Controlled Free-Radical Miniemulsion Polymerization of Styrene Using Degenerative Transfer

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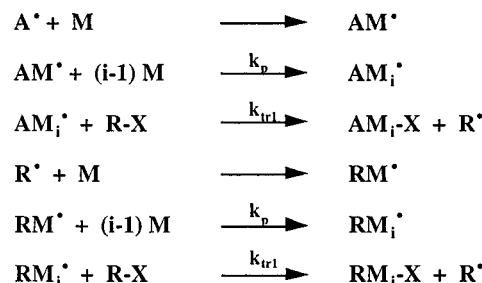*Elf-Atochem, Groupement de Recherches de Lacq, B.P. 34, 64170 LACQ, France*

ABSTRACT: Controlled free-radical polymerization of styrene was performed in aqueous dispersed medium using a degenerative transfer process with iodine atom exchange. The transfer agent was the commercially available perfluorohexyl iodide. Its efficiency was shown to be low in conventional batch emulsion polymerization since polymer had molar mass higher than expected. This was explained by a slow rate of diffusion of the perfluorinated transfer agent through the water phase, from the monomer droplets to the active latex particles. This problem was overcome by using a batch miniemulsion process. In that case, 100% efficiency of the chain transfer agent was reached, and the experimental molar masses fit well with the theoretical ones. With that technique, the transfer agent could be directly located in the polymer particles without transportation. Moreover, when using a continuous addition of monomer, a linear increase of the number-average molar mass with conversion was observed.

Introduction

Controlled free-radical polymerization enables to apply free-radical polymerization to the synthesis of well-defined polymers with predictible molar mass, narrow molar mass distribution, and complex architectures.[1,2] The different methods that lead to controlled free-radical polymerization are based either on a reversible termination reaction (mainly nitroxide-mediated radical polymerization[1−3] and atom transfer radical polymerization[1,2,4]) or on a reversible chain transfer reaction.[5,6] In both cases, macromolecular chains undergo successive activation/deactivation cycles. In the case of reversible transfer, the activation process is based on a bimolecular reaction between an active macromolecule and a dormant one, leading to the exchange of the ω-end group. It can be a direct exchange like in the so-called degenerative transfer technique where an iodine atom is exchanged.[5] Another more recent approach is the reversible addition−fragmentation chain transfer (RAFT),[6] in which case chains are end-functionalized by a dithioester that is exchanged via an addition−fragmentation process. In such systems, a conventional radical initiator is needed together with the specific transfer agent, and a great advantage of the reversible transfer technique is that the experimental conditions can be very close to conventional ones, in terms of temperature, concentrations, and processes. Molar mass control is achieved according to the different reactions reported in Scheme 1. The average molar mass increases with monomer conversion, and the number-average degree of polymerization at final conversion can be calculated by the ratio of the initial concentration of monomer to the initial concentration of transfer agent, providing that the initial concentration of initiator is small with respect to that of the transfer agent. Block copolymers were synthesized in bulk, the limitation being the unavoidable contamination by the two respective homopolymers. They had particularly narrow molar

Scheme 1

1) Transfer reaction to RX

$$A^{\bullet} + M \longrightarrow AM^{\bullet}$$

$$AM^{\bullet} + (i\text{-}1)\,M \xrightarrow{\ k_p\ } AM_i^{\bullet}$$

$$AM_i^{\bullet} + R\text{-}X \xrightarrow{\ k_{tr1}\ } AM_i\text{-}X + R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow RM^{\bullet}$$

$$RM^{\bullet} + (i\text{-}1)\,M \xrightarrow{\ k_p\ } RM_i^{\bullet}$$

$$RM_i^{\bullet} + R\text{-}X \xrightarrow{\ k_{tr1}\ } RM_i\text{-}X + R^{\bullet}$$

2) Degenerative transfer (extension of existing chains)

$$RM_i\text{-}X + RM_j^{\bullet} \underset{k_{tr2}}{\overset{k_{tr2}}{\rightleftharpoons}} RM_i^{\bullet} + RM_j\text{-}X$$
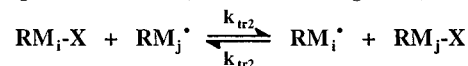
with   A :   Radical initiator fragment
       R-X :   Transfer agent
       M :   Monomer
       k_p :   Rate constant of propagation
       k_{tr1} :   Rate constant of transfer to RX
       k_{tr2} :   Rate constant of transfer to RM_i-X

mass distribution when the RAFT technique was applied.[6c]

Since water is a friendly medium for radical polymerization, it is therefore possible to carry out controlled polymerization in aqueous dispersed systems. Attempts using the systems based on reversible termination were published,[7−15] but difficulties remain and the technique still has to be improved.

In this work, we present a study on the controlled free-radical polymerization of styrene using degenerative transfer based on the iodine atom exchange. This system, which gave interesting results in bulk,[5] was carried out for the first time with this monomer in emulsion and miniemulsion polymerizations. The trans-

fer agent we used was the commercially available perfluorohexyl iodide (C$_6$F$_{13}$I) which was previously used by Yutani and Tatemoto for fluorinated monomers.[16] It was first applied in batch polymerization processes. Further incremental monomer additions were also performed using a semicontinuous feed process.

Experimental Part

Materials. Styrene (St) was distilled under reduced pressure before use. The radical initiators α,α′-azobis(isobutyronitrile) (AIBN, >98% from Fluka) and 4,4′-azobis(4-cyanopentanoic acid) (ACPA, 75%, remainder water from Aldrich), the transfer agent perfluorohexyl iodide (C$_6$F$_{13}$I, 99% Aldrich), the anionic surfactant sodium dodecyl sulfate (SDS, 98%, from Acros), and the buffer sodium hydrogen carbonate (NaHCO$_3$, Prolabo) were used as received.

Bulk Polymerization of Styrene. Bulk polymerizations of styrene in the presence of C$_6$F$_{13}$I were carried out at 70 °C in sealed tubes after degassing by two freeze−pump−thaw cycles. AIBN was used as a radical initiator. The transfer constant of C$_6$F$_{13}$I was determined at low conversion (45 min reaction, conversion < 10%) using the Mayo equation: the concentration of AIBN was 0.028 mol L^{-1}, and the concentration of C$_6$F$_{13}$I was varied between 0 and 0.03 mol L^{-1}. After reaction, the polymers were precipitated in methanol and dried. Conversion was determined by gravimetry, and molar masses were measured by size exclusion chromatography.

Emulsion and Miniemulsion Polymerization Procedures. Batch emulsion polymerizations were carried out at 70 °C under nitrogen atmosphere, using a conventional 250 mL thermostated reactor. A typical recipe is described below. Deionized water (169 mL), NaHCO$_3$ (0.15 g), and SDS (0.5 g, 0.010 mol/L$_{water}$) were introduced into the reactor, and the solution was bubbled with nitrogen. The mixture of styrene (18 g: τ = 10 wt % polymer content in the latex at final conversion) and C$_6$F$_{13}$I was then added under mechanical stirring, and the emulsion was heated to 70 °C. After stabilization of the temperature, 3 mL of an alkaline aqueous solution of the initiator (ACPA, 0.15 g: 3 × 10^{-3} mol/L$_{water}$) was added which corresponded to time zero of the reaction.

For miniemulsion polymerizations,[17] experimental conditions were the same, except that a high molar mass polystyrene (1 wt % with respect to monomer, $M_w = 3.3 \times 10^5$ g mol^{-1}) was initially introduced in the monomer phase in order to enhance nucleation in the monomer droplets.[17] In the presence of C$_6$F$_{13}$I, neither cosurfactant nor hydrophobe was used. The monomer in water emulsion was prepared outside of the reactor and was strongly homogenized by ultrasonification. When a water-soluble initiator (ACPA) was used, the emulsion was introduced into the preheated reactor and deoxygenated by nitrogen bubbling, and the aqueous solution of initiator was finally added, marking time zero of the reaction. When a monomer-soluble initiator (AIBN) was used, it was dissolved in styrene before ultrasonification. The formed stable emulsion was deoxygenated at room temperature and then introduced into the preheated reactor which corresponded to time zero of the polymerization.

For some reactions, a second load of monomer was fed into the reactor after miniemulsion polymerization of the first load. This was done by continuous addition of neat monomer at a flow rate of 6.7 mL/h.

Latex Characterization. Samples were periodically withdrawn during polymerization in order to follow monomer conversion by gravimetry and to measure particles diameter by dynamic light scattering (Zetasizer4 from Malvern). The particle concentration (number of particles per milliliter of latex) was calculated according to the classical equation

$$N_p = \frac{6\tau}{\pi D_p^3 d_p}$$

with τ the polymer content (g mL^{-1}), D_p the particle's diameter (cm), and d_p the polymer density (1.05 g mL^{-1}).

Polymer Characterization. Polymers were recovered from the latexes by water evaporation. Molar masses were measured by size exclusion chromatography (SEC) using a Waters apparatus working at room temperature with stabilized tetrahydrofuran eluent at a flow rate of 1 mL min^{-1} and equipped with four PL-gel 10μ columns (100, 500, 10^3, and 10^4 Å). A differential refractive index detector was used, and molar masses were derived from a calibration curve based on polystyrene standards.

Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in linear mode. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polymer solutions (2−5 g L^{-1}) were prepared in THF. The matrix, 1,8-dihydroxy-9[10*H*]anthracenone (dithranol), was also dissolved in THF (10 g L^{-1}). The polystyrene solution (10 μL) was mixed with 50 μL of the matrix solution. Silver trifluoroacetate (10 μL of a 2 g L^{-1} solution in THF) was added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems.

Results and Discussion

Bulk Polymerization of Styrene. According to Scheme 1, the transfer process takes place following two simultaneous steps. The first one is the conventional transfer to the chain transfer agent C$_6$F$_{13}$I, creating new chains with a perfluorohexyl group at one end and an iodine atom at the other end. The other process is the transfer of the iodine atom from an end-functionalized chain to a propagating macroradical, which is a thermodynamically neutral process. This second step does not create new chains but contributes to the extension of existing chains. If the initial concentration of radical initiator is small with respect to the initial concentration of transfer agent, a large majority of the macromolecules have the same expected structure. The evolution with time of the number-average degree of polymerization DP$_n$ can be calculated by the following equation:

$$DP_n = \frac{[M]_0 - [M]_t}{([C_6F_{13}I]_0 - [C_6F_{13}I]_t) + f([I]_0 - [I]_t)} \quad (1)$$

with [M]$_0$ and [M]$_t$ the monomer concentration respectively at time 0 and at time *t*, [I]$_0$ and [I]$_t$ the initiator concentration respectively at time 0 and at time *t*, *f* the initiator efficiency, and [C$_6$F$_{13}$I]$_0$ and [C$_6$F$_{13}$I]$_t$ the transfer agent concentration respectively at time 0 and at time *t*.

At very low monomer conversion, the Mayo equation can be applied and gives, if the contribution of the initiator is neglected

$$DP_{n0} = \frac{k_p[M]_0}{k_{trl}[C_6F_{13}I]_0} = \frac{1}{C_{trl}} \frac{[M]_0}{[C_6F_{13}I]_0} \quad (2)$$

Therefore, the plot of DP$_n$ versus monomer conversion starts at DP$_{n0}$ and follows eq 1 when time and hence conversion increase. The chain concentration becomes constant and close to the initial concentration of the transfer agent once the latter has been completely
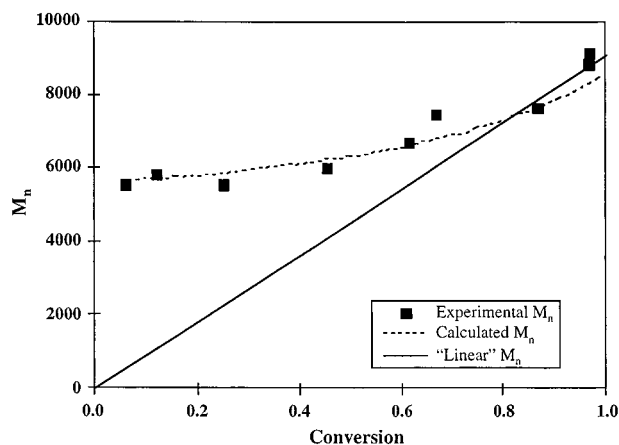
Figure 1. Bulk polymerization of styrene at $T = 70$ °C with $[C_6F_{13}I]_0 = 0.1$ mol L^{-1} and $[AIBN]_0 = 0.03$ mol L^{-1}. M_n is calculated by modified eq 1: $M_n = 104\{[[M]_0(1 - \exp(-k_p[P^\bullet]\cdot t))]/[[C_6F_{13}I]_0(1 - \exp(-k_{tr1}[P^\bullet]t)) + f[I]_0((1 - \exp(-k_dt))]\}$ using a decreasing value of f with monomer conversion,[20] a rate constant of decomposition of AIBN at 70 °C, $k_d = 4.7 \times 10^{-5}$ s^{-1},[21] a rate constant of propagation of styrene at 70 °C, $k_p = 477$ L mol^{-1} s^{-1},[22] and the value of $[P^\bullet] = 10^{-7}$ mol L^{-1} was calculated from the slope of the $\ln(1/1 - \text{conversion})$ versus time plot. Linear $M_n = \text{conversion} \times 104([M]_0/[C_6F_{13}I]_0)$.

consumed. At that stage only, and if the reversible transfer takes place, a linear increase of DP_n with monomer conversion can be observed. Thus, $C_{tr1} = k_{tr1}/k_p$ should be larger than 1 in order to totally consume the transfer agent before complete monomer conversion. This is the case with $C_6F_{13}I$ in the polymerization of styrene, since a value of $C_{tr1} = 1.4$ was experimentally determined at 70 °C, using the classical Mayo equation (see Experimental Part). Nevertheless, this value is not large enough to lead to a linear DP_n versus conversion plot with intercept close to 0. For instance, with a concentration of $C_6F_{13}I$ of 0.1 mol L^{-1} in bulk styrene (8.75 mol L^{-1}), the initial theoretical DP_n at low conversion is 63 ($M_n = 6500$ g mol^{-1}). It should increase to 87 ($M_n = 9100$ g mol^{-1}) at final conversion. In addition, the constant of the degenerative transfer reaction $C_{tr2} = k_{tr2}/k_p$ should be large enough, since it influences the molar mass distribution: $M_w/M_n = 1 + 1/C_{tr2}$ at final conversion.[18] A value of $C_{tr2} = 3.8$ was calculated by Goto et al. at 70 °C for the same system,[19] indicating that the polydispersity index cannot be lower than 1.26.

Bulk polymerization of styrene was performed at 70 °C using an initial concentration of AIBN of 0.03 mol L^{-1} and an initial concentration of $C_6F_{13}I$ of 0.1 mol L^{-1}. The evolution of the experimental molar masses versus monomer conversion is plotted in Figure 1. It should be noted that there is a good agreement with the calculated molar masses given by eq 1. The observed shift of the SEC peak between 6% monomer conversion ($M_n = 5550$ g mol^{-1}, $M_w/M_n = 1.72$) and 97% ($M_n = 9100$ g mol^{-1}, $M_w/M_n = 1.41$) together with the decrease of M_w/M_n is a good indication that a chain extension process has occurred as expected when a degenerative transfer reaction takes place. Moreover, the theoretical molar mass was reached at final conversion, indicating the complete consumption of the transfer agent. Thus, it is very likely that chains have an iodine atom at the end and can be extended by degenerative transfer when a second load of monomer is added. This was experimentally verified as illustrated in Figure 2. However, the tailing on the low molar mass side of the chromato-
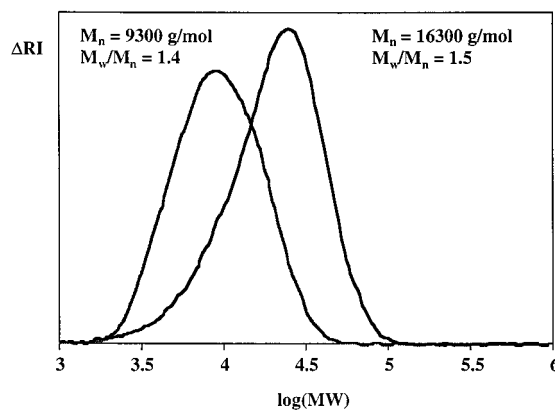

Figure 2. Chain extension in bulk polymerization of styrene. First step: bulk polymerization of styrene at 70 °C with $[C_6F_{13}I]_0 = 0.1$ mol L^{-1} and $[AIBN]_0 = 0.03$ mol L^{-1} until 72% conversion. Second step: addition of styrene (same amount as for the first step). For the second step, polymerization was stopped at 60% conversion.
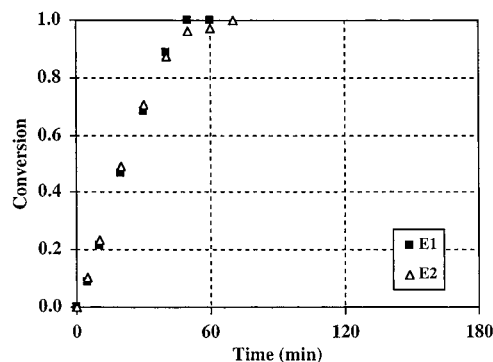

Figure 3. Conversion versus time for the batch emulsion polymerizations of styrene using ACPA initiator at 70 °C. **E1**: $[C_6F_{13}I]_0 = 0.1$ mol/L$_{St}$; final diameter = 73 nm; $N_p = 4.5 \times 10^{14}$ mL^{-1}. **E2**: $[C_6F_{13}I]_0 = 0.2$ mol/L$_{St}$; final diameter = 70 nm; $N_p = 5.2 \times 10^{14}$ mL^{-1}.

gram is an indication of the existence of dead chains which cannot be avoided when using a reversible transfer process.

Emulsion Polymerization of Styrene. Emulsion polymerizations of styrene were carried out according to a conventional batch process as described in the experimental part. The transfer agent $C_6F_{13}I$ was used at two initial concentrations in the monomer phase: 0.1 mol/L$_{St}$ (experiment **E1**) and 0.2 mol/L$_{St}$ (experiment **E2**). In that case, the theoretical number-average molar masses are respectively $M_n = 9100$ g/mol and $M_n = 4550$ g/mol at final monomer conversion. It is observed in Figure 3 that polymerization was fast and that neither kinetics nor particles diameter was affected by the addition of the perfluorinated compound. Moreover, the final latexes were stable and did not form any coagulum. However, in contrast to bulk polymerization, the final molar masses were strongly above the linear theoretical line, even at complete conversion (Figure 4). This is the indication that an unexpectedly small number of chains were formed, i.e., that the chain transfer agent had a low efficiency. This efficiency was calculated to be approximately 50% for both experimental conditions. This means that the transfer agent was not totally consumed before complete monomer conversion, which is in contradiction with the transfer constant value. This behavior can be explained by a slow diffusion of the perfluorohexyl iodide from the monomer droplets to the
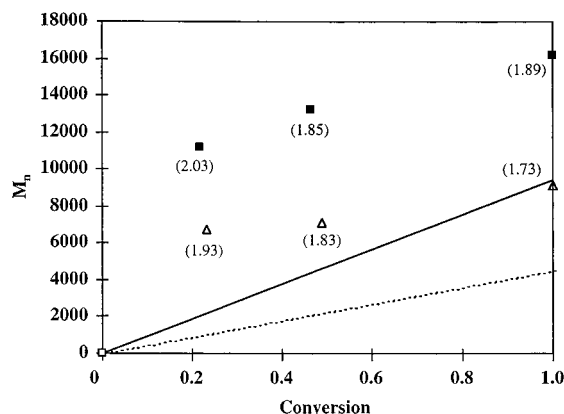
Figure 4. Number-average molar mass versus monomer conversion for the batch emulsion polymerizations of styrene using ACPA initiator at 70 °C. **E1**: $[C_6F_{13}I]_0 = 0.1$ mol/L$_{St}$. **E2**: $[C_6F_{13}I]_0 = 0.2$ mol/L$_{St}$. **E1**: (■) experimental M_n; (—) linear theoretical M_n. **E2**: (△) experimental M_n; (- - -) linear theoretical M_n. M_w/M_n values are given in parentheses.

active particles during polymerization, which is not surprising owing to its very hydrophobic character.

This situation prevents the use of $C_6F_{13}I$ in controlled free-radical emulsion polymerization since, in addition to a poor molar mass control, remaining transfer agent might further react with a second monomer load, leading to the creation of new chains instead of chain extension by degenerative transfer.

Miniemulsion Polymerization of Styrene. To increase the transfer agent efficiency in aqueous dispersed system, a miniemulsion process was applied. Because of the ultrasonification of the initial monomer in water emulsion, very small monomer droplets are formed, the diameter of which is significantly below a micron. Stability of the emulsion is usually improved by the use of a cosurfactant such as hexadecanol or of a hydrophobe such as hexadecane. In our study however it was not used, the perfluorinated compound being supposed to play the role of a hydrophobe. The small droplet size enables their direct nucleation. If it is the case, then the monomer and the organic compounds are initially located in the particles where polymerization takes place, and no transportation is needed. Thus, the transfer agent should be consumed following the same kinetics as in bulk polymerization which might lead to a high efficiency, i.e., the formation of polymer with the expected molar mass.

The miniemulsion polymerizations were carried out using the same concentrations as in the previously described emulsion polymerizations. Experimental conditions and final characteristics of the latexes are reported in Table 1. Monomer conversion versus time curves are plotted in Figure 5. In all cases, stable latexes were recovered with no coagulum. Fast and complete polymerizations were obtained when using the water-soluble ACPA initiator, similar to the case for the previous emulsion polymerizations. It should however be noted that the addition of $C_6F_{13}I$ led to a slight decrease of the polymerization rate, which is correlated with a decrease of the final number of particles (i.e., an increase of the final particle's diameter). The use of the oil-soluble AIBN as a radical initiator led to a comparatively slower polymerization reaction. The short inhibition period which could be observed with the latter initiator corresponds to the time that was required for

heating the reaction mixture to the desired temperature (see Experimental Part).

The most interesting feature of the batch miniemulsion polymerizations is that the final polymer had the expected molar mass as displayed in Figure 6. Like in bulk polymerizations, molar mass increased with monomer conversion, and the curve did not pass through the origin because of the low value of the chain transfer constant. In all cases, the polydispersity index values, M_w/M_n, decreased with monomer conversion from approximately 2 to approximately 1.5−1.6. Polymer with molar mass as high as $M_n = 47\,000$ g mol^{-1} could be obtained with relatively narrow polydispersity ($M_w/M_n = 1.50$) and with high final monomer conversion (92%) (see Table 1, experiment **ME6**). Those results show that the transfer agent efficiency was considerably improved in batch miniemulsion polymerization as compared with that in emulsion polymerization.

The structure of the final polymer from the **ME2** experiment was analyzed by MALDI-TOF mass spectrometry. As illustrated in Figure 7, two main series are visible in the spectrum, both corresponding to a molar mass distribution of polystyrene with 104.15 u between the peaks. For a given series and a given degree of polymerization, the multiplicity of the peak corresponds to the isotopic distribution which is a function of the various atoms existing in the structure, including the metal cation. Both series correspond to the same structure being cationized either with silver (as expected) or with sodium (because the samples contain large amounts of Na$^+$, coming from the initiator, the surfactant, and the buffer). This structure is $C_6F_{13}-$(styrene)$_n-CH{=}CH(C_6H_5)$. It corresponds to polymer chains with the transfer agent fragment at the α-end. The ω-end unsaturation is the result of HI elimination which could have taken place during the synthesis, during the storage of the dried polymer and mainly during the MALDI-TOF MS analysis. Unfortunately, it is not possible to detect the iodine end group which would be proof of the living character of the chains. Furthermore, the lability of the C−I bond does not enable to isolate the polymer without elimination, which precludes accurate quantitative analysis. No series with the initiator fragment could be observed which is not surprising since the amount was small with respect to the transfer agent; moreover, only a fraction of it has decomposed during 2 h at 70 °C. It is also interesting to note that no chain resulting from termination by recombination can be observed with either ACPA fragment or C_6F_{13} at each end.

Therefore, the final latexes, prepared by the miniemulsion process, are composed of particles containing a majority of polystyrene chains with the expected C_6F_{13} tail at the α-end. To check whether the macromolecules have an iodine atom at the ω-end, chain extension has been performed by the addition of a second load of monomer. When this addition was performed in one shot after a first step of polymerization, coagulation of the latexes occurred. For that reason, a semicontinuous process was applied. A latex similar to **ME2** was prepared in order to be used as a seed for continuous monomer addition. After 90% conversion, this seed latex was poststabilized by the addition of SDS (to reach an overall concentration of 0.015 mol/L$_{water}$). The same amount of monomer as in the initial load was continuously fed into the reactor as described in the Experimental Part and in Table 1 (latex **ME7**). A slow rate of
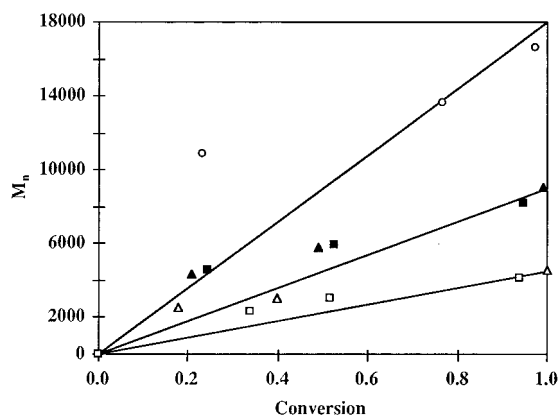
Table 1. Miniemulsion Polymerizations of Styrene at 70 °C in the Presence of $C_6F_{13}I$: Experimental Conditions and Latex Characterization

expt	process	symbol (Figs 5 and 6)	initiator	final diam (nm)	final N_p $\times 10^{-14}$ (mL^{-1})	$[C_6F_{13}I]_0$ (mol/L$_{St}$)	theor M_n at final conversion[a]	exptl M_n as a function of monomer conversion	
								conversion	M_n (M_w/M_n)
ME1	batch	■	ACPA	89	2.5	0.1	9100	0.25	4600 (2.2)
								0.53	5960 (1.84)
								0.95	8200 (1.69)
ME2	batch	□	ACPA	114	1.1	0.2	4550	0.16	2350 (1.65)
								0.52	3070 (1.61)
								0.94	4150 (1.50)
ME3	batch	▲	AIBN	116	1.0	0.1	9100	0.21	4360 (2.4)
								0.49	5780 (1.98)
								0.99	9060 (1.91)
ME4	batch	△	AIBN	140	0.5	0.2	4550	0.18	2570 (1.74)
								0.40	3020 (1.63)
								1.0	4560 (1.55)
ME5	batch	○	ACPA	104	1.6	0.05	18200	0.23	10900 (1.97)
								0.77	13600 (1.87)
								0.98	16600 (1.66)
ME6	batch		ACPA[b]	112	1.2	0.02	45000	0.25	27500 (1.91)
								0.57	35000 (1.73)
								0.92	47000 (1.50)
ME7[c]									
1st step	batch		ACPA	114	1.10	0.2	4550	0.47	4130 (1.54)
2nd step	continuous addition of St			153	0.94	0.1[e]	9500	0.60	4900 (1.58)
								0.75	7060 (1.53)
								0.99[f]	9240 (1.73)
ME8[d]	continuous addition of St		ACPA	91	2.3	0.1	10900	0.16	1900 (1.26)
								0.34	3980 (1.70)
								0.54	6900 (1.90)
								0.84	10900 (2.3)

[a] Calculated by 104([M]$_0$/[C$_6$F$_{13}$I]$_0$). [b] Concentration of ACPA was divided by 5 (reaction time = 2 h). [c] **ME7**: first load of styrene: 17.7 g; second load = 18.1 g (addition was started at a reaction time of 52 min) (overall conversion is calculated on the basis of the final amount of added monomer). [d] **ME8**: initial styrene in the reactor: 0.98 g; second load = 17.1 g (addition was started at $t = 0$) (overall conversion is calculated on the basis of the final amount of added monomer). [e] Due to dilution. [f] Overall conversion.
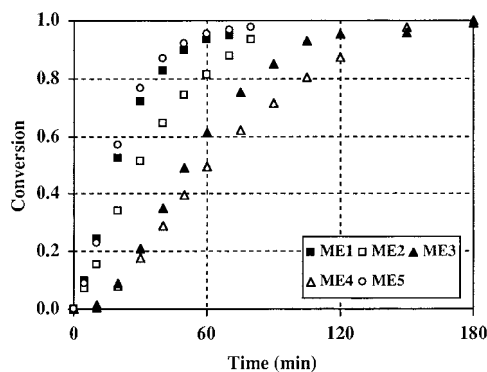
Figure 5. Conversion versus time for the batch miniemulsion polymerizations of styrene using ACPA or AIBN as initiators at 70 °C (see Table 1).

Figure 6. Number-average molar mass versus monomer conversion for the batch miniemulsion polymerizations of styrene using ACPA or AIBN initiators at 70 °C (see Table 1).

addition was used, and no new initiator was added because a sufficient amount was supposed to remain from the first step. If no new particles are created, the existing particles would grow by propagation of the added monomer, and the existing chains would be extended according to the reversible transfer process. A secondary nucleation would have a dramatic effect not only on the particle size distribution but also on the molar mass distribution since in the newly formed particles no controlled polymerization would take place, owing to the absence of macromolecules with an iodine end group. As reported in Table 1, the expected characteristics were experimentally observed: no secondary nucleation (the diameter increased and N_p remained the same) and a good agreement between the final experimental M_n and the theoretical one. Moreover, during the second step a linear increase of M_n with monomer

conversion was observed (Figure 8), but in contrast to batch conditions, there was a simultaneous increase of M_w/M_n.

It has been shown above that, owing to a value of C_{tr1} larger than 1, $C_6F_{13}I$ was consumed before complete monomer conversion in the first batch step. Thus, upon decreasing in that first step the proportion of monomer with respect to the overall amount, without changing the amount of transfer agent, the linear increase of M_n would start at smaller overall monomer conversion. Therefore, for a second experiment with semicontinuous addition (**ME8**), a minimum amount of styrene (1 g) and the overall transfer agent were emulsified in water using ultrasonification. Afterward, the remaining styrene was continuously fed into the preheated reactor,
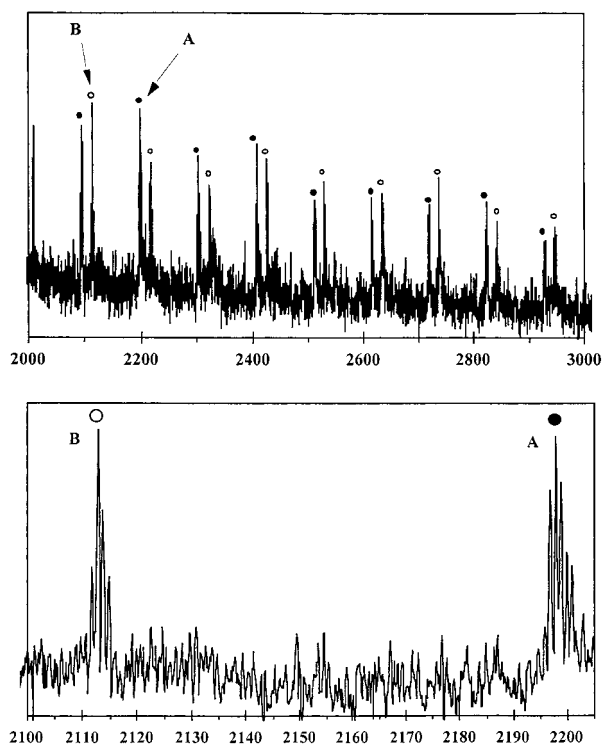
Figure 7. MALDI-TOF-MS spectrum of polymer **ME2** at final conversion: expansion between $m/z = 2000$ u and $m/z = 3000$ u and expansion between $m/z = 2100$ u and $m/z = 2205$ u. (●) Series A: [C$_6$F$_{13}$−(styrene)$_n$−CH=CH(C$_6$H$_5$), Ag$^+$] (for $n = 16$, $m/z = 2196.5$ u). (○) Series B: [C$_6$F$_{13}$−(styrene)$_n$−CH=CH-(C$_6$H$_5$), Na$^+$] (for $n = 16$, $m/z = 2111.6$ u).
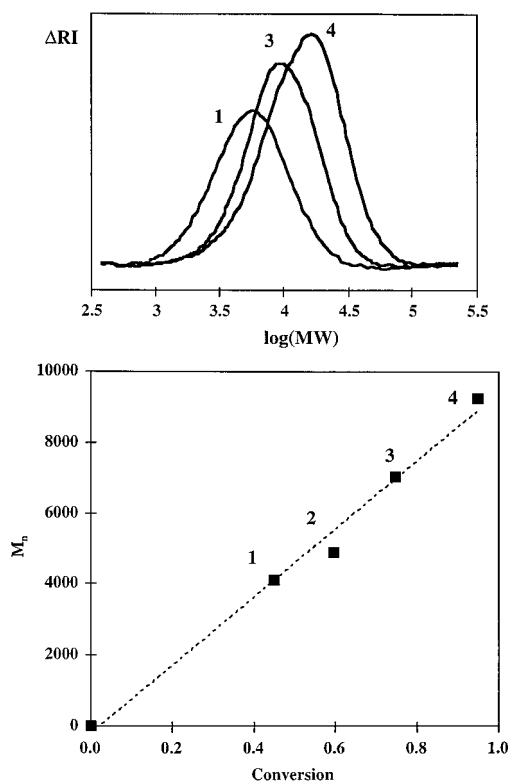

Figure 8. SEC chromatograms and plot of the number-average molar mass versus overall monomer conversion for the miniemulsion polymerization **ME7** with continuous addition of styrene in the second step; first step was based on the recipe of latex **ME2** (see Table 1).

the beginning of addition corresponding to time zero of the reaction. The initiator was added just prior to
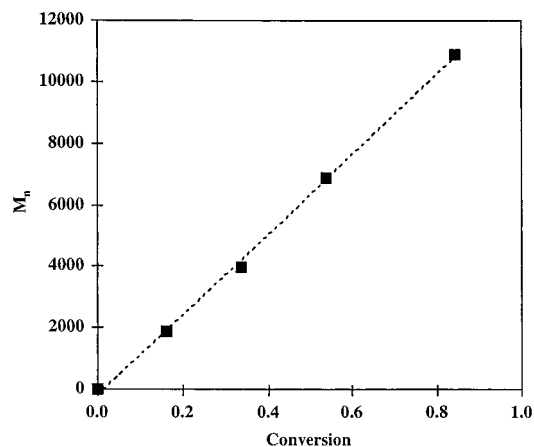

Figure 9. Number-average molar mass versus overall monomer conversion for the miniemulsion polymerization **ME8** with continuous addition of styrene (see Table 1).

styrene addition. Results are reported in Table 1, and the M_n versus conversion plot is shown in Figure 9. As expected, a linear increase of M_n is observed throughout the polymerization. However, like for the previous semicontinuous experiment **ME7**, the M_w/M_n value increased with monomer conversion. This can be a consequence of the fact that the activation/deactivation reaction is an exchange between two macromolecular chains, a propagating one and a dormant one. In that case, the rate constant of this reaction (k_{tr2}) is most probably dependent upon chain length and medium viscosity. With slow continuous addition of monomer, the particles contain low monomer concentration and have high viscosity which can lead to a decrease of k_{tr2}. The consequence is, thus, a decrease of $C_{tr2} = k_{tr2}/k_p$, leading to a significant broadening of the molar mass distribution as experimentally observed.

Conclusion

Controlled free-radical polymerization of styrene was performed in an aqueous dispersed medium using a degenerative transfer process with iodine atom exchange. The transfer agent was the commercially available perfluorohexyl iodide. Its efficiency was shown to be low (i.e., 50%) in conventional batch emulsion polymerization since polymer had molar mass higher than expected. This was explained by a slow rate of diffusion of the perfluorinated transfer agent through the water phase, from the monomer droplets to the active latex particles. However, when using a batch miniemulsion process, 100% efficiency was reached, and the experimental molar masses fit well with the theoretical ones. With that technique, the transfer agent could be directly located in the polymerization locus without transportation. An increase of the molar mass with monomer conversion was observed together with of a decrease of M_w/M_n, although the curve did not cross the origin. This result could be easily explained by the relatively low transfer constant of C$_6$F$_{13}$I, which is 1.4 for styrene polymerization. The proportionality of M_n with monomer conversion was observed when styrene was continuously fed into the polymerization medium. In that case, however, the molar mass distribution broadened with monomer conversion, and this was explained by a decrease of the rate constant of the activation/deactivation reaction with chain length and viscosity of the polymerization medium. The synthesis of block copoly-

mers in miniemulsion polymerization is now under investigation.

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