DOI: 10.1002/masy.200750224

Unusual Kinetics in Aqueous Heterophase Polymerizations

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Summary: The heterogeneous nature of aqueous heterophase polymerizations is the base for an easy route to unique block copolymers, for the development of new and more effective polymerization strategies, and the abilities to unique studies of radical polymerization kinetics. Thermo-sensitive double hydrophilic block copolymers and micro- or nano-gel particles of poly(N-isopropyl acrylamide) as thermo-responsible block and charged or uncharged hydrophilic polymers can easily be prepared if the polymerization of N-isopropyl acrylamide is started with the corresponding polymeric radicals. The application of extremely fast microwave heating allows the development of highly effective pulsed thermal polymerization strategies and the production of polymers with desired molecular weight distributions over wide ranges. 2,2′-azobisisobutyronitrile simultaneously initiates the polymerization in both the monomer and the aqueous phase and leads, even under surfactant-free conditions, to stable latex particles.

Keywords: 2,2′-azobisisobutyronitrile; block copolymers; heterophase polymerization; microwave heating; particle nucleation

Introduction

Aqueous heterophase polymerization is not only an industrially important radical polymerization technique but also scientifically challenging as well as offering unique possibilities for basic scientific studies. All advantages as well as all kinetic peculiarities of heterophase polymerizations are grounded on the heterogeneous nature of the reaction system creating at least two, extremely different reaction loci. The potential ability to produce amphiphilic block copolymers via a simple radical polymerization mechanism under such circumstances was recognized already 1952.[1]

This paper emphasizes the utilization of unusual kinetic effects in aqueous heterophase polymerizations regarding (1) the comparably facile synthesis of block copolymers, (2) the advantages of the use of microwave heating, and (3) the abilities to study radical polymerization reactions taking place simultaneously in both the monomer and the continuous aqueous phase if monomer soluble initiators are employed mainly during the particle nucleation period.

Experimental Part

Block Copolymer Formation

All polymerization experiments were carried out at 70 °C in 100 ml all - glass reactors. The precursor polymers were synthesized with the following recipe: 100 g of water, 20 g of monomer, 0.32 g of 2,2-azobis(2-methyl-N-(2-hydroxyethyl)propionamide) (VA-086 from Wako) as initiator. The recipe for the production of the linear and cross-linked block copolymers with N-isopropyl acrylamide (NIPAm) was 100 g of water, 2 g of the corresponding precursor polymer as reductant, 4 g of NIPAm, 0.4 g of ceric

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ammonium nitrate dissolved in 5 ml of concentrated nitric acid as oxidant, and 0.1 g of N,N′-methylenebis(acrylamide) ylenebis(acrylamide) (MBAm), respectively. After polymerization all polymers were cleaned by ultrafiltration through DIAFLO membranes with a molecular weight cut-off of 10^4 g/mol (type YM 10 from Amicon, Inc., USA) as long as the amount of original water was replaced ten times. Then, the polymers were isolated by freeze drying. The molecular weight distributions of the precursor polymers with hydroxymethyl terminal groups were analyzed by analytical ultracentrifugation according to standard procedures.[2,3] The particle size (D_i, intensity weighted average particle size) in solution or in dispersion was measured using a NICOMP particle sizer (model 370). Additionally some samples were investigated with transmission electron microscopy (TEM) with a Zeiss EM 912 Omega microscope.

Pulsed Thermal Polymerizations with Microwave Heating

The experimental and analytical procedures are described in great detail elsewhere.[4] Miniemulsions were prepared according to standard procedures from an organic phase that consisted of 6 g of styrene 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). After pre-emulsification for 1 h homogenization was carried out by ultrasonicating the macroemulsion with a sonicatortip (Branson sonifier W450 Digital) under ice cooling for 2 min. Oil-soluble radical initiators were added to the organic phase before homogenization, and water-soluble radical initiators were added to the miniemulsion after homogenization.

Investigations of Particle Nucleation with 2,2′-Azobisisobutyronitrile

These investigations were carried out at 70 °C in an experimental setup allowing on-line measurement of optical transmission and conductivity of the aqueous phase as described in.[5] First, the reactor was filled with 400 g of de-ionized and degassed water from a Seral purification system (PURELAB Plus) with a conductivity of 0.06 μS/cm. Then, styrene was placed on top of the water confined in a glass funnel maintaining a constant monomer – water interface of 31 cm^2 throughout the experiment (the remaining water – air interface is 80 cm^2). 120 minutes after styrene addition the polymerizations were started by adding 76 mg of 2,2′-azobisisobutyronitrile (AIBN) dissolved in 1.2 g of styrene. The total amount of styrene for all experiments was 3.7 g. The AIBN in styrene solution was added either to the monomer reservoir in the glass funnel or directly into the aqueous phase. At the end of the polymerizations the monomer phase was separated from the aqueous phase and the polymers formed in both phases were characterized regarding their molecular weight distributions by means of SEC. Additionally, the latex particles were imaged by TEM.

Block Copolymer Formation

The production of block copolymers via radical polymerization premises at least a much shorter radical formation period compared with the duration of the propagation reaction, a negligible probability of radical termination throughout the whole polymerization process, and a sequential monomer addition. The latter requirement is the easiest to fulfill. In contrast, the realization of the two other points strongly requests much more efforts. To block the radical termination means to restrict the probability of radical encounters which is possible by either decreasing the number density of radicals per unit volume or by the generation of high molecular weight radicals. A low number density of growing radicals per unit volume is successfully realized by the various controlled or living radical polymerization techniques.[6] The creation of a situation where only high molecular weight radicals grow during the entire polymerization reaction is possible by the application of polymeric initiators.[7–9] Under such conditions block copolymer formation is the more effective the higher the molecular weight of the initiating radicals as radical termination decreases according to a power law with increasing molecular weight.[10] In general, the requirement of timely separated radical formation and propagation can be realized in different ways. Any kind of radiation-induced radical formation allows controlling the duration of the period of initiation of growing chains. For the first synthetic block copolymers ever described BOLLAND & MELVILLE used UV-light.[11] These authors reported as early as 1939 the formation of poly(methyl methacrylate)-*b*-polychloroprene-*b*-poly(methyl methacrylate) triblock copolymers by radical gas phase polymerization. After switching off the UV-light growing radicals deposited at the reactor walls survived quite a long time and continued to grow after addition of new monomer. Another remarkable example how heterophase conditions can be used to make block copolymers by conventional radical polymerization is the application of a special initiating system in emulsion polymerization.[12] HORIE & MIKULASOVA used a polymeric redox-initiator system. Though, the initiator system was removed after 30 minutes the polymerization in the latex continued until complete styrene conversion and moreover, after the addition of methyl methacrylate block copolymer formation was proven. Obviously, growing radicals can easily survive inside latex particles as it was also proven by electron spin resonance investigations of MMA emulsion polymerization. [13] The continuation of a radical polymerization reaction after ending primaryradical formation is known as 'post-effect' and is characterized by non-steady state free radical polymerization kinetics.[14] O'SHAUGHNESSY & YU have demonstrated that the 'infinite' lifetime in the post-effect situation emerges directly from principles of polymer physics after the onset of entanglements under homogeneous reaction conditions.[14,15]

These considerations allow the conclusion that under the conditions of emulsion polymerization initiated with polymeric radicals a latex particle is the perfect place for polymeric radicals to survive not only in the glassy but also in the swollen state which is a high concentrated polymer in monomer solution (about 50 weight-%). Consequently, an optimum reaction system for producing block copolymers by ordinary radical polymerization is a heterophase polymerization with the generation of polymeric radicals. It was experimentally proven that a redox initiator system with Ce^{4+} as oxidant and a hydrophilic polymer with hydroxymethyl end groups as reductant leads to the formation of single polymeric radicals at the terminal carbon atom (cf. Figure 1).

For monomethoxy terminated poly(ethylene glycol) as reductant it was shown that during the polymerization of N-isopropyl acrylamide (NIPAm) the formation of primary poly(ethylene glycol) radicals stops after about five minutes whereas the growing poly(ethylene glycol)-*b*-PNIPAm radicals survive many hours.

The polymerization could be restarted many times after the addition of new batches of monomer.[16] In these experiments the survival of radicals was observed even after the aggregation of the growing poly(ethylene glycol)-*b*-PNIPAm chains to

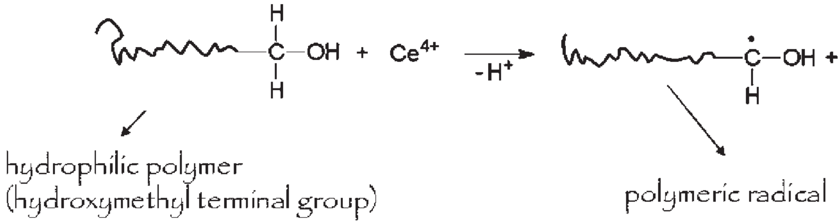

Figure 1.
Illustration of the formation of poly-meric radicals.

latex particles as the polymerization temperature was above the critical solution temperature of PNIPAm. This experimental fact was utilized to produce a huge variety of amphiphilic block copolymers by adding, after the polymerization of the first batch of NIPAm was completed, other hydrophobic monomers which swell the PNIPAm core of the latex particles.[17,18]

Hydrophilic precursor polymers with hydroxymethyl end groups can easily be prepared by polymerization in aqueous solution with corresponding initiators such as 2,2-azobis(2-methyl-N-(2-hydroxyethyl)-propionamide) or symmetrical poly(ethylene glycol)-azo initiators.[7] Apparently, the average molecular weight and the molecular weight distribution (MWD) of the precursor polymers is not crucial as poly(ethylene glycols) with a molecular weight of 5000 g/mol and the hydrophilic polymers mentioned in Table 1 with much higher average molecular weights and much broader MWD have been successfully employed as polymeric reductants in NIPAm polymerization.

These precursor polymers lead to hydrophilic thermo-sensitive block copolymers, which form at room temperature (RT) transparent solutions which convert during heating into electrosterically stabilized PSS-PNIPAm, PAA-PNIPAm, PDADMAC-PNIPAm, and PDEAMEMA-PNIPAm block copolymer particles.

For the PSS-PNIPAm, PDADMAC-PNIPAm, and PDEAEMA-PNIPAm block copolymers the average particle size of the aggregates decreases with increasing temperature up to 35 °C and remains constant at higher temperatures (cf. Figure 2). The size of the aggregates at temperatures below the critical solution temperature of the PNIPAm–block depends strongly on the nature of the other block. The observed order PSS > PDADMAC > PDEAEMA indicates both an influence of the electrical nature and the chain length. The PNIPAm-block possesses a quite strong aggregation power as not only the uncharged PDEAEMA chains but also the polyelectrolyte chains are brought into much closer contact in the aggregated state. Interestingly, the thermal behavior of the PAA-PNIPAM block copolymers is the opposite as the aggregate size increases with increasing temperature over the whole range. This indicates a specific acid – base interaction and hence, a partly ampholytic nature of this block copolymer causing colloidal destabilization.

Table 1.
Precursor polymers with hydroxymethyl end groups.

Precursor polymer	Range of the MWD
Poly(styrene sulfonate) (PSS)	$1.0 \cdot 10^5$–$1.6 \cdot 10^6$
Poly(diallyldimethylammonium chloride) (PDADMAC)	$1.0 \cdot 10^4$–$2.0 \cdot 10^5$
Poly(acrylic acid) (PAA)	$5.0 \cdot 10^5$–$3.0 \cdot 10^6$
Poly(diethylaminoethyl methacrylate) (PDEAEMA)	$1.0 \cdot 10^5$–$2.5 \cdot 10^6$

Thermo-sensitive micro- or nano-gel particles can be obtained if the block copolymer formation is carried out in the presence of MBAm as a cross-linker.

Expectedly, the thermo-sensitivity of the gels is much lower that that of the uncross-linked counterparts as D_i decrease during heating by only 100 nm. TEM images of the block copolymer gel particles reveal an interesting effect of the nature of the hydrophilic block on the morphology (Figure 3). The anionic PSS and PAA – blocks collapse on the PNIPAm cores but the cationic PDADMAC blocks remain stretched on the sample grids and reveal nicely the core shell morphology of the block copolymer gel particles.

Microwave Heating

Aqueous heterophase polymerizations may be carried out in microwave ovens because the polar nature of the continuous phase allows for efficient microwave coupling. This dielectric heating is extremely fast as the reaction mixture can be warmed up within about 12 seconds from room temperature to >90 °C. Comparable with radiation induced polymerization pulsed thermal polymerizations (PTP) with alternating ‘hot’ and ‘cold’ stages as illustrated in Figure 4 give rise to

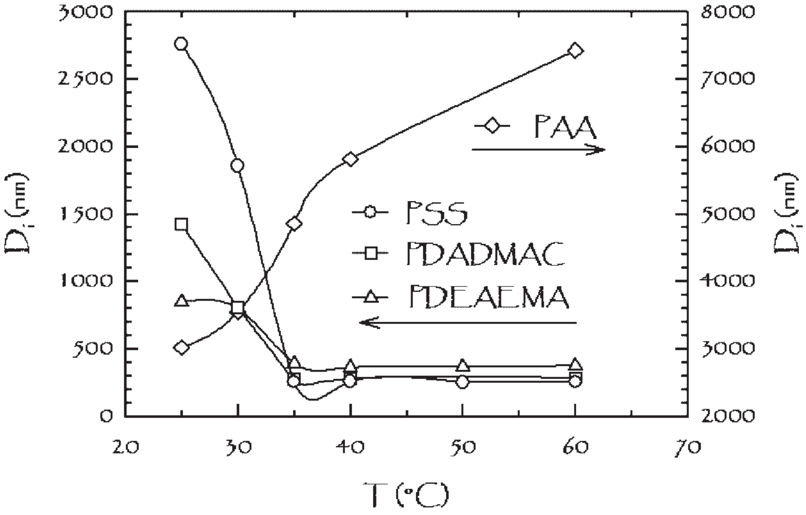

Figure 2.
Average aggregate size (D_i) in dependence of the temperature (T) for PNIPAm block copolymers with various hydrophilic blocks.

conditions, in which the cold stages are perfect post-effect situations in the above sense.

In a comprehensive study about the initiator influence during PTP of styrene in miniemulsions it turned out that medium hydrophobic initiators such as AIBN and PEGA200 lead to largely enhanced conversion (Table 2) compared to the much more hydrophilic potassium peroxodisulfate (KPS) or the much more hydrophobic 2,2′-azobis(2-methyl-butyronitrile) (V59).[4]

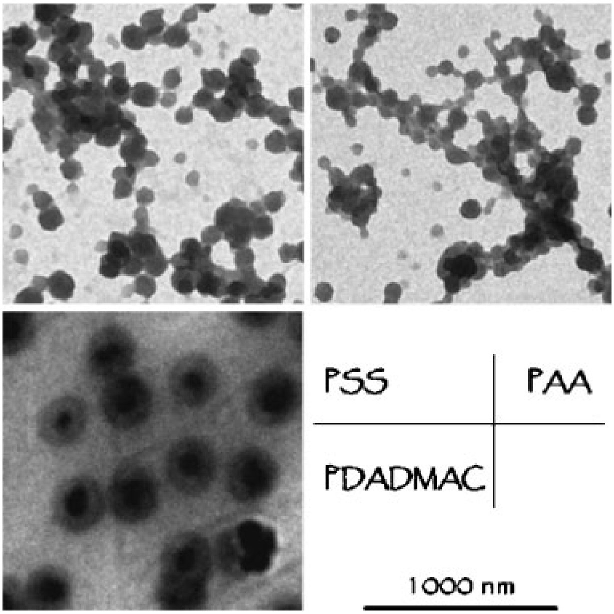

Figure 3.
TEM images of PNIPAm block copolymer gel particles with various hydrophilic blocks.

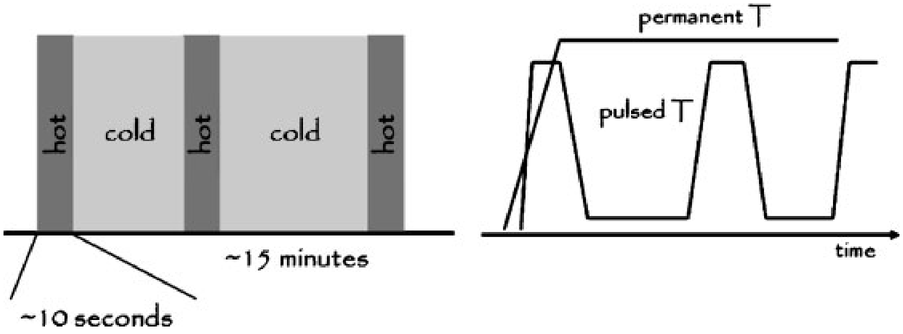

Figure 4.
Illustration of the pulsed thermal polymerization (PTP) procedure (left) with cycles of alternating hot and cold stages and the temperature profiles during polymerizations with pulsed and permanent heating (right).

Table 2.
Conversion during PTP of styrene miniemulsions after 4 pulses of 1kW power and an initiator concentration of 450 μmol except V59, where 900 μmol were used.

Initiator	V59	AIBN	PEGA200	KPS
Conversion	39.8%	88.4%	80.4%	39.0%
Water solubility	<1 mM	2.44 mM[19]	4.58 mM[7]	18.5 mM[20]

The temperature profile during the polymerization has no influence on the achievable conversion for a given initiator concentration but a strong influence on the average molecular weight (cf. Figure 5). The PTP results in polymers with much higher molecular weights than the polymerizations with permanent microwave heating.

The MWD changes during PTP in a very specific way in dependence on both the initiator concentration and the number of pulses as exemplarily shown for AIBN in

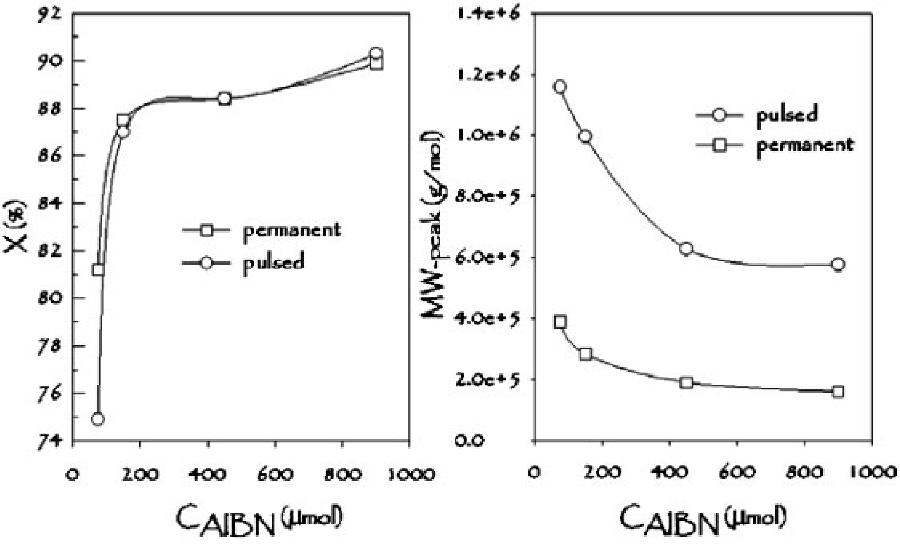

Figure 5.
Dependence of the monomer conversion and the peak molecular weight (MW-peak) on the AIBN concentration and the temperature profile obtained in styrene miniemulsion polymerization with microwave heating.

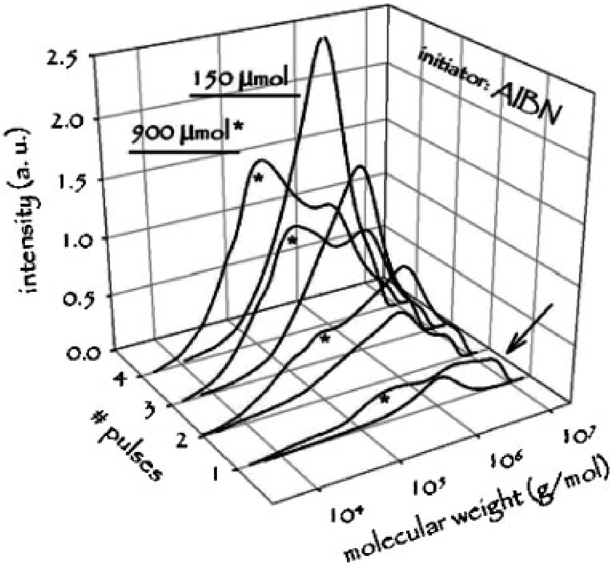

Figure 6.
Development of the MWD during the PTP of styrene miniemulsions at low and high initiator concentration (AIBN) after an increasing number of microwave pulses; the target temperature during the microwave pulse was 92 °C.

Figure 6. This graph contains conversion weighted MWD in which the area under the SEC traces is directly proportional to the monomer conversion. This kind of presentation makes it easy to see how much polymer in a certain molecular weight range has been formed in a given conversion range or microwave pulse.

The monomer conversion for the polymerizations of Figure 6 after each cycle at the end of the 'cold period' obeys common experience. It is the higher the higher the initiator concentration and after 4 temperature pulses it reaches 87 and 90% for 150 and 900 μmol of AIBN, respectively. But the MWD's as depicted elucidate the peculiarities of PTP.

In the range of the MWD below 10^6 g/mol the expected influence of the AIBN concentration is observed as higher amounts of initiator cause the formation of higher portions of polymer chains in the low molecular weight region. But also in the high molecular weight region, close to the exclusion limit of the SEC apparatus, a large portion of polymer chains is present especially for the high AIBN concentration (indicated by the arrow in Figure 6). Particularly, after the first two cycles the maximum in the MWD is in the high molecular weight region above 10^6 g/mol. This is an unusual but interesting feature of PTP and illustrates the possibilities to realize high rates and high molecular weights simultaneously.

Another unusual result of PTP is illustrated in Figure 7. These data show for both the mass average molecular weight (M_w) and the conversion a clear tendency to decrease with increasing energy input during the radiation period.

The parallel change of conversion and average molecular weight with increasing energy input is not clear at a glance as it apparently contradicts the 'normal' expectation of radical kinetics. However, an explanation is possible considering the peculiarities of both the pulsed thermal polymerization procedure and the heterophase conditions.

During the hot stage of the cycle the rate of radical formation is high and the huge number of low molecular weight radicals favors bimolecular termination as it scales

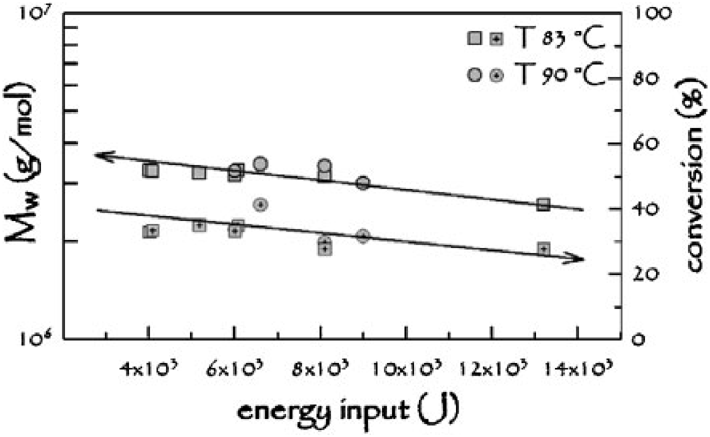

Figure 7.
Change of conversion and mass average molecular weight (M_w) after the first cycle with the energy input (microwave power times duration of the pulse) for two different target temperatures; one single pulse, initiator: 450 μmol PEGA200.

with the radical concentration squared. However, a few radicals survive and continue to grow during the cold stage where no radicals are generated. The heterophase nature of the reaction system supports the surviving of some radicals due to the compartmentalization and the high viscosity inside the particles. The chain transfer limit of the average molecular weight for radical styrene polymerization at 0 °C can be estimated to be about 10^7 g/mol.[21–23] The following model calculation elucidates the importance of the cold stage for the PTP. An average miniemulsion droplet with a diameter of 100 nm contains about $3 \cdot 10^6$ styrene molecules. Assuming 40% monomer conversion after the first cycle (that is the highest value obtained so far) and chain growth until the transfer limit means that a single radical per particle has to generate about 12 chains or 11 times to do radical transfer to monomer. This scenario would require at most a duration of the cold stage of about $12 \cdot (10^5/k_p[M]) =$ 4400 s if a propagation frequency at 0 °C of $k_p[M] = 270.6$ 1/s is assumed. [24] These estimations – though quite rough – seem to be not unrealistic as the gap between two pulses is at least 900 s and the temperature has to decrease from 90 °C to zero within this time. Moreover, as the propagation frequency at 90 °C is only 30 times of that at 0 °C most of the monomer conversion is generated by the surviving radicals during the cold stage.

An increasing rate of primary radical formation (higher initiator concentration or energy input) increases the number of surviving radicals. However, if this number is above a critical value and if there is more than one growing radical per particle the small radical formed after chain transfer to monomer can cause termination. This might explain the dependence of the conversion and the average molecular weight on the energy input.

In conclusion of this section, the extremely fast heating capabilities of microwaves can be used to tailor the MWD during aqueous heterophase polymerizations only by physical means. The PTP scenario or the generation of alternating sequences of steady state and non-steady state conditions regarding the concentration of growing radicals allows a certain control over the MWD. Broad MWD are accessible, which might be of interest for practical applications as they combine easy processibility with good mechanical properties.

Particle Nucleation in the Case of Monomer Soluble Initiators

Thermodynamics requires in any heterophase system an exchange of matter between all phases. It will take place as soon as it is kinetically possible. This is important for any kind of heterophase polymerization and is one reason that aqueous phase kinetics plays a crucial role even if hydrophobic initiators are employed.[25–27] As shown in the former section medium hydrophobic initiators such as AIBN are very useful carrying out PTP of styrene miniemulsions and hence, an interesting question might be what happens in surfactant–free polymerizations? Is it possible to get latex particle if the polymerization is started with AIBN, which is predominantly dissolved in the monomer phase? What differences exist between the polymerization inside the monomer and the water phase? In order to investigate these points a procedure as depicted in Figure 8 was employed.[5]

The polymerization was started by adding an AIBN in styrene solution 120 minutes after placing the styrene monomer in the funnel on top of the aqueous phase. The initiator was injected either into the monomer phase (mode 1) or into the water phase (mode 2). At the end of the polymerization the monomer phase was separated from the aqueous phases and the products formed in any phase were analyzed. Surprisingly, polymerization was observed in both phases. Besides the expected bulk polymer in the monomer phase also latex particles were obtained (cf. Figure 9).

The reactions in the aqueous phase lead initially to a change in the conductivity and subsequently to the formation of latex particles accompanied by the drop in the transmission (cf. Figure 10). Moreover, the shape of the conductivity curve is qualitatively the same as observed for surfactant-free emulsion polymerizations initiated with potassium peroxodisulfate.[5,28] The bend of the conductivity curves marks the onset of particle nucleation as conducting species are captured in the diffuse electrical double layer of the particles. These results clearly prove that side reactions of carbon radicals in water lead to conducting species. The zeta-potential of the particles is pH-dependent and negative at pH >4. First hints that such radicals can attack water molecules have been obtained by NMR investigations of polymers made by 'normal' emulsion polymerization (i.e. in the presence of surfactants) initiated with azo-initiators.[29] Ongoing studies try to clarify the reaction mechanisms.

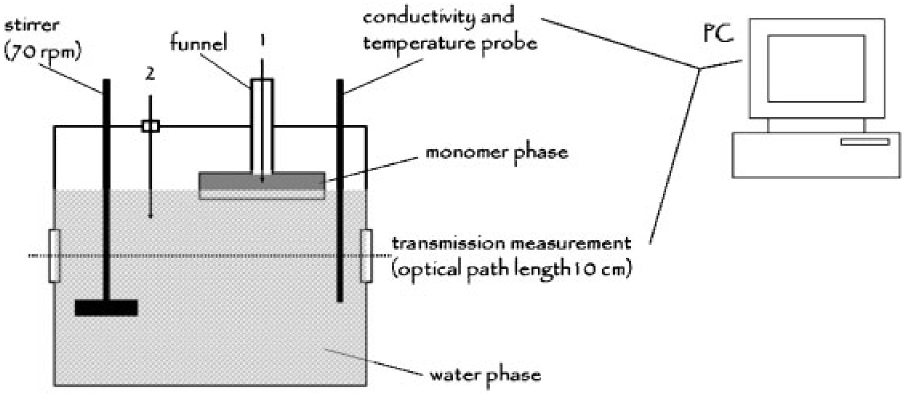

Figure 8.
Illustration of the reactor and the methodology to investigate the initial period of heterophase polymerizations with on-line monitoring of transmission and conductivity (not to scale); 1 and 2 denote possibilities to inject AIBN; the stirrer speed is just enough to avoid concentration gradients in the continuous phase and does not cause the formation of monomer droplets.

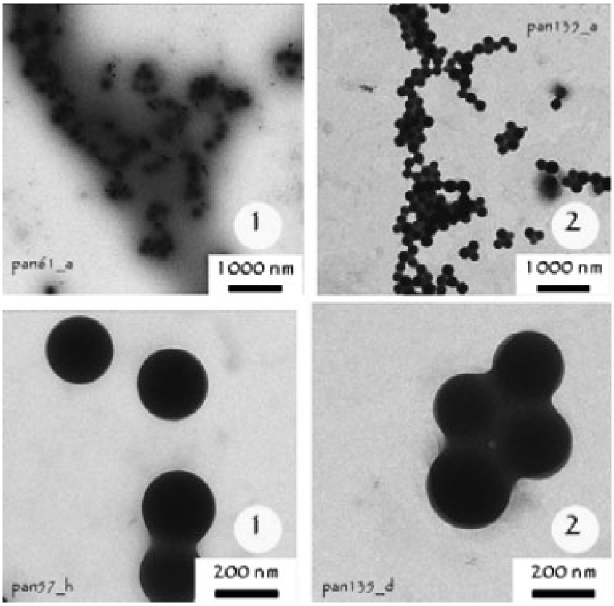

Figure 9.
TEM images of latex particles obtained during surfactant-free emulsion polymerization of styrene initiated with AIBN; 1,2 – AIBN injection modes.

The differences in the averaged curves between both injection modes are only marginal. The higher is the amount of AIBN in the bulk monomer phase (mode 1 vs. mode 2) the lower the initial slope of the conductivity – time curve, the longer the pre-nucleation period, and the later the transmission starts to drop.

Interestingly, after the bend (i.e. after particle nucleation) the slopes of both

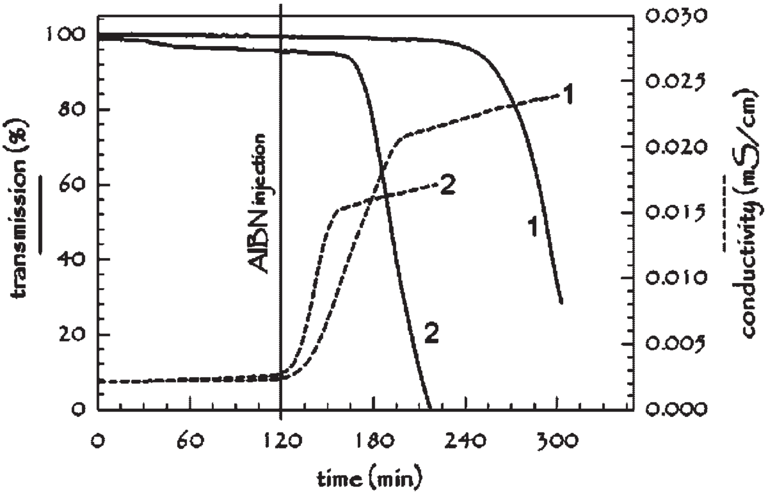

Figure 10.
On-line record of the changes in transmission (solid lines) and conductivity (dashed lines) during AIBN-initiated surfactant-free styre-ne heterophase polymerize-tion; the curves represent averages of 5 repeats; 1, 2 AIBN addition into the monomer and the water phase, respectively.

conductivity curves are almost identical and thus, indicating the same overall surface area of the nucleated particles. This conclusion is confirmed by the average size of the particles which is almost the same (D_i of 190 and 184 nm for mode 1 and 2, respectively, cf. also Figure 9). Note, the initiator addition mode 2 leads to a thin monomer layer at the water air interface, which obviously facilitates AIBN diffusion into the water phase compared to mode 1, which favors a higher AIBN concentration in the thicker bulk monomer phase possessing a smaller interface to the water phase.

The average molecular weight of the polymer depends on both the AIBN addition mode and the reaction locus (cf. Table 3). The molecular weight data scatter a lot, especially those obtained for the polymer formed in the latex particles after AIBN addition to the monomer phase (mode 1). Despite the scatter, which might be due to a post-effect situation in the latex particles before isolating the polymer, the order of the molecular weights can be explained as follows. The polymerization to high molecular weight polymers starts in the monomer phase soon after initiator addition. Whereas the formation of polymers in the latex can start only after nucleation, which is 30 (for mode 2) or 70 minutes (for mode 1) after initiation (cf. Figure 10). The polymer formed during this pre-nucleation period inside the monomer phases retains the monomer and reduces swelling of the particles with monomer. Thus, the polymerization inside the monomer phase prevents the formation of high molecular weight polymers inside the latex particles.

In conclusion, the formation of latex particles in surfactant-free emulsion polymerization of styrene initiated with AIBN obeys the same rules of aggregative nucleation as verified for KPS.[5,28] The latex particles are electrostatically stabilized by ionic or ionizable groups which are formed by side reactions of carbon radicals under participation of water.

Table 3.
Number average molecular weight (g/mol) of the polymer formed during surfactant-free emulsion polymerization of styrene in dependence on the AIBN addition mode and the polymerization locus; average values and standard deviation of 6 repeats.

	Latex	Bulk
Initiation mode 1	11200 ± 11000	31400 ± 4100
Initiation mode 2	1900 ± 190	21200 ± 6500

Acknowledgements: The authors thank the Max Planck Society for financial support and the director of the colloid chemistry department of the Max Planck Institute of Colloids and Interfaces, Markus Antonietti, for many encouraging and fruitful discussions. M.M. gratefully acknowledges a fellowship from the DAAD (German Academic Exchange Service) and J.L. a joint fellowship from the Korea Science and Engineering Foundation (KOSEF) and the DAAD. The authors are indebted for the analytical ultracentrifugation to Mrs. A. Völkel and for the electron microscopy images to Mrs. R. Pitschke and Mrs. H. Runge.

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