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Lipase-mediated synthesis of six-membered cyclic carbonates from trimethylolpropane and dialkyl carbonates: Influence of medium engineering on reaction selectivity

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ABSTRACT

Six-membered cyclic carbonates are potential monomers for aliphatic polycarbonates and polyurethanes in a process without using toxic phosgene and isocyanate. Lipase catalyzed transesterification of the polyol, trimethylolpropane (TMP) with dimethyl carbonate (DMC) or diethyl carbonate (DEC) followed by thermal cyclization was used for synthesis of six-membered cyclic carbonates with pendant hydroxyl and alkoxycarbonyloxyl groups. Immobilized lipase B from *Candida antarctica* (Novozym®435) was used as the catalyst. Mixture of a hydrophilic solvent such as THF for high solubility of TMP, and a hydrophobic solvent such as toluene, were selected as the best solvent system for achieving high substrate conversion and selectivity. A relationship between polyol conversion and solvent hydrophobicity (log *P*) and solvent type, respectively, was established. THF:toluene system at a ratio of 0.5:1.0 (v/v) provided high degree of TMP conversion to product with high proportion of cyclic carbonates (>80%). The cyclic carbonate with pendant hydroxyl group was obtained with almost 85% selectivity at TMP conversion of 68.6% using 10% (w/w) Novozym®435 at TMP:DMC ratio of 1:1. However, at TMP:DMC ratio of 1:5 and the same biocatalyst concentration, the TMP conversion was 100% with 72% selectivity for the cyclic carbonate with pendant alkoxycarbonyloxyl group. The product formed was without or with less content of linear carbonates, bis and tris(methoxycarbonyloxy)-TMP, as compared to that in a solvent-free system. The reactivity of DEC was lower than that of DMC. The reaction pathway leading to the formation of cyclic carbonate in this process comprised enzymatic carbonation of TMP with alkylcarbonates and thermal cyclization of linear carbonates. The process affords high degree of conversion of polyol to cyclic carbonates and provides a potentially attractive synthetic route for monomers of polycarbonates and polyurethanes.

1. Introduction

Cyclic carbonates have attracted attention in recent years to provide an alternative route for the production of aliphatic polycarbonates and polyurethanes by ring-opening polymerization [1–6]. These aliphatic polymers, besides having traditional applications in engineering, optical devices, seatings, seals, coatings and high performance adhesives, are expected to find applications in the field of biomedicine because of their biocompatibility and low toxicity [7–10]. Furthermore, they are considered to be environmentally benign due to their promising features of biodegradability and recyclability [11,12]. The process for their manufacture however involves toxic chemicals.

Aliphatic polycarbonates are currently produced industrially by reacting an alkanediol with phosgene, triphosgene or dialkylcarbonates [6]. Polyurethanes are produced using polyols, such as alkanediols and glycerol, and isocyanate, which is derived from the reaction between an amine and phosgene [13,14]. Since phosgene and low-molecular weight isocyanates have disadvantageous toxicological profiles, attempts have been made to develop routes to make polyurethanes from other sources however none of these have yet been commercially established [14]. Recent studies have reported on the syntheses of five- and six-membered cyclic carbonates by different procedures, including addition of carbon dioxide to epoxides using metal containing catalysts under pressure [1–4,15], and by transesterification of polyols with dialkylcarbonate using metal- [16], or enzymatic (lipase) catalysis [17,18]. Six-membered cyclic carbonate is the preferred monomer for the ring-opening polymerization process, since in contrast to the five-membered monomer it is thermodynamically less stable than the ring-opened polymer, and thus retains CO_2 during the polymerization reaction [16,19,20].

In an earlier report, enzymatic synthesis of the six-membered cyclic trimethylene carbonate from 1,3-diol and dimethyl or diethyl

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Table 1
Summary of the reactions between TMP and dialkylcarbonates (DMC or DEC) catalyzed by Novozym®435 under different conditions.

Run	N435 (%, w/w)	Solvent	Ratio of TMP:DMC	Reaction temp. (°C)	Reaction time (h)	TMP conversion (%)	Products (%)					Cyclic carbonates (**4**+**6**)
							3	**4**	**5**	**6**	**7**	
1	50	ACN:toluene (0.5:1)	1:1.5	60	93	47.7	10.3	89.7	0	0	0	89.7
2	50	t-BuOH:*n*-hexane (0.5:1)	1:1.5	60	93	68.4	28.5	33.2	20.2	12.3	5.8	45.5
3	50	THF (1.5)	1:1.5	60	72	64.5	50.9	30.2	11.6	7.3	0	37.5
4	20	THF:toluene (1:0.5)	1:1.5	60	72	85.6	10.4	73.0	3.4	13.2	0	86.2
5	20	THF:toluene (0.5:1)	1:1.5	60	72	95.7	16.9	41.3	0	41.8	0	83.1
6	10	THF:toluene (0.5:1)	1:1	60	115	68.6	10.8	84.7	0	4.6	0	89.2
7	10	THF:toluene (0.5:1)	1:2	60	115	96.3	9.1	53.5	6.4	31.0	0	84.5
8	10	THF:toluene (0.5:1)	1:5	60	115	100	0.2	14.0	4.0	72.1	9.7	86.1
9	5	THF:toluene (0.5:1)	1:1	60	72	20.3	1.4	98.6	0	0	0	98.6
10	10	THF:toluene (0.5:1)	1:2	50	121	93.5	13.0	46.2	9.3	30.8	0.7	76.9
11	10	THF:toluene (0.5:1)	1:1 (DEC)	60	115	40.0	33.2	62.0	4.8	0	0	62.0
12	10	THF:toluene (0.5:1)	1:2 (DEC)	60	115	86.7	26.1	47.9	8.0	18.0	0	65.9
13	10	THF:toluene (0.5:1)	1:5 (DEC)	60	115	99.4	7.3	39.2	6.5	47.0	0	86.2

carbonate has been achieved in a solvent system of acetonitrile and toluene (4:1, v/v) using very high concentration (600–900%, w/w of the diol) of the immobilized *Candida antarctica* lipase B, Novozym®435, however with moderate yield (53%) and low productivity [18]. Synthesis of the cyclic carbonates with functional groups from poly-functional alcohols such as trimethylolpropane (TMP) and pentaerythritol (PE) have required more complicated reaction steps and harsh conditions such as thermal disproportionation of the transesterification products followed by distillative depolymerization both at >200 °C under reduced pressure, resulting in low yields (30%) [21].

We have recently investigated the synthesis of six-membered cyclic carbonates with functional groups using lipase-mediated reaction between TMP and dialkylcarbonate under solvent free conditions [22]. The product formed was a mixture of cyclic and linear (mono-, di- and tri-) carbonates, the proportions of which depended on the reaction conditions used. Subjecting the product mixture to thermal disproportionation at 60–80 °C without the biocatalyst converted the linear carbonates to the cyclic ones. The present study investigates the influence of different solvent types and their hydrophobicity, and other reaction parameters on the reaction efficiency and selectivity of cyclic carbonate production during the reaction between the polyol and dialkylcarbonate catalyzed by Novozym®435.

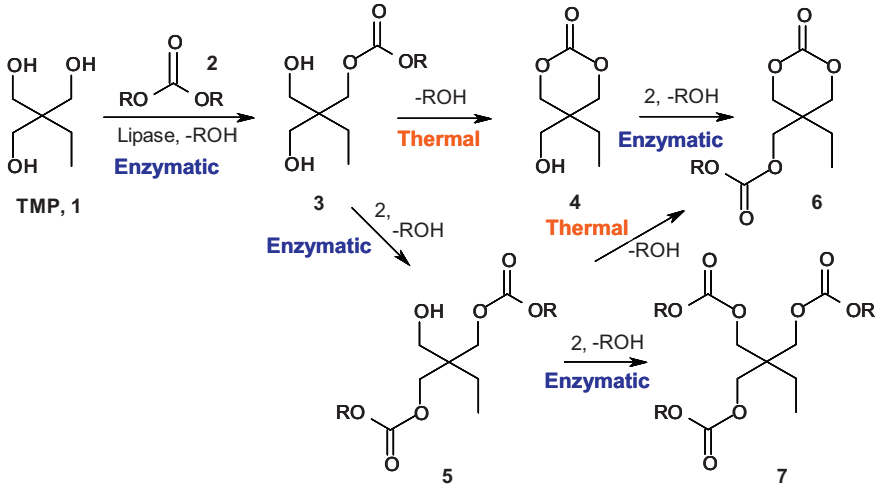
2. Experimental

2.1. Materials

Trimethylolpropane (TMP) was a product of Perstorp AB (Sweden). Immobilized lipase B from *C. antarctica* (CALB, Novozym®435) was kindly provided by Novozymes A/S (Bagsvaerd, Denmark). Dimethyl carbonate (97%), diethyl carbonate (97%), and molecular sieves (4 Å beads, 8–12 mesh) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Tetrahydrofuran (THF), toluene, n-hexane, *tert*-butanol and acetonitrile of HPLC grade (<0.1% water) were purchased from MERCK (Germany). All chemicals were used without further treatment.

2.2. Reaction procedures

The reactions were performed in 5 mL capped vials on a thermomixer (MKR 13, HLC Biotech, Germany). Typically, 50 mg (0.37 mM) TMP was dissolved in 1.5 mL solvent by mild shaking at 700 rpm at the defined reaction temperature, prior to addition of 0.2 g molecular sieves and certain amounts of dialkylcarbonate and Novozym®435 (N435) to start the reaction. The amount of biocatalyst (w/w) was calculated based on the TMP amount used in the reaction. Small aliquots were withdrawn from the reaction media at



Scheme 1. Possible reaction pathway of synthesis of carbonates from TMP and DMC or DEC in solvent system by lipase-catalyzed and thermal reactions (R = methyl from DMC or ethyl from DEC).

different time intervals for analysis of the polyol and the products. Effects of solvent type, biocatalyst amount, molar ratio of substrates and reaction temperature on the reaction were investigated.

2.3. Quantitative analyses and elucidation using GC, GC–MS and NMR

Quantitative analyses were performed by gas chromatography (GC, 430-GC, Varian, Palo Alto, USA) equipped with FactorFour Capillary column, VF-1 ms (Varian, 15 M × 0.25 mm) and a flame ionization detector. The initial column oven temperature was increased from 50 to 250 °C at a rate of 20 °C/min. The samples diluted at concentration of 0.1–0.5 mg/mL in acetonitrile were injected in a split injection mode of 10% at 275 °C. The degree of TMP conversion and concentration of products formed were calculated from the peak areas on the chromatograms. The identity of the products was confirmed by measuring the molecular masses of products by GC–MS (Varian 431-GC, Varian 210-MS) equipped with FactorFour Capillary column, VF-5 ms (Varian, 30 M × 0.25 mm), and structure elucidation by ^{1}H and ^{13}C NMR using 400 MHz NMR (Bruker, UltraShield Plus 400, Germany) as described earlier [22].

3. Results and discussion

3.1. Selection of solvent system for lipase-catalyzed reaction between TMP and DMC

Although the most desirable strategy from a green chemistry perspective is to carry out the reaction in a solvent free medium, different solvents can influence both the selectivity and yield of the reaction [23,24]. It is also known that the stability of an enzyme is usually higher in a more hydrophophic solvent, i.e. with higher log *P* (logarithm of partition coefficient between water and octanol). In contrast, solvents with lower log *P* value such as pyridine, dimethylformamide (DMF) and acetonitrile can solubilise many polar molecules like TMP, but often inactivate the enzyme by their ability to remove water of hydration, and promote accumulation of water in the reaction media [25–28].

To investigate the effect of the solvents, THF, *t*-butanol and acetonitrile were chosen as hydrophilic solvents, and toluene and n-hexane as the hydrophobic ones. These solvents were used individually and in mixture systems for reactions at 60 °C. In pure solvents, the highest TMP conversion of 60% was obtained in THF after 72 h reaction using 40% (w/w) N435, while in *t*-butanol and acetonitrile the highest conversion values obtained were 44% and 12%, respectively, after 92 h of reaction with the same concentration of the biocatalyst. TMP was generally not soluble in the hydrophobic solvents, n-hexane and toluene, and there was practically no reaction with DMC in these solvents. The conversion of TMP was significantly increased by using mixtures of hydrophilic and hydrophobic solvents (Fig. 1). THF is freely miscible with toluene, and varying the ratio of these solvents showed that the reactivity was improved with decreasing THF:toluene ratio (Fig. 1A). At THF:toluene ratio of 0.5:1, conversion of 94% was achieved already after 24 h using 20% (w/w) biocatalyst, while at a ratio of 1.0:0.5 similar degree of conversion was reached after 72 h of reaction. Other solvent mixtures, *t*-butanol/*n*-hexane and acetonitrile/toluene, gave significantly lower conversions (Fig. 1B and C).

Fig. 2 shows TMP conversion obtained after 92 h of reactions with respect to the log *P* of different solvent mixture systems. The log *P* of the solvent mixtures was calculated from the log *P* values of the component solvents and the ratio of the solvents used. It is clear from the figure that for each solvent mixture the TMP conversion was increased with increase in log *P* but the extent of conversion in the THF/toluene system was significantly higher than that in the other solvent mixtures under conditions of similar log *P*. An earlier study by Tasaki et al. reported the synthesis of cyclic trimethylene carbonate in a solvent system of acetonitrile:toluene (4:1, v/v), which has a log *P* value of 0.236 that is in the lower end of the curve for the solvent mixture in Fig. 2. This was expected to give low conversion yield, which was actually 53% in the report [18]. However, besides log *P* even other features of the solvent systems affecting the reactants and products (such as solubility, miscibility, and stabilization) and the biocatalyst (e.g. stability and activity) influence the reaction rate and yield.

Besides the substrate conversion, the product profile for the different systems was also determined. Table 1 shows the degree of conversion and ratio of different products formed in some selected

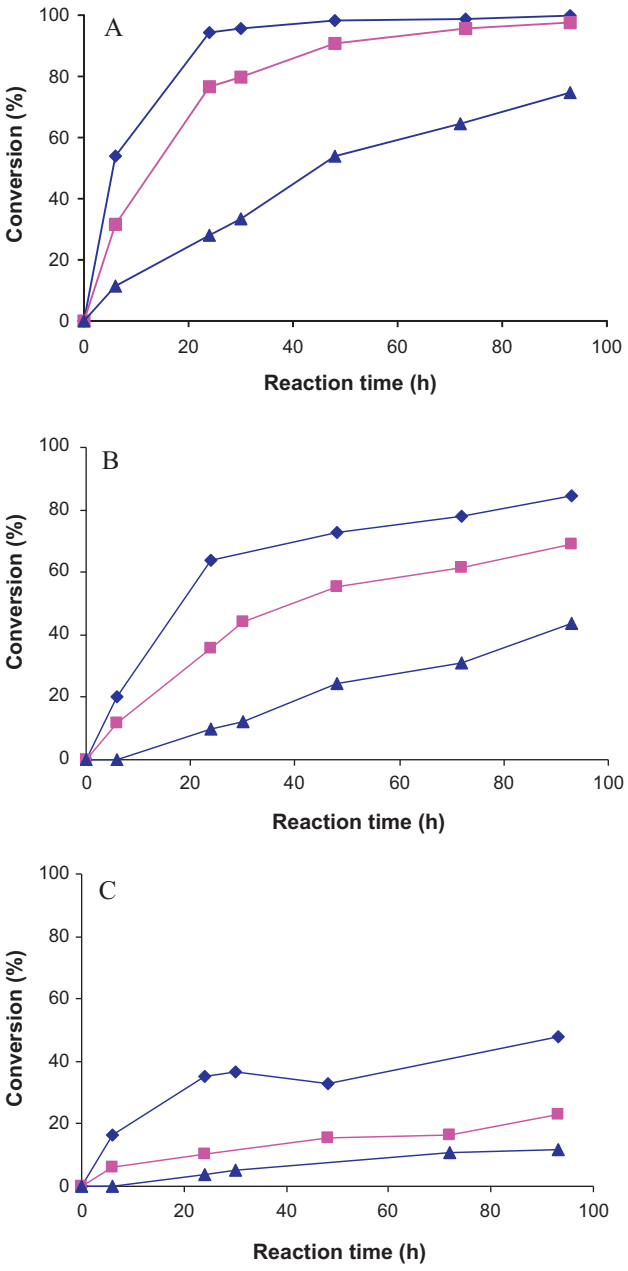


Fig. 1. Selection of solvent system for synthesis of cyclic carbonates by lipase mediated reaction between TMP and DMC at a ratio of 1:1.5, 60 °C. Profiles of TMP conversion (A) using 20% (w/w) N435 in THF:toluene system, at ratios of 0.5:1.0 (♦), 1.0:0.5 (■), and 1.5:0 (▲); (B) using 50% (w/w) N435 in *t*-butanol:*n*-hexane system at ratios of 0.15:1.35 (♦), 0.5:1.0 (■) and 1.5:0 (▲); (C) using 50% (w/w) N435 in acetonitrile:toluene at ratios of 0.5:1.0 (♦), 1.0:0.5 (■) and 1.5:0 (▲).

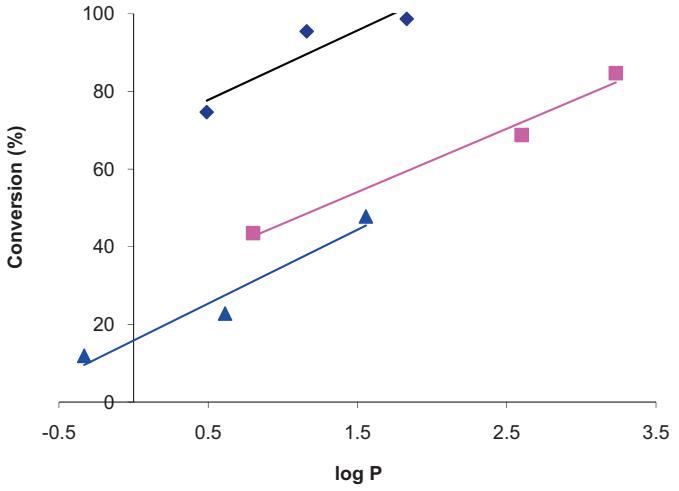


Fig. 2. Relationship between TMP conversion (at 92 h) and hydrophobicity (log *P*) of THF:toluene system (♦), *t*-butanol:*n*-hexane system (■) and acetonitrile:toluene (▲). Data obtained in Fig. 1 is used.

systems. In majority of the reactions (except in *t*-butanol:*n*-hexane and THF systems, Runs 2 and 3), cyclic carbonates of TMP, product **4** (with pendant hydroxyl group) and/or product **6** (with pendant methoxycarbonyloxyl group) were the predominant products with either none or low proportions of the linear carbonate derivatives of TMP (mono-(**3**), bis (**5**) and tris(methoxycarbonyloxy) (**7**)-TMP) (Scheme 1). In the acetonitrile:toluene system, nearly 90% of the product formed was 4 but the TMP conversion was as low as 48% (w/w) using 50% (w/w) N435 (Run 1). The system of *t*-butanol and hexane gave low product selectivity besides incomplete conversion (Run 2). THF:toluene system (Runs 4–10) provided high yields (except at equimolar ratio of TMP:DMC) as well as high proportion of cyclic carbonate products **4** and **6** (>80%). Based on these observations, mixture of THF:toluene at a ratio of 0.5:1 was selected as the best solvent system, and employed for further optimization of the processes.

3.2. Analysing the influence of temperature on cyclic carbonate formation

Reducing the reaction temperature from 60 °C to 50 °C reduced both the reaction rate as well as the proportion of cyclic carbonates formed (for comparison see Runs 7 and 10 in Table 1). This is in line with our earlier observations in the solvent free system, which indicated that cyclization of the linear carbonate, formed by lipase catalysis was promoted at higher temperature [22]. Since THF has a boiling point of 66 °C and N435 is not very stable above 60 °C, higher temperatures were not investigated in the present study.

In order to distinguish between the enzymatic and temperature effects, the reaction mixture obtained after a certain time of biocatalyst treatment was further processed with or without the biocatalyst. For this, 50 mg (0.37 mM) TMP was reacted with 75 mg (0.83 mM) DMC in THF:toluene (0.5:1.0 mL) using 5 mg N435 and 0.2 g molecular sieves at 60 °C for 22 h (Fig. 3A). Subsequently, processing of one part of the reaction mixture was continued under the same conditions, while the other part was centrifuged to remove

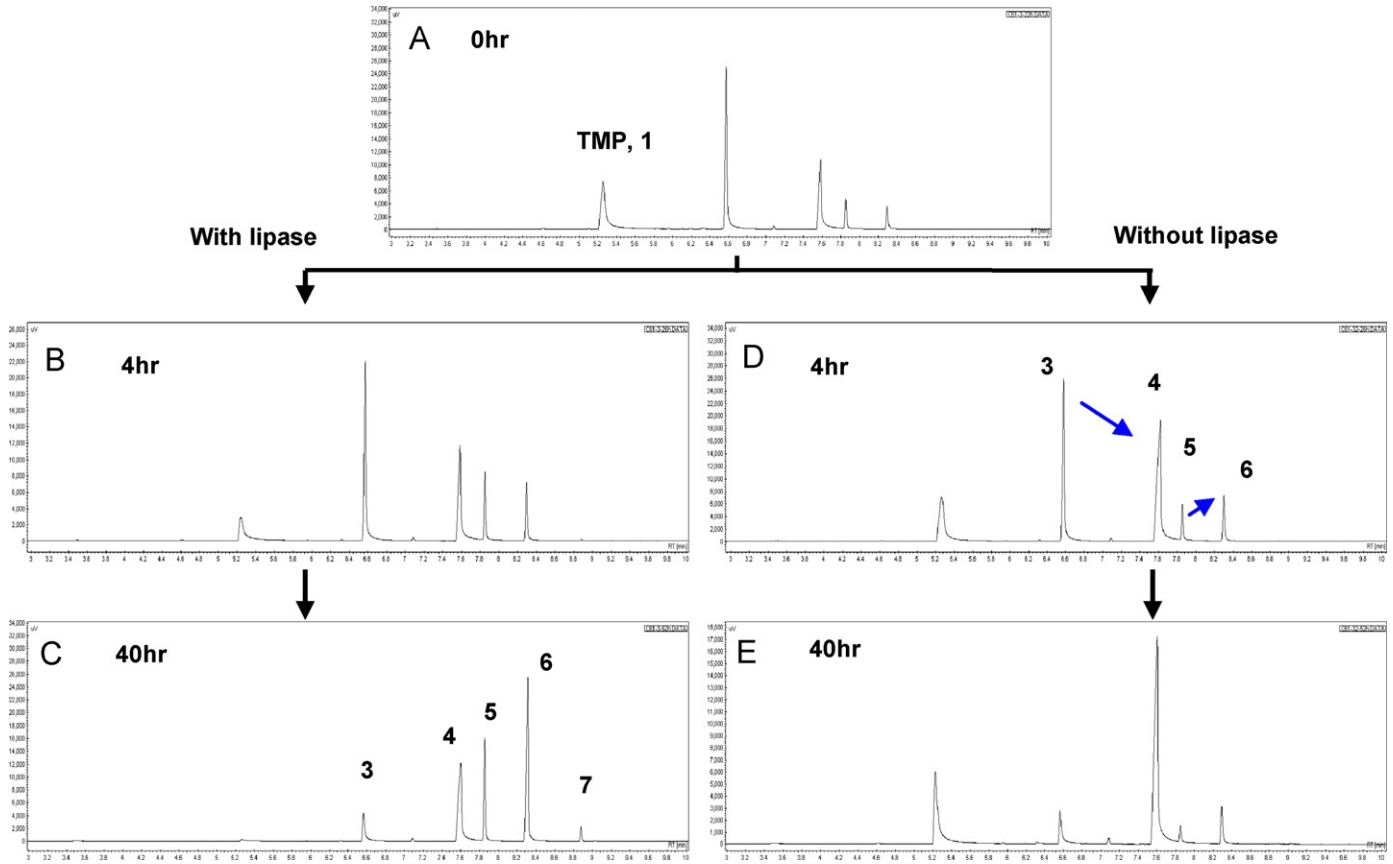


Fig. 3. Gas chromatograms of reaction products prepared by N435-catalyzed reaction between TMP and DMC, and thermal reaction. Peaks were assigned by GC–MS and ^{1}H NMR in previous report [22]. Peaks 1, 3, 4, 5, 6, and 7 indicate the structures shown in Scheme 1. Reaction solution A, prepared by N435-catalyzed reaction at 60 °C for 22 h, was subjected to further reaction under initial conditions and analysed after 4 h (B) and 40 h (C). Solution A was incubated at 60 °C after removal of N435 and analysed after 4 h (D) and 40 h (E).

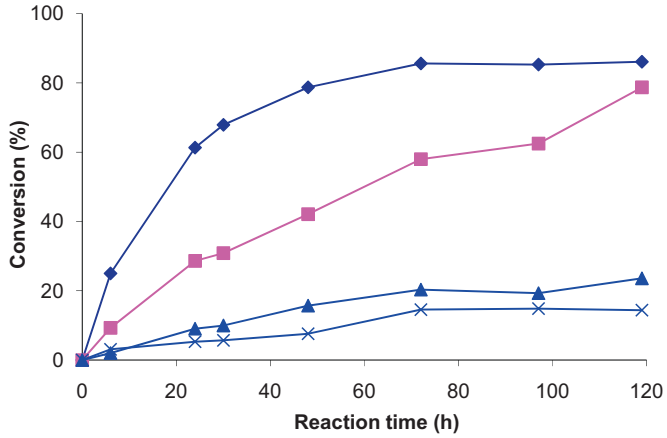


Fig. 4. Effect of the amount of Novozym®435 on synthesis of cyclic carbonates at TMP:DMC ratio of 1:1 (0.37 mM) at 60 °C in THF:toluene (0.5:1.0) system. N435 was used at concentrations of 2.5% (x), 5% (▲),10% (■), and 20% (♦) (w/w), respectively.

solids including the immobilized lipase preparation, and then supplemented with 0.2 g molecular sieves prior to incubation at 60 °C. In the reaction with the biocatalyst, the remaining TMP was further converted to different products (Fig. 3B and C). On the other hand, the TMP level remained unchanged in the reaction without the biocatalyst, and product **3** was decreased with corresponding increase in the cyclic carbonate product **4**, and product **5** was decreased with increase in **6** (Fig. 3D and E). Further conversion of **4** to **6** did not take place. Therefore the cyclizations from **3** to **4**, and from **5** to **6** seem to be caused by thermal reaction at 60 °C. This would also imply that in the sample containing the lipase, TMP is sequentially converted to **3**, **5** and **7**, while **4** is converted to **6** (Fig. 3B and C, Scheme 1). This indicates that only dialkylcarbonate served as the acyl-donor for the lipase active site, while mono- and di-carbonated TMP (**3**, **5**), and cyclic carbonate (**4**) were acyl-acceptors in the lipase catalyzed reaction. The reaction conditions providing higher rate of thermal cyclization led to a higher proportion of the desired cyclic carbonate products.

3.3. *Effect of biocatalyst concentration and TMP–DMC ratio in THF/toluene system*

The amount of biocatalyst used is one of the important parameters for determining reaction yield, selectivity of products and process cost. N435 was used at 2.5, 5, 10, and 20% (w/w) of TMP in THF:toluene (0.5:1.0) system at 60 °C. As shown in Fig. 4, the reactions employing higher biocatalyst amounts (10 and 20%, w/w) showed increasing TMP conversion with time, reaching 78% with 10% (w/w) N435 after 120 h of reaction, and 86% with 20% (w/w) biocatalyst after 72 h. The product yield per gram of biocatalyst was however higher, and showed higher proportion (85%) of product **4** with 10% (w/w) N435. The reaction yields achieved are also much higher with significantly lower biocatalyst concentration than those reported earlier for the six-membered cyclic trimethylene carbonate (1,3-dioxane-2-one) monomer [18] and five membered cyclic glycerol carbonate [17].

The ratio of two reactants also influenced the reaction and proportion of products as shown in Fig. 5. At TMP:DMC ratios of 1:5, 1:2 and 1:1, TMP conversion reached 100%, 96.3% and 68.6%, respectively, after 115 h of reaction (Fig. 5A). At TMP:DEC of 1:5, the conversion had reached 95% already at 48 h. The product proportions were very different with reaction time for the different substrate ratios. For the TMP:DMC ratio of 1:1, the proportion of the cyclic carbonate **4** increased with time reaching 84.7% at 115 h (Table 1 (Run 6), Fig. 5B). With increasing concentration of DMC,

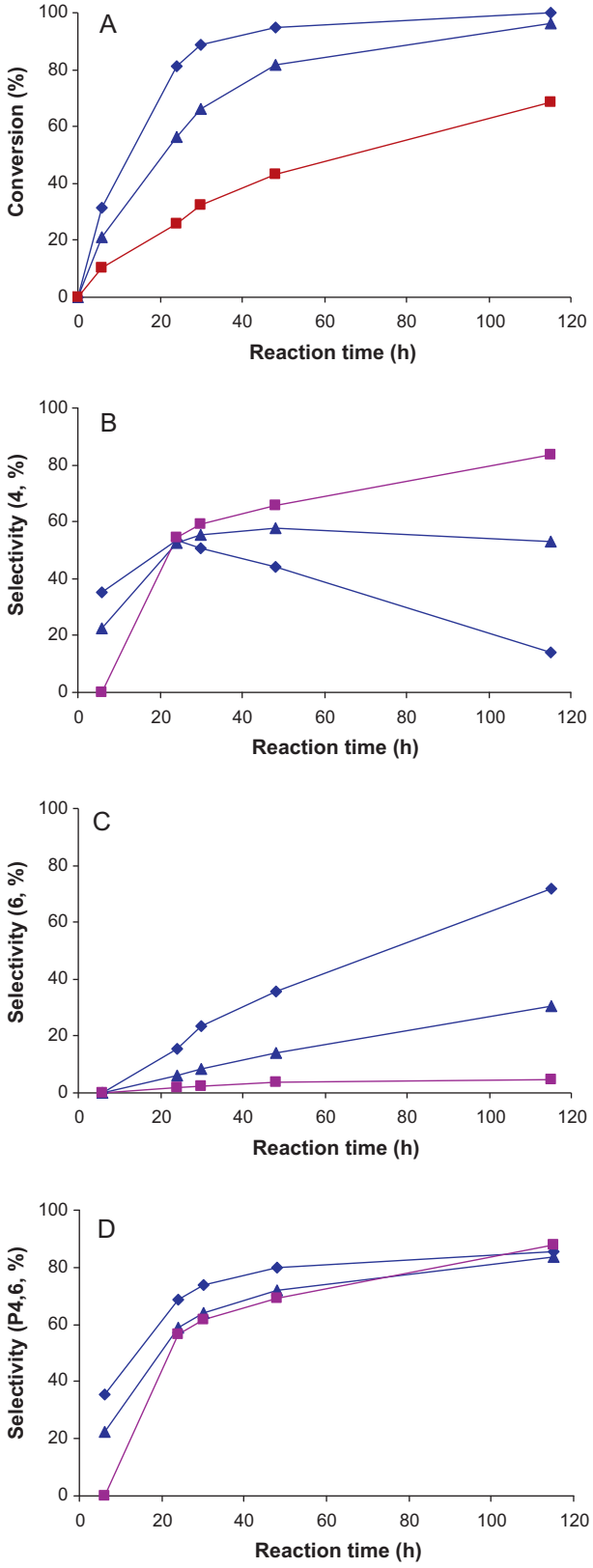


Fig. 5. Effect of TMP:DMC ratio on (A) TMP conversion, (B) formation of cyclic carbonate 4, (C) formation of cyclic carbonate 6, and (D) 4 and 6, using 10% (w/w) N435 at 60 °C in THF:toluene (0.5:1.0). The ratios of TMP:DMC used were 1:5 (♦), 1:2 (▲) and 1:1 (■), respectively.

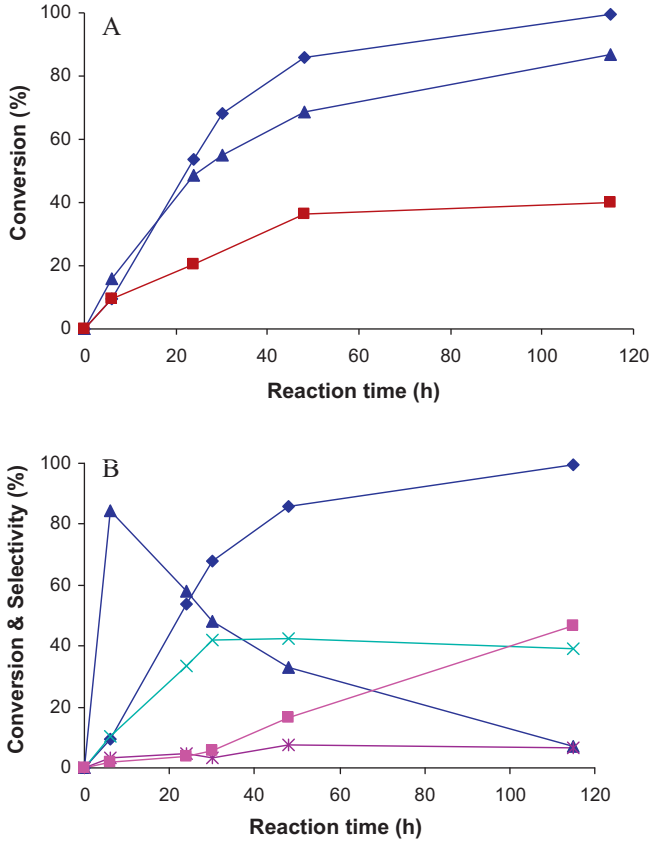


Fig. 6. Effect of TMP:DEC ratio on synthesis of cyclic carbonates using 10% (w/w) N435 at 60 °C in THF:toluene (0.5:1.0) system. (A) TMP conversion (%) at TMP:DEC ratios of 1:5 (♦), 1:2 (▲) and 1:1 (■), respectively. (B) Conversion of TMP (♦), and production of 3 (▲), 4 (x), 5 (✳) and 6 (■) in the reaction at TMP:DEC ratio of 1:5.

the content of product **4** decreased after an initial increase. At TMP:DMC ratio of 1:5, product **4** constituted the highest proportion of 50% after 24 h reaction (at TMP conversion of 80%), and subsequently decreased to 14%. This was attributed to its further conversion to the other cyclic carbonate derivative, product **6** by the lipase catalyzed transesterification at the remaining hydroxyl group with excess DMC. This was seen in increase in the content of product **6** to 72.1% (Table 1 (Run 8), Fig. 5C). Regardless of the TMP:DMC ratio, the total amount of cyclic carbonates, **4** and **6** was maintained over 80% (Table 1, Fig. 5D).

3.4. Comparison of reactivity and selectivity between DMC and DEC

Although DMC and DEC undergo the same type of reaction with TMP, differences in their physicochemical properties such as molecular size and hydrophobicity influence their interaction with the enzyme. As observed in the solvent-free system [22], the reactivity of DEC with TMP was lower than that of DMC (Fig. 6A, Table 1). For example, at substrate ratio (TMP:DEC or DMC) of 1:1 and 1:2 at 60 °C, the conversion using 10% N435 after 115 h of reaction with DEC reached 40% and 86.7%, respectively (Fig. 6), while the corresponding conversions with DMC were 68.9% and 96.3%, respectively (Fig. 5). Additionally, further conversion of the initially formed product **3**′ (mono-carbonated TMP) to the other products progressed slowly with DEC, and 33 and 26% of **3**′ remained in the product at TMP:DEC ratio of 1:1 and 1:2, respectively (Table 1). Highest degree of TMP conversion (99.4%) was achieved at TMP:DEC ratio of 1:5 which was similar to that with DMC but at a slower rate (Table 1, Figs. 5A and 6A). Fig. 6B shows the profiles of TMP conversion and products in the reaction with TMP:DEC ratio of 1:5 using 10% N435 at 60 °C. The highest proportion of the cyclic carbonate **4** in the reaction was 40% at 30 h and subsequently remained quite stable while the cyclic carbonate with pendant ethoxycarbonyloxyl group, **6**′ level increased gradually to just over 40%. This implies also a slower reaction rate in conversion of **4** to **6**′ in comparison with the reaction with DMC at a similar reactant ratio (see Fig. 4B). At 115 h, 99% of TMP was consumed and the product mixture contained predominantly (>86%) **4** and **6** (in almost equal proportions) with minor contents of **3**′ and **5**′ (Fig. 5B). The slower reaction rate with DEC could be due to the lower leaving rate of the acyl group for DEC as compared with DMC at 60 °C, and perhaps lower adsorption (mass transfer) rate of resulting ethanol into pore (4 Å) of molecular sieves.

4. Conclusion

Synthesis of functional six-membered cyclic carbonates by lipase-mediated reaction between TMP and DMC or DEC was achieved with high yield in a single step by using a mixture of hydrophilic and hydrophobic solvents. A useful relationship of solvent hydrophobicity (log *P*) and solvent type with conversion yield was established to choose a suitable solvent system. The proportion of the cyclic carbonate products, **4** and **6** were particularly influenced by the ratio of TMP and dialkylcarbonate used. The reaction starts with the formation of a linear mono-carbonated derivative of TMP, which undergoes further conversion to other linear carbonates with higher degree of substitution and cyclic carbonates depending on the reaction conditions. The reaction conditions providing highest TMP conversion rate and cyclic carbonate yield were the solvent mixture comprising THF:toluene at a ratio of 0.5:1, TMP:dialkylcarbonate at 1:5 ratio and 10% Novozym®435. In order to further enhance the rate of cyclic carbonate formation, especially product **4**, a useful strategy would be to obtain rapid conversion to **3** and subjecting the product to high temperature. Further development of this synthetic route is in progress for production of polyurethane without using toxic phosgene and isocyanate.

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