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Living Radical Polymerization in Miniemulsion Using Reversible Addition−Fragmentation Chain Transfer

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ABSTRACT: Living radical polymerizations using reversible addition−fragmentation chain transfer (RAFT) have been conducted successfully in miniemulsions stabilized by nonionic surfactants. The miniemulsion stability was found to be a key issue. Both anionic and cationic surfactants were not able to maintain the original droplet morphology during the reaction. The application of nonionic surfactants allowed the controlled polymerization of methacrylate and styrene monomers, resulting in stable dispersions free of coagulate. Typical particle sizes for these latices were around 200−300 nm. The molar mass of the polymer was close to the predicted value, and polydispersity was typically below 1.20, never exceededing 1.40. The "living" character of the latex material was further exemplified by its transformation into block copolymers. The increased polymerization rate of the compartmentalized system allowed for improved block copolymer purity compared to that of homogeneous systems. Furthermore, it was shown that latex blends containing particles with very different characteristics could be prepared in a single polymerization by a careful choice of reaction conditions allowing the design of sophisticated materials.

Introduction

Living radical polymerization has been shown to be a versatile tool for the preparation of well-defined polymer architectures. In the early stages of its development, the technique was restricted to a limited number of monomers and confined to extraordinary polymerization conditions. Nitroxide-mediated polymerization, for example, required high temperatures,[1] whereas the disulfides applied by the iniferter technique required UV irradiation.[2] During the past few years, however, existing techniques have been refined and new ones developed so that nitroxide-mediated polymerizations can now be conducted with monomers other than styrene at more modest temperatures,[3] while atom transfer radical polymerization (ATRP)[4] and reversible addition fragmentation chain transfer (RAFT)[5,6] allow the controlled polymerization of nearly all vinyl monomers under conditions comparable to those in conventional radical polymerization.

A new challenge confronting living radical polymerization is its application in dispersed (i.e., heterogeneous) media. Water-borne polymerizations are an industrially preferred way to conduct radical polymerizations as they eliminate the need for organic solvents,[7] provide an excellent medium to remove the heat of reaction, and guarantee a product that has a low viscosity and is easy to handle. If controlled radical polymerizations could be conducted in such systems, the range of possible industrial applications and products will be greatly enhanced through intelligent design of the polymer architecture.

Recent literature reports several attempts to perform living radical polymerization in dispersed media, applying techniques based on reversible termination (ATRP, nitroxides).[8] The disadvantage is the troublesome partitioning of the small deactivating species over the two phases, which complicates the kinetics.[9] If the deactivating species moves into the water phase, it will slow the growth of aqueous phase radicals, hampering radical entry, while at the same time decreasing the rate of polymerization. Control of molecular weight at the main locus of polymerization (i.e., inside the particle) will suffer from the reduced concentration of deactivating species. Besides, it has been argued that the persistent radical effect, which adds to the control in bulk and solution polymerizations, will cause a exceedingly low polymerization rate in such compartmentalized systems.[10]

Techniques based on degenerative transfer form a more likely candidate for this type of application since the number of free propagating radicals remains unaffected in theory. Another advantage is that the controlling species is (attached to) a dormant polymer chain and thus will not be able to diffuse out of the particle, negating the effect of exit and the corresponding lack of molecular weight control. Several studies reported the successful application of such techniques in waterborne systems, but all of these studies use relatively inactive species to control the polymerization. The alkyl iodides used by several groups[10,11] have a transfer constant only slightly greater than unity. A similarly slow consumption of the compound can be expected for the RAFT agents applied by Kanagasabapathy et al. and in our own group, because of a poor homolytic leaving group[12] and a rather unactivated carbon−sulfur double bond,[13] respectively. Although these systems allow the preparation of complex architectures (e.g., block copolymers), polydispersity is usually high (~2) since the conversion of transfer agent into polymer chains takes place during a prolonged interval of the polymerization and because the exchange reaction between growing radicals and dormant chains is slow in comparison with propagation.

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The transition from transfer agents with low activity to those with a high activity appears to be straightforward, but in practice this turns out to be more complicated. In our previous work several RAFT agents have been applied in conventional emulsion polymerizations, both seeded[14] and ab initio.[15] While low-activity xanthates could easily be used,[13] high-reactivity agents based on the dithiobenzoate group invariably led to colloidal stability problems.[14,15] A large amount of the transfer agent was lost in the form of an (oligomeric) coagulate, resulting in a much higher molar mass than expected for the emulsion material.

In this paper we will present our results on the preparation of low-polydispersity homopolymers and block copolymers using highly reactive RAFT agents via miniemulsion polymerization.

In miniemulsion polymerization, the initial droplet size is at least 1 order of magnitude smaller than that of the droplets in conventional (macro)emulsions. The resulting increase in the interfacial area of the droplet phase and the reduced number of micelles ensure that radical entry into the droplets becomes the dominant particle nucleation mechanism. In the ideal case the resulting polymer dispersion is a copy of the initial emulsion in terms of particle size, number, and identity,[16] thus eliminating the need for transport of the RAFT agent through the water phase.

Several factors may cause reality to deviate from this rather simplistic model. First, the presence of competing nucleation mechanisms cannot be ruled out. Although micellar nucleation is unlikely, homogeneous nucleation has been shown to lead to the formation of new particles.[17] The extent to which this occurs depends on numerous factors, the most important being the amount of surfactant and monomer in the water phase, the type of initiator used, and the stability of the monomer droplets. In the case of RAFT polymerizations, secondary nucleation is highly undesired as the newly formed particles will not contain any RAFT agent, and the polymerization in these particles will not be controlled.

Second, not all of the droplets may be converted to particles. Miniemulsions are in principle unstable systems. Albeit small, the Gibbs free energy of the system is above zero, and finite differences in osmotic pressure among the droplets will cause monomer to be transported from the small droplets to the larger ones, thereby increasing the driving force for this process and finally resulting in phase separation. The difference in osmotic pressure among the droplets will also be increased if in the course of the reaction some become nucleated while others do not. The droplets lacking polymer will eventually supply monomer to the growing polymer particles and act as monomer reservoirs. The RAFT agent contained within these resevoirs will then need to be transported to the growing particles through the water phase. This may have two different, but both undesirable, effects. First, the RAFT agent, arriving later at the locus of polymerization, will start new chains later in the polymerization and therefore broaden the molar mass distribution. Second, if the RAFT agent has already been converted into (oligomeric) dormant species in these droplets, transportation may no longer be possible because of their low water solubility. The most probable event is that these oligomers coagulate as monomer is depleted from these droplets.

To avoid these transportation phenomena, it is important to closely approach the "ideal" miniemulsion system where the droplets can be considered as nanoscale bulk reactors, acting independently while being converted into polymer particles.

Table 1. Ionically Stabilized Miniemulsions[a]

stabilization type	anionic	cationic
surfactant	SDS	CTAB
monomer	styrene, BMA, EHMA	styrene
costabilizer	hexadecane	hexadecane, PS, Kraton
initiator	KPS, KPS/$Na_2S_2O_5$, AIBN, V-40, AIBN/V40	VA-086, AIBN, V-40
RAFT agent	**1**, **2**, **3**	**2**, **3**, **4**, **5**

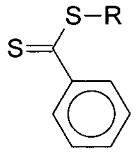
[a] These recipes typically contain 80 g of water, 20 g of monomer, 0.2 g of surfactant, 0.2−0.5 g of costabilizer, 0.2−0.6 g of RAFT agent (2−4 g for **4** and **5**), and 0.1−0.2 g of initiator.

Results and Discussion

Stability Issues. The stability of miniemulsions is a key issue as discussed above. Although they are thermodynamically unstable, the droplet size should be preserved for a time span, long enough to conduct a polymerization reaction. Surfactant alone cannot provide this stability, and a suitable costabilizer has to be used such that the droplets will be guarded against Oswald ripening for periods of weeks or months. A well-known costabilizer is cetyl alcohol, which is believed to form a structured complex together with the hydrophobic surfactant tails of, for example, sodium dodecyl sulfate (SDS), thereby creating an electrostatically charged barrier that prevents droplet coalescence and slows the diffusion of monomer out of the droplets. Completely hydrophobic materials like hexadecane,[18] dodecylmercaptan,[19] and stearyl methacrylate[20] were found to work even better. It is unlikely that these hydrophobes will reside in the surfactant layer. Their effectiveness is attributed to a lowering of the Gibbs free energy on entropic grounds by becoming highly dilute with the monomer. Larger hydrophobic species like polystyrene and poly(methyl methacrylate) have also been used to improve the particle stability, causing higher reaction rates and a more robust nucleation process.[21]

The combination of SDS and either cetyl alcohol or hexadecane as the costabilizer is beyond any doubt the most commonly applied stabilizer system for conventional miniemulsion polymerization. The first patent on RAFT polymerization[5] mentions two examples of styrene miniemulsions using precisely these components. A similar system was taken as the starting point for our investigations. A series of miniemulsions were prepared using SDS as surfactant. Table 1 and Scheme 1 summarize the various monomers, RAFT agents, and costabilizers that were used. Polystyrene, hexadecane, and Kraton L1203 were employed separately and in varying combinations to halt Oswald ripening, and in most cases a stable miniemulsion was obtained. The particle size was typically between 60 and 100 nm. The unreacted miniemulsions showed no visible signs of phase separation for at least a week. During this period the conductivity was monitored and remained constant for the blanks without RAFT, whereas the addition of RAFT agent caused a slight increase in conductivity after a period of 3−4 days, indicating that the stability is affected, but this effect is unimportant on the polymerization time scale.

Scheme 1. RAFT Agents Applied in This Study



1. R = $C(CH_3)_2CN$
2. R = $C(CH_3)_2C_6H_5$
3. R = $C(CH_3)_2COOC_2H_5$
4. R = $C(CH_3)(CN)CH_2CH_2COO$-
-poly(ethylene-*co*-butylene)
5. R = poly(methyl methacrylate)

When miniemulsions were polymerized with potassium persulfate (KPS), some phase separation became apparent as soon as the reaction started. A clear red monomer phase formed in the vortex of the stirred miniemulsion, and as the reaction proceeded, this organic phase slowly increased in volume. The red color indicates the presence of species containing the dithiobenzoate group, and GPC analyses revealed that the layer consisted of monomer swollen oligomers/polymers, usually of a considerably lower molar mass than the emulsion polymer and with a broader molar mass distribution (polydispersity typically between 3 and 5). Neither polystyrene nor Kraton was present in the organic layer when these polymers were employed as stabilizers, indicating that the red phase does not originate from droplet coalescence. This suggests that monomer is extracted from the existing particles. In the course of this process, the conductivity rapidly increases while in miniemulsions that do not employ RAFT agents the conductivity remains roughly constant during the reaction.

The effect of the initiator was investigated by the use of 2,2′-azobis(isobutyronitrile) (AIBN) and 1,1′-azobis(1-cyclohexanecarbonitrile) (V-40), which are azo initiators that partition preferentially into the droplet phase. The aim of this set of experiments was to determine whether the stability problems were a consequence of the water-soluble initiator, KPS. In addition, it has been argued that organic phase initiation also suppresses secondary particle formation and thus the possibility of transportation problems of RAFT into new particles. The colloidal stability obtained with the azo initiators was similar to that with KPS. Here it should also be noted that the majority of radicals that partake in the polymerization are not derived from the initiator but originate from the applied RAFT agent. Its fast exchange reactions combined with its high concentration relative to that of the initiator cause the majority of both propagating and dormant species to have the R group, which was originally attached to the RAFT agent (Scheme 1), as end group. Nonetheless neither a different initiator nor another RAFT agent could reduce the phase separation to any significant degree.

To achieve efficient nucleation of all particles, the radical flux was varied by changing the initiator from AIBN to V-40. While the stability remained poor, it was found that the rate at which the organic layer was formed was correlated to the speed of reaction: faster reactions exhibited faster formation of a separate organic phase. Therefore, reaction products formed by the polymerization appear to play a crucial role in the destabilization process. It should be noted that further enhancement of droplet nucleation by the application of a redox system proved ineffective.

The stability problems were not specific to styrene polymerizations. The same phenomena could be observed in polymerizations using *n*-butyl methacrylate (BMA) and (2-ethyl)hexyl methacrylate (EHMA). Although polydispersities remained below 2, stability was equally poor and up to 35% of the organic material would be lost due to coagulation.

In our attempts to circumvent this stability issue, a different stabilization strategy was adopted from literature where it was shown that cetyl trimethylammonium bromide (CTAB), a cationic surfactant, could stabilize miniemulsions with an efficiency similarity to that of SDS.[22] A series of miniemulsions were conducted employing this surfactant while using 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086) as initiator. Again stable miniemulsions were obtained after sonication, but phase separation was induced by the polymerization. Similar variations were made in the choice of hydrophobe and RAFT agent as in the series of SDS experiments, all with similar results in terms of stability. These systems typically react until the monomer is depleted from the "emulsion phase". In the end situation the organic layer would contain up to 40% of the total amount of monomer, of which a substantial part had been polymerized. The emulsion material itself was of very low molar mass and had a multimodal distribution. In these experiments, polymeric RAFT agents (Scheme 1, agents **4** and **5**) were also investigated, but these could not completely suppress the instability. Although the dithiobenzoate moiety was attached to a hydrophobic material, a small organic phase with a light red color would form.

The third alternative way to stabilize miniemulsions comprises the use of nonionic surfactants. Recent literature reports the successful application of such surfactants in polymerizable miniemulsions.[22,23] We used a variety of nonionic surfactants in conjunction with either hexadecane or Kraton as the hydrophobe. Application of surfactants with relatively high HLB values (15.3−17.8) in most cases led to stable miniemulsions. Samples taken from the unreacted emulsions were monitored for at least a week. During this period a few cases showed some signs of creaming or destabilization after 4−5 days, but the majority remained homogeneous to the eye. These miniemulsions typically reacted in the absence of an organic layer. Under some circumstances minor phase separation was observed 10−20 min after the start of polymerization, but quickly thereafter it would disappear without notable effect on the molar mass distribution and without the formation of any coagulate. The products from the polymerizations were stable for at least several months. The results of several such polymerizations are detailed in the sections "controlled polymerization" and "block copolymers".

The exact cause of the instability in the ionically stabilized systems is currently under investigation and will be addressed in a future publication. Speculating, one could say that phenomena occurring during the first few percent of conversion appear to be crucial. During this stage, all the RAFT agent is transformed into dormant oligomeric species, which will partition to some extent in the water phase. The presence of water phase oligomers is known to promote homogeneous nucleation.[16] In this case the high concentration of such species may create a substantial driving force for monomer to migrate to the water phase, thereby destroying the traditional miniemulsion system. Beside the increased level of oligomers, miniemulsions containing RAFT agent lack the added stability from the presence of high molar mass polymer that would otherwise be formed in the early stages of the reaction. This suggests that the stability would benefit from avoiding the sustained presence of oligomers by low RAFT concentrations, rapidly reacting monomers, and low-reactivity transfer agents. Only the latter effect has been has been confirmed in the literature.[10−12] Furthermore, the stability issues are not expected to be specific of the RAFT system (e.g., the applied sulfur chemistry, unknown impurities in the product, etc.) as remarkably similar observations have been reported in a recent paper by Matyjaszewski et al.[24] concerning waterborne ATRP reactions.

Controlled Polymerization. Once stability was guaranteed, miniemulsions could be used as a tool in the preparation of sophisticated polymer architectures. Table 2 provides details on a series of miniemulsions that was conducted in the presence of either Igepal890 or Brij98, both nonionic surfactants.

Figure 1 shows conversion−time profiles for several miniemulsion polymerizations. When the rate of EXP1 is compared with that of EXP2, it is shown that the addition of RAFT agent to the system causes a large decrease in the rate of polymerization. The reaction rates for the various methacrylates are comparable, which was to be expected as they have similar propagation rate constants. Only the methyl methacrylate (MMA) polymerization showed deviating behavior. Because of its smaller particle size and consequently larger number of particles, it was expected to react faster. It initially, however, starts at a comparable polymerization rate but shows a notable acceleration during the next 40 min. It is unlikely that this can be attributed to the gel effect that is quite commonly observed in methyl methacrylate polymerization, since over this time interval the average polymer chain length does not exceed 30 repeat units. For a PMMA sample of such a chain length prepared in solution polymerization, the glass transition temperature (T_g) was found to be 85 °C, well below the literature value for high molar mass material of approximately 110 °C. As the droplets consist of only 20% of this polymeric material dissolved in about 80% of monomer at a reaction temperature of 70 °C, the gel effect is unlikely to occur. Another explanation is that additional particles are generated during this interval. The more hydrophilic MMA monomer and its oligomers may promote homogeneous nucleation and in this way increase the number of particles and thus the reaction rate. The newly formed particles would be deficient in RAFT agent, resulting in uncontrolled polymerization. However, no evidence for such a process is found in the molar mass distributions.

The most likely explanation is the increased entry efficiency of MMA compared to that of *n*-BMA, *i*-BMA, and EHMA. It has been calculated that the entry efficiency for MMA and BMA at 50 °C and at a KPS concentration of 0.01 mol dm^{-3} was 94% and 15%, respectively,[7] and therefore MMA will have a higher average number of radicals per particle compared to the case of BMA. The origin of this effect can be traced back to the greater water solubility of MMA.

The styrene polymerization is exceptionally slow due its lower propagation rate constant (k_p).

Table 2. Miniemulsions Stabilized with Nonionic Surfactants[e]

expt	monomer	time (min)	x (%)	$M_{n,theory}$ ($\times 10^{-3}$ Da)	M_n ($\times 10^{-3}$ Da)	M_w/M_n	DP (nm)
EXP1[a]	EHMA	25	100		>3000		
EXP2[b]	EHMA	29	5				
		47	22				
		81	53	4.1	5.4	1.07	
		94	71	5.4	6.1	1.08	
		114	84	6.4	6.7	1.08	
		136	96	7.3	7.3	1.09	
		161	100	7.6	7.6	1.09	290
EXP3[c]	STY	66	5	8.0	8.0	1.12	
		99	9	8.3	8.1	1.14	
		180	16	8.8	8.4	1.17	
		305	28	9.7	9.0	1.20	
		2525	87	14	12	1.38	340
EXP4[c]	MMA	32	41	9.3	9.1	1.23	
		67	96	13	11	1.40	
		140	100	13	11	1.40	240, 340
EXP5[b]	MMA	32	14	1.3			
		51	38	3.2	5.3	1.07	
		64	84	6.7	7.9	1.15	
		81	95	7.4	8.3	1.17	160
EXP6[b]	*i*-BMA	17	4	0.57			
		31	9	0.90	2.0	1.10	
		47	15	1.3			
		64	26	2.1	4.9	1.07	
		82	40	3.1	5.5	1.11	
		121	70	5.3	6.8	1.19	
		182	96	7.3	8.2	1.25	300
EXP7[b]	*n*-BMA	31	8	0.93			
		50	17	1.6			
		80	29	2.6	4.9	1.06	
		105	45	3.9	5.5	1.10	
		157	76	6.5	7.0	1.17	
		203	99	8.4	8.5	1.20	300
EXP8[d]	EHMA	27	9	0.99			
		42	29	2.6	3.5	1.09	
		55	39	3.5	3.9	1.11	
		67	56	4.8	4.6	1.13	
		99	89	7.5	6.4	1.13	
		125	99	8.4	7.1	1.10	
	+MMA/MA	165			7.9	1.11	
		190			9.1	1.13	
		215			1.0	1.16	230
EXP9[b]	STY	108	6	0.72	0.73	1.07	
		170	7	0.86	0.78	1.06	
		245	11	1.2	0.94	1.08	
		348	14	1.4	1.3	1.13	
		1280	42	4.0	4.3	1.12	221

[a] Recipe based on 80 g of water, 20 g of monomer, 0.4 g of hexadecane, 4 g of Igepal890, and 0.20 g of KPS. [b] Recipes based on 80 g of water, 20 g of monomer, 0.4 g of hexadecane, 4 g of Igepal890, 0.60 g of RAFT (type **1**), and 0.20 g of KPS. [c] Recipe based on 35 mL of the product from EXP2, 7 g of monomer, 0.5 g of Igepal890, 20 mL of water, and 35 mg of KPS. [d] Recipe based on 80 g of water, 20 g of monomer, 4 g of Brij98, 0.4 g of hexadecane, 0.6 g of RAFT, 0.20 g of KPS. At full conversion a feed stream of 15 g of monomer (MMA:methacrylic acid, 12:1) was started at a rate of 0.1 mL/min. [e] Experimental molar masses are determined by GPC against polystyrene calibrants.

The following equation is used for evaluation of the number-average molar mass with conversion and time:

$$\bar{M}_n = M_{RAFT} + \frac{x[M]_0 M_M}{[RAFT]_0 + 2f[I]_0(1 - e^{-k_d t})} \qquad (1)$$

where M_{RAFT} is the molar mass of the RAFT agent which constitutes the end groups of the polymer chain; M_M is the molar mass of a single monomer unit; x equals the fractional conversion; $[M]_0$, $[I]_0$, and $[RAFT]_0$ are the initial concentrations of the monomer, the initiator, and the RAFT agent; k_d is the dissociation rate constant of the initiator at the reaction temperature; and f is an

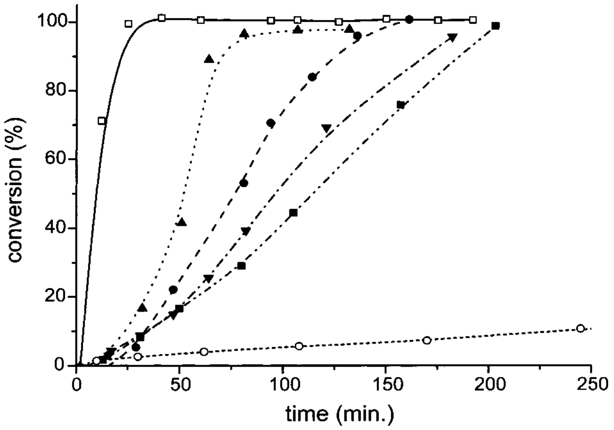


Figure 1. Conversion–time profiles for miniemulsion polymerizations: EXP1 (□), EXP2 (●), EXP5 (▲), EXP6 (▼), EXP7 (■), EXP9 (○). See Table 2 for experimental details.

efficiency factor, a measure of the fraction of radicals that will form polymer chains. f contains contributions from both the initiator efficiency and the efficiency for water phase radicals to enter polymer particles. Note that eq 1 assumes rapid and full conversion of the RAFT agent into dormant species.

Under most circumstances the second term of the denominator can be neglected relative to the concentration of RAFT agent since typical recipes apply a small amount of initiator compared to RAFT agent. The ratio of these two ingredients dictates the amount of dead material as indicated by formula 2:

$$n_{\mathrm{L}} = 1 - n_{\mathrm{D}} = \frac{[\mathrm{RAFT}]_0}{[\mathrm{RAFT}]_0 + 2f[\mathrm{I}]_0(1 - \mathrm{e}^{-k_{\mathrm{d}}t})} \qquad (2)$$

where n_{D} and n_{L} are the number fractions of dead material and living material. Terminated material not only excludes itself from further polymerization procedures (e.g., block copolymer preparation), but it also causes a broadening of the molar mass distribution. When the polymer molar mass and the maximum tolerable level of dead material are set, formulas 1 and 2 give the ratio of monomer, raft agent, and initiator. In solution and bulk polymerizations when a relatively pure or high molar mass material is desired, this often leads to extremely slow rates of polymerization. The situation is expected to be more favorable in dispersed systems where termination is reduced due to radical compartmentalization.Figure 2 shows two predictions for molar mass. An overestimation is obtained when the initiator-derived chains are neglected, denoted by the continuous straight line. The dashed curve is an underestimation of the molar mass and depicts the situation when f is 0.7, assuming that entry efficiency is 1 and initiator efficiency is 0.7 similar to solution experiments. As mentioned previously, the difference between the two predictions often is negligible, but it becomes clear from Figure 2 that for slow polymerizations the time-dependent term describing the initiator contribution plays a role. The styrene polymerization (Figure 2, bottom) closely follows the predicted values over the studied conversion range while the butyl methacrylate polymerization (Figure 2, top) seems to start above theory and slowly converges on the theoretical values. A reason for this behavior should not be sought in the miniemulsion kinetics as the same trend was observed in solution polymerizations. The difference can be explained by the fact that the experimental molar mass has been determined by gel permeation chromatography (GPC) against polystyrene standards. Although Mark–Houwink parameters are available for the applied methacrylates, such a correction procedure is known to yield unreliable results for low molar mass polymer. The same drift is observed in the polymerization of EHMA, depicted on the left-hand side of Figure 3. All of these polymerizations show living behavior with low polydispersities (<1.20).

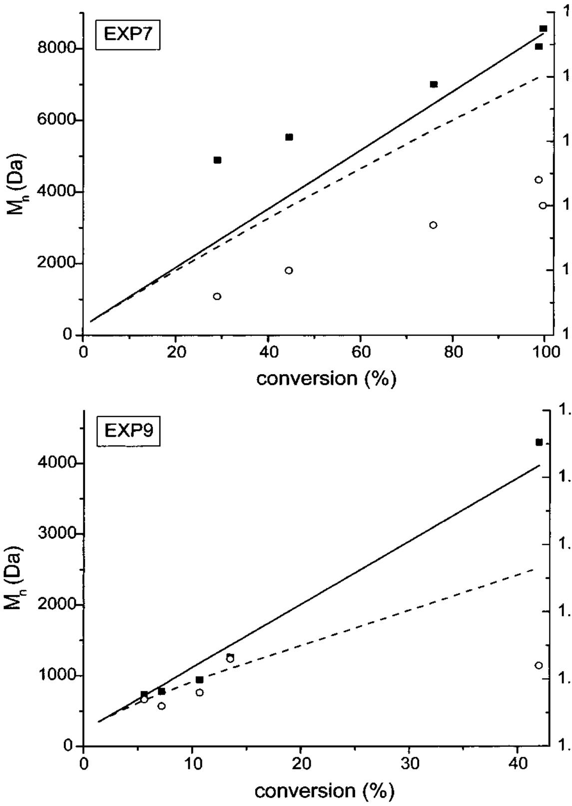


Figure 2. Results for the polymerizations of *n*-BMA (EXP7, top) and styrene (EXP9, bottom). Number-average molar mass: experimental values (■, in PS equivalents); theroretical values based on the dormant species (—); theoretical values corrected for initiator derived chains (- - -). Polydispersity index of the polymer (○, right axis).

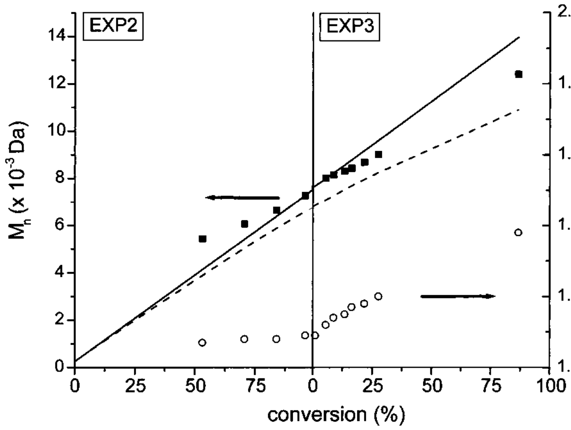


Figure 3. Molar mass data (left axis) for the preparation of the seed latex (EXP2) and the subsequent seeded polymerization of styrene (EXP3). Number-average molar mass: experimental values (■, in PS equivalents); theroretical values based on the dormant species (—); theoretical values corrected for initiator derived chains (- - -). Polydispersity index of the polymer (○, right axis).

Block Copolymers. The living character of the miniemulsions was further exemplified by their transformation into block copolymers. This was done either by two subsequent batch polymerizations where the initially prepared miniemulsion serves as a seed for the second polymerization or by a semicontinuous procedure where a second monomer was added to the polymerization reaction over a certain period of time, just after the first monomer had reached full conversion.

In the batch polymerizations the product of EXP2 was applied as the seed latex for experiments EXP3 and EXP4. For each of these experiments the seed was swollen with an amount of monomer equal to the amount of polymer already present (on weight basis). A small amount of surfactant was added to stabilize the increased surface area of the particles, and the amount of initiator was increased to the same starting level applied in EXP2.

In polymerization EXP3, styrene is employed, and due to its low propagation rate constant, the rate of polymerization is much lower than that of EXP2. Figure 3 shows the continued increase in molar mass of the seed latex material. Again the low polymerization rate suggests that eq 2 be implemented to account for chains started by initiator. The experimental values are between the theoretical line not taking into account initiator and the curve using eq 2 with f equal to 0.7. Although the polydispersity increased during this second stage polymerization, it remains low (1.38). The particle size (number-average) increased from 0.29 μm for EXP2 to 0.34 μm for EXP3. If a constant number of particles is assumed, then adding 87% to the volume of the particles (conversion of EXP3) should increase their diameter by approximately 23%, going up to 0.36 μm. The difference between theory and measurement is small, and no evidence for secondary particle formation could be found.

In polymerization EXP4, in which the seed latex is swollen with MMA, the reaction proceeds faster than the seed preparation (EXP2), though the k_p of MMA is slightly lower than that of EHMA.[25] Again the high entry efficiency found for MMA polymerizations may play a role, but a more important effect in this case is the generation of a new crop of particles. This process is confirmed by the particle size distribution as well as the evolution of the molar mass distribution. Doubling the volume of the original particles would increase their diameter from 0.29 to 0.37 μm. The particle size distribution shows that the original population has grown only to 0.34 μm and that new particles are generated with a particle size of 0.25 μm. The newly formed particles will not contain any dithioester groups as these are securely attached to polymer chains in the original population of particles. For this reason polymerization in these particles will proceed uncontrolled, and high molar mass PMMA homopolymer will be formed. This can be observed in the GPC traces depicted in Figure 4.

The signal at an elution volume of 16.8 mL THF corresponds to the nonionic surfactant and has been used for normalization. During the polymerization of EHMA (EXP2), low-polydispersity material is formed with a number-average molar mass of 7.6×10^3 Da (PS equivalents). During the seeded polymerization (EXP4), this material continues to grow as it is being converted into poly(EHMA-*b*-MMA) and retains its narrow distribution. Simultaneously, material of high molar mass and higher polydispersity is formed which we expect to be PMMA homopolymer in the second crop of particles. It grows in a conventional uncontrolled fashion due to the absence of dithiobenzoate species, confirmed by the absence of the dithioester chromophore in the chromatogram generated by the UV detector at a wavelength of 320 nm (not shown).

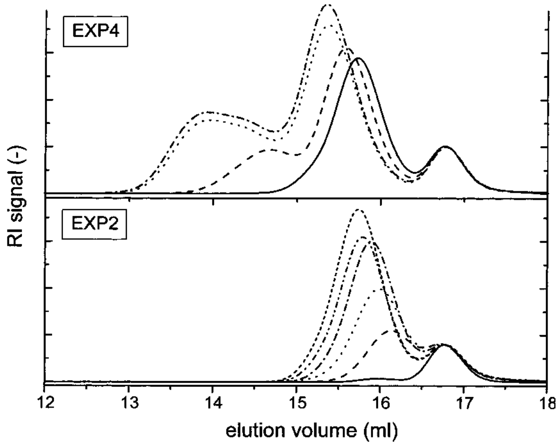


Figure 4. GPC traces (refractive index detector) for the preparation of the seed latex (EXP2, bottom) and the subsequent seeded polymerization of MMA (EXP4, top). The peak at 16.8 mL corresponds to the applied nonionic surfactant. This peak was used for normalization.

Here we have prepared a latex, which may have very intriguing properties as it contains both high-T_g particles of high molar mass and particles consisting of a low molar mass block copolymer that can act as in situ compatibilizer for the PMMA spheres and a different material. Alternatively, the hard PMMA spheres may act as reinforcement filler for the block copolymer film cast from this latex. Indeed, living radical polymerization in miniemulsion can open up the way to a whole new class of “designer latices”.

Experiment EXP8 differs from EXP2 in that it utilizes Brij98 as surfactant. In this polymerization block copolymer is prepared by a semicontinuous procedure. First EHMA is polymerized to full conversion. The molar mass is again close to the theoretical value, and polydispersity remained below 1.2 (Figure 5). A feed stream of a 10 g monomer mixture of MMA and methacrylic acid (12:1 on weight basis) was started at a rate of 0.1 mL/min. Samples taken during this part of the polymerization again show controlled growth of the block copolymer. The GPC traces showed no evidence of any nonblock copolymers formed during this stage (in this case poly(MMA-*co*-methacrylic acid)). This type of polymer is unavoidably formed to some extent, and although the amount can be minimized, it is usually observable as low molar mass material in the GPC trace when block copolymers are prepared in bulk or solution.[26] The combination of a high polymerization rate and a low radical flux per particle, typical for compartmentalized systems, allows the preparation of block copolymers with a higher degree of purity than in homogeneous systems.

To further establish the effectiveness of this procedure, the samples were precipitated in water/methanol (3:1) to remove the surfactant and analyzed by HPLC (Figure 6). Chromatograms were normalized on the Kraton, which had been applied as hydrophobe (together with hexadecane). Several samples of different PEHMA chain lengths were injected, and these gave two peaks

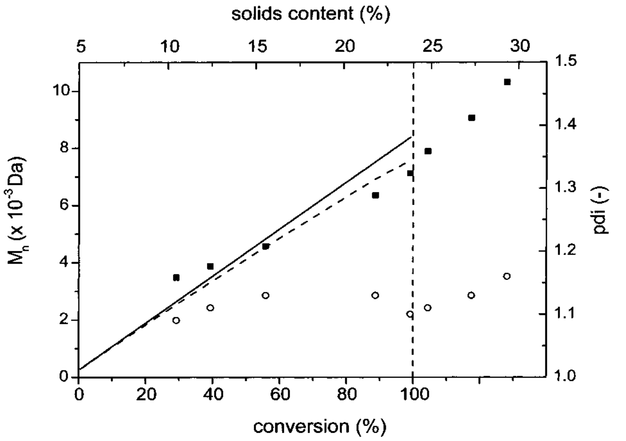


Figure 5. Molar mass data (left axis) for polymerization of EHMA (EXP8) and its transformation into poly(EHMA-*b*-[MMA-*co*-methacrylic acid]). Number-average molar mass: experimental values (■, in PS equivalents); theroretical values based on the dormant species (—); theoretical values corrected for initiator derived chains (- - -). Polydispersity index of the polymer (○, right axis).

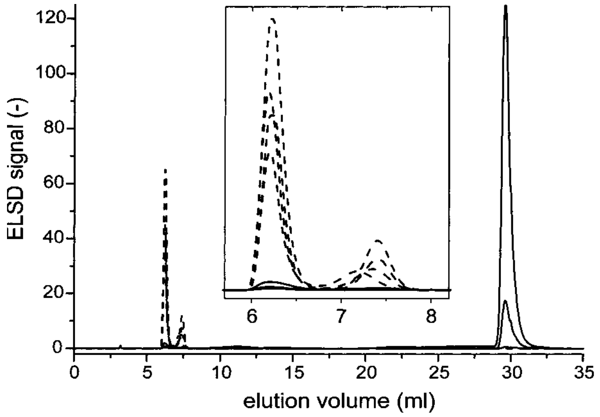


Figure 6. Gradient HPLC chromatograms of samples taken from miniemulsion EXP8. Samples taken during the polymerization of EHMA (- - -) and samples taken during the addition of the second monomer feed stream of MMA and methacrylic acid (—).

between 6 and 8 mL elution volume. The three samples taken during the second stage of the polymerization (see Table 2) had much higher elution volumes. The first has added an average number of only seven monomer units per chain, resulting in a very broad multimodal signal between 9 and 32 mL elution volume. The exact elution volume is strongly dependent on the number of polar monomer units that has been added and especially on the incorporation of methacrylic acid. As the chains grow further and all start to contain methacrylic acid, the polymer elutes at 30 mL. The nonionic surfactant Brij98 eluted at 34 mL and was not present in the precipitated samples. Integration of the peaks revealed that less than 2% of the poly(EHMA) prepared in the first stage remained, and the absence of its signal in the UV chromatogram ($\lambda = 320$ nm) showed that these chains no longer have a dithiobenzoate end group. No peaks other than this one and the one attributed to the block copolymer were observed. This leads us to conclude that narrow-polydispersity poly[EHMA-*block*-(MMA-*co*-methacrylic acid)] was prepared with the surfactant as the single significant contaminant. The product was easily isolated by precipitation in water/methanol.

Conclusion

The application of RAFT polymerizations in dispersed media is not as simple as might be expected from its straightforward free-radical chemistry. After previously reported difficulties using ab initio and seeded emulsion polymerizations, it was expected that elimination of the need of the RAFT agent to be transported through the water phase would alleviate the encountered stability problems. This was found not to be the case with these miniemulsions. Both anionic and cationic surfactants were found inadequate in maintaining the original droplet morphology upon the onset of reaction. Only when nonionic surfactants were used were miniemulsions obtained that were stable during the polymerization. The precise reason for the observed phase separation is not yet clear, but as ATRP reactions show similar behavior we assume that the presence of a large amount of oligomers and the absence of truly high molar mass polymer during the initial phase of the reaction play an important role.

A number of controlled polymerizations were performed where the advantages of compartementalized systems were exploited. Their relatively low termination rate allowed for the controlled preparation of several methacrylate and styrene block copolymers with a much higher level of block purity than obtainable in typical solution polymerizations. Finally, it was shown that living radical polymerization could be conducted simultaneously with conventional radical polymerization in a single reactor leading to a blend of latex particles with completely different characteristics. This novel process allows sophisticated materials engineering by a careful choice of reaction conditions.

Experimental Section

Chemicals and Equipment. 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086) and 1,1′-azobis(1-cyclohexanecarbonitrile) (V-40) were obtained from Wako Chemicals and used without purification. AIBN (98%) was purchased from Merck and recrystallized from methanol before use.

Demineralized Super Q water, conductivity below 10^{-7} S cm^{-1}, was used for the preparation of the miniemulsions. Monomers were obtained from Aldrich Chemicals. Before use they were distilled (except for EHMA) and past through an inhibitor removal column (Aldrich).

2-Cyanoprop-2-yl dithiobenzoate (**1**, Scheme 1),[27] 2-phenylprop-2-yl dithiobenzoate (**2**, Scheme 1),[5] and 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**3**, Scheme 1)[5] were prepared as described in the literature. Polymeric RAFT agents were prepared by either organic procedures (**4**, Scheme 1) or solution polymerization (**5**, Scheme 1) of methyl methacrylate in the presence of **1** (Scheme 1). The preparation and characterization of **4** have been described in a previous publication.[26] RAFT agent **5** has an apparent number-average molar mass of 3.5 × 10^3 Da and a polydispersity of 1.07, determined by GPC against polystyrene standards.

Kraton L1203 (a monohydroxyl copolymer of ethylene and butylene $M_n \approx 4 \times 10^3$ Da, polydispersity ≤ 1.05) was received from Shell Chemicals. All other chemicals were obtained from Aldrich and used as received.

GPC analyses were performed on a Waters system equipped with 2 PLgel Mixed-C columns and a UV and an RI detector. All molecular weights reported in this paper are apparent values expressed in polystyrene equivalents. Although Mark–Houwink parameters were available for the polymers studied, a correction procedure was not applied, as its validity is only established for molar masses exceeding approximately 2.0 × 10^4 Da.

The HPLC analyses were performed using an Alliance Waters 2690 separation module. Detection was done using a

PL-EMD 960 ELSD detector (Polymer Laboratories) and using a 2487 Waters dual UV detector at wavelengths of 254 and 320 nm.

All samples were analyzed by injecting 10 μL of a solution of the dried polymer in tetrahydrofuran at a concentration of 5 mg/mL. Columns were thermostated at 35 °C.

Samples were analyzed on a NovaPak CN column (Waters, 3.9 × 150 mm) by the application of a gradient from heptane to THF in 40 min. Data for both GPC and HPLC were acquired by Millennium 32 3.05 software.

Particle diameters were determined by light scattering on a Malvern 4700. For this purpose, samples were diluted with water. Emulsion EXP9 was diluted with water saturated with styrene to preserve the original droplet size.

Miniemulsion Procedure. Monomer was mixed with RAFT agent, hydrophobe, and oil-soluble initiator (AIBN, V-40, if applicable). This organic phase was mixed well until it was completely homogeneous. While stirring vigorously (magnetic stirrer), the organic phase was added dropwise to a solution of surfactant in water. The flask was left stirring to homogenize for 60 min after which a sonicating probe (400 W, Dr. Hielscher UP400S) was immersed into this preemulsion. Stirring continued for 12 min while sonicating (amplitude 30%, cycle 1.0). During this process, the miniemulsion was cooled by a water bath to keep its temperature below 20 °C. The miniemulsion was then transferred into a three-necked 250 mL round-bottom flask equipped with reflux cooler and containing water-soluble initiator (potassium persulfate or VA-086, if applicable). The round-bottom flask was then immersed into an oil bath that had been preheated to the reaction temperature (70 °C), and polymerization was carried out under an argon atmosphere. During regular time intervals, samples were taken for light scattering, conversion measurement, and GPC analyses.

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