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Reverse Iodine Transfer Polymerization (RITP) in Emulsion

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Summary: Reverse iodine transfer polymerization (RITP) is a new controlled radical polymerization technique based on the use of molecular iodine I_2 as control agent. This paper aims at presenting the basics of RITP and the strategy that we have followed for the development of this process in the past three years, from the validation in homogeneous solution polymerization up to recent results in heterogeneous aqueous polymerization processes. Typical examples of RITP of butyl acrylate in emulsion and RITP of styrene in miniemulsion are discussed.

Keywords: emulsion polymerization; miniemulsion polymerization; reverse iodine transfer polymerization

Introduction

The area of radical polymerization has seen a real breakthrough with the invention of controlled/''living'' radical polymerization techniques (CRP).[1] These techniques make it possible to design copolymers with unusual chain microstructures (e.g. gradient copolymers, well-defined graft copolymers), copolymers of complex architectures that were only accessible by other specific methods such as living ionic polymerizations (e.g. block copolymers, star polymers, ...), copolymers with functional groups (e.g. homo- or hetero-telechelic polymers, macromonomers, functional star polymers, ...), and composites (e.g. polymer brushes from modified surfaces). The CRP techniques rely on a reversible activation-deactivation of the polymer chains, i.e. an equilibrium between a reservoir of dormant chains (capped polymer chains) and a tiny population of active chains (propagating chains) (Figure 1). Two main strategies have been used so far: the first one deals with a reversible termination mechanism and the quality of the control is then essentially based on the persistent radical effect (i.e. an accumulation of the persistent species $[X\text{-}(Y)] \gg [P^\bullet]$ leading to a favored cross-coupling rather than self-termination $R_c = k_c\ [X\text{-}(Y)][P^\bullet] \gg R_t = k_t\ [P^\bullet]^2$), the second one deals with a reversible chain transfer mechanism and the quality of the control is then essentially based on the high probability of reversible transfer reactions in comparison with termination (i.e. domination of degenerative chain transfer $R_{ex} = k_{ex}\ [P^\bullet][P\text{-}X(+Y)] \gg R_t = k_t\ [P^\bullet]^2$)[2] Sometimes, the two processes (reversible termination and reversible transfer) can operate simultaneously (example: living radical polymerizations mediated by organocobalt porphyrin complexes reported by Wayland et al.[3,4]). Several CRP techniques have been developed in the past thirty years, but their implementation at an industrial scale, especially in heterogeneous aqueous processes which are of major importance nowadays, remains a challenge.[5,6] In this paper, we report our strategy to set up a new CRP technique based on simple, readily available and economical chemicals and our attempts to control the polymerization in aqueous emulsion polymerizations. Experimental details are given elsewhere.[7–11]

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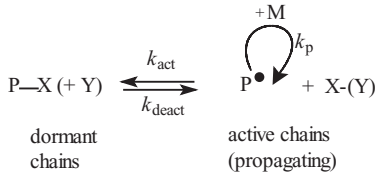

Figure 1.
General scheme of reversible activation in controlled radical polymerization.

Strategy

The first CRP techniques were developed as early as in the late seventies (iodine transfer polymerization, ITP)[12] and early eighties (photo-INIFERTERS)[13] (nitroxide-mediated polymerization, NMP).[14] In the nineties, the CRP mechanisms were rationalized thanks to an intensive research particularly based on kinetics, and other CRP techniques have been proposed (atom transfer radical polymerization, ATRP)[15] (reversible addition-fragmentation chain transfer, RAFT).[16] Since then, new CRP techniques are still appearing (e.g. based on cobalt, tellurium,...) and the subtleties of the CRP mechanisms are often still subject to debate (example: side reactions with the radical intermediate in RAFT[17]). It is interesting to note that each CRP technique can be applied according to at least two important alternatives: a) on the one hand a R-X(+Y) can be directly used (e.g. an alkoxyamine R-ONR_1R_2 in the case of NMP), b) on the other hand a X-(Y) can be used together with a source of radicals to form in situ the R-X(+Y) compound (e.g. a nitroxide $R_1R_2NO\bullet$ in the presence of an azo initiator R-N=N-R in the case of NMP). It is also interesting to note that in the second case a powerful radical scavenger is required (the nitroxide $R_1R_2NO\bullet$ is the radical scavenger for the case mentioned above) to limit the propagation during the initialization period.[18] A last observation is that ITP is an attractive CRP technique because it does not require complicated chemicals and it has already led to commercial products,[12] but the second variant was not reported yet in the literature although molecular iodine I_2 is known to be a powerful radical scavenger.[19] We have decided to fill this gap by developing the reverse iodine transfer polymerization (RITP) technique, based on the use of molecular iodine I_2 as a control agent.[7,20–22]

Validation of the Concept in Solution Polymerization

The concept of RITP was first checked in solution polymerization.[7,8,20] The basic mechanism of RITP is presented in Figure 2. It was shown that the use of molecular iodine I_2 allowed the controlled polymerization of a wide range of monomers such as acrylates, alpha-fluoro acrylates, styrenics, vinylidene halides, and methacrylates. A typical result is given in Table 1 (run 1) for RITP of butyl acrylate in butyl acetate at 85 °C with 2,2′-azobis-(isobutyronitrile) AIBN as the initiator.[7]

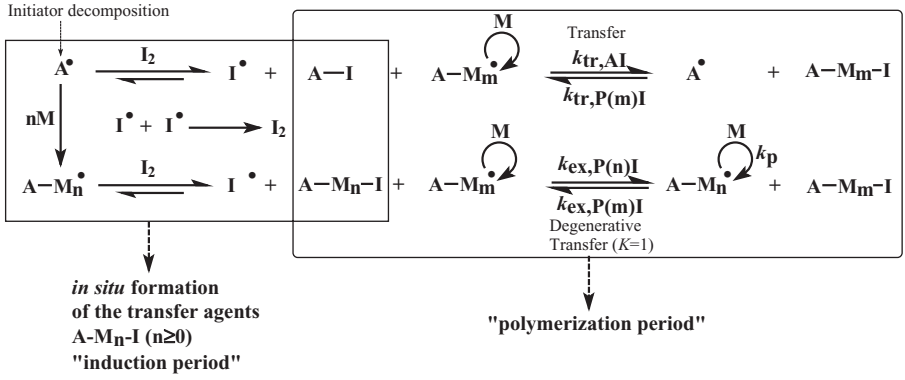

Figure 2.
Basic mechanism of reverse iodine transfer polymerization.

Table 1.
Reverse iodine transfer polymerization in solution, emulsion and miniemulsion.[a)]

Run	Solvent	Monomer	Additive	Time (h)	Conv. (%)	$M_{n,th}$[b)] ($g \cdot mol^{-1}$)	$M_{n,SEC}$ ($g \cdot mol^{-1}$)	M_w/M_n	pH	d_p[c)] (nm)
1	Butyl acetate	Butyl acrylate	No	5	95	9 500	9 700	1.83	n.a.	n.a.[d)]
2	Water (emulsion)	Butyl acrylate	No	7	99	10 300	31 000	1.98	5.2	106
3	Water (emulsion) (surfactant-free)	Butyl acrylate	No	15	83	8 700	22 000	1.88	5.1	443
4	Water (miniemulsion)	Styrene	No	16	72	7 500	13 900	1.73	2.4	334
5	Water (miniemulsion)	Styrene	H_2O_2/HCl	16	78	7 900	7 900	1.46	3.4	316

a) Run 1: polymerization of *n*-butyl acrylate at 80% w/v versus butyl acetate as solvent ([BuA] = 3.30 M) in the presence of 2,2′-azobisisobutyronitrile as initiator with $[AIBN]/[I_2] = 1.9$, $T = 85\ ^\circ C$. Run 2: polymerization of BuA in emulsion at $T = 85\ ^\circ C$ ($[ACPA]/[I_2] = 1.7$, $[SDS] = 0.15 \times CMC$, $M_{n,targeted} = 10\,400\ g \cdot mol^{-1}$). Run 3: polymerization of BuA in emulsion at $T = 85\ ^\circ C$ ($[ACPA]/[I_2] = 1.6$, no SDS, $M_{n,targeted} = 10\,100\ g \cdot mol^{-1}$). Run 4: polymerization of styrene in miniemulsion at $T = 60\ ^\circ C$ in the presence of Perkadox 16S as initiator, $[Perkadox]/[I_2] = 1.99$. Run 5: polymerization of styrene in miniemulsion at $T = 60\ ^\circ C$ in the presence of Perkadox 16S as initiator, $[Perkadox]/[I_2] = 2.44$. BuA: *n*-butyl acrylate; ACPA: 4,4′-azobis(4-cyanopentanoic acid); AIBN: 2,2′-azobisisobutyronitrile; SDS: sodium dodecyl sulfate; *CMC*: critical micelle concentration; Perkadox 16S: bis(4-tert-butylcyclohexyl) peroxydicarbonate.

b) Calculated by $M_{n,theoretical} = (\text{mass of monomer}) \times \text{Conversion}/(2 \times (\text{moles of } I_2)) + M_{A\text{-}I}$ in which $M_{A\text{-}I}$ is the molecular weight of the chain ends.

c) Particle diameter.

d) Not applicable.

The kinetic analysis in the case of RITP of methyl acrylate at 70 °C showed the existence of an initialization period during which iodine is consumed to form short A-M_n-I telomers which can further act as reversible transfer agents (reversible chain transfer) (Figure 3). For high monomer to iodine $[M]/[I_2]$ ratio, the monomer conversion during this period is negligible: this is the reason why in most cases this period can be called ''inhibition period'' or ''induction period''. This favored reaction of radicals

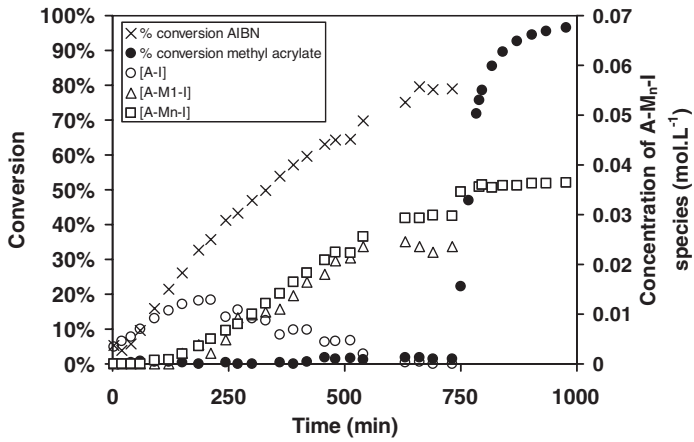

Figure 3.
Typical evolution of monomer conversion, initiator conversion, and concentrations of A-M_n-I species in reverse iodine transfer polymerization of methyl acrylate at 70 °C in deuterated benzene (determined by ^{1}H-NMR analyses) ([methyl acrylate] = 5.47 M, $[C_6D_6] = 5.70$ M, $[2,2'\text{-azobis(isobutyronitrile)}] = 3.78 \times 10^{-2}$ M, and $[I_2] = 2.22 \times 10^{-2}$ M).

with iodine is due to the high reactivity of iodine.[23,24] Indeed, the scavenging of alkyl radicals by iodine I_2 is nearly a diffusion-controlled reaction (typically in the range 10^9–$10^{10}\ M^{-1} \cdot s^{-1}$) and it was reported that there are certainly no spin effects in the scavenging of alkyl radicals by iodine and that steric effects can be expected to be small.[24] Furthermore, iodine radicals $I_\bullet$ produced by the scavenging reaction can recombine to form I_2 and this reaction is again a very fast nearly diffusion-controlled reaction (in the range 10^9– $10^{10}\ M^{-1} \cdot s^{-1}$).[24,25] Actually, the observed rate constants for the scavenging of alkyl radicals by iodine $R_\bullet + I_2$ and for the recombination of iodine radicals $I_\bullet + I_\bullet$ were not found to be completely proportional to the inverse of the viscosity of the media, indicating that they are not solely diffusion rate-controlled, but they could be described with a combination of a diffusion-controlled rate constant and an activation-controlled rate constant.[24]

After the induction period, the polymerization takes place and is dominated by the degenerative chain transfer mechanism. A typical evolution of the molecular weight and polydispersity index with conversion is given in Figure 4 in the case of RITP of methyl methacrylate in toluene.[8] The experimental data are in relatively good agreement with the theoretical evolutions of the molecular weight M_n (Eq. 1) and polydisersity index *PDI* (Eq. 2).[12]

$$M_n = (p[M]_0 M_{monomer})/\{2[I_2]_0 \times [1-(1-p)^{Cex}]\} \quad (1)$$

$$PDI = \{1 + ([M]_0/(2[I_2]_0)) \times [2 + (2-p)(1-C_{ex})/C_{ex}]\}/\{p[M]_0/(2[I_2]_0[1-(1-p)^{Cex}])\} \quad (2)$$

in which p is the fractional monomer conversion, $M_{monomer}$ is the molecular weight of the monomer, $[I_2]_0$ is the initial concentration of iodine, and C_{ex} is the degenerative chain transfer constant.

In the case of poly(methyl acrylate) where the polymers chain-ends are stable enough to survive during a Maldi-Tof analysis (in addition to ^{1}H-NMR, ^{13}C-NMR, and SEC characterizations), the expected structure A-M_n-I was confirmed, supporting the proposed mechanism of RITP.[7]

Ab Initio Emulsion Polymerization

Ab initio emulsion polymerization is one of the most used heterogeneous processes in

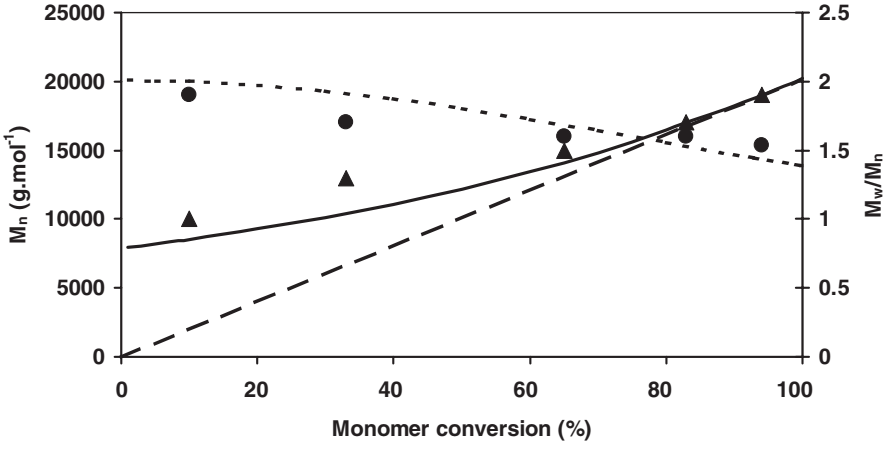

Figure 4.
Evolution of molecular weight M_n (▲) and polydispersity index M_w/M_n (●) with monomer conversion in reverse iodine transfer polymerization of methyl methacrylate in toluene at 80 °C in the presence of AIBN as initiator with $[AIBN]/[I_2] = 1.7$ ($M_{n,targeted} = 20\,200\ g \cdot mol^{-1}$). Theoretical evolutions are given by Eq. 1 (—) and Eq. 2 (- - -) with $C_{ex} = 2.6$. The ideal behavior of M_n assuming a high C_{ex} is also given for comparison (– – –).

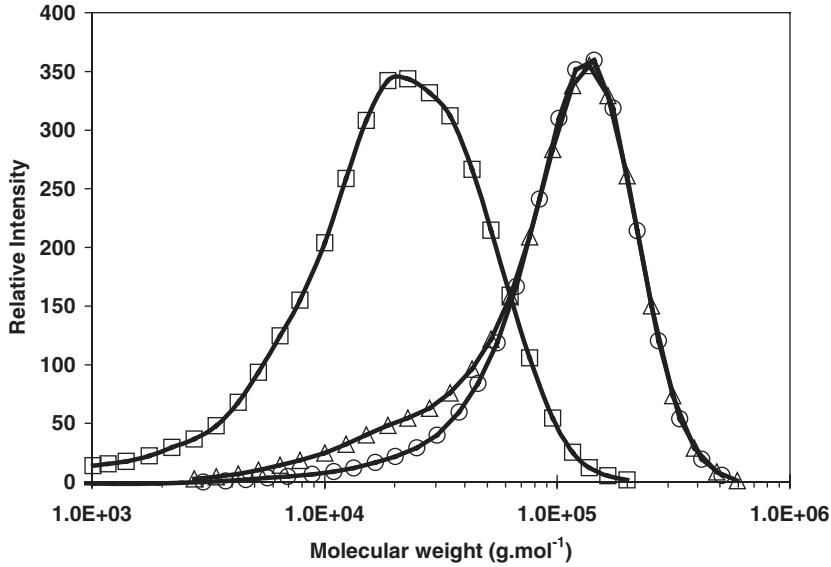

Figure 5.
Molecular weight distributions of the seed poly(BuA) latex ($M_{n,SEC} = 15\,900\ g \cdot mol^{-1}$) prepared by RITP and of the block copolymer latex poly(butyl acrylate)-bock-poly(styrene-*co*-butyl acrylate) ($M_{n,SEC} = 53\,400\ g \cdot mol^{-1}$) prepared by seeded emulsion polymerization at 85 °C: (□) refractive index detector (seed latex), (○) UV detector at 254 nm (copolymer latex), (△) refractive index detector (copolymer latex). Seed: [ACPA]/[I_2] = 1.6, [SDS] = 0.15 × *CMC*, targeted $M_n = 2\,500\ g \cdot mol^{-1}$, conversion = 40%, particle diameter = 127 nm; Block copolymer: second monomer = styrene; $Monomer_{Feed}/Monomer_{Seed}$ = 4.7 w/w, conversion = 32%, particle diameter = 203 nm.

the industry.[26] It initially involves two phases: a monomer phase dispersed in an aqueous phase containing a hydrosoluble radical initiator and a surfactant. The polymerization creates a new phase of polymer particles (nucleation). The nucleation step is very important since it will determine the number of particles (and so the final latex particle size) which in turn will partly determine the kinetics of the polymerization.[27] Most CRP techniques tested so far failed in ab initio emulsion polymerization because they encountered difficulties related to the nucleation step (e.g. instability of the latex, slow diffusion of hydrophobic control agents,...)[5,6,28] and only a few works gave promising results.[29] In our first attempts, we tested ab initio emulsion RITP of *n*-butyl acrylate, using 4,4′-azobis(4-cyanopentanoic acid) (ACPA) neutralized with sodium hydroxide as initiator and sodium dodecyl sulfate (SDS) as surfactant.[9] It was possible to obtain a stable and uncolored (white) monodisperse

$$I_{2,aq} + H_2O \rightleftharpoons I^- + H^+ + HOI \quad (1)$$

$$3HOI \rightleftharpoons IO_3^- + 2I^- + 3H^+ \quad (2)$$

$$3\,I_{2,aq} + 3\,H_2O \rightleftharpoons IO_3^- + 5\,I^- + 6\,H^+ \quad (3)$$

$$I_{2,aq} + I^- \rightleftharpoons I_3^- \quad (4)$$

Figure 6.
Some important reactions of iodine I_2 in the aqueous phase: hydrolytic disproportionation of iodine I_2 and triiodide I_3^- formation.

$$H_2O_2 + 2H^+ + 2I^- \rightleftharpoons I_2 + 2H_2O$$

Figure 7.
Oxydation of iodide by hydrogen peroxide.

latex with high monomer conversion (Table 1, run 2). The potentially surface-active iodinated transfer agents synthesized in situ during the process (A-M_n-I oligomers in which A is a hydrophilic moiety from the radical initiator) can take part in the nucleation step and contribute to the electrostatic stabilization of the latex, as indicated by a successful surfactant-free RITP experiment in emulsion (Table 1, run 3). It was checked that the molecular weight of the latex could be tuned by varying the initial concentration of iodine $[I_2]$. Furthermore, the successful preparation of a block copolymer latex poly(butyl acrylate)-block-poly(styrene-*co*-butyl acrylate) proved that the polymer chains could be reactivated (living character) (Figure 5). Nevertheless, it was also noticed that the molecular weights of the latexes prepared by RITP were much higher than the theoretical values, as shown in Table 1 runs 2-3. In order to account for this upward deviation of the molecular weights, the peculiarities of emulsion polymerization (partitioning of the reactants between the different phases) and the chemistry of iodine in water must be considered (Figure 6).[10] Indeed, although the partitioning of iodine is in favor of the butyl acrylate monomer phase ($K = [I_2]_{aq}/[I_2]_{BuA} = 2.03 \times 10^{-3}$ at 25 °C), the disproportionation of iodine in water plays a serious deleterious role in the control of the polymerization. By following the evolution of the concentration of iodide $[I^-]$ by a selective electrode for the experiment of Table 1 run 2, it was shown that the side reaction of hydrolysis

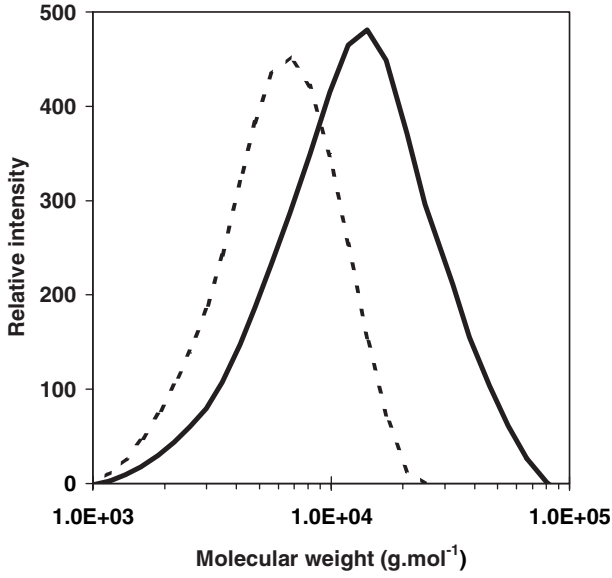

Figure 8.
Molecular weight distributions of the seed polystyrene latex prepared by reverse iodine transfer polymerization in miniemulsion ($M_{n,SEC} = 4\,900$ g·mol^{-1}, $M_w/M_n = 1.48$, $M_{n,th} = 4\,100$ g·mol^{-1}, – – – –) and the final polystyrene latex prepared by iodine transfer polymerization of styrene in seeded emulsion polymerization ($M_{n,SEC} = 8\,900$ g·mol^{-1}, $M_{n,th} = 9\,800$ g·mol^{-1}, —). Seed latex (miniemulsion polymerization at $T = 60$ °C): water (150 g), I_2 (0.3833 g, 1.51 mmol), n-hexadecane (0.45 g, 1.99 mmol), styrene (15 g, 144 mmol), Perkadox 16S (1.495 g, 3.75 mmol), dodecyl sulfate sodium salt (0.4 g, 1.39 mmol) and addition of hydrogen peroxide (0.7 g H_2O_2 30% wt. solution in water, 6.23 mmol) in 15 g of water during 3 hours; Chain extension (seeded emulsion polymerization at 75 °C): seed PS-I latex (42.5 g, $M_n = 4\,900$ g·mol^{-1}, 0.54 mmol), α,α′-azobisisobutyronitrile (0.0233 g, 0.142 mmol), styrene (3.01 g, 28.9 mmol).

was actually very important and that only 33% of the initial iodine was effectively consumed through the RITP mechanism ($\alpha = n_{I2,effective}/n_{I2,initial} = 33\%$). Based on this value of 33%, the experimental molecular weight now matches the corrected targeted value ($M_{n,targeted\ (corrected)} = (mass\ of\ monomer)/(2 \times \alpha \times n_{I2,initial}) + M_{A\text{-}I} = 31\,000\ g \cdot mol^{-1}$). The identification of the side reactions was a key step toward the development of improved RITP procedures in heterogeneous aqueous processes as described below.

Miniemulsion Polymerization

In order to counterbalance the hydrolytic disproportionation of iodine in water, a modified RITP procedure was developed. The new procedure is based on the use of an oxidant to regenerate iodine I_2 by oxidation of iodide I^-. In this section, this new concept is illustrated in the case of miniemulsion polymerization of styrene by RITP initiated by bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16S) at $T = 60\,^{\circ}C$ with dodecyl sulfate sodium salt as surfactant and hexadecane as hydrophobe.[11] The continuous addition of hydrogen peroxide (as oxidant) in acidic conditions leads to the oxidation of iodide I^- to form iodine I_2 and water (Figure 7). This new concept allowed us to prepare a stable polystyrene latex with a much better agreement between theoretical and experimental molecular weight (Table 1, run 5) than the corresponding RITP in the absence of hydrogen peroxide (Table 1, run 4). Furthermore, the successful chain-extension (resuming the polymerization with a new shot of styrene and AIBN) indicates that the living character of the RITP polymerization is maintained with this new procedure (Figure 8).

Conclusion

The RITP process has been invented few years ago and it has rapidly led to promising results in heterogeneous aqueous processes. Stable and uncolored (white) monodisperse poly(butyl acrylate) latex could be obtained by RITP in emulsion. However, a large deviation of the molecular weights from the theoretical values was observed in the early attempts of RITP in emulsion: hydrolytic disproportionation of iodine has been identified as a serious deleterious side reaction. Based on this knowledge, an improved RITP procedure has been set up that is based on the use of an oxidant to regenerate iodine. For instance, RITP of styrene in miniemulsion has been successfully performed with a continuous addition of hydrogen peroxide as oxidant. Thanks to this new concept, in addition to the living character of the latex, a good correlation between theoretical and experimental molecular weights can now be obtained, reinforcing the interest of RITP for the industrial development of controlled radical polymerization in dispersed aqueous processes. Our current efforts focus on the application of this new concept to a wide range of experimental conditions to test its robustness.

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