

Study of Compartmentalization in the Polymerization of Miniemulsions of Styrene and Butyl Methacrylate

K. Ouzineb, C. Graillat, T. F. McKenna

CNRS-LCPP/CPE, Bât. F308, 43 Bd. du 11 Novembre 1918, B.P. 2077, 69616, Villeurbanne Cedex, France

Received 22 November 2002; accepted 28 May 2003

ABSTRACT: Different surfactant and costabilization systems were studied for the miniemulsion polymerizations of styrene (St) and of butyl methacrylate (BMA). It was found that the combination of sodium dodecyl sulfate, Triton X-405, and octadecyl acrylate yielded excellent results. With this system all of the droplets initially present in the reactor polymerized. This stabilization system was then used in the study of compartmentalization of the monomer droplets in miniemulsion polymerization. Blends of BMA and St miniemulsions were prepared separately and polymerized together to study mass transfer in this system. It was observed

that no matter is exchanged between the different phases. This compartmentalization was also demonstrated and exploited by producing a bimodal molecular weight distributions latex, achieved with a semicontinuous process. The lower MWD was created by adding a second miniemulsion containing a transfer agent. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 115–124, 2004

Key words: miniemulsion polymerization; polymerizable costabilizer; mass transfer; molecular weight distribution; compartmentalization

INTRODUCTION

In conventional emulsion polymerization, particles are generated by micellar, homogeneous, or coagulative nucleation. The number and size of particles, as well as the mechanism of polymerization, depend on the physical and chemical nature of the monomer and the surfactants used. It is generally accepted that emulsified monomer droplets do not significantly contribute to the particle nucleation because their surface area is negligible compared to that of the micelles or primary particles, and as a result they cannot compete for the incoming oligomeric radicals formed in the aqueous phase. However, it was found that these droplets can become the main loci of polymerization if their diameters are reduced below 1 μm .¹ In fact, in miniemulsions this property is exploited in such way that the final polymer particles are created by polymerizing directly in small droplets and, ideally, no nucleation of particles takes place once the reaction begins.

Droplets used to make miniemulsions are typically stabilized using a combination of an ionic surfactant and a hydrophobic agent. The latter is generally a long-chain alkane [e.g., hexadecane (HD)] or an alcohol (e.g., hexadecanol). The surfactant prevents the droplets from coalescing, whereas the hydrophobic agent reduces the diffusion of the monomer from the

smaller droplets to the larger ones (Ostwald ripening) so that droplets of different sizes and compositions can exist together.² It is this property (among others) that we will exploit in the current study.

A miniemulsion is prepared by dissolving the anionic surfactant in water and a costabilizer (or hydrophobe) in the monomer. The oil and aqueous solutions are mixed with a mechanical agitator for a few minutes and then in a high-shear mixer (e.g., an ultrasonifier, homogenizer, or microfluidizer). This mechanical shearing breaks the oil phase into submicron droplets. The resultant miniemulsion is then polymerized with a free-radical initiator as in classical emulsion systems.

A successful miniemulsion polymerization could be defined as a system where all the droplets present in the initial emulsion polymerize and no new particles are created. The challenge, inherent in choosing a system to stabilize the droplets, is to reduce or to eliminate micellar or homogeneous nucleation. Micellar nucleation can be avoided by keeping the aqueous concentration of the surfactant below its critical micelle concentration (cmc). Homogeneous nucleation can be kept to a minimum by producing droplets with a high surface area. Nonetheless, it is difficult to prove whether homogeneous nucleation has occurred.

As we mentioned above the idea is to choose the stabilization system to ensure that the droplets are the main loci of polymerization. If we consider miniemulsion in terms of an energy balance at the surface of the particles, the hydrophobic agent dissolved in the droplets provides an osmotic pressure that counteracts the Laplace pressure. The Laplace pressure

Correspondence to: T. McKenna (mckenna@cpe.fr).

(P_{Laplace}) can be calculated with the following equation:

$$P_{\text{Laplace}} = \frac{2\gamma_{\text{LL}}}{R} \quad \text{where}$$

$$\gamma_{\text{LL}} = \frac{A_d}{A_{\text{surf}}} \gamma_{\text{LL},d} + \left(1 - \frac{A_d}{A_{\text{surf}}}\right) \gamma_{\text{LL},n}$$

where R is the droplet radius, A_d is the surface area of the droplets, A_{surf} is the surface area covered by surfactant molecules, γ_{LL} is the interface tension of oil droplet, $\gamma_{\text{LL},n}$ is the interfacial tension between the aqueous and the organic phases without surfactant, and $\gamma_{\text{LL},d}$ is the interfacial tension between the aqueous and the oil droplet covered with surfactant.

The interfacial tensions can be measured with the "drop method" in which experiments consist of measuring the volume of a drop large enough to fall under the influence of gravity alone from a capillary in a surrounding fluid.^{3,4}

The osmotic pressure (P_{osmotic}) created by the costabilizer is calculated by

$$P_{\text{osmotic}} = \frac{RT[C]}{M}$$

where R is the ideal gas constant, T is the reaction temperature, $[C]$ is the costabilizer concentration, and M is its molecular weight.

The challenge is to maintain this osmotic pressure equal to or just slightly greater than the Laplace pressure throughout the reaction so that all the droplets can act as individual batch reactors.²

With an efficient costabilizer this condition can be easily satisfied in the initial unpolymerized miniemulsion. However, because this osmotic pressure can decrease as the polymer is formed, combined with the fact that droplets can contain monomer at concentrations higher than the saturation value found in the particles obtained in classic emulsion polymerization of the same monomer, it is theoretically possible to have a monomer desorption from the particles during a miniemulsion polymerization.

Ugelstad et al.¹ appear to have been the first to have studied miniemulsions, even though they did not call it such at this time. They polymerized submicron droplets of styrene by mixing the monomer phase in an aqueous phase containing different types of surfactants. They reported similarities between the final particle size distribution and the initial droplet size distribution and obtained a bimodal distribution of polymer particles. This indicates that the droplets were a main locus of polymerization, but not the only one. The principal conclusion of their study was that as the chain length of the costabilizer increased, the stability

of the miniemulsion increased, and the finer the droplet size, the more likely it was that all the droplets would be polymerized. A number of investigators have followed up on this and have shown that polymers dissolved in the monomer can enhance droplet stability.⁵⁻¹⁴

In addition to favoring the formation of stable droplets, polymeric costabilizers offer the advantage of not increasing the level of volatile organic compounds (VOCs) present in the final latex, whereas long-chain alkanes or fatty alcohols must be removed at the end of the polymerization. On the other hand, they have the disadvantage of needing to be prepared ahead of time in solution polymerization to obtain polymer with low molecular weight to facilitate its dissolution and improve its compatibility with the monomer. Chern et al.¹⁵⁻¹⁷ suggested using polymerizable hydrophobes to circumvent these difficulties.

One of the key advantages of miniemulsion is the control of the final number of particles (N_p) that can be achieved. Another, less-exploited advantage is that it is possible to create rather high solids content (>50%) directly in the reactor without needing to use a semi-batch stage to concentrate an initial seed. Masa et al.¹⁸ and Lopez de Arbin and Asua¹⁹ reported experiments at 55 wt % solid content latices using miniemulsion and classical emulsion terpolymerization. The viscosity was found to be 6.5 times higher for the conventional emulsion latices. It is therefore possible that the way in which miniemulsions are created makes them attractive for high solid content latices.

The objectives of the work presented here were to gain a better understanding of miniemulsion polymerization in terms of stabilization and transfer phenomena, and to propose different ways to exploit the unique aspects of miniemulsion polymers. In the first part of the study, different stabilization systems are tested for styrene and butyl methacrylate miniemulsions to select the most efficient one. In the second part we will look at the degree of mass transfer taking place in the systems and look at the production of polymers with bimodal molecular weight distributions (MWDs) or particle size distributions (PSDs).

EXPERIMENTAL

Styrene (St), butyl methacrylate (BMA), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), Triton X-405 (70% in aqueous solution), and octadecyl acrylate (ODA) were obtained from Acros Organics (Geel, Belgium) and used as received. The chain-transfer agent employed was dodecyl mercaptan (Acros Organics) and was used as received. The molecular weight of SDS was 288 g mol⁻¹. Its cmc was found to be 1.6 g L⁻¹ at 25°C.²⁰ The molecular weight of Triton was taken to be 1966 g mol⁻¹.²¹ Deionized water was

TABLE I
Experimental Recipes (Variables Studied)

Reaction	St (% wt/total)	HD (% wt/total)	SDS (× CMC)	Triton (× CMC)	PS (% wt/St)	PMMA (% wt/St)	ODA (% wt/St)	KPS (% wt/total)
RB1	15	10	2.8	—	—	—	—	0.03
RB2	15	12	2.8	—	—	—	—	0.03
RB3	20	5	1.6	—	—	—	—	0.03
RB4	20	2.8	1.6	—	1.25	—	—	0.03
RB5	15	10	2.8	—	—	7	—	0.03
RB6	20	—	2.8	2.3	—	7	—	0.03
RB7	26	—	0.4	2.3	—	1	2	0.12
RB8	26	—	0.4	2.3	—	—	2	0.12
RB9	35	—	0.4	2.3	—	—	2	0.26
RB10	58	—	1.4	4.4	—	—	2	0.43

used throughout the investigation. The polymers used as hydrophobes [polystyrene (PS) or polymethylmethacrylate (PMMA)] were prepared using a well-known method of solution polymerization. Their low molecular weight facilitated their dissolution in the monomer phase [$M_{w(\text{Psty})} = 49,400$, $M_{n(\text{Psty})} = 25,333$, $M_{w(\text{PMMA})} = 18,000$, $M_{n(\text{PMMA})} = 7000$]. The emulsification was ensured by an ultrasonifier at 90% amplitude, corresponding to a power input of 540 W. Miniemulsions were prepared by sonifying 500-mL batches of the different formulations for 4 min. Gravimetric measurements were performed on a limited number of the sonified samples to verify that no polymerization occurred during this step.

Polymerizations were carried out in a 2-L glass reactor equipped with a reflux condenser, anchor stirrer, and nitrogen inlet. The reaction temperature was controlled at 70°C by circulating water from a thermostatic bath in the reactor jacket. Dissolved oxygen was removed from the initial charge by bubbling nitrogen through it for 0.5 h before each run. At the end of the degassing period, the initiator was added to start the polymerizations. A summary of the different batches discussed in this work is provided in Table I. Samples were withdrawn during the process and placed in vials containing hydroquinone to stop the reaction. Overall conversions were determined gravimetrically, and average particle sizes were measured with quasi-elastic light scattering (QELS; Malvern Lo-C or variable angle QELS, Malvern 4800; Lyon, France). Average particle sizes reported here are an average of 10 measurements per sample.

In the polymerizations carried out in a semicontinuous mode, the monomer was added at a constant rate under gravity flow, and the aqueous surfactant solution with a programmable syringe pump. The MW and glass-transition temperature measurements were performed using a GPC calibrated with standard polystyrene (Waters 710plus autosampler) and a DSC (Setaram DSC 131; Lyon, France), respectively.

RESULTS AND DISCUSSION

Stabilization systems for styrene miniemulsions

In the first part of this study we will use different formations to gain more insight into the process of droplet/particle stabilization for the monomers we chose to use, and especially to help us to select a well-adapted stabilization system for the miniemulsion polymerization of St and of BMA. Different stabilization systems were tested (SDS/HD, SDS/HD/PS, SDS/HD/PMMA, SDS/Triton/ODA/PMMA, SDS/Triton/ODA) and the concentrations of the different hydrophobes, surfactants, and initiator as well as the solid content were all varied (see Table I). Several authors reported the effect of sonication conditions on droplet size.^{22,23} The main conclusion is that we can produce smaller initial droplets at the same surfactant and hydrophobe concentrations by providing more energy during this stage of emulsification. Thus, the time of ultrasonification was kept constant during all of the preparations so we would be able to compare the runs on an equal footing. The initial droplet size ($d_{m,i}$) and the final particle size ($d_{p,f}$), with their respective polydispersity indices (PI_{initial} , PI_{final}) obtained for all the runs, are summarized in Table II.

The first experiments were carried out with hexadecane (HD) as costabilizer. This long-chain alkane has been widely used to minimize the monomer diffusion into the aqueous phase (RB1, RB2, RB3).² As one may observe from Table II, increasing the HD concentration leads to a noticeable reduction in the average droplet size and the PI_{initial} . The significant decrease in particle size during runs RB1 and RB3 leads us to conclude that micellar nucleation probably occurred in these runs, so that the final particle size in both reactions reach an average value close to the final particle size obtained in RB2, which is why no significant polymerization rate difference was observed among these three reactions. If we look at the ratio between the initial number of droplets and the final

TABLE II
Experimental Results Obtained for the Styrene Miniemulsion Polymerizations Stabilized with SDS/HD, SDS/HD/PS, SDS/HD/PMMA, SDS/Triton/ODA/PMMA, and SDS/Triton/ODA

	d_m (nm)	d_p final (nm)	P_{osmotic} (bar)	P_{Laplace} (bar)	$N_{m,i}/N_{p,f}$	PI _{initial}	PI _{final}
RB1	270	101.6	11.89	1.32	0.06	0.25	0.05
RB2	105.3	117.1	15.10	4.91	1.64	0.15	0.07
RB3	399.1	123.9	6.44	4.33	0.03	0.30	0.07
RB4	200.2	157.6	5.74	5.52	0.57	0.18	0.08
RB5	192.7	126.1	12.55	2.53	0.32	0.15	0.06
RB6	181.8	118.8	2.93	2.73	0.32	0.15	0.07
RB7	193.2	172.5	1.78	1.50	0.79	0.16	0.08
RB8	191.4	185.1	1.67	1.48	1.04	0.14	0.06
RB9	260	256.1	1.28	1.23	1.10	0.15	0.05
RB10	240.1	239.4	1.57	0.95	1.14	0.16	0.07

number of particles for these runs in Table II, the predominance of micellar nucleation is confirmed for RB1. With the stabilization recipe provided here, the initial droplets were very large ($d_m = 270$ nm) and the SDS concentration was fairly high. In fact, if we use a value of $a_s = 45 \text{ \AA}^2$ for SDS on St, we are at a surface coverage of 120% before the reaction begins. In other words, there is an excess of SDS in the water phase, which means that we have not eliminated the conditions for the formation of micelles. Given the final size of the particles, this is most likely what has happened. On the other hand, only part of the initial droplets are found in the final latex for RB2, and, as one can see from Table II, the final particle size is larger than the initial droplet size. It would seem that the smaller initial particle size (why this occurs is not clear because the sonification conditions are thought to be the same) means that the surface area of the droplets is much higher. In fact we can calculate that SDS occupies about 47% of the droplet surface. It is possible then that this recipe allowed some of the particles to flocculate during the reaction to better stabilize the surface.

Runs RB3, RB4, and RB5 allow us to see the effect of changing the stabilization system. Comparing RB3 to RB1 shows us that decreasing the relative amounts of SDS and HD leads to an even lower number of droplets being initiated. In these runs the concentration of SDS was decreased, and the initial droplets were smaller than those in RB1 so we expect fewer problems in terms of micellar nucleation. However, the initial polydispersity index given by the Lo-C was fairly high, which means that there were many droplets of different sizes and we probably experienced Ostwald ripening here. Adding PS and PMMA in runs RB4 and RB5, respectively, improved the fraction of droplets being initiated. This agrees well with the results of Miller et al.^{9,24,25}

For these reasons we carried out a reaction with PMMA as the unique hydrophobe (RB6), and added a small amount of Triton to complete the surfactant

stabilization. In this case the droplet size remained under 200 nm, and approximately one third of the initial droplets were nucleated (see Table II). We can therefore consider that PMMA and HD provide similar levels of stabilization when the surfactant concentrations are adjusted.

In our first series of experiments it was found that increasing the hydrophobicity of the organic phase seemed to improve droplet nucleation in the sense that the ratio $N_{m,i}/N_{p,f}$ increased from close to zero to about 0.5. However, this was insufficient, so other experiments were performed to improve the droplet nucleation. Furthermore we decided to test a different kind of hydrophobe. Although the polymer used in runs RB4–RB6 seemed to provide adequate stability, it was still necessary to prepare them ahead of time in a separate reaction; moreover, the ratio $N_{m,i}/N_{p,f}$ was still not close to unity. Of course HD can be added directly to the mixture, but as we mentioned above, it must be removed if miniemulsions are ever used industrially. In an attempt to overcome these inconveniences, we tested octadecyl acrylate (ODA) as the hydrophobe in runs RB7–RB10. The results of these runs, shown in Table III, allowed us to conclude that the combination of SDS at a concentration lower than the cmc with Triton and ODA is an effective stabilization system that prevents Ostwald ripening, and allows us to maintain control of the particle size throughout the reaction. The ratio between the initial number of droplets and final number of particle is close to unity (see Table II). Chern et al.^{15–17} presented the same conclusion about the efficiency of ODA to retard the diffusional degradation of the monomer droplets. Nevertheless, they found with the system SDS/ODA that only 49% of the initial droplets were converted. The mixed surfactant SDS/Triton provides a synergetic stabilization with SDS producing a repulsive force between similar charges, and Triton providing a steric stabilization. This combination of surfactants seems to provide better results than using SDS alone.

TABLE III
Kinetic Constants for Styrene and BMA

	k_p at 70°C ($\text{dm}^{-3}/\text{mol}^{-1}/\text{s}^{-1}$)	r_1	r_2	C_p^{sat} at 50°C ^a (mol dm^{-3})	C_w^{sat} at 50°C (mol dm^{-3})	T_g (°C)	References
Styrene (1)	4.8×10^2	0.45		5.5	5.0×10^{-3}	100	28, 29
BMA (2)	8.9×10^2		0.5	3.8	2.5×10^{-3}	34	28, 29

^a This is the value available in classical emulsion.

In reactions RB9 and RB10 we increased both the solids content and the initiator concentration. The stabilization system was kept at the same concentrations with respect to monomer content. The ratio between $N_{m,i}$ and $N_{p,f}$ was once again close to unity. The fact that the vast majority of the droplets were nucleated even if we increased the initiator concentration confirms the efficiency of this stabilization system. In addition, we can also see that the polydispersity of the PSD is relatively low (0.1 is assumed to be monodisperse with the Malvern Lo-C that we used in this study), which offers additional proof that the monomer droplets are the principal polymerization sites, and that they keep their individuality throughout the reaction.

To test the feasibility of using miniemulsions to make a high solids content latex, or at least to serve as initial seeds for such a process, the mass fraction of the monomer phase was increased to 58% (RB10). The surfactant and initiator concentrations were adjusted both to ensure an efficient stabilization of the higher number of droplets generated and to maintain the reaction time at the same level as before. The results indicate that we can still maintain control over the PSD, even at these high concentrations. It should be noted that the rate of polymerization is slightly lower in RB9 and RB10 than in the preceding batch runs (complete conversion in 5 and 7 h, respectively, with respect to less than three for the preceding runs) attributed to the lower surface area offered by the droplets at high solids. Nevertheless, if we look at the total time needed to achieve a polymer content of 58% in this system and compare it with the 6–10 h needed in conventional emulsions (see, e.g., Schneider et al.²⁶) then the advantage of miniemulsions is clear.

To get a better understanding of the results of the previous section, let us consider the runs in terms of the Laplace and osmotic pressures measurements (also shown in Table II). The stabilization of droplets can be understood in terms of the interfacial energy. How well the droplets maintain their stability after sonification depends on the type and the level of both the surfactant and the hydrophobic agent. As we discussed in the preceding section, the osmotic pressure should be equal to or slightly higher than the Laplace pressure to maintain stable droplets. If this condition is satisfied, the droplets are protected against coales-

cence and monomer diffusion for several weeks. As one may observe from the measurements summarized in Table III, the osmotic pressure exceeds the Laplace pressure in all the first seven miniemulsions (RB1–RB7). However, better results are obtained for the SDS/Triton/ODA stabilization system where the osmotic pressure is just slightly greater than the Laplace pressure (RB8, RB9, RB10). When the Laplace pressure is too low compared to the osmotic pressure (RB1–RB6), the majority of the initial droplets are not nucleated. The Laplace pressure is directly related to the surfactant surface coverage of the droplets; if this surface coverage is insufficient, the droplets are not protected against coalescence (e.g., runs RB1 and RB3). The same events occur for runs RB4–RB7 at a different level.

Note that we need the average diameter of droplets for the calculation of the Laplace pressure. The fact that we have a very broad droplet size distribution (DSD) in the initial runs means that the difference between the pressures is much more significant in reality and that we cannot have an accurate determination of the initial number of droplets. Therefore it is difficult to draw a strong conclusion about the mechanism governing the miniemulsion polymerization. Nevertheless, it seems clear that the DSD is one of the most important parameters in monomer miniemulsion and this parameter is directly related to the stability and nucleation mechanism of droplets.

In conclusion we have to ensure that there is an equilibrium between the osmotic pressure and the Laplace pressure. For this to be so we need a DSD as narrow as possible with an average size between 100 and 250 nm. When the surfactant and costabilizer concentrations are well adjusted, all the droplets need to receive the same quantity of mechanical energy. This means that the sonication time must be long enough to ensure that all the droplets are treated equally because of the fact that only a small volume of the fluid near the probe is directly influenced by the ultrasound waves at a given instant. We applied the same sonication time to the same mass of latex in all of the runs, and it is possible that for the runs stabilized with HD an increase in the time of sonication could allow a nonnegligible decrease in droplet size. Nevertheless, the minimum droplet size that can be reached is fixed by the type and the amount of surfactant and

costabilizer. Asua²⁷ reported an interesting review of the homogenization conditions, and the reader is referred to this work for a more in-depth discussion.

Thus results shows that, by adjusting the stabilization system, we were able to perform an efficient styrene miniemulsion. In the following section we will use the stabilization system defined here and look at the degree of mass transfer between droplets during polymerization. This is an important question because it will allow us to better understand the kinetics of the reaction, as well as to search for interesting applications of this type of polymerization.

TRANSFER PHENOMENA IN MINIEMULSION

The previous results obtained with SDS/Triton/ODA for St miniemulsion polymerization allow us to consider the droplets as separate objects that keep their individuality throughout the reaction. However, it remains unclear as to whether the monomer can be exchanged between them during the reaction. To answer this question, and also to look at the possibility of making complex molecular weight or composition distributions in a single reactor, we decided to blend two separately prepared miniemulsions of different monomers (St, BMA) and then to polymerize the two populations of droplets together. Because the two homopolymers have very different glass-transition temperatures (see Table III), it was thought that by performing DSC analysis of the final polymer we could distinguish whether any copolymer was formed. Before looking at the degree of mass transfer in such configuration we performed an experiment to test the efficiency of the stabilization system defined above on the second monomer, BMA.

BMA miniemulsions

We carried out a BMA miniemulsion polymerization with the stabilization system providing the best result

TABLE IV
Experimental Results Obtained for the BMA Miniemulsion Polymerization and for BMA and Styrene Miniemulsion Polymerized Together

	RB11	RB12
St, % wt/total	—	14
BMA, % wt/total	28	14
SDS, × CMC	0.4	0.4
TritonX-405, × CMC	2.3	2.3
ODA, % wt/monomer	2	2
$d_{m/BMA}$, nm	152.3	155.1
$d_{m/PS}$, nm	—	190.4
$N_{m,i}^{BMA} \times 10^{-17} / (1/L \text{ H}_2\text{O})$	2.8	2.9
$N_{m,i}^{St} \times 10^{-16} / (1/L \text{ H}_2\text{O})$	—	3.8
$N_{p,f} \times 10^{-17} / (1/L \text{ H}_2\text{O})$	3.1	1.2

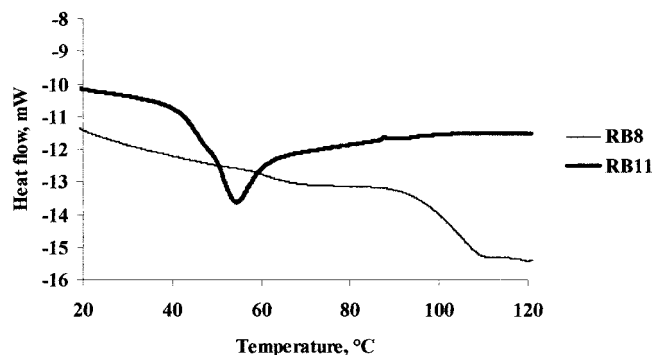


Figure 1 DSC measurements obtained for the final latex of runs RB8 and RB11.

in the preceding section (SDS/Triton/ODA). The initial condition between the Laplace and the osmotic pressure was satisfied, and in the same conditions as defined above we obtained a smaller droplet size for BMA compared to that of St (see Table IV). This is probably attributable to the higher surface area per surfactant molecule (a_s) of SDS and Triton in the case of BMA. This means that the surface charge density needed to stabilize an object is lower for BMA droplets than for St. In other words, we need less surfactant for BMA than for St to reach the same droplet size. As we can see from Table IV (run RB11), the ratio between $N_{m,i}$ and $N_{p,f}$ is close to unity, and the system SDS/Triton/ODA provides an adequate stabilization for BMA as well as for St.

In addition we performed a DSC measurement on the final latex to determine the glass-transition temperature (T_g) of PBMA in our experimental conditions (Fig. 1). The temperature evolution of the heat flow shows a single glass transition. We also precisely weighed the mass of dried polymer so that we could deduce the variation of the heat capacity (ΔC_p) of PBMA in our experimental conditions. The results are shown in Table V.

Blending of two miniemulsions

In this experiment two separate miniemulsions were prepared, one of St, the other of BMA. The two dispersions were then mixed (50% by volume of each

TABLE V
Glass-Transition Temperatures for RB8, RB11, and RB12 and Variation of the Heat Capacity Obtained by DSC

	RB8	RB11	RB12
T_{g1} , °C	—	42	39
T_{g2} , °C	89	—	87
ΔC_p , mW/g	3	10	—

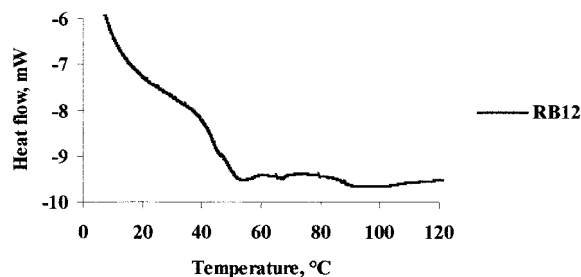


Figure 2 DSC measurement obtained for the final latex of RB12.

emulsion), and polymerized together with KPS (Table IV, run RB12).

The ratio between the initial number of droplets and the final number of particles of each miniemulsion could not be calculated precisely because we had access only to the average particle size of the final latex. However, there is no reason to believe that we would encounter problems of stability given the results presented above.

The DSC measurements of the final latex, shown in Table V and Figure 2, reveal two clearly defined glass-transition temperatures (T_g). To identify them clearly we also performed a DSC analysis on RB8 to determine the T_g of PS in our experimental conditions. The comparison between all the DSC results (RB12, RB11, RB8) revealed several things. First of all the lower and higher T_g values seen in RB12 correspond to the T_g of RB11 and RB8. In addition the heat flow variation for the first glass transition is more pronounced than the second one, which is in concordance with the difference between ΔC_p (RB11) and ΔC_p (RB8) (Table IV). As may be observed from Table V, ΔC_p (PBMA) is three times that of ΔC_p (PS). Finally, each glass transition was located in a narrow temperature interval. All these results allow us to conclude that the higher glass-transition temperature corresponds to PS and the lower one to PBMA. Consequently, the final latex (RB12) was composed of only two homopolymers, thereby demonstrating that no significant monomer exchange occurred between the two miniemulsions and thus between the polymerizing droplets. This is also another way to confirm that droplet nucleation is the predominant means of particle formation. The negligible mass transfer between polymerizing droplets opens up interesting applications, not just in the control of PSD. In the following section we will see how this compartmentalization can be exploited.

Miniemulsions with bimodal MWD

In this last section we explore the potential of exploiting the compartmentalized nature of miniemulsions to produce a bimodal MWD latex in a single reactor. To

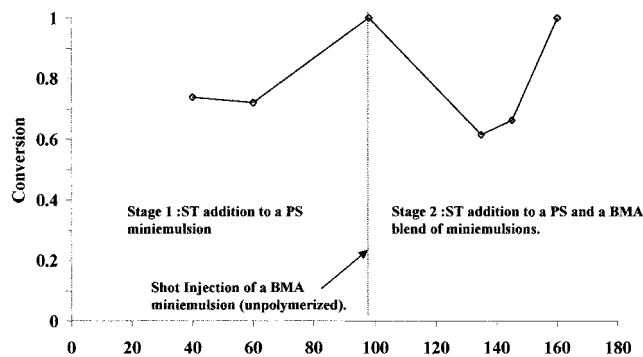


Figure 3 Monomer conversion as a function of time for the bimodal MWD latex.

allow a mechanical separation of these two peaks we decided to produce a latex with a bimodal PSD at the same time, where the large and the small populations correspond to the high and low MW populations, respectively. It can be seen from Table III that the k_p values for the two monomers are not very different, and that the reactivity ratios are such that composition drift in this system should be at a minimum.

Figure 3 shows the evolution of the conversion for the semicontinuous process RB13 as a function of time. During the first stage of the process the St monomer was added at a feed flow set at a level such that no monomer accumulation occurred in the aqueous phase. We continuously added an aqueous solution of Triton throughout the entire reaction to ensure the stabilization of the growing particles. At the end of the first stage, the PS latex had a monodisperse PSD with a mean diameter of 460 nm, as shown in Figure 4. We found no evidence to show that secondary nucleation occurred. During the second part of the process the BMA miniemulsion with a droplet size of 150 nm and a polydispersity index of 0.15 was added over the course of a few minutes in a proportion such that it

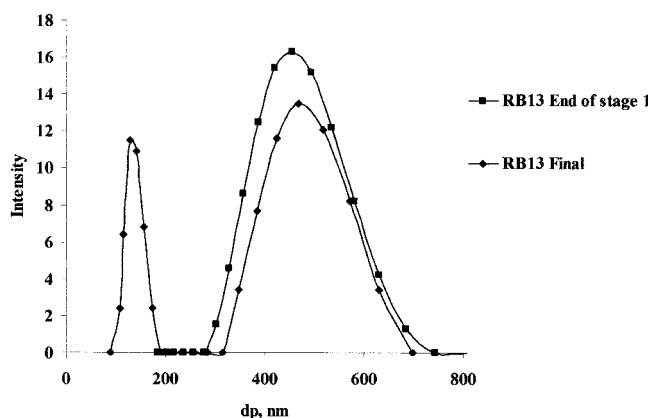


Figure 4 Particle size distribution obtained with multiangle light scattering at 90° for the latices obtained at the end of stage 1 and at the end for run RB13.

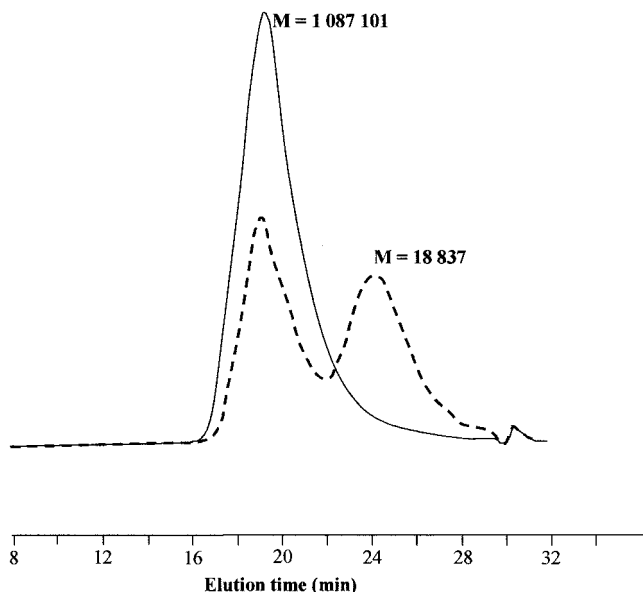


Figure 5 GPC result: (—) RB13 stage 1; (---) RB13 final latex.

represents 20% by volume of the total organic phase in the reactor. At the same time we continued to feed the St for 40 min at 2.0 g/min. This second stage lasted 40 min so that the mass of St added did not lead to a significant increase in size for the PS particles.

We performed multiangle QELS, gel permeation chromatography (GPC), and DSC measurements to determine the PSD, the MWD, and the glass-transition temperature obtained for the final latex, respectively. As we can see from Figures 4 and 5 the final latex shows both bimodal PSD and MWD. The smaller population has a mean diameter of 147 nm, very close to the mean diameter of the BMA droplets introduced during the second stage of RB13, and the larger one has a mean diameter of 468 nm. The difference in diameter corresponds closely to the mass of St added during the second stage.

Figure 5 shows that the polymer at the end of the first stage had a monomodal distribution, observed with an M_w of about 1.1×10^6 and that the polymer at

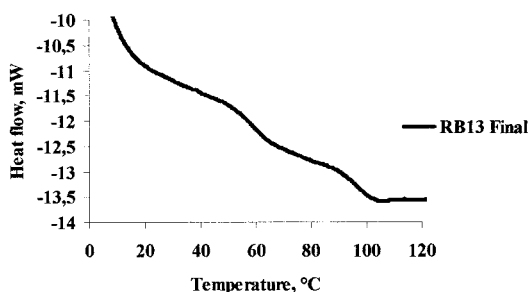


Figure 6 DSC measurement performed on the final latex RB13.

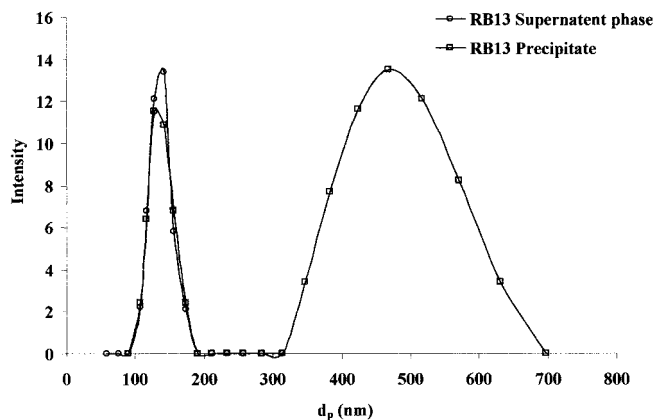


Figure 7 Particle size distribution obtained with multiangle light scattering at 90° for the two phases resulting from centrifugation of the final latex RB13.

the end had a bimodal distribution with a peak corresponding clearly to that of the polystyrene homopolymer, and a lower M_w corresponding to that of the smaller particles. Figure 6 shows that the final latex has two different T_g values: the first one corresponds closely to the T_g of PBMA obtained in run RB11; and the second transition is similar to the one obtained for PS in run RB8.

The fact that we had a significant difference in size between the two populations allowed us to mechanically separate them with centrifugation. PSD, MWD, and DSC measurements were performed on each phase issued from the centrifugation (the smaller particles are of course found in the supernatant liquid, and the larger ones in the concentrated phase at the bottom of the tubes).

As we can see the particles in the supernatant phase present a monomodal PSD (Fig. 7), corresponding exactly to the smaller PSD obtained for the final latex, and a monomodal MWD (Fig. 8) with a peak at the same position as the lower MW fraction obtained for

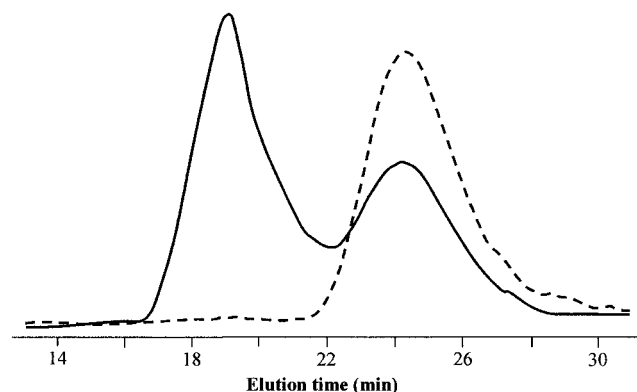


Figure 8 GPC results: (—) RB 13 precipitate phase; (---) RB13 supernatant phase.

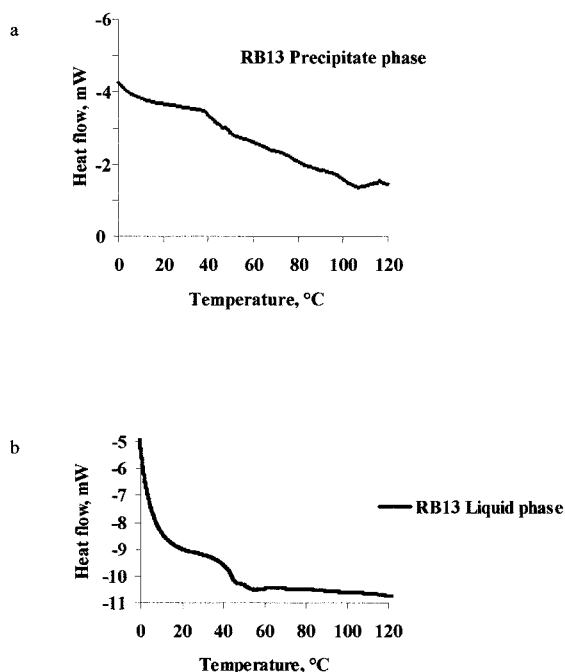


Figure 9 DSC measurements performed on the two phases resulting from centrifugation of the final latex RB13: (a) precipitate; (b) supernatant phase.

the final latex. Similarly, the polymer in the precipitated phase shows a bimodal PSD and MWD identical to those obtained for the final latex. It should also be noted that a mass balance showed that a nonnegligible amount of small particles were precipitated with large particles during the centrifugation; however, this did not seem to alter the results significantly.

Figure 9 shows the results of the DSC measurement on the supernatant phase containing only the small particles. We can see that there is a single $T_{g'}$ corresponding to that of PBMA obtained in run RB11 (see Fig. 1). In addition, the precipitate of the final latex presents two distinctive T_g values. The first one can be attributed to PBMA, and the second one occurs at the same position as the T_g of PS obtained in run RB8. Furthermore, and more important, no glass transition appears between these two peaks, which means that no significant exchange occurred between the polymerizing BMA miniemulsion and the growing PS particles. We succeeded in maintaining the initial characteristics of BMA droplets. This system allowed us to

obtain a constant particle size evolution with a low MWD, and consequently the PS particles continued to grow during the entire reaction producing polymer with high MW.

The identity of each peak obtained for the PSD and MWD of the final latex allowed us to calculate the ratio between the initial number of droplets and the final number of particles for the BMA miniemulsion and between the initial number of PS particles and the final one. As we can see from Table VI these ratios are close to unity, which confirms once again that the majority of BMA droplets are nucleated, and no significant renucleation of PS particles occurred during the semicontinuous process.

All these results lead to the conclusion that no significant exchange of transfer agent and monomer occurred between the PBMA and PS particles. In addition no renucleation or autoflocculation phenomena occurred during the reaction because, if they had occurred, we would have found a significant amount of copolymer in the final latex.

The properties of PS particles at stage 1 are maintained until the end of the reaction, and the addition of the BMA miniemulsion allowed us to create a latex with two bimodal distributions: one in particle size, and one in MWD. Interestingly enough, the BMA droplets were not destabilized by the presence in the reactor of PS particles polymerizing, and the addition of St monomer at the same time. The balance between the Laplace and the osmotic pressure was satisfied all along the second stage; consequently, the majority of the droplets introduced in the second population were nucleated, and no monomer or transfer agent desorption occurred. The PBMA particles did not adsorb St monomer because in miniemulsion, the concentration of monomer into the droplets is twice the saturation value obtained in classical emulsion (Table II). When the reaction begins in the second state, this concentration remains over 60% of conversion, and there is no driving force for mass transfer.

In the preceding section it was shown that no monomer transfer occurred when two miniemulsions (BMA, St), prepared separately, were polymerized together.

When the droplets are well stabilized against coalescence and Ostwald ripening, they act as individual batch reactors, regardless of whether there is one pop-

TABLE VI
Experimental Results Obtained for the Semicontinuous Miniemulsion Polymerization of St and BMA with a Bimodal PSD and MWD

	$N_{m,i \text{ St}}/N_{p,f \text{ PS}}$	$N_{m,i \text{ BMA}}/N_{p,f \text{ PBMA}}$	PI	T_{g1} (°C)	T_{g2} (°C)
RB13	1.01	0.98	0.23	35.8	87.2
RB13 precipitate	1.05	0.96	0.25	36.3	93.7
RB13 supernatant	—	0.95	0.05	34.9	—

ulation or two populations of droplets in the reactor. The fact that the initial component dissolved in monomer droplets remains inside throughout the reaction opens an interesting application in the control of specific properties. This compartmentalized nature of miniemulsions has a great deal of potential in producing latices with different properties. One of the more interesting possibilities is that of making high solids content latices with bimodal PSD (and MWD). This will be the object of a subsequent study from this group, so we will not discuss this much further. Suffice to say that because we need to make a bimodal PSD at a solids content less than 60%, then concentrate the emulsion to make such products, the fact that we can do so *and* control the MWD before the concentration stage makes this last series of experiments pertinent.

CONCLUSIONS

In the present study, we looked at two aspects of miniemulsions: (1) to gain a fundamental understanding of the mechanisms of miniemulsion polymerizations; and (2) to find ways of exploiting the compartmentalization of the droplets during the reaction.

The ability to nucleate all the droplets of either styrene and/or butyl methacrylate is possible with a stabilization system that combines a mixed surfactant system in reasonable amounts, and a polymerizable hydrophobe (SDS, Triton, ODA). When the equilibrium between the Laplace and the osmotic pressures is ensured in the initial miniemulsion and during the entire reaction, the majority of the droplets initially present polymerized.

This type of stabilization that ensures that Ostwald ripening is kept to a minimum, and that there is no degradative transfer, implies that we can polymerize two (or more) populations of different compositions (in monomer, chain-transfer agent, or size) together. This idea was tested with DSC measurements. The analyses performed on the final latex showed that no copolymer was formed during the reaction, which means that no significant monomer transfer occurred between the different populations of miniemulsions, and consequently between the polymerizing droplets. This simultaneously demonstrates that the majority of the droplets polymerized and that the system is in fact compartmentalized in terms of mass transfer.

We decided to test the compartmentalization of the miniemulsion in a semicontinuous process to illustrate the potential applications and not just in the control of PSD. The objectives were to produce a final latex with a bimodal MWD by using two miniemulsions, one of BMA containing some transfer agent and one of St, each distribution constituted by a single miniemul-

sion: the lower MWD corresponding to PBMA and the higher one to PS. We also imposed a bimodal PSD on the final latex. The results clearly reveal that no monomer and transfer agent exchange occurred during the two populations, and that the BMA miniemulsion was not perturbed by the presence of PS particle polymerizing and by the continuous addition of St. This result has potentially very interesting applications in bimodal, high solids content systems.

References

- Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. *Polym Lett Ed* 1973, 11, 503.
- Antonietti, M.; Landfester, K. *Prog Polym Sci* 2002, 27, 689.
- Harkins, W. D.; Brown, F. E. *J Am Chem Soc* 1919, 41, 499.
- Lando, J. L.; Oakley, H. T. *J Colloid Interface Sci* 1967, 25, 526.
- Fontenot, K. J.; Reimers, J. L.; Schork, F. J. In 4th International Workshop on Polymer Reaction Engineering; Reichert, K. H., Moritz, H., Ed.; Dechema Monographs: Weinheim, 1992; pp 127, 429–439.
- Ugelstad, J.; Mork, P. C.; Kaggerud, K. H.; Ellingsen, T.; Berge, A. *Adv Colloid Interface Sci* 1980, 13, 101.
- Reimers, J. L.; Schork, F. J. *J Appl Polym Sci* 1996, 60, 251.
- Miller, C. M.; Blythe, J. P.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 2365.
- Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* 1995, 28, 2765.
- Blythe, P. J.; Morrison, B. R.; Mathauer, K. A.; Sudol, E. D.; El-Aasser, M. S. *Langmuir* 2000, 16, 898.
- Blythe, P. J.; Sudol, E. D.; El-Aasser, M. S. *Macromol Symp* 2000, 150, 179.
- Reimers, J.; Schork, F. J. *J Appl Polym Sci* 1996, 59, 1833.
- Aizpurua, I.; Amalvy, J. I.; Barandiaran, M. J. *Colloid Surf A Physicochem Eng Aspects* 2000, 166, 59.
- Chern, C. S.; Liou, Y. C.; Chen, T. J. *Colloid Surf A Physicochem Eng Aspects* 1998, 138, 65.
- Chern, C. S.; Liou, Y. C.; Chen, T. J. *Macromol Chem Phys* 1998, 199, 1315.
- Chern, C. S.; Liou, Y. C.; Chen, T. J. *Polymer* 1998, 16, 3767.
- Masa, J. A.; Lopez de Arbina, L.; Asua, J. M. *J Appl Polym Sci* 1993, 48, 205.
- Lopez de Arbina, L.; Asua, J. M. *Polymer* 1992, 33, 4832.
- Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A: Polym Chem* 1997, 35, 3813.
- Ash, M.; Ash, I., Eds. *Handbook of Industrial Surfactants*; Gower Press: Aldershot, UK, 1993.
- Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* 1999, 32, 5222.
- Mujumdar, S.; Kumar, P. S.; Pandit, A. B. *Indian J Chem Technol* 1997, 4, 277.
- Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* 1995, 28, 2754.
- Miller, C. M.; Blythe, P. J.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 2365.
- Schneider, M.; Graillat, C.; Guyot, A.; McKenna, T. F. *J Appl Polym Sci* 2002, 84, 1897.
- Asua, J. M. *Prog Polym Sci* 2002, 27, 1283.
- Gilbert, R. G. *A Mechanistic Approach*; Academic Press Inc.: London, 1995; pp 31, 60.
- Andrews, R. J.; Grulke, E. A. *Polymer Handbook*, 4th edition; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999.