High Temperature Initiator-Free RAFT Polymerization of Methyl Methacrylate in a Microwave Reactor

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The reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate (MMA) was investigated under microwave irradiation. At first, a comparison was made between microwave and thermal heating for the RAFT polymerization of MMA with azobis(isobutyronitrile) (AIBN) as initiator and 2-cyano-2-butyldithiobenzoate (CBDB) as RAFT agent, revealing comparable polymerization kinetics indicating the absence of non-thermal microwave effects. Second, the CBDB-mediated RAFT polymerization of MMA was investigated at high temperatures (120°C, 150°C, and 180°C, respectively) in the absence of a radical initiator, showing a linear increase of the molar masses with conversion. The polydispersity indices remained below 1.5 up to 25% MMA conversion at 120°C and 150°C, indicating a controlled polymerization. This control over the polymerization was confirmed by the ability to control the molar masses by the concentration of RAFT agent.

Introduction

The control over polymer structure and architecture is one of the major aspects in contemporary polymer science because it allows an accurate tuning of the macroscopic properties. As a result, the use of controlled radical polymerization (CRP) techniques flourished in the past decade. CRP provides excellent control over the polymer structure based on a wide variety of monomers, such as acrylates, methacrylates, and styrenics. The major advantages of CRP are the relatively simple experimental procedures as well as the tolerance to almost all functional groups. The most commonly used CRP techniques are atom transfer radical polymerization (ATRP),[1,2] nitroxide-mediated polymerization (NMP),[3,4] and reversible addition–fragmentation chain transfer polymerization (RAFT).[5–7] RAFT has gained increased attention in recent years owing to its versatility for polymerizing a large variety of monomers, including difficult to control monomers such as vinyl acetate[8,9] and vinyl pyrrolidone.[10,11] The RAFT polymerization process includes several different reaction steps of which a simplified version is represented in Scheme 1. During the initial stage of the RAFT polymerization, radicals (I•) are formed, which react with monomer until they are stabilized by reaction with the RAFT agent (2-cyano-2-butyldithiobenzoate, CBDB, in the present study) as represented in Step 1. Subsequently, the leaving group of the RAFT agent will form a radical that initiates a new oligomeric chain (Step 2) and this equilibrium will evolve into the final RAFT equilibrium as represented in Step 3. In this final equilibrium, the

majority of polymer chains are in dormant states, whereby most of the dormant polymers are end-capped with dithiobenzoate and only a minor fraction is present as dormant radical with two polymer chains attached to the RAFT agent. Only this minor dormant radical fraction equilibrates to free radical polymer chains that can react with monomer as well as with dormant polymer chains with the dithiobenzoate. As a result of this equilibrium, there is only a small concentration of free radical polymer chains in solution and, thus, the rate of termination is suppressed, leading to control over the polymerization. In general, RAFT polymerizations are performed at intermediate temperatures ranging from ambient temperature up to 90°C in the presence of a radical initiator such as azobis(isobutyronitrile) (AIBN). Higher temperatures are mostly avoided because it is known that thermolysis of the RAFT agent can occur above 120°C.[12–15] Nonetheless, Vana and coworkers reported the autoinitiated RAFT polymerization of styrene at temperatures ranging from 120°C to 180°C, whereby no substantial decomposition of the RAFT agent was observed.[16] Furthermore, Busch, Barner-Kowollik and coworkers reported a linear increase of the molar mass with conversion for the polymerization of ethene at 175°C in the presence of a fluorinated RAFT agent.[17]

The use of microwave irradiation as an alternative to convective thermal heating has been demonstrated to sometimes result in higher yields, improved selectivity, and faster reactions in organic chemistry[18–23] and polymer chemistry.[24–27] However, only a limited number of studies have been reported
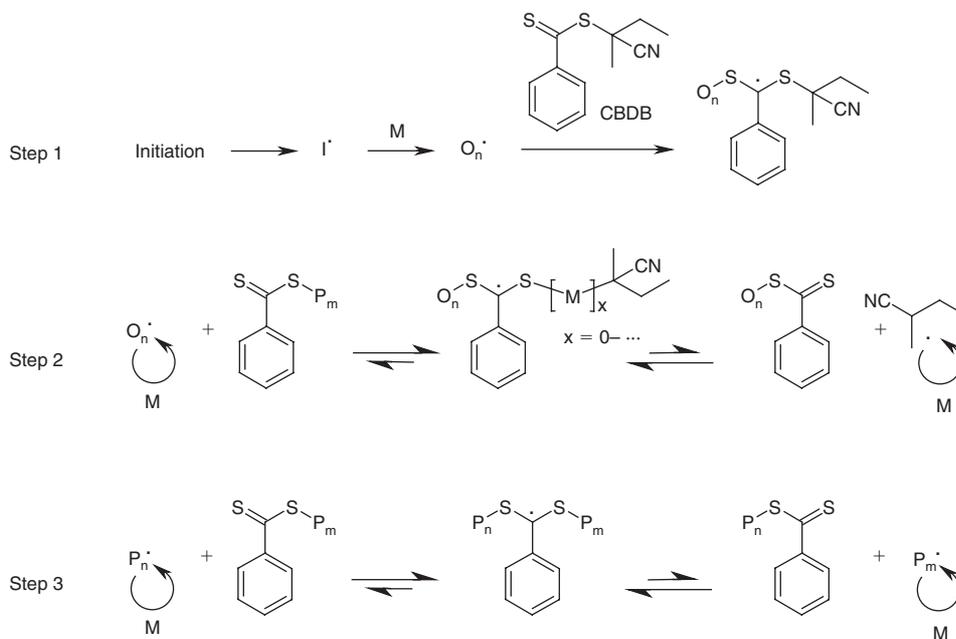
Scheme 1. Simplified schematic representation of the reversible addition–fragmentation chain transfer (RAFT) polymerization process. Step 1 represents the initiation and oligomerization as well as oligomer addition to the RAFT agent; Step 2 represents the initial equilibration between the leaving group of the RAFT agent and the oligomer radicals; Step 3 shows the final RAFT polymerization equilibrium. I = initiating group, M = monomer, O_n = oligomer chain, CBDB = 2-cyano-2-butyldithiobenzoate RAFT agent, and P = polymer chain.

dealing with the effect of microwave irradiation on the RAFT polymerization process.[28–31] Even though an acceleration of the microwave-assisted polymerization was found in these studies, the temperature determination in the microwave-assisted polymerizations was not unambiguous owing to the use of a conventional kitchen microwave[28] or due to the use of simultaneous cooling in combination with temperature determination at the outside of the reaction vessel via an IR probe.[29–31] Nonetheless, Perrier and coworkers demonstrated an ultra-fast microwave RAFT polymerization procedure that could not be reproduced with conventional heating at elevated temperatures.[30]

In the present study, we investigated the effect of microwave irradiation on the RAFT polymerization of methyl methacrylate (MMA) using CBDB as RAFT agent, AIBN as initiator, and toluene as solvent. Besides, we report a simple high-temperature initiator-free RAFT polymerization procedure for MMA. The control over the polymerization and the initiation mechanism as well as potential side reactions are discussed.

Experimental

Materials

MMA (Aldrich 99%) was purified by passing over basic alumina. Azobis(isobutyronitrile) (Aldrich) was recrystallized from methanol. 2-Cyano-2-butyl dithiobenzoate was prepared in a similar way to that described in the literature for a related compound.[32] Analytical grade solvents were purchased from Biosolve Ltd. All solutions were deoxygenated by bubbling for 30 min with argon gas before use.

Instrumentation

The microwave-assisted polymerizations were performed using the Biotage Initiator Sixty. Polymerizations were performed under temperature control utilizing an IR temperature sensor.

Size exclusion chromatography (SEC) was measured on a Shimadzu system with an SCL-10A system controller, an LC-10AD pump, an RID-6A refractive index detector, an SPD-10A UV detector, and a PLgel 5 µm Mixed-D column with chloroform/triethylamine/2-propanol (94:4:2) as eluent at a flow rate of 1 mL min^{-1} and the column oven set to 50°C (poly(MMA) (PMMA) calibration).

^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer using deuterated chloroform as solvent.

Microwave Polymerization with AIBN

To obtain an inert atmosphere, all microwave vessels were filled in a Chemspeed ASW2000 automated synthesizer. The hood of the synthesizer was flushed for at least 30 min with argon. From stock solutions of MMA (monomer), AIBN (initiator), and CBDB (RAFT agent) in toluene, a total volume of 4.2 mL was transferred into the microwave vessels, prefilled with a stirring bar, resulting in 2.2 M concentration of monomer with a RAFT:initiator ratio of 1:0.25. These vessels were capped inside the synthesizer and transferred to the autosampler of the Biotage Initiator Sixty and heated to 70°C for different predefined reaction times. After the polymerization, samples were taken from the microwave reactors (100 µL crude sample) and diluted (1.0 mL chloroform) for GC analysis to calculate the monomer conversions. A second sample (100 µL crude sample) was withdrawn from the reactors and diluted (1.0 mL chloroform/triethylamine/2-propanol (94:4:2) mixture) for SEC analysis in order to calculate the molar masses and polydispersity indices against PMMA standards.

Microwave Polymerization without AIBN

The polymerizations without AIBN were performed in a similar manner to that described above. The polymerization

mixtures were prepared in the ASW2000 synthesis robot with a CBDB concentration of $0.5 \times 10^{-2}, 1.0 \times 10^{-2}, 2.0 \times 10^{-2}$, and 4.0×10^{-2} mol L^{-1}. The microwave polymerizations were performed at 120°C, 150°C, and 180°C. Besides the SEC sample, a sample (100 µL crude sample) was taken after the polymerization from the microwave reactors and diluted (500 µL [D3]chloroform) for ^{1}H NMR analysis to calculate the monomer conversions from the signals of the COOCH_3 of the polymer and the monomer.

Results and Discussion

Comparison of Microwave and Thermal Heating

The effect of microwave heating on the RAFT polymerization process was investigated for the polymerization of MMA with CBDB as chain-transfer agent and AIBN as initiator in toluene. Therefore, the polymerization kinetics under microwave irradiation were determined using the previously optimized polymerization conditions, namely 70°C, 2.2 M monomer concentration and [MMA]:[CBDB]:[AIBN] = 100:1:0.25.[33,34] As a result of the relatively low polymerization temperature, only little microwave power (less than 20 W) was applied to the polymerization mixture after the initial heating ramp. The resulting microwave polymerization kinetics were compared with the previously reported conventionally heated RAFT polymerization as depicted in Fig. 1. The first-order kinetic plot, Fig. 1a, shows a close agreement between conventional thermal heating and microwave heating, indicating that microwave irradiation does not accelerate the polymerization process, which concurs with the growing concept that microwave irradiation does not influence homogeneous reactions, i.e. the non-existence of non-thermal microwave effects.[35–40] In addition, comparable polydispersity indices were obtained for the thermal and microwave polymerizations, indicating a similar control over the polymerizations.

The observed differences in the number average molecular weight (M_n) against conversion plot for the different thermal polymerizations are in the same range scattered around the theoretical number average molecular weight ($M_{n,th}$) as the difference with the microwave polymerization. Therefore, no conclusions can be drawn on the effect of microwave irradiation on the molar masses of the resulting PMMA. The relatively large error in the SEC data can be ascribed to measuring the polymers at different times and, unfortunately, analyzing with outdated calibration curves. Based on the kinetic investigations, it can be concluded that microwave heating with low microwave power does not influence the RAFT polymerization process investigated.

High Temperature Initiator-Free RAFT Polymerization

As microwave irradiation does not influence the RAFT polymerization, the possibility of attaining higher reaction temperatures with the microwave synthesizer was explored. Thermal polymerization of MMA under ambient pressure is limited to the boiling point of MMA, namely 100°C. However, the microwave oven utilized allows superheating, i.e. heating beyond the boiling point, of the polymerization mixture because it operates with closed reaction vessels. To avoid a high radical concentration at higher temperatures, the polymerizations were performed in the absence of a radical initiator. Finally, the polymerization was further simplified by exclusion of the solvent; thus, a solution of CBDB in MMA was investigated. The investigated polymerization temperatures were 120°C, 150°C, and 180°C and the CBDB
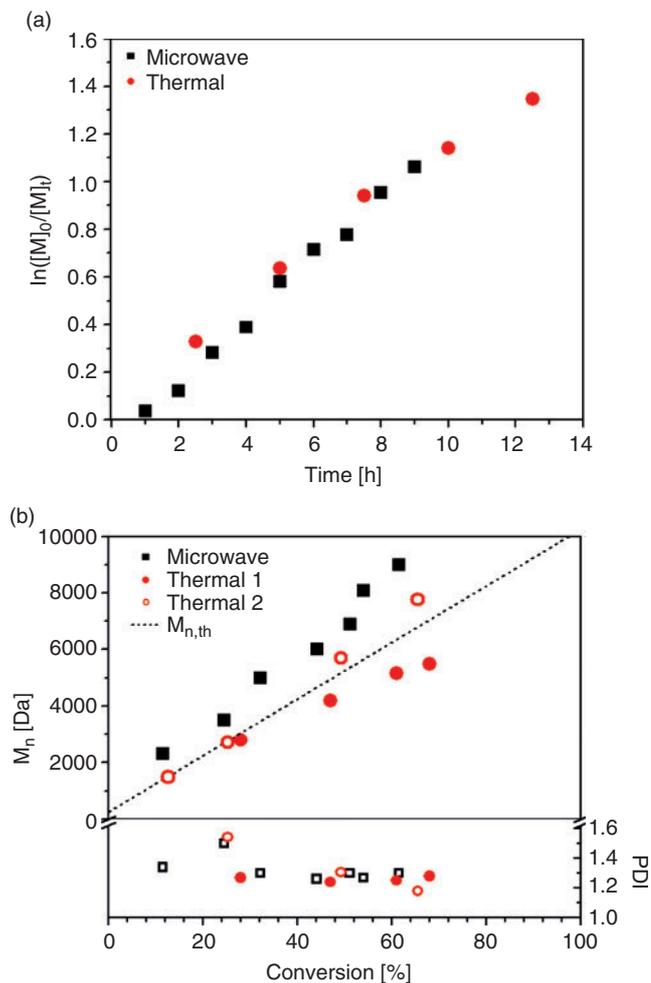

Fig. 1. Kinetic plot for the reversible addition–fragmentation chain transfer (RAFT) polymerizations of methyl methacrylate (MMA) in toluene using 2-cyano-2-butyldithiobenzoate (CBDB) as RAFT agent and azobis(isobutyronitrile) (AIBN) as initiator at 70°C with conventional thermal heating and microwave irradiation heating (a). [MMA]:[CBDB]:[AIBN] = 100:1:0.25; [MMA] = 2.2 M. Molar mass and polydispersity index versus conversion plot for these polymerizations with 'Thermal 1' as averaged data from ref. [33] and 'Thermal 2' from ref. [34] (b).

concentration was set to 4.0×10^{-2} mol L^{-1}, corresponding to a [MMA]:[CBDB] ratio of 234. Fig. 2 shows the first-order kinetic plots and the M_n against conversion plot for the RAFT polymerization of MMA at 120°C, 150°C, and 180°C, respectively. Surprisingly, significant monomer conversions were obtained at all three temperatures in the absence of a radical source. In contrast, a reference experiment of heating MMA to 150°C resulted in only 2% conversion after 4 h, confirming a previous report on the thermal polymerization of MMA.[41] As indicated by the successful RAFT polymerizations in the absence of a radical initiator, another radical source should have supplied the radicals to start the polymerization. Even though thermal decomposition of dithiobenzoate RAFT agents does occur via an elimination process at temperatures higher than 120°C,[12,14,15] the formation of radicals from the thermal decomposition of CBDB is unlikely. The potential formation of radicals by the decomposition of the RAFT agent by UV irradiation[42,43] from, for example, sunlight can be excluded because the microwave polymerizations are performed in the dark. Therefore, it is proposed
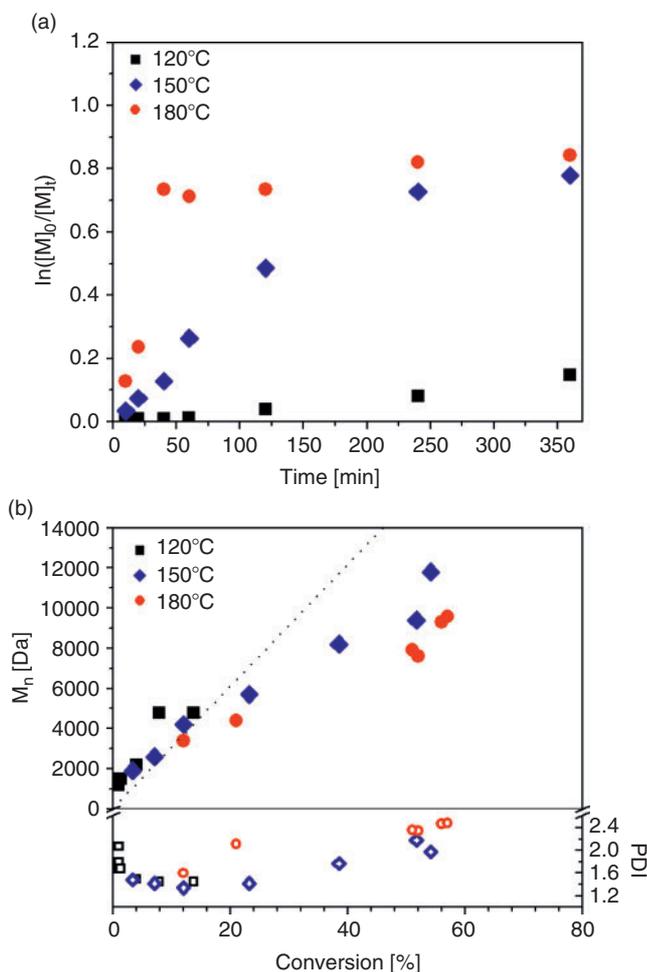
(a)

(b)

Fig. 2. Kinetic plots for the reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate in bulk using 2-cyano-2-butyldithiobenzoate as RAFT agent with a concentration of 4.0×10^{-2} mol L^{-1} at 120°C, 150°C, and 180°C under microwave irradiation (a). Corresponding molar mass and PDI against conversion plot (b).

Fig. 3. Size exclusion chromatography traces for the reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate in bulk using 2-cyano-2-butyldithiobenzoate as RAFT agent with a concentration of 4.0×10^{-2} mol L^{-1} at 120°C, 150°C, and 180°C under microwave irradiation.

results can be rationalized by a very low radical flux in the RAFT polymerization. The SEC traces of the polymerization at 120°C in Fig. 3 reveal bimodal distributions except for the final polymer trace. The bimodularity and relatively high molar masses at low conversion have been previously ascribed to the occurrence of a combination of conventional chain-transfer and RAFT free radical polymerization during the RAFT of MMA, which is known as 'hybrid' behaviour.[44] Similar bimodal SEC traces are observed for the polymerization at 150°C at low conversion (Fig. 3). Nonetheless, the polymerization at 150°C is controlled up to 1 h and ∼25% conversion. At higher monomer conversion, chain coupling occurs, as indicated by the high molar mass fraction in the SEC traces, resulting in increasing polydispersity index (PDI) values up to ∼2 at 50% conversion. The observed chain coupling is most likely chain transfer to polymer, which is more pronounced at higher temperatures.[41,45]

In the previous part, it was found that the initiator-free RAFT polymerization of MMA proceeded relatively fast with good control at 150°C. In a next step, RAFT polymerizations of MMA were investigated at 150°C with CBDB concentrations of 0.5×10^{-2}, 1.0×10^{-2}, 2.0×10^{-2}, and 4.0×10^{-2} mol L^{-1}. Fig. 4 depicts the kinetic plots obtained. The M_n against conversion plot clearly shows that with lower CBDB concentration, i.e. higher [MMA]:[CBDB] ratio, higher molecular weights are obtained. Furthermore, the difference between the $M_{n,th}$ and M_n at low monomer conversion becomes larger with decreasing CBDB concentration, which can be ascribed to 'hybrid' behaviour as discussed previously. All polymers have reasonably well-defined molar mass distributions with PDI values of ∼1.5 up to 25% conversion, indicating, together with the possibility of controlling the polymer molecular mass by the CBDB concentration, that the high-temperature RAFT polymerization of MMA proceeds in a controlled manner in the absence of a radical initiator. At higher monomer conversion, chain coupling is observed, resulting in significant high molar mass fractions in the SEC traces (Fig. 5).

Similar observations were made in the first-order kinetic plot (Fig. 4a). All polymerizations demonstrate similar linear

that the small amount of radicals formed by heating MMA, i.e. thermal initiation as indicated by the reference experiment and literature,[41] is sufficient to start the RAFT polymerization process. This proposed mechanism is further supported by the increased polymerization rate at higher temperatures because the radical flux from MMA will be higher at higher temperatures. In contrast, if the radicals were only formed by decomposition of CBDB, the total number of radicals would be the same at all temperatures and, thus, the effect of temperature would be expected to be smaller.

All three RAFT polymerizations at 120°C, 150°C, and 180°C revealed a linear increase of M_n with conversion close to the $M_{n,th}$, indicating a controlled polymerization mechanism. However, the polymerization at 180°C resulted in broad molar mass distributions (Fig. 3) and the monomer conversion levelled off after reaching ∼50% conversion after 40 min. As such, it can be concluded that 180°C is too high to have a controlled polymerization, which is most likely owing to too high a radical flux. At 120°C, the RAFT polymerization proceeded very slowly, reaching only 14% conversion after 6 h. Nonetheless, the polydispersity indices were below 1.50 after 2% monomer conversion, indicating good control over the polymerization. These
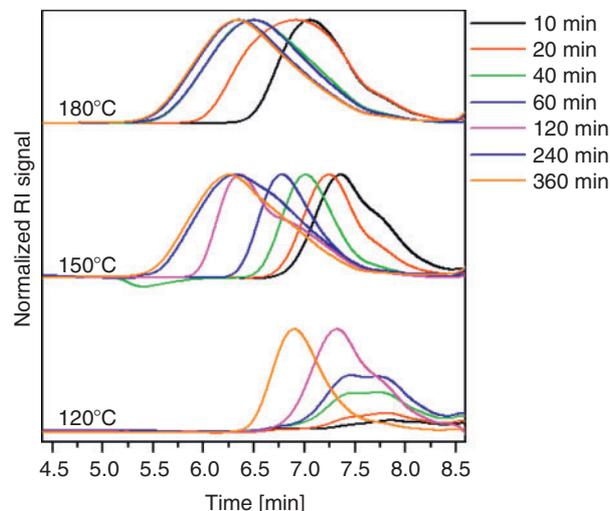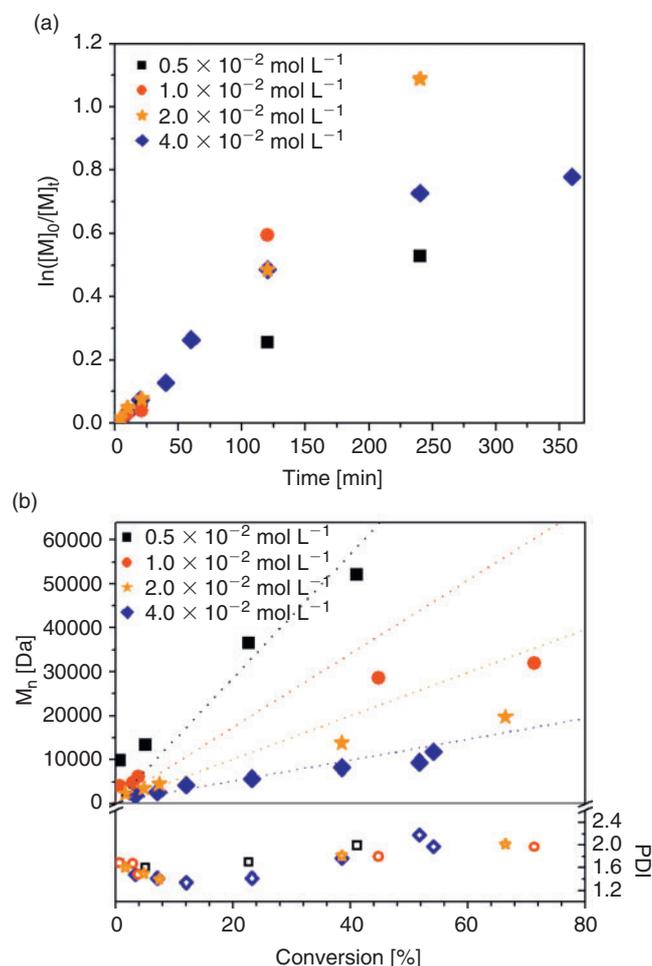
(a)

(b)

Fig. 4. Kinetic plots for the reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate in bulk using 2-cyano-2-butyldithiobenzoate as RAFT agent with a concentration of 0.5×10^{-2}, 1.0×10^{-2}, 2.0×10^{-2}, and 4.0×10^{-2} mol L^{-1} at 150°C under microwave irradiation (a). Corresponding molar masses and polydispersity index values against conversion plot with the theoretical molar masses as dotted lines (b).
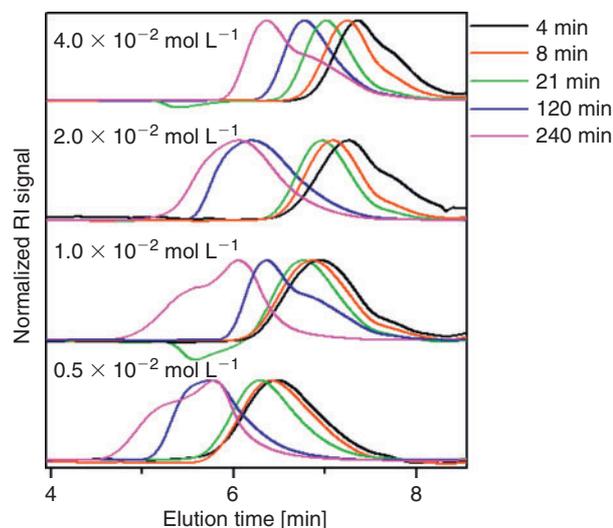

Fig. 5. Size exclusion chromatography traces for the reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate in bulk using 2-cyano-2-butyldithiobenzoate as RAFT agent with a concentration of 0.5×10^{-2}, 1.0×10^{-2}, 2.0×10^{-2}, and 4.0×10^{-2} mol L^{-1} at 150°C under microwave irradiation.

first-order kinetics up to 50 min, indicating that the polymerization rate is independent of the RAFT agent concentration. After 50 min, the polymerization with 0.5×10^{-2} mol L^{-1} becomes slower, which can be ascribed to the higher viscosity resulting from the longer polymer chains. Surprisingly, the polymerization with 4.0×10^{-2} mol L^{-1} CBDB significantly deviates from linearity after 2 h, whereas the remaining polymerizations with intermediate CBDB concentrations still exhibit linear first-order kinetics up to 4 h. This observed difference at different CBDB concentrations is not fully understood at this moment, but might be related to the higher radical concentration with higher CBDB concentration resulting in a larger probability of termination as well as chain transfer to polymer. Nonetheless, the main important observation is that the high-temperature initiator-free MMA RAFT polymerization proceeds in a controlled manner, at least up to 25%, at 150°C.

Conclusions

The microwave-assisted RAFT polymerization of MMA using CBDB as chain-transfer agent and AIBN as initiator was found

to proceed with comparable polymerization kinetics to thermal polymerization, indicating the absence of non-thermal microwave effects. Nonetheless, the easy access to superheated conditions in modern microwave synthesizers allowed the exploration of high-temperature conditions for the CBDB-mediated initiator-free RAFT polymerization of MMA in bulk. The polymerization was investigated at 120°C, 150°C, and 180°C, demonstrating significant MMA polymerization at all temperatures in the absence of a radical initiator. Based on literature and a model thermal polymerization of neat MMA, it is proposed that the initiator-free RAFT polymerization is started by thermal auto-initiation of MMA. Even though all polymerizations revealed a linear increase of conversion, 180°C was found to be too high to have a controlled polymerization, as indicated by broad molar mass distributions. Furthermore, the polymerizations at 120°C and 150°C revealed a controlled polymerization behaviour with PDI values below 1.50 up to ∼25% monomer conversion, whereby the polymerization at 120°C was very slow. Therefore, 150°C was chosen to investigate the effect of the RAFT-agent concentration on the polymerization behaviour, indicating that the molar masses can be tuned by the RAFT-agent concentration as expected for a controlled polymerization. Again, up to 25% conversion, the polymerizations were found to be controlled, after which presumably chain transfer to polymer becomes more prominent, resulting in broadened molar mass distributions.

The present work shows for the first time a simplified synthetic protocol for the controlled RAFT polymerization of MMA. As such, it might serve as a basis for the future development of improved initiator-free RAFT protocols by, for example, variation of the RAFT agent, use of additional solvent and further temperature optimization. An important aspect that needs further clarification in future work is the presence of the RAFT agent at the polymer chain end, which is an important prerequisite for the formation of chain-extended polymers and block copolymers.

Acknowledgement

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