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Ultrafast Conversion and Molecular Weight Control through Temperature Programming in Microwave-Induced Miniemulsion Polymerization

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ABSTRACT: Microwave-mediated miniemulsion polymerization of styrene with consecutive periods of heating and cooling exhibits — compared to continuously heated polymerizations — a very unique behavior. For medium-hydrophobic azo-initiators under optimized conditions, polymer radicals survive the heating pulse and grow during the cooling period to ultrahigh molecular weights $>10^7$ g/mol. This “surviving radical effect” is accompanied by unexpectedly high conversion after the first polymerization cycle, comprising of a temperature pulse of less than 10 s duration and a subsequent cooling period. Besides the ultrarapid heating by the microwaves, the surviving radical effect is purely thermal in nature and can be explained by the elemental reactions of radical heterophase polymerizations.

Introduction

Microwave radiation as a fast and efficient means of heating reaction media has been evoking rapidly growing interest in chemical engineering since the first publication of microwave-assisted organic synthesis in 1986.[1] Nowadays, commercially available microwave ovens allow homogeneous heating of polar molecules with excellent control of temperature in very short times since the heating process does not depend on heat conduction or convection. Although many publications claim the existence of specific microwave effects, increasing evidence is found in modern microwave ovens providing on-line temperature measurement that mechanisms in microwave-induced reactions do not differ from those observed in conventionally heated samples. This result is not surprising because the low energy of photons with a wavelength of 12.25 cm does not suffice to change the electronic structure of molecules, but only couple to rotation processes of polar molecules. Their interaction with matter usually causes only dielectric heating of polar samples. However, in many cases reaction rates are found to increase by up to 4 orders of magnitude, since numerous reactions may now be carried out under conditions that were impossible when applying conventional heating, e.g., solvent-free syntheses. For more details on microwave synthesis, elaborated review articles can be recommended.[2,3] While microwave-assisted synthesis is a fairly young field of research, microwave heating has originally been used extensively in analytical applications such as moisture analysis, wet ashing procedures of biological and geological materials, and the dissolution of ore samples, which do not require elaborate heat control.

It is no wonder that also microwave-assisted polymerization reactions have been performed. Whereas early work was focused on microwave-generated plasmas near metals for local polymerization and curing, also heterophase polymerization reactions in water were considered starting from 1996.[4,5] For polymerization reactions, it is important to have a polar solvent (or monomer) as a microwave absorber to couple efficiently the microwave energy into the system. This is why heterophase polymerization in water seems to be ideally suited for this purpose. As known from earlier work on the microwave curing of expoxies,[6] there is, however, again no mechanistic difference between traditional heating and microwaves.

Microwave heating in heterophase polymerization as an ultrafast heating method is suited for the thermal activation of polymerization reactions and may cause considerable savings of energy, compared with classical heating circuits. There are a few reports on microwave-mediated heterophase polymerizations,[4,5,7−10] and a recently published review on general aspects of microwave-induced polymer synthesis might be useful for the reader as well.[11]

The heterophase-polymerization techniques which presumably combine in a most favorable fashion with microwave heating are both seeded emulsion polymerization and miniemulsion polymerization. In both cases, significant parts of the monomer phase prior to polymerization are dispersed in the continuous phase in form of kinetically stable droplets with diameters between 50 and 500 nm. The mechanism of either polymerization has been found to be predominantly based on polymerization inside the preformed droplets, which act as nanoreactors,[12] and thus the particle nucleation step of ab-initio emulsion polymerizations is avoided (cf. Scheme 1). Moreover, these facts make both techniques suitable for a continuous polymerization in so-called tube reactors,[13] which would offer also new perspectives for technology and industrial applications.

In this contribution, a detailed report on an experimental study of microwave-enhanced miniemulsion polymerization of styrene is given. The results prove the potential of this unique combination for polymer synthesis as at high polymerization rates the molecular weight distribution can be tuned over broad ranges.

Experimental Section

Chemicals. Styrene was purchased from Fluka (purum; ≥99%, stab. with 0.005% 4-*tert*-butylcatechol). It was freshly distilled and stored at −10 °C. Hexadecane (99%), sodium dodecyl sulfate (98%), and 3-chloroperoxybenzoic acid (57−86%, containing

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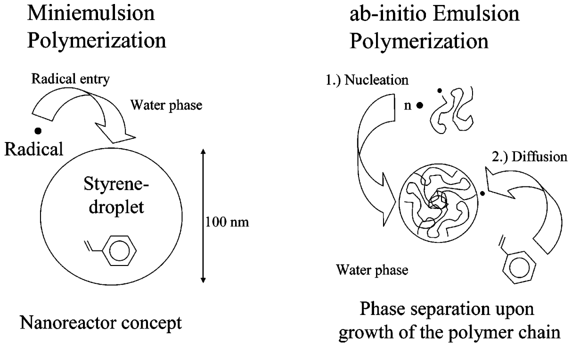
Scheme 1. Schematic Comparing the Reaction Mechanisms of Miniemulsion and ab-Initio Emulsion Polymerization[a]



[a] The rate-limiting step in miniemulsion polymerization is radical entry into the monomer droplets and in ab-initio emulsion polymerization the nucleation of particles that afterward swell with monomer.

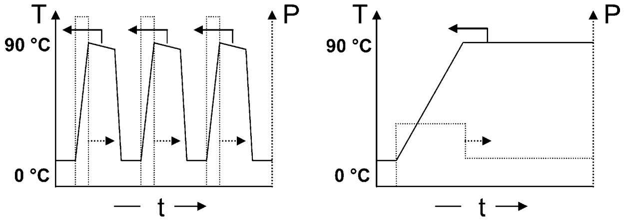
residual water) were purchased from Aldrich and used without further purification. Azoisobutyronitrile (AIBN, purum; $\geq$98%), potassium peroxodisulfate (KPS, p.a.; $\geq$99%), and *tert*-butyl perbenzoate (for synthesis, $>$98%) were purchased from Fluka and used without further purification. 2,2′-Azobis(2-methylbutyronitrile) (V 59) was purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Bis(α,α-dimethylbenzyl) peroxide was purchased from Merck-Schuchardt and used without further purification. PEGA 200 was synthesized in our lab according to literature procedures.[14]

Preparation of Styrene-in-Water Miniemulsions. All samples were prepared from an organic phase that consisted of 6 g of styrene (monomer) and 250 mg of hexadecane (hydrophobe) and an aqueous phase that consisted of 24 g of water (continuous phase) and 74 mg of SDS (surfactant). Oil-soluble radical initiators (AIBN, V59, *tert*-butyl perbenzoate and bis(α,α-dimethylbenzyl) peroxide) were added to the organic phase before homogenization, and water-soluble radical initiators (KPS, PEGA 200, and 3-chloroperoxybenzoic acid) were added to the miniemulsion after homogenization. Homogenization was carried out in two steps after uniting the aqueous and the organic phase: at first (pre)emulsification was achieved by stirring the two phases at maximum speed with a magnetic stirrer for 1 h, yielding an unstable macroemulsion. Immediately afterward, in a second step, homogenization was carried out by ultrasonicating the macroemulsion with a sonicator-tip (Branson sonifier W450 Digital) under unstirred ice cooling for 2 min.

Processing Conditions for Microwave-Assisted Miniemulsion Polymerization. In the experiments, the duration of microwave irradiation was adjusted to heat the reaction media to a predefined temperature. Pulses of 9−12 s at constant 1000 W proved to be sufficient to heat up 30 g of miniemulsion from room temperature to preset values between 75 and 95 °C, which are well suited for rapid decomposition of the employed radical initiators and do not exceed the boiling point of water.

If the outcome of a chemical synthesis performed using microwave heating differs from its thermally heated counterpart, specific microwave effects are present.[3] Such effects may be divided into two types: (1) effects in which the reaction is enhanced through the specific excitation of rotational states in the molecules and (2) effects that are caused merely by the particular temperature profile, e.g., great heating rates. The prospective of this contribution is to test the benefits of very fast processing using microwave heating. However, it is necessary to also check for the first type of microwave effects. Therefore, the following two different processing conditions in the microwave oven were examined: (i) Quasi-conventional experiments: heating the miniemulsion slowly to a preset temperature and keeping it at that temperature (see Scheme 2, right) until full conversion is reached yields temperature profiles equal to those of conventional heating. However, microwave radiation is present throughout polymerization. (ii) Pulsed experiments: rapid heating at high microwave power with subsequent cooling in a stirred ice bath (see Scheme 2, left) allows to keep the conditions of thermal heating short.

Scheme 2. Diagrams of Temperature and Power over Time[a]



[a] (left) Pulsed processing: Schematic of the temperature and power profile of a sample, which is repeatedly heated through microwave radiation of great power and cooled in an ice bath immediately afterward. (right) Conventional and quasi-conventional processing: schematic of the temperature profile of a sample, which is slowly heated to a preset temperature and kept at this temperature either in an oil bath or through microwave radiation (the power profile refers to controlled microwave heating).

To compare the results with standard batch processing, miniemulsions were polymerized conventionally by transferring them into flasks of 50 mL, which were then inserted into stirred oil baths and kept at a preset temperature for 4 h. Because of the exothermal reaction, temperatures in the flask exceeded those of the oil bath and were therefore monitored with a digital thermometer (P 310 Temp).

In quasi-conventional experiments, 30.4 g of the miniemulsion was heated at 110 W microwave power to a preset temperature of 92 °C. The microwave oven was then set to maintain this temperature for a certain time. All quasi-conventional experiments were carried out as batch experiments in a beaker under stirring to yield results that are directly comparable to the conventionally processed experiments. The applied microwave oven, model MLS-Ethos 1600 by MLS Mikrowellen Laborsysteme, features online measurement with a thermocouple that is inserted into the reaction media, providing the data for temperature control.

If the product of quasi-conventionally processed experiments is different from that obtained with conventional heating, a microwave effect of the first type is present. If only the products of pulsed processing are different from those obtained with conventional heating, a microwave effect of the second type is present.

Analysis. Conversion of the prepared polystyrene latexes was determined gravimetrically after evaporation of residual styrene and water at room temperature. All conversion values given in this paper were corrected by the value of a blind sample of the same unpolymerized miniemulsion in order to account for nonvolatile components (initiator, surfactant, and hexadecane).

Molecular weight and weight distributions were determined by dissolving the isolated and dried polystyrene in THF and performing GPC analysis with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å (from Polymer Standard Service), using a P1000 pump with an UV2000 detector (l = 260 nm) (both from Thermo Separation Products) and an RI detector (Shodex RI-71), in THF with a flow rate of 1 mL min^{-1} at 30 °C. The molecular weights were calculated with a calibration relative to polystyrene standards. All molecular weights and weight distributions in this contribution are based on the data obtained from RI detection.

The molecular weights of selected samples were investigated with static light scattering. Measurements were taken at angles between 15° and 150° using a device by ALV, Langen, with a step-motor controlled goniometer (ALV SP-86). A frequency-doubled Nd:YAG laser by Adlas, model DPY 42511, with a maximum power output of 400 mW served as light source. The laser beam was focused on a 10 mm quartz cuvette in a toluene bath. The scattering intensity was recorded using a photomultiplier (Thorn EMI, PM 28 b). The results were plotted in the Zimm representation for elaboration.

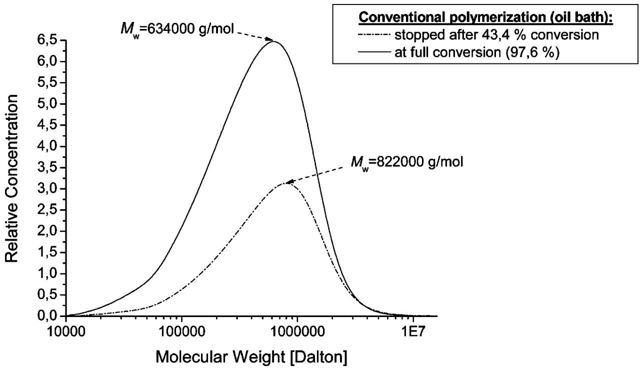


Figure 1. Example of a conversion weighted molecular weight distribution (MWD) for the latex of a conventional styrene-in-water miniemulsion polymerization carried out in an oil bath at 83 °C. 450 μmol of PEGA 200 was applied as radical initiator. Samples of the same miniemulsion were taken during polymerization (43.4% conversion) and at full conversion (97.6%). The area between the curves represents the polymer formed during the second half of the polymerization. The MWD is monomodal throughout polymerization.

Results and Discussion

Conventional Miniemulsion Polymerization. Batch miniemulsion polymerization with conventional thermal heating in an oil bath is performed as a default experiment to relate to all further experiments. Figure 1 shows molecular weight distributions obtained in such polymerization using 262 mg of PEGA 200 (450 μmol). PEGA 200 is an azo-initiator derived from AIBN by reacting poly ethylene glycol oligomers of 200 g/mol on its nitrile moieties, rendering PEGA 200 water-soluble. Throughout this paper, the molecular weight distribution (MWD) curves are corrected for conversion by relating the area of the elugrams to the particular conversion and subsequent transformation into the MWDs. This kind of presentation makes it easy to see how much polymer of a certain molecular weight has been produced in a given conversion range or microwave pulse.

The molecular weight distribution of conventionally processed experiments shows no anomalies, and Figure 1 depicts the usual monomodal molecular weight distribution for PEGA 200 initiated polystyrene throughout the miniemulsion polymerization process. The decrease in molecular weight toward full conversion is expected for radical polymerization, as the monomer concentration at the reaction loci decreases. This is particularly true for miniemulsion polymerization. Moreover, the thermal experiments were carried out in oil baths on temperature-controlled hot plate stirrers. Their temperature control is not capable of providing perfectly isothermal conditions. As a result of the exothermal polymerization reaction, the temperature of the miniemulsion rises, and due to the accelerated initiator decomposition the kinetic chain length decreases. Note that the data show no evidence of chain transfer under the applied conditions and at the initiator concentration used in the experiment.

Quasi-Conventional Polymerization with Constant Microwave Heating. Quasi-conventional processing in the microwave oven using both AIBN and PEGA 200 as radical initiators yielded qualitatively identical products as obtained in conventional experiments. All molecular weight distributions (MWD) using AIBN (see Figure 2) and PEGA 200 (not represented) were found to be monomodal.

Table 1 shows the experimental conditions and results. With increasing AIBN concentration, the peak values are shifted toward lower molecular weights. The reaction rates were comparable to those of the conventionally heated reference experiments at the same temperature. All data are in line with previous observations on radical polymerization in heterophases and are indicative for the absence of a microwave specific effect on the initiator decomposition or radical polymerization.

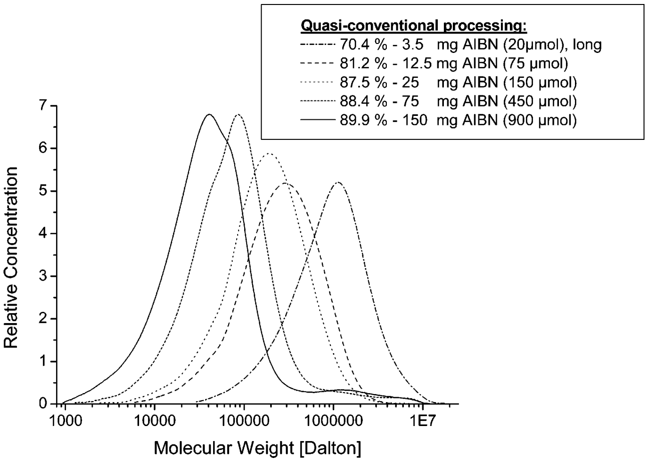


Figure 2. Quasi-conventional miniemulsion polymerization through continuous heating of a sample in the microwave oven using different concentrations of AIBN; the temperature was 92 °C. All molecular weight distributions (MWD) are monomodal. For the experimental details of these samples, see Table 1. Note: the high molecular weight polymer in the samples containing high concentrations of AIBN is produced during the emulsification step (ultrasound initiation) and does not originate from microwave heating.

Pulsed Processing: Optimization of the Initiator and the Difficulties of Droplet Nucleation. To check for specific effects at high microwave power, blind experiments with no added radical initiator were performed. They showed negligible conversion even after five temperature-pulses up to 90 °C at 1000 W. This underlines sufficient purity, temperature homogeneity and shows that none of the added components can generate radicals under the influence of microwave irradiation. Especially, the duration of the heating cycles was short enough to prevent thermal self-initiation of styrene.

Then, seven different radical initiators (lipophilic, hydrophilic, and amphiphilic) were tested in order to determine their efficiency in microwave-assisted miniemulsion polymerization.

The experiments listed in Table 2 were carried out in batches of 30 g standard miniemulsion, to which the indicated amounts of radical initiator were added. Fractions of 2 g were taken from the batch after each temperature pulse for analysis.

Bis(α,α-dimethylbenzyl) peroxide, *tert*-butyl perbenzoate, and 3-chloroperoxybenzoic acid are peroxo-initiators which need fairly high decomposition temperatures (usually above 100 °C). The first two compounds are lipophilic and yield hydrophobic radicals. Contrarily, 3-chloroperoxybenzoic acid is amphiphilic in nature and decomposes into a lipophilic and a strongly hydrophilic OH radical. *tert*-Butyl perbenzoate and even more pronounced 3-chloroperoxybenzoic acid are asymmetric with respect to the O−O bond, resulting in a polarization of the bond. They may therefore be sensitive against dielectric heating, and an initiator specific effect of microwave radiation is most likely to occur in these molecules. However, after eight pulses of 90 °C less than 5% conversion was found in the case of 3-chloroperoxybenzoic acid; no polymer at all was detected with the other two initiators. This clearly proves that specific cleavage of O−O bonds using dielectric heating cannot be achieved under the particular experimental conditions in direct miniemulsions as the generated temperature pulses were not high enough for a noticeable thermal decomposition.

Table 1. Quasi-Conventional Miniemulsion Polymerization[a]

name	radical initiator (mg)	radical initiator (μmol)	temp (°C)	duration (min)	final conv (%)	M_w mean value
AIBN-0	3.5	20	75 → 89	>40	70.4	1.338×10^6
AIBN-1	12.5	75	92	24	81.2	0.390×10^6
AIBN-2	25	150	92	24	87.5	0.284×10^6
AIBN-3	75	450	92	24	88.4	0.191×10^6
AIBN-4	150	900	92	24	89.9	0.161×10^6

[a] The amount of initiator, preset temperature, duration, final conversion, and average molecular weight (M_w) are given for various amounts of AIBN.

Table 2. Pulsed Processing: Experimental Results of Microwave-Assisted Miniemulsion Polymerization Using Various Radical Initiators[a]

name	radical initiator (mg)	radical initiator (μmol)	total no. of *T* pulses	final conv (%)	mol wt M_w
KPS	100	370	5	39.0	0.218×10^6
bis(α,α-dimethylbenzyl) peroxide	124.7	450	8	−0.8	
tert-butyl perbenzoate	91.7	450	8	−0.3	
3-chloroperoxybenzic acid	79.3	450	8	4.5	$\approx 1.02 \times 10^6$
V59-2	29.3	150	5	30.7	0.945×10^6
V59-4	175.6	900	4	39.8	0.245×10^6
AIBN-1	12.5	75	6	74.9	1.159×10^6
AIBN-2	25	150	4	87.0	0.995×10^6
AIBN-3	75	450	4	88.4	0.628×10^6
AIBN-4	150	900	4	90.3	0.577×10^6
PEGA-2	88.4	150	4	65.5	1.844×10^6
PEGA-3	262	450	4	80.4	1.665×10^6
PEGA-4	520	900	4	80.2	1.536×10^6
blind	0	0	5	1.1	

[a] The amounts of initiator refer to 30 g of styrene miniemulsion containing 6 g (20%) of styrene. The number of temperature pulses at 1000 W microwave power with subsequent cooling in an ice bath is given. Final conversion was determined gravimetrically. Negative values of conversion are due to the correction with the mass of the blind experiments' residue and indicate the experimental error. Mean molecular weights of the resulting polymer were determined from GPC measurements using RI detection.

Table 3. Decomposition Rate Constants in the Given Solvents and Water Solubilities of Radical Initiators Applicable to Microwave-Mediated Miniemulsion Polymerization of Styrene

initiator	k_d [s^{-1}], 67 °C	k_d [s^{-1}], 90 °C	[I_w] [M], 25 °C	data measured in
PEGA 200	1.06×10^{-5} (ref 16)	2.03×10^{-4} (ref 16)	4.58×10^{-3} (ref 16)	toluene
KPS	1.45×10^{-5} (ref 17)	2.99×10^{-4} (ref 17)	1.85×10^{-2} (ref 18)	water
V59	1.92×10^{-5} (ref 19)	/		styrene
AIBN	2.26×10^{-5} (ref 20)	3.96×10^{-4} (ref 20)	2.44×10^{-3} (ref 21)	styrene

Potassium peroxodisulfate (KPS) also does not possess a dipole moment across its cleavable O−O bond, but it decomposes at much lower temperatures yielding purely hydrophilic radicals. Surprisingly, also KPS showed only a low efficiency in our setup. Typically, after five pulses the conversion was lower than 50% and the reproducibility poor. In contrast, the azo-compounds AIBN and PEGA 200 gave full monomer conversion after only four heating pulses.

The order of conversion obtained with KPS, PEGA 200, AIBN, and V59 is not easily explainable as it correlates neither with the decomposition rate constant (k_d) nor with the water solubility [I_w] of the initiators. The k_d values of all four systems are between 2 and 4×10^{-4} s^{-1} and 1 and 2×10^{-5} s^{-1} at 67 and 90 °C, respectively, so that they cannot account for the different reaction rates. The water solubilities are quite different, but also they cannot serve as sole reason as the most hydrophilic (KPS) and the most hydrophobic initiator (V59) lead to similar conversion.

AIBN and PEGA 200 are located in the middle of the hydrophobic−hydrophilic scale of the investigated initiators and gave fast polymerization and excellent conversions. These results suggest that under the particular conditions optimum hydrophobic−hydrophilic properties of the initiator are required for getting high polymerization rate and conversion. These optimum properties obviously have to be within quite a narrow range. Note that for both PEGA 200 and AIBN the applied concentration range of 6.6−38 mM and 3.2−38 mM, respectively, exceeds the water solubility of the initiators. Considering partition between the monomer and the water phase, larger amounts of both initiators are inside the monomer droplets, and hence, radical generation predominantly takes place there. A sufficient hydrophilicity of the formed radicals is then obviously needed that at least one of them can leave the droplets in order to get an odd number of radicals per droplet and to avoid instantaneous recombination of all generated radicals within a short period of time. An odd number of radicals per droplet can also be obtained if an odd number of radicals from the continuous phase enter the droplet. The partition coefficient of AIBN and V59 between styrene and water at 25 °C is about 120 and 2560, respectively.[15] The comparison between AIBN and V59 (cf. Table 3) shows how much an additional methylene group can matter in radical heterophase polymerization.

In addition to the conversion data, also the molecular weight distributions reveal interesting differences between the four initiators. The comparison of the conversion corrected MWDs as depicted in Figure 3 proves a typical advantage of heterophase polymerization techniques which is the ability to realize simultaneously high polymerization rates and high molecular weights. The peak molecular weight changes in the order PEGA 200 > AIBN > V59 > KPS; for PEGA 200 and AIBN the distribution reaches the high molecular weight exclusion limit of the GPC apparatus.

Varying the Amounts of AIBN and PEGA 200 Initiators. For the analysis of how different amounts of AIBN and PEGA 200 affect conversion and molecular weight distribution of the formed polymer, multistep processing of the miniemulsions was applied. Each step involved heating of 30 g miniemulsion to 90 °C in about 12 s, immediately followed by a rapid

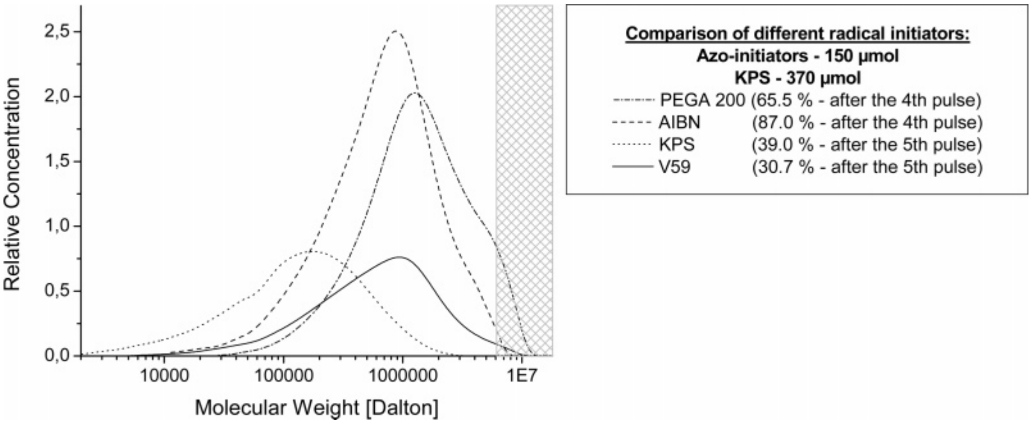


Figure 3. Conversion weighted molecular weight distributions using different initiators in pulsed, microwave-assisted miniemulsion polymerization. The gray shaded area in the diagram marks the exclusion limit of the GPC.

temperature quench to 0 °C. After every step, a sample of 2 g was taken and characterized. Figures 4 show the MWD's obtained in corresponding experiments at various concentrations of PEGA 200. The experiments represented in the diagrams are already listed in Table 2. The values of conversion after every step are given in percent within the graphs. Essentially the same trends were observed for AIBN, however, with a tendency toward lower molecular weights. The corresponding diagrams may be found in the Supporting Information.

The data in Figure 4 are indeed astonishing as they break, at least partly, with common experiences and expectations gained in emulsion and miniemulsion polymerization and prove that the applied time–temperature program creates special molecular weight distributions of the polymer in the latex particles (compare to Figure 1). Figure 5 replots those data and those of analogous experiments with AIBN (see Supporting Information) by comparing the MWDs at high conversions for both initiators.

Contrary to the common behavior as described by the conventional and quasi-conventional processing, increasing amounts of initiator do not significantly alter the final conversion, and also the MWDs stay about unchanged. The average molecular weight is in many cases highest after the first pulses, in particular for higher initiator concentrations (see Figure 4 and data in the Supporting Information). In addition, all these experiments yield polymers with bimodal MWD comprising significant fractions with high and ultrahigh molecular weight generated in the early stages of the experiments.

Figure 6 shows the conversion as a function of the number of pulses for the two azo-initiators. The conversion obtained after the first pulse can be as high as 35%, formally received after 12 s of heating. This underlines the great potential of microwave-mediated miniemulsion polymerizations with pulsed processing regarding the space–time yield compared to the conventional conditions. Additionally, Table 4 compares the formal residence time in the reactor for miniemulsion polymerization to obtain a monomer conversion higher than 80% for the different heating modes.

Optimizing the Pulse Peak Profiles. Investigation of the origin of the very high conversions with at the same time very high molecular weights involves the variation of the processing conditions. For this reason small fractions of 5 g of miniemulsion were heated in the microwave oven at different microwave powers, allowing to heat the samples even more rapidly, which is due to the smaller sample volumes: At 1000 W microwave power, the sample can be heated from room temperature to 90 °C in about 8 s. Table 5 shows a systematic investigation of the influence of the temperature pulse profile on conversion and the molecular weight in miniemulsions that were initiated with PEGA 200. All experiments were subjected to one temperature pulse only.

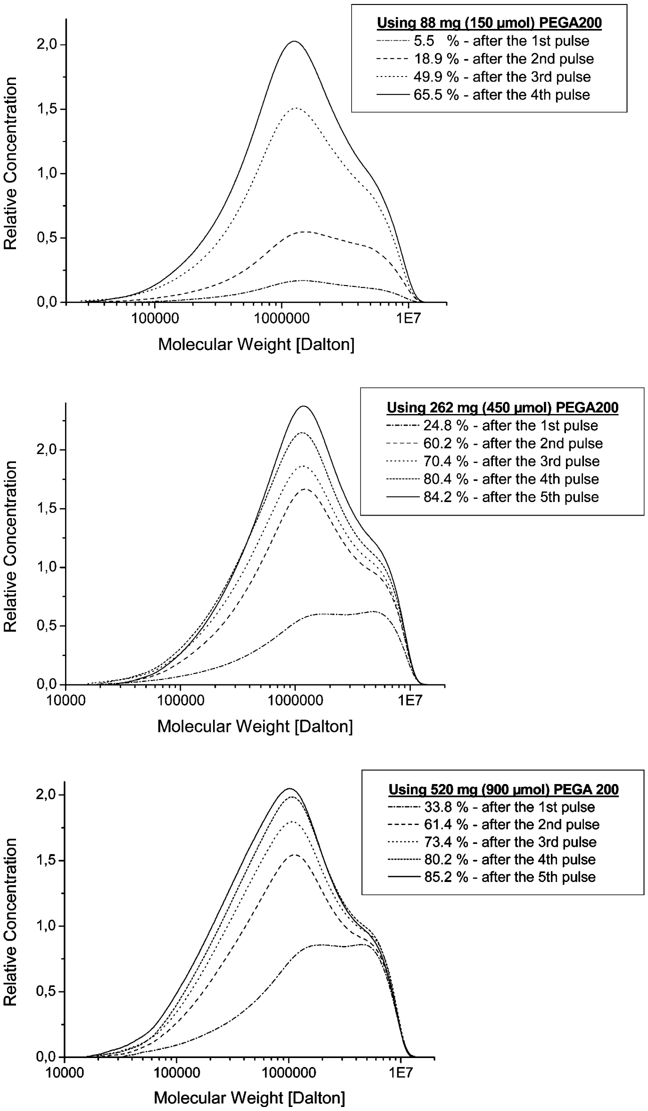


Figure 4. Conversion weighted molecular weight diagrams of the molecular weight development in pulsed, microwave-assisted miniemulsion polymerization using three different amounts of PEGA 200. The number of pulses, after which samples were taken, is given with the respective conversion in percent.

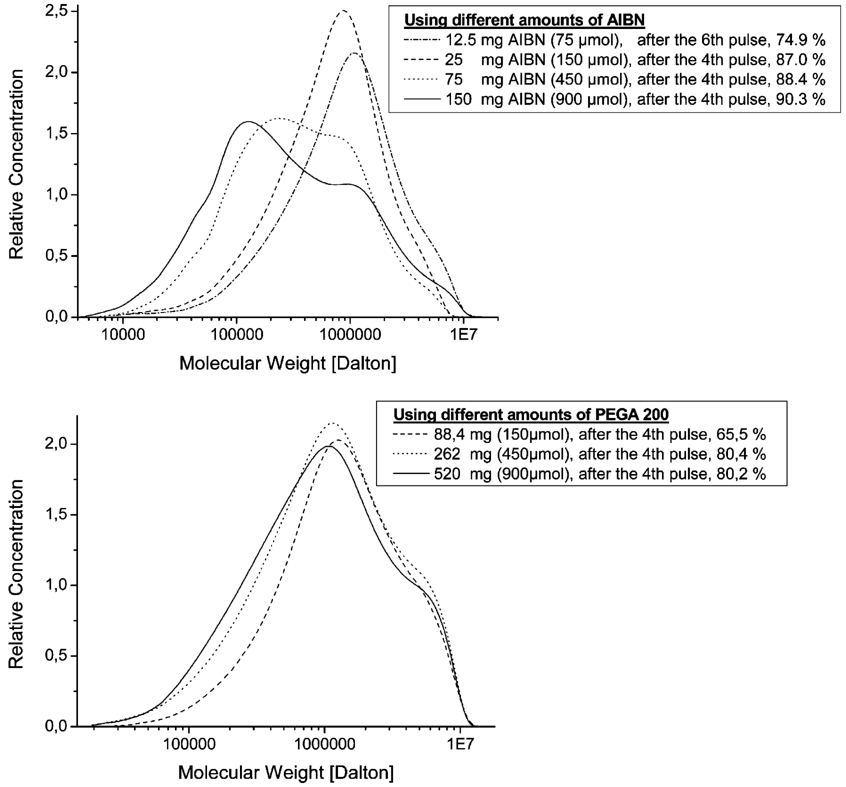


Figure 5. Conversion weighted molecular weight distributions for the direct comparison of the molar mass distribution yielded in experiments with different amounts of AIBN and PEGA 200.

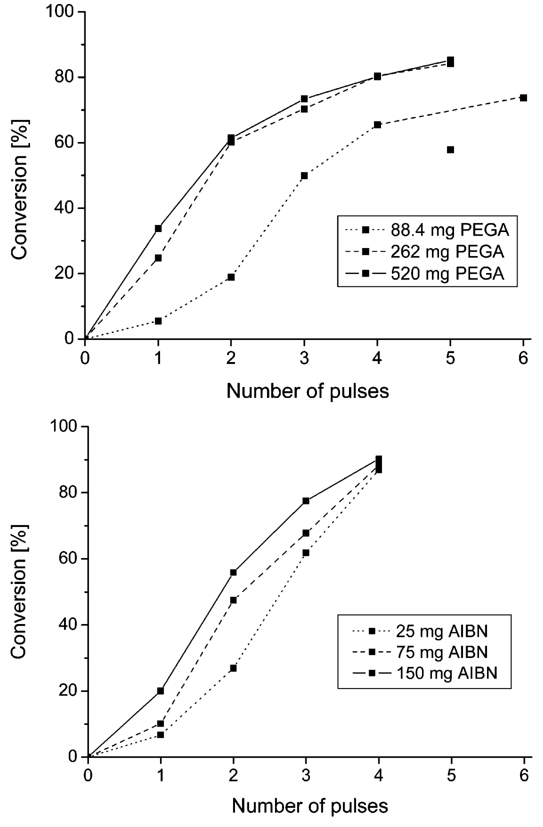


Figure 6. Representation of the increase in conversion in the course of a pulsed, microwave-assisted miniemulsion polymerization using different concentrations of PEGA 200 and AIBN as radical initiator.

High conversions of up to more than 40% were preferentially found after short temperature pulses using high microwave powers. Conversion seems to depend mostly on the heating rate as determined by the microwave power and the cooling procedure (see Figure 7) but also seems to be related to the maximal preset temperature (compare samples 1, 2, 3, 4 with samples 5, 6, 8, 10).

It is a striking observation that polymer molecules with molecular weights on the order of 10^7 Da are produced in great yields after the first pulse. A significant part of the polymers is that large that even with the employed optimized GPC setup it was not possible to separate them. Static light scattering investigations in THF of samples 1 and 4 confirmed molecular weights (M_w) of 7.9×10^6 and of 6.4×10^6 g/mol, respectively. Because of the large size of the polymers in solution, these values may be regarded as lower estimates.

Contrary to "normal" radical polymerization under homogeneous conditions, an increased radical flux or higher rate of initiation (either by greater initiator concentration or higher preset temperature or greater power of the pulses) enhances the tendency to generate those high molecular weight species with high yields. However, this specific effect as observed during microwave-induced miniemulsion polymerization can be explained by fundamental rules of radical heterophase polymerizations. Under pulsed temperature conditions, all reaction steps including radical generation predominantly take place inside confined reaction loci of quite small size (droplets of about 100 nm in diameter), and the radicals are generated only during a certain period of the whole reaction. During the hot phase of radical formation, the standard processes of radical polymerization take place, including termination. In fact, the very high radical flux occurring in those 5−10 s is essentially removing all the impurities, and most of the radicals recombine rapidly, until in the end either zero or one radical is left (0/1 rule).

The special effects occur because the applied processing times were made that short that they are shorter or of the order of the typical molecular polymerization times (the time it takes to

Table 4. Direct Comparison of Heating and Reaction Times Using Different Processing Conditions[a]

	processing condition	total time above $T_{\mathrm{decomposition}}$ $\approx$ 70 °C	total heating time time in reactor)
pulsed processing in a tube reactor	4−5 T pulses, 1000 W, 15 s each	100 s	70 s (1000 W)
quasi-conventional microwave heating	heating at 110 W + 16 min at ≈100 W	16 min	24 min (100 W)
conventional heating in an oil bath	oil bath, 75 °C; 55 min	45 min	55 min (75 °C, oil bath)

[a] In all cases, 450 μmol of PEGA 200 was added to 30 g of styrene standard miniemulsion as radical initiator, and the samples were heated to 74 °C. Final conversion was between 80% and 93%.

Table 5. Influence of the Temperature Profile on Microwave-Assisted Miniemulsion Polymerization[a]

name	conv (%)	microwave power (W)	heating time (s)	mean M_w (g/mol)	max temp (°C)	cooling procedure
1	29.8	1000	8.1	3.402×10^6	90	ice
2	41.3	750	8.8	3.445×10^6	90	ice
3	33.7	400	15.0	3.283×10^6	90	ice
4	31.6	200	45.0	3.007×10^6	90	ice
5	27.8	1000	8.1	3.156×10^6	83	ice
6	34.9	750	8.1	3.298×10^6	83	ice
7	35.0	550	9.4	3.232×10^6	83	ice
8	32.9	400	10.0	3.302×10^6	83	ice
9	33.4	300	13.6	3.280×10^6	83	ice
10	33.2	200	30.0	3.188×10^6	83	ice
11	27.8	100	132.0	2.592×10^6	83	ice
12	45.1	1000	8.1	2.932×10^6	83	air
13	42.7	200	30.0	3.061×10^6	83	air

[a] Only one isolated temperature pulse was applied in the microwave oven to small fractions of 5 g of miniemulsion. Microwave power and hence the heating rate, the preset maximal temperature, and the cooling procedure were varied (quenching in an ice bath or cooling with air at ambient temperature). Note: the MWD as measured by GPC and the M_w values listed in the table are apparent values, as an important part of the very high molecular weight polymer was trapped in the filters and/or excluded from the GPC column due to its size and therefore has not been accounted for.

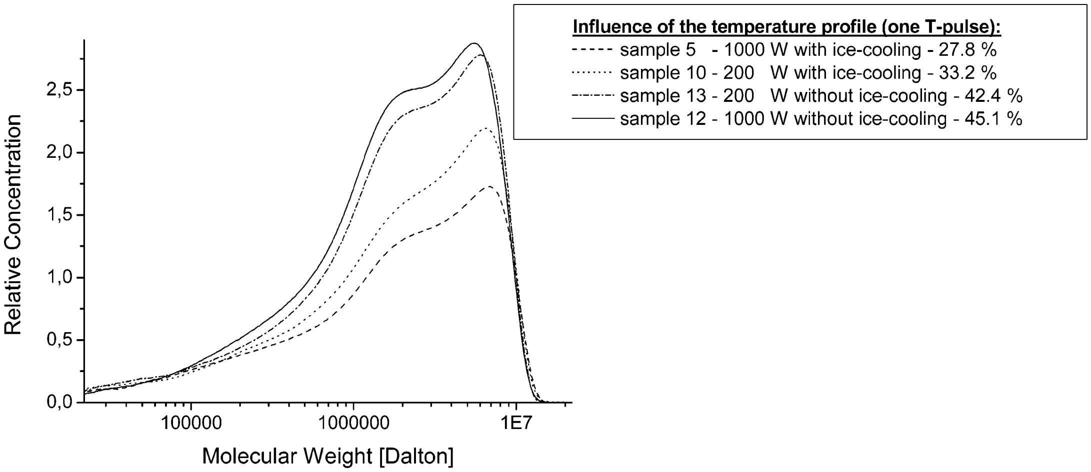


Figure 7. Conversion weighted molecular weight distributions of miniemulsions after one temperature pulse showing the influence of the pulse shape. The heating was performed at 1000 and 200 W; the preset maximal temperature was 83 °C for the presented cases. Cooling in an ice bath was compared to cooling at air at ambient temperature. Conversion is given in percent.

complete one chain). In other words, quick pulsed heating creates practically independent of the initiator concentration, a very clean, "radical-purged" monomer droplet with either zero or one radical. This scenario guarantees that in the confined reaction space the number of growing radicals decreases so rapidly that the conversion obtained in the hot step of the pulse can be neglected.

An Illustration: The Model of Surviving Radicals. The qualitative explanation of the experimental results leads to what shall be called the model of "surviving radicals": At the end of the hot phase neither polymer of very high molecular weight nor great conversion has been yielded. However, while cooling the system down to very low temperatures, the one radical left in the droplet finds itself in a cleaned environment, with practically no chance to terminate. Chain growth is stopped only by transfer events which might occur to monomer, initiator, stabilizer, or at higher conversion also to polymer. For styrene at monomer conversion up to 40% (as obtained after the first microwave pulse) the growth of a single chain is practically only stopped by transfer to monomer, which has however no effect on conversion.[22,23]

The fact that polymerization takes place predominantly after − and not during − the actual temperature pulse can be illustrated by a model calculation assuming a miniemulsion droplet with a diameter of 100 nm contains almost 3×10^6 styrene molecules, which would lead to a potential molecular weight of 300×10^6 g/mol. The limiting size of a polymer molecule is determined by the so-called transfer limit, which is the ratio of the temperature-dependent rate constants of propagation, k_p, and transfer to monomer, k_{tM} (e.g., see ref 24 for k_{tM} at 70 °C and refs 22 and 23 for k_{tM} at 0 °C). As chain transfer to monomer has a higher activation free energy than propagation, lower temperatures favor higher molecular weights. Accordingly, polystyrene molecules with molecular weight of more than 5×10^6 Da can only be produced with radical polymerization at temperatures lower than room temperature; hence, the ultrahigh molecular weights in the experiments cannot have been formed during the hot phase. Particularly, for 0 °C a transfer limit of M_n of about 10^7 Da is estimated.[22,23] As experimental data for 0 °C are not available, estimated values were used assuming that the activation free energies of the kinetic processes obtained at higher temperatures can be applied.

The found maximal 40% monomer conversion, together with the 0/1 rule, transcribes simplistically into 50% of droplets with no conversion, whereas 50% show 80% conversion. This means that in a single, polymerizing droplet 25 chains with an average molecular weight of 10^7 g/mol must be formed. Accordingly, the surviving radical has to generate 25 chains, clearly a situation which can only be provided by chain transfer to the monomer.[17,25] To reach a M_n of 10^7 Da at 0 °C takes about 15 min; that is, the single radical survives at least for 6 h, producing all the time ultralong polymer chains. In comparison, getting a polystyrene of 10^6 Da ($P_n = 10^4$) polymerized at 90 °C needs a little more than 2 s.[26] Thus, throughout the heating pulse of 9 s, a maximum of four polymer chains per latex particle with an average molecular weight of 10^6 Da are formed, which corresponds to only 1.33% conversion in the hot stage of the process. Obviously these calculations are rough estimates. A detailed mathematical description of the system is beyond the scope of this article and will be addressed in our future research.

Radical desorption from a droplet/particle as a possible source of radical loss is rather unlikely in the present system: It could occur only for monomer (or small oligomer) radicals, as polymer radicals cannot leave the droplets due to their hydrophobicity. Over the course of polymerization the viscosity increases dramatically in those droplets carrying a radical. As in this way the mobility/diffusion of the radicals is greatly slowed down, desorption even of small monomer radicals becomes more and more unlikely with increasing conversion.

Radical mobility inside the droplets containing a radical is already hindered after the first chain transfer. This may be illustrated by our static light scattering data, which show that a single polymer chain of 10^7 g/mol forms a Gaussian coil of about 250 nm. This polymer chain, however, will have to squeeze into a 100 nm miniemulsion droplet, which already contains up to four shorter polymer chains formed during the hot stage of the reaction. Consequently, even after the first ultrahigh molecular weight chain is formed, the viscosity inside the droplet is greatly increased. Moreover, mobility generally decreases with decreasing temperature. At temperatures as low as 0 °C, when chain transfer to monomer occurs, desorption of radicals from the droplets will be slowed down significantly. It is therefore reasonable to assume that the probability of exit even for those monomer radicals generated after the first chain transfer to monomer at low temperature is quite low.

The model of surviving radicals and the above calculations illustrate the experimental interrelation of very high conversion and ultrahigh molecular weight polymer molecules. The high conversion after one or two microwave pulses can occur only, if the one surviving radical finds a very clean nanodroplet after the hot stage. The high radical flux during the hot stage serves to remove all terminating impurities, which is particularly efficient at very high temperatures and high radical initiator concentrations. For the sake of completeness, it must be mentioned that radicals with extremely long lifetimes are well-known in some heterophase polymerization scenarios, especially for small nanodroplets or cases where radical mobility is sufficiently restricted to avoid the termination of radicals.[27−29]

Radicals that survive for minutes and even hours and days in highly segregated systems have also been detected by electron spin resonance in emulsion polymers after completing conversion.[30] The molecular weight distributions in Figures 4 and 7 closely resemble those of experiments that were carried out at room temperature using great amounts of initiator,[31] further evidencing that polymerization was in fact carried out at low temperatures. Moreover, they resemble the results of polymerizations with ultrasound initiation in an ice bath.[32]

At later stages of the reaction beyond 40% conversion and increasing number of heat pulses (see Figure 4) polymer in the molecular weight range of 10^6 Da is produced. This can be simply due to the increasing viscosity inside the polymerizing droplets causing an increasing average number of surviving and hence growing radicals per droplet. Further growing viscosity inside the drops stops eventually the monomer consumption (glass effect) during the cold stages at an overall conversion between 80 and 90% (cf. data in Figure 6).

Conclusion and Outlook

A new polymerization strategy is described, which combines the advantages of the confinement of the polymerization inside nanoreactors during heterophase polymerization with the very rapid and efficient microwave heating. Alternating short pulses of microwave heating (about 10 s) and longer intervals of cooling (at least 15 min) were applied. Under optimized conditions this leads to very high molecular weights on the order of 10^7 g/mol and high conversion of up to 40% conversion after the first cycle. The molecular weight of the polymer chains is governed by their so-called low-temperature transfer limit, which is the maximal value at a given temperature.

The system and its special effects turned out to be sensitive against the choice of initiator, and best results were obtained for medium-hydrophobic azo-compounds as thermal initiators, such as AIBN and PEGA 200. Microwave-specific effects such as coupling to dipolar moieties of the initiator can be excluded, and all experimental facts can be explained with common radical heterophase polymerization kinetics.

The results can be explained by the model of "surviving" radicals. Here, the heat pulse generates a large number of radicals which mainly terminate and generate only about 1% of conversion in each nanodroplet during the hot phase. At the same time these radicals remove very efficiently all impurities which can terminate polymer radicals. After this hot phase, the system consolidates to a situation where zero or one radical is left inside the nanodroplets. The surviving radicals grow during the cold phase undisturbed until − according to the chosen temperature − chain transfer to monomer occurs. Experimental molecular weight data model calculations show that most of the monomer conversion is realized during the cold stage of the process and that a single surviving radical produces about 25 polymer chains per droplet.

The approach of microwave-pulsed heterophase polymerization represents presumably the most simple and the most efficient access to polymers of such high molecular weight. It is evident that by appropriately programmed temperature steps and/or addition of other monomers/transfer agents between the steps a wide variety of bi- and multimodal molecular weight distributions can be accessed.

The basic reason for these new possibilities is that processing times come into the range of molecular polymerization times, e.g., we can cool and heat at a rate that is comparable to the time it takes for a chain to polymerize. This tool obviously allows controlling and handling molecular events down to the scale of a single polymer chain.

In summary, pulsed miniemulsion polymerization including programmed steep temperature pulses possesses promising potential for commercial application as it allows the comparatively easy realization of tailored molecular weight distributions, especially including species with extremely high molecular weights of up to $>10^7$ g/mol. Moreover, it is straightforward that this polymerization strategy is not restricted to batch miniemulsion polymerization, which has been chosen as it is convenient to carry out in lab-scale experiments. It can also be carried out with swollen seed particles instead of miniemulsion droplets and even continuously in tube reactors, which easily allow the realization of consecutive heating and cooling zones.

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Supporting Information Available: Effect of different amounts of AIBN on conversion and molecular weight distribution in a multistep process. This material is available free of charge via the Internet at http://pubs.acs.org.

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