

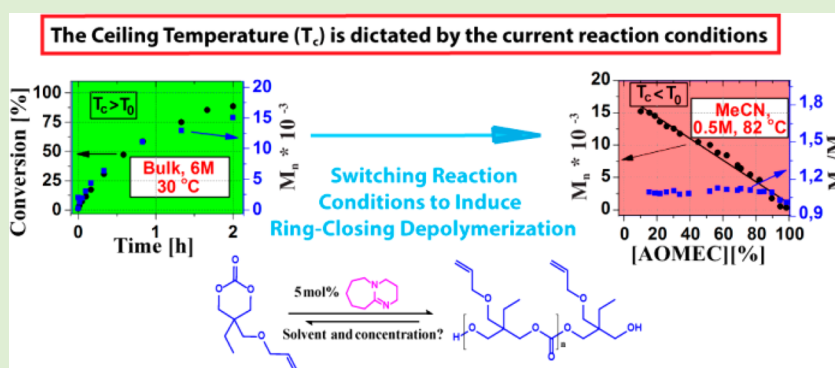
Switching from Controlled Ring-Opening Polymerization (cROP) to Controlled Ring-Closing Depolymerization (cRCDP) by Adjusting the Reaction Parameters That Determine the Ceiling Temperature

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S Supporting Information



ABSTRACT: Full control over the ceiling temperature (T_c) enables a selective transition between the monomeric and polymeric state. This is exemplified by the conversion of the monomer 2-allyloxymethyl-2-ethyl-trimethylene carbonate (AOMECE) to poly(AOMECE) and back to AOMECE within 10 h by controlling the reaction from conditions that favor ring-opening polymerization ($T_c > T_0$) (where T_0 is the reaction temperature) to conditions that favor ring-closing depolymerization ($T_c < T_0$). The ring-closing depolymerization (RCDP) mirrors the polymerization behavior with a clear relation between the monomer concentration and the molecular weight of the polymer, indicating that RCDP occurs at the chain end. The T_c of the polymerization system is highly dependent on the nature of the solvent, for example, in toluene, the T_c of AOMECE is 234 °C and in acetonitrile $T_c = 142$ °C at the same initial monomer concentration of 2 M. The control over the monomer to polymer equilibrium sets new standards for the selective degradation of polymers, the controlled release of active components, monomer synthesis and material recycling. In particular, the knowledge of the monomer to polymer equilibrium of polymers in solution under selected environmental conditions is of paramount importance for in vivo applications, where the polymer chain is subjected to both high dilution and a high polarity medium in the presence of catalysts, that is, very different conditions from which the polymer was formed.

INTRODUCTION

The assumption of an increasing future demand for more refined polymeric materials with niche properties for niche applications cannot be easily refuted.^{1,2} The trend is not only to construct polymers in a controlled manner but also to equip the polymer chain with functions. Functions predesigned into the monomeric structure or generated via a postpolymerization modification that targets a specific site or performs an exquisite task in vivo or in natura, resulting in a desired macroscopic change.^{3,4} In other words, we aim to achieve, via synthesis, the specificity of biological systems.

One highlighted group of materials for a diverse set of applications, especially in the biomedical arena, are degradable aliphatic polymers with repeating units of either ester or carbonate groups.^{5–7} These polymers, which are most often

obtained by ring-opening polymerization of the respective cyclic monomers, allow, through different addition schemes or inherent reactivity behavior, the construction of refined macromolecular architectural features.^{8–10} This enables control of many polymer properties, such as degradation,^{11–13} mechanical performance,^{11,14} and the placement of functional groups along the polymer chain.^{15,16}

A particular class of monomers/polymers that has evoked strong interest and shown high potential for a diverse set of applications is the substituted cyclic six-membered carbonates and the corresponding polycarbonates.^{17–20} Their potential lies

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in the abundance of a large variety of 1,3-propane diols that are selectively substituted at the 2-position with residues carrying functional handles, such as hydroxyl and carboxyl groups, that are subsequently easily derivatized.^{21–27} Together with recent advances in organocatalyzed ROP, these monomers/polymers have opened the possibility to construct highly refined functional polycarbonate materials at high rates, at ambient temperatures and with few side reactions.^{28–33}

Additionally, a factor immensely important but alluring the lime-light is the favorable thermodynamic equilibrium polymerization behavior of six-membered cyclic carbonates. Cyclic six-membered carbonates, even though heavily substituted, possess good equilibrium polymerization behavior, that is, favorable thermodynamics of polymerization,^{34–36} compared to the cyclic ester analogs.^{37–40} The thermodynamic description of polymerization was first discussed in the seminal paper by Dainton and Ivin in the late 1940s, where they coined the expression “the ceiling temperature (T_c) of polymerization”.⁴¹ In addition to being indicative of the highest temperature at which conversion of the monomer can be achieved, the ceiling temperature (T_c) is a measure of the propensity of the monomer to undergo polymerization. T_c is independent of the catalytic system used but dependent on the monomer concentration, and there are indications in the literature that suggest very different polymerization behavior in different surrounding media, even at the same concentration,^{38,42,43} especially for the cationic polymerization of THF.^{44,45} A specific understanding of how the monomer–polymer equilibrium is altered as a function of the reaction medium may be regarded as a black box, but it is highly important for the behavior of the polymer chain in real applications.

Our hypothesis is that the monomer–polymer equilibrium is dictated by the current state of the system. Our aim is to tailor the thermodynamic equilibrium by changing the surrounding reaction conditions. This will enable a reversible transition between the monomeric and polymeric states in the system. If successful, this process would enable both predesigned control of polymerization as well as a means to fine-tune the final behavior of the polymeric system in different environments, aspects that are highly important not only in the biomedical arena but also in the recycling of polycarbonates and polyesters.^{46,47}

To explore this, the same monomer, 2-allyloxymethyl-2-ethyl-trimethylene carbonate (AOMECE), is polymerized in very different surroundings by varying the solvent type, temperature, and monomer concentration. We have centered our investigation on the perspective of the thermodynamics of ring-opening polymerization. The equilibrium polymerization behavior of AOMECE is thermodynamically intermediate, meaning that the equilibrium should be easily disturbed by changing the surrounding environment, such as the temperature, solvent type, and concentration.⁴⁸

EXPERIMENTAL SECTION

Materials. Hexanediol (Sigma-Aldrich, Sweden) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Sigma-Aldrich, Sweden) were stored under an inert gas atmosphere prior to use. Chloroform (HPLC grade, Fisher Scientific, Germany), methanol (general purpose grade, Fisher Scientific, Germany), dichloromethane (anhydrous, $\geq 99.8\%$, Sigma-Aldrich), toluene (anhydrous, $\geq 99.8\%$, Sigma-Aldrich), acetonitrile (anhydrous, $\geq 99.8\%$, Sigma-Aldrich), dichloromethane (DCM) (Fisher Scientific, Germany), sodium hydride (NaH) (60% dispersion in mineral oil, Sigma-Aldrich, Sweden), diethyl carbonate (99%, Sigma-Aldrich, Sweden), trimethylolpropane allyl ether (98%,

Sigma-Aldrich, Sweden), acetic acid (technical grade, Fisher Scientific, Germany), and acetic acid anhydride (ReagentPlus, $\geq 99\%$, Sigma-Aldrich, Sweden) were used as received.

Synthesis of 2-Allyloxymethyl-2-ethyl-trimethylene Carbonate (AOMECE). The monomer was synthesized via ring-closing depolymerization according to a previously reported protocol,^{36,49} along with a consecutive distillation step with the addition of acetic anhydride (0.1 eq. to AOMECE) and triethylamine (0.1 eq. to AOMECE) to ensure that the residual hydroxyl groups were capped.

Polymerization of AOMECE. General Preparation and Polymerization Setup. All reaction vessels were equipped with a magnetic stirrer and were dried in an oven at 150 °C for 48 h, followed by further drying with a heating gun and three consecutive vacuum/ N_2 (g) cycles. All reactants were weighed under an inert gas atmosphere (N_2) in a glovebox (Mbraun MB 150-GI). All reactions were stirred at a constant temperature that was maintained (± 2 °C) using an IKAMAG RCT basic safety thermostat. At different time intervals, samples were taken and analyzed by 1H NMR spectroscopy and size exclusion chromatography (SEC). Samples (0.1 mL, 0.6 mmol) were withdrawn from the reaction vessel using disposable syringes followed by termination with a solution of acetic acid (0.05 mL, 0.88 mmol) in dichloromethane (DCM, 1 mL).

Bulk Polymerization of AOMECE. AOMECE (1 g, 5 mmol) was weighed inside a glovebox into a dry 25 mL two-necked round-bottom flask, followed by the addition of the catalyst DBU (0.038 mL, 0.25 mmol) and polymerization at the selected temperatures.

Solution Polymerization of AOMECE. First, a stock solution containing 0.25 mmol DBU per ml of the selected solvent (toluene or acetonitrile) was prepared. Then, AOMECE (1 g, 5 mmol) was weighed inside a glovebox into a dry 25 mL two-necked round-bottom flask. To the reaction mixture, 1 mL of the stock solution and a prespecified amount of solvent were added. For more details of the polymerization setup, see general preparations and polymerization setup and Supporting Information Tables S1, S2 and S3. Additionally, for information regarding the instruments see Supporting Information.

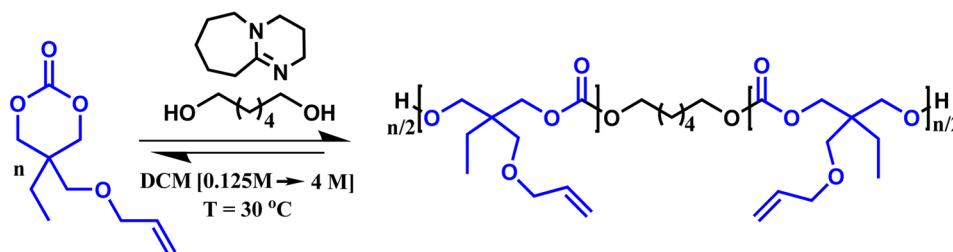
RESULTS AND DISCUSSION

The ability of a monomer to polymerize is highly dependent under which conditions the synthesis is performed. Parameters such as temperature, concentration, and perhaps even surrounding solvent dictate the final outcome of the polymerization and shift the equilibrium concentration between monomer and polymer.^{50,51} Understanding how the equilibrium is influenced by external factors is immensely important during polymer synthesis and monomer synthesis but also for the final application of the envisioned polymeric material. The relationship between the enthalpy and entropy change, ΔH_p and ΔS_p , in the system, the monomer concentration, and temperature is summarized by the Dainton–Ivin equation, eq 1 ($T = T_c$), which states the ceiling temperature (T_c) of polymerization decreases with decreased initial monomer concentration.⁵² However, the influence of the solvent polarity on the enthalpy and entropy changes in the system with dilution, which may play a crucial role for the equilibrium state of the polymer, is omitted.

$$T = \frac{\Delta H_p}{\Delta S_p + R \ln([M]_{eq})} \quad (1)$$

Influence of the Initial Monomer Concentration on Its Equilibrium Concentration. In the first paper on anionic ring-opening polymerization of cyclic carbonates with a lithium alcoholate as the initiator, it was observed that in the thermodynamic regime of the polymerization, a ring–chain equilibrium is established, which is dependent on the monomer concentration, temperature, and nature of the solvent.⁴² However, no quantitative, systematic investigation of the

Scheme 1. Polymerization of AOMECE ([M]) with Hexanediol ([I]) as the Initiator Catalyzed with DBU ([C]), [M]/[I]/[C] = [100]:[1]:[5] at Different Concentrations Ranging from 0.125 to 4 M in DCM



phenomenon was performed. Recent reports on the polymerization of substituted trimethylene carbonates in dichloromethane (DCM) catalyzed by organocatalysts, that is, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), resulted in the respective polymer under mild condition in the absence of side reactions; low to no degree of decarboxylation was observed.⁷ Although, likewise to the first paper a clear ring–chain equilibrium is established. Specifically, polymerization of TMC catalyzed by DBU has been reported to reach 99% monomer conversion at equilibrium after 40 h in 2 M DCM at ambient temperature.⁵³ However, when the TMC monomer was substituted with a triethylene glycol chain at the 2-position and the polymerization was performed under more dilute conditions (0.8 M DCM) with the same DBU catalyst, the polymerization reached an equilibrium point of 70% conversion after 8 h at ambient temperature.⁵⁴

Inspired by these results, the first experiments on ring-opening polymerization of AOMECE were performed in dichloromethane (DCM) with different initial monomer concentrations using hexamethylenediol as initiator and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst for 72 h (to reach equilibrium) at 30 °C (Scheme 1).

As observed from Figure 1, with increasing initial monomer concentration ($[AOMECE]_0$), the monomer concentration at

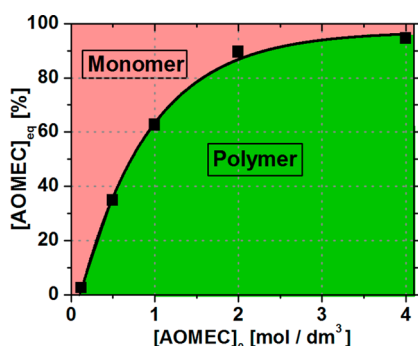


Figure 1. Equilibrium monomer conversion as a function of the initial monomer concentration for the polymerization of AOMECE ([M]) with hexanediol ([I]) as initiator and DBU as catalyst ([C]). [M]/[I]/[C] = [100]:[1]:[5] in DCM at 30 °C and ambient pressure.

equilibrium ($[AOMECE]_{eq}$) decreases: $[AOMECE]_0 = 0.5 \text{ M} \Rightarrow [AOMECE]_{eq} = 66\%$, $[AOMECE]_0 = 1 \text{ M} \Rightarrow [AOMECE]_{eq} = 38\%$, $[AOMECE]_0 = 2 \text{ M} \Rightarrow [AOMECE]_{eq} = 10\%$, that is, the final concentration of the repeating units in the polymer increases. Hence, the carbonate monomer AOMECE, exhibits a ceiling temperature of $T_c = 30 \text{ °C}$ in DCM at an initial monomer concentration of 0.125 M (Supporting Information Table S1 and Figure 1).

The initial monomer concentration plays a crucial role in the concentration of AOMECE at equilibrium. However, the contribution of the enthalpy (ΔH_p) and entropy (ΔS_p) of polymerization in conjunction with the reaction environment remains unknown, that is, when the system is diluted, is this purely an entropic effect or is the ring strain influenced by other factors, such as the polarity of the medium.

Polymerization Thermodynamics in Different Environments. The influence of the reaction medium on the thermodynamics of the polymerization was determined by analyzing the influence of the initial monomer concentration, temperature and solvents with different polarity on the change in the monomer–polymer equilibrium and consequently on the enthalpy (ΔH_p) and entropy (ΔS_p) of polymerization and the ceiling temperature (T_c). The requirements for the choice of solvents are (i) a reasonably high boiling point combined with a reasonably high vapor pressure to ensure easy removal of the solvent; (ii) a solvent that is unable to initiate polymerization or deactivate the catalyst, meaning that it is inert under the polymerization conditions; and (iii) solvents with very different polarities. The two selected solvents that fulfill these criteria are toluene (PhMe with a boiling point of 111 °C and a relative polarity to water of 0.10 and acetonitrile (MeCN) with a boiling point of 82 °C and a relative polarity to water of 0.46.

The polymerization of AOMECE was performed with 5 mol % DBU (relative to the initial monomer concentration) as catalyst at different temperatures accompanied by the evaluation of the kinetic behavior to ensure that equilibrium conversion was reached (Scheme 2 and Supporting Information Tables S2–S4 and Figures S1–S16).

The thermodynamic equilibrium polymerization of bulk AOMECE ($[AOMECE]_0 = 6 \text{ M}$) revealed similar thermodynamic parameters as found by Endo et al.⁵⁵ for 2,2-disubstituted trimethylene carbonates. According to Dainton's eq 1, the values obtained for $[AOMECE]_0 = 6 \text{ M}$ are $\Delta H_p = -3.6 \text{ kJ mol}^{-1}$ and $\Delta S_p = -6.9 \text{ mol}^{-1} \text{ K}^{-1} \text{ J}$ (with a corresponding ceiling temperature of $T_c = 247 \text{ °C}$ (Figure 2)). Compared to the more thoroughly studied lactones, the ceiling temperature of this monomer is between that of ϵ -caprolactone and δ -valerolactone.⁴⁸ This result likely originates from the higher ring strain in a six-membered cyclic carbonate monomer than in a lactone with the same ring size.^{56,57}

The bulk thermodynamic equilibrium polymerization occurs at an initial monomer concentration of 6 M, Figure 2 and Table 1). Furthermore, AOMECE was polymerized in toluene at 2, 1, 0.5, and 0.25 M at 30, 60, 75, and 90 °C for each concentration and in acetonitrile at 2, 1, 0.5, and 0.25 M at 30, 45, and 75 °C for each concentration. Tables S2–S4 present the experimental details for these experiments, and Supporting Information Figures S1–S16 display the results.

Scheme 2. Polymerization of AOMEc in PhMe and in MeCN with 5 mol % DBU (Relative to the Initial Monomer Concentration) as Catalyst Using Different Initial Monomer Concentrations and Polymerization Temperatures: Evaluation of the Equilibrium Conversion

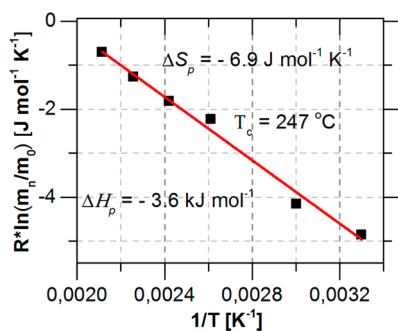
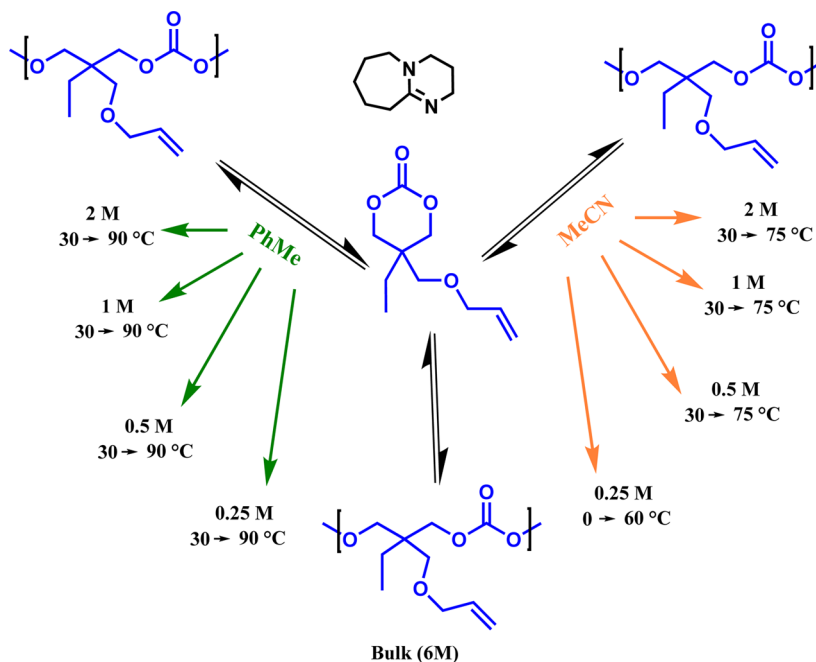


Figure 2. Thermodynamic equilibrium polymerization of bulk AOMEc (6 M) with hexanediol as initiator and DBU as catalyst at different temperatures: $R \ln(m_n/m_0) = \Delta H_p/T - \Delta S_p$. The intercept is used to calculate the ΔS_p , and the slope of the line gives ΔH_p . The ratio $\Delta H_p/\Delta S_p = T_c$.

All the results are summarized in Table 1. The polymerization behavior differs substantially based on the solvent. With a 2 M solution of AOMEc in PhMe, a ceiling temperature of $T_c = 234$ °C is obtained, while in MeCN at the same concentration, $T_c = 142$ °C (Table 1). Specifically, in a 2 M

solution of toluene at 30 °C, the concentration of AOMEc at equilibrium ($[AOMEc]_{eq}$) is $100 - 97.6\% = 2.4\%$, whereas in acetonitrile under the same conditions $[AOMEc]_{eq} = 100 - 73.0\% = 27\%$ (Figures S1 and S9).

The ring strain (the enthalpy of polymerization ΔH_p may serve as a measure of the ring strain) and the contribution of the polymerization entropy ΔS_p are strongly affected by solvents of different polarity (Figure 3): ΔH_p in PhMe (1 M) = -22.0 kJ mol $^{-1}$, whereas ΔH_p in MeCN (1 M) = -10.1 kJ mol $^{-1}$. A more than a 2-fold increase in ring strain is observed in the nonpolar solvent toluene. The ring strain increases with dilution toward a maximum value in both cases; a larger increase in ΔH_p is observed when using PhMe as the solvent (Figure 3a). The dielectric constants for a number of cyclic carbonates have been determined,⁵⁸ and within this selection the chemical structure that most closely resembles AOMEc is propylene carbonate, which has a dielectric constant of 64 at 25 °C (for comparison, the dielectric constant of MeCN is 37.5 and that of PhMe is 2.4). All cyclic carbonates have high dielectric constants due to their highly polar carbonate group. It is our hypothesis that solvents with different dielectric constants (different polarity) induce changes in the con-

Table 1. Thermodynamic Data for the Polymerization of AOMEc in PhMe and MeCN at Different Concentrations

entry	solvent	C [mol L $^{-1}$]	temp [°C]	ΔH_p [kJ mol $^{-1}$]	ΔS_p [J mol $^{-1}$ K $^{-1}$]	T_c [°C]
1	bulk	6 M	30 → 200	-3.6 ± 0.006	-6.9 ± 0.28	247
2	toluene	2 M	30 → 90	-11.1 ± 0.026	-21.9 ± 1.5	234
3	toluene	1 M	30 → 90	-22.0 ± 0.048	-46.6 ± 2.6	199
4	toluene	0.5 M	30 → 90	-38.8 ± 0.072	-89.2 ± 4.0	162
5	toluene	0.25 M	30 → 90	-43.2 ± 0.156	-105.2 ± 6.8	137
6	acetonitrile	2 M	30 → 75	-7.6 ± 0.072	-18.3 ± 1.0	142
7	acetonitrile	1 M	30 → 75	-10.1 ± 0.025	-26.8 ± 1.4	104
8	acetonitrile	0.5 M	30 → 75	-12.7 ± 0.048	-35.8 ± 2.3	82
9	acetonitrile	0.25 M	0 → 60	-13.7 ± 0.06	-39.1 ± 3.5	77

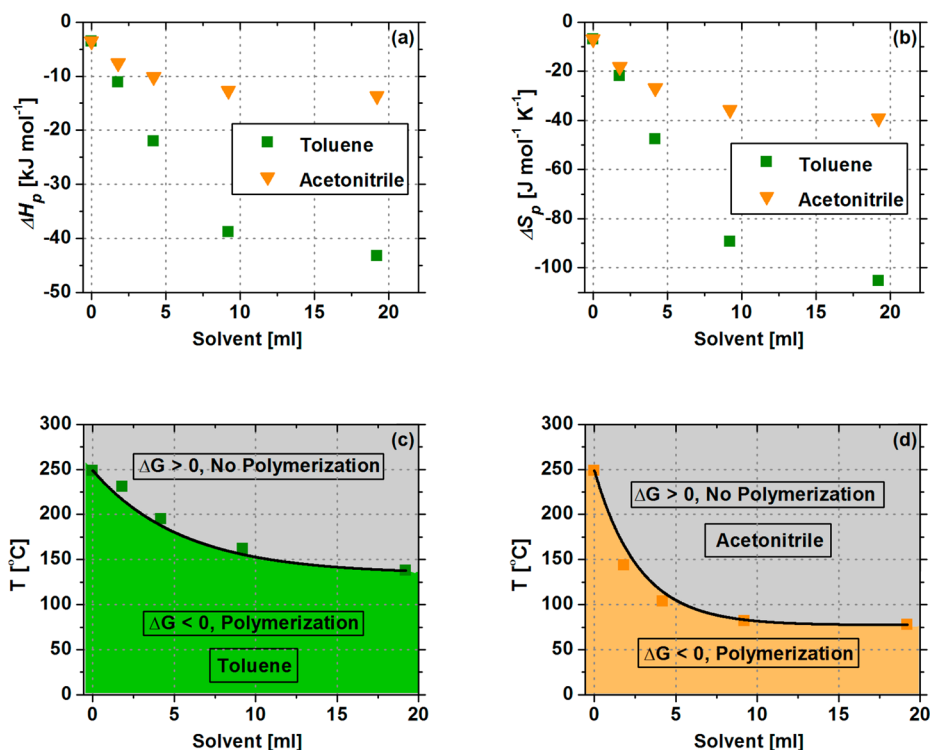


Figure 3. Thermodynamic equilibrium polymerization of AOMEc in PhMe and MeCN as a function of different initial monomer concentrations. (a) and (b) show the change in ΔH_p and ΔS_p , respectively, (c) and (d) display $\Delta H_p/\Delta S_p = T_c$ as a function of different degrees of solvation (different monomer concentrations): (c) in PhMe and (d) in MeCN. (For numerical values, see Tables S2–S4).

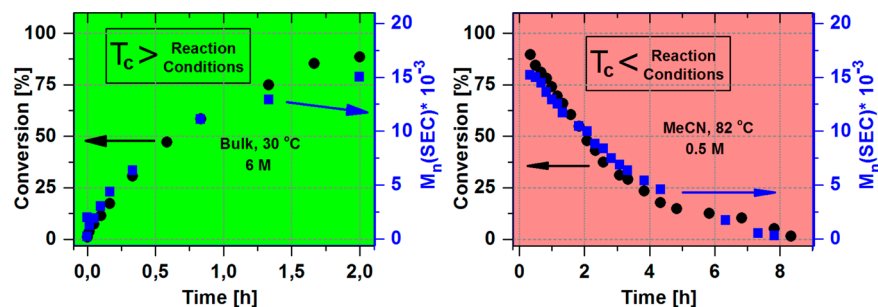


Figure 4. Bulk polymerization of AOMEc ($[AOMEc]_0 = 6$ M catalyzed with 10 mol % DBU): conversion of AOMEc versus time and $M_n(SEC)$ versus time (green area). Depolymerization of poly(AOMEc) ($[AOMEc]_{in} = 0.5$ M with 10 mol % DBU) in MeCN at $T = 82$ °C: conversion of AOMEc_{in} versus time and $M_n(SEC)$ versus time (red area).

formation of the cyclic carbonate monomer, forcing the monomer into a more or less favored conformation, which in turn determines the ring strain and ΔH_p . A larger deviation in polarity between the monomer and solvent, that is, a larger difference in the dielectric constants, leads to increased ring strain in the monomer and consequently to a higher absolute value for ΔH_p and a lower concentration of AOMEc at equilibrium. The increase in the ΔS_p with dilution is an inescapable consequence of the change in system thermodynamics; however, the magnitude is related to the nature of the solvent. At 0.25 M in PhMe, $\Delta S_p = -105.2$ J mol⁻¹ K⁻¹, and in MeCN, $\Delta S_p = -39.1$ J mol⁻¹ K⁻¹, which is more than 2.5 times higher for the less polar solvent toluene (Table 1 and Figure 3b). Because of the more favorable interactions between the solvent and monomer, a more ordered solvent network is produced. For MeCN, which has a more similar dielectric constant to cyclic carbonates, a more ordered solvent network is formed, which prevents a stronger decrease in entropy with

dilution, and this is in contrast to PhMe, where the entropic increase is more pronounced (Figure 3b). This is however a hypothetical explanation, although the scientific literature regarding protein–ligand binding⁵⁹ and halogen bonding in different solvents supports this explanation.⁶⁰

The solvent polarity and monomer concentration that influence both ΔH_p and ΔS_p , which respected magnitudes in conjunction to temperature, determine the conditions at which polymerization occurs ($\Delta G_p = \Delta H_p - T\Delta S_p < 0$) and at which depolymerization is favored ($\Delta G_p = \Delta H_p - T\Delta S_p > 0$). We determined the polymerizability of AOMEc at different temperatures and different concentrations in PhMe and MeCN, which revealed substantial differences between the two solvents (Figure 3c,d). T_c was equivalent for the two solvents at very different degrees of solvation, T_c (PhMe, 0.25 M) = 137 °C and T_c (MeCN, 2 M) = 142 °C (Table 1, Figure 3c,d). The T_c of polymerization is indicative of the temperature at which $\Delta G_p = 0$, that is, monomer conversion occurs only up

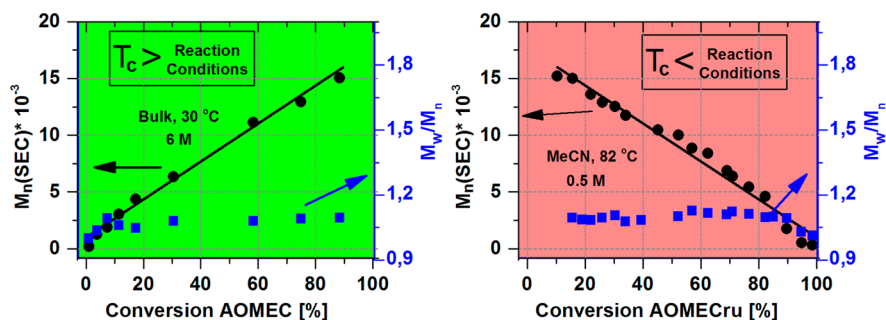


Figure 5. Bulk polymerization of AOMECE ($[M]_0 = 6$ M catalyzed with 10 mol % DBU): $M_n(\text{SEC})$ and M_w/M_n versus conversion of AOMECE (green area). Depolymerization of poly(AOMECE) ($[\text{AOMECE}_{\text{ru}}]_0 = 0.5$ M with 10 mol % DBU) in MeCN at $T = 82$ °C: $M_n(\text{SEC})$ and M_w/M_n versus conversion of AOMECE_{ru} (red area).

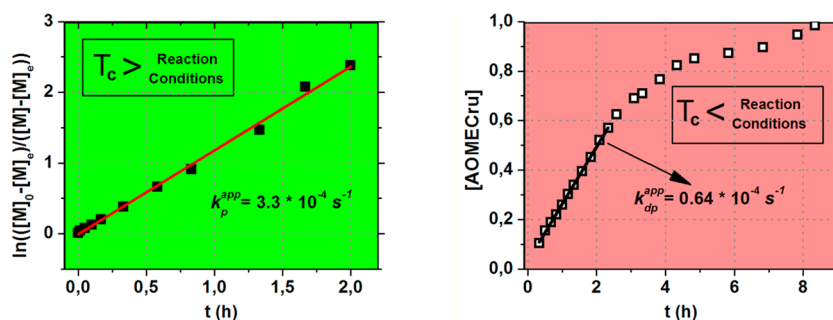


Figure 6. Bulk polymerization of AOMECE ($[M]_0 = 6$ M catalyzed with 10 mol % DBU): first order, $\ln([M]_0 - [M]_e) / ([M] - [M]_e) = k_p^{\text{app}} t$, where the slope of the line gives k_p^{app} (green area). Depolymerization of PAOMECE ($[\text{AOMECE}_{\text{ru}}] = 0.5$ M with 10 mol % DBU) in MeCN at $T = 82$ °C: zero order, $[\text{AOMECE}_{\text{ru}}] = k_{\text{dp}}^{\text{app}} t + [\text{AOMECE}]$, where the slope of the line gives $k_{\text{dp}}^{\text{app}}$ (red area).

to this temperature, and if a polymer is subjected to temperatures above these conditions, depolymerization occurs.

The on/off between the monomeric and polymeric state, hence the T_c regime, was recently explored for the homopolymerization of γ -butyrolactone, a monomer that was previously considered “not polymerizable”. Polymerization was achieved at -40 °C; increasing the temperature to well above T_c enabled depolymerization and recycling of the monomer.^{61,62} The T_c for the polymerization of a specific monomer can be adjusted by copolymerization; to increase the ceiling temperature of a specific monomer, a comonomer with a higher T_c can be added.^{63–66} Adjustment of the monomer–polymer equilibrium by changing the concentration was also achieved for a highly substituted ϵ -caprolactone monomer.⁶⁷

Polymerization with in Situ Change in the Reaction Conditions. To prove the ability of the AOMECE–poly(AOMECE) system to respond to changes in the environment, we performed sequential changes to the reaction conditions: (i) AOMECE was first reacted in bulk ($[\text{AOMECE}]_0 = 6$ M) at 30 °C. Under these conditions, polymerization occurred because $T_c > T_0$. (ii) After reaching equilibrium conversion of AOMECE, poly(AOMECE) was dissolved in MeCN to produce 0.5 M concentration of repeating units (AOMECE_{ru}), and the temperature was increased to 82 °C. Under these conditions ($T_c < T_0$) ring-closing depolymerization occurred. The time conversion plots and the change in the number-average molecular weight versus time for the polymerization of AOMECE and the depolymerization of poly(AOMECE) are shown in Figure 4; the corresponding numeric values are shown in Tables S5 and S6. Specifically, 30% conversion of AOMECE to poly(AOMECE) was achieved after 20 min, whereas the corresponding value of the depolymerization of 30% of poly(AOMECE) to AOMECE

was achieved after 70 min, as shown in Tables S5 and S6 and Figure 4.

The ability of AOMECE to be in the polymeric state or the monomeric state is dependent on the surrounding environment (Figures 4 and 5). The initial polymerization conditions of the $[\text{AOMECE}]_0 = 6$ M and 30 °C system favors polymerization ($T_c > T_0$), and the conversion and molecular weight follow the conventional trend. After 2 h, when the system environment is changed to one that disfavors polymerization (solution of MeCN, $[\text{AOMECE}]_0 = 0.5$ M and 82 °C, $T_c < T_0$) direct ring-closing depolymerization is observed (the concentration of AOMECE_{ru} decreases, where subscript ru indicates the repeating units).

The depolymerization follows an analogous trend to the polymerization (Figures 4 and 5), indicating that depolymerization occurred via ring-closing depolymerization from the chain end. This is further supported by the similar values of the molecular weight at the same conversion of AOMECE_{ru} (where subscript ru indicates the repeating units) and AOMECE. However, in terms of kinetic behavior, the polymerization and depolymerization behave very differently, as shown in Figures 4 and 6. The polymerization follows the classical pseudo first order kinetics, $k_p^{\text{app}} = 3.3 \times 10^{-4} \text{ s}^{-1}$, whereas the depolymerization follows pseudo zero order kinetics, $k_{\text{dp}}^{\text{app}} = 0.64 \times 10^{-4} \text{ s}^{-1}$ (Figure 6). Therefore, the depolymerization of poly(AOMECE) is initially independent of the concentration. However, as the system approaches equilibrium, that is, $\Delta G_p = 0$, polymerization–depolymerization equilibrium is established, and a change in the kinetics is observed (Figure 6). This observation cannot be generalized to ring-closing depolymerization but reflects the features of this particular system. The selected reaction parameters for depolymerization, MeCN 0.5 M and 82 °C, are at the borderline at which $\Delta G = 0$ for the

system. If the selected reaction parameters shift to more strongly favor depolymerization ($T_c \ll T_0$, hence $\Delta G_p \ll 0$), it is believed that the entire depolymerization process would follow pseudo zero order kinetics.

CONCLUSIONS

The surrounding conditions of cyclic carbonates and the corresponding polymers dictate their monomer–polymer equilibrium. In DCM at 30 °C and ambient pressure with an initial monomer concentration of $[AOME C]_0 = 0.125$ M, no monomer conversion is observed, $\Delta G_p = 0$, and the system is at its ceiling temperature, whereas at 4 M monomer, 95% equilibrium conversion is observed. The monomer–polymer equilibrium is highly dependent on the nature of the reaction conditions and the polarity of the surrounding medium. For AOME C at $[AOME C]_0 = 1$ M and 75 °C in PhMe, the equilibrium monomer concentration is (100–86.6) 13.4%; in MeCN and at the same conditions, the equilibrium monomer concentration is (100–23.1) 76.9%. Tailoring the thermodynamic equilibrium via the reaction conditions enables selective transition between the monomeric and polymeric states. Exemplified by changing the reaction from conditions that favor polymerization (bulk polymerization at 30 °C) to conditions that disfavor polymerization ($[AOME C]_0 = 0.5$ M in MeCN and $T = 82$ °C) reformation of the cyclic monomer AOME C is observed within 10 h.

These results indicate that the polymeric state should not be viewed only from the vantage point of its respective synthesis but rather as a continuing equilibrium between monomer and polymer. This underlines the importance of considering how the polymer will behave during its application. Specifically, if we consider in vivo applications where the polymer is subjected to a highly polar reaction conditions at low concentrations actively brings to question the most preferable state of the polymer under these reaction conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.6b01375.

Data regarding experimental setup, determination of equilibrium conversion, and GPC values for the polymerization and concentration-induced depolymerization of AOME C/PAOME C (PDF)

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Notes

The authors declare no competing financial interest.

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