186 *Macromolecules* **2007,** *40,* 186−190

Controlled Radical Polymerization of Styrene by Reverse Iodine Transfer Polymerization (RITP) in Miniemulsion: Use of Hydrogen Peroxide as Oxidant

Jeff Tonnar, Patrick Lacroix-Desmazes,* and Bernard Boutevin

Ingénierie et Architectures Macromoléculaires, Institut Charles Gerhardt FR 1878−CNRS,
UMR−CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale,
34296 Montpellier Cedex 5, France

Received July 21, 2006; Revised Manuscript Received November 6, 2006

ABSTRACT: The use of molecular iodine I_2 in controlled radical polymerization, called reverse iodine transfer polymerization, represents a new, straightforward way to prepare controlled macromolecular architectures. Herein, miniemulsion polymerization of styrene in the presence of molecular iodine has been successfully performed. The polymerization of styrene was initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate at $T = 60$ °C with dodecyl sulfate sodium salt as surfactant and hexadecane as hydrophobe, yielding a stable and uncolored latex. A certain amount of iodine reacted with water to form hydroiodic acid, leading to an upward deviation of the experimental molecular weight from the theoretical value. However, when the iodine lost by hydrolysis was regenerated by continuous addition of hydrogen peroxide in acidic conditions, it led to the expected molecular weight (e.g., $M_{\mathrm{n,SEC}} = 7900$ g mol^{-1}, $M_w/M_n = 1.46$, styrene conversion = 78%, $M_{\mathrm{n,theoretical}} = 7900$ g mol^{-1}). Hence, the molecular weight of the polymer chains could be accurately controlled by changing the concentration of iodine. Last, a chain extension was successfully performed in seeded emulsion polymerization, proving the living character of the polymerization.

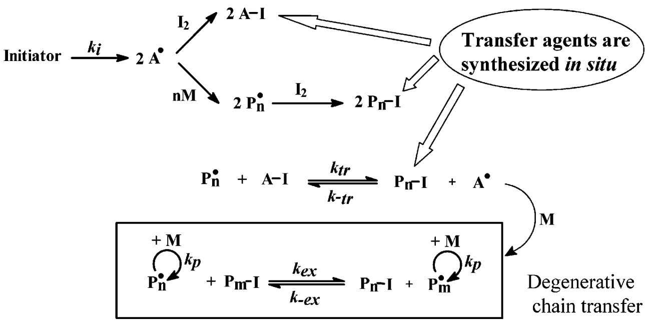
Introduction

During recent years, controlled radical polymerization (CRP)[1−3] has provided several simple and robust routes to synthesize well-defined low-dispersity polymers and the fabrication of novel functional materials[4−8] like block, graft, or star copolymers. The main difference with free radical polymerization is that in CRP a reversible activation−deactivation process between dormant (or capped) chains and active chains (or propagating radicals) enables all polymer chains to grow at the same rate. Different CRP methods have been developed so far among which nitroxide−mediated polymerization (NMP),[6] atom transfer radical polymerization (ATRP),[5] iodine transfer polymerization (ITP),[9−12] and reversible addition−fragmentation chain transfer polymerization (RAFT/MADIX)[13] are the most widely studied. Considering more specifically ITP in aqueous dispersed medium which is of industrial interest, promising results were obtained in miniemulsion polymerization of styrene[14−17] and seeded emulsion polymerization of *n*-butyl acrylate[16] leading to a PS-*b*-PBuA block copolymer.

A new CRP method, which relies on molecular iodine I_2 to control the polymerization, was developed by our group[18−20] and patented.[21−23] The basic mechanism of reverse iodine transfer polymerization (RITP) is shown in Scheme 1. The initiator decomposes (e.g., thermally) to form radicals which react with iodine or add a few monomer units before reacting with iodine to form the iodinated transfer agents (A−I adduct or A−M_n−I transfer agents) in situ. Once the whole free iodine has been consumed, the degenerative transfer mechanism establishes itself. One main difference between RITP and ITP is that in RITP the transfer agents are synthesized in situ. There is no need to synthesize and store transfer agents. One molecule of iodine can control two polymer chains and the targeted molecular weight is given by eq I.

$$M_{\mathrm{n,targeted}} = (\text{mass of monomer})/(2 \times n_{\mathrm{I2,initial}}) + M_{\mathrm{A-I}} \quad \text{(I)}$$

Scheme 1. Simplified Mechanism of Reverse Iodine Transfer Polymerization in Solution (A•, Radical from the Initiator; I_2, Molecular Iodine; M, Monomer Unit; *n*, Number Average Degree of Polymerization)



Recently, our group polymerized butyl acrylate by RITP in ab initio emulsion polymerization.[24,25] Although the molecular weight was efficiently tuned by varying the concentration of iodine, iodine hydrolysis was responsible for an upward deviation of the molecular weight from the theoretical value. Herein, we propose a major improvement of RITP in dispersed aqueous medium. Hydrogen peroxide is added as oxidant to counterbalance the side reactions of iodocompounds in water. This method is assessed in RITP of styrene in miniemulsion[26] and leads to a very good control of the molecular weight.

Experimental Section

Materials. Styrene (Acros, 99%) was purified by vacuum distillation before use. Dodecyl sulfate sodium salt (SDS, Aldrich, 98%, critical micelle concentration = 2.6 g.L^{-1}), bis(4-*tert*-

---

* Corresponding author. Telephone: 33 4 67 14 72 05. Fax: 33 4 67 14 72 20. E-mail: patrick.lacroix-desmazes@enscm.fr.

10.1021/ma061649c CCC: \$37.00

butylcyclohexyl) peroxydicarbonate (Perkadox 16S, Akzo Nobel, 95%), hydrogen peroxide (Acros, 30 wt % solution in water), *n*-hexadecane (Acros, 99%), and iodine (I_2, Aldrich, 99.8%) were used as received. α,α′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization in methanol. Water was deionized (4 μS/cm) by passing through columns packed with ion exchange resins.

General Procedure for Miniemulsion Polymerization. [Styrene]/[Perkadox]/[I_2] = 189/2.44/1, $M_{n,targeted} = 10\,100$ g mol^{-1}. Typically, 140 g of water were placed in a 250 mL glass reactor and thoroughly purged with argon for 30 min. The reaction medium was acidified by addition of 1 mL of chlorhydric acid, HCl, 0.1 N. A solution of SDS (400 mg, $M = 288.28$ g mol^{-1}, 1.39 mmol) in water (10 g) was added in the reactor under argon flow, followed by a solution of Perkadox 16S (746 mg, $M = 398.5$ g mol^{-1}, 1.87 mmol), iodine (0.1943 g, $M = 253.81$ g mol^{-1}, 0.766 mmol), and *n*-hexadecane (0.45 g, $M = 226.45$ g.mol^{-1}, 1.99 mmol) in styrene (15.05 g, $M = 104$ g mol^{-1}, 145 mmol). Then, the solution was miniemulsified by ultrasonication (Bioblock Scientific Vibra Cell 75043, 5 min, 8 kHz) under argon flow and the miniemulsion was purged for another 15 min with argon. The reactor was thermostated at 60 °C and the reaction proceeded for 16 h under argon atmosphere and magnetic stirring in the absence of light. In the experiments where iodine was regenerated by hydrogen peroxide, an aqueous solution of hydrogen peroxide (0.3 g of H_2O_2 30 wt % solution in water, $M = 34$ g mol^{-1}, 2.65 mmol) in 15 g of water was injected during the first 3 h with a Compact Braun perfusor equipped with a 20 mL Terumo syringe. Monomer conversion was determined by gravimetric analysis. Results: polymerization time = 16 h, styrene conversion = 78%, theoretical number-average molecular weight $M_{n,th} = 7900$ g mol^{-1}, number-average molecular weight determined by size exclusion chromatography $M_{n,SEC} = 7900$ g mol^{-1}, polydispersity index PDI = 1.46, particle diameter d_p = 316 nm (monomodal), and uncolored latex.

Chain Extension. The seed latex was prepared as above: [styrene]/[Perkadox]/[I_2] = 95.5/2.48/1 ($M_{n,th} = 5200$ g mol^{-1}) and continuous addition of hydrogen peroxide (0.7 g H_2O_2 30 wt % solution in water, $M = 34$ g mol^{-1}, 6.17 mmol) in 15 g of water during 3 h. Results: styrene conversion = 76%, $M_{n,th} = 4100$ g mol^{-1}, $M_{n,SEC} = 4900$ g mol^{-1}, PDI = 1.48, and particle diameter d_p = 339 nm (monomodal). This seed latex was used to resume the polymerization (chain extension). The seed latex (42.5 g, M_n = 4900 g mol^{-1}, 0.54 mmol) was introduced in a 100 mL glass reactor and purged by argon bubbling during 20 min. A solution of AIBN (0.0233 g, $M = 164$ g mol^{-1}, 0.142 mmol) in styrene (3.01 g, $M = 104$ g mol^{-1}, 28.9 mmol) was added to the seed latex. The latex was stirred during 1 h to allow styrene diffusion and then the reaction proceeded in the dark under argon atmosphere with magnetic stirring during 22 h at $T = 75$ °C. Results: styrene conversion = 69%, $M_{n,th} = 9800$ g mol^{-1}, $M_{n,SEC} = 8900$ g mol^{-1}, PDI = 1.80, and particle diameter d_p = 419 nm (monomodal).

Characterizations. Size exclusion chromatography (SEC) was performed on dried samples dissolved in tetrahydrofuran, with a Spectra Physics Instruments SP8810 pump equipped with a Shodex RIse-61 refractometer detector and two 300 mm columns thermostated at 30 °C (columns mixed-C PL-gel 5 μm from Polymer Laboratories : 2×10^2 to 2×10^6 g mol^{-1} molecular weight range). Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL·min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories. The particle size of the latex was determined with a Nanotrac 250 particle analyzer (Microtrac Inc.). pH measurements were performed with a Consort P500 apparatus from Bioblock Scientific. Iodide concentrations [I^-] were measured with a PHM 210 Standard pH Meter from Radiometer Analytical with an iodide selective electrode ISE25I-9 and a reference electrode REF201 from Radiometer Analytical.

Results and Discussion

Kinetics of Styrene Miniemulsion Polymerization by RITP. Iodine, I_2, is known to be a strong radical inhibitor. As long as free iodine is present in the reaction medium, all formed radicals are deactivated by iodine, forming the iodinated transfer agents in situ. Therefore, the polymerization can be divided into two separate periods: first an inhibition period, where all formed radicals are deactivated by iodine and monomer conversion is very low, and a second polymerization period controlled by degenerative transfer mechanism, where the polymerization takes place (Figure 1).

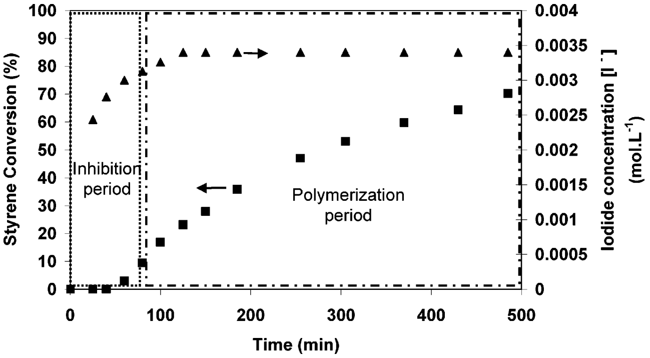


Figure 1. Evolution of monomer conversion (■) and iodide concentration (▲) vs time for reverse iodine transfer polymerization of styrene in miniemulsion at $T = 60$ °C ([Perkadox 16S]/[I_2] = 1.99, [dodecyl sulfate sodium salt] = 2.6 g·L^{-1}, $M_{n,targeted} = 10\,300$ g mol^{-1}).

Scheme 2. Main Equilibria Involved in the Hydrolytic Disproportionation of Iodine

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

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

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

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

One important feature of RITP in aqueous media is the formation of iodide I^- by side reactions between water and iodo compounds.[25] The concentration of I^- was measured with an iodide selective electrode. Figure 1 indicates that the iodide concentration [I^-] increases during the inhibition period and reaches a plateau shortly after the end of the inhibition period.

An important reaction to consider is the hydrolytic disproportionation of iodine in the aqueous phase (Scheme 2).[27,28] Iodine hydrolysis involves the formation of hypoiodous acid (HOI) (pKa $_{HOI/IO-}$ = 11),[29] iodide (I^-) (p$K_{a(HI/I-)}$ = −10),[30] iodate (IO_3^-) (p$K_{a(HIO3/IO3-)}$ = 0.8),[29] and triiodide (I_3^-). It also forms protons and thus it tends to lower the pH.

Iodine hydrolysis (equilibrium 3) is composed of two main equilibria.[28] The first one (equilibrium 1) is a rapid equilibrium[31] whereas the second step (equilibrium 2)[28] is a slow but complete decomposition of HOI. The complexation of iodide by iodine to form triiodide (equilibrium 4) is a fast equilibrium.[31]

During the polymerization period, iodide concentration [I^-] remained constant, indicating that the whole iodine was consumed at the end of the inhibition period (one part to form the iodinated transfer agents in situ and the other part by iodine hydrolysis). One can conclude that the upward deviation from the theoretical molecular weight is due to the hydrolysis of iodine or the hydrolysis of the rather unstable A-I adduct, diminishing the efficiency of iodine ($\alpha = n_{I2,effective}/n_{I2,initial} <$ 1) to control the polymerization. Indeed, the experimental molecular weight at 72% styrene conversion ($M_{n,experimental}$ = 13 900 g mol^{-1}, M_w/M_n = 1.73) is fully consistent with both the final pH = 2.36 ([H^+] = $10^{-2.36}$ = 4.36×10^{-3} mol L^{-1}) and the final iodide concentration [I^-] = 3.4×10^{-3} mol L^{-1},

Scheme 3. Reactions of Hydrogen Peroxide

$$H_2O_2 + 2H^+ + 2I^- \rightleftharpoons I_2 + 2H_2O \qquad (5)$$

$$2\,H_2O_2 \rightleftharpoons O_2 + 2H_2O \qquad (6)$$

$$H_2O_2 + IOH \rightleftharpoons O_2 + H_2O + I^- + H^+ \qquad (7)$$

corresponding to an efficiency of iodine $\alpha \cong 0.58$ and leading to a theoretical molecular weight $M_{n,th}$ = (mass of monomer) × conversion/($2\alpha n_{I2,initial}$) + M_{A-I} = 12 700 g mol^{-1}.

New Concept: Iodine Regeneration through the Addition of an Oxidant. Iodine hydrolysis in aqueous medium cannot be avoided. However, in order to gain a good control of the molecular weight, we investigated the possibility to take advantage of the reductive nature of iodide I^- to regenerate iodine by oxidation. Hydrogen peroxide H_2O_2 and iodinated species present different reactions in aqueous medium (Scheme 3). The simplest one is the reaction of hydrogen peroxide and iodide (reaction 5).[32] In order to favor the reaction of hydrogen peroxide with iodide, the proton concentration $[H^+]$ has to be high. Moreover, to avoid an important disproportionation of hydrogen peroxide (reaction 6) to water and oxygen (which would act as a radical inhibitor), the amount of hydrogen peroxide has to be kept as low as possible; but this reaction is rather slow. Last, hydrogen peroxide can react with HOI to form iodide, water and oxygen (reaction 7).[32] In order to avoid this side reaction, it is again better to work in acidic conditions because the oxygen resulting from this reaction would inhibit the polymerization.

Validation of the New Concept: Influence of Hydrogen Peroxide on RITP in Miniemulsion. In order to compensate the loss of iodine by hydrolysis, an aqueous solution of hydrogen peroxide (whose quantity was not optimized) was continuously added into the reaction medium during the first 3 h (duration of hydrogen peroxide addition > inhibition time). The role of hydrogen peroxide is to oxidize iodide I^- (created by hydrolysis) into iodine I_2.

Run 1 (Table 1) corresponds to the reference experiment without hydrogen peroxide addition. The experimental molecular weight was higher than expected because of iodine disproportionation as explained before. In run 2 (Table 1), there was a continuous addition of hydrogen peroxide during the inhibition period. A lower molecular weight and a smaller polydispersity index (PDI) were observed, but the monomer conversion was limited to 58%.

pH influences greatly the equilibrium concentrations of the oxido-reduction reaction between hydrogen peroxide and iodide. At neutral or basic pH, the kinetics of reaction 5 will be very slow because of the low proton concentration. If hydrogen peroxide does not react onto iodide, the dismutation of hydrogen peroxide (reaction 6) and the reaction of H_2O_2 with HOI (reaction 7) can become significant. These reactions produce oxygen which can inhibit the polymerization and therefore limit the conversion. Thus, the rather low conversion obtained in run 2 (Table 1) can be ascribed to a too high pH (final pH = 6.75).

By working in acidic medium, the extent of these side reactions producing oxygen can be minimized and the rate of iodine regeneration maximized. Indeed, in run 3 (Table 1), the reaction medium was acidified by addition of 1 mL of HCl 0.1 N, resulting in a final monomer conversion of 78% and a good correlation between theoretical and experimental molecular weights together with a low PDI. The final iodide concentration $[I^-]$ is around 10^{-7} mol L^{-1}, indicating that the iodide I^- is fully converted back to iodine I_2 by oxidation.

Influence of Iodine Concentration on the Molecular Weight. To get a reasonable monomer conversion, a small amount of HCl was added to the following polymerizations. Moreover, hydrogen peroxide was continuously added to regenerate iodine I_2 and to keep a good control of the molecular weights. Typically, an aqueous solution of hydrogen peroxide was injected during the first 3 h into the reaction medium. In order to check the controlled character of the polymerization, the concentration of iodine was varied (while keeping the excess of initiator over iodine constant at about 2.5) to target molecular weights of 5200, 10 100, and 20 300 g mol^{-1} (runs 1−3 in Table 2). In all cases, the final concentration of iodide I^- was negligible and the results indicate that the experimental molecular weights were very close to the theoretical values. Furthermore, Figure 2 shows that the whole molecular weight distribution was shifted toward higher molecular weights when the concentration of iodine was decreased. Last, the reference experiment without iodine (run 2b, Table 2) led to a higher molecular weight and a much broader polydispersity (PDI = 2.40) than the corresponding RITP experiment (PDI = 1.46) (run 2a, Table 2). In iodine transfer polymerization the minimum polydispersity index is given by PDI = 1 + [chain transfer agent]$_0$/[M]$_0$ + 1/C_{ex} in which C_{ex} is the degenerative chain transfer constant ($C_{ex} = k_{ex}/k_p$).[12] In ITP, C_{ex} values are rather low (typically C_{ex} = 3.6 for ITP of styrene at 80 °C)[11,12] leading to slightly higher PDIs than ATRP, RAFT or NMP where the exchange between propagating and dormant chains is usually faster. All these findings prove that RITP of styrene in miniemulsion allows the control of molecular weights of the

Table 1. Effect of a Continuous Addition of Hydrogen Peroxide[a]

run	[Perkadox]/[I_2]	addition of H_2O_2	addition of HCl 0.1 N	$M_{n,targeted}$ (g mol^{-1})	time (h)	convn (%)[b]	$M_{n,th}$ (g mol^{-1})[c]	$M_{n,exp}$ (g mol^{-1})	PDI	pH	d_p (nm)[d]
1	1.99	no	no	10 300	16	72	7500	13 900	1.73	2.36	334
2	2.59	yes	no	9800	18	58	5800	4500	1.35	6.75	309
3	2.44	yes	yes	10 100	16	78	7900	7900	1.46	3.36	316

[a] Polymerization of styrene in miniemulsion polymerization at T = 60 °C in the presence of Perkadox 16S as initiator. [b] Conversion determined by gravimetry. [c] $M_{n,th}$ = (mass of monomer) × (monomer conversion)/(2 × n_{I2}) + M_{AI} in which M_{AI} = 282 g mol^{-1}. [d] d_p : particle diameter.

Table 2. Effect of Iodine Concentration[a]

run	[Perkadox]/ [I_2]	$M_{n,targeted}$ (g mol^{-1})	time (h)	convn (%)[b]	$M_{n,th}$ (g mol^{-1})[c]	$M_{n,exp}$ (g mol^{-1})	PDI	d_p (nm)[d]
1	2.48	5200	20	76	4100	4900	1.48	339
2a	2.44	10 100	16	78	7900	7900	1.46	316
2b	no iodine	n.a.	16	85	n.a.	13 300	2.40	204
3	2.51	20 300	14	77	15 700	18 200	1.75	301

[a] Polymerization of styrene in miniemulsion polymerization at T = 60 °C in the presence of Perkadox 16S as initiator and hydrogen peroxide as oxidant, [b] Conversion determined by gravimetry. [c] $M_{n,th}$ = (mass of monomer)×(monomer conversion)/(2 × n_{I2}) + M_{AI} in which M_{AI} = 282 g mol^{-1}. [d] d_p : particle diameter; n.a.: not applicable.

Table 3. Chain Extension of the Polystyrene Chains[a]

run	type	time (h)	convn (%)	$M_{n,targeted}$ (g mol^{-1})	$M_{n,th}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	PDI	d_p (nm)
1	seed PS latex[b]	20	76	5200	4100	4900	1.48	339
2	chain extension of PS block[c]	22	69	12 000	9800	8900	1.80	419

[a] Chain extension of the polystyrene chains in seeded emulsion polymerization at 75 °C. [b] Seed latex (miniemulsion): 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 h. [c] Chain extension : seed PS−I latex (42.5 g, M_n = 4900 g mol^{-1}, 0.54 mmol), α,α′-azobis(isobutyronitrile) (0.0233 g, 0.142 mmol), styrene (3.01 g, 28.9 mmol).

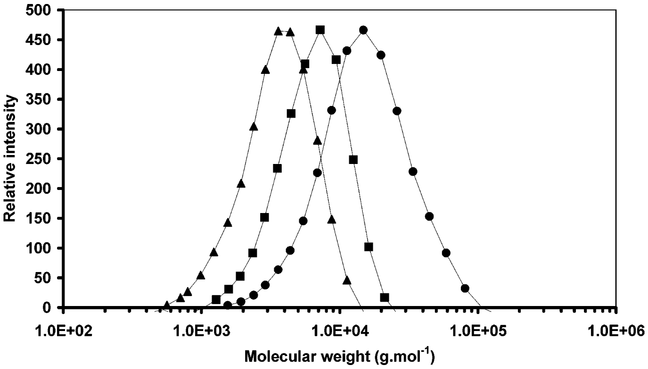


Figure 2. Molecular weight distributions of polystyrene samples prepared by reverse iodine transfer polymerization in miniemulsion at $T = 60$ °C with addition of hydrogen peroxide ([Perkadox 16S]/[I_2] ≅ 2.5, [dodecyl sulfate sodium salt] = 2.6 g·L^{-1}). Targeted molecular weight: (▲) 5200 g mol^{-1}; (■) 10 100 g mol^{-1}; (●) 20 300 g mol^{-1}.

polymer latexes (if iodine is regenerated by the addition of hydrogen peroxide).

Chain Extension. To check the living character of the final polymer latex prepared by miniemulsion polymerization, a PS−I latex (monomer conversion of 76%) (Table 3, run 1) was further used as a seed in seeded emulsion polymerization of styrene. The reaction was conducted at 75 °C with the following concentrations: [styrene]/[AIBN]/[PS−I] = 68/0.26/1. The results in Table 3 (run 2) show that the molecular weight increases as theoretically expected: $M_{n,SEC}$ = 8900 g mol^{-1}, PDI = 1.80. The theoretical molecular weight $M_{n,th}$ can be calculated using eq II ($M_{n,theoretical}$ = 9800 g mol^{-1}).

$$M_{n,th} = M_{n,first\ block} + (\text{mass of monomers}) \times \text{conversion}/(\text{moles of first block}) \quad \text{(II)}$$

The final latex has a diameter particle size of 419 nm. The number of particles N_p remained constant (4.39×10^{12} to 4.32×10^{12} particles per mL of water) during the seeded emulsion polymerization. This shows that no renucleation and no destabilization or particle coagulation occurred. Furthermore, although the polydispersity broadened slightly during this second step, a clear shift of the molecular weight distribution (MWD) toward higher molecular weights was observed (Figure 3). Thus, the chain extension was successfully performed.

Conclusion

The new controlled radical polymerization method named RITP, based on the use of molecular iodine I_2 as a radical trap, is an easy-to-make method which does not require the synthesis nor storage of control agents. RITP can be performed in dispersed aqueous media and it has been successfully applied to control the radical polymerization of styrene in miniemulsion. In order to overcome side reactions between water and iodo-compounds that were responsible for an upward deviation of the molecular weight, iodine I_2 was regenerated by oxidation of iodide I^- with hydrogen peroxide in acidic conditions. Thanks to this improved version of the RITP process, a good correlation between theoretical and experimental molecular weights was obtained in miniemulsion. Finally, the living character of the polystyrene chains was demonstrated by a successful chain extension in seeded emulsion polymerization. These results definitely reinforce the interest of RITP for the industrial development of controlled radical polymerization in dispersed aqueous processes.

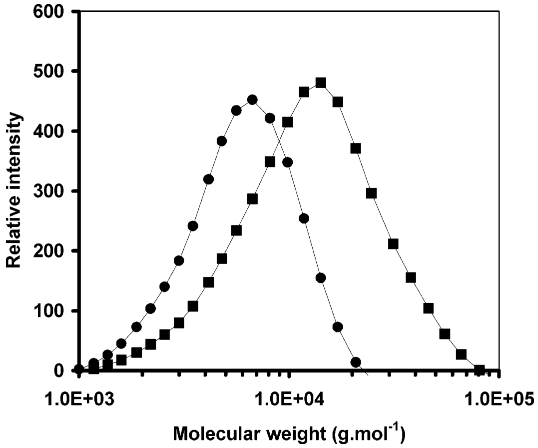


Figure 3. Molecular weight distributions of the seed latex prepared by reverse iodine transfer polymerization in miniemulsion (●) and the final polystyrene latex prepared by iodine transfer polymerization of styrene in seeded emulsion polymerization (■).

Acknowledgment. Vincent Bodart and Christophe Fringant (Solvay) are acknowledged for their constant interest in the RITP process.

References and Notes

(1) Matyjaszewski, K. *ACS Symp. Ser.* **1998**, *685*, 2−30.
(2) Matyjaszewski, K.; Ed. *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT. (Proceedings of a Symposium on Controlled Radical Polymerization held on 22−24. August 1999, in New Orleans.)* ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.
(3) Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1383−1415.
(4) Fukuda, T.; Goto, A. *ACS Symp. Ser.* **2000**, *768*, 27−38.
(5) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(6) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(7) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039−1067.
(8) Matyjaszewski, K. *ACS Symp. Ser.* **2003**, *854*, 2−9.
(9) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S. *Macromolecules* **1995**, *28*, 2093−2095.
(10) Tatemoto, M. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 5, pp 3847−3860.
(11) Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809−2814.
(12) David, G.; Boyer, C.; Tonnar, J.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. *Chem. Rev.* **2006**, *106*, 3936−3962.
(13) Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3189−3204.
(14) Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J.-P.; Pirri, R. *Macromolecules* **1999**, *32*, 7354−7360.
(15) Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2000**, *33*, 3485−3487.

(16) Farcet, C.; Lansalot, M.; Pirri, R.; Vairon, J. P.; Charleux, B. *Macromol. Rapid Commun.* **2000**, *21*, 921−926.
(17) Pouget, E.; Tonnar, J.; Eloy, C.; Lacroix-Desmazes, P.; Boutevin, B. *Macromolecules* **2006**, *39*, 6009−6016.
(18) Lacroix-Desmazes, P.; Severac, R.; Otazaghine, B.; Boutevin, B. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2003**, *44*, 683−684.
(19) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B. *Macromolecules* **2005**, *38*, 6299−6309.
(20) Boyer, C.; Lacroix-Desmazes, P.; Robin, J.-J.; Boutevin, B. *Macromolecules* **2006**, *39*, 4044−4053.
(21) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B.; Bodart, V.; Kurowsky, V. In PCT Int. Appl.; Solvay SA, Belg, WO 03097704 A1, 2003.
(22) Boutevin, B.; Otazaghine, B.; Lacroix-Desmazes, P.; Dubreuil, M.; Bodart, V. PCT Int. Appl.; Solvay SA, Belg, WO 03097705 A1, 2003.
(23) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B.; Bodart, V.; Kurowski, V. PCT Int. Appl.; Solvay SA, Belg, WO 2004094356 A1, 2004.
(24) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2005**, *46*, 280−281.
(25) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *ACS Symp. Ser.* **2006**, *944*, Chapter 41, 604−619.
(26) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283−1346.
(27) Murray, H. D. *J. Chem. Soc., Abstr.* **1925**, *127*, 882−885.
(28) Nagy, K.; Koertvelyesi, T.; Nagypal, I. *J. Solution Chem.* **2003**, *32*, 385−393.
(29) Kolthoff, I. M. In *Treatise on Analytical Chemistry*; Kolthoff, I. M., Elving, P. J. Eds.; Interscience Publishers: New York, 1959; Vol. 1, pp 405−420.
(30) Brownstein, S.; Stillman, A. E. *J. Phys. Chem.* **1959**, *63*, 2061−2062.
(31) Lengyel, I.; Epstein, I. R.; Kustin, K. *Inorg. Chem.* **1993**, *32*, 5880−5882.
(32) Kessi-Rabia, M.; Gardes-Albert, M.; Julien, R.; Ferradini, C. *J. Chim. Phys. Phys.−Chim. Biol.* **1995**, *92*, 1104−1123.

MA061649C