

University of Groningen

RAFT Polymerization of a Biorenewable/Sustainable Monomer via a Green Process

Versteeg, Friso G; Hegeman, Niels C; Sebakhy, Khaled O; Picchioni, Francesco

Published in:
Macromolecular Rapid Communications

DOI:
[10.1002/marc.202200045](https://doi.org/10.1002/marc.202200045)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2022

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Versteeg, F. G., Hegeman, N. C., Sebakhy, K. O., & Picchioni, F. (2022). RAFT Polymerization of a Biorenewable/Sustainable Monomer via a Green Process. *Macromolecular Rapid Communications*, 43(13), [e2200045]. <https://doi.org/10.1002/marc.202200045>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

RAFT Polymerization of a Biorenewable/Sustainable Monomer via a Green Process

Friso G. Versteeg, Niels C. Hegeman, Khaled O. Sebakhy, and Francesco Picchioni*

A biorenewable polymer is synthesized via a green process using the RAFT principle for the first time in supercritical CO₂ at 300 bar and 80 °C. α -Methylene- γ -butyrolactone polymers of various chain lengths and molecular weights are obtained. The molecular weights vary from 10 000 up to 20 000 with low polydispersity indexes (PDI <1.5). Furthermore, the monomer conversion in supercritical CO₂ is substantially higher, respectively 85% for ScCO₂ compared to \approx 65% for polymerizations conducted in dimethyl formamide (DMF) solvent. Chain extensions are carried out to confirm the livingness of the formed polymers in ScCO₂. This opens up future possibilities of the formation of different polymer architectures in ScCO₂. The polymers synthesized in ScCO₂ have glass transition temperature (T_g) values ranging from 155 up to 190 °C. However, the presence of residual monomer encapsulated inside the formed polymer matrix affects the glass transition of the polymer that is lowered by increasing monomer concentrations. Hence, additional research is required to eliminate the remaining monomer concentration in the polymer matrix in order to arrive at the optimal T_g .

aspects is to use biorenewable monomers, like α -methylene-butyrolactones. Those biobased monomers are cyclic analogues of methyl methacrylate (MMA), containing a five membered exocyclic butyrolactone ring. α -Methylene- γ -butyrolactone (α -MBL) monomer can be found in extremely small quantities in tulips, hence it is also called Tulipalin A. A better way to obtain methylene lactones is to synthesize them from itaconic acid, which is present and readily available from biomass sources like rice and corn.^[8] A few studies have been performed on transforming itaconic acid into compounds similar to cyclic lactones.^[8–13] The polymerization of these monomers will lead to plastics with advanced thermal properties. On average the glass transition temperature of these cyclic lactones is \approx 195 °C. For the sake of comparison, poly-methylmethacrylate (PMMA) and polystyrene (PSTY) only have a glass

transition temperature of \approx 100 °C, making them unsuitable for higher temperature applications. Additionally, polymers obtained from α -methylene- γ -butyrolactone monomers possess solvent and scratch resistance and advanced optical properties.^[8,15]

By employing reversible addition–fragmentation chain-transfer (RAFT) polymerization technique, the control over the polymerization can be achieved.^[14–15] The molecular weight can be predetermined by choosing the right amount of RAFT agent, monomer, and initiator concentration, while maintaining chain end fidelity and a low polydispersity index (PDI). By reactivation of the chain end groups of the functional polymer, new monomers can be added to the already existing polymer (i.e., chain extension) to produce block-, graft-, and star- (co)polymers and more other complex architectures.^[16–18] However, many efforts in polymerizing this class of monomers still relies on the use of classical organic solvents with the corresponding, generally high, environmental impact. In this the use of a green solvent would ideally render the overall product and process to make it much more attractive from an environmental point of view.

Among all possible choices, the use of supercritical fluids, and more specifically supercritical carbon dioxide (ScCO₂), as an alternative solvent or extraction medium has been on the rise the past decade.^[19–22] One of the important aspects why CO₂ is being used is the general low parameter criteria to realize supercritical conditions ($P = 73$ bar and $T = 31$ °C) and the low-toxicity and nonflammable aspect. Supercritical CO₂ is a unique fluid with high diffusivity where it can be seen as a hybrid between a gas

1. Introduction

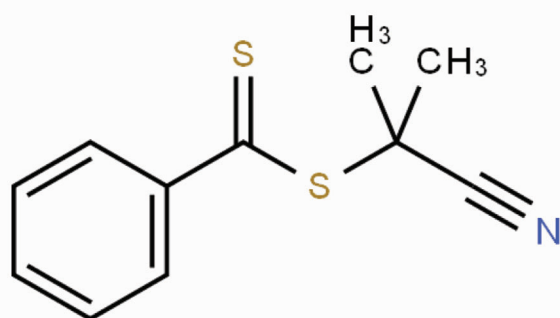
Current environmental constraints along with the depletion of fossil fuels necessitates the use of greener materials in society. Thus, research on biorenewable plastics has tremendously increased over the past 20–30 years, now that the consequences of using oil based plastics unfold on the environment.^[1–3] Not only is the focus placed on the recycling of already made plastics but also on the green chemistry' of producing new plastics from different biomass sources.^[4–6] Biobased monomers are the most sustainable, renewable, abundant, and ubiquitous biomass available in nature, as they are present in plants.^[7] Hence, one of those

F. G. Versteeg, N. C. Hegeman, K. O. Sebakhy, F. Picchioni
 Department of Chemical Engineering – Product Technology
 University of Groningen
 Nijenborgh 4, Groningen 9747 AG, The Netherlands
 E-mail: f.picchioni@rug.nl

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/marc.202200045>

© 2022 The Authors. Macromolecular Rapid Communications published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/marc.202200045



Scheme 1. Chemical structure of the RAFT agent used in this work.

and a liquid, meaning the density of a liquid and the viscosity of a gas. Above the critical point of CO_2 , it is possible to adjust the parameters for each specific process. Typically, higher pressures are being used for the polymerization reaction (≈ 300 bar) as that increases the solvation power of the ScCO_2 , due to an increase of the density. RAFT polymerization of styrene and methyl methacrylate in ScCO_2 have already been extensively researched but, to the best of our knowledge, the use of a biorenewable monomer for RAFT polymerization in ScCO_2 has not been reported yet which highlights the novelty of this work.^[23–30]

In this study, we report the first controlled radical polymerization of α -MBL via RAFT in ScCO_2 to produce thermally stable and sustainable polymers. Besides the ongoing transition to environmentally benign solvents by eliminating the need for organic solvents, an emerging interest is to replace conventional monomers (derived from fossil fuels) by biorenewable substitutes (derived from biomass) to produce sustainable polymers and natural alternatives to petroleum sourced plastics in a green environment. Furthermore, high conversions are reported in ScCO_2 ($>85\%$) in comparison to solution polymerization ($\approx 65\%$).

2. Experimental Section

2.1. Materials

α -Methylene- γ -butyrolactone (α -MBL) ($>95\%$ purity) was purchased from TCI Chemicals and used as received without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) free radical initiator was purchased from Sigma-Aldrich and was purified by recrystallization in methanol twice. 2-cyanoprop-2-yl dithiobenzoate (RAFT agent, see **Scheme 1** for chemical structure) was purchased from SigmaAldrich and used without further purification. Poly(dimethyl siloxane monomethyl methacrylate) ($M_n = 10\,000$ g mol⁻¹) stabilizer was purchased from Fluorochem and used without further purification. All chemicals were stored in a freezer at -18 °C.

2.2. Methods

RAFT-mediated polymerizations were carried out in a 100 mL stainless steel Parr batch reactor with maximum pressure of 350 bar and a temperature range of -10 to 350 °C. **Figure 1** shows a schematic representation of the reactor with: 1) being the compressor; 2) stirrer; 3) pressure indicator; 4) inlet for solution; 5)

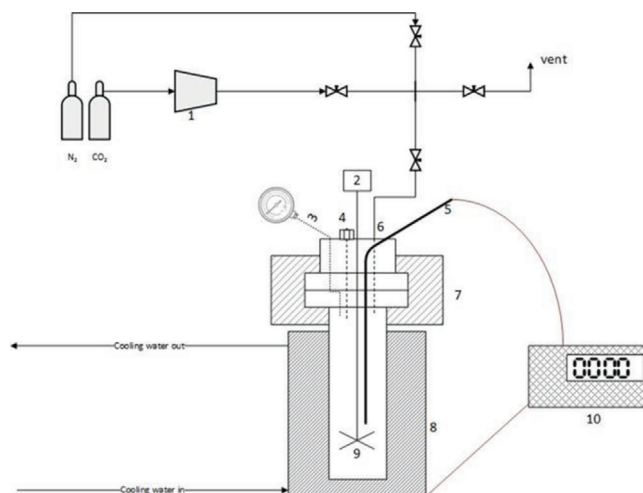


Figure 1. Schematic representation of the experimental setup.

thermocouple; 6) main inlet of reactor; 7) clamps for the reactor; 8) heating jacket; 9) stirrer; and 10) temperature controller.

2.3. RAFT-Mediated Polymerizations

2.3.1. Experimental Procedure for Polymerization of α -MBL in ScCO_2 at Different Temperatures

A 25 mL round bottom flask was charged with AIBN (0.04 g), RAFT agent (0.11 g), PDMS-MA (5 wt.% of α -MBL), and α -MBL (10 g). When the AIBN and RAFT agent were fully dissolved the flask was purged under Argon atmosphere and flushed for ≈ 30 –45 min. The reactor was leak tested by pressurizing the reactor to 150 bar. Afterward the solution was transferred into a 100 mL batch Parr reactor against a slow nitrogen purge flow to eliminate oxygen from creeping in. Then the reactor was sealed, pressurized, and heated to the desired temperature. When the desired temperature was reached, additional CO_2 was added into the system to reach the final reaction pressure of ≈ 300 bar. Agitation was set at 500 rpm and the reaction was left to proceed for 24 h to ensure full conversion of the monomer. After the reaction was completed, the reactor was cooled down to room temperature with a cooling jacket. When room temperature was reached, pressure was released slowly from the system until atmospheric pressure was attained. The reactor was opened and the polymer powder was discharged. The polymer was collected and dried in a vacuum oven at 200 °C overnight to remove impurities and residual monomer. This purification method was chosen among at least seven other methods. Eight milligrams of the product were dissolved in 2 mL dimethyl formamide (DMF) with 0.01×10^{-3} M LiBr, the solution was then filtered into a GPC vial for molecular weight analysis.

2.3.2. Experimental Procedure for Polymerization of α -MBL in ScCO_2 to Study the Effect of Reaction Time at 80 °C

The same preparation, as for the temperature influence experiments, were conducted, however, the temperature for this set of

experiments were all carried out at 80 °C. To determine polymerization rate the reaction was stopped at different reaction times. Conversions were calculated gravimetrically by drying in the vacuum oven at 200 °C.

2.3.3. Experimental Procedure to Target Various Molecular Weights

Finally, a set of experiments were conducted to target molecular weights between 10–25 kg mol⁻¹ by varying the monomer starting concentration and/or the RAFT initial concentration. The exact numbers are given in Table S1 (Supporting Information).

2.3.4. Experimental Procedure for the Chain Extension Experiments

Chain extensions were performed in solution. In a 25 mL round bottom flask 2 g of macroRAFT was dissolved in 15 g of DMF. When fully dissolved 2 g of additional monomer (α -MBL) were added together with AIBN in a ratio of macroRAFT to AIBN = [5]:[1]. The solution was then purged under Argon for 30 min and placed in an oil bath at 80 °C. The polymerization was left to proceed for 15 h before being quenched in an ice bath and the polymer precipitated out in cold methanol and filtered. Finally, the collected polymer was dried under vacuum at 100 °C overnight.

2.3.5. RAFT Polymerization of α -MBL in DMF

Two polymers were synthesized in DMF to compare conversion and polydispersity between the two different methods. A typical solution RAFT polymerization was carried out as follows: first, 2 g of α -MBL were dissolved in 10 g of DMF. To this solution, AIBN and the RAFT agent were added in a [5]:[1] molar ratio before purging this flask with Argon for 25 min. This solution was then stirred at 350 rpm for 24 h at 100 °C, then the polymer was extracted by precipitation in cold methanol and dried in a vacuum oven at 140 °C.

2.3.6. Polymers Characterization

To quantify the polymers being made, three different methods were used to analyze the polymers. Gel permeation chromatography (GPC), Differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). All GPC analysis was performed using an Agilent (Santa Clara, California, United States) model 1200 series with 3x PSS GRAM analytical linear columns (300 × 8 mm 10 μ m) at a flowrate of 1 mL min⁻¹ at 50 °C with an injection volume of 20 μ L. The eluent of the system was DMF with 10 × 10⁻³ M LiBr and Mn, Mw, and PDI were determined from refractive index chromatograms using polystyrene standards by using an Agilent 1200 refractive index detector with toluene as reference peak. DSC analysis of polymer samples was performed on a TA instruments Discovery DSC 25 equipped with a cooler and auto sampler. Sampler were prepared using Tzero aluminum pan and were analyzed in the following method: 100 to 220 °C

Table 1. Experimental results of RAFT polymerization of α -MBL in ScCO₂ after 24 h at 300 bar with stirring of 500 rpm. Concentrations of [α -MBL]:[CPDB]:[AIBN]=[419]:[2]:[1].

Entry	Mn [g mol ⁻¹]	PDI	T [°C]
T65	19 500	5.92	65
T70	28 900	4.91	70
T75	14 100	4.26	75
T80	14 000	1.38	80
T85	12 500	1.35	85
T90	14 000	1.38	90
T95	13 000	1.47	95
T100	14 100	8.0	100

Table 2. Experimental results of RAFT polymerization of α -MBL in DMF after 24 h at 100 °C with 350 rpm stirring.

Entry	Conversion [%]	Mn [g mol ⁻¹]	PDI
6	65	6200	1.37
7	70	11 000	1.49

at 10 °C min⁻¹ heating rate, 220 to 100 °C at 10 °C min⁻¹ cooling rate and finally 100 to 220 °C at 10 °C min⁻¹ heating rate. The T_g of the polymers was detected in the second heating cycle and processed by the software Trios v5.1.1.46572. Decomposition temperature was determined by thermogravimetric analysis on a Perkin Elmer TGA 4000. Under nitrogen atmosphere, samples were heated from 25 to 600 °C at 20 °C min⁻¹.

Data were processed using Pyris series TGA 4000 software. Finally, a ¹H NMR analysis was performed on an Oxford NMR AS 400 spectrometer operating at 400 MHz NMR spectra were recorded (8 scans) in deuterated DMSO-d₆. Elemental analysis was performed using a CHNS micro analyzer from Elementar. 2 mg were heated up to 1150 °C in a high-temperature combustion unit. The micro cube is equipped with three gas-specific adsorption columns. VarioMicro software was used to analyze the results.

3. Results and Discussion

3.1. Influence of Temperature

To find out the influence of the temperature on the RAFT polymerization a small study was performed using different temperatures. From **Table 1**, relatively high conversions (>85%) are reached after \approx 24 h. These values are significantly higher than the ones obtained in DMF (only 60–65%) after 24 h at higher temperature (**Table 2**). This statement holds true also in comparison to other published works,^[8] where only 50% monomer conversion was reached in benzene after 10–20 h before gelation of the polymerization medium took place. One key difference between ScCO₂ properties and that of DMF is the viscosity, ScCO₂ has a viscosity of \approx 0.05 cP being less viscous than DMF which has a viscosity of 0.67 cP at 40 °C, which may improve the diffusion and transfer of radical species and monomer mobility in the propagation steps, respectively.^[31–34] Another effect that ScCO₂ has on

Table 3. Results of kinetic experiments performed at 80 °C and 300 bar. Concentrations of $[\alpha\text{-MBL}]:[\text{CPDB}]:[\text{AIBN}] = [419]:[2]:[1]$ with stirring of 500 rpm.

Entry	Conversion [%]	M_n [g mol ⁻¹]	PDI	Time [h]
K_0.5	66%	14 800	1.61	0.5
K_1	72%	12 200	1.53	1
K_2	74%	13 000	1.50	2
K_3	81%	15 700	1.32	3
K_4	85%	20 000	1.40	4
K_5	93%	19 000	1.34	18

the system is the swelling of the polymer. Üzer et al. reported 9–25% swelling of PMMA in ScCO₂ in a range of 35–45 °C and 80–150 bar, while Shinkai et al. reported a swelling ratio of up to 25% at 300 bar.^[35,36] It is within reason to assume that during the polymerization process the produced polymer is also swelling, making the growing polymer chains more accessible for propagation with fresh monomer.

At higher temperatures the deviation tends to increase significantly. Below 80 °C no control was observed on the polymerization of α -MBL in ScCO₂. Above 100 °C, the control over the polymerization is lost. This may be due to the thermal degradation of the RAFT agent, for which a kinetic degradation constant of $2.57 \times 10^{-6} \text{ s}^{-1}$ at 60 °C has been reported.^[37] Another widely used dithio raft agent, cumyl dithiobenzoate (CDB), also underwent drastic thermal degradation when used in a temperature range of 90–120 °C.^[38] However, it must be noted that in DMF solution the RAFT agent was still active at 100 °C. When comparing conventional solution RAFT polymerization with ScCO₂ it seems that there is no difference in control over the polymerization in ScCO₂. Normally a homogeneous or bulk polymerization gives a better control, and thus a lower PDI, than heterogeneous polymerizations.^[39] This seems to confirm, albeit indirectly, our preliminary hypothesis that in ScCO₂, due to the swelling effect (vide supra), the polymerization seems to proceed in a more homogeneous way. Indeed, it is known that ScCO₂ has a plasticizing and swelling effect on the polymer particles and when combined with excellent mass-transfer this results in a high conversion RAFT polymerization when compared to conventional heterogeneous polymerization. Namely, plasticization may facilitate diffusion of monomer and initiator into the polymer phase of heterogeneous polymerization.^[40,41]

3.2. Kinetic Study

From the temperature dependence results it was concluded that 80 °C was the best temperature to conduct the kinetic experiments on the RAFT polymerization of α -MBL in ScCO₂. A kinetic study on the RAFT polymerization of α -MBL was performed at 80 °C at various reaction times, as shown in Table 3. In this table, the conversion, molecular weight and PDI are given.

From Table 3 the results of the kinetic experiment are shown. Noteworthy is that high level of conversions are reached after only 4 h. In Figures S3 and S4 (Supporting Information), the two plots are made in which the molecular weight vs the conversion and the $\ln([M]_0/[M]_t)$ is shown. Both graphs indicate clear limi-

Table 4. Results of experiments targeting different molecular weights at 80 °C and 300 bar, polymerizations run for 24 h with a stirring of 500 rpm.

Entry	M_n [g mol ⁻¹]	PDI
1	7500	1.41
2	10 000	1.50
3	14 000	1.38
4	14 700	1.26
5	18 600	1.22

tations in the control of the polymerization at larger conversion values and reaction times. ¹H NMR spectra of all experiments were taken and can be found in the supporting information Figures S5–S9 (Supporting Information). At longer reaction times higher conversions were observed as the peak area at 5.6 and 6.2 ppm decrease over time which corresponds to the C=C bond of the monomer, as seen in Figure 2. A few small peaks are observed in the spectra as well; this is attributed to the monomer not being >99% pure. The ¹H NMR spectra of the monomer can be found in the supporting information Figure S6 (Supporting Information).

However, due to losses of monomer during the ScCO₂ removal it is difficult to obtain accurate representations of the monomer conversion during the polymerization. Nevertheless, a consistent increase in molecular weight in time is observed for the kinetic experiments with one outlier at 0.5 hours.

3.3. Different Chain Lengths

A series of experiments were conducted to synthesize PMBL of various chain lengths between 10 and 20 kg mol⁻¹ polymers (under the assumption of 100% conversion). This was done by varying the monomer concentration and/or the raft concentration at 80 °C. The results of those are given in Table 4.

We might notice that the control of the polymerization seems to improve (relatively lower PDI values) when targeting higher molecular weights.

3.4. Chain Extension

A key feature of RAFT polymerization is the ability to reinitiate the polymer chain with AIBN to continue the propagation. This opens up the ability to make different kind of polymer architectures like block and star polymers.^[25] In this study chain extensions were done with additional monomer of α -MBL in solution. For the chain extension two MacroRAFT samples were chosen that were synthesized in ScCO₂ and dissolved in DMF with additional monomer and AIBN. The results of these experiments are shown in Table 5.

In Figure 3, the GPC graphs are plotted against the original MacroRAFT being used. The GPC traces display an increase of molecular weight of the PMBL sample. Dissolving of the made MacroRAFT and reinitiating of this polymer showed the chain-end fidelity of the polymers synthesized in supercritical CO₂ with relative narrow PDI's and close molecular weight compared to

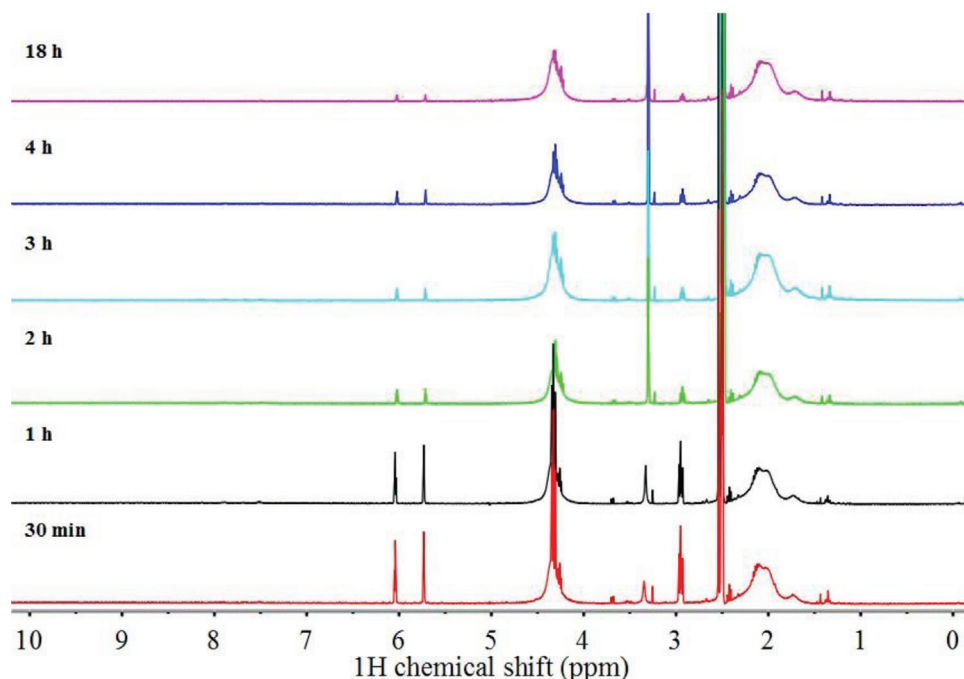


Figure 2. Stack plot of ^1H NMR spectra in d_6 -DMSO.

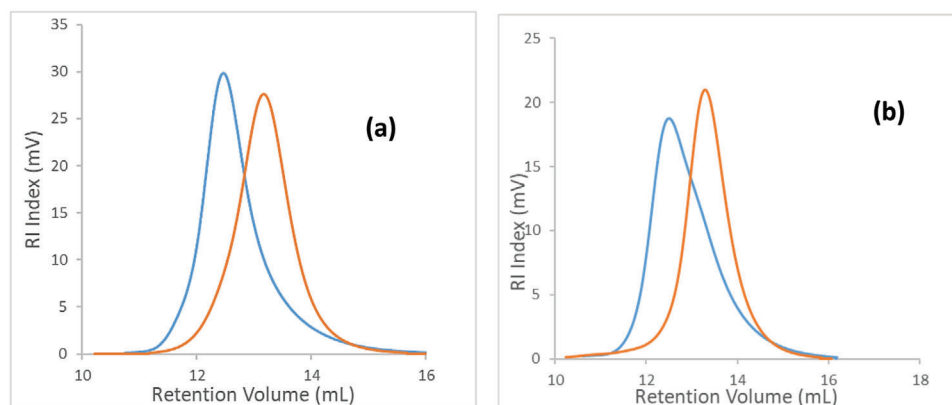


Figure 3. Chain extension experiments. a) CE_1 and b) CE_2.

Table 5. Results of Chain-Extension experiments. Reactions performed at $80\text{ }^\circ\text{C}$ in a 25 mL reactor for 15 h with stirring of 350 rpm.

Entry	M_n MacroRAFT [g mol^{-1}]	M_n [g mol^{-1}]	PDI
CE_1	14 800	22 500	1.6
CE_2	13 000	18 433	1.7

theoretical weight. In future work chain extensions experiments in supercritical CO_2 will be considered as well as the use of different kind of monomers.

To ensure that the polymerization was indeed a success, IR spectra and ^1H NMR of the monomer and of the polymers were recorded and compared in **Figure 4** and **Figure S10** (Supporting Information) with **Figure S11** (Supporting Information).

The distinctive $\text{C}=\text{C}$ peak that is present in the monomer α -MBL at 1666 cm^{-1} cannot be found anymore in the spectrum of the formed polymer, confirming that the polymerization was successful.

In **Figure S11** (Supporting Information), a ^1H NMR is taken from entry 3 of the RAFT polymerization of α -MBL in supercritical CO_2 . It is clear that some residual monomer is left inside the polymer as there are two distinctive peaks at 5.6 and 6.2 ppm that indicates the $\text{C}=\text{C}$ bond of α -MBL. Nonetheless the backbone of the polymer can also be found at the 2 ppm region, indicating that RAFT polymerization did occur. By dissolving the formed polymer and precipitate it back into methanol, the residual monomer and impurities were removed as can be seen in **Figure S12** (Supporting Information). Furthermore, another way of removing the monomer from the polymer is by using a vacuum oven at $200\text{ }^\circ\text{C}$ for 3 h see **Figure S13** in Supporting Information.

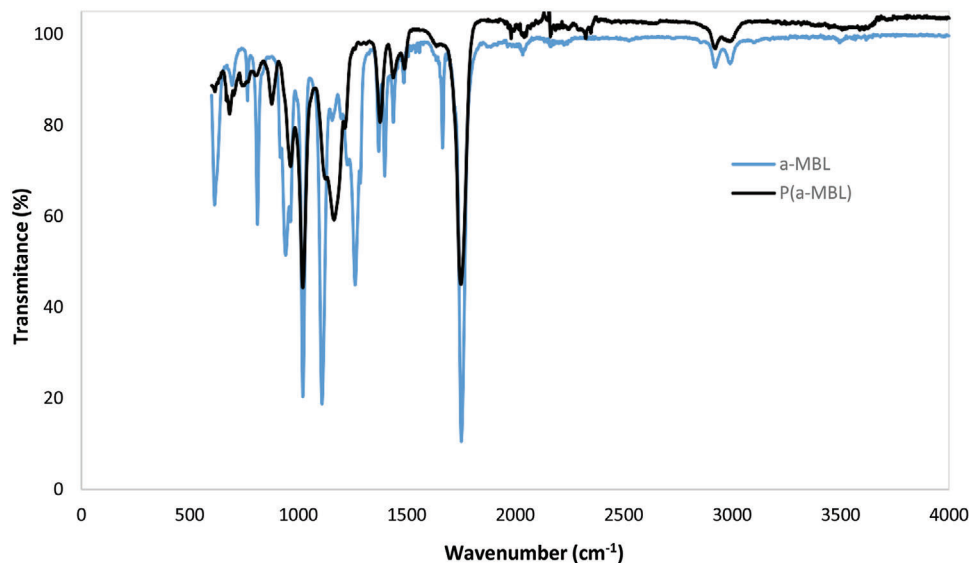


Figure 4. IR spectrum of α -MBL and PMBL.

Poly(methylene butyrolactones) are known for their high glass transition temperatures and solvent resistance.^[8] Typically glass transition temperatures are ≈ 195 °C, where the estimated entanglement molecular weight from rheological measurements is ≈ 10.6 kg mol⁻¹.^[15] For the RAFT polymerizations in supercritical CO₂, lower T_g is observed than is expected (Figure S14, Supporting Information).

This is due to the low residual monomer concentration inside the polymer. It has been shown that residual monomer in the polymer can act as a plasticizer and decrease the T_g significantly.^[41–44]

Due to the robust nature of the polymer, when venting off the CO₂, a hard rock solid is formed at the bottom of the reactor in which it is shown that residual monomer is getting entrapped. On the ¹H NMR graphs, distinctive monomer peaks are shown that indicates the presence of α -MBL. To further quantify this theory, a small part of the polymer is dissolved in DMF and stirred overnight at 100 °C before being precipitated in cold methanol and dried in the vacuum oven overnight at 100 °C. The collected polymer was analyzed again in the DSC and a T_g of 195 °C was found, indicating no residual monomer being left (see supporting info). In Figure S15 (Supporting Information), the difference is shown of entry 3 in glass transition temperature before and after purification. A clear shift to the desired 195 °C is evident.

Also two different values for the T_g of the poly(α -MBL) are shown in DMF. The M_n of this entry (6) is 6200 g mol⁻¹ which is below the entanglement molecular weight resulting in a lower T_g .^[15] When entry 11 was above M_c (11 000 g mol⁻¹), the T_g corresponds to the previously reported value of 195 °C.

4. Conclusion

Biomass-derived monomers based on five-membered γ -butyrolactone ring (e.g. α -MBL) represent suitable and attractive candidates to replace sources of fossil origin. We envisage a state-of-art process using a green solvent (ScCO₂) to polymerize bio renewable/sustainable monomer (α -MBL) in a controlled

fashion with the RAFT technique. Various polymers of molecular weights varying from 10 000 up to 20 000 g mol⁻¹ were produced at 80 °C with low polydispersity indexes (PDI < 1.5). Also the effect of the reaction temperature was studied, where the ideal temperature for this polymerization is between 80 and 95 °C. Furthermore, the conversion of the polymerization in supercritical CO₂ is substantially higher, respectively 85% for ScCO₂ compared to $\approx 65\%$ for polymerizations carried out in DMF. The livingness of the formed polymers was confirmed by chain extension experiments in solution, with a clear growth in molecular weight before and after. This further indicates that controlled radical polymerization of a high temperature stable polymer is possible in supercritical CO₂ and opens up possibilities of the formation of different polymer architecture structures in CO₂. The polymers synthesized in ScCO₂ have T_g values varying from 155 up to 190 °C. However, the presence of residual monomer encapsulated inside the formed polymer matrix affects the glass transition of the polymer that lowers it. Therefore, additional research is required to control the remaining monomer concentration in the polymer matrix in order to arrive at the optimal T_g without adding extra purification steps. Possibly this can be realized via changes to the experimental procedure used and/or changes to the set-up to overcome this effect. Finally, those sustainable polymers can find potential applications at high temperatures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

α -methylene- γ -butyrolactone, biorenewables, glass transition (T_g), RAFT, supercritical CO₂, sustainability

Received: January 19, 2022
Revised: April 4, 2022
Published online: June 9, 2022

- [1] M. Hoel, S. Kverndokk, *Resour. Energy Econ.* **1996**, *18*, 115.
- [2] L. Allen, M. J. Cohen, D. Abelson, B. Miller, *The World's Water* **2012**, 73.
- [3] N. Raddadi, F. Fava, *Sci. Total Environ.* **2019**, *679*, 148.
- [4] R. V. Nonato, P. E. Mantelatto, C. E. V. Rossell, *Appl. Microbiol. Biotechnol.* **2001**, *57*, 1.
- [5] W. Wei, C. C. K. Keh, C.-J. Li, R. S. Varma, *Clean Technol. Environ. Policy* **2004**, *6*, 250.
- [6] F. L. Hatton, *Polym. Chem.* **2020**, *11*, 220.
- [7] H. Fouilloux, C. M. Thomas, *Macromol. Rapid Commun.* **2021**, *42*, 2000530.
- [8] J. T. Trotta, M. Jin, K. J. Stawiasz, Q. Michaudel, W.-L. Chen, B. P. Fors, *J. Polym. Sci. Part A Polym. Chem.* **2017**, *55*, 2730.
- [9] S. Xu, J. Huang, S. Xu, Y. Luo, *Polymer (Guildf)*. **2013**, *54*, 1779.
- [10] G. Qi, M. Nolan, F. J. Schork, C. W. Jones, *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 5929.
- [11] J. Mosnáček, K. Matyjaszewski, *Macromolecules* **2008**, *41*, 5509.
- [12] J. Mosnáček, J. Ae Yoon, A. Juhari, K. Koynov, K. Matyjaszewski, *Polymer (Guildf)*. **2009**, *50*, 2087.
- [13] D. C. Green, K. W. Allen, J. Chem Soc, C. Commun, M. L. Kaplan, R. C. Haddon, F. Wudl, E. D. Feit, J. Org, U. Pittman, W. J. Patterson, S. P. McManus, *J. Polym Sci and M.*
- [14] M. K. Akkapeddi, *Macromolecules* **2002**, *12*, 546.
- [15] M. Fetizon, M. Golfier, J. M. Louis, *Tetrahedron* **1975**, *31*, 171. 15 J. T. Trotta.
- [16] G. Moad, J. Chiefari, Y. Chong, J. Krstina, R. T. Mayadunne, A. Postma, E. Rizzardo, S. H. Thang, <https://doi.org/10.1002/1097-0126>
- [17] J. Chiefari, Y. K. (B) Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559.
- [18] Y. K. Chong, T. P. T. Le, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1999**, *32*, 2071.
- [19] L. Barner, C. Barner-Kowollik, T. P. Davis, M. H. Stenzel, *Australian Journal of Chemistry* **2004**, *57*, 19.
- [20] G. Moad, E. Rizzardo, S. H. Thang, *Chem. – An Asian J.* **2013**, *8*, 1634.
- [21] H. Pekar, M. P. Srinivasan, J. M. Smith, B. J. Mccoy, *AIChE J.* **1992**, *38*, 761.
- [22] J. M. Desimone, Z. Guan, C. S. Elsbernd, *Science (80-)* **1992**, *257*, 945.
- [23] S. P. Nalawade, F. Picchioni, L. P. B. M. Janssen, *Prog. Polym. Sci.* **2006**, *31*, 19.
- [24] J. L. Kendall, D. A. Canelas, J. L. Young, J. M. Desimone, *Chem. Rev.* **1999**, *99*, 543.
- [25] A. M. Gregory, K. J. Thurecht, S. M. Howdle, *Macromolecules* **2008**, *41*, 1215.
- [26] K. J. Thurecht, A. M. Gregory, W. Wang, S. M. Howdle, *Macromolecules* **2007**, *40*, 2965.
- [27] T. Arita, S. Beuermann, M. Buback, P. Vana, *Macromol. Mater. Eng.* **2005**, *290*, 283.
- [28] T. Arita, S. Beuermann, M. Buback, P. Vana, *E-Polymers* **2004**, *4*, 1.
- [29] G. Jaramillo-Soto, P. R. García-Morán, F. J. Enríquez-Medrano, H. Maldonado-Textle, M. E. Albores-Velasco, R. Guerrero-Santos, E. Vivaldo-Lima, *Polymer (Guildf)*. **2009**, *50*, 5024.
- [30] P. B. Zetterlund, F. Aldabbagh, M. Okubo, *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 3711.
- [31] E. Heidaryan, T. Hatami, M. Rahimi, J. Moghadasi, *J. Supercrit. Fluids* **2011**, *56*, 144.
- [32] C. Yang, G. He, Y. He, P. Ma, *J. Chem. Eng. Data* **2008**, *53*, 1639.
- [33] S. I. Cauët, K. L. Wooley, *J. Polym. Sci. A. Polym. Chem.* **2010**, *48*, 2517.
- [34] J. Collins, T. G. Mckenzie, M. D. Nothling, S. Allison-Logan, M. Ashokkumar, G. G. Qiao, *Macromolecules* **2019**, *52*, 185.
- [35] T. Shinkai, K. Ito, H. Yokoyama, *J. Supercrit. Fluids* **2014**, *95*, 553.
- [36] G. Akman, O. Hortaçsu, *J. Supercrit. Fluids* **2006**, *38*, 119.
- [37] Y. Zhou, J. He, C. Li, L. Hong, Y. Yang, *Macromolecules* **2011**, *44*, 8446.
- [38] J. Xu, J. He, D. Fan, W. Tang, Y. Yang, *Macromolecules* **2006**, *39*, 3753.
- [39] M. Hölderle, M. Baumert, R. Mülhaupt, *Macromolecules* **1997**, *30*, 3420.
- [40] M. Aerts, *Chemical Reactor Engineering* <https://doi.org/10.6100/IR723144>
- [41] A. I. Cooper, *J. Mater. Chem.* **2000**, *10*, 207.
- [42] D. T. Turner, A. Schwartz, *Polymer (Guildf)*. **1985**, *26*, 757.
- [43] M. E. Valencia Zapata, J. H. Mina Hernandez, C. D. Grande Tovar, C. H. Valencia Llano, J. A. Diaz Escobar, B. Vázquez-Lasa, J. San Román, L. Rojo, *Int. J. Mol. Sci.* **20**, 2938, <https://doi.org/10.3390/IJMS20122938>
- [44] A.-D. Ayman, *Electron. Physician* **2017**, *9*, 4766.