Polym. Bull. (2012) 68:141–150
DOI 10.1007/s00289-011-0537-5

ORIGINAL PAPER

Ring-opening polymerization of 2,2-dimethyltrimethylene carbonate using imidazol-2-ylidenes

Zhenzhong Wang · Lifang Zhang · Junwen Wang · Yan Wang · Rui Zhang · Xingna Guo · Chunling Liu

Received: 7 April 2011 / Revised: 13 May 2011 / Accepted: 29 May 2011 /
Published online: 7 June 2011

Abstract The ring-opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) catalyzed with imidazol-2-ylidenes substituted by benzyl, isopropyl, and methyl was conducted. The influences of substitutional group, monomer, catalyst, and initiator (benzyl alcohol) concentration, as well as polymerization temperature and reaction time were investigated in detail. The kinetics studies indicate that the polymerization rate is first-order with respect to both monomer and catalyst concentrations. The overall activation energy amounts to 51.06 kJ/mol. Mechanistic studies reveal that the 2,2-DTC polymerization proceeds according to a monomer-activated process.

Keywords Imidazol-2-ylidene · Ring-opening polymerization · 2,2-Dimethyltrimethylene carbonate

Introduction

As a class of the most attractive biomaterials, aliphatic polyesters attract much attention because of their wide applications in biomedical fields such as tissue engineering and drug controlled release, due to the surface erosion degradation mechanism [1], high permeability, and the good biocompatibility.

Z. Wang · L. Zhang (✉) · J. Wang (✉) · Y. Wang · R. Zhang · X. Guo
Institute of Material Chemistry, Shanxi Normal University, Linfen 041004, China
e-mail: zhanglf0015@163.com

J. Wang
e-mail: wjwchlwx@yahoo.com.cn

C. Liu
Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, Xi'an 710062, China

Various organometallic catalysts have been used for the ring-opening polymerization of cyclic carbonates [2–10]. However, it is difficult to remove the metal contaminants which compromised the resultant polymer performance in biomedical and microelectronic applications [4, 11]. Considering the problems surrounding the use of metal catalysts, a few efforts were devoted to using metal-free organocatalyts [12–21] such as *N*-heterocyclic carbenes (NHCs), 4-*N*,*N*-dimethylaminopyridine and so on for cyclic esters polymerization such as ε-caprolactone, lactide exception of 2,2-dimethyltrimethylene carbonate (DTC), to the best of our knowledge.

In this article, we report the ring-opening polymerization of DTC using imidazol-2-ylidenes substituted by benzyl, isopropyl, methyl (Scheme 1) as catalysts separately and present the relation between the structures and catalytic activity of imidazol-2-ylidenes, with emphasis on the polymerization characteristics, kinetics, and mechanism.

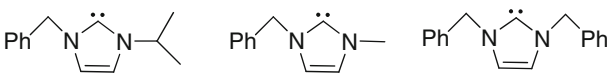
Experimental

Materials

2,2-DTC was synthesized according to ref [22], and dried over phosphorus pentoxide. Benzyl alcohol (BnOH) was dried over calcium hydride for 48 h, and then distilled under reduced pressure before use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone before use. All other materials were analytical grade and used as received.

Catalyst preparation

All catalyst preparations were performed with Schlenk tubes and a vacuum-line technique under purified nitrogen. Imidazol-2-ylidenes (Scheme 1) were prepared by already reported methods [23–25], and those compounds were characterized by ^{1}H NMR [1-isopropyl-3-benzylimidazol-2-ylidene (**1**) ^{1}H NMR ($CDCl_3$, 600 MHz):1.54–15.6 (d, 6H); 4.55–4.62 (m, 1H); 5.30 (s, 2H); 7.16–7.19 (d, 2H); 7.33–7.35 (q, 5H). 1-methyl-3-benzylimidazol-2-ylidene (**2**) ^{1}H NMR ($CDCl_3$, 600 MHz):3.27 (s, 3H); 5.34 (s, 2H); 7.16–7.18 (d, 2H); 7.33–7.36 (q, 5H). 1,3-dibenzylimidazol-2-ylidene (**3**) ^{1}H NMR ($CDCl_3$, 600 MHz):5.40 (s, 4H); 7.16–7.18 (d, 4H); 7.35–7.38 (q, 10H)]. As the precursor of carbene catalysts, hydrophobic imidazolium hexafluorophosphates were prepared from its halogen salt which slightly modified in literature [26–28].



Scheme 1 The structures of imidazol-2-ylidenes

Measurements

^{1}H NMR spectra of obtained polymer was performed on a Bruker AV-600MHz spectrometer using $CDCl_3$ or DMSO-d_6 at 25 °C with TMS as internal standard. Differential scanning calorimetry (DSC) was performed two heating and cooling cycles in the temperature range −60 to 150 °C at a heating rate of 10 °C/min with a DSC 2010 instrument. Number average molecular weight (M_n) and polydispersity (PDI) of PDTC were measured in THF at 40 °C by Gel permeation chromatography 220 (GPC) with a refractive index detector and a set of columns (PL gel 10 m Mixed-B 300 × 7.5 mm and PL gel 10 m Guard 50 × 7.5 mm) and calibrated using polystyrene standards.

Polymerization procedure

All polymerizations were carried out in glass ampoules under inert gases. Monomer and solvent were added into the ampoules successively and kept thermostated. Initiator and catalyst were added to the ampoule according to priority by syringe. The polymerization was quenched by distilled water. The polymer was washed with methanol twice, and then dried to constant weight under vacuum at 40 °C.

Results and discussion

Characteristics of the polymerization

Three imidazol-2-ylidenes substituted by different groups as catalysts were utilized to examine their catalytic activity for the DTC ring-opening polymerization. The polymerization results are summarized in Table 1. As experimental results shown, the order of catalytic effect is **1** > **2** > **3**. It indicated that catalytic activity of NHC/BnOH system is dramatically influenced by the donation-electronic inductive effect. When electron-donating ability of group on *N*-imidazol-2-ylidenes becomes greater, the catalytic activity of imidazol-2-ylidenes is also increasing.

Using **1** as catalyst, the effects of DTC concentration and initiator amount have been investigated in detail and the result is shown in Figs. 1 and 2, respectively. As shown in Fig. 1, the monomer conversion and molecular weight of PDTC tend to rise with increasing DTC concentration till [DTC] > 3.0 mol/L. With higher concentration, the monomer conversion and the M_n of polymer decrease and the PDI

Table 1 Effect of different NHCs on polymerization of DTC initiated by BnOH

No.	Catalyst	Cov. (%)	Mn × 10^{-4} (g mol^{-1})	PDI
1	**1**	99.2	2.82	1.31
2	**2**	68.8	1.57	1.37
3	**3**	49.5	1.11	1.27

Condition: [DTC] = 3.0 mol/L, [DTC]/[*I*]/[*C*] = 200/1/1, 25 °C, 70 min, in THF

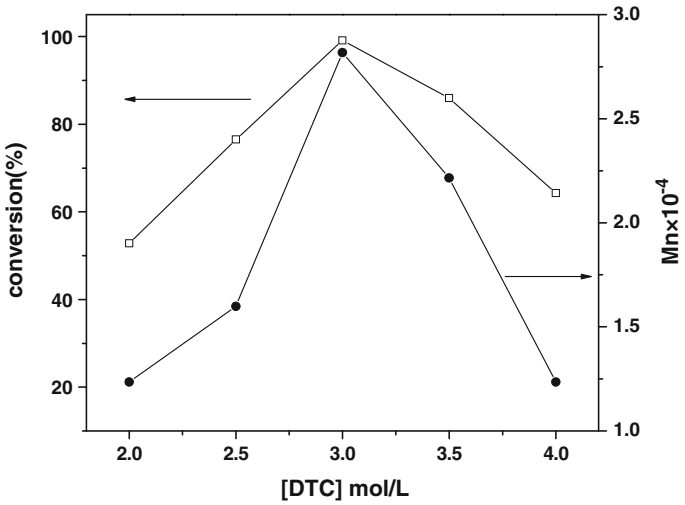


Fig. 1 Effect of monomer concentration on polymerization of DTC; conditions: [DTC]/[*I*] = 200, [*C*]/[*I*] = 1, 0 °C, 70 min, in THF

broadens. Figure 2 illustrates that [DTC]/[*I*] of 200 molar ratio is essential for preparing high yield and molecular weight polymer. The polymerization could not happen when further decreasing initiator content, yet increasing initiator content presumably leads to forming more and shorter polymeric chains, thus decreasing the molecular weight of polymer. Therefore, the optimum DTC concentration and initiator amount on the polymerization are as follows: [DTC] = 3.0 mol/L, [DTC]/[*I*] = 200.

The influences of polymerization time and temperature, catalyst to initiator molar ratio ([*C*]/[*I*]) were systematically conducted in Table 2. As seen in Table 2, the monomer conversion, M_n and PDI of PDTC can be controlled by varying factors mentioned above. The M_n of PDTC obtained is in the range of (1.07–2.82) × 10^4.

It was also found that the relation between M_n of PDTC with the conversion of DTC, as shown in Fig. 3, indicating that there is a linear relationship, consistent with a living polymerization.

The DSC measurement of the PDTC sample displays two different crystalline modifications (Fig. 4). Modification A gives a transition temperature of 89.2 °C and modification B has a melting point of 115.2 °C at first heating. Upon cooling and reheating, modification A completely disappears and a melting point of 115.4 °C is only observed. This is due to the sample no longer exists solution crystallization of condition, then modification A cannot take shape, while melt crystallization is the condition to form modification B, therefore it can only form modification B.

Kinetics of 2,2-DTC polymerization

The kinetics of the DTC polymerization with **1** initiated by BnOH in THF was investigated. Linear plots of $\ln([DTC]_0/[DTC]_t)$ versus time at four different catalyst concentrations at conversions below 41% indicate that the polymerization is of first

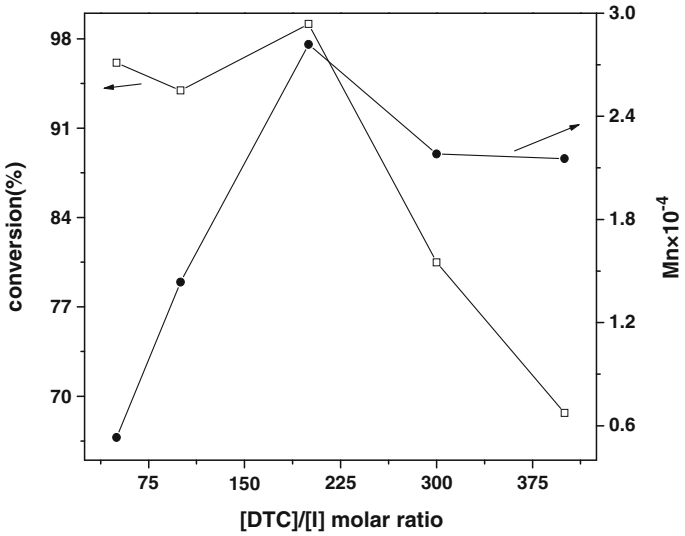


Fig. 2 Effect of the initiator concentration on polymerization of DTC; conditions: [DTC] = 3.0 mol/L, [*C*]/[*I*] = 1, 25 °C, 70 min, in THF

Table 2 Polymerization of DTC with **1** initiated by BnOH

No.	*C*/*I*	Temp (°C)	Time (min)	Conv. (%)	Mn × 10^{-4} (g mol^{-1})	PDI
1	1.00	25	50	88.7	2.20	1.27
2	1.00	25	60	94.2	2.36	1.30
3	1.00	25	70	99.2	2.82	1.31
4	1.00	25	80	96.7	2.51	1.33
5	1.00	25	90	95.8	2.48	1.36
6	1.00	5	70	61.6	2.00	1.21
7	1.00	15	70	87.2	2.22	1.24
8	1.00	35	70	92.4	2.23	1.51
9	1.00	45	70	88.4	1.97	1.65
10	0.50	25	70	47.8	1.07	1.15
11	0.75	25	70	87.8	1.74	1.25
12	1.25	25	70	94.6	2.38	1.44
13	1.50	25	70	86.1	1.98	1.74

Conditions: [DTC] = 3.0 mol/L, [DTC]/[*I*] = 200, in THF

order with respect to monomer (Fig. 5). A first order in the catalyst was also obtained from the slopes of the plots in Fig. 6. Therefore, the polymerization follows an overall kinetic law of the following form:

$$R_p = k_p[\mathrm{DTC}][\mathbf{1}]$$

where k_p is the polymerization rate constant. The relationship between the $\ln R_p$ and the reciprocal of polymerization temperature ($1/T$) has been plotted in Fig. 7.

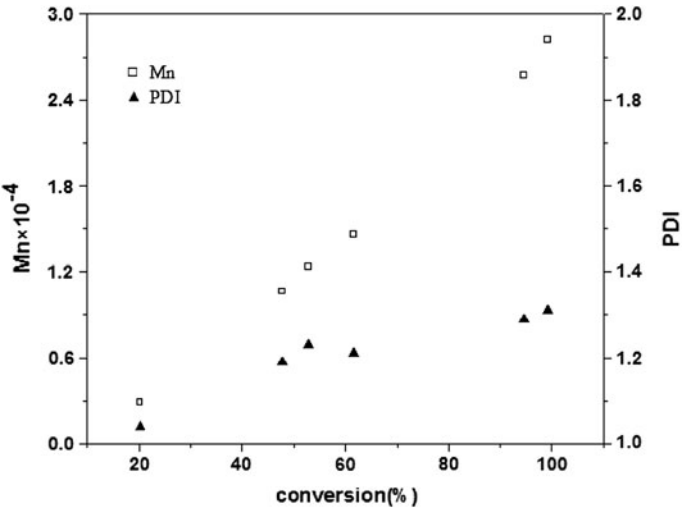


Fig. 3 Relation between molecular weight and the conversion; conditions: [DTC] = 3.0 mol/L, [DTC]/[*I*] = 200, [*C*]/[*I*] = 1, 25 °C, in THF

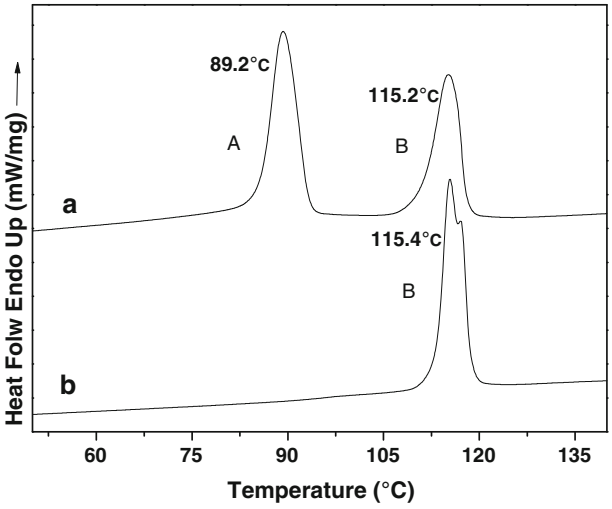


Fig. 4 DSC curves of PDTC. (*a*) First heating and (*b*) second heating

According to the Arrhenius equation, the overall activation energy is 51.06 kJ/mol (Scheme 2).

Mechanism of 2,2-DTC polymerization

The possible mechanism catalyzed by NHCs can catalyze polymerization is a monomer-activated mechanism commonly accepted by majority experts analogous

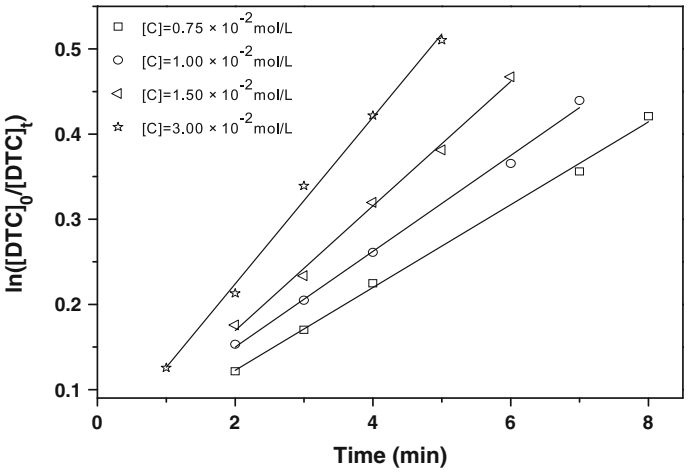


Fig. 5 ln ($[DTC]_0/[DTC]_t$) as a function of time; conditions: [DTC] = 3.00 mol/L, [DTC]/[*I*] = 200, 25 °C, in THF

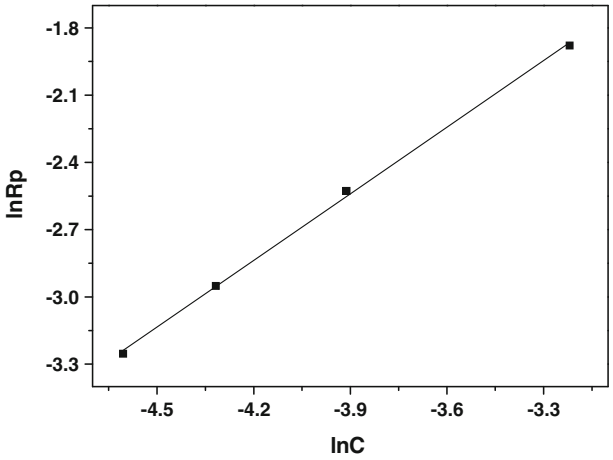


Fig. 6 Plot of lnR_p versus ln[*C*]; conditions: [DTC] = 3.00 mol/L, [DTC]/[*I*] = 200, 25 °C, in THF

to the pathway of the ring-opening polymerization of cyclic esters with enzymes [14, 29]. According to the mechanism, initiation occurs when the nucleophile BnOH reacts with the DTC catalyst complex to form the ring-opened adduct, the α-chain end of the PDTC bears the ester from the initiating BnOH and the ω-chain end is a primary alcohol and serves as the nucleophile in subsequent propagation. Consistent with this mechanism, the ^{1}H NMR spectrum of the PDTC, initiated with BnOH in the presence of **1**, shows the resonances associated with the phenmethyl ester as well as the hydroxyl chain-end (Fig. 8).

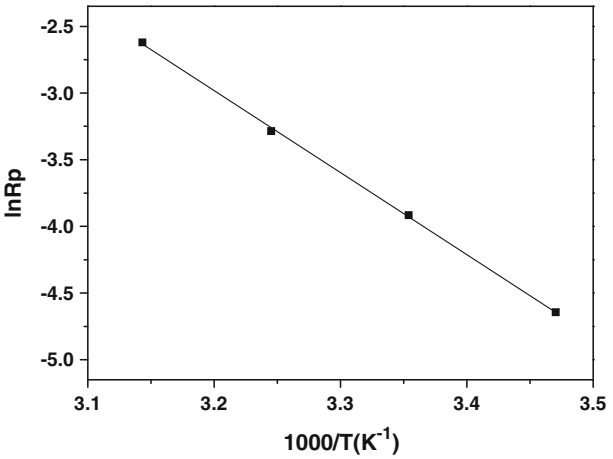
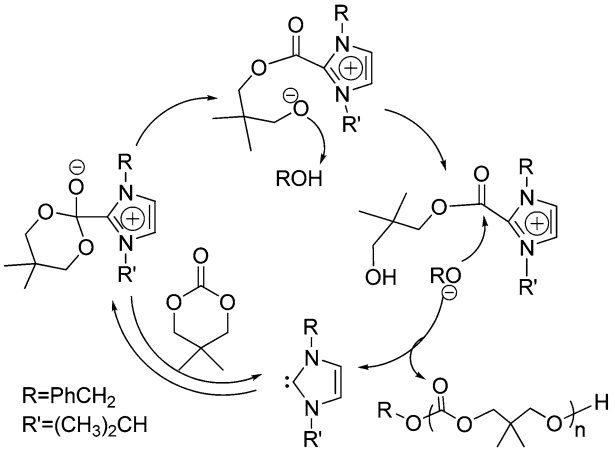


Fig. 7 Effect of the reaction temperature on polymerization rate; conditions: [DTC] = 3.0 mol/L, [DTC]/[*I*]/[*C*] = 200/1/1, in THF



Scheme 2 Proposed Mechanism for polymerization of DTC catalyzed by **1** with BnOH

Conclusions

Imidazol-2-ylidenes synthesized are effective catalysts for the ring-opening polymerization of DTC. **1** has higher effective and gives higher molecular weight polymer after 70 min at [DTC]/[*C*]/[*I*] = 200/1/1, in THF, at 25 °C. The kinetics of **1**/BnOH system demonstrates that the polymerization reaction proceeds with first-order rate dependence on DTC monomer and catalyst concentration, respectively, and the overall activation energy amounts to 51.06 kJ/mol. The proposed process is through a monomer-activated mechanism.

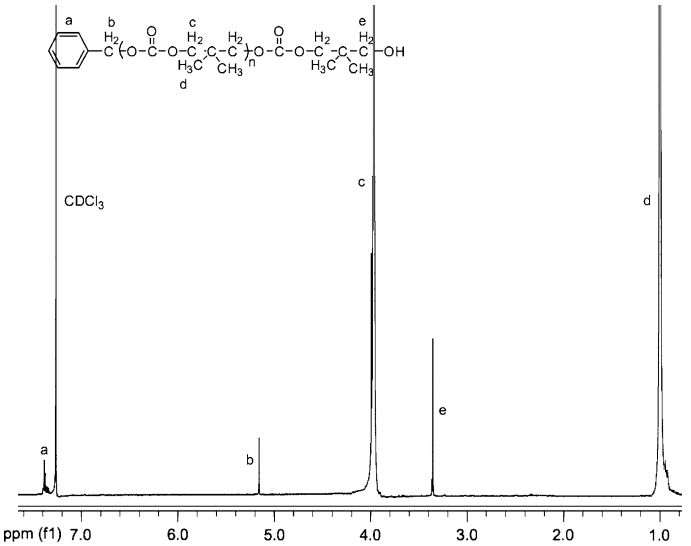


Fig. 8 ^{1}H NMR spectrum of PDTC catalyzed by **1** with BnOH

Acknowledgments This study was supported by the Shanxi Natural Science Foundation of China (Grant No. 2006011069), the Opening Foundation of Key Laboratory of Shanxi Province (Grant No. 2009011059-7), the Research Found for Education Department of Shanxi Province (Grant No. 2010111), and the Opening Foundation of Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education (Grant No. 201002).

References

1. Hu B, Tu YY, Yan GP, Zhuo RX, Bottle SE, Wu Y, Fan CL, Duan YJ (2011) Polycarbonate microspheres containing mitomycin C and magnetic powders as potential hepatic carcinoma therapeutics. Colloids Surf B Biointerfaces 84:550–555
2. Save M, Schappacher M, Soum A (2002) Controlled ring-opening polymerization of lactones and lactides initiated by lanthanum isopropoxide, 1. General aspects and kinetics. Macromol Chem Phys 203:889–899
3. Stevels WM, Ankone MJK, Dijkstra PJ, Feijen J (1996) A versatile and highly efficient catalyst system for the preparation of polyesters based on lanthanide tris(2,6-di-tert-butylphenolate)s and various alcohols. Macromolecules 29:3332–3333
4. Ling J, Shen ZQ, Huang QH (2001) Novel single rare earth aryloxide initiators for ring-opening polymerization of 2,2-dimethyltrimethylene carbonate. Macromolecules 34:7613–7616
5. Zhang LF, Shen YQ, Yu CP (2003) Ring-opening polymerization of ε-caprolactone by lanthanide tris (2,6-dimethylphenolate)s. Chin J Chem 21:1236–1237
6. Ling J, Zhu WP, Shen ZQ (2004) Controlling ring-opening copolymerization of ε-caprolactone with trimethylene carbonate by scandium tris(2,6-di-tert-butyl-4-methylphenolate). Macromolecules 37: 758–763
7. Zhang LF, Niu YH, Wang Y, Wang P, Shen LJ (2010) Ring-opening polymerization of ε-caprolactone by lanthanide tris(2,4,6-tri-tert-butylphenolate)s: characteristics, kineticsand mechanism. Sci China Chem 53:599–604
8. Zhou LY, Yao YM, Zhang Y, Xue MQ, Chen JL, Shen Q (2004) Synthesis and characterization of homoleptic lanthanide guanidinate complexes and their catalytic activity for the ring-opening polymerization of trimethylene carbonate. Eur J Inorg Chem 10:2167–2172

9. Sheng HT, Zhou LY, Zhang Y, Yao YM, Shen Q (2007) Anionic lanthanide phenoxide complexes as novel single-component initiators for the polymerization of ε-caprolactone and trimethylene carbonate. J Polym Sci Part A Polym Chem 45:1210–1218
10. Zhou LY, Sun HM, Chen JL, Yao YM, Shen Q (2005) Living carbocationic copolymerization of isobutylene with styrene. J Polym Sci Part A Polym Chem 43:1778–1786
11. Khedher A, Mimouni MF (2010) Sensorless-adaptive DTC of double star induction motor. Energy Convers Manag 51:2878–2892
12. Connor EF, Nyce GW, Myers M, Möck A, Hedrick JL (2002) First example of N-heterocyclic carbenes as catalysts for living polymerization: organocatalytic ring-opening polymerization of cyclic esters. J Am Chem Soc 124:914–915
13. Dove AP, Pratt RC, Lohmeijer BGG, Culkin DA, Hagberg EC, Nyce GW, Waymouth RM, Hedrick JL (2006) N-heterocyclic carbenes: effective organic catalysts for living polymerization. Polymer 47:4018–4025
14. Csihony S, Culkin DA, Sentman AC, Dove AP, Waymouth RM, Hedrick JL (2005) Single-component catalyst/initiators for the organocatalytic ring-opening polymerization of lactide. J Am Chem Soc 127:9079–9084
15. Coulembier O, Kiesewetter MK, Mason A, Dubois P, Hedrick JL (2007) A distinctive organocatalytic approach to complex macromolecular architectures. Angew Chem Int Ed 46:4719–4721
16. Nederberg F, Lohmeijer BGG, Leibfarth F, Pratt RC, Choi J, Dove AP, Waymouth RM, Hedrick JL (2007) Organocatalytic ring opening polymerization of trimethylene carbonate. Biomacromolecules 8:153–160
17. Culkin DA, Jeong W, Csihony S, Gomez ED, Balsara NP, Hedrick JL, Waymouth RM (2007) Zwitterionic polymerization of lactide to cyclic poly(lactide) by using N-heterocyclic carbene organocatalysts. Angew Chem Int Ed 46:2627–2630
18. Coulembier O, Dove AP, Pratt RC, Sentman AC, Culkin DA, Mespouille L, Dubois P, Waymouth RM, Hedrick JL (2005) Latent, thermally activated organic catalysts for the on-demand living polymerization of lactide. Angew Chem Int Ed 44:4964–4968
19. Kamber NE, Jeong W, Gonzalez S, Hedrick JL, Waymouth RM (2009) N-heterocyclic carbenes for the organocatalytic ring-opening polymerization of ε-caprolactone. Macromolecules 42:1634–1639
20. Helou M, Miserque O, Brusson J, Carpentier J, Guillaume SM (2010) Organocatalysts for the controlled "immortal" ring-opening polymerization of six-membered-ring cyclic carbonates: a metal-free, green process. Chem A Eur J 16:13805–13813
21. Kamber NE, Jeong W, Waymouth RM (2007) Organocatalytic ring-opening polymerization. Chem Rev 107:5813–5840
22. Sarel S, Pohoryles LA (1958) The stereochemistry and mechanism of reversible polymerization of 2,2-disubstituted 1,3-propanediol. J Am Chem Soc 80:4596–4599
23. Arduengo AJ, Basika Dias HV, Harlow RL, Kline MJ (1992) Electronic stabilization of nucleophilic carbenes. J Am Chem Soc 114:5530–5534
24. Arduengo AJ, Krafczyk R, Schmutzler R, Craig HA, Goerlich JR, Marshall WJ, Unverzagt M (1999) Imidazolylidenes, imidazolinylidenes and imidazolidines. Tetrahedron 55:14523–14534
25. Kuhn N, Kratz T (1993) Synthesis of imidazol-2-ylidenes by reduction of imidazole-2-(3H)-thiones. Synthesis 6:561–562
26. Bonhôte P, Dias A, Papageorgiou N, Kalyanasundaram K, Grätzel M (1996) Hydrophobic, highly conductive ambient-temperature molten salts. Inorg Chem 35:1168–1178
27. Samantaray MK, Katiyar V, Pang KL, Nanavati H, Ghosh P (2007) Silver N-heterocyclic carbene complexes as initiators for bulk ring-opening polymerization (ROP) of l-lactides. Organomet Chem 692:1672–1682
28. Thomas F, Mehran Y, John PR (2003) A structure–permeability study of small drug-like molecules. Bioorg Med Chem Lett 13:719–722
29. Coulembier O, Lohmeijer BGG, Dove AP, Pratt RC, Mespouille L, Culkin DA, Benight SJ, Dubois P, Waymouth RM, Hedrick JL (2006) Alcohol adducts of N-heterocyclic carbenes: latent catalysts for the thermally-controlled living polymerization of cyclic esters. Macromolecules 39:5617–5628