

Sn-catalyzed synthesis of propylene carbonate from propylene glycol and CO₂ under supercritical conditions

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Abstract

Dibutyltin oxide or dibutyltin dimethoxide was first used as a remarkable selective catalyst for the synthesis of propylene carbonate from propylene glycol and carbon dioxide. The effects of the reaction parameters, such as reaction time, temperature and CO₂ pressure on the amount of propylene carbonate were also experimentally studied. Under the optimized conditions, the amount of propylene carbonate was nearly proportional to PG concentration. The use of *N,N*-dimethylformamide as a co-solvent in this study significantly enhanced the catalytic activity, and the ketals as dehydrating agents greatly improved the yield of PC, which can be limited by the equilibrium. A postulated mechanism for the dibutyltin oxide-catalyzed carboxylation of propylene glycol was also discussed.

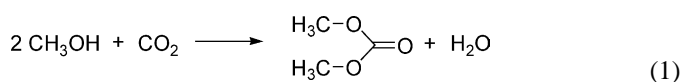
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Keywords: Supercritical carbon dioxide; Propylene glycol; Propylene carbonate; Tin compound; Ketal

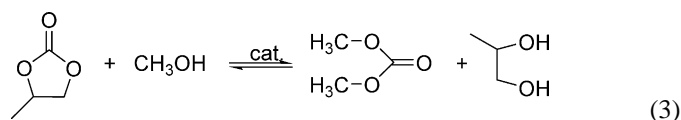
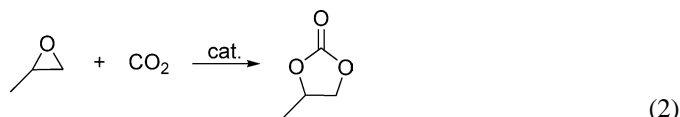
1. Introduction

The efficient transformation of carbon dioxide that is an abundant greenhouse gas and a cheap C₁ building block into useful chemicals is very attractive for synthetic chemists in view of resource utilization and pollution prevention [1–3]. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC) via the coupling of CO₂ with epoxides [4–10]. In this process, one carbon atom and two oxygen atoms can be incorporated in one step without forming any co-products with high atom efficiency. Moreover, these carbonates are valuable as precursors for polymeric materials, aprotic polar solvents, electrolytic elements of lithium secondary batteries and chemical ingredients for pharmaceutical/fine chemicals in many other biomedical applications [11,12]. Furthermore, a possible utilization of cyclic carbonates, such as PC and EC is the transesterification with methanol to form dimethyl carbonate (DMC) and the corresponding glycol. It is known that the

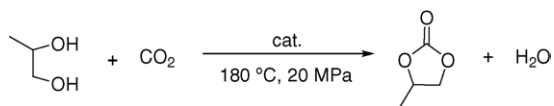
process of synthesizing DMC from methanol and PC is one of the industrial synthetic processes utilizing carbon dioxide as a raw material [13].



Although synthesis of DMC directly from carbon dioxide and methanol catalyzed by transition metals has also been developed (Eq. (1)) [14–18], the process has not been yet applied for industrial exploitation because of the low productivity, as resulted from catalyst deactivation and hydrolysis of DMC by co-produced water. Hence, the process for producing DMC via the transesterification of PC with methanol has drawn much attention from the standpoint of “green chemistry” [19–22].



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Scheme 1. Synthesis of propylene carbonate from propylene glycol and supercritical carbon dioxide.

The process is comprised of two steps: the cycloaddition of propylene oxide and carbon dioxide to give PC (Eq. (2)), and the transesterification of PC with methanol (Eq. (3)). In this process, propylene glycol (PG) is always a co-product with DMC. If PC can be synthesized from PG and CO₂ (Scheme 1), the process becomes more valuable since PG can be recycled. Overall, the reaction can be regarded as PC synthesis from PG and CO₂ according to Scheme 1 and Eq. (3). In this context, the synthesis of cyclic carbonates from carbon dioxide and glycols could be more promising. Recently, CeO₂–ZrO₂ has been developed to catalyze the synthesis of PC from PG and carbon dioxide in supercritical conditions [23,24]. In addition, Cu, Fe, Zn complexes have been used for EC manufacture from CO₂ and the dehydrated derivative ketal, which was formed from EG and cyclohexanone [25].

In the present paper, the Sn-compound like Bu₂SnO or Bu₂Sn(OMe)₂ was used to catalyze the formation of PC from PG and carbon dioxide under supercritical conditions. The use of DMF as a co-solvent in this study significantly promoted the catalytic activity. The effects of the reaction conditions, such as reaction time, temperature and CO₂ pressure have been carefully examined in the “PG + CO₂” reaction. Furthermore, a postulated mechanism is also discussed.

2. Experiment

2.1. Reagents

Propylene glycol was stored over anhydrous sodium sulfate for 2 days and distilled under reduced pressure. *N,N*-Dimethylformamide was stirred over CaH₂ overnight and distilled prior to use. 4-Methyl-2,2-pentamethylene-1,3-dioxolane (ketal **1**) and 2,2,4-trimethyl-1,3-dioxolane (ketal **2**) were prepared according to the published procedures [26,27]. Other reagents and solvents were of analytic grade and available commercially.

2.2. Representative procedure for the preparation of PC from PG and carbon dioxide

The reaction was carried out in a stainless-steel autoclave reactor with an inner volume of 25 ml. A typical procedure is as follows: In an autoclave equipped with a magnetic stirrer, Bu₂Sn(OMe)₂ or Bu₂SnO (5 mmol) was added to a solution of propylene glycol (7.3 ml, 100 mmol), dimethyl formamide (2 ml) and biphenyl (80 mg, as an internal standard for GC) under nitrogen atmosphere. And then CO₂ was introduced into the autoclave with an initial pressure of ca. 5.0 MPa at room temperature. The pressure was generally adjusted to 15 MPa at 180 °C. The mixture was stirred for 12 h, and the temperature

was kept constant during the reaction. At the end of the reaction, the autoclave was cooled to ambient temperature and then was further cooled to 0 °C in an ice-water bath. The excess of carbon dioxide was vented slowly. The products were detected by gas chromatograph equipped with a flame ionization detector and a capillary column (Agilent technologies 6890, HP-5. 0.25 mm i.d. × 30 m), and further determined by GC–MS (HP G1800A) by comparing retention times and fragmentation patterns with authentic samples.

3. Results and discussion

3.1. PC synthesis from PG and CO₂ catalyzed by tin compound

Dibutyltin oxide or dibutyltin dimethoxide catalyzed the reaction of propylene glycol with CO₂ at 180 °C, 20 MPa for 12 h to afford propylene carbonate (Scheme 1).

The results for PC synthesis from PG and supercritical CO₂ catalyzed by the Sn-compounds under various reaction conditions are summarized in Table 1. Without a catalyst, either in the presence of DMF or in the absence of DMF, the carboxylation of PG did not occur (Table 1, entries 4 and 5). While in the presence of catalytic amounts of dibutyltin oxide or dibutyltin dimethoxide (Table 1, entries 1 and 2), considerable turnover number (>30) of the product was obtained. As a result, the TON of catalytic production for Bu₂SnO or Bu₂Sn(OMe)₂ is much higher than that for the reported heterogeneous catalyst (CeO₂–ZrO₂), which the turnover number was calculated to be 4.4 [23]. In addition, the present PC synthesis is very selective. Indeed, PC is substantially the sole product as judged by gas chromatography. It should be noted that the catalytic activity of dibutyltin oxide was very close to that of dibutyltin dimethoxide (Table 1, entry 1 versus entry 2). It is noteworthy that dibutyltin oxide has advantages over dibutyltin dimethoxide in terms of stability in air, easy handling and low cost. As for DMF effect, the amount of PC produced (1.8 mmol) in the presence of DMF was about four times as large as that without DMF (0.45 mmol) (Table 1, entry 2 versus entry 3). Whereas DMF (2 ml) alone was used, no reaction occurred (Table 1, entry 5). Consequently, DMF as a co-solvent is essential to promote this reaction.

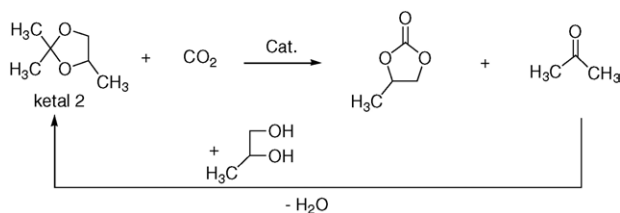
In terms of the productivity, the yield of PC is very low, and the maximum PG conversion was about 2% in this study, which is in accord with the published result [23]. The problem of this procedure is ascribed to the thermodynamic limitations. Accordingly, the removal of H₂O from the reaction system is essential to overcome this restriction. Thus, we first dehydrated PG to form dehydrated derivatives, such as ketal **1** and ketal **2** and then reacted the dehydrated derivative with carbon dioxide as illustrated in Scheme 2. The co-produced acetone can be easily converted to the ketal **2**. Overall, the reaction can be regarded as PC synthesis from PG and CO₂. In this way, there is no need to remove water from the reaction mixture for the PC synthesis.

It was reported that ketal **2** reacted with supercritical CO₂ in the presence of the catalyst to afford the cyclic carbonate with high TON [25]. In this study, the reaction of ketal **1** or ketal **2** alone with CO₂ without PG in the presence of the catalytic

Table 1

Sn-catalyzed synthesis of propylene carbonate from propylene glycol and supercritical CO₂^a

Entry	Cat.	Cat. (mmol%)	DMF (ml)	PC ^b (mmol)	TON ^c
1	Bu ₂ SnO	0.05	2	1.7	32
2	Bu ₂ Sn(OMe) ₂	0.05	2	1.9	36
3	Bu ₂ Sn(OMe) ₂	0.05	0	0.4	8
4	–	0	0	0	–
5	–	0	2	0	–
6 ^d	Bu ₂ SnO	1	2	0	0
7 ^e	Bu ₂ SnO	1	2	0	0
8 ^f	Bu ₂ SnO	1	2	2.1	42
9 ^g	Bu ₂ SnO	1	2	1.1	22
10 ^h	Bu ₂ Sn(OMe) ₂	0.05	2	3.4	68
11	Ti(OPr) ₄	0.05	2	1.2	24

^a Reaction conditions: PG (100 mmol), biphenyl (80 mg) as an internal standard for GC, total pressure (15 MPa), 180 °C, 12 h.^b Determined by GC using an internal standard technique.^c TON, turnover number: moles of PC per mole of catalyst.^d 4-Methyl-2,2-pentamethylene-1,3-dioxolane (ketal **1**, 5 mmol) alone without PG.^e 2,2,4-Trimethyl-1,3-dioxolane (ketal **2**, 5 mmol), without PG.^f PG (5 mmol), ketal **2**, 5 mmol and DMF (2 ml).^g PG (5 mmol) without ketal.^h In the presence of 5 mmol of ketal **1**.

Scheme 2.

amount of Bu₂SnO did not take place (entries 6 and 7, Table 1). In contrast, a significant amount of PC was produced in the presence of 5 mmol of PG under the same reaction conditions (entry 8, Table 1). Hence, the presence of PG is inevitable for PC formation (Table 1, entry 7 versus entry 8). Furthermore, the requirement of PG is clearly shown in Fig. 1 (vide infra). This indicates that PC is, in fact, formed from PG and CO₂ according to Scheme 2. The ketal is probably working as a chemical dehydrating agent. As easily seen, the catalytic activity of Bu₂SnO or Bu₂Sn(OMe)₂ in the presence of ketal **2** or ketal **1** was about two times greater than that in the absence of any dehydrating agent like ketal **2** (Table 1, entries 8 versus entry 9, and 2 versus 10). Thus, the ketals as dehydrating agents greatly improved the yield of PC, which can be limited by the equilibrium.

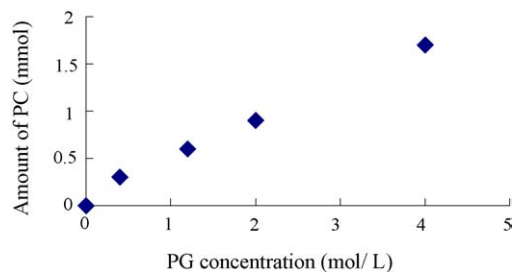


Fig. 1. Plot of PC amount as a function of PG concentration for the reaction of PG and CO₂ catalyzed by Bu₂SnO. Reaction conditions: DMF (2 ml), Bu₂SnO (0.25 mmol%), 200 °C, 15 MPa, 12 h.

It worth mentioning that titanium *n*-butoxide, a less toxic reagent, also exhibited catalytic activity for the reaction of PG and CO₂ to form PC under the same reaction conditions (Table 1, entry 11).

3.2. Effects of the reaction parameters on PC formation

Shown in Fig. 1 is the effect of the concentration of PG on the amount of PC formed. The reactions were performed in the presence of Bu₂SnO (0.25 mmol) at 200 °C and 15 MPa. As illustrated in Fig. 1, the amount of PC is nearly proportional to PG concentration, which is presumably assignable to the intrinsic property of the equilibrium reaction (Scheme 1). A similar relation between the DMC yield and the methanol concentration was observed for DMC synthesis from acetal and CO₂ [18]. Notably, the selectivity of PC (up to 99.9%) is independent of PG concentration.

Reaction time dependence on the amount of PC is given in Fig. 2. The results indicate that the amount of PC increases gradually with increasing reaction time. As shown in Fig. 2, the reaction proceeded rapidly within first 12 h, whereas further increase in the reaction time caused a slight decrease in the yield of PC,

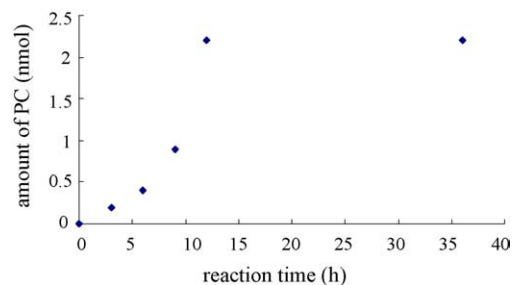


Fig. 2. Reaction time—the amount of PC profile for the reaction of “PG + CO₂” by Bu₂Sn(OMe)₂. Reaction conditions: PG (100 mmol), Bu₂Sn(OMe)₂ (0.05 mmol%), 20 MPa, 180 °C.

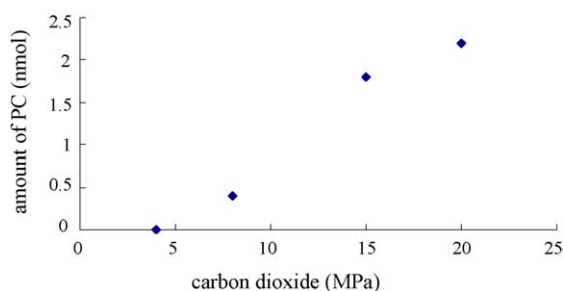
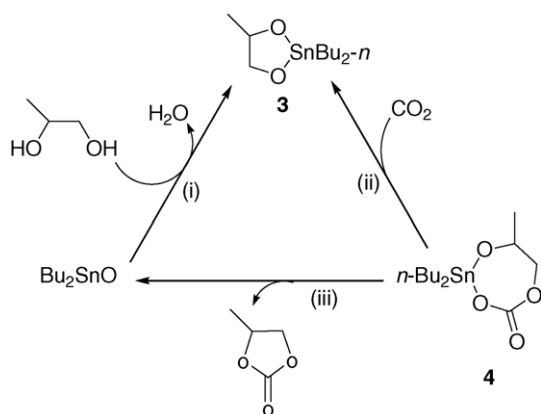


Fig. 3. The amount of PC vs. CO₂ pressure for the reaction of PG with CO₂ mediated by Bu₂Sn(OMe)₂. Reaction conditions: PG (100 mmol), Bu₂Sn(OMe)₂ (0.05 mmol%), 180 °C, 12 h.



Scheme 3. A postulated mechanism for PC synthesis from PG and CO₂ catalyzed by Bu₂SnO.

as a consequence of more by-products formed with prolonging reaction time and the reversibility of the reaction. Obviously, 12 h was the optimal reaction time for the “PG + CO₂” reaction.

The effect of CO₂ pressure on PC synthesis was also investigated (Fig. 3). The amount of PC is nearly proportional to the reaction pressure in the range of 4–20 MPa. A similar relation between the DMC yield and the CO₂ pressure was reported in previous work [18]. As shown in Fig. 3, a higher CO₂ pressure is favorable for achieving higher activity, which could probably be attributable to that higher concentration of CO₂ can shift the equilibrium to the right or enhance insertion of CO₂ into the metal–oxygen bond as depicted in a possible mechanism (Scheme 3). This demonstrates that the supercritical conditions have the preferential effect for promoting the reactivity of CO₂.

It is found that the amount of PC is affected by reaction temperature under supercritical conditions. As listed in Table 2, the

Table 2
Reaction temperature dependence on the amount of PC for Bu₂Sn(OMe)₂ in the reaction of “PG + CO₂”

Entry	Temperature (°C)	Pressure (MPa)	PC (mmol)	TON
1	100	20	0	–
2	150	20	0.4	8
3	180	20	2.2	44
4	240	20	0.2	4

Reaction conditions: PG (100 mmol), Bu₂Sn(OMe)₂ (0.05 mmol%), 20 MPa, 12 h.

amount of PC increases as reaction temperature increases up to 180 °C (entries 1–3), whereas further increase in the temperature causes sharp decrease in the yield (entry 4, Table 2), possibly due to the formation of side-products, such as dipropylene glycol, and PC decomposition. In contrast, PC was not detected by GC at all when reaction temperature was lower than 100 °C (entry 1, Table 2). Conclusively, 180 °C could be the suitable reaction temperature.

3.3. A possible mechanism for the present Sn-catalyzed carboxylation of PG

R₂Sn(OMe)₂ and Bu₂SnO are reported as active catalysts for various reactions, such as DMC synthesis [14–17], polycarbonate synthesis from carbon dioxide and epoxide [28], stereoselective ring-opening polymerization of β-lactones [29]. However, Bu₂Sn(OMe)₂ or Bu₂SnO has never been reported that could be used as a catalyst for preparing of PC from PG and CO₂. In present paper, the organotin compounds are first used as catalysts for the synthesis of PC from PG and CO₂ under supercritical conditions. The catalytic activity of Bu₂Sn(OMe)₂ is very close to that of Bu₂SnO in this study as listed in Table 1 (entry 1 versus entry 2). Therefore, a plausible catalytic cycle for the present Bu₂SnO-catalyzed carboxylation of the 1,2-diol like PG with CO₂ has been proposed as illustrated in Scheme 3. This proposal is closely related to that of Bu₂SnO-catalyzed carboxylation of 1,2-aminoalcohols with CO₂ [30]. It involves three steps: (i) the reaction of dibutyltin oxide and PG to give 2,2-dibutyl-1,3,2-dioxastannolan **3** [31]; (ii) since Sn–O bond is known to be susceptible to CO₂ insertion [32], a cyclic tin carbonate **4** may be formed through the insertion of CO₂ to **3**; (iii) subsequent intramolecular nucleophilic attack of alkoxy group on a carbonyl carbon atom may cause the elimination of propylene carbonate regenerating the dibutyltin oxide [31]. In addition, 2,2-dibutyl-1,3,2-dioxastannolan **3** is also derived from Bu₂Sn(OMe)₂ and propylene glycol by elimination of methanol [33]. It is possible that Bu₂Sn(OMe)₂ which acts as an active catalyst for synthesizing PC from PG and CO₂ may pass through the same catalytic cycle. Indeed, Bu₂Sn(OMe)₂ displayed comparable activity with Bu₂SnO, as rationalized on the basis of the proposed mechanism in Scheme 3.

4. Conclusions

Propylene carbonate was synthesized via the reaction of propylene glycol with CO₂ catalyzed by Bu₂SnO or Bu₂Sn(OMe)₂ with a remarkable selectivity. No by-product was formed at all under the optimum reaction conditions. Bu₂SnO exhibited comparable catalytic activity with Bu₂Sn(OMe)₂ in this study. Under the optimized conditions, the amount of propylene carbonate was nearly proportional to PG concentration. The reaction was enhanced by DMF as a co-solvent, and the turnover number of the catalytic production was improved by the ketal as a dehydrating agent. In addition, titanium *n*-butoxide as a less toxic reagent also displayed catalytic activity for PC synthesis from PG and CO₂.

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References

- [1] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, R.C. Stair, B.R. Stults, W. Tumas, *Chem. Rev.* 101 (2001) 953.
- [2] P.T. Anastas, *Green Chem.* 5 (2003) G29.
- [3] P.T. Anastas, R.L. Lankey, *Green Chem.* 2 (2000) 289.
- [4] D.J. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* 153 (1996) 155 (and references therein).
- [5] H. Yasuda, L.N. He, T. Sakadura, C. Hu, *J. Catal.* 233 (2005) 119.
- [6] Y. Du, F. Cai, D.-L. Kong, L.-N. He, *Green Chem.* 7 (2005) 518.
- [7] M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *Appl. Catal. A: Gen.* 255 (2003) 5.
- [8] M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J. Mol. Catal. A: Chem.* 204 (2003) 245.
- [9] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* 896 (2003).
- [10] R.L. Paddock, S.T. Nguyen, *Chem. Commun.* 1622 (2004).
- [11] K. Biggadike, R.M. Angell, C.M. Burgess, R.M. Farrel, A.P. Hancock, A.J. Harker, A.J. Irving, W.R. Irving, C. Ioannou, P.A. Procopiou, R.E. Shaw, Y.E. Solanke, O.M.P. Singh, M.A. Snowden, R. Stubbs, S. Walton, H.E. Weston, *J. Med. Chem.* 43 (2000) 19.
- [12] A.-A.G. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [13] 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.
- [14] J. Kizlink, I. Pastucha, *Collect Czech Chem. Commun.* 60 (1995) 687.
- [15] J. Kizlink, I. Pastucha, *Collect Czech Chem. Commun.* 59 (1994) 2116.
- [16] J. Kizlink, *Collect Czech Chem. Commun.* 58 (1993) 1399.
- [17] N. Yamazaki, S. Nakahama, F. Higashi, *Rep. Asahi Glass Found. Ind. Technol.* 33 (1978) 31.
- [18] J.-C. Choi, L.-N. He, H. Yasuda, T. Sakakura, *Green Chem.* 4 (2002) 230 (and references therein).
- [19] D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A* 221 (2001) 241.
- [20] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
- [21] M. Aresta, E. Quaranta, *CHEMTECH* (1997) 32.
- [22] D. Gillerman, B.M. Trost, *Science* 254 (1991) 1471.
- [23] K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kuni-mori, *Green Chem.* 6 (2004) 206.
- [24] K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kuni-mori, *Catal. Lett.* 95 (2004) 45.
- [25] M. Aresta, A. Dibenedetto, C. Dileo, I. Tommasi, E. Amodio, *J. Supercrit. Fluids* 25 (2003) 177.
- [26] A.D. Ronald, E.L. Eliel, J.R. Edman, B.C. Mckusick, *Org. Synth. Coll. Vol.5* (1973) 303.
- [27] F.A.J. Meskens, *Synth.* (1981) 501.
- [28] L. Vogdanis, W. Heitz, *Makromol. Chem., Rapid Commun.* 7 (1986) 543.
- [29] J.E. Kemnitzer, S.P. McCarthy, R.A. Gross, *Macromolecules* 26 (1993) 6143.
- [30] H.E. Ramsden, C.K. Banks, *US Patent* 2,789,994 (1957).
- [31] K.-I. Tominaga, Y. Sasaka, *Synlett.* (2002) 307.
- [32] J. Choi, T. Sakakura, T. Sako, *J. Am. Chem. Soc.* 121 (1999) 3793.
- [33] A. Shanzer, J. Libman, H. Gottlieb, F. Frolow, *J. Am. Chem. Soc.* 104 (1982) 4220.