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Supercritical RROP: Exploring the radical ring-opening polymerisation of 2-methylene-1,3,6-trioxocane in supercritical CO_2 as a green solvent

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ABSTRACT

Radical ring opening polymerisation (RROP) of cyclic ketene acetals (CKAs) is an attractive technique to synthesize branched, (bio)degradable polyesters. However, CKAs as monomers of RROP suffer from hydrolysis lability, making aqueous heterogeneous precipitation polymerisations challenging. In order to explore the precipitation polymerisation of 2-methylene-1,3,6-trioxocane (MTC) and avoid the hydrolysis of monomer, kinetic studies in supercritical CO_2 ($scCO_2$) were performed. Tuning the reaction pressure and temperature allowed for synthesis in varying viscosity domains. Importantly, we describe the precipitation polymerisation of low T_g PMTC (−65 °C) in $scCO_2$. In contrast to literature, where a particle-driven polymerisation mechanism has been described for high T_g polymers, a slurry-like precipitation polymerisation was observed for PMTC. Depending on the reaction temperature, polymers with either (i) a defined density of branches (DB) and a scattering of molar mass values, or (ii) a scattering of DB values and relatively defined molar mass were prepared.

1. Introduction

Due to the climate crisis, environmental pollution, and the limitation of natural resources there is a growing need for sustainable materials and the adaptation towards greener chemistry. This involves the use of greener solvents, concepts for the end-of life of products such as degradability and reducing the carbon footprint in the production of plastics [1–4]. One approach to tackle the issue of environmental pollution is the implementation of (bio)degradable materials in daily life products with non-toxic degradation products. To achieve this degradability, cleavable groups that can be broken down hydrolytically or enzymatically can be incorporated into polymer backbones [5]. Rather than accumulating in the environment as microplastics, (bio)degradable polymers break down to low molar mass products, that can be digested by microorganisms [6].

For many years, polyesters were prepared by polycondensation [7], ring-opening polymerisation [8] and metathesis reactions [9,10] allowing for their application in multiple disciplines ranging from biomedical, drug delivery and cosmetic applications [7,11,12]. An alternative method for polyester synthesis that has attracted interest more recently is the radical ring-opening polymerisation (RROP) of cyclic ketene acetals (CKAs) [5,11–21]. RROP of CKAs was first reported by Bailey et al. and combines a radical initiation and propagation mechanism with a ring-opening step [22].

Following the ring-opening, unique polyesters with ether, amino [5,20] and phenol-functionalities [14,23,24] in the polymer backbone can be prepared (see Fig. 1). By choosing the right CKA, properties, such as pH-responsiveness (alkyl-2-methylene-1,3,6-dioxazocane (alk-MACs)) [20], stiffness (5,6-benzyl-2-methylene-1,3-dioxepane (BMDO)) [25] and varying hydrophilicity (2-methylene-1,3-dioxepane (MDO) or 2-methylene-1,3,6-trioxocane (MTC)) [19] can be tailored [5,15,17,26,27]. Exploiting the radical character of RROPs, copolymerisation of CKAs with vinylic monomers could be used to incorporate degradable functions into poly(acrylic acid) [28] or polyethylene [29,30]. A unique feature of RROP is the ability to produce branched polyesters [19]. It has been shown that incorporation of branching can be used to expand the

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property range of established polymers like poly(ε-caprolactone) (PCL) and in turn the scope of potential applications [19,31]. A method to quantify the number of repeating units involved in branching is based on ^{1}H NMR spectroscopy. There the integral intensity of the branching units was divided by the integral intensity of ring-opening units. By varying the DB, PCL-analogues with a broad range of melting temperatures and crystallinities can be synthesised [18,19,21,31]

While branching can be beneficial for certain applications, in many instances this is an unwanted side effect of using a radical polymerisation process to make the polyesters. The branches are formed via intra- or intermolecular transfer which increase the molar mass dispersity and alter the architecture of the polymer [21]. As such, a key challenge for homopolymerisation of CKAs via RROP remains in gaining an understanding of the branching reaction with a view to being able to control it. Attempts to optimize the reaction conditions to control dispersity, molar mass or DB have been met with limited success [5,21]. Across a range of the reaction conditions, comparable polymers are obtained. To date, only increasing the energy put into the reactions, by UV light and/or high temperature, have promoted the reaction to give higher molar mass samples of high dispersity (i.e. Đ >6). [5,12].

Due to the ability to access different kinetic regimes, exploiting heterogeneous polymerisation processes (e.g. emulsion polymerisation), appears attractive for investigating the RROP of CKAs [32,33]. Unfortunately, due to the presence of the hydrolytically-sensitive acetal moiety present in these monomers, water needs to be avoided to prevent monomer degradation [33]. One approach to avoid this issue was reported by Agarwal et al., who replaced CKAs with the hydrolytically stable cyclic vinyl acetals [33,34]. However, to prepare materials derived from existing CKAs, alternative reaction conditions have to be explored.

In the following work, we explore RROP in supercritical fluids (scRROP) by providing kinetic insights of the precipitation polymerisation of MTC. Here supercritical carbon dioxide ($scCO_2$) was used, since it turns supercritical under mild conditions (31.1 °C and 73.8 bar) [35]. Embracing $scCO_2$ as an abundant, non-toxic solvent with tuneable density will help to push experimental boundaries in terms of viscosity [36]. It can be removed by simply venting the reaction vessel, avoiding energy intense drying processes and toxic solvent residues. With that, a notable drawback of conventional RROP: the use of petroleum-based solvents can be avoided [37]. The established knowledge on the particle-driven mechanism for precipitation polymerisation [38] (for high T_g polymers) will be examined and a data set for modelling the kinetics during the synthesis of poly(MTC) (a low T_g polymer of −65 °C [18]) established. With that, a greener approach for RROP can be established and data for further modelling in $scCO_2$ provided.

2. Materials and methods

All chemicals were purchased from Sigma-Aldrich, Merck Millipore, Fischer Scientific and Acros Organics. Diethylene glycol, chloroacetaldehyde dimethylacetal, potassium *tert*-butoxide and 2,2′-azobis (2-methylpropionitrile) (AIBN) were purchased from Sigma Aldrich. *tert*-Butanol was purchased from Thermo Scientific. Carbon Dioxide (CO_2, SCF grade 5.5, 99.9995 %) was obtained from Air Products and Chemicals Inc. Except for AIBN, that was recrystallized to remove stabilizers, all chemicals were used without further purification.

2.1. Synthetic procedures

2.1.1. 2-Chloromethyl-1,3,6-trioxocane (MTC-Cl) and 2-methylene-1,3,6-trioxocane (MTC)

The synthesis of MTC and MTC-Cl was performed as reported in literature and is described in detail in section 1 of the SI [18]. Briefly, diethylene glycol, chloroacetaldehyde dimethylacetal and DOWEX WX2 was mixed at 120 °C, the product was distilled to obtain the MTC-Cl. The chloroacetal was then mixed with *tert*-butanol and potassium *tert*-butoxide and heated to 120 °C. The product was extracted with diethyl ether and distilled multiple times to gain MTC as a clear, transparent liquid.

2.1.2. Polymerisation of MTC

All polymerisation reactions were performed in a high-pressure autoclave with a stirring rate of 250 rpm. After the system was purged for 10 min with CO_2, a degassed solution of 0.5 g MTC and 1 mol% AIBN was added. The reaction mixture was injected through the key hole of the autoclave safety valve, keeping a constant counterflow of CO_2. In order to dissolve the reaction mixture as fast as possible, the autoclave was sealed, heated to 31 °C and pressured to 1200 PSI (83 bar). With that, the CO_2 became supercritical and the respective reaction temperature and pressure was set. Setting temperature and pressure took less than 20 min and when the desired conditions were reached, the starting time t_0 was defined. After that, the reactions were left stirring for the

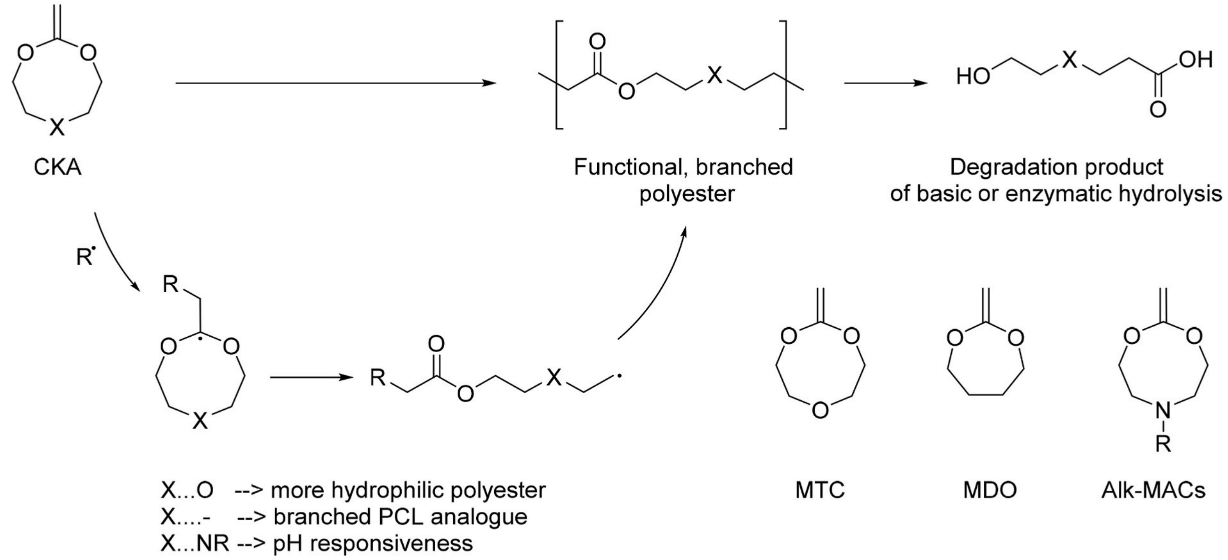

Fig. 1. Illustration of the polymerisation mechanism of RROP as a method to prepare functional, branched polyesters. RROP of cyclic ketene acetals, allowing for the incorporation of heteroatoms into the polymer backbone by substitution of the ring. The reaction starts with the initiation by a radical at the exocyclic double bond, leading to a tertiary radical which undergoes ring opening leading to a functional, branched polyester.

respective time and to finish the reaction, the reaction vessels were cooled to 25 °C. Subsequently, the autoclave was vented and the polymer recovered. The residual polymer was dissolved in tetrahydrofuran (THF) and dried to constant mass in a vacuum oven.

2.2. Size exclusion chromatography

To analyse the samples for their molar mass, a similar protocol to previous studies was used [19,21]. SEC coupled with a triple detection setup was used comprised of a degasser, an isocratic pump (both series Agilent 1200), an autosampler (Agilent series 1100) and 2 × SEC columns PLgel MIXED-C columns (300–7.5 mm; 5 μm particle size) by Agilent Technologies Inc. (USA).The downstream detection system was comprised of a multi angle light scattering MALS DAWN® HELEOS® II, a viscometric detector Viscostar® III and a differential refractometer Optilab® T-rEX, all by Wyatt Technology Corp. (USA). Separations were performed in THF (stabilized with 0.025 % BHT) as eluent with a flow rate of 1 mL/min. For that, 53 μL of polymer solution were injected having an analyte concentration of 4 mg/mL. Data recording and analysis was done using the Software Astra® by Wyatt Technology Corp. (USA), version 7.3.2. Initial MALS detector normalisation, delay volume alignment and band broadening correction were adjusted by measuring a narrowly distributed PS standard with a M_w of 30,000 g/mol (PS80317, Pressure Chemicals Co, USA) and of $Đ \leq 1.06$ and validated by measurements of other PS standards with higher M_w of 200,000 g/mol. Following the protocol discussed in literature, a deviation of 5 % was implemented for the molar mass determination [19,21].

2.3. NMR spectroscopy

^{1}H NMR measurements were performed using a Bruker Advance III 500 spectrometer operating at 500.13 MHz for ^{1}H and at 125.74 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used as solvent and reference ($\delta(^1H) = 7.26$ ppm; $\delta(^{13}C) = 77.0$ ppm). The measurements were carried out at 30 °C using standard pulse sequences of the TopSpin 3.2 software package (Bruker Biospin). Following the protocol discussed in literature, a deviation of 5 % was implemented for the determination of the DB [19, 21].

3. Results and discussion

To gain insights into the scRROP, kinetic studies were performed. Making use $scCO_2$ as non-toxic, abundant solvent system, Kwon et al. reported the synthesis of PMDO with a low dispersity (i.e. $Đ < 2$), but branching or variation of polymerisation conditions was not discussed [39]. In this work, the scRROP of MTC will be reported in-depth for the first time discussing the impact of the density of the $scCO_2$ and reaction temperature.

Separate batches of the reaction mixture were polymerised in a time frame of 0–24 h and analysed for their conversion and DB by ^{1}H NMR and for their M_n and $Đ$ by size exclusion chromatography with multiple-angle-light-scattering detection (SEC-MALS). In Fig. 2, the schematic experimental setup is illustrated. To investigate the impact of temperature and pressure, the polymerisation was carried out at 65 °C, 75 °C or 85 °C with 1 mol% AIBN as radical initiator at a pressure of either 2000 PSI (138 bar) or 3600 PSI (248 bar) to represent the maximum and minimal pressure domains achievable under safe conditions at the experimental setup. Sample series will be referred to as ‘x-y’ with ‘x’ being the reaction temperature and ‘y’ the applied pressure. For instance, sample series 65–3600 was carried out at 65 °C and 3600 PSI. In $scCO_2$ a variation in temperature and pressure typically leads to a variation of viscosity. For instance, at 85 °C a viscosity from 27.6 to 53.0 μPa•s, at 75 °C a viscosity of 30.0 and 59.1 μPa•s and at 65 °C a viscosity of 36.0 and 66 μPa•s is expected at 2000 PSI and 3600 PSI, both being approximately 5–10 % of the viscosity of a typical solution [40,41].

Since MTC has not been polymerised in $scCO_2$ previously, solubility tests were performed. A beaker in a fixed volume view cell (100 mL) was employed, with a maximum working pressure of 4350 PSI and a maximum working temperature of 150 °C, which contains two sapphire windows at either end of its body allowing for a visual determination of

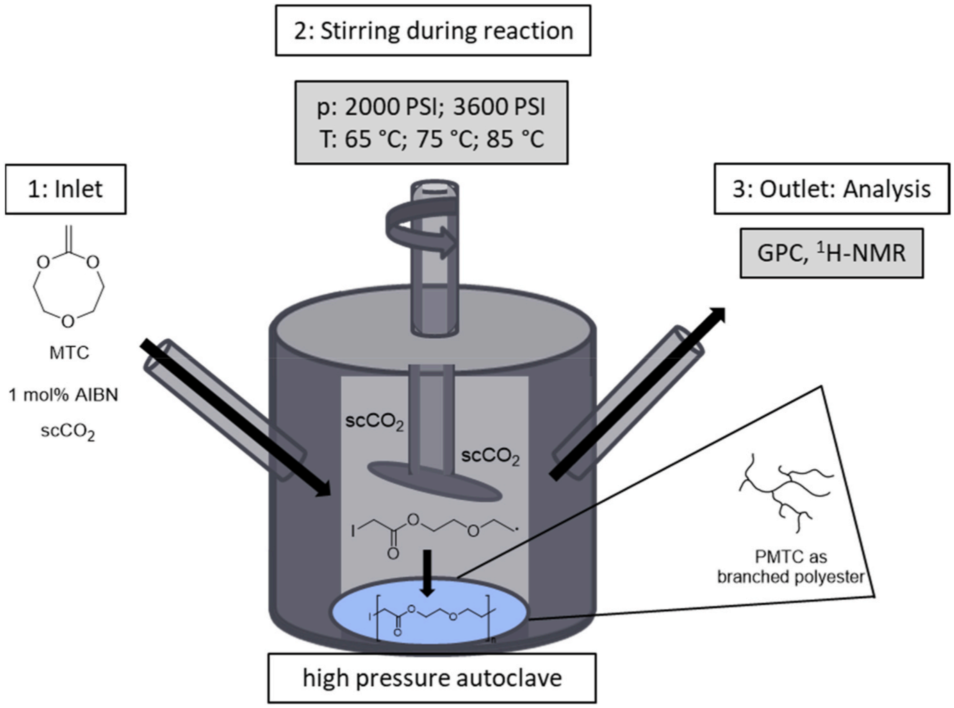

Fig. 2. Schematic of a high-pressure autoclave and the reaction taking place: (1) first a mixture of monomer and initiator (MTC + AIBN) was added to the reactor, (2) reaction was performed with varying solvent capacities at different pressure and temperature and (3) the branched, precipitated polymer was analysed after a certain time by SEC and ^{1}H NMR.

solubility in $scCO_2$. Below the critical point, a two-phase system consisting of the gaseous CO_2 and the liquid MTC phase was observed (Fig. 3A). When the pressure was increased above its critical point (31.1 °C, 1070 PSI (73.8 bar)), CO_2 became a supercritical fluid [35]. At this point, the CO_2 mixed with MTC and a solution of the monomer in $scCO_2$ formed immediately. Optically this was determined when the sample height of the MTC in the beaker decreased until liquid MTC could no longer be observed (Fig. 3B). Increasing temperature and pressure did not significantly increase the solubility of the MTC in CO_2 since the turbidity remained comparable (Fig. 3C). Since PMTC was insoluble in CO_2 (Fig. S4 of the SI), the reaction will be considered a radical ring opening precipitation polymerisation.

In accordance to earlier work, the impact of reaction temperature was investigated when samples were polymerised at 65 °C, 75 °C and 85 °C for 24 h [21]. The conversion, molar mass, dispersity and DB are presented in Table 1 for representative samples of these reaction conditions. For none of the samples, a notable amount of hydrolysis or ring-retaining products were observed (see Fig. S16). To set a starting point for further discussion, the impact of reaction temperature 65°, 75 °C and 85 °C at a constant pressure of 3600 PSI will be discussed first. Please note, that the DB only describes the overall number of branched repeating units, but does not discriminate between short-chain and long-chain branching. Rather than stating clear trends, the discussion hence has to be treated as an attempt to examine the process of branching better.

For sample 65–3600, the conversion was limited to 40 %. The conversion was surprisingly low compared to relevant literature, but the reasoning for the limited conversion will be discussed later. A sample with a molar mass of 3.8 kg/mol, a dispersity of 1.5 and a DB of 15 % was isolated. We postulate, that this low molar mass and dispersity compared to literature is caused by the precipitation of polymer chains during the reaction interrupting chain growth [21]. In literature, for low conversion domains, a dispersity of 1.5 was reported to be a typical value for termination by recombination [42]. Long chain branching was reported to increase the dispersity, whilst short chain branching would not have much impact [43]. Having a DB of 15 % and a dispersity of 1.5 suggested dominant short chain branching. However, more detailed analysis has to be conducted in future work.

In order to accelerate the polymerisation rate, the reaction temperature was increased to 75 °C keeping the pressure at 3600 PSI. The conversion was successfully increased to 55 % and samples with an increased molar mass of 5.5 kg/mol, a dispersity of 2.2 and a DB of 17 % were obtained. Having a comparable DB to 65–3600, the molar mass increased, but also the dispersity.

Table 1
Compilation of samples polymerised by scRROP at different temperature and pressure, conversion, M_n, $Đ$ determined by SEC-MALS and the DB for the five data series polymerised in supercritical CO_2. In order to allow a comparability to bulk polymerisation (with lower reaction time but comparable conversion), the M_n, $Đ$ and DB range for reference samples from literature were added. The literature samples were polymerised at 65 °C and 85 °C [21].

Sample series [T-p of reaction]	Conversion after 24 h [%]	**M_n [kg/mol] after 24h**	**$Đ$ after 24 h**	**DB [%] after 24 h**
65–3600	40	3.8 ± 0.2	1.5 ± 0.1	15 ± 0.8
75–3600	55	5.5 ± 0.3	2.2 ± 0.1	17 ± 0.9
85–3600	80	6.2 ± 0.3	3.1 ± 0.2	18 ± 0.9
75–2000	55	73.0 ± 3.7[a]	3.3 ± 0.2	19 ± 1.0
85–2000	80	8.6 ± 0.4	6.6 ± 0.3	18 ± 0.9
Bulk from literature [21]	80	20–30	<2.5	10–12

[a] The phenomenon of the higher molar mass will be discussed in the main text.

Since the dispersity was above 1.5, termination only by recombination was not likely. Termination by disproportionation would lead to a dispersity of around 2.0 at relatively low conversion, but no disproportionation products were observed by ^{1}H NMR (see Fig. S16) [43]. Since, this increased dispersity is most likely caused by transfer reactions, it is reasonable, that the increased temperature favoured long chain branching.

Since a conversion of 55 % was not satisfying, the reaction temperature was increased further to 85 °C in sample 85–3600, and the conversion increased to 80 %. Following the trend discussed for samples 65–3600 and 75–3600, the molar mass increased to 6.2 kg/mol, the dispersity rose to a value of 3.1 and the DB to 18 %. The DB hence increased slightly by 3 % compared to 65–3600 and the dispersity was almost double, suggesting a further relative increase in long chain

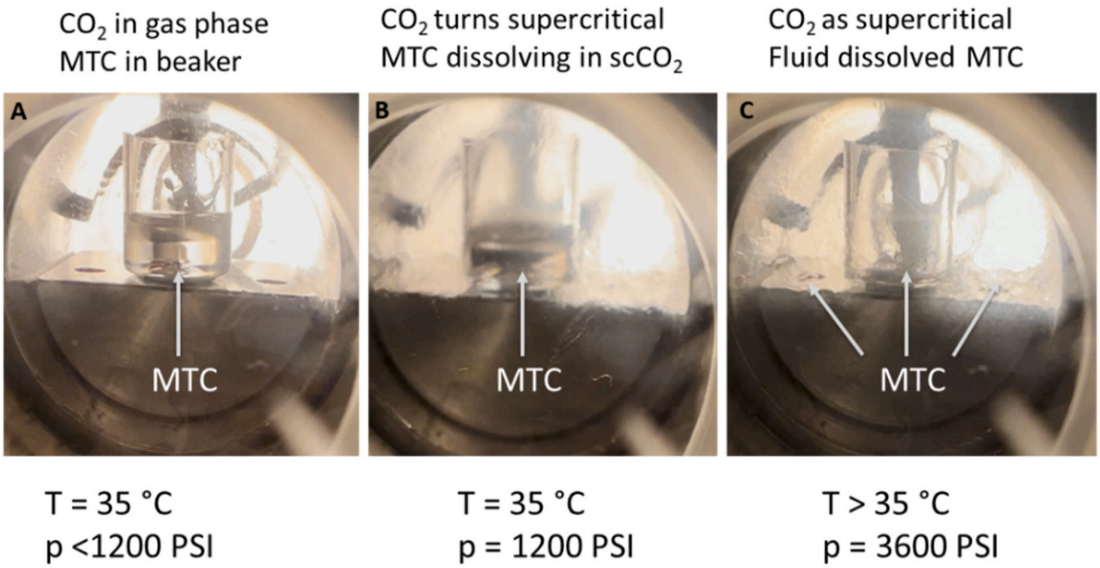

Fig. 3. Solubility experiment of MTC in $scCO_2$. A) The MTC was placed in a beaker within the high-pressure view cell at different times and pressures. First a two-phase system with MTC in the beaker and the gaseous CO_2 was observed. B) When the pressure was increased, the CO_2 became supercritical and dissolved the MTC from the beaker (process of dissolving in the middle picture), C) at higher temperatures the MTC stays dissolved (right picture).

branching. With that, temperature was identified as a crucial parameter that impacts the reaction and the polymers obtained from the scRROP.

The second most significant parameter to vary reaction conditions is pressure. The pressure of $scCO_2$ in the autoclave defines its density and also viscosity of this green solvent and the plasticised polymer that is formed. To investigate, the pressure was decreased to 2000 PSI for sample series 75–3600 and 85–3600. Series 65–3600 was excluded from these experiments, since the conversion was too low. When decreasing the pressure, a similar conversion of 55 % and 80 % was observed for samples 75–2000 and 85–2000, respectively. For sample 75–2000, an increased molar mass, dispersity and DB of 73.0 kg/mol, 3.3 and 19 % compared to entry 75–3600 was observed. With decreasing pressure, the molar mass was increased by a factor of more than 10 from 5.5 kg/mol to 73.0 kg/mol. While this may give the impression of an outlier, a polymer after 16h of polymerisation also gave a higher M_n of 30.0 kg/mol and will be discussed below. DB only increased slightly from 17 to 19 %, but dispersity increased notably from 2.2 to 3.3, suggesting the promotion of long chain branching.

Decreasing the pressure for sample 85–3600 to 2000 PSI, lead to an increased molar mass from 6.2 kg/mol to 8.6 kg/mol, a yet higher dispersity of 6.6 (compared to 3.1) and a similar DB of 18 %. Similar to the sample series at 75 °C, the DB was the same but the dispersity more than doubles. The increased dispersity again suggests that the density of $scCO_2$ influences the long chain branching.

Since both sample series 75–3600/2000 and 85–3600/2000 had a similar DB, but significantly different dispersities this suggests a shift in the ratio of long chain branching and short chain branching. This has to be treated as a hypothesis, because detailed structural insights were missing. In order to verify the branching discussion, further investigation is necessary. A promising approach to understand this mechanism on a deeper level would be rheology and viscosimetric analysis of higher molar mass samples and linear references, which will be target in future studies. From a synthetic point of view the density and solubility power of $scCO_2$ strongly depends on temperature and pressure. At 2000 PSI compared to 3600 PSI the density of CO_2 was significantly lowered from 0.66 to 0.35 g/ml at 85 °C and from 0.71 to 0.41 g/ml at 75 °C [41]. With that, it appeared reasonable that the low density of CO_2 fails to supress transfer reactions leading to high dispersity values and increased long-chain branching, but further analysis is needed. Comparing the molar mass of the samples to literature values, scRROP lead to decreased molar mass, increased dispersity and increased DB. Except for the sample 75–2000, all polymers prepared in $scCO_2$ had a number average molar mass below 10 kg/mol, which is less than 50 % of the reference with 20–30 kg/mol. At a comparable conversion, the dispersity of sample series 85–3600 was with 3.1 higher by a value of 0.6 and 85–2000 with a value of 6.6 more than twice the value of the thermal reference. The DB of the $scCO_2$ samples was 6–8 % higher with 18 % DB. All of these phenomena are likely an effect of the precipitation-type polymerisation in scRROP. When low molar mass samples with a lower dispersity are targeted, an increase in the applied pressure can help to impact the outcome of the reaction. However, to get further insights into the polymerisation mechanism kinetic studies were performed.

In the next step the evolution of the polymers (DB and molar mass) over the course of the reaction will be discussed. Controlling the branching reaction remains crucial to prepare better defined polymers obtained from RROP. Here, the evolution of branching as the most significant side reaction of RROP with increasing conversion was focussed upon (illustrated in Fig. 4A). Interestingly, a deviation from the exponential increase of DB with increasing conversion reported in earlier work was observed [21]. For sample series 65–3600 being in the low conversion domain (40 %), a scattered DB ranging from 8 % to 22 % was found. Increasing the reaction temperature to 75 °C (55 % conversion), the DB scattered less, being in the range of 11–21 %. Only the polymerisation of data series 85–3600 with the highest conversion (80 %) lead to polymers with a defined range of DB from 15 to 20 %. A second correlation was exposed in Fig. 4B. For sample series 65–3600, independent of the reaction time a comparable molar mass ranging from 2 to 5 kg/mol was obtained. When the reaction temperature was increased in the 75–3600 series, the molar mass scattered more being in the range of 4–8 kg/mol. Following this behaviour, for sample series 85–3600 a scattering molar mass ranging from 6 to 15 kg/mol was observed.

In combination, a relevant finding of this work becomes clearer: samples with either (i) a defined, low molar mass with a scattered DB at 65 °C or 75 °C, or (ii) samples with a defined DB and scattered, but increased, molar mass at 85 °C can be prepared. Interestingly, all the molar masses reported in this study are below the molar mass obtained with conventional RROP. Instead of growing to long polymer chains, the precipitation polymerisation stops the propagation process to generate lower molar mass samples with a M_n below 20.0 kg/mol and so effectively provides a method to control the molar mass without using chain transfer agents.

In order to understand this behaviour better, and with that the heterogeneous polymerisation, the polymerisation mechanism of scRROP is

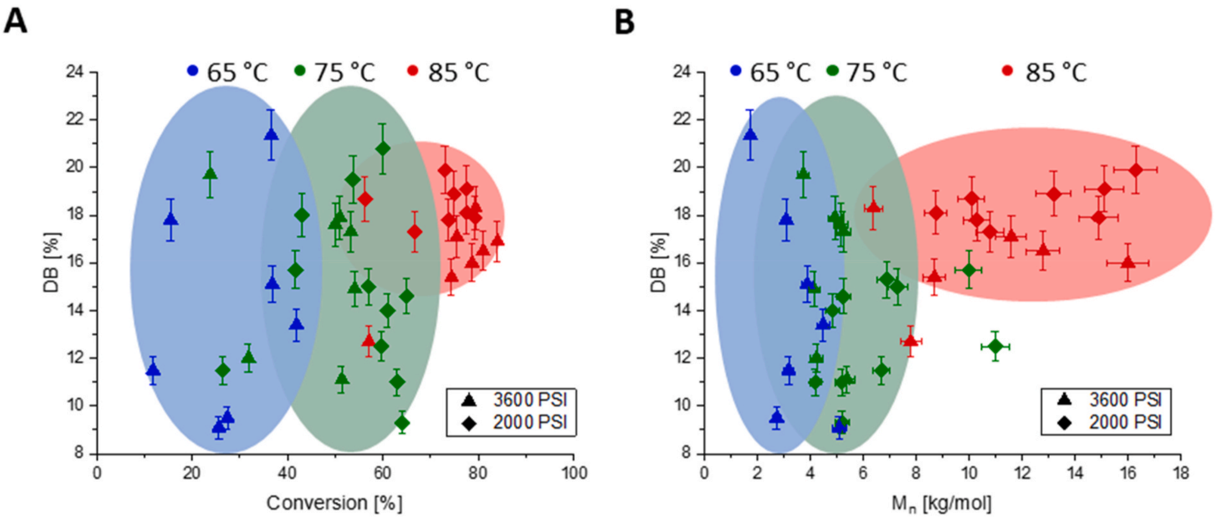

Fig. 4. Compilation of the resulting polymers depending on their reaction conditions ((blue: 65 °C, green: 75 °C, red: 85 °C): A) Dependency of DB with conversion, B) Dependency of DB with M_n deviating from the expected behaviour of radical polymerisation. All samples were grouped similar to Fig. 3 by their maximum conversion. No significant impact of the applied pressure was observed.

discussed next. Keeping in mind, that PMTC is a low T_g polymer with a T_g around - 65 °C [18] and most of the literature is focussed on the synthesis of high T_g polymers, a difference in the polymerisation behaviour is expected.

In the literature, there are various reports of precipitation polymerisation in $scCO_2$, focussing on a particle driven process causing a slow polymerisation rate in an induction period of the precipitation polymerisation [38,44,45]. As depicted in Fig. 5A, for the RROP of MTC, the conversion increased immediately after t_0 as it was expected for conventional free radical polymerisation. Different to conventional RROP, the reaction effectively stopped after approximately 6 h for sample series 65–3600 and after 1 h for sample series 75–3600/2000 and 85–3600/2000. An increase in the polymerisation rate at higher temperature was expected and observed by a steeper increase of conversion. However, the limitation of conversion was surprising. The cessation of polymerisation is not due to depletion of AIBN; there is more than sufficient amounts of AIBN to allow polymerisation to continue (66 % at 65 °C, 20 % at 75 °C and 0 % only for 85 °C after 6 h, calculation see SI 3.4) [42]. This suggests the reaction is encumbered by a phase segregation between monomer and initiator. With that, the initiator efficiency decreases dramatically and the reaction slows down to a stage, where no measurable conversion is observed. In agreement with the missing induction phase, that was postulated earlier, the reaction started right away. Rather than being accelerated by precipitation as known for high T_g polymers, we postulate that precipitation caused a deceleration effect brought on by phase segregation [38,45]. The effect of this phase segregation has been discussed in various works in literature [38,45,46].

However, these works were not comparable to the polymerisation of PMTC, since the polymer with a T_g of −65 °C could not form stable particles [18,39]. Kwon et al. faced a similar issue when copolymerising MDO with vinylpyrrolidone [39]. In their work, particles of a high quality were prepared for a copolymer system of MDO and vinylpyrrolidone as long as the T_g was around 50 °C. When the T_g decreased due to an increasing incorporation of MDO to a value of 8 °C, the formed particles merged and did not meet the requirements for their application for their work. Thus, they stopped looking into the details of the polymerisation mechanism for polymers with a T_g below 8 °C [39]. Following the decreasing yield at lower T_g, a similar effect to the scRROP of MTC is possible, but rather a suggestion towards a different polymerisation mechanism.

In an attempt to explain the mechanism of scRROP, we postulate a difference of two mechanisms for the precipitation polymerisation in $scCO_2$: (i) a particle-driven accelerated mechanism for high T_g polymers reported in literature [36,38,44,45,47,48] and (ii) a segregation-limited decelerated mechanism for the scRROP of MTC reported in this work. The differences in the mechanism were illustrated in Fig. 5B.

In brief, for mechanism (i), polymer precipitates and forms polymer particles. Once a critical number of particles is formed, they accelerate the polymerisation on its surface, causing the conversion to increase faster. Reaction takes place in, or on the surface of particles, or solely in the $scCO_2$ phase (detailed discussion see SI chapter 4) [36,38]. We postulate, that PMTC follows a different mechanism (ii): first CO_2 is pumped into the autoclave and temperature is increased until CO_2 becomes supercritical. It then dissolves the initiator as illustrated in Fig. 5B–I. The polymerisation starts and once PMTC precipitates from the monomer rich CO_2-phase it does not provide stable particles, but forms a slurry-like polymerisation product at the bottom of the reaction vessel. (Fig. 5B–II). Rather than accelerating the reaction, the formation of a polymer-rich solid phase, decreases the chain mobility and separates monomer from initiator. With that, the initiator efficiency is decreased and the reaction stops at a time point, where at least 66 % (for 65 °C) or 20 % (for 75 °C) AIBN had to be present following the Arrhenius equation (Fig. 5B–III) [42]. The effect of increased conversion with increasing temperature could be either due to increased chain mobility, or a higher radical flux, that allows a higher conversion of monomer in the same time frame.

4. Conclusion

In this work, kinetic insights into the polymerisation of MTC in $scCO_2$ were gained. Being a precipitation polymerisation, the reaction stopped after approximately 6 h, potentially caused by a segregation effect between initiator and monomer. The reaction temperature was the most important parameter to control the outcome of the reaction. A maximum conversion of 40 % was observed at 65 °C, 60 % conversion was observed at 75 °C and 80 % conversion was obtained at 85 °C. Increasing the temperature also led to polymers with higher molar mass ranging from 2 to 4 kg/mol at 65 °C, 4–8 for 75 °C and 6–15 kg/mol for samples polymerised at 85 °C. Since increasing temperature also favoured transfer to polymer leading to long chain branching, the dispersity also increased from 1.5 to 3.1 for sample series 65–3600 and 85–3600. The low dispersity of sample series 65–3600 suggests termination by recombination is dominant and favours short chain branching. Decreasing pressure led to higher molar mass samples, but also higher dispersities suggesting more transfer to polymer. High pressure appeared to be a suitable tool to supress transfer reactions leading to lower dispersity values and likely less long chain branching. Temperature on the other hand appeared to be the most important parameter to

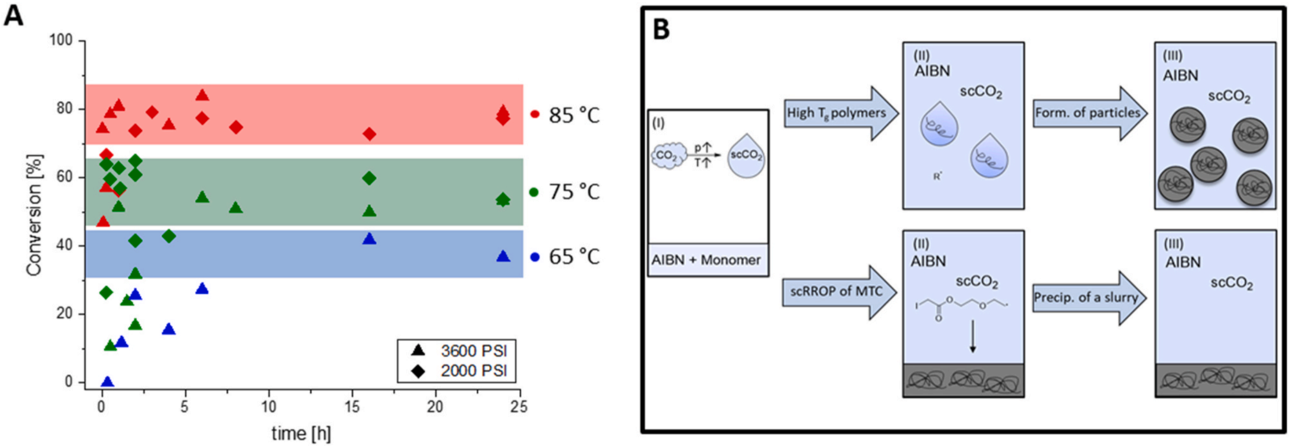

Fig. 5. A) Development of conversion over time at different reaction conditions (blue: 65 °C, green: 75 °C, red: 85 °C) for the polymerisation of PMTC exhibiting an immediate increase of conversion without induction period, B) Models for the precipitation polymerisation of high T_g polymers yielding polymer particles after the precipitation as reported in literature (top) and a model for low T_g polymer(-65 °C) leading to a slurry-like product as polymerisation product (bottom). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

control the conversion and molar mass. Except for samples polymerised at 85 °C, the DB scattered broadly between 8 and 22 %, not following the conversion dependency reported earlier. An effect, that could not be found for the polymerisation of CKAs in solution or bulk before was revealed at 85 °C: a reaction condition supressing the DB. When changing the pressure of sample series 85–3600/2000 a defined DB in the range of 15–20 % was observed. A trend of a decreased DB for sample series 85–3600 appeared, with a DB in the range of 15–17 %. In line with the lower dispersity at high pressure, transfer reactions were most likely supressed highlighting the potential of the use of $scCO_2$.

Polymerisations in $scCO_2$ appear to be an interesting method to solve challenges of RROP in terms of sustainability. Avoiding energy-intense drying processes and potentially toxic solvents from petroleum-based feedstocks in heterogeneous polymerisation helped to optimize polymerisation protocols of RROP. However, a deviating behaviour from typical polymerisation in CO_2 for high T_g polymers was observed for PMTC as low T_g polymer. Instead of following a particle-driven and accelerated polymerisation, a precipitation-deceleration effect was observed. We postulate, that conversion limitation was caused by a phase segregation between monomer and initiator which slows down the reaction until it effectively stops. A data set for further modelling was provided motivating investigations of low T_g polymers in $scCO_2$ and their mechanistic behaviour.

With that, the toolbox of RROP was broadened by the use of $scCO_2$ combining the advantages of polymerisation in supercritical fluids with RROP as tool to obtain degradable polymers. Embracing the potential to impact DB, molar mass and aiming for low dispersities should be adapted to other CKAs, potentially helping to synthesize new functional, degradable materials.

5. Notes

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The supporting information is available and contains additional information on synthetic aspects (incl. key data on all polymers discussed), additional ^{1}H NMR spectra, examples for all calculations.

CRediT authorship contribution statement

Fabian Mehner: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Bradley Hopkins:** Writing – review & editing, Methodology. **Morgan Reynolds-Green:** Writing – review & editing, Methodology. **Daniel J. Keddie:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Conceptualization. **Steven M. Howdle:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Jens Gaitzsch:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2024.127373.

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