

Quaternary ammonium salt-functionalized chitosan: An easily recyclable catalyst for efficient synthesis of cyclic carbonates from epoxides and carbon dioxide

Yuan Zhao^{a,b}, Jie-Sheng Tian^a, Xin-Hua Qi^b, Zhe-Nan Han^b,
Yuan-Yi Zhuang^b, Liang-Nian He^{a,*}

^a State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, PR China

^b College of Environmental Science and Engineering, Nankai University, Tianjin 300071, PR China

Received 6 February 2007; received in revised form 17 March 2007; accepted 20 March 2007

Available online 24 March 2007

Abstract

A quaternary ammonium salt covalently bound to chitosan is reported as an efficient and recyclable single-component catalyst for the synthesis of propylene carbonate (PC) from propylene oxide (PO) and carbon dioxide without any organic solvent or co-catalyst. The catalyst can be easily recovered by filtration and reused for at least five times without obvious loss of its catalytic activity. The effects of the catalyst structure and various reaction parameters on the catalytic performance were in detail investigated. Moreover, the catalyst was found to be applicable to a variety of terminal epoxides, producing the corresponding cyclic carbonates in high yield and selectivity. Notably, this environmentally benign and cost-effective process has great potential to be applied in various continuous flow reactors in industry.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Chitosan-supported catalyst; Quaternary ammonium salt; Carbon dioxide; Propylene oxide; Propylene carbonate

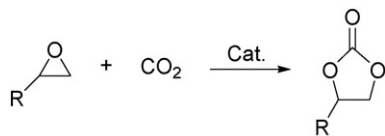
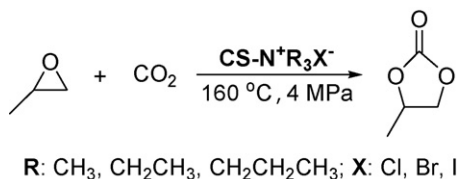
1. Introduction

Conversion of carbon dioxide into industrially useful chemicals has dual significances in view of both environmental protection and sustainable chemistry [1,2]. One of the most promising methodologies in this area is the synthesis of cyclic carbonates via the cycloaddition of epoxides and CO₂ (Scheme 1) [3]. High atom efficiency of the reaction and the wide applications of the cyclic carbonate products are the main reasons for the constant interests paid to this simple reaction [4–7]. Since cyclic carbonates were produced on an industrial scale more than 40 years ago [8,9], many catalysts have been developed to promote carbon dioxide insertion into oxiranes, such as amines and phosphines [10], alkali metal halides and onium salts [11,12], organometallic compounds [13–17], and ionic liquid [18–20]. In current processes of cyclic carbonate production employed by industry, various homogeneous catalysts

were used. However, to separate the catalyst from the product by a purification process, such as distillation after the reaction, is a complicated process and may result in the decomposition of the catalyst or formation of by-products. Therefore, many heterogeneous catalysts have been proposed for this reaction, such as metal oxides [21–24] or oxychlorides [25], Cs-loaded zeolite and alumina [26], etc. However, these catalysts generally suffer from insufficient activity and an additive or co-catalyst is necessary for realizing high yield of the product. In this context, one strategy is that the active species can be chemically or physically attached to a support like natural or synthesized polymers [27–31], silica [32–34], zeolite [35] and other materials [36], in order to get a better product separation and make the catalyst recovery more facile. To be delighted, a synergistic acceleration of the catalyst activity was found by immobilization of homogeneous catalyst on the support [34].

Quaternary ammonium salts (such as Bu₄NBr, Et₄NBr, etc.) are currently used as cheap and efficacious homogeneous catalysts for the industrial preparation of cyclic carbonates [37,38]. Chitosan (abbreviated as CS) is the *N*-deacetylated derivative of chitin which is one of the most abundant biopolymers next to

* Corresponding author. Tel.: +86 22 2350 4216; fax: +86 22 2350 9634.
E-mail address: heln@nankai.edu.cn (L.-N. He).

Scheme 1. Cycloaddition reaction of epoxides and CO₂.Scheme 2. The CS-N⁺R₃X⁻-catalyzed synthesis of propylene carbonate.

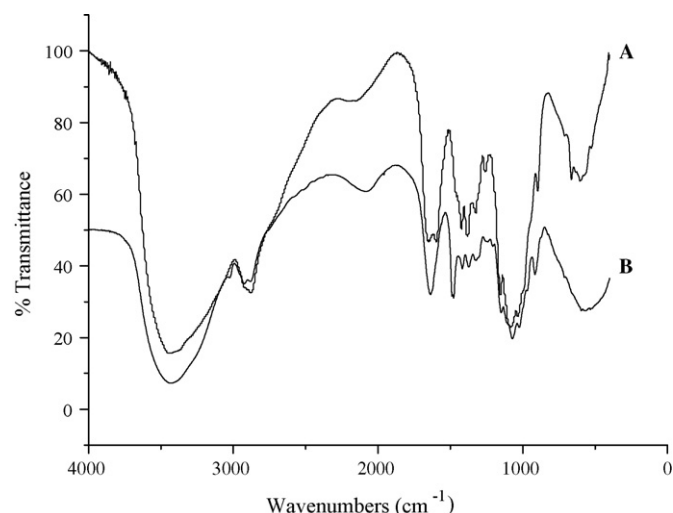
cellulose and a by-product of fishing industry. Besides the biocompatibility, biodegradability and non-toxicity, chitosan can be easily chemically or physically modified which make it an excellent supporting material of catalyst [39]. Recently many attempts have been made to explore new applications of chitosan in this purpose [30,40–48]. A chitosan-supported zinc chloride in combination with 1-butyl-3-methylimidazole halides was shown to be active for the cycloaddition of PO and CO₂ [31]. In this article, we designed and synthesized a functionalized biopolymer—chitosan-supported quaternary ammonium salt (abbreviated as CS-N⁺R₃X⁻), which was shown to be a single-component active catalyst for the cycloaddition reaction of epoxides and CO₂ (Scheme 2). Very high PC yield and selectivity were attained with high catalyst recyclability and stability.

2. Experimental

2.1. Materials and analysis

Chitosan was purchased from Zhejiang Jinke (Golden Shell) Bio. Chem. Company. The degree of deacetylation was 91% and viscosity average molecular weight was 5×10^4 . 3-Chloro-2-hydroxypropyl trimethylammonium chloride (CTA, 65 wt% water solution) was purchased from Fluka Company and other quaternizing agents were prepared according to the published procedure [49,50]. Carbon dioxide of 99.99% purity was commercially available and epoxides were supplied from Aldrich Company. Other reagents were of analytical grade and were used as received.

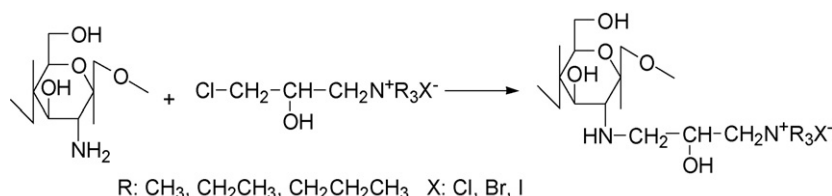
The products were analyzed on a gas chromatograph (Shimadzu 2014 chromatographer) equipped with a RTX-5 capillary column (30 m × 0.25 μm) using a flame ionization detector

Fig. 1. FT-IR spectra of the unmodified chitosan (A) and the CS-N⁺Me₃Cl⁻ (B).

(FID). The FT-IR spectra were recorded on a MAGNA-560 FT-IR spectrophotometer using KBr tablets. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury-plus 400 spectrometer using tetramethylsilane (TMS) as an internal standard.

2.2. Catalysts preparation and characterization

According to the procedures reported in literature [51], the supported catalysts (quaternary ammonium salts covalently bound to chitosan, CS-N⁺R₃X⁻) were synthesized as shown in Scheme 3. The representative procedure for the preparation of the quaternary ammonium salt-functionalized chitosan (CS-N⁺Me₃Cl⁻) was as follows: chitosan (4 g), 10 g of 40 wt% NaOH solution, and 50 ml of isopropanol were added into a flask. The reactants were stirred at 55 °C for 4 h, and then an aqueous solution of 3-chloro-2-hydroxypropyl trimethylammonium chloride (65 wt%, 30 ml) was gradually added to the reaction mixture. Then the reaction was magnetically stirred at 70 °C for another 15 h. When the reaction was complete, the resulting mixture was neutralized by adding dilute hydrochloric acid. The product was isolated by precipitation via the addition of alcohol into the reaction mixture, followed by filtration, washing with anhydrous alcohol, and drying under vacuum at 80 °C. The supported catalyst was characterized by the FT-IR (Fig. 1), ¹H NMR and ¹³C NMR spectra [52], showing that hydroxypropyl trimethylammonium chloride (CTA) was covalently linked to the nitrogen atom of chitosan [43].



Scheme 3. Preparation of the quaternary ammonium salts covalently bound to chitosan.

2.3. Synthesis of PC from PO and CO₂

Typical procedure for the synthesis of PC from PO and CO₂ was as follows: a stainless steel autoclave (25 ml inner volume) was purged with CO₂ to evacuate air, and then 0.3 g (1 mmol) of CS-N⁺Me₃Cl⁻, 0.08 g of biphenyl (internal standard of GC) and propylene oxide (4 ml, 57.2 mmol) were added successively. CO₂ was charged in the reactor and the pressure was adjusted to 4 MPa at 160 °C. The autoclave was heated at that temperature for 6 h, and the pressure was kept constant during the reaction. After reaction, the autoclave was allowed to be cooled, and then the excess of CO₂ was vented. The product yields were determined by GC with a flame ionization detector and were further identified using GC–MS by comparing retention times and fragmentation patterns with authentic samples. The products structures were also identified by ESI–MS and NMR spectra as previously reported [29,32]. The solid catalyst was recovered by filtration, followed by rinsing with anhydrous alcohol and drying.

3. Results and discussion

3.1. The effects of catalyst structures on the catalytic performance

A series of the quaternary ammonium salt-functionalized chitosan, such as hydroxypropyl trimethylammonium bromide of chitosan (CS-N⁺Me₃Br⁻), hydroxypropyl trimethylammonium iodide of chitosan (CS-N⁺Me₃I⁻), hydroxypropyl triethylammonium chloride of chitosan (CS-N⁺Et₃Cl⁻), and CS-N⁺Me₃Cl⁻ were investigated for PC synthesis. For comparison with the supported catalysts, the catalytic activity of the corresponding lower molecular weight compounds such as Bu₄N⁺Cl⁻, Bu₄N⁺Br⁻, Bu₄N⁺I⁻, Me₄N⁺Cl⁻, Et₄N⁺Cl⁻ were also examined for the reaction of PO with CO₂. The results are listed in Table 1. Without a catalyst, the reaction of CO₂ and PO afforded no product at all (entry 11, Table 1). It is important to note that the CS alone was found to be inactive for PC synthesis (entry 1). In general, the quaternary ammonium salts (entries 7–10) except Me₄N⁺Cl⁻ (entry 6) and the chitosan-supported ones (entries 2–5) exhibited high activity under the identical reaction conditions (140 °C, 4 MPa, 6 h). It is worth mentioning that no halogenated organic compounds were detected by GC–MS.

Notably, the catalyst performance depended on the anions of the chitosan-supported catalysts. The order of catalytic activity was as follows: I⁻ > Br⁻ > Cl⁻ (entries 2–4), in accord with its leaving ability and nucleophilicity [11]. However, the cations of the catalysts among the unsupported ammonium salts except Me₄N⁺Cl⁻ have little influence on the performance of the catalysts (entries 6–10). It is interesting that the support (chitosan) may play an appreciable role in promoting PC synthesis though it did not show any activity at all when used alone (entry 2 versus 6). The similar synergetic effect of the support with the active catalytic species was recently reported by Sakakura et al. [34].

As a consequence, CS-N⁺Me₃Cl⁻ was chosen as a model catalyst for further investigation due to its easy availability and

Table 1
PC synthesis catalyzed by the quaternary ammonium halides^a

Entry	Catalyst	Yield ^b (%)	Selectivity (%)
1	CS	Trace	–
2	CS-N ⁺ Me ₃ Cl ⁻	73	>99
3	CS-N ⁺ Me ₃ Br ⁻	95	>99
4	CS-N ⁺ Me ₃ I ⁻	100	>99
5	CS-N ⁺ Et ₃ Cl ⁻	81	>99
6	Me ₄ N ⁺ Cl ⁻	1	90
7	Et ₄ N ⁺ Cl ⁻	91	99
8	Bu ₄ N ⁺ Cl ⁻	99	89
9	Bu ₄ N ⁺ Br ⁻	88	89
10	Bu ₄ N ⁺ I ⁻	92	91
11	None	0	–
12 ^c	CS-N ⁺ Me ₃ Cl ⁻	98	>99
13 ^d	CS-N ⁺ Me ₃ Cl ⁻	83	>99

^a Reaction conditions: 140 °C, 4 MPa, 6 h, PO (57.2 mmol), catalyst (1.7 mmol%, relative to PO).

^b Determined by GC using an internal standard technique. The yield in this work is defined as follows: yield of product (%) = (moles of product/moles of PO added) × 100.

^c Reaction conditions: 160 °C, 4 MPa, 6 h, catalyst (1.7 mmol%, relative to PO).

^d Reaction conditions: 160 °C, 4 MPa, 6 h, catalyst (0.2 mmol%, relative to PO).

stability. Indeed, almost quantitative yield of PC was attained at 160 °C in the presence of a catalytic amount of CS-N⁺Me₃Cl⁻. The high activity was still maintained even at low catalyst loading (0.2 mmol% relative to PO, entry 13).

3.2. Effect of temperature on PC synthesis

Fig. 2 shows the influence of reaction temperature on PC yield. Reaction temperature is the most important factor for the heterogeneously catalyzed cycloaddition reaction. As shown in Fig. 2, the PC yield increased up to 160 °C and selectivity was kept at a high level as temperature increasing, whereas, further increase in the temperature caused a slight decrease in PC yield, presumably due to side-products formed at the higher temperature. The lower yield of the product at lower temperature was possibly due to the lower activity of catalyst. Accordingly, 160 °C could be the optimal temperature for the reaction.

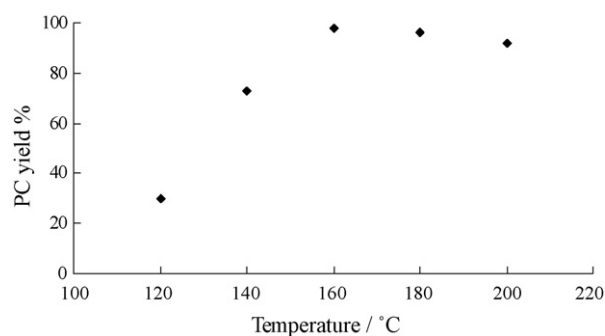


Fig. 2. Influence of temperature on PC yield. Reaction conditions: propylene oxide, 57.2 mmol; catalyst (CS-N⁺Me₃Cl⁻), 0.3 g (1.7 mmol% relative to PO); pressure, 4 MPa; time, 6 h.

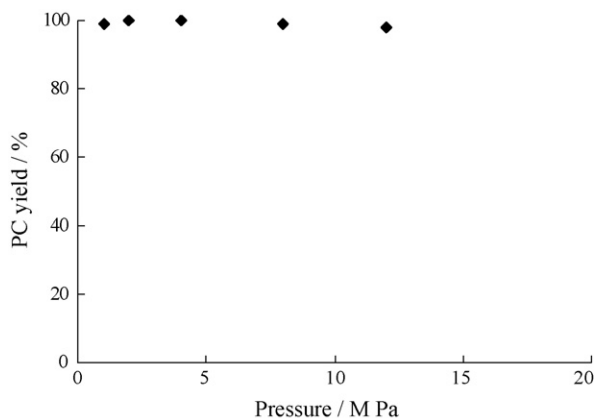


Fig. 3. Pressure influence on PC yield. Reaction conditions: propylene oxide, 57.2 mmol; catalyst ($\text{CS-N}^+\text{Me}_3\text{Cl}^-$), 0.3 g (1.7 mmol% relative to PO); temperature, 160 °C; time, 6 h.

3.3. Pressure effect on PC synthesis

As illustrated in Fig. 3, a remarkable feature of the reaction is that the CO_2 pressure shows no effect on the PC yield at 160 °C in the range of 1–12 MPa. Indeed, the catalyst efficiently operated even under the pressure as low as 1 MPa. The good absorbency of chitosan to CO_2 [48] could be of benefit to the reaction.

The reaction in supercritical CO_2 is also advantageous in terms of product separation from the reaction media. Thus, the phase behaviour of the reaction visually inspected through a sapphire window attached to the autoclave reveals that propylene oxide and supercritical CO_2 initially form a uniform phase while PC is separated out and forms a new phase after the reaction. In addition, the catalyst ($\text{CS-N}^+\text{Me}_3\text{Cl}^-$) exists as solid during the reaction. Accordingly, this procedure could be applied to development of fixed-bed continuous flow reactors, avoiding the use of organic solvent to isolate the products.

3.4. Reaction time dependence of PC yield for $\text{CS-N}^+\text{Me}_3\text{Cl}^-$

Fig. 4 shows the influence of reaction time on PC yield. The $\text{CS-N}^+\text{Me}_3\text{Cl}^-$ -catalyzed PC synthesis from PO and CO_2 proceeded rapidly and more than 60% PC yield was obtained within first 1 h at 160 °C. The PC yield experienced a continuing growth

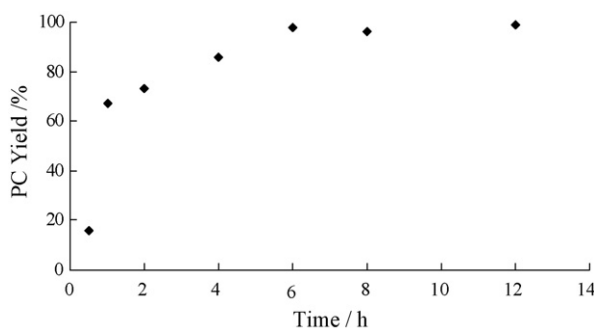
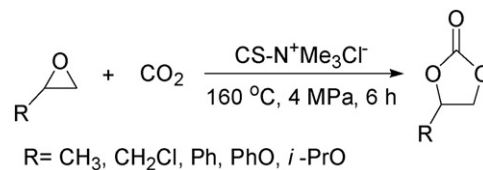


Fig. 4. Reaction time dependence of PC yield for $\text{CS-N}^+\text{Me}_3\text{Cl}^-$. Reaction conditions: PO, 57.2 mmol; $\text{CS-N}^+\text{Me}_3\text{Cl}^-$, 0.3 g (1.7 mmol% relative to PO); 1 mmol; pressure, 4 MPa; temperature, 160 °C.



Scheme 4. The $\text{CS-N}^+\text{Me}_3\text{Cl}^-$ -catalyzed coupling of CO_2 and epoxides.

within 6 h, while the selectivity of PC almost kept a constant during the whole reaction course. Consequently, a reaction time of 6 h was required for almost complete PO conversion.

3.5. Cycloaddition reaction of various epoxides and CO_2 catalyzed by $\text{CS-N}^+\text{Me}_3\text{Cl}^-$

A series of epoxides were examined for the synthesis of the corresponding carbonates in the presence of $\text{CS-N}^+\text{Me}_3\text{Cl}^-$ under the optimized reaction conditions (Scheme 4). The results were summarized in Table 2. The catalyst was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in high yields and selectivities. Propylene oxide was found to be the most reactive epoxide, while styrene oxide exhibited relatively low activity among the epoxides surveyed. Consequently, this solvent-free process reserves the primary benefits of a heterogeneous catalysis, while co-opting the benefits of a homogeneous catalysis.

Table 2
Cycloaddition reaction of various epoxides catalyzed by $\text{CS-N}^+\text{Me}_3\text{Cl}^-$

Epoxide	Product	Yield ^a (%)	Selectivity (%)
		98	>99
		92	92
		88	88
		91	91
		96	96

^a Reaction conditions: catalyst ($\text{CS-N}^+\text{Me}_3\text{Cl}^-$, 0.3 g, 1.7 mmol% relative to PO), 160 °C, 4 MPa, 6 h.

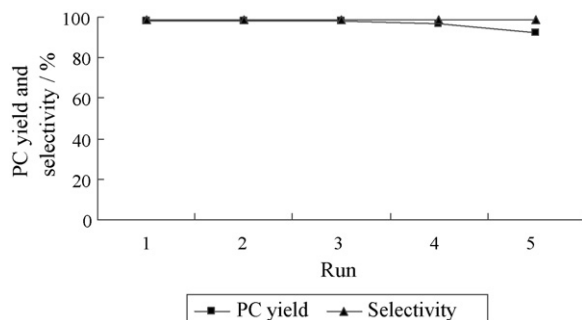


Fig. 5. Catalyst recycle. Reaction conditions: propylene oxide, 57.2 mmol; catalyst ($\text{CS-N}^+\text{Me}_3\text{Cl}^-$), 0.3 g (1.7 mmol% relative to PO); 160 °C; 4 MPa; 6 h.

3.6. Catalyst recycling

The catalyst was simply recovered by filtration after reaction and reused for next run after drying. The results were summarized in Fig. 5. We delightedly found that $\text{CS-N}^+\text{Me}_3\text{Cl}^-$ can be recycled for at least five times without obvious loss in activity and the selectivity was constant at a high level. The leaching of the active ingredient of the catalyst was tested. The solid catalyst was thoroughly filtered from the product solution, and the content of chloride ion in the resulting filtrate was measured by ion chromatography with a DIONEX DX-120 Ion Chromatographic instrument. The content of chloride ion was at the level of 43 ppm, demonstrating the thermal stability of the chemically modified chitosan [53,54]. The experimental results also confirmed that $\text{CS-N}^+\text{Me}_3\text{Cl}^-$ in the fifth run still maintained high activity.

4. Conclusion

A quaternary ammonium salt-functionalized chitosan was shown for the first time to be an active and readily recyclable single-component catalyst for the synthesis of carbonates from epoxides and CO_2 without any additive or co-catalyst. The workup procedure is simple and the catalyst can be easily recovered by filtration and reused for five times without significant loss of activity. This organic solvent-free process presented here could show much potential application in industry due to its simplicity, easy product separation, using a biopolymer as a support, and ease of catalyst recycling. Further study concerning the applications in continuous flow reactors are in progress.

Acknowledgements

We are grateful to the financial supports of the National Science Foundation of China (grant nos. 20472030, 20421202, and 20672054), and the Committee of Science and Technology of Tianjin (grant no. 05YFJMJC00800).

References

[1] H. Arakawa, M. Aresta, J.N. Armor, et al., *Chem. Rev.* 101 (2001) 953–996.
 [2] P.T. Anastas, T.C. Wilimson (Eds.), *Green Chem.* ACS Symposium Series 626, American Chemical Society, Washington, DC, 1996.

[3] D.J. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* 153 (1996) 155–174.
 [4] A.A.G. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951–976.
 [5] M. Yoshida, M. Ihara, *Chem. Eur. J.* 10 (2004) 2886–2893.
 [6] J.H. Clements, *Ind. Eng. Chem. Res.* 42 (2003) 663–674.
 [7] J.P. Parrish, R.N. Salvatore, K.W. Jung, *Tetrahedron* 56 (2000) 8207–8237.
 [8] J.F. Cooper, M. Lichtenwalter, US Patent 2,773,070 (1956).
 [9] P.P. McClellan, US Patent 2,873,282 (1959).
 [10] J.W. Huang, M. Shi, *J. Org. Chem.* 68 (2003) 6705–6709.
 [11] N. Kihara, N. Hara, T. Endo, *J. Org. Chem.* 58 (1993) 6198–6202.
 [12] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* 4 (2002) 2561–2563.
 [13] F.W. Li, C.G. Xia, L.W. Xu, W. Sun, G.X. Chen, *Chem. Commun.* (2003) 2042–2043.
 [14] W.J. Kruper, D.V. Dellar, *J. Org. Chem.* 60 (1995) 725–727.
 [15] R.L. Paddock, S.T. Nguyen, *J. Am. Chem. Soc.* 123 (2001) 11498–11499.
 [16] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* 44 (2003) 2931–2934.
 [17] X.B. Lu, H. Wang, R. He, *J. Mol. Catal. A: Chem.* 186 (2002) 33–42.
 [18] H.Z. Yang, Y.L. Gu, Y.Q. Deng, F. Shi, *Chem. Commun.* (2002) 274–275.
 [19] F.W. Li, L.F. Xiao, C.G. Xia, B. Hu, *Tetrahedron Lett.* 45 (2004) 8307–8310.
 [20] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* (2003) 896–897.
 [21] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, *Appl. Catal. A: Gen.* 219 (2001) 259–266.
 [22] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* 121 (1999) 4526–4527.
 [23] M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J. Mol. Catal. A: Chem.* 204/205 (2003) 245–252.
 [24] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* (1997) 1129–1130.
 [25] H. Yasuda, L.N. He, T. Sakakura, *J. Catal.* 209 (2002) 547–550.
 [26] M. Tu, R.J. Davis, *J. Catal.* 199 (2001) 85–91.
 [27] T. Nishikubo, A. Kameyama, J. Yamashita, M. Tomoi, W. Fukuda, *J. Polym. Sci., Part A: Polym. Chem.* 31 (1993) 939–947.
 [28] Y. Du, F. Cai, D.L. Kong, L.N. He, *Green Chem.* 7 (2005) 518–523.
 [29] Y. Du, J.Q. Wang, J.Y. Chen, F. Cai, J.S. Tian, D.L. Kong, L.N. He, *Tetrahedron Lett.* 47 (2006) 1271–1275.
 [30] H.S. Kim, J.J. Kim, H.N. Kwon, M.J. Chung, B.G. Lee, H.G. Jang, *J. Catal.* 205 (2002) 226–229.
 [31] L.F. Xiao, F.W. Li, C.G. Xia, *Appl. Catal. A: Gen.* 279 (2005) 125–129.
 [32] J.Q. Wang, D.L. Kong, J.Y. Chen, F. Cai, L.N. He, *J. Mol. Catal. A: Chem.* 249 (2006) 143–148.
 [33] H.B. Xie, H.F. Duan, S.H. Li, S.B. Zhang, *New J. Chem.* 29 (2005) 1199–1203.
 [34] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* 1664–1666 (2006).
 [35] R. Srivastava, D. Srinivas, P. Ratnasamy, *Appl. Catal. A: Gen.* 289 (2005) 128–134.
 [36] R. Srivastava, D. Srinivas, P. Ratnasamy, *J. Catal.* 233 (2005) 1–15.
 [37] C.H. McMullen, J.R. Nelson, B.C. Ream, J.A. Sims Jr., US Patent 4,314,945 (1982).
 [38] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* 5 (2003) 497–507.
 [39] E. Guibal, *Prog. Polym. Sci.* 30 (2005) 71–109.
 [40] J.H. Tong, Y. Zhang, Z. Li, C.G. Xia, *J. Mol. Catal. A: Chem.* 249 (2006) 47–52.
 [41] K.R. Reddy, K. Rajgopal, C.U. Maheswari, M.L. Kantam, *New J. Chem.* 30 (2006) 1549–1552.
 [42] G. Huang, C.C. Guo, S.S. Tang, *J. Mol. Catal. A: Chem.* 261 (2007) 125–130.
 [43] E. Loubaki, M. Ourevitch, S. Sicsic, *Eur. Polym. J.* 27 (1991) 311–317.
 [44] M. Fan, Chinese Patent CN 1752111A (2006).
 [45] S.H. Lim, S.M. Hudson, *Carbohydr. Res.* 339 (2004) 313–319.

- [46] V.A. Spinelli, M.C.M. Laranjeira, V.T. Fávere, *React. Func. Polym.* 61 (2004) 347–352.
- [47] G. Lang, H. Wendel, E. Konrad, US Patent 4,921,949 (1990).
- [48] H.B. Xie, S.B. Zhang, S.H. Li, *Green Chem.* 8 (2006) 630–633.
- [49] H.K. Reimschuessel, M.A. Kocur, US Patent 4,594,452 (1986).
- [50] J.L. Deavenport, B.I. Lopez, US Patent 5,463,127 (1995).
- [51] C.S. Yang, Z.S. Cai, J.T. Wang, Q. Xu, J.L. Yan, *J. Func. Polym.* 17 (2004) 649–652.
- [52] ^1H NMR (D_2O , 400 MHz): δ 2.33–2.34 (CH), 2.53–2.54 (CH_2), 2.56 (CH_3), 3.01–3.19 (CH_2), 3.2–3.43 (CH and CH_2), 4.31–4.32 (CH); ^{13}C { ^1H } NMR (D_2O , 100.6 MHz): δ 51.83, 54.27, 60.41, 62.65, 65.31, 69.19, 73.11, 74.91, 78.03, 102.35.
- [53] J.J.E. Hardy, S. Hubert, D.J. Macquarrie, A.J. Wilson, *Green Chem.* 6 (2004) 53–56.
- [54] C.C. Guo, G. Huang, X.B. Zhang, D.C. Guo, *Appl. Catal. A: Gen.* 247 (2003) 261–267.