Reverse Iodine Transfer Polymerization of Methyl Acrylate and *n*-Butyl Acrylate

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ABSTRACT: Solution polymerization of methyl acrylate initiated by 2,2′-azobis(isobutyronitrile) (AIBN) at 65 °C in the presence of molecular iodine I_2 has been studied. The process, called reverse iodine transfer polymerization (RITP), efficiently controls the molecular weight (determined by size exclusion chromatography, SEC) and the structure of the polymer. For instance, poly(methyl acrylate) samples of $M_{n,SEC}$ = 5700 g mol^{-1} and M_w/M_n = 1.79 ($M_{n,theoretical}$ = 5500 g mol^{-1}), $M_{n,SEC}$ = 10 900 g mol^{-1} and M_w/M_n = 1.91 ($M_{n,theoretical}$ = 10 500 g mol^{-1}), and $M_{n,SEC}$ = 21 800 g mol^{-1} and M_w/M_n = 1.98 ($M_{n,theoretical}$ = 20 700 g mol^{-1}) were successfully prepared. The polymerization was followed by on-line ^{1}H NMR spectroscopy to investigate the evolution of several compounds in the reaction medium, especially the adduct between primary radicals and iodine (A−I, where A stands for the radical fragment from the initiator), the monoadduct A−M$_1$−I (where M stands for the monomer unit), and the monomer conversion. The iodine-end-capped structure of the polymers (A−M$_n$−I, where n is the mean number degree of polymerization) was further demonstrated by mass-assisted laser desorption ionization time-of-flight (MALDI-TOF). The inhibition period in RITP of *n*-butyl acrylate was shortened at higher temperature (about 30 min at 95 °C) without detrimental effect on the control of the molecular weight of the final polymer: $M_{n,SEC}$ = 8600 g mol^{-1} and M_w/M_n = 1.88 ($M_{n,theoretical}$ = 9200 g mol^{-1}). Furthermore, RITP of acrylates was successfully performed in a large variety of media (in bulk, toluene, α,α,α-trifluorotoluene, anisole, methyl ethyl ketone, butyl acetate, propylene carbonate, propionitrile, and dimethylformamide). Last, the living nature of the polymer was confirmed by the preparation of a poly(methyl acrylate)-*b*-polystyrene block copolymer.

Introduction

Controlled/living free-radical polymerization is one of the most effective routes to prepare well-defined polymers (predetermined molecular weight, narrow distribution, and tailored architectures).[1] Reversible termination and degenerative chain transfer are two ways for controlled radical polymerization. Nitroxide-mediated polymerization (NMP)[2] and atom transfer radical polymerization (ATRP)[3] use a reversible termination mechanism in which the propagating radical reacts with the control agent to give a dormant chain. The control of the polymerization is achieved by the persistent radical effect.[4] In reversible addition−fragmentation chain transfer (RAFT)[5] (the same process was named MADIX, which stands for macromolecular design through interchange of xanthates, by the researchers of Rhodia)[6] and in iodine transfer polymerization (ITP),[7] the control of the polymerization is achieved through degenerative chain transfer with transfer constant values C_{tr} typically ranging from about unity for xanthates and iodoalkyls and up to several hundreds for dithioesters.[8] The ITP process was first applied to the copolymerization of vinylidene fluoride with hexafluoropropene and occasionally with tetrafluoroethylene.[7,9] More recently, some works reported the application of this process to styrene,[10−15] methyl and *n*-butyl acrylates,[10,11,14] vinyl acetate,[16−18] vinyl chloride,[19] and vinylidene chloride.[20] However, the chain transfer agents used in ITP were iodoalkyl compounds (such as 2-iodo-perfluoropropane, 1-iodo-perfluorohexane, 1-iodo-1-chloroethane, 1-phenylethyl iodide, methyl-2-iodopropionate, and iodoacetonitrile) which are unstable due to the weak C−I bond and thus prone to alteration upon storage. Furthermore, ITP of monomers involving tertiary propagating radicals (such as methacrylates) was not successful[11] because it would require iodoalkyl compounds with a better leaving group[21] such as ethyl 2-iodo-2-methylpropionate, although such compounds are inherently even more unstable.[22] To overcome these limitations, we have proposed a new process that is based on a direct reaction of radicals with molecular iodine I_2. In this way, the reversible chain transfer agent is generated in situ in the reaction mixture (Scheme 1). By analogy with the reverse ATRP process where the alkyl halide initiator (e.g., R−Cl) is synthesized in situ by reaction of radicals with the complex in the oxidized state (e.g., $CuCl_2$/ligand),[3] we called this new process reverse iodine transfer polymerization (RITP). Nevertheless, beyond the acronyms, the differences between reverse ATRP and RITP must be kept in mind. In the case of reverse ATRP, the formation of dormant chains is carried out using the equilibrium between dormant and active chains imposed by the ATRP reaction. In RITP, it is better to talk about in situ formation of the dormant chains, since the reaction forming the dormant chains is not the same reaction that later will mediate the polymer growth (degenerative transfer). The aim of our work is to understand the RITP process by the survey of several classes of monomers. Several patents based on the RITP process have been recently published by Solvay[23−25] and Akzo.[26,27] Sekisui Chemical reported a similar process to prepare styrenic polymers with controlled structure.[28] The detailed RITP of styrene and methyl methacrylate as well as a more in-depth kinetic

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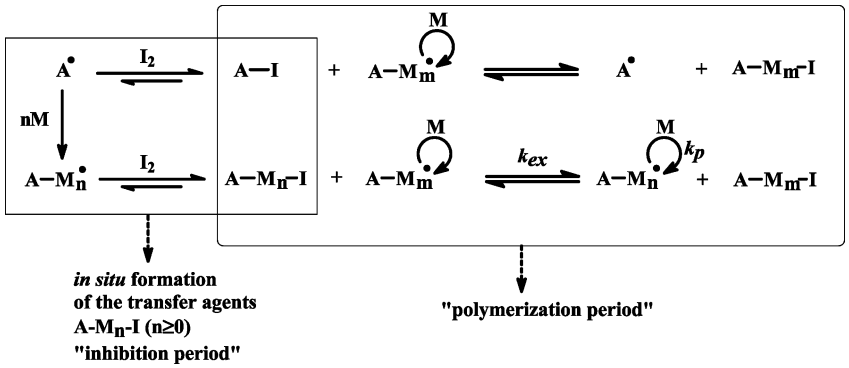
Scheme 1. Simplified Mechanism of Reverse Iodine Transfer Polymerization (RITP)[a]



[a] A• = radical from the initiator; I_2 = molecular iodine; M = monomer unit; n = mean number degree of polymerization; k_{ex} = degenerative chain transfer rate constant; k_p = propagation rate constant.

Table 1. Polymerization of Methyl Acrylate by Reverse Iodine Transfer Polymerization (RITP)[a]

run	$M_{n,targeted}$ (g mol^{-1})	[AIBN]/[I_2]	$t_{loss\ of\ coloration}$	$t_{inh,theor}$[b]	t_{polym}	conv (%)[c]	$M_{n,theoretical}$[d] (g mol^{-1})	$M_{n,exp}$[e] (g mol^{-1})	M_w/M_n
1	5600	1.3		∞	48 h	4	400	400	1.25
2	10700	1.3		∞	48 h	3	500	300	1.29
3	21000	1.3		∞	48 h	3	800	400	1.28
4	5600	1.5		44 h	48 h	2	300	300	1.11
5	10700	1.5		44 h	48 h	3	500	400	1.22
6	21000	1.5		44 h	48 h	3	800	400	1.22
7	5700	1.7	26 h	27 h	45 h	97	5500	5600 (5700)[f]	1.75 (1.79)[f]
8	10700	1.7	22 h	27 h	45 h	98	10500	11100 (10900)[f]	1.83 (1.91)[f]
9	21100	1.7	30 h	27 h	45 h	98	20700	21500 (21800)[f]	1.92 (1.98)[f]
10	5600	2.0	22 h	18 h	28 h 30 min	97	5400	5300	1.95
11	10700	2.0	21 h	18 h	28 h 30 min	98	10500	10100	1.89
12	21200	2.0	24 h	18 h	28 h 30 min	92	19500	21700	1.98

[a] Polymerization of methyl acrylate ([MA] = 5.26 M) in benzene ([benzene] = 5.88 M) at 65 °C in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. [b] Calculated by $t_{inhibition,theoretical} = -\ln(1 - [I_2]_0/(f\,[initiator]_0))/k_d$ with $k_d = 1.90 \times 10^{-5}$ s^{-1} and $f = 0.7$. [c] Determined by ^{1}H NMR in $CDCl_3$: fractional conversion = $1 - I_1/I_2$ where the integral I_1 refers to the resonances at 6.4 ppm (H_A), 6.1 ppm (H_B), and 5.8 ppm (H_C) (3H, $H_AH_CC{=}CH_B-$, J_{trans} = 17.3 Hz, J_{cis} = 10.3 Hz, J_{gem} = 1.4 Hz) and the integral I_2 refers to the resonances at 3.5−3.8 ppm (3H, $-OCH_3$, singlet + broad peak). [d] Calculated by $M_{n,theoretical}$ = (mass of monomer) × conversion/(2 × (moles of I_2)) + M_{A-I}, where $M_{A-I} = M_{chain\ ends}$ = 195 g mol^{-1}. [e] Polystyrene calibration. [f] Calculated with Mark−Houwink coefficients of polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, α = 0.716) and poly(methyl acrylate) ($K = 19.5 \times 10^{-5}$ dL g^{-1}, α = 0.660).

study based on numerical simulations will be reported elsewhere. This paper describes for the first time in more detail the RITP process in the case of methyl acrylate as a model monomer for acrylates.

Experimental Section

Materials. Methyl acrylate (MA, Aldrich, 99%) and *n*-butyl acrylate (*n*-BuA, Aldrich, 99%) were purified by vacuum distillation over anhydrous CaH_2. 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was recrystallized from methanol. Iodine (I_2, Aldrich, 99,8%), benzene (SDS, 99.9%), propylene carbonate (Aldrich, 99%), and benzene-d_6 (C_6D_6, Aldrich, 99%) were used as received. All other solvents—toluene (Carlo Erba, 99.5%), trifluorotoluene (Lancaster, 99%), methyl ethyl ketone (SDS, 99%), anisole (Aldrich, 99%), butyl acetate (Aldrich, 99%), dimethylformamide (SDS, 99%), and propionitrile (Aldrich, 99%)—were vacuum-distilled before use.

Polymerization of Methyl Acrylate. In a typical procedure of MA polymerization by RITP process (run 9 in Table 1), methyl acrylate (6.00 g, 6.97×10^{-2} mol), benzene (6.08 g, 7.78×10^{-2} mol), AIBN (3.99×10^{-2} g, 2.43×10^{-4} mol), and iodine (3.67×10^{-2} g, 1.44×10^{-4} mol) were introduced in a Schlenk flask. After three freeze−thaw−pump cycles, the flask was heated at 65 °C in an oil bath. The polymerization was conducted in the dark under argon atmosphere with magnetic stirring. Samples were withdrawn from the reactor with a glass syringe through a septum and under positive argon flow. Conversion was determined by ^{1}H NMR analysis on crude samples in $CDCl_3$. We used the integral I_1 of the resonances at 6.4 ppm (H_A), 6.1 ppm (H_B), and 5.8 ppm (H_C) (3H, $H_AH_CC{=}CH_B-$, J_{trans} = 17.3 Hz, J_{cis} = 10.3 Hz, J_{gem} = 1.4 Hz) relative to the residual monomer and the integral I_2 of the resonances at 3.5−3.8 ppm (3H, $-OCH_3$, singlet + broad peak) relative to polymer and monomer. The fractional conversion was given by $1 - I_1/I_2$. Molecular weights were determined by size exclusion chromatography (SEC).

For kinetics followed by on-line ^{1}H NMR, in a typical run, the reaction mixture of methyl acrylate (1.00 g, 1.16×10^{-2} mol), benzene-d_6 (1.02 g, 1.22×10^{-2} mol), AIBN (1.32×10^{-2} g, 8.02×10^{-5} mol), and iodine (1.20×10^{-2} g, 4.72×10^{-5} mol) was introduced in a glass flask, then gently flushed with argon for 30 min to remove oxygen, and finally placed in a 5 mm NMR tube. The NMR tube was introduced into the spectrometer and was equilibrated at 70 °C. Each spectrum was performed with 16 scans for 150 s.

Block Copolymerization. Methyl acrylate (6.07 g, 7.05×10^{-2} mol), butyl acetate (6.72 g, 5.78×10^{-2} mol), AIBN (108.5 mg, 6.60×10^{-4} mol), and iodine (85.5 mg, 3.37×10^{-4} mol) were reacted under argon atmosphere at 65 °C for 22 h to form a first block of poly(methyl acrylate): conversion = 97% (^{1}H NMR), $M_{n,theoretical}$ = 8900 g mol^{-1}, $M_{n,SEC}$ = 8400 g mol^{-1}, and M_w/M_n = 1.94. Then, a solution of styrene (6.00 g, 5.76×10^{-2} mol), butyl acetate (6.63 g, 5.70×10^{-2} mol), and AIBN (24.7 mg, 1.50×10^{-4} mol) was added, and the polymerization proceeded for 29 h to prepare a poly(methyl acrylate)-*b*-poly(styrene) block copolymer: methyl acrylate conversion = 100% and styrene conversion = 68% (^{1}H NMR), copolymer composition methyl acrylate/styrene 63/37 molar ratio (^{1}H NMR),

$M_{n,theoretical}$ = 14 800 g mol^{-1}, $M_{n,SEC}$ = 13 300 g mol^{-1}, and M_w/M_n = 1.73.

Analyses. Size exclusion chromatography (SEC) was performed on crude samples with a Spectra Physics Instruments SP8810 pump equipped with a Shodex RIse-61 refractometer detector and either two 300 mm columns mixed-D PL-gel 5 μm (2×10^2–4×10^5 g mol^{-1} molecular weight range) or two 300 mm columns mixed-C PL-gel 5 μm (2×10^2–2×10^6 g mol^{-1} molecular weight range) from Polymer Laboratories (at T = 30 °C). Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories. When Mark–Houwink coefficients were applied, the following values were used: polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$),[29] poly(methyl acrylate) ($K = 19.5 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.660$),[30] and poly(*n*-butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.700$).[29]

^{1}H NMR analyses were performed on a Bruker 250 MHz in benzene-d_6 or $CDCl_3$.

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 equipped with a nitrogen laser (337 nm). It was operated at an accelerating potential of 20 kV in positive linear mode and reflectron mode. The matrix used was α-cyanohydroxycinnamic acid in the absence of cationization agent. The concentrations of sample and matrix solutions were 10 g L^{-1} in tetrahydrofuran, and the analyte-to-matrix ratio was 1/10 v/v. 1 μL of the mixture was deposed on a stainless steel target, air-dried, and introduced in the spectrometer under vacuum.

Preamble

Brief Historical Survey. Molecular iodine I_2 has already been reported as a strong inhibitor in free-radical polymerization. For instance, Bartlett et al. followed the monomer conversion for the peroxide-induced polymerization of vinyl acetate and showed that iodine behaves as an efficient inhibitor, the polymerization being apparently totally arrested for a period during which iodine stops two chains per molecule.[31] A tentative interpretation of the kinetics was proposed based on the formation of $I_3^\bullet$ radicals which would react with growing chains, but this hypothesis encountered some difficulties and no molecular weight data were given for the polymers after the inhibition period. Bartlett et al. also established that iodine strongly inhibits the free-radical polymerization of styrene.[32] Ghosh et al. studied the thermal polymerization of methyl methacrylate initiated by AIBN in the presence of iodine, and by plotting the reciprocal degree of polymerization $1/DP_n$ vs molar ratio $[I_2]/[monomer]$ in a set of experiments, they concluded that iodine (or some adducts it could give with the monomer) acts as a chain transfer agent (C_{tr} = 6, expressed in terms of transfer constant of iodine); however, the evolution of monomer conversion with time was not investigated, and the authors did not mention any inhibition period.[33] On the contrary, Lissi et al. also studied the thermal polymerization of methyl methacrylate initiated by AIBN and emphasized that iodine is not consumed in a chain reaction but acts as an efficient inhibitor even at extremely low concentration; however, after the inhibition period, no molecular weight data of the polymers were reported.[34] There are no discrepancies and/or contradictions between the conclusions of these studies if the whole RITP process is considered. Indeed, reverse iodine transfer polymerization (RITP) takes advantage of the powerful inhibitor ability of iodine to generate in situ the iodinated reversible chain transfer agents A–M_n–I ($n \geq 0$), where A stands for the primary radical fragment from the initiator, M stands for the monomer unit, n stands for the mean number degree of polymerization, and I stands for the iodine atom.[35] The RITP mechanism can be described as a conventional free radical polymerization using a very effective terminator. Typically, the RITP process is split into two different periods (Scheme 1). During the first period, the primary free radicals A$^\bullet$ arising from the initiator react directly or indirectly (after few propagation steps) with iodine I_2 to form A–M_n–I telomers. If the reaction rate constant with iodine is high (i.e., much faster than propagation), as expected from the values reported in the literature for the bimolecular reaction of alkyl radicals with iodine ($k > 10^8$ L mol^{-1} s^{-1} at 25 °C),[36–38] this period lasts until the quantitative consumption of iodine. Consequently, for high monomer-to-iodine ratio, the monomer conversion during this period is essentially negligible. This is the reason why this period can be called "inhibition period". After this inhibition period during which the iodinated transfer agents are formed, the polymerization follows the kinetics of a conventional free-radical polymerization governed by degenerative chain transfer.[8] The theoretical mean number degree of polymerization DP_n is given by eq 1

$$DP_n = \Delta[monomer]/(2[I_2]_0 + \Delta[AIBN]) \cong \Delta[monomer]/(2[I_2]_0) \quad (1)$$

where $\Delta[monomer]$ is the consumption of the monomer, $[I_2]_0$ is the initial concentration of iodine in the reaction medium, and $\Delta[AIBN]$ is the excess amount of AIBN used to initiate and propagate the polymerization. $\Delta[AIBN]$ can be evaluated by kinetic analyses and is usually negligible compared to the term $2[I_2]_0$. (A typical detailed example is given later in this paper.) Therefore, the theoretical molecular weight of the polymers prepared by RITP can be calculated by eq 2

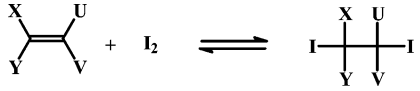
$$M_{n,theoretical} = (mass\ of\ monomer) \times conversion/(2 \times (moles\ of\ I_2)) + M_{A-I} \quad (2)$$

where M_{A-I} stands for the molecular weight of the A–I adduct. This equation is simplified assuming a high degenerative chain transfer constant and a low fraction of dead chains. Alternatively, in the case of rather low degenerative chain transfer constant (but still higher than unity), a good approximation of the molecular weight can be given by eq 2 at high conversion.

Reactions with Iodine. The reactivity of iodine is complex. Iodine has been reported in different kind of reactions. For instance, iodine can react with double bonds, initiate some ionic polymerizations, and form acceptor–donor complexes. For a better understanding of the RITP mechanism, these three possible reactions were considered.

The addition of halogen to double bonds is well-known. Most double bonds are easily halogenated with bromine, chlorine, or mixed halogen compounds. Iodination has also been accomplished, but the reaction is slower, unless radical conditions are used (for instance in inert atmosphere, under UV irradiation, at −50 °C).[39–41] The order of reactivity for some of the reagents is BrCl > ICl > Br_2 > IBr > I_2.[42] Furthermore, *vic*-diiodinated compounds are generally very unstable at room temperature or in the presence of light and tend to revert to iodine and the olefin (Scheme 2).[32,43] NMR studies with 1,2-disubstituted olefins have shown that

Scheme 2. Reversible Formation of *vic*-Diiodinated Compounds from Iodine and Olefins



the reaction with iodine in the absence of light is reversible and follows a mechanism of trans-addition and cis-elimination.[44] If such I−M−I compound interacts with the RITP process, it would lead to a population of polymers with a I−M_n−I structure, which should be revealed by either a SEC analysis (the molecular weight of this population should be twice the molecular weight of the theoretical molecular weight given by eq 2) or a MALDI-TOF analysis (different chain ends as compared to the A−M_n−I structure indicated in Scheme 1).

Another use of iodine is the initiation of cationic polymerization. However, the experimental conditions of this kind of polymerization are usually very different compared to the free-radical polymerizations studied herein. For instance, cationic polymerizations of *n*-butyl vinyl ether by HI/I_2 catalysts require a high purity of the reactants and are usually carried out in the range −45 to −5 °C.[45] Ring-opening polymerization of tetrahydrofuran at 80 °C has been reported with iodine as catalyst,[46] and therefore this solvent will not be used in this study.

Last, iodine is an acceptor able to form complexes with donor compounds.[47] Iodine forms weak complexes with benzene (and its derivatives), ketones, ethers, and esters in apolar solvents, and the equilibrium constant decreases when the temperature increases.[48−51] For comparison, stronger complexes are formed with amino compounds such as pyridine and triethylamine.[49,50] From the data of the literature (Supporting Information), however, and because the role of solvent is very important in the case of weak complexes,[51] it is very difficult to predict at this stage the effect of such complexes on the RITP process.

Results and Discussion

Before studying the kinetics, some experiments were performed to check the efficiency of the RITP process with methyl acrylate (Table 1). One of the key parameters is the ratio [initiator]/[I_2]. In ITP as well as in RAFT, the ratio [initiator]/[transfer agent] must be as low as possible (generally lower than unity, typically in the range 0.1−0.5) because it determines the extent of dead chains.[11] In the RITP process, during the inhibition period, the free radicals predominantly react with iodine to form in situ the reversible chain transfer agent. When all the iodine is consumed, at the end of the inhibition period, the degenerative transfer equilibrium takes place. In this way, the ratio [initiator]/[I_2] is a very important parameter because it will determine both the duration of the inhibition period and the subsequent kinetics of the polymerization. Thus, taking into account the efficiency of the initiator *f* and its rate constant of dissociation k_d, the inhibition time $t_{inhibition,theor}$ can be calculated by eq 3.

$$t_{inhibition,theor} = -\ln(1 - [I_2]_0/(f\,[initiator]_0))/k_d \quad (3)$$

First of all, the results given in Table 1 indicate that a ratio [AIBN]/[I_2] higher than 1.5 is needed to pass the inhibition period. This is because the efficiency of AIBN is lower than unity ($f < 1$). Then, the molecular weights

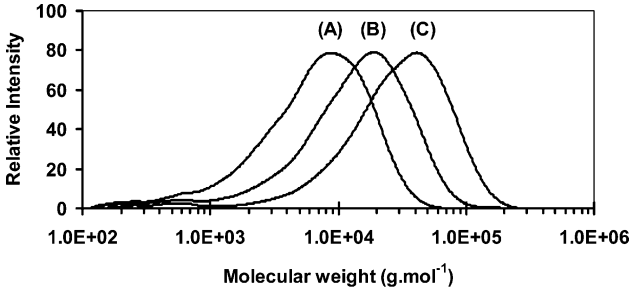


Figure 1. Size exclusion chromatograms of polymers prepared by reverse iodine transfer polymerization (RITP) of methyl acrylate ([MA] = 5.26 M) in benzene ([benzene] = 5.88 M) at 65 °C for 45 h: (A) [2,2′-azobis(isobutyronitrile)] = 6.94×10^{-2} M, [I_2] = 4.13×10^{-2} M, conversion = 97%, $M_{n,theoretical}$ = 5500 g mol^{-1}, $M_{n,SEC}$ = 5600 g mol^{-1}, and M_w/M_n = 1.75; (B) [2,2′-azobis(isobutyronitrile)] = 3.75×10^{-2} M, [I_2] = 2.14×10^{-2} M, conversion = 98%, $M_{n,theoretical}$ = 10 500 g mol^{-1}, $M_{n,SEC}$ = 11 100 g mol^{-1}, and M_w/M_n = 1.83; (C) [2,2′-azobis(isobutyronitrile)] = 1.83×10^{-2} M, [I_2] = 1.08×10^{-2} M, conversion = 98%, $M_{n,theoretical}$ = 20 700 g mol^{-1}, $M_{n,SEC}$ = 21 500 g mol^{-1}, and M_w/M_n = 1.92 (polystyrene calibration).

obtained by polymerization of MA with RITP process are close to the theoretical values, and the polydispersity index values (around 1.8) are in good agreement with iodine transfer polymerization (i.e., corresponding to a rather low transfer constant as usually reported in ITP of acrylates).[10,11] In contrast, in a blank experiment previously reported elsewhere by us in the absence of iodine, the polymerization led to a high molecular weight and a broad molecular weight distribution (M_n = 452 500 g mol^{-1}, M_w/M_n = 2.52).[52] Another important fact is the correlation between the end of the inhibition period and the coloration vanishing of the reaction mixture. The visual observation of the reaction mixture indicates that the solution is brown at the beginning of the polymerization (due to the presence of iodine). In runs 1−6, the color is still present at the end of the reaction, whereas for runs 7−12 the final solution is uncolored. Furthermore, the discoloration time agrees well with the theoretical inhibition time calculated by eq 3. The disappearance of the brown color reveals the consumption of iodine. These first results show the efficiency of the RITP process to control MA polymerization in accordance with the expected mechanism. Furthermore, the good control of the final molecular weight according to eq 2 indicates that the possible side reaction (iodination of methyl acrylate) leading to I−M_n−I structures is not significant here.

The chromatograms of entries 7−9 in Table 1 are shown in Figure 1. Although the molecular weight distribution is quite broad, the chromatogram is monomodal in all cases. Furthermore, the shift of the whole distribution toward higher molecular weights for higher targeted M_n is clearly visible.

To understand better the RITP mechanism, the kinetics of the polymerization was followed by on-line ^{1}H NMR in order to determine the monomer conversion and to follow the evolution of several compounds in the reaction media. Indeed, the concentration of AIBN and A−I could be followed by ^{1}H NMR analysis. The assignments of the peaks for AIBN (δ = 1.25 ppm), $(CH_3)_2$-(CN)CC$(CH_3)_2$(CN) (A−A) (δ = 1.01 ppm), and $(CH_3)_2$-(CN)C−I (A−I) (δ = 1.62 ppm) were determined from a solution of AIBN and iodine in C_6D_6 after heating at 70 °C ([AIBN] = 8.20×10^{-1} M, [I_2] = 5.47×10^{-1} M, [C_6D_6] = 1.13×10^1 M). These assignments agree with the literature.[22,53,54] The chemical shifts given above were

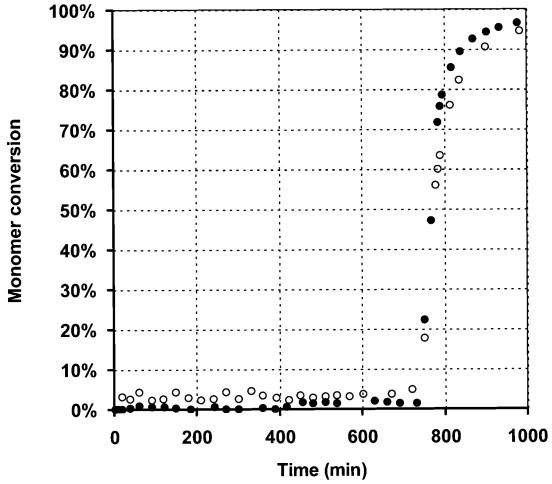


Figure 2. Evolution of monomer conversion vs time for the polymerization of methyl acrylate ([methyl acrylate] = 5.47 M, $[C_6D_6]$ = 5.70 M) by reverse iodine transfer polymerization (RITP) initiated by 2,2′-azobis(isobutyronitrile) (AIBN) at T = 70 °C: [AIBN] = 3.78×10^{-2} M and $[I_2] = 2.22 \times 10^{-2}$ M (closed circle ●), [AIBN] = 2.02×10^{-2} M and $[I_2] = 1.16 \times 10^{-2}$ M (open circle ○).

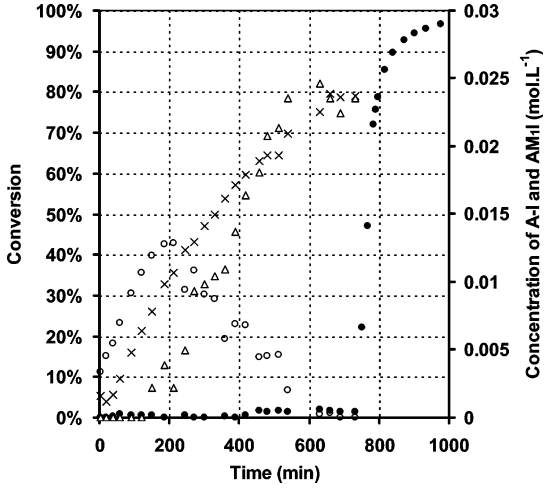


Figure 3. Evolution of methyl acrylate conversion (closed circle ●), 2,2′-azobis(isobutyronitrile) conversion (cross symbol ×), concentration of $(CH_3)_2(CN)C-I$ (A−I) (opened circle ○), and concentration of $(CH_3)_2(CN)C-CH_2-CH(CO_2CH_3)-I$ (A−M_1−I) (opened triangle △) vs time for the polymerization of methyl acrylate by reverse iodine transfer polymerization (RITP) at 70 °C: [methyl acrylate] = 5.47 M, $[C_6D_6]$ = 5.70 M, [2,2′-azobis(isobutyronitrile)] = 3.78×10^{-2} M, and $[I_2] = 2.22 \times 10^{-2}$ M.

determined at room temperature in C_6D_6. Slight changes (i.e., AIBN (δ = 1.49 ppm), $(CH_3)_2(CN)CC(CH_3)_2(CN)$ (A−A) (δ = 1.29 ppm), and $(CH_3)_2(CN)C-I$ (A−I) (δ = 1.95 ppm)) were observed at 70 °C and in the presence of monomer. MA was polymerized by RITP for two different targeted M_n (10 800 and 20 700 g mol^{-1}) with $[AIBN]/[I_2] = 1.7$ (Figure 2). In both cases, the evolution of monomer conversion with time clearly shows an inhibition period prior to the polymerization period. The experimental inhibition time is about 720 min (12 h), independent of the targeted molecular weight, consistent with the theoretical value calculated by eq 3 (in the range 600−820 min with $k_d = 3.70 \times 10^{-5}$ s^{-1} and $f = 0.7-0.8$).[55,56] Alternatively, by matching the experimental inhibition time by eq 3, the initiator efficiency can be estimated to be $f = 0.74$ in these conditions. This value of $f = 0.74$ is coherent with the evolution of the concentration of A−A adduct (around 13% based on the decomposed AIBN from ^{1}H NMR, leading to an upper limit value[57,58] of $f = 1-0.13 = 0.87$). Since the inhibition period is well predicted by eq 3 which does not take into account complex formation with iodine, one can conclude that complex formation with iodine does not seem to disturb the RITP of methyl acrylate in benzene (i.e., the neat process is well described in Scheme 1 although complexes with iodine might take part in intermediate reactions).

Figure 3 shows that the inhibition period itself can be divided into two main stages (the concentration of A−I higher than zero at time zero is most probably due to the initiator decomposition, estimated to less than 10%, during the preparation of the sample and the rise in temperature in the spectrometer). The A−I adduct is formed and consumed during the inhibition period. In the first stage, the concentration of A−I increases up to a maximum. At this point, the rates of formation and consumption of A−I are the same. At the beginning of the inhibition period, the formation of A−I is more favored than the formation of A−M_n−I telomers because the coupling of A$^\bullet$ with iodine (R_c) is faster than propagation (R_p): a very rough estimation with rate constants from the literature for alkyl radicals R$^\bullet$ gives $R_c/R_p = (k[R^\bullet][I_2])/(k_p[R^\bullet][M]) = (k[I_2])/(k_p[M]) = (C[I_2]/[M]) \cong 3610 \times 2.22 \times 10^{-2}/5.47 = 14.6$ (with $k > 10^8$ L mol^{-1} s^{-1} at 25 °C,[36-38] k_p = 27 700 L mol^{-1} s^{-1} at 70 °C,[30] [methyl acrylate] = 5.47 M, and $[I_2] = 2.22 \times 10^{-2}$ M). Then, in the second stage of the inhibition period, the concentration of A−I decreases and becomes negligible at the end of the inhibition period. Thus, A−I adduct is produced by reaction of A$^\bullet$ with iodine and consumed by chain transfer to form A−M_n−I telomers. Indeed, as the concentration of iodine decreases with time, the probability for A$^\bullet$ to propagate for a few steps before reacting with iodine or A−I increases. In a minor extent, owing to its rather unstable nature, the A−I adduct might also undergo a unimolecular thermal dissociation to give A−M_n−I telomers after few propagating steps. The evolution of the concentration of A−M_n−I species vs time was tentatively assessed by ^{1}H NMR, and a good agreement was obtained between $M_{n,NMR}$ values determined by end-group analyses (α- and ω-end groups at 1.02−1.15 and 4.22−4.75 ppm, respectively) and the theoretical value $M_{n,theoretical}$ calculated with eq 2 (Supporting Information). For instance, at the end of the inhibition period (1.5% conversion of methyl acrylate, polymerization time of 731 min), we obtained $M_{n,NMR}$(ω-end group at 4.22−4.75 ppm) = 340 g mol^{-1}, $M_{n,NMR}$(α-end group at 1.02−1.15 ppm) = 420 g mol^{-1}, and a theoretical value $M_{n,theoretical}$ = 350 g mol^{-1}, indicating a mean number degree of polymerization DP_n = 2. It means that the in situ synthesized iodinated transfer agents which are present in the reaction medium at the end of the inhibition period are very small iodo-telomers A−M_n−I (essentially n = 1, 2, and 3). At 94% conversion of methyl acrylate (polymerization time of 903 min), we obtained $M_{n,NMR}$(ω-end group at 4.22−4.75 ppm) = 11 500 g mol^{-1} and $M_{n,NMR}$(α-end group at 1.02−1.15 ppm) = 12 400 g mol^{-1}, close to the theoretical value $M_{n,theoretical}$ = 10 200 g mol^{-1}. In particular, the monoadduct $(CH_3)_a(CH_3)_b(CN)C-CH_cH_d-CH_e(CO_2CH_{3f})-I$ (named A−M_1−I) was unambiguously identified by ^{1}H NMR during the inhibition period (H(e), 4.57 ppm; H(c), 2.66 ppm; H(d), 2.11 ppm; H(b), 1.15 ppm; H(a), 1.10 ppm; J(c,d) = 14.5 Hz,

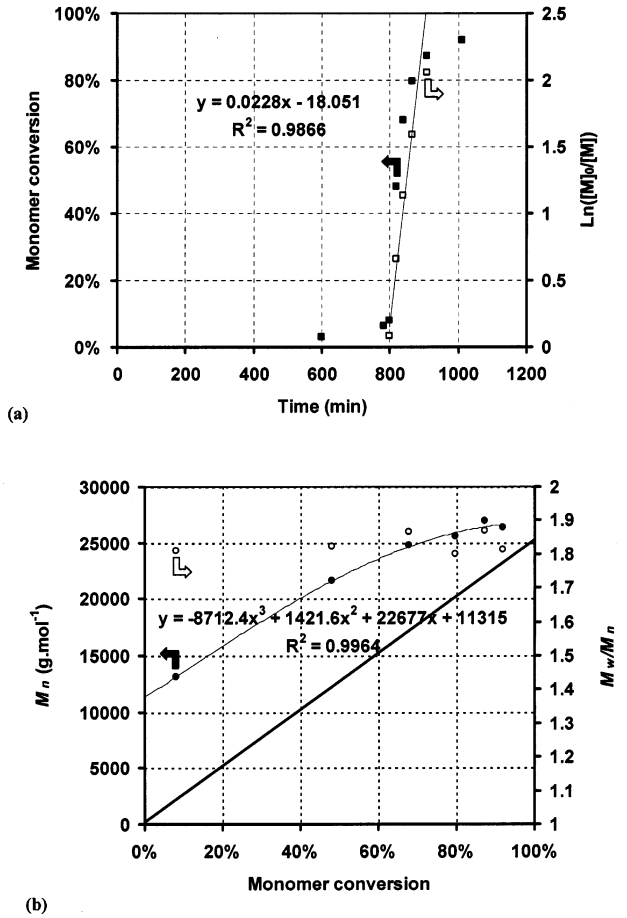


Figure 4. Polymerization of methyl acrylate by reverse iodine transfer polymerization (RITP) at 70 °C, [methyl acrylate] = 5.26 M, [benzene] = 5.88 M, [2,2′-azobis(isobutyronitrile)] = 1.54×10^{-2} M, and $[I_2] = 9.1 \times 10^{-3}$ M: (a) evolution of methyl acrylate conversion (closed square ■) and $\ln([M]_0/[M])$ (open square □, and first-order fit) vs time; (b) evolution of molecular weight M_n (closed circle ●, and third-order fit) and polydispersity index M_w/M_n (open circle ○) by size exclusion chromatography vs monomer conversion.

J(c,e) = 10.5 Hz, J(d,e) = 3.4 Hz), and the evolution of its concentration according to the integral at 2.66 ppm is also shown in Figure 3. Therefore, the evolution of the concentrations determined by ^{1}H NMR is consistent with the mechanism of RITP presented in Scheme 1.

The evolutions of monomer conversion vs time as well as $M_{n,SEC}$ and M_w/M_n vs monomer conversion are shown in Figure 4. First, the evolution of monomer conversion vs time (Figure 4a) indicates a fast polymerization period following the inhibition period: the monomer conversion increases from 6% to 92% in 229 min. In this period of time, the excess amount of AIBN used to initiate and propagate the polymerization is $\Delta[AIBN] = 7.5 \times 10^{-4}$ M (with a rate constant of dissociation $k_d = 3.70 \times 10^{-5}$ s^{-1} for AIBN at 70 °C[55] and $f = 0.7$). Therefore, the excess amount of AIBN contributes for only $\Delta[AIBN]/(2[I_2]_0 + \Delta[AIBN]) = 4\%$ of the polymer chains, indicating that the approximation of eq 1 is valid (i.e., the contribution of the excess amount of AIBN on $M_{n,theoretical}$ is negligible). Furthermore, the slope $k_p[P^\bullet]$ (3.8×10^{-4} s^{-1}) of the corresponding plot $\ln([M]_0/[M])$ vs time (where [M] is the concentration of monomer) gives a concentration of propagating radicals $[P^\bullet] = 1.4 \times 10^{-8}$ mol L^{-1} (with a propagation rate constant $k_p = 27\,700$ L mol^{-1} s^{-1} at 70 °C).[30] Figure 4b indicates that $M_{n,SEC}$ increases with conversion and approaches the theoretical line to finally reach the targeted value at high conversion. Moreover, the polydispersity index is almost constant around 1.8. A similar trend was previously observed by Matyjaszewski et al. in bulk iodine transfer polymerization of methyl acrylate in the presence of 1-phenylethyl iodide as transfer agent.[11] At low monomer conversion, the upward deviation of $M_{n,SEC}$ compared to $M_{n,theoretical}$ accounts for a low degenerative chain transfer constant. Indeed, the iodinated species at the end of the inhibition period are very small iodotelomers (mainly $n = 1$, 2, and 3 according to the results of ^{1}H NMR discussed above). These very small A−M$_n$−I telomers are gradually consumed by degenerative chain transfer during the polymerization period, in the same manner as 1-phenylethyl iodide in the work of Matyjaszewski et al.,[11] to form a distinctive population of polymers of higher molecular weight. The upward deviation of $M_{n,SEC}$ compared to $M_{n,theoretical}$ (or $M_{n,NMR}$) at low monomer conversion can thus be ascribed to the fact that the SEC results do not take into account the population of very small telomers, whereas ^{1}H NMR analysis permits to follow all the A−M$_n$−I species. Therefore, the very small telomers A−M$_n$−I (essentially $n = 1$, 2, and 3) are involved in a living polymerization by degenerative chain transfer with a degenerative chain transfer constant $C_{ex} = k_{ex}/k_p$, where k_{ex} is the rate constant for the degenerative chain transfer of A−M$_n$−I species and k_p is the propagation rate constant of methyl acrylate (Scheme 1). The average lifetime of propagating radicals (τ) and the average number of monomer units (ν) added during this period of time are given by eqs 4 and 5 where k_t is the termination rate constant ($k_t = 6.44 \times 10^8$ L mol^{-1} s^{-1} at 70 °C),[59,60] [P$^\bullet$] is the concentration of propagating radicals, and [M] is the concentration of monomer.

$$\tau = 1/(k_{ex}[A{-}M_n{-}I] + k_t[P^\bullet]) \cong 1/(k_{ex}[A{-}M_n{-}I]) \cong 1/(2k_{ex}[I_2]_0) \quad (4)$$

$$\nu = k_p[M]\tau \cong k_p[M]/(2k_{ex}[I_2]_0) = [M]/(2C_{ex}[I_2]_0) \quad (5)$$

In first approximation, an estimation of the degenerative chain transfer constant is given by $C_{ex} \cong [M]_0/(2\nu_0[I_2]_0)$ with $\nu_0 = (M_{n,x=0} - M_{A-I})/M_{methyl\ acrylate}$ where $M_{n,x=0}$ is the $M_{n,SEC}$ extrapolated at zero conversion (Figure 4b). Thus, $\nu_0 = (11300 - 195)/86.09 = 129$ and $C_{ex} \cong 5.26/(2 \times 129 \times 9.1 \times 10^{-3}) \cong 2.2$ (i.e., $k_{ex} = C_{ex}k_p \cong 6.09 \times 10^4$ L mol^{-1} s^{-1}). This quite low degenerative chain transfer constant $C_{ex} \approx 2.2$ is also consistent with a polydispersity index M_w/M_n in the range 1.7−2.[8,61] The approximation in eqs 4 and 5 is fulfilled since $k_{ex}[A{-}M_n{-}I] \cong 2k_{ex}[I_2]_0 = 6.09 \times 10^4 \times 2 \times 9.1 \times 10^{-3} = 1.1 \times 10^3 \gg k_t[P^\bullet] = 6.44 \times 10^8 \times 1.4 \times 10^{-8} = 9$. It actually means that the characteristic time for activation−deactivation by degenerative chain transfer $\theta_{ex} = 1/(k_{ex}[A{-}M_n{-}I]) \cong 0.9$ ms is much smaller than the characteristic time for deactivation by irreversible termination (coupling of two propagating radicals) $\theta_{termination} = 1/(k_t[P^\bullet]) \cong 0.11$ s: as expected, degenerative chain transfer dominates the polymerization.

MALDI-TOF analysis of a polymer sample prepared by RITP ([methyl acrylate] = 5.18 M, [benzene] = 5.97 M, [AIBN] = 6.96×10^{-2} M, and $[I_2] = 4.16 \times 10^{-2}$ M, $T = 70$ °C, 18 h, conversion = 99%, $M_n = 5800$ g mol^{-1}, $M_w/M_n = 2.07$) was performed in both linear mode (Figure 5) and reflectron mode (Figure 6) in order to confirm the mechanism. Several populations could be

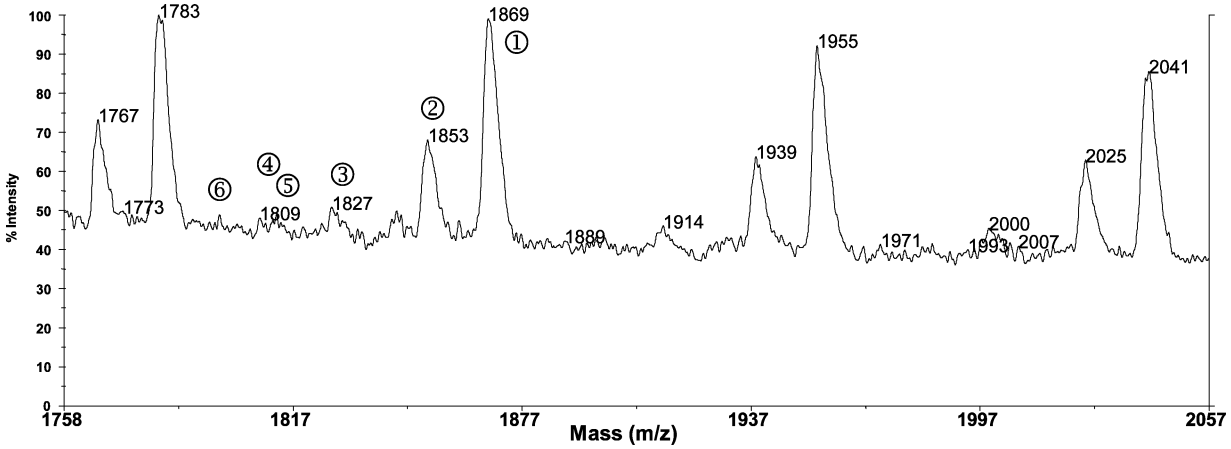


Figure 5. Portion of the MALDI-TOF spectrum (linear mode) of a poly(methyl acrylate) sample synthesized by reverse iodine transfer polymerization (RITP) ([methyl acrylate] = 5.18 M, [benzene] = 5.97 M, [2,2′-azobis(isobutyronitrile)] = 6.96×10^{-2} M, and $[I_2] = 4.16 \times 10^{-2}$ M, $T = 70$ °C, 18 h, conversion = 99%, $M_n = 5800$ g mol^{-1}, $M_w/M_n = 2.07$). Operating conditions: nitrogen laser (337 nm), accelerating potential of 20 kV, α-cyanohydroxycinnamic acid as matrix, sample of 1 μL of a 1/10 v/v analyte-to-matrix mixture prepared at 10 g L^{-1} in tetrahydrofuran.

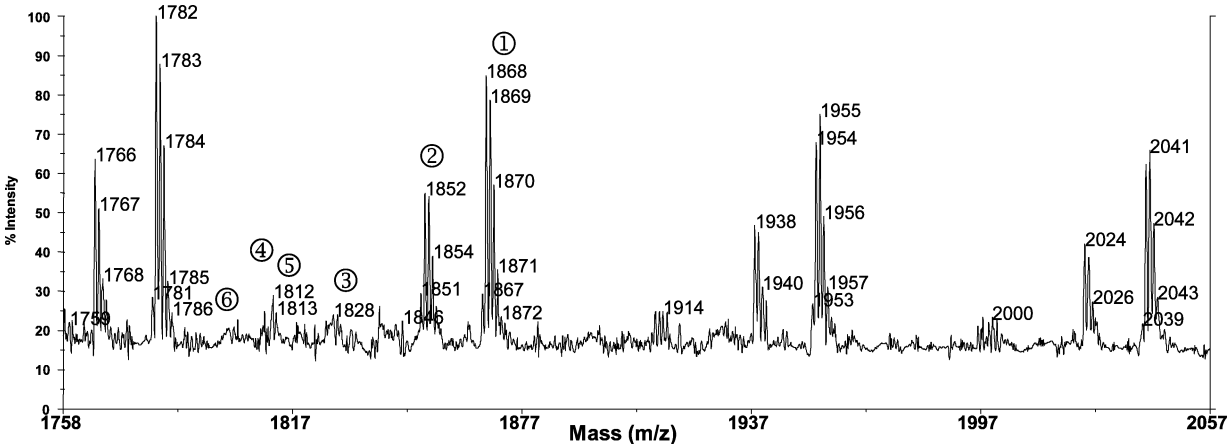
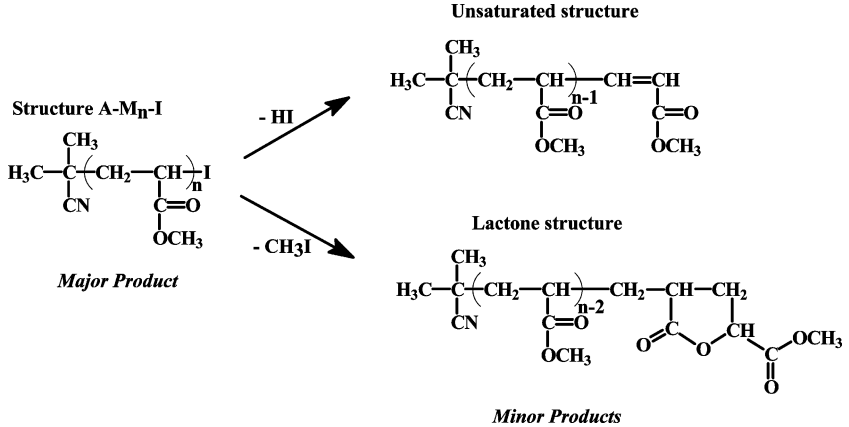


Figure 6. Portion of the MALDI-TOF spectrum (reflectron mode) of a poly(methyl acrylate) sample synthesized by reverse iodine transfer polymerization (RITP) ([methyl acrylate] = 5.18 M, [benzene] = 5.97 M, [2,2′-azobis(isobutyronitrile)] = 6.96×10^{-2} M, and $[I_2] = 4.16 \times 10^{-2}$ M, $T = 70$ °C, 18 h, conversion = 99%, $M_n = 5800$ g mol^{-1}, $M_w/M_n = 2.07$). Operating conditions: nitrogen laser (337 nm), accelerating potential of 20 kV, α-cyanohydroxycinnamic acid as matrix, sample of 1 μL of a 1/10 v/v analyte-to-matrix mixture prepared at 10 g L^{-1} in tetrahydrofuran.

Scheme 3. Structures Identified in the MALDI-TOF Spectra of a Poly(methyl acrylate) Sample Synthesized by Reverse Iodine Transfer Polymerization (RITP)[a]



[a] [Methyl acrylate] = 5.18 M, [benzene] = 5.97 M, [2,2′-azobis(isobutyronitrile)] = 6.96×10^{-2} M, and $[I_2] = 4.16 \times 10^{-2}$ M, $T = 70$ °C, 18 h, conversion = 99%, $M_n = 5800$ g mol^{-1}, $M_w/M_n = 2.07$. Major product: A−M_n−I; minor products: unsaturated and lactone structures.

identified (Scheme 3 and Table 2). The two major populations of the spectra (Figure 5, linear mode: at $m/z = 1869.4$ and 1853.3; Figure 6, reflectron mode: at 1868.3 and 1852.3) have been assigned to A−M_n−I polymer chains, cationized with either K^+ or Na^+, respectively. Four other minor populations of much lower intensity were tentatively assigned by closer inspection of the data. The population at 1827.9 (Figure

Table 2. Assignments of Peaks in the MALDI−TOF Spectra of a Poly(methyl acrylate) Sample Synthesized by Reverse Iodine Transfer Polymerization (RITP)[a]

	linear mode			reflectron mode		
structure	*n*	exptl mass (*m/z*)	theor mass (*m/z*)[b]	*n*	exptl mass (*m/z*)	theor mass (*m/z*)[c]
$A-M_n-I$, K^+	19	1869.43	1869.80	19	1868.29	1868.61
$A-M_n-I$, Na^+	19	1853.30	1853.69	19	1852.30	1852.64
unsaturated, K^+ ($A-M_n-I$, $-HI$), K^+	21	1914.38	1914.07	21	1913.44	1912.77
unsaturated, Na^+ ($A-M_n-I$, $-HI$), Na^+	24	2156.12	2156.23	18	1638.49	1638.69
lactone, K^+ ($A-M_n-I$, $-CH_3I$), K^+	20	1814.60	1813.96	20	1812.52	1812.72
lactone, Na^+ ($A-M_n-I$, $-CH_3I$), Na^+	24	2142.87	2142.21	24	2140.51	2140.89

[a] [Methyl acrylate] = 5.18 M, [benzene] = 5.97 M, [2,2′-azobis(isobutyronitrile)] = 6.96×10^{-2} M, and $[I_2] = 4.16 \times 10^{-2}$ M, $T = 70$ °C, 18 h, conversion = 99%, $M_n = 5800$ g mol^{-1}, $M_w/M_n = 2.07$. [b] Chemical mass. [c] Monoisotopic mass.

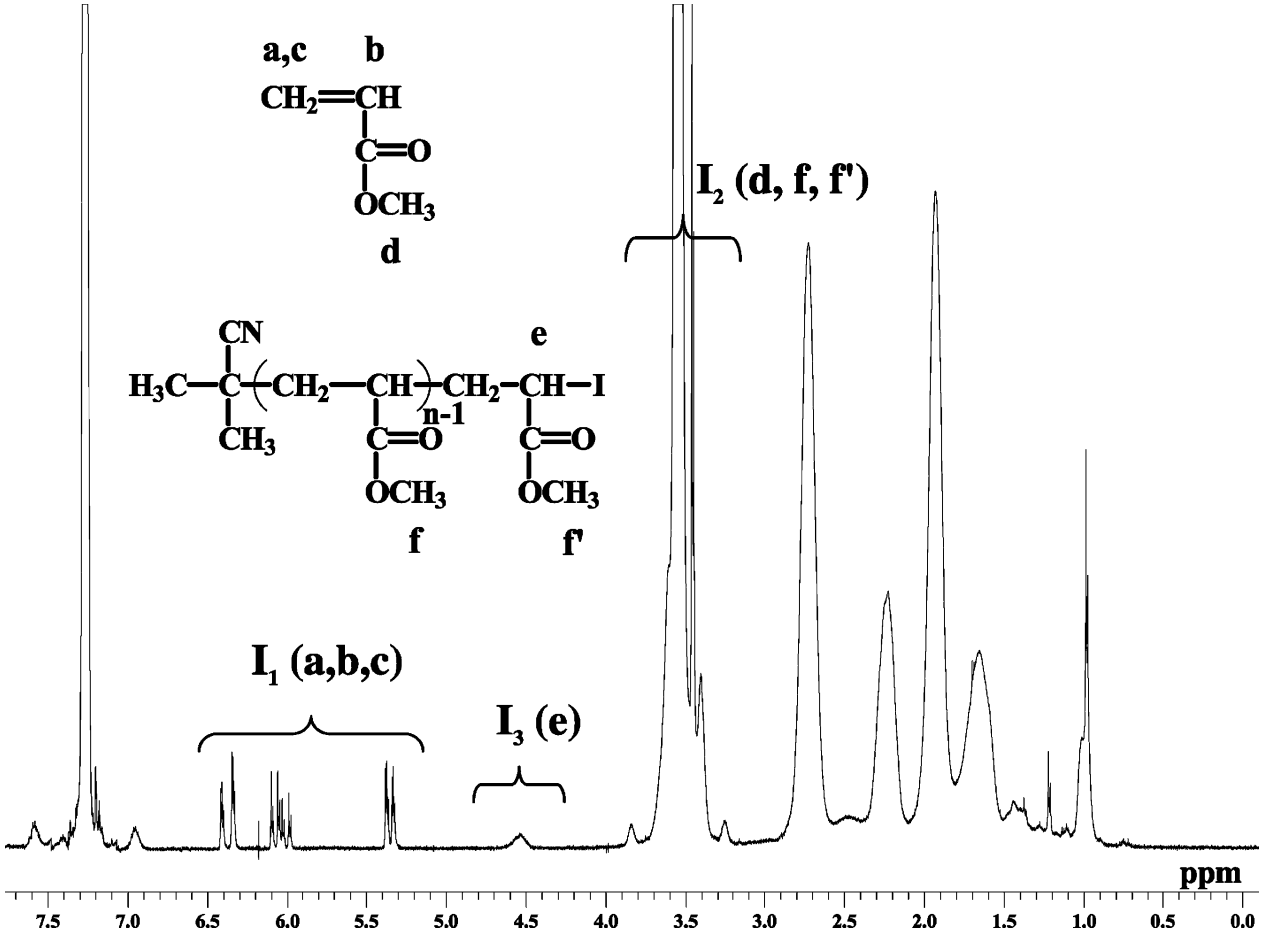


Figure 7. ^{1}H NMR spectrum in C_6D_6 of a poly(methyl acrylate) sample at the end of the polymerization ([methyl acrylate] = 5.26 M, [benzene] = 5.88 M, [2,2′-azobis(isobutyronitrile)] = 6.94×10^{-2} M, $[I_2] = 4.13 \times 10^{-2}$ M, $T = 65$ °C, 45 h, conversion = $1 - I_1/I_2 = 97\%$, $M_{n,theoretical} = 5500$ g mol^{-1}, $M_{n,SEC} = 5700$ g mol^{-1}, and $M_w/M_n = 1.79$, $DP_{n,SEC} = 64$, $DP_{n,NMR} = (I_2 \times \text{conversion})/(3I_3) = 67$).

5, linear mode) could correspond to $A-M_{n-1}-CH=CHCO_2Me$ (formed by HI elimination from $A-M_n-I$ during MALDI-TOF analysis) cationized with K^+ (population also visible at 1828.4 in Figure 6, reflectron mode). Such phenomenon (HI elimination during MALDI-TOF analysis) was already reported in the case of iodo-terminated polystyrene synthesized by ITP[13] and RITP[52] processes. Elimination of HX (X = Br, Cl) was also reported during MALDI-TOF analysis of poly(acrylates) and poly(methacrylates) prepared by ATRP.[62−64] Since no unsaturated end groups have been detected in ^{1}H NMR of these samples, the fragmentation was attributed to the MALDI-TOF technique. The population at 1809.1 (Figure 5, linear mode) could be ascribed to the same structure $A-M_{n-1}-CH=CHCO_2Me$ cationized by Na^+. Furthermore, a population at 1814.0 (Figure 5, linear mode, peak value not mentioned on the spectrum) could correspond to a lactone derivative (formed by CH_3I elimination from $A-M_n-I$) cationized with K^+ (population also visible at 1812.5 in Figure 6, reflectron mode). The loss of CH_3X (X = Br, Cl)[64,65] and the formation of a lactone end group[65] during MALDI analysis was already reported in the case of halogen end-capped poly(methyl methacrylate). Last, another population (not distinguished in the figures) could be ascribed to the same lactone derivative cation-

Table 3. Polymerization of Methyl Acrylate by Reverse Iodine Transfer Polymerization (RITP) in Various Solvents[a]

run	solvent	conversion (%)[b]	$M_{n,theoretical}$[c] (g mol^{-1})	$M_{n,exptl}$[d] (g mol^{-1})	M_w/M_n
1	bulk[e]	88	8800	8600 (8500)[f]	1.91 (1.98)[f]
2	toluene	69	7000	7200 (6900)[f]	1.82 (1.89)[f]
3	α,α,α-trifluorotoluene	92	9400	10000 (9700)[f]	2.01 (2.11)[f]
4	anisole	81	8100	11300 (11200)[f]	1.80 (1.85)[f]
5	methyl ethyl ketone	98	9800	11500 (11400)[f]	2.08 (2.17)[f]
6	butyl acetate	87	8200	6800 (6600)[f]	1.75 (1.78)[f]
7	propylene carbonate	99	9600	11000 (10800)[f]	2.10 (2.26)[f]
8	propionitrile	98	9700	10200 (9700)[f]	2.06 (2.20)[f]
9	dimethylformamide	89	8600	7300 (6900)[f]	1.90 (2.00)[f]

[a] Polymerization of methyl acrylate at 80% w/v vs solvent ([methyl acrylate] = 5.06 M) at 65 °C in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator with [AIBN]/[I_2] = 2, for 24 h. [b] Determined by ^{1}H NMR. [c] Calculated by $M_{n,theor}$ = (mass of monomer) × conversion/(2 × (moles of I_2)) + M_{A-I} where $M_{A-I} = M_{chain\ ends}$ = 195 g mol^{-1}. [d] Polystyrene calibration. [e] Without solvent. [f] Calculated with Mark−Houwink coefficients of polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, α = 0.716) and poly(methyl acrylate) ($K = 19.5 \times 10^{-5}$ dL g^{-1}, α = 0.660).

Table 4. Polymerization of *n*-Butyl Acrylate by Reverse Iodine Transfer Polymerization (RITP) at Various Temperatures[a]

run	T (°C)	$t_{loss\ of\ coloration}$	t_{polym}	conversion (%)[b]	$M_{n,theoretical}$[c] (g mol^{-1})	$M_{n,exptl}$[d] (g mol^{-1})	M_w/M_n
1	65	>15 h	24 h	97	10300	12000 (12600)[e]	2.14 (2.16)[e]
2	85	≈1 h 40 min	5 h	95	9500	9700 (10000)[e]	1.83 (1.85)[e]
3	95	≈0.5 h	1 h	95	9200	8300 (8600)[e]	1.85 (1.88)[e]

[a] Polymerization of *n*-butyl acrylate at 80% w/v vs butyl acetate as solvent ([*n*-BuA] = 3.30 M) in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator with [AIBN]/[I_2] = 1.9. [b] Determined by ^{1}H NMR. [c] Calculated by $M_{n,theor}$ = (mass of monomer) × conversion/(2 × (moles of I_2)) + M_{A-I} where $M_{A-I} = M_{chain\ ends}$ = 195 g mol^{-1}. [d] Polystyrene calibration. [e] Calculated with Mark−Houwink coefficients of polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, α = 0.716) and poly(*n*-butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, α = 0.700).

ized by Na^+. In summary, A−M_n−I was the major product in the sample, further confirming the relevance of the mechanism presented in Scheme 1.

To confirm the conclusions drawn from the MALDI-TOF analyses, a poly(methyl acrylate) sample was analyzed by ^{1}H NMR at room temperature in C_6D_6 at the end of the polymerization (Table 1, run 7, conversion = $1 - I_1/I_2 = 97\%$, $M_{n,theoretical}$ = 5500 g mol^{-1}, $M_{n,SEC}$ = 5700 g mol^{-1}, and M_w/M_n = 1.79). The signal of the proton of the ω-end group −CH_2−C*H*(CO_2CH_3)−I was identified at 4.5 ppm (Figure 7). Thus, from the integral I_3 of this peak at 4.5 ppm and the integral I_2 of the methoxy protons −OCH_3 at 3.5 ppm, the DP_n was given by (I_2 × conversion)/(3I_3), giving DP_n = 67 and $M_{n,HNMR}$ = 5900 g mol^{-1}. The good agreement between both M_n values derived form SEC and ^{1}H NMR analyses confirms that the polymer chains are functionalized with iodine at the ω-chain end; i.e., the A−M_n−I structure is the main population of the poly(methyl acrylate) chains prepared by RITP.

Different classes of solvent were tested for RITP of methyl acrylate: aromatics, ether, ketone, ester, carbonate, nitrile, and amide. Although a detailed study for each solvent would deserve attention, the results in Table 3 show that all the solvents which were considered here gave a reasonable control of the final molecular weight, indicating that RITP is a rather flexible and robust process. Furthermore, first results on RITP of *n*-butyl acrylate in aqueous emulsion, which will be the scope of a separate communication, show that the molecular weight of the polymer can be tuned, indicating that the RITP process should be applicable to heterogeneous processes which are of major industrial importance.

For industrial developments, long inhibition period may be crippling. Therefore, attempts were made to fasten the RITP process by increasing the temperature. The results are given in Table 4 in the case of the polymerization of *n*-butyl acrylate which was chosen owing to its higher boiling point at atmospheric pressure compared to methyl acrylate. It shows that the inhibition period can be shortened efficiently, thus decreasing the overall time of polymerization, while keeping a good control of the final molecular weight of the polymer.

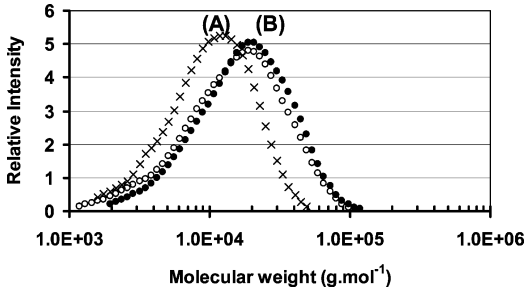


Figure 8. Size exclusion chromatrograms of a poly(methyl acrylate) (chromatogram A, refractive index detector, cross symbol ×) and a poly(methyl acrylate)-*b*-polystyrene block copolymer (chromatograms B: UV detector at 254 nm, closed circle ●, and refractive index detector, open circle ○) prepared by sequential reverse iodine transfer polymerization (RITP) of methyl acrylate (methyl acrylate (6.07 g, 7.05 × 10^{-2} mol), butyl acetate (6.72 g, 5.78 × 10^{-2} mol), 2,2′-azobis(isobutyronitrile) (108.5 mg, 6.60 × 10^{-4} mol), iodine (85.5 mg, 3.37 × 10^{-4} mol), T = 65 °C, 22 h, conversion = 97%, $M_{n,SEC}$ = 8400 g mol^{-1}, and M_w/M_n = 1.94) and iodine transfer polymerization (ITP) of styrene (one shot addition of styrene (6.00 g, 5.76 × 10^{-2} mol), butyl acetate (6.63 g, 5.70 × 10^{-2} mol), 2,2′-azobis(isobutyronitrile) (24.7 mg, 1.50 × 10^{-4} mol), T = 65 °C, 29 h, methyl acrylate conversion = 100%, styrene conversion = 68%, copolymer composition methyl acrylate/styrene 63/37 molar ratio by ^{1}H NMR, $M_{n,SEC}$ = 13 300 g mol^{-1}, and M_w/M_n = 1.73).

Finally, a block copolymer poly(methyl acrylate)-*b*-polystyrene was prepared by sequential RITP polymerization of methyl acrylate followed by addition of styrene. The conversion of methyl acrylate was quantitative before the addition of styrene (conversion = 97%, $M_{n,theo}$ = 8900 g mol^{-1}, $M_{n,exp}$ = 8400 g mol^{-1}, M_w/M_n = 1.94). Then, the molecular weight of the polymer increased while the polydispersity index decreased (styrene conversion = 68%, $M_{n,theo}$ = 14 800 g mol^{-1}, $M_{n,exp}$ = 13 300 g mol^{-1}, M_w/M_n = 1.73). The SEC

analysis of the block copolymer with two detectors (refractive index and UV) showed an unimodal distribution (Figure 8) with a visible shift toward higher molecular weights compared to the macroinitiator, confirming that most of the poly(methyl acrylate) chains were living and took part in the formation of the desired block copolymer. Hence, the living nature of the RITP process opens the door to a wide range of well-designed macromolecular architectures.

Conclusions

The strong reactivity of molecular iodine I_2 toward alkyl radicals was advantageously used to control the polymerization of methyl acrylate and *n*-butyl acrylate. The process, called reverse iodine transfer polymerization (RITP), was detailed for the first time in the case of acrylates. It follows a mechanism that involves the reaction of primary or oligoradicals with iodine to form in situ iodinated compounds which can further react in a living fashion through degenerative chain transfer. RITP proved to be a very efficient method to obtain polyacrylates of well-defined molecular weight, and it is extremely simple to perform since no sophisticated control agent or catalyst needs to be synthesized. Furthermore, RITP is compatible with a large number of solvents (such as aromatics, ether, ester, carbonate, nitrile, and amide). Last, block copolymers can be prepared upon addition of a second monomer, illustrating the living nature of the process.

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Supporting Information Available: ^{1}H NMR spectra, peak assignments, and determination of $M_{n,NMR}$ by end-group analyses; MALDI-TOF spectra and simulated distribution; and equilibrium constants of complexes with iodine. This material is available free of charge via the Internet at http://pubs.acs.org.

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