49. Finally, very small quantity of polyether was produced, which could be controlled less than one percent by controlling water content less than 16 parts of million. These results collectively suggest that the rate-determining step in the
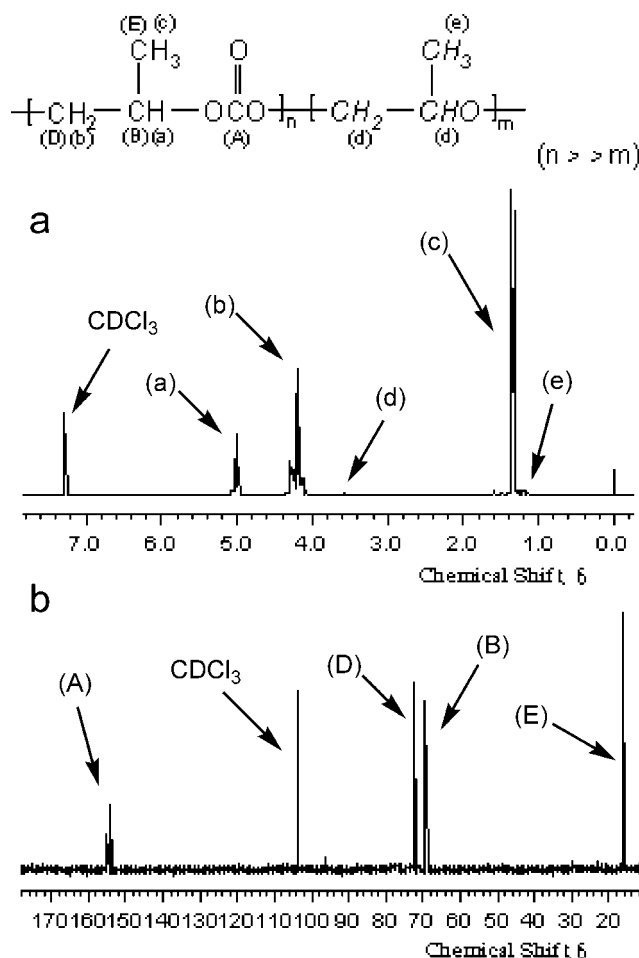
Figure 1 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectrum of the methanol insoluble copolymer.

TABLE I
Effect of Water on the Copolymerization of CO_2 with PO

Run	Concentration of water ($\times 10^{-6}$)[a]	Yield[b]	Polyether (wt %)	Propylene carbonate (wt %)[c]	f_C (mol %)[d]	M_n/M_w/MWD[e]
1	5.6	6263	0.3	2.8	49.4	72,013/238,756/3.32
2	10.7	5912	0.4	3.7	49.3	68,804/269,336/3.91
3	16.2	4741	0.9	5.6	49.3	62,540/267,561/4.28
4	22.1	4390	2.0	7.7	49.2	52,547/271,411/5.17
5	25.4	3902	2.6	8.6	49.2	48,122/256,218/5.32

[a] Percentage of water in PO by mass.
[b] g polymer/mol Zn.
[c] Determined by GC.
[d] Determined by ^{1}H NMR spectroscopy.
[e] Determined by gel-permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

copolymerization is actually the insertion of PO into a zinc carbonate bond. That is, the rate of CO_2 insertion into zinc oxide bond at the active site is fast than that of PO insertion into zinc carbonate bond, otherwise a mass of polyether units would be produced because ZnGA shows high activity for the homopolymerization of PO into poly(propylene oxide) or polyether in the absence of CO_2.[27] It was supposed that only one metal binding site is favorable for the copolymerization, but two binding sites are needed for competitively consecutive epoxide insertions during very rapid CO_2 insertion process.[28] The single-crystal structure of ZnGA revealed that all Zn(II) centers coordinate to four carboxyl oxygen atoms on different glutarate ligands via four syn-anti bridges, forming a distorted tetrahedral geometry, thus a three-dimensional network is generated.[29] It appears that this typical structure is correlated to the characteristic of ZnGA as catalysts for producing alternating polycarbonates with little polyether. Nevertheless, some base catalysts like alkylammonium or phosphonium halides seem to favor the formation of the five-membered ring product propylene carbonate.[30] Propylene carbonate is certainly not the intermediate during the PPC formation because propylene carbonate cannot be used as the monomer for the PPC synthesis.[31]

The observations that the molecular weight of PPC decreased and the molecular weight distribution became broad (from 3.32 to 5.32) with increasing water content, imply that water may act as the chain transfer agent during the formation of PPC.

Effect of ethanol on the coupling reactions of CO_2 and PO

Alcohols are often used as molecular weight regulators in polymerization process. Therefore, we selected ethanol as a proton donor to assess its influences on the coupling reactions of CO_2 and PO. As listed in Table II, compared to the system containing trace water, the PPC yield decreased dramatically in the presence of ethanol. Presumably, two reasons account for this phenomenon. First, ethanol can coordinate favorably to active site of metal catalyst than water can. According to the results reported by Kim et al.,[32] it is necessary for PO to coordinate first to metal in active site prior to the insertion of CO_2 into metal-oxygen bond. The impurities containing heteroatom, such as water, ethanol, etc., competing with PO, not only coordinate to metal of catalyst but also coordinate with metal of active propagation chains, leading to both longer induction period and lower propagation rate. This is consistent with the results

TABLE II
Effect of Ethanol on the Copolymerization of CO_2 with PO

Run	Concentration of ethanol ($\times 10^{-6}$)[a]	Yield[b]	Polyether (wt %)	Propylene carbonate (wt %)[c]	f_C (mol %)[d]	M_n/M_w/MWD[e]
1	6.1	4331	1.0	3.5	49.3	67,909/265,653/3.91
2	10.5	2107	3.1	12.9	49.6	40,616/261,112/6.43
3	15.8	1054	6.4	13.4	49.4	37,577/256,128/6.82
4	22.1	293	ND[f]	ND[f]	ND[f]	ND[f]

[a] Percentage of water in PO by mass.
[b] g polymer/mol Zn.
[c] Determined by GC.
[d] Determined by ^{1}H NMR spectroscopy.
[e] Determined by gel-permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.
[f] Not detected.

TABLE III
Effect of Propanal on the Copolymerization of CO_2 with PO

Run	Concentration of propanal ($\times 10^{-6}$)[a]	Yield[b]	Polyether (wt %)	Propylene carbonate (wt %)[c]	f_C (mol %)[d]	M_n/M_w/MWD[e]
1	6.4	7746	2.3	3.2	49.1	88,931/271,513/3.05
2	11.4	9190	2.9	4.1	49.5	84,865/283,235/3.34
3	15.0	7629	3.6	6.9	49.5	56,226/185,873/3.31
4	20.9	3317	6.8	12.0	49.3	47,579/173,587/3.65
5	22.6	2302	7.3	15.4	49.5	27,442/15,9005/5.79

[a] Percentage of water in PO by mass.
[b] g polymer/mol Zn.
[c] Determined by GC.
[d] Determined by ^1H NMR spectroscopy.
[e] Determined by gel-permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

of the copolymerization of PO and CO_2 catalyzed by double metal cyanide complex.[33] On the other hand, ethanol exhibits stronger chain transfer ability than water does. Based on the MS data of copolymer from reaction of CO_2 and PO catalyzed by zinc catalysts, water, ethanol, and even hydroxyl-terminated polymer chain all could act as the chain transfer agents.[34] The addition of ethanol resulted in more seriously decrease of molecular weight and broadening of molecular weight distribution when compared to water, demonstrating that ethanol did act as the chain transfer agent in copolymerization process. This is in agreement with what has been previously observed for other catalyst system in the copolymerization reaction of CO_2 and PO,[33] for example, either 1,4-butanediol or 1,6-hexanediol, compared to water, possess greater chain transfer constants. Moreover, the presence of ethanol showed greater effect on the contents of both propylene and polyether when compared to water.

Effect of propanal on the coupling reactions of CO_2 and PO

In previous work, we found that the higher yields of PPC could be afforded in case that PO was carefully treated prior to use by using potassium hydroxide to remove propanal impurity in PO. These interesting phenomena promoted us to explore the influences of propanal on the reactions of CO_2 and PO. The experimental results are summarized in Table III. When propanal content in PO was less than 15 parts of million, the yields of PPC were at high levels with maximum value of 9190 g PPC per mol of zinc, but the molecular weight decreased gradually with increasing propanal content. It appears that propanal can regulate the molecular weights of PPC to some extent without decreasing the catalytic activity of the catalyst, offering a potential method to obtain PPC with controlled molecular weight, which is one of subjects that are explored in many chemical corps

and academes.[35,36] Interestingly, the observations that the yields of PPC increased gradually at levels of propanal content less than 11.4 parts of million indicated that traces of propanal could indeed enhance the catalytic activity of ZnGA for the copolymerization of CO_2 and PO. As the promoting effect of water on CO_2 insertion into ruthenium hydride bond to form formate complex,[37] we propose that propanal could stabilize the transition state formed prior to PO insertion into zinc oxygen bond of active propagation chain, by forming rather stable five-membered cycle through intermolecularly H-bonded to the transition state intermediate (Scheme 2). Owing to PO insertion reaction being a rate-determining step in the copolymerization process, the chain propagation rate could be accelerated to some extent in the presence of traces of propanal, resulting in a higher yield of PPC. However, when the propanal content in PO increased to 20.9 parts of million, the yields of PPC reduced to 3317 g PPC per mol of zinc significantly. This observation listed in Table III showed that the chain transfer reactions occurred under condition where the excess of propanal was present, leading to an inactivation of propagation chain. It should be noted that the propanal content had not shown significant influence in wide ranges on molecular weight distribution compared with both water and ethanol.
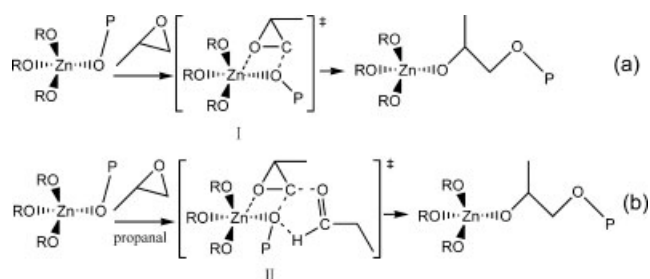
Scheme 2 Insertion of PO into Zn—O bond in propagation reactions of chains (a) without and (b) with a propanal molecule.

About the initiation mechanism

Little information has been disclosed for the initiation reaction in the copolymerization of CO_2 and PO catalyzed by ZnGA. It has been reported that the PPCs produced using zinc oxide–benzenedicarboxylic acid as catalyst have aromatic rings as end groups originating from the said catalyst.[38] The low molecular weight chains were identified by MALDI-TOF-MS as an alternating copolymer represented as $(PO)n$-alt-$(CO_2)m$, where $m = n - 1$, $n - 2$, $n - 3$, $n - 4$, $n - 5$, with —OH and —H end groups, but were free of glutarate units in the molecular chains. These results indicate Zn—OH groups as the active initiating species.[27] In this work, no proton and carbon signals of glutarate units in both ^{1}H-NMR and ^{13}C-NMR spectra were found due to the extremely low concentration of glutarate units in high molecular weight PPC. We infer that PO might insert into the Zn—OH bond instead of insertion into zinc carbonate bond from ZnGA in the initiation step of ZnGA catalyst system for the copolymerization of CO_2 and PO. In this case, Zn—OH groups act as the active initiating species. Hydroxy groups that may come from adventitious water in environment act as ligands to satisfy coordination saturation of coordinatively unsaturated zinc on the surface of ZnGA crystal. This process is the same as aluminum oxide and silicon oxide when used as catalyst supports that absorb a number of hydroxy groups on the surface. For further understanding of the initiation reactions, the compounds containing active protons with varying activity should be used and studied with respect to the catalytic activity of ZnGA catalyst.

CONCLUSIONS

The coupling reaction of CO_2 and propylene oxide catalyzed by ZnGA was investigated in the presence of water, ethanol, and propanal impurity. The impurities showed obviously influence on the molecular weight, the yield, or copolymerization rate, and the byproduct content. The yields of PPC polymer were remarkably reduced by the presence of traces of water and ethanol added. Ethanol appeared to show obvious effect on the coupling reaction. Interestingly, the presence of a small quantity of propanal was helpful to give high yields of PPC. All three impurities appeared to act as the chain transfer agents in copolymerization process, resulting in lower molecular weight and broaden molecular weight distribution. All three impurities showed no significant effects on the concentration of carbonate linkages in PPC's backbone. The contents of the byproducts, such as propylene carbonate and polyether increased with increasing the concentration of three used impurities.

References

1. Inoue, S.; Koinuma, H.; Tsuruta, T. J Polym Sci Part B: Polym Lett 1969, 7, 287.
2. Kobayashi, M.; Inoue, S.; Tsuruta, T. Macromolecules 1971, 4, 658.
3. Inoue, S.; Kobayashi, M.; Koinuma, H.; Tsuruta, T. Makromol Chem 1972, 155, 61.
4. Gorecki, P.; Kuran, W. J Polym Sci Part C: Polym Lett 1985, 23, 299.
5. Kobayashi, M.; Inoue, S.; Tsuruta, T. J Polym Sci Polym Chem Ed 1973, 11, 2383.
6. Inoue, S. J Polym Sci Part A: Polym Chem 2000, 38, 2861.
7. Sugimoto, H.; Ohshima, H.; Inoue, S. J Polym Sci Part A: Polym Chem 2003, 41, 3549.
8. Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. J Am Chem Soc 1999, 121, 107.
9. Paddock, R. L.; Nguyen, S. T. J Am Chem Soc 2001, 123, 11498.
10. Eberhardt, R.; Allmendinger, M.; Rieger, B. Macromol Rapid Commun 2003, 24, 194.
11. Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. J Am Chem Soc 2002, 124, 14284.
12. Chen, X. H.; Shen, Z. Q.; Zhang, Y. F. Macromolecules 1991, 24, 5305.
13. Tan, C. S.; Hsu, T. J. Macromolecules 1997, 30, 3147.
14. Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C.; Phelps, A. L. Inorg Chem 2003, 42, 7809.
15. Coates, G. W.; Moore, D. R. Angew Chem Int Ed Engl 2004, 43, 6618.
16. Bechman, E. J. Science 1999, 283, 946.
17. Kim, J. S.; Kim, H.; Yoon, J.; Heo, K.; Ree, M. J Polym Chem 2005, 43, 4079.
18. Darensbourg, D. J.; Holtcamp, M. W. Coord Chem Rev 1996, 153, 155.
19. Inoue, S. J Macromol Sci Chem 1979, 13, 651.
20. Motika, S. A.; Pickering, T. L.; Rokicki, A. J.; Stein, B. K. U.S. Pat. 5,026,676 (1991).
21. Yang, S. Y.; Chen, L. B.; Yu, A. F.; He, S. J. Acta Polym Sinica 1998, 3, 339.
22. Doskocil, E. J. J Phys Chem B 2005, 109, 2315.
23. Meng, Y. Z.; Du, L. C.; Tjong, S. C.; Zhu, Q.; Hay, A. S. J Polym Sci Part A: Polym Chem 2002, 40, 3579.
24. Ree, M.; Bae, J. Y.; Jung, J. H.; Shin, T. J. J Polym Sci Part A: Polym Chem 1999, 37, 1863.
25. Wang, S. J.; Du, L. C.; Zhao, X. S.; Meng, Y. Z. J Appl Polym Sci 2002, 85, 2327.
26. Darensbourg, D. J.; Nicole, W. S.; Takumi, K. J Mol Catal A 1995, 104, L1.
27. Chisholm, M. H.; Diana, N. L.; Zhou, Z. P. Macromolecules 2002, 35, 6494.
28. Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. Inorg Chem 2000, 39, 1578.
29. Kim, J. S.; Kim, H.; Ree, M. Chem Mater 2004, 16, 2981.
30. Behr, A. Carbon Dioxide Activation by Metal Complexes. VCH: New York; 1988; p 91.
31. Kuran, W.; Listos, T. Makromol Chem 1992, 193, 945.
32. Kim, J. S.; Ree, M.; Lee, S. W.; Oh, W.; Baek, S.; Lee, B.; Shin, T. J.; Kim, K. J.; Kim, B.; Lüning, J. J Catal 2003, 218, 386.
33. Wu, L. C.; Yu, A. F.; Zhang, M.; Chen, L. B. Acta Polym Sinica 2004, 1, 98.
34. Meerendonk, W. J. V.; Duchateau, R. Koning, C. E.; Gruter, G. J. Macromolecules 2005, 38, 7306.
35. Rokicki, A. J.; Pu, A. U.S. Pat. 4,943,677 (1990).
36. Soga, K.; Hyakkoku, K.; Lkeda, S. Makromol Chem 1978, 179, 2837.
37. Yin, C. Q.; Wu, L.; Fu, X. B.; Xu, Z. T.; Siuman, N. G. J Mol Catal (China) 2003, 17, 22.
38. Hino, Y.; Yoshida, Y.; Inoue, S. Polym J 1984, 16, 159.