1. Introduction

Biodegradable polymers have attracted great attention from the scientific community because of their extensive applications in biomedical fields, such as drug delivery, designing of artificial human tissues and organ repair etc. Aliphatic polycarbonates (APCs) are one of very important class of biodegradable polymers owing to their excellent optical, thermal, and mechanical properties alongside their non-toxicity, biodegradability, and biocompatibility. Aliphatic polycarbonates are extensively used in the advancement of synthetic degradable polymers that are employed in automotives, aircrafts, electronics, and construction and biomedical materials as well as in the polyurethane and surfactant industry.

Inherently staggering application properties and biocompatibility of APCs are also accompanied by non-acid biodegradation products in vivo. Furthermore, the degradation rate of polycarbonates is lower than that of polyesters, a prerequisite for applications requiring long-term availability in the body. Properties of the polymers have a direct correlation with their synthesis methods.

Low to fairly high molar mass polycarbonates with narrow molar mass distributions can be prepared by ring-opening polymerization (ROP) of cyclic carbonates via cationic, anionic, coordinated, or enzymatic catalysis. Among several cyclic carbonates, ethylene carbonate and propylene carbonate have been used as inert solvent at lower temperature, and as reactive reagent at high temperature. Both ethylene carbonate and propylene carbonate are biodegradable, have high boiling and flash points, low toxicities, low odour levels and evaporation rates. They are synthesized by reaction of carbon dioxide with ethylene oxide or propylene oxide, therefore, are economically feasible.

High polymerization enthalpy of ethylene carbonate (125.6 kJ mol⁻¹) makes it impossible to synthesize pure poly(ethylene carbonate). Polymerization of ethylene carbonate at high temperature generally result in a copolymer comprising of ether linkages alongside targeted carbonate linkages, due to formation of carbon dioxide during polymerization. Decarboxylation during polymerization makes this reaction thermodynamically feasible by increasing entropy of the polymerization.

Ring-opening polymerization of EC by several different catalysts has been reported. All the catalysts used for polymerization of ethylene carbonate result in the copolymers having different content of ether and carbonate linkages. Polymerization by lewis acids or transesterification catalyst (metal alkoxides of tin, zirconium, and metal acetylacetonates) produces copolymers that contain about 40–50% ethylene carbonate units along with unwanted ethylene oxide units. Carbonate linkages of the copolymers decrease further in the products synthesized by basic catalysts. The high molar mass polycarbonates are obtained under conditions of high catalyst content, temperature, and monomer-to-initiator ratio.
catalysts (KOH, CH₃OK, NaI, and NaCl etc.) to only about 10–20%.³⁷,³⁸,³⁹,⁴⁰ Alternative ether and carbonate linkages in the copolymers and presence of 1,4,6,9-tetraoxaspiro[4.4]nonane intermediate has been shown in Al(acac)₃ or Ti(OBu)₄ catalyzed EC polymerizations.²⁸ Major hydrolysis by-product of ethylene carbonate polymerization by organometallic catalysis is diethylene glycol. Relative content of carbonate to ether linkages decreases with increase of the alkalinity of the catalyst.²⁷–³² Heterogeneous catalysis by using sodium stannate trihydrate has been reported for ethylene carbonate polymerization by Harris and McDonald.³³–³⁴ Presence of 2-hydroxyethylearbonate and 2-hydroxyethylether and diethylene glycol in the reaction mixture was noticed. Ionic ring-opening polymerization of ethylene carbonate also result in a copolymer with different relative amounts of carbonate and ether linkages.³³–³⁴ The polymer synthesized by ROP of EC contains both ether and carbonate linkages, therefore, it is referred as poly(ethylene ether-carbonate), PEEC, in the proceeding text.

In this study, we report on the ring-opening polymerization of ethylene carbonate by using sodium stannate trihydrate as a heterogeneous transesterification catalyst. The main target of this study is to analyze the molecular structure of poly(ethylene ether-carbonate), PEEC, by advanced 1D and 2D-NMR spectroscopic techniques such as ¹H, ¹³C, ¹H–¹H COSY (homonuclear correlation spectroscopy), ²H–¹³C HMQC (heteronuclear multiple-quantum correlation), ²H–¹³C HMBC (heteronuclear multiple-bond correlation), and MALDI-TOF mass spectrometry. Optimization of reaction conditions with regard to conversion, molar mass propagation and relative amount of carbonate linkages was conducted. Selectivity of polymerization with respect to polymerization temperature, catalyst concentration, monomer to initiator ratio, and polymerization solvent was evaluated.

This is first paper of the series of the project targeted to synthesize novel, amphiphilic and biodegradable block copolymers based on PEEC as hydrophobic segment for drug delivery and other biological applications. Optimization of polymerization conditions and meticulous structure elucidation of individual PEEC block is imperative for development of real structure–property correlations of the block copolymers. Several papers addressing synthesis, characterization, self-assembly behaviour, and their applications in drug delivery are in line to be published in due course of time.

2. Experimental

2.1. Materials

Ethylene carbonate-99% extra pure (Daejung, Korea), diethylene glycol-99% (Scharlau, Spain), Sodium Stannate trihydrate-95% (Sigma Aldrich, USA) were used as received. Solvents for synthesis such as 1,4-dioxane-99.5%, toluene-99.5% (Merck, Germany), dimethylformamide-99.8%, dichloromethane-99.8%, tetrahydrofuran-99.9% (RCI Labscan, Thailand), acetonitrile-99.9%, acetone-99.9% (Fisher Scientific, USA), and benzene-99.5% (Sigma-Aldrich, Germany) were used as received. HPLC grade chloroform-99.8% (RCI Labscan, Thailand) was used for size exclusion chromatography.

2.2. Polymerization

Ring-opening polymerization of EC was conducted in a three necked round bottom flask that is equipped with a magnetic stir bar, a thermometer, and an evacuating/purging assembly. Calculated amounts of diethylene glycol (initiator), sodium stannate trihydrate (catalyst) and ethylene carbonate (monomer) were added in an oven-dried flask that is subjected to three evacuation and purging cycles, to attain inert atmosphere. The polymerization was then conducted at high temperature for required time. The polymers were used directly for analysis without any further purification. For the synthesis of PEEC-5K 0.106 g (1 mmol) of DEG, 4.4 g (50 mmol) of EC, and 0.022 g (0.5 wt% of monomer) of sodium stannate trihydrate (catalyst) were taken in a 10 mL round bottom flask and polymerized at 175 °C for 10 hours. The variations in the quantity of reagents, and polymerization conditions for selectivity analysis are given in the corresponding section.

2.3. Characterization

2.3.1. Size exclusion chromatography (SEC). An Agilent SEC instrument (infinity 1200 series) equipped with an isocratic pump, manual injector, column oven and a RI detector, was used for SEC analysis. A set of three PLgel columns (300 × 7.5 mm, 5 μm, Mixed D) (Agilent Technologies, UK), connected in series to a PLgel guard column (50 × 7.5 mm) in front, is used. The temperature of column oven was maintained at 30 °C. Chloroform (HPLC grade) was used as an eluent at a flow rate of 1.0 mL min⁻¹. The SEC system was calibrated with narrow molar mass polystyrene standards (ranging from 165 g mol⁻¹ to 3 × 10⁶ g mol⁻¹) by Polymer Standard Services (Germany). Therefore, all the molar mass values obtained by SEC analysis are equivalent to linear PS. Sample concentrations were kept between 3.0 and 5.0 mg mL⁻¹ and 100 μL of sample solution was injected. The data was processed by using Agilent OpenLAB ChemStation (AgilentGPC data analysis software, 32 bit version).

2.3.2. NMR analysis. ¹H (500 MHz), ¹³C (125 MHz), ¹³C DEPT, and COSY NMR spectra were recorded on a Bruker AVANCE AN-500 MHz spectrometer. CDCl₃ was used as solvent, and ¹H and ¹³C were referenced to residual solvent signals.³⁶ ¹H–¹³C correlation experiments were performed on a Bruker AVANCE AN-500 MHz spectrometer (Bruker, Switzerland). With a 5 mm PABBI probe by using gs-HSQCT³⁷ and gs-HMBC³⁸ pulse sequences. Coupling constant were calculated in hertz (Hz), multiplicities were labelled as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), and the prefixes br (broad) or app (apparent) were used. The HSQC experiment was optimized for C–H coupling of 145 Hz with decoupling applied during acquisition, while the HMBC experiment was optimized for coupling of 8 Hz without decoupling during acquisition. 2D-NMR data were acquired with 1024 points in t₁, the number of increments for t₂ was 256. Thirty two scans and sixteen dummy scans were used for HSQC and HMBC experiments. A relaxation delay of 1 s and 2 s was used for 1D and 2D experiments, respectively.
2.3.3. MALDI-TOF MS analysis. Bruker ultraflex speed mass spectrometer was used for MALDI-TOF mass spectrometry. The instrument is equipped with a 2 kHz smart beam-II laser. The irradiations slightly above the threshold laser power were used to generate ions. Positive ion spectra were recorded in reflectron mode. To improve the signal-to-noise ratio, the spectra of 200 shots were averaged.

Dithranol (30 mg mL\(^{-1}\)), analyte (5 mg mL\(^{-1}\)), sodium trifluoroacetate (20 mg mL\(^{-1}\)) in THF were mixed in a ratio of 1 : 10 : 1 (v/v/v). 0.5 mL of the resulting mixture were deposited on the stainless steel sample plate and is allowed to dry in air.

3. Results and discussion

3.1. Synthesis of poly(ethylene ether carbonate)

Ring opening polymerization of ethylene carbonate is associated with several side reactions that lead to ether linkages alongside targeted carbonate linkages in the polymer chain.\(^{27,31,33–37,39–41}\) The proposed mechanism of ring-opening polymerization of EC by heterogeneous transesterification catalyst sodium stannate trihydrate is shown in Scheme 1. The chain propagation reaction in ROP of EC proceeds by two different mechanisms: attack on the carbonyl carbon and attack on the ethylene carbon.\(^{31,42,43}\) The chain propagation by attack on the carbonyl carbon is kinetically favourable, however, reversible. The positive enthalpy of this propagation step makes it unlikely to happen exclusively, therefore, it is almost impossible to synthesize pure poly(ethylene carbonate).\(^{27}\) On the other hand, the attack on the ethylene carbon is irreversible due to removal of carbon dioxide. The propagation by latter mechanism leads to formation of ethylene ether units in the polymer chain. The final product is the result of the competition between these two propagation mechanisms, hence, contains both ethylene carbonate and ethylene ether units. Scheme 2 displays the ROP of EC by using DEG as initiator and sodium stannate trihydrate as catalyst, the polymer chains contain both ether and carbonate units.

The first question when synthesizing new polymers is the rational propagation of the molar mass. Size exclusion chromatography is the most widely used technique for this purpose. As can be seen in Fig. 1, the elution volume decreased with the increase of the molar mass. The naming of various products in the figure is according to relative monomer to initiator ratio (targeted molar mass).

3.2. Structural elucidation of poly(ethylene ether-carbonate) by NMR spectroscopy

Structural characterization of poly(ethylene ether-carbonate) is performed by advanced techniques of NMR spectroscopy. The \(^{1}H\)-NMR spectrum of polymer is shown in Fig. 2, where a singlet at \(\delta\) 4.49 ppm corresponds to the monomer, ethylene carbonate. The other three signals confirm the polymer formation bearing three different types of protons in the polymer chain. The peak at \(\delta\) 4.25 ppm corresponds to the methylene protons (CH\(_2\)-3) adjacent to carbonate group, while the peak at \(\delta\) 3.62 ppm correspond to the carbon atoms (CH\(_2\)-4) adjacent to CH\(_2\)-3. Carbon atoms (CH\(_2\)-5) between the ether–ether linkages appear at \(\delta\) 70.5 ppm. Highly downfield signal at \(\delta\) 155.08 ppm is the characteristic peak of the carbonyl carbon (C=O-2).

Distortionless enhancement of polarization transfer using a 135 degree decoupled pulse (DEPT-135) allows differentiation between carbons attached to odd or even number of hydrogens. The carbons attached to odd number of hydrogen (1 and 3) have positive phase (up) while carbons attached to even number of hydrogen (2) have a negative phase (down). A DEPT-135 spectrum of the same product is shown in Fig. 3B. Spectrum confirms the presence of only methylene (–CH\(_2\)-) groups in the polymer chain.

Signals assigned by \(^{13}C\)-NMR were further confirmed by 2D-NMR analysis (HSQC and HMBC), discussed in detail in proceeding text.
Homonuclear correlation spectroscopy ($^1$H–$^1$H COSY) is used to identify the different proton signals (CH$_2$-3, CH$_2$-4 and CH$_2$-5) via coupling with each other. The assignment of signals CH$_2$-3 and CH$_2$-4 was confirmed by 2D COSY measurements. Methylene proton (CH$_2$-3) (connected to the carbonate group) have a clear correlation with protons CH$_2$-4 of ether linkage, Fig. 4 (Table 1).

Heteronuclear single quantum coherence spectroscopy (HSQC) reveals information on the correlation of two different nuclei separated by a single bond. 2D $^1$H–$^{13}$C HSQC technique is utilized for accurate assignment of $^{13}$C-NMR spectra. X-Axis depicts the $^1$H-NMR while Y-axis belongs to $^{13}$C-NMR. Correlation of three different protons can be unambiguously established with three different carbons (see Fig. 5). Direct correlation of proton at δ 4.25 ppm (CH$_2$-3) with carbon at δ 66.9 ppm (CH$_2$-3), proton at δ 3.69 ppm (CH$_2$-4) with carbon at δ 68.8 ppm (CH$_2$-4), and proton at δ 3.62 ppm (CH$_2$-5) with carbon signal at δ 70.5 ppm (CH$_2$-5) can be noticed in the contour plot. On the basis of this direct correlation data, signals at δ 66.9 and δ 68.8 ppm could be related to the two carbon atoms in ethylene carbonate (EC) units; −CH$_2$ group (CH$_2$-3) adjacent to the oxygen of carbonyl group (C=O-2) and −CH$_2$ group (CH$_2$-4) adjacent to the oxygen of ether unit, respectively. The signal at 70.5 ppm could be assigned to the CH$_2$ groups (CH$_2$-5) in the ethylene oxide (EO) units (ether linkage), Table 1.

Sequences of carbonate functionality and ether linkages in the polymer were further conﬁrmed by the 2D $^1$H–$^{13}$C heteronuclear multiple bond correlation (HMBC) technique. Heteronuclear multiple bond correlation has ability to develop a correlation over a longer range of 2–4 bonds. $^1$H–$^{13}$C HMBC spectra depicts that $^1$H-NMR signal at δ 4.25 ppm (CH$_2$-3) is related to $^{13}$C-NMR signals at δ 155.1 ppm (C=O-2) and δ 68.8 ppm (CH$_2$-4), Fig. 6. This conﬁrms the presence of carbonate-ether sequences in the copolymer chain. Additionally, proton at δ 3.69 ppm (CH$_2$-4) has a direct correlation with carbon atom at δ 66.9 ppm (CH$_2$-3) and δ 70.5 ppm (CH$_2$-5). HMBC correlation data demonstrated that the proton at δ 4.25 ppm (CH$_2$-3) and proton at δ 3.62 ppm (CH$_2$-5) are connected through CH$_2$ group (CH$_2$-4) at δ 3.69 ppm adjacent to −CH$_2$ group of the carbonate unit (CH$_2$-3), Table 1. Meticulous 2D coupling of proton and carbon NMR conﬁrms the presence of ether linkages (equivalent to ethylene oxide repeat units). Presence of peak at δ 3.69 ppm (CH$_2$-4) in $^1$H-NMR clearly indicates the presence of EO units that are formed by decarbonylation of EC. Furthermore, equal intensity of peaks at δ 3.69 (CH$_2$-4) and δ 4.25 (CH$_2$-3) is an indication of absence of EC–EC joining in the polymer chain. The most populated sequence (triad) of EC and EO in copolymer seems to be EC–EO–EO.

3.3. MALDI-TOF MS

To confirm the presence of ether linkages in the polymers obtained by polymerization of ethylene carbonate, MALDI-TOF MS analysis of the products is conducted. Ideally, if there is no carbon dioxide emission during polymerization, the oligomers should have molar mass increment of 88.06
Emission of carbon dioxide results in reduction in the molecular weight of the repeat unit by 44.01 amu (formula weight of carbon dioxide). In this case, MALDI-TOF MS of the polymer obtained by polymerization of ethylene carbonate should be similar to polyethylene oxide (mass increment of 44.05), as can be seen in Fig. 7. Nevertheless, NMR analyses revealed that average carbonate content in the polymer chains is nearly 50%. Therefore, the product should be a combination of carbonate and ether linkages. MALDI-TOF MS reveals numbers \( m/z \) that need to be justified by molecular structure. In this particular case, one number can be true for several combinations of ether and carbonate linkages (see Table 2).

### 3.4. Conversion and quantification of carbonate and ether linkages by NMR

Percent conversion and relative amounts of carbonate and ether linkages in the polymer chain can be calculated by \(^1\)H-NMR spectra (Fig. 2). As discussed above, peak at \( \delta \) 4.49 ppm of \(^1\)H-NMR is attributed to EC monomer. Peaks at \( \delta \) 4.25 (CH\(_2\)-3) and \( \delta \) 3.69 ppm (CH\(_2\)-4) in \(^1\)H-NMR are assigned to the two carbon atoms in EC unit, and peak at \( \delta \) 3.62 ppm (CH\(_2\)-5) is assigned to the carbon atom of EO unit. The conversion of monomer and the polymer composition can be calculated by using intensities of the above mentioned peaks in \(^1\)H-NMR spectra. Following formulas are used for the calculations, where \( I_1, I_2, I_3, \text{ and } I_4 \) represent the intensities of the corresponding signals in \(^1\)H-NMR spectra.
Monomer conversion (%) = \frac{I_3 + I_4 + I_5}{I_3 + I_4 + I_5 + I_1} \times 100 \quad (1)

EC content (%) = \frac{I_3 + I_4}{I_3 + I_4 + I_5} \times 100 \quad (2)

3.5. Selectivity of ethylene carbonate polymerization

Selectivity of polymerization of ethylene carbonate with regard to conversion, evolution of molar mass and ether content is evaluated by variations in polymerization temperature, monomer to initiator ratio, catalyst content, and polymerization solvent. Molar mass values obtained by size exclusion chromatography are relative to linear PS. The values of molar mass at the maxima (M_p) are used in all the selectivity plots. Percent conversion and relative ratio of carbonate to ether linkages are calculated by \textsuperscript{1}H-NMR as explained in the previous section.

3.5.1. Polymerization temperature. Arrhenius equation describes that rate of reaction increases exponentially with temperature. Same is true for ethylene carbonate polymerization. To evaluate the temperature selectivity, polymerizations were carried out at various temperatures ranging from 120 to 175 °C. Evolution of molar mass as a function of reaction time is shown in Fig. 8A. As can be seen, there is no appreciable reaction progress at 120 °C. As expected, the polymerization proceeds faster at higher temperature. As a next step, we took 10
hours as a standard polymerization time and products are evaluated for molar mass and dispersity, conversion, and content of carbonate/ether linkages, Fig. 8B. Nearly complete conversion of the monomers is observed at 175 °C in 10 hours, and polystyrene equivalent molar mass of polymers with maximum number of molecules in the sample is 7500 g mol⁻¹ (value at peak maximum, M_p). Molar mass and conversion decreased if the polymerization is conducted at lower
temperature for similar period of time. Polymerization proceeded faster at higher temperature without any considerable increase in the average ether content of the polymer chains. PDI of the products also did not vary to large extent and ranged from 1.6 to 1.8.

3.5.2. Amount of catalyst. Amount of catalyst should have an impact on the progression of the polymerization. In this context, amount of catalyst was varied systematically and polymerizations of EC were conducted at 175 °C (the optimized temperature). Molar mass propagation, relative carbonate linkages and time required for complete conversion as a function of catalyst amount are shown in Fig. 9. The conversion and molar mass progression is directly proportional to the amount of catalyst. Most importantly, average carbonate content of the polymer chains is not affected to large extent and remained in the range of 40–45%. In this case, polymerizations were continued till more than 90% conversions. The amount of catalyst does not have any considerable effect on the conversion, molar mass and relative ether and carbonate linkages; however, polymerization proceeded at much faster rate with higher catalyst amount.

3.5.3. Monomer to initiator ratio. An increase in monomer to initiator ratio with almost complete conversion should result in an augmented molar mass. The polymerizations were performed at optimized conditions (temperature and catalyst amount) till almost complete conversion of the monomers. Progression of the molar mass, time required for complete conversion and average carbonate content of the polymer chains as a function of monomer to initiator ratio is shown in Fig. 10. Molar mass and time required for complete conversion increases linearly with monomer content. However, the average carbonate content of the polymer chains remains in the same range of 40–45%.

![Fig. 7](https://example.com/figure7.png)  
A representative MALDI-TOF MS spectrum of the poly(ethylene ether-carbonate), PEEC; possible combinations of number of ether and carbonate units with m/z value of 1010 are given in Table 2.

| Sr. Nr | Number of EC units (a) | Number of EE units (b) | Molecular formula [DEG-(EC)\textsubscript{a}(EE)\textsubscript{b} + Na] | Theoretical molecular weight (Da) |
|--------|------------------------|------------------------|-------------------------------------------------|----------------------------------|
| 1      | 10                     | 0                      | C\textsubscript{34}H\textsubscript{50}O\textsubscript{33}Na                  | 1009.74                          |
| 2      | 9                      | 2                      | C\textsubscript{35}H\textsubscript{54}O\textsubscript{32}Na                  | 1009.79                          |
| 3      | 8                      | 4                      | C\textsubscript{36}H\textsubscript{58}O\textsubscript{31}Na                  | 1009.83                          |
| 4      | 7                      | 6                      | C\textsubscript{37}H\textsubscript{62}O\textsubscript{30}Na                  | 1009.87                          |
| 5      | 6                      | 8                      | C\textsubscript{38}H\textsubscript{66}O\textsubscript{29}Na                  | 1009.92                          |
| 6      | 5                      | 10                     | C\textsubscript{39}H\textsubscript{70}O\textsubscript{28}Na                  | 1009.96                          |
| 7      | 4                      | 12                     | C\textsubscript{40}H\textsubscript{74}O\textsubscript{27}Na                  | 1010.00                          |
| 8      | 3                      | 14                     | C\textsubscript{41}H\textsubscript{78}O\textsubscript{26}Na                  | 1010.05                          |
| 9      | 2                      | 16                     | C\textsubscript{42}H\textsubscript{82}O\textsubscript{25}Na                  | 1010.09                          |
| 10     | 1                      | 18                     | C\textsubscript{43}H\textsubscript{86}O\textsubscript{24}Na                  | 1010.13                          |
| 11     | 0                      | 20                     | C\textsubscript{44}H\textsubscript{90}O\textsubscript{23}Na                  | 1010.18                          |
3.5.4. Solvent effect. To evaluate the solvent effect on the polymerization, solvents of different polarities are used that include acetone, dichloromethane (DCM), tetrahydrofuran (THF), dioxane, benzene, toluene and dimethylformamide (DMF). Solvents with lower boiling points could not go beyond their boiling point under reflux conditions, therefore, no reasonable progress in polymerization is observed. High boiling solvents such as toluene and DMF allowed to achieve reasonably high temperatures, polymerization proceeded to some extent. However, conversion and molar mass could not go beyond 20 percent and 1500 g mol⁻¹ respectively, even after 24 hours.

4. Conclusion

This study reports on successful ring-opening polymerization of ethylene carbonate by using sodium stannate trihydrate catalyst. The comprehensive structural elucidation of the products is performed by advanced NMR techniques. It is concluded that ethylene carbonate polymerization is associated with decarboxylation during polymerization. This side reaction results in polymer chains that contain ether linkages alongside targeted carbonate linkages. Results of one-dimensional NMR (¹H and ¹³C) and two-dimensional NMR (COSY, HSQC, and HMBC) complement each other. Two-dimensional NMR analysis revealed peculiar structural features of the polymer chains that are not possible by only one-dimensional NMR analysis. MALDI-TOF MS results support the outcome of detailed NMR analysis. The EC–EE–EE triad seems to be the major repeating unit in the polymer chain. Molar mass progression, conversion, and relative ratio of carbonate to ether linkages are calculated by size exclusion chromatography and ¹H-NMR, respectively. Progress of polymerization is affected by reaction conditions such as temperature, amount of catalyst, monomer to initiator ratio and solvent. Nonetheless, the relative content of carbonate repeat units in the PEEC synthesized under varying polymerization conditions remained in the range of 40–45%. Synthesis, characterization, and drug encapsulation efficiency of

Fig. 8 (A) Propagation of molar mass of PEEC as a function of time at various polymerization temperatures, (B) molar mass, conversion and carbonate content as a function of temperature; polymerization conditions: monomer : initiator = 50 : 1, catalyst amount = 0.5 wt%; \( M_p \) obtained from size exclusion chromatography (equivalent to linear PS), monomer conversion and average ether content from ¹H-NMR.

Fig. 9 Molar mass, conversion and carbonate content as a function of amount of catalyst; polymerization conditions: monomer : initiator = 50 : 1, temperature = 175 °C; \( M_p \) obtained from size exclusion chromatography (equivalent to linear PS), monomer conversion and average ether content from ¹H-NMR.

Fig. 10 Molar mass, conversion and carbonate content as a function of monomer to initiator ratio (M/I); polymerization conditions: monomer : initiator = 50 : 1, temperature = 175 °C; \( M_p \) obtained from size exclusion chromatography (equivalent to linear PS), monomer conversion and average ether content from ¹H-NMR.
amphiphilic, biodegradable block copolymers based on PEEC as a hydrophobic segment is in process.

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