Notes

Miniemulsion Living Free Radical Polymerization of Styrene

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Introduction

"Living" free-radical polymerization (LFRP) represents a promising technique to produce polymers with highly controlled structures. Several possible systems, such as nitroxide-mediated living polymerization[1] (NMLP), degenerative transfer[2] (DT), atom transfer living polymerization[3] (ATRP), and reversible addition fragmentation polymerization[4] (RAFT), have been tested extensively under bulk polymerization conditions. In particular, both ATRP and RAFT seem very promising since they can be applied to a broad range of monomers and at low temperatures.

The industrial application of these systems is however unlikely, despite the advantages offered by LFRP in terms of polymer architecture control. Emulsion polymerization could overcome many existing problems connected to the LFRP industrial development, since (i) it accepts water as reaction medium, (ii) it achieves large reaction rates together with high solid content, and (iii) it represents a well-established commercial process.

However, only a few applications of LFRP in emulsion are reported in the literature. Seeded[5] and ab initio[6] NMLP of styrene with TEMPO have been attempted. In general, the high-temperature values required by TEMPO to be effective ($\geq$110 °C) made the latex unstable, besides leading to strong chain transfer to monomer. Qui et al.[7] performed a reverse ATRP of styrene, with good results in terms of control of the molecular weight distribution (MWD), but with low productivities. Furthermore, the final particle size distribution (PSD) characterized by a relatively large average particle diameter (d_n = 2.51 μm) indicates the presence of coagulation.

In this work a new process is presented that allows to realize simultaneously high productivity and good MWD control.

Experimental Section

Reactions are conducted in a jacketed reactor equipped with magnetic stirrer, condenser, and baffles. The temperature is regulated within $\pm$1 °C. Samples are withdrawn with a syringe at regular time intervals. In bulk reactions, all the reactants are charged into the reactor, which is then purged with nitrogen for 20 min at ambient temperature before raising the

temperature to the set value. Miniemulsions (mE) are prepared by adding to a water and surfactant (sodium dodecyl sulfate, SDS) solution an organic solution of styrene, initiator, transfer agent ($C_6F_{13}I$), and hexadecane as stabilizer under vigorous agitation. The resultant emulsion is sonified by a B.Braun Labsonic 1510 at a power of 30 W for 1.5 h. The reaction procedure is then the same as in the case of bulk reactions. Conversion is measured gravimetrically, MWD by a Hewlett-Packard GPC equipped with three PL MIXED-C columns, and PSD by light scattering (Malvern Zetasizer 5000). All the reactants are used as received without any purification. The operating conditions and the characteristics of the polymer produced in all the experimental runs are summarized in Table 1.

Results and Discussion

To identify a convenient LFRP in emulsion, we have to first select the most appropriate system among NMLP, ATRP, and RAFT (or DT). Since in emulsion the polymer particles are typically very small, i.e., with mean particle diameter (d_p) ranging from 50 to 300 nm, bimolecular termination of the growing radicals tends to be much faster than all the other reactions that change the number of radicals per particle. This confines styrene emulsions to a number of radicals per particle less than or at most equal to two. This effect is usually referred to as *compartmentalization*.

Let us now consider reactions responsible for the livingness of the polymerization that also involve a change in the number of radicals per particle, such as NMLP or ATRP. Typical activation and deactivation rate constants for a styrene ATRP are k_a = 0.45 L/(mol s) and k_d = 1.1 $\times$ 10^7 L/(mol s), respectively,[8] so that the ratio between the deactivation (τ_d) and the activation (τ_a) characteristic times is as follows:

$$\frac{\tau_d}{\tau_a} = \frac{k_a}{k_d} \frac{[RX][Mt^n]}{n_R n_{CR}} (N_A V_p)^2 \tag{1}$$

where [RX] and [Mt^n] are the dormant chains and metal concentrations, respectively, n_R and n_{CR} indicate the number of growing radicals and "counter radicals" per particle, V_p is the particle volume, and N_A the Avogadro number. Let us consider a typical particle with d_p = 100 nm, [RX] = [Mt^n] = 0.02 mol/L, and one growing radical. At the beginning of the polymerization, the counter radical concentration is low, and then growing radicals produced by the activation reaction can accumulate in the particle and terminate by bimolecular termination. This produces an accumulation of counter radicals which soon makes the deactivation process faster than the activation one. For example, by considering 20 counter radicals in the particle, i.e., n_{CR} = 20, the ratio above becomes 0.08. This implies that when an activation takes place in a particle with no radicals, the counter radical traps the growing radical in a time that is short compared to the time scale for activation. That is, the produced radical is deactivated by the counter

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Table 1. Recipes of the Experimental Runs in Bulk and in Miniemulsion[a]

run	type	ϕ	d_p [nm]	$[M]_0/[D]_0$	$[M]_0/[AIBN]_0$	conversion [%]	time [h]	M_n [g/mol]	P_d
A	bulk			200	4000	40.7	89	13 060	1.66
B	mE	0.23	152.4	200	4000	91.1	2.5	17 730	1.57
C	mE	0.16	137.3	100	2000	96.3	2.0	8990	1.47
D	mE	0.16	136.2	400	2000	96.2	2.0	35 960	1.51
E	mE	0.16	136.9	800	2000	97.0	2.0	63 000	1.67
F	mE	0.20	134.1	100	900	94.4	2.0	10 650	1.51
G	mE	0.20	139.8	200	900	93.3	2.0	20 060	1.53
H	mE	0.20	133.8	∞	900	84.7	1.0	303 200	3.17

[a] All reactions have been conducted at 80 °C with hexadecane:styrene = 1:28 and SDS:water = 1:175 (by weight). $[M]_0/[D]_0$ and $[M]_0/[AIBN]_0$ indicate molar ratios, while ϕ indicates the styrene weight over the overall weight ratio. D = $C_6H_{13}I$
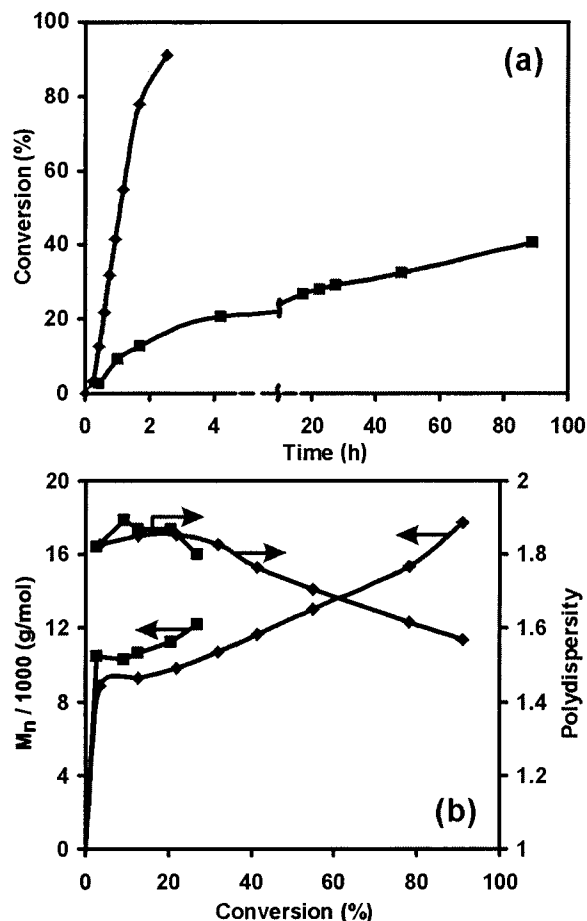

Figure 1. (a) Conversion vs reaction time and (b) number-average molecular weight (M_n) and polydispersity vs conversion for a bulk (■: run A, Table 1) and a miniemulsion (◆: run B, Table 1) reaction.

Figure 2. (a) Number-average molecular weight (M_n) and polydispersity vs conversion for different miniemulsion reactions (■, run C; ◆, run D; ●, run E, Table 1). (b) GPC normalized signal vs elution volume for run D (Table 1) at increasing conversions (3.65, 33.2, 70.9, and 96.2%).

radical before a second radical can be produced by activation. Therefore, the average number of growing radicals per particle remains far below the value of 0.5 typical for a styrene emulsion, thus leading to exceedingly low polymerization rates.

When the livingness of the process is instead obtained by a chain transfer reaction, such as DT or RAFT, this does not affect the number of radicals per particle, and thus the same kinetics as in a classical styrene emulsion polymerization can be realized. Of course, the number of entry events should be regulated in order to have a number of bimolecular terminations that is far below the number of dormant chains per particle, so as to preserve the livingness of the process. In the following, some experimental results are presented where these concepts are applied.

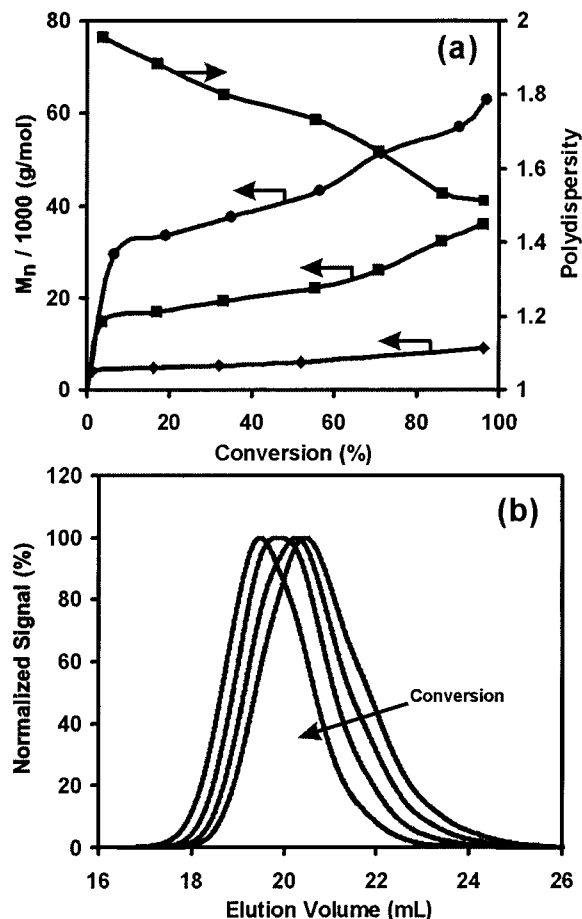Before starting the polymerization the transfer agent is introduced in the monomer droplets which are the main loci of particle nucleation in a mE. It is worth mentioning that, when a water-soluble initiator is used, it has been seen experimentally that no control over the MWD is obtained. A possible explanation is that, under these conditions, homogeneous nucleation becomes competitive with droplet nucleation.[9] The transfer agent is water-insoluble; thus, no control over the MWD is obtained in the particles formed by homogeneous nucleation. This can be avoided using low concentrations of an oil-soluble initiator, such as AIBN.[10] Under these conditions, each particle behaves as an isolated bulk reactor, but because of radical compartmentalization, the average value of 0.5 radicals per particle is achieved, thus leading to large productivities. Figure 1a shows the comparison between conversion in bulk and mE as a function of time (runs A and B, Table 1). Despite the same oil-phase composition, mE has reached 90%

conversion in 2.5 h while after 90 h the conversion in bulk is still below 45%. This is so because, while in bulk the radical concentration is $[R^\bullet] = (R_i/k_t)^{0.5}$, where R_i represents the global rate of initiation, in mE the radical concentration is much larger being of the order of $0.5/N_A V_p$. In Figure 1b the obtained values of number-average molecular weight (M_n) and polydispersity (P_d) are compared as a function of time. It is seen that despite the different reaction time, both bulk and mE achieve a similar control over the MWD. The significant nonlinear increase of M_n at low conversion values is typical of these chain transfer mechanisms and is independent of radical concentration (cf. Mayo equation). Therefore, it is similar in both reaction types shown in Figure 1b.

In Figure 2a, M_n and P_d versus conversion are shown for runs C, D, and E in Table 1. A satisfactory control over the MWD is obtained. The initial M_n increase is again present, and as expected, it decreases by decreasing the $[M]_0/[D]_0$ ratio. Figure 2b shows the GPC elution diagram at different conversions for the polymer obtained for run D. The decrease of the average elution volume for increasing conversions together with the decrease of the P_d is a clear indication of the livingness of the process. For a comparison, run H in Table 1 indicates that when miniemulsion is prepared without transfer agent, no control over the MWD is obtained.

Conclusions

In this work it has been shown that in order to realize LFRP in emulsion, while preserving high polymerization rates, reactions that do not imply a change in the radical number, such as DT or RAFT and not NMLP and ATRP, should be used. Experimental data using 1-iodotridecafluorohexane as transfer agent indicate that good control over the MWD can be obtained in combination with large polymerization rates, using a miniemulsion with oil-soluble initiator. This procedure can be in general applied to a variety of monomers. The developed analysis indicated that better performances would be obtained using transfer agents characterized by larger transfer rates.

During the preparation of this paper similar results as those discussed previously have appeared in this same journal.[11] We believe that the material presented in this work contributes on one hand to confirm the earlier results and on the other hand to provide a rationale for the selection of the reacting system to carry out a controlled polymerization in emulsion. This may stimulate the development of new systems for the realization of a more efficient controlled polymerization.

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