Living Radical Polymerization

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Use of Sodium Iodide as the Precursor to the Control Agent in Ab Initio Emulsion Polymerization**

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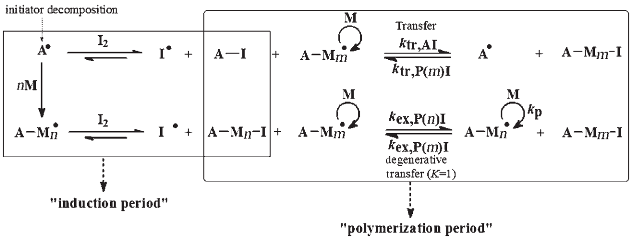
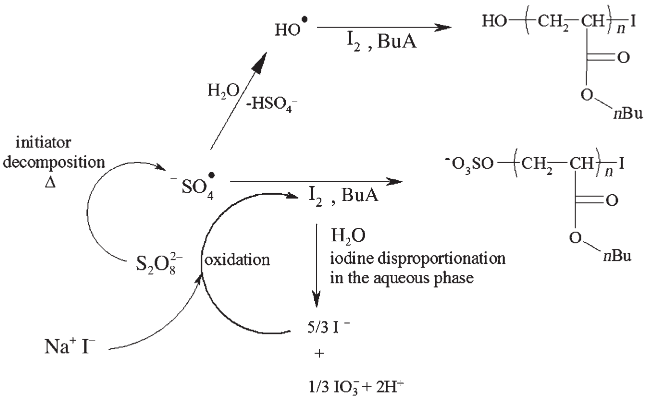
In recent years, controlled/living radical polymerization (CRP) has emerged beside ionic polymerization as a major synthetic route for the preparation of complex macromolecular architectures, such as block or gradient copolymers.[1] The most widely used methods of CRP are nitroxide-mediated polymerization (NMP),[2] atom-transfer radical polymerization (ATRP),[3] iodine-transfer polymerization (ITP),[4] and reversible addition–fragmentation chain-transfer polymerization (RAFT).[5] All these methods rely on a reversible activation–deactivation of the growing polymer chains.[6] The implementation of CRP in dispersed aqueous media and especially in ab initio emulsion polymerization[7,8] has been met with many problems,[9] such as a loss of colloidal stability,[10] the presence of an oily red layer,[10–12] loss of control over the molecular weight or polydispersity index, and slow polymerization rates. Improvements were made by implementing multistep procedures and/or continuous monomer addition,[13,14] but no effective single-step ab initio emulsion polymerization by a traditional CRP method, such as ATRP, NMP, or RAFT, has yet been described.

Recently, we developed and patented a new CRP technique named reverse iodine transfer polymerization (RITP).[15–17] RITP relies on the use of molecular iodine as a control agent (Scheme 1). We synthesized poly(butyl acrylate) by RITP on the basis of ab initio emulsion polymerization initiated by 4,4′-azobis(4-cyanopentanoic acid). However, the hydrolytic disproportionation of I_2 in the aqueous medium caused an upward deviation of the molecular weights of the polymers.[18] This problem was overcome in the miniemulsion polymerization of styrene[19] by using hydrogen peroxide as an oxidant to regenerate the hydrolyzed iodine.



Scheme 1. Simplified mechanism of reverse iodine transfer polymerization (RITP) in solution ($A^\bullet$: radical from the initiator; I_2: molecular iodine; M: monomer unit; *n*: mean number degree of polymerization).

The RITP procedures reported to date rely on the use of molecular iodine. However, as iodine is only slightly soluble in water, it has to be dissolved in the monomer before use. Moreover, I_2 is reactive toward a large number of chemical compounds and is potentially hazardous upon storage and handling (especially because of the risk of the formation of iodine vapor, which is harmful when inhaled). Thus, there may be practical difficulties associated with the use of molecular I_2 on an industrial scale. In contrast, iodides are water soluble, are less reactive and less toxic than iodine, and require fewer precautions in terms of storage and handling. Therefore, the replacement of iodine by iodide ions would be of great practical interest. In our constant effort to facilitate the implementation of RITP under industrially acceptable conditions, we propose the generation of I_2 in situ from sodium iodide by oxidation with potassium persulfate ($K_2S_2O_8$, KPS; Scheme 2). We describe herein the polymerization of butyl acrylate at a constant temperature of 85 °C, whereby NaI is used as the precursor to the control agent (I_2 is generated in situ), potassium persulfate serves as both the oxidant [Eq. (1)] and the radical initiator [Eq. (2)], and sodium 1-hexadecanesulphonate is used as the surfactant



Scheme 2. Main reactions in the aqueous phase: in situ synthesis of I_2 by oxidation, iodine disproportionation in the aqueous phase, iodine regeneration by potassium persulfate, initiator decomposition, and in situ formation of the iodinated transfer agent.

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(critical micelle concentration: 0.25 $\mathrm{g\,L^{-1}}$; Krafft point: 47–57 °C).

$$S_2O_8^{2-} + 2\,I^- \rightarrow I_2 + 2\,SO_4^{2-} \quad (1)$$

$$S_2O_8^{2-} \rightarrow 2\,SO_4^{\cdot -} \quad (2)$$

Once molecular iodine has formed in the aqueous phase, its hydrolytic disproportionation[20] has to be counterbalanced to avoid a deviation of the molecular weight from the targeted value. Iodide ions react with potassium persulfate,[21] which also acts as the radical-polymerization initiator,[22] to generate iodine I_2 in situ and to regenerate the disproportionated iodine (Scheme 2). One experimental constraint on the use of KPS as both the oxidant and the initiator is that the KPS concentration and the reaction temperature must be high enough for KPS not only to oxidize iodide ions (a redox reaction that is already fast at room temperature) but also to create radicals at a reasonable rate, so that KPS is not consumed completely by multiple redox cycles within the inhibition period.

After an inhibition period (the end of which is indicated by the loss of the characteristic purple color of iodine and by particle nucleation), a stable white latex (74 % monomer conversion) with a mean particle diameter of 124 nm and a monomodal particle-size distribution was obtained when NaI was used as the precursor to the control agent (Table 1, entry 2). A very similar result was obtained in the equivalent ab initio emulsion polymerization with molecular iodine (Table 1, entry 1). The slightly larger particle size observed with NaI might be ascribed to the higher ionic strength of the aqueous phase.[8] The pH value of the medium dropped noticeably during the polymerization to a final value of approximately pH 2 as a result of the decomposition of potassium persulfate. Indeed, the sulfate radical anion produced by the thermal decomposition of KPS [Eq. (2)] can react with a water molecule to form a hydrogen sulfate anion and a hydroxyl radical [Eq. (3)]. The final pH value is related to the formation of hydrogen sulfate anions ($\mathrm{p}K_a \approx 2$), which dissociate in the water phase to form sulfate anions and protons. The low pH values associated with this process should enhance the initiation rate.[23] Importantly, a low pH value is also beneficial in limiting the hydrolytic disproportionation of iodine.[18]

$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + HO^{\cdot} \quad (3)$$

The final iodide concentration $[I^-]$ in the poly(butyl acrylate) (PBuA) latex was determined with an iodide-selective electrode to be approximately $5 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$. This value corresponds to about 0.5 % of the sodium iodide introduced initially. Thus, virtually all of the iodide was transformed successfully into iodine, which could control the polymerization. This conclusion was confirmed by analysis by size-exclusion chromatography (SEC), which showed a good correlation between experimental and theoretical molecular weights. A monomodal molecular-weight distribution and a reasonable polydispersity index of 1.84 were observed for the RITP of butyl acrylate.[15,18] These results with sodium iodide are nearly identical to those obtained when molecular iodine was used directly as a control agent (Table 1) and indicate that molecular iodine can be replaced by nonhazardous and water-soluble sodium iodide without a detrimental effect on the controlled nature of the polymerization.

The ^{1}H NMR spectrum of the polymer produced with NaI is shown in Figure 1. The number-average molecular weight can be calculated by integrating the signal at $\delta = 4.79$ ppm[24] due to the hydrogen atom at the iodinated chain end ($-CH_2C\mathit{H}(CO_2Bu)-I$, H_d) and the reference signal at $\delta =$

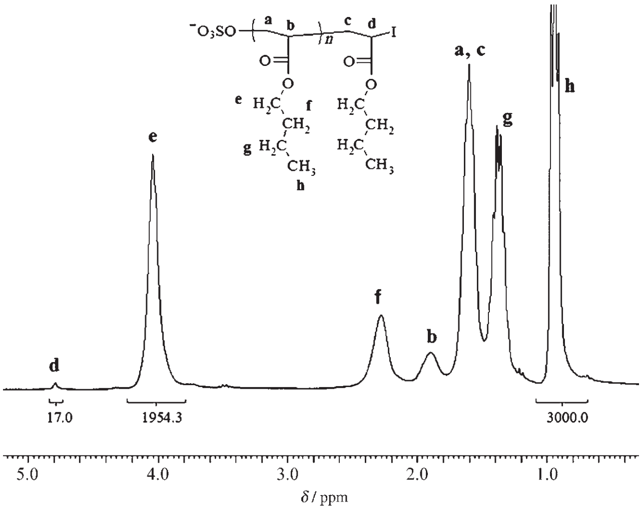


Figure 1. ^{1}H NMR spectrum in $CDCl_3$ of a PBuA–I latex synthesized by reverse iodine transfer polymerization (through ab initio emulsion polymerization) with NaI and coagulated in an aqueous $CaCl_2$ solution ($[BuA]/[K_2S_2O_8]/[NaI] = 76.5:2.83:1$, conversion of butyl acrylate: 74 %, $M_{n,th} = 7490\ \mathrm{g\,mol^{-1}}$, $M_{n,SEC} = 7470\ \mathrm{g\,mol^{-1}}$, polydispersity index: 1.84, $M_{n,NMR} = 7750\ \mathrm{g\,mol^{-1}}$): $\delta = 0.94$ (t, H_h), 1.37 (m, H_g), 1.60 (m, H_a, H_c), 1.90 (m, H_b), 2.28 (m, H_f), 4.04 (t, H_e), 4.79 ppm (m, H_d).

Table 1: Influence of the use of NaI instead of I_2 on the ab initio emulsion RITP of butyl acrylate.

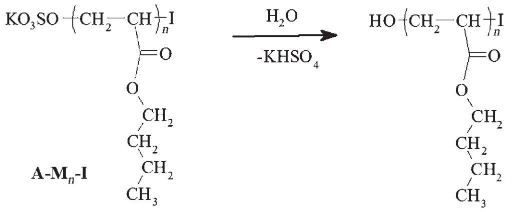
Entry	Iodine source	$[K_2S_2O_8]/[I_2]$	t [h]	Conv. [%][a]	$M_{n,th(100\%)}$ [$\mathrm{g\,mol^{-1}}$][b]	$M_{n,th(conversion)}$ [$\mathrm{g\,mol^{-1}}$][c]	$M_{n,SEC}$ [$\mathrm{g\,mol^{-1}}$]	M_w/M_n	d_p [nm][d]
1[e]	I_2	4.4	7	75	10190	7700	7770	1.80	93
2[f]	NaI	4.7	7	74	10040	7490	7470	1.84	124

[a] Conversion was determined by gravimetry. [b] $M_{n,th} = (\text{mass of monomer}) \times (\text{monomer conversion})/(2 \times n_{I_2}) + M_{A-I}$, in which $M_{A-I} = 223\ \mathrm{g\,mol^{-1}}$ (calculation with chain ends SO_4^- and I) and $n_{I_2} = n_{I_2,0}$ for entry 1 and $n_{I_2} = n_{NaI,0}/2$ for entry 2. [c] Calculated value of M_n at the level of conversion observed experimentally. [d] Particle diameter. [e] The ab initio emulsion polymerization of butyl acrylate at $T = 85$ °C in the presence of potassium persulfate as both the initiator and the oxidant, with iodine dissolved in the monomer as the control agent. [f] The ab initio emulsion polymerization of butyl acrylate at $T = 85$ °C in the presence of potassium persulfate as both the initiator and the oxidant, with sodium iodide dissolved in the aqueous phase as the precursor to iodine. In entry 2, $[K_2S_2O_8]/[I_2]$ is given by $([K_2S_2O_8]_0 - ([NaI]_0/2))/([NaI]_0/2)$.

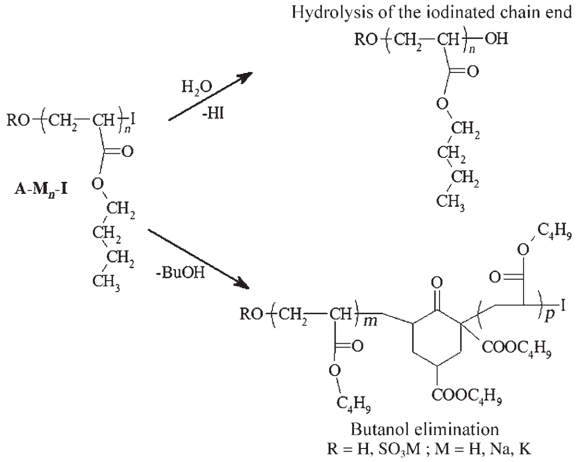
0.94 ppm due to the methyl protons (H_h) in the BuA units and comparing the two values [Eq. (4)]. Very good agreement was observed between the theoretical molecular weight ($M_{n,th} = 7490\,g\,mol^{-1}$) and the experimental molecular weights ($M_{n,SEC} = 7470\,g\,mol^{-1}$, $M_{n,NMR} = 7750\,g\,mol^{-1}$).

$$M_n = M_{A-I} + \frac{I_h/3}{I_d} \times M_{BuA} \tag{4}$$

We carried out MALDI-TOF analysis in reflectron mode of a polymer sample prepared by RITP in ab initio emulsion with NaI to confirm the mechanism. The MALDI-TOF spectrum of the polymer is rather complex (see the Supporting Information). Indeed, the polymerization can be initiated by two different radicals to give either a sulfate- or a hydroxy-terminated polymer chain (Scheme 2). Furthermore, several degradation processes can take place during the emulsion polymerization. In particular, at low pH values (< 2, as in our experiments), the sulfate chain end derived from the radical initiator (persulfate) and/or the iodinated chain end derived from the control agent (iodine) can be hydrolyzed to give hydroxy chain ends (Schemes 3 and 4). Additionally, in the emulsion polymerization of butyl acrylate with persulfate as the initiator, 1-butanol can be released by intramolecular cyclization (Scheme 4).[25,26] The distributions in the MALDI spectrum are compatible with these structures (see the Supporting Information).



Scheme 3. Hydrolysis of the sulfate chain end during the polymerization.



Scheme 4. Hydrolysis of the iodinated chain end and butanol elimination during the emulsion polymerization.

Finally, the living character of the PBuA seed ($M_{n,seed} = 6640\,g\,mol^{-1}$) was demonstrated by the successful synthesis of a PBuA-*b*-poly(BuA-*co*-styrene) block-copolymer latex ($M_{n,th} = 13\,990\,g\,mol^{-1}$, $M_{n,SEC} = 14\,100\,g\,mol^{-1}$; see the Supporting Information).

The implementation of CRP in ab initio emulsion polymerization with commercial, cheap, nontoxic, and nonhazardous control agents is of great interest for the development of CRP on an industrial scale. Until now, all ab initio emulsion polymerization systems relied on the use of multiple-step procedures and rather expensive or noncommercial control agents. In this study, stable white poly(butyl acrylate) latexes were obtained by ab initio emulsion polymerization in a single step by using a combination of sodium iodide and potassium persulfate to control the polymerization. Good agreement between theoretical and experimental molecular weights was observed. Furthermore, the synthesis of a PBuA-*b*-poly(BuA-*co*-styrene) block copolymer proved the living character of the PBuA–I seed latex. In conclusion, the successful replacement of water-insoluble, hazardous molecular iodine by water-soluble, harmless sodium iodide makes way for a new generation of living radical polymerization processes and represents a milestone for the development of CRP in aqueous media.

Experimental Section

n-Butyl acrylate (BuA, Aldrich, 99%) and styrene (Acros, 99%) were purified by vacuum distillation before use. NaI (Acros, 99%), I_2 (Aldrich, 99.8%), $K_2S_2O_8$ (Aldrich, 99%), Mersolat H40 (Lanxess, 40% aqueous solution), and sodium 1-hexadecanesulphonate (Lancaster, 99%) were used as received. Water was deionized by passing it through columns packed with ion-exchange resins.

General procedure: Water (110 g) was placed in a 250-mL glass reactor and purged thoroughly with argon for 30 min. A solution of sodium 1-hexadecanesulphonate (30 mg, 0.091 mmol) in water (10 g) was added under a flow of argon, followed by a solution of NaI (230 mg, 1.53 mmol) in water (10 g). BuA (15.00 g, 117 mmol) was then added, followed by a solution of $K_2S_2O_8$ (1.178 g, 4.36 mmol) in water (20 g), and the reactor was heated under thermostat control at 85 °C with magnetic stirring. The polymerization proceeded under an argon atmosphere in the absence of light for 7 h. Monomer conversion was determined by gravimetric analysis (74% conversion, $M_{n,SEC} = 7470\,g\,mol^{-1}$, $M_w/M_n = 1.84$, $d_p = 124\,nm$).

Characterization: SEC was performed with dried samples dissolved in THF with a Spectra Physics Instruments SP8810 pump equipped with a Shodex Rise-61 refractometer detector, a Milton Roy ultra-violet spectrometer detector, and two columns of 300 mm in length (mixed-C PLgel 5-μm columns from Polymer Laboratories; molecular-weight range: 2×10^2–$2 \times 10^6\,g\,mol^{-1}$), which were maintained at a temperature of 30 °C with a thermostat. THF was used as the eluent at a flow rate of $1.0\,mL\,min^{-1}$. Calibration was performed with polystyrene standards from Polymer Laboratories. The Mark–Houwink coefficients for polystyrene ($K = 11.4 \times 10^{-5}\,dL\,g^{-1}$, $\alpha = 0.716$)[27] and poly(*n*BuA) ($K = 12.2 \times 10^{-5}\,dL\,g^{-1}$, $\alpha = 0.700$)[27] were used for the calculations. The particle size of the latex was determined with a Nanotrac 250 particle analyzer (Microtrac). Measurements of pH values were made with a Consort P500 apparatus from Bioblock Scientific. Iodide concentrations [I^-] were measured with a PHM 210 standard pH meter from Radiometer Analytical with the iodide-selective electrode ISE25I-9 and the reference electrode REF201. To avoid possible chain-end degradation, the PBuA latex was coagulated in an aqueous solution of calcium chloride before ^{1}H NMR spectroscopy and MALDI-TOF analysis. ^{1}H NMR spectroscopy was performed with a Bruker Avance 250-MHz instrument and the solvent $CDCl_3$.

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