Reverse Iodine Transfer Polymerization (RITP) of Methyl Methacrylate

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ABSTRACT: The polymerization of methyl methacrylate (MMA) initiated by 2,2′-azobis(isobutyronitrile) (AIBN) as radical initiator in the presence of iodine (I_2) was studied at different temperatures (T = 70 °C and 80 °C). This process, called reverse iodine transfer polymerization (RITP), is based on the direct reaction of radicals with molecular iodine. RITP efficiently controls the molecular weight (determined by size exclusion chromatography, SEC) and the structure of the polymer chains (confirmed by ^{1}H and ^{13}C NMR spectroscopy). For instance, PMMA samples of $M_{n,SEC}$ = 2300 g mol^{-1} and polydispersity index PDI = M_w/M_n = 1.5 ($M_{n,theoretical}$ = 2300 g mol^{-1}), $M_{n,SEC}$ = 4600 g mol^{-1} and PDI = 1.6 ($M_{n,theoretical}$ = 4700 g mol^{-1}), $M_{n,SEC}$ = 9600 g mol^{-1} and PDI = 1.6 ($M_{n,theoretical}$ = 10 000 g mol^{-1}), and $M_{n,SEC}$ = 19 200 g mol^{-1} and PDI = 1.5 ($M_{n,theoretical}$ = 18400 g mol^{-1}) were successfully prepared by RITP. The polymerization was followed by on-line ^{1}H NMR spectroscopy, and the conversion of iodine was followed by titration with a thiol (thioglycolic acid). It was shown by SEC, titration of iodine, gas chromatography, and NMR analyses that RITP was split into two different periods: a first "inhibition" period during which iodine is consumed to form very short ω-iodotelomers, and a second period where the polymerization follows the kinetics of a conventional free radical polymerization governed by degenerative chain transfer. The degenerative chain transfer constant was estimated to be $C_{ex} \approx 2.6$ at T = 80 °C. Last, the iodine-end-capped structure of the polymers was demonstrated by different analytical techniques, and the iodine functionality of the PMMA chains was up to 95%.

Introduction

The synthesis of new polymers with interesting properties (innovative polymers) may use two different strategies: the synthesis of new monomers or the development of new polymerization methods. Since the 1980s, with the discovery of new controlled polymerization methods, it is now possible to obtain quite easily new macromolecular architectures such as block, graft copolymers, or telechelic polymers.[1−4] Although judicious strategies (e.g., condensation of functional telomers,[5,6] telomerization with particular transfer agents,[7,8] dead end polymerization with particular initiator[9]) had previously been used to obtain such copolymers, all of them present some important drawbacks or limitations: formation of a mixture of block copolymers with undesirable homopolymers or formation of copolymers with relatively low molecular weights. Only ionic polymerizations are able to reach perfectly controlled architectures, but their cost and their difficult implementation limit their application in the industry. The invention of living/controlled free radical polymerizations such as atom transfer radical polymerization,[10−13] nitroxide-mediated radical polymerization,[14−16] and reversible addition−fragmentation chain transfer polymerization (RAFT[17−21] or MADIX[22]) has permitted preparation of this new type of block copolymers and, thus, to obtain innovative properties. One of the oldest method is iodine transfer polymerization (ITP), discovered by Tatemoto.[23−29] Indeed, this process has been used in the eighties for the polymerization of vinylidene fluoride.[24,30−32] Despite this precedence, only a few studies dealing with ITP have been reported in the literature. Works of Matyjazsewski et al. in 1995[33,34] reactivated the interest for this type of polymerization in studying different monomers: styrene,[35−38] *n*-butyl acrylate,[39] vinyl chloride,[40−46] vinylidene chloride,[47] and last, vinyl acetate.[48] ITP permits controlling molecular weights for a wide range of monomers, such as acrylates and vinyl acetate, and appears with RAFT, the most universal technique. ITP can also lead to diblock or triblock copolymers. For example, the synthesis of thermoplastic elastomers (TPE) was pioneered by the Daikin Company in 1979 (producing Daiel TPE[23,25−27] nowadays), then studied by DuPont[49−51] and developed later by Ausimont (now Solvay Solexis).[52−54] Furthermore, ITP can be performed in heterogeneous processes such as aqueous miniemulsion polymerization.[37] ITP is a simple method because only a radical initiator (such as 2,2′-azobis(isobutyronitrile), AIBN), a iodinated transfer agent, like $C_6F_{13}I$, and a monomer are necessary. Last, purification steps are easy because no catalyst has to be eliminated. Nevertheless, ITP has two important drawbacks: first, iodinated transfer agents are not very stable under storage,[35] which is due to the weak C−I bond. Indeed, iodinated transfer agents are light-sensitive, temperature-sensitive, and are prone to decomposition to give free iodine (I_2) or hydriodic acid (HI) by elimination reaction. The presence of free iodine may cause an inhibition period and consume the initiator, leading to nonreproducible results. Furthermore, ITP of monomers involving tertiary propagating radicals (such as ITP of methyl methacrylate with 1-phenylethyliodide as transfer agent) was not successful[34] because it would require more activated iodoalkyl transfer agents (sterically hindered or activated by electronic effects), which are inherently even more unstable. To overcome these two limitations, a new technique developed in our laboratory has been successfully applied to the polymerization of methyl acrylate,[55,56] styrene,[55] butyl α-fluoroacrylate,[55,57] and vinylidene chloride.[55,58] This technique, called "reverse iodine transfer polymerization" (RITP), is based on the in situ synthesis of the iodinated transfer agent, thus avoiding its preliminary synthesis and storage.

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The aim of this work is to describe RITP and demonstrate that it is applicable to methyl methacrylate (as a model for methacrylates). Iodine is a simple molecule but its reactivity is complex: iodine can react onto double bonds, acts as catalyst or reactant, and therefore, side reactions may be envisaged. ITP of methyl methacrylate reported so far in the literature was unsuccessful because no alkyl iodide was adapted to the polymerization of MMA.[34] Therefore, RITP appears very attractive to fill this gap.[59,60] This paper reports a detailed study on the RITP mechanism of methyl methacrylate and examines different aspects such as the inhibition period and the polymerization period.

Experimental Section

1. Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice in methanol, dried at 0 °C under vacuum (0.01 mmHg) for 6 h, and stored at −4 °C. Methyl methacrylate (MMA, Aldrich, 99%) was distilled under reduced pressure (20 mmHg) before use and stored at −4 °C. Iodine (I_2, Aldrich, 99.8%), hydroquinone monomethyl ether (MEHQ, Aldrich, 99%), toluene (SDS, 99%), toluene-d_8 (Aldrich, 99%), benzene (SDS, 99.5%), pentane (SDS, 95%), and tetrahydrofuran (THF, SDS, 99%) were used as received.

2. Characterization. ^{1}H NMR (250 and 400 MHz) and ^{13}C NMR (62.8 MHz) were performed at room temperature on Bruker AC 250 and AC 400 spectrometers in deuterated chloroform $CDCl_3$ or toluene-d_8 as solvent (tetramethylsilane as reference). In ^{13}C NMR, a long relaxation time (10 s) was chosen to allow quantitative analysis.

Kinetics were studied by ^{1}H NMR at 80 °C in deuterated toluene on a Bruker 250 MHz spectrometer. The temperature of the apparatus was standardized with DMSO by measuring the coupling constant.

Size exclusion chromatography (SEC) was performed at 30 °C with a Spectra-Physics SP8810 pump, three columns PLgel 5 μm MIXED-D, 500 Å, and 100 Å from Polymer Laboratories, and a Spectra-Physics SP8430 refractometer detector. THF was used as solvent at 0.8 mL min^{-1}. Calibration was established with poly(methyl methacrylate) standards from Polymer Laboratories. The samples were injected using a Shimadzu automatic injector (injection volume 20 μL).

Gas chromatography analyses (GC) were performed on a Delsi Instruments Serial 330 apparatus coupled with a Shimadzu C-R6A integrator. A 2-m-long Carbowax 20M (poly(ethylene glycol)) column was used with nitrogen as the gas vector at 1 bar. The analyses were achieved in isothermal mode at 130 °C ($T_{injector} = T_{detector} = 200$ °C). GC was used to determine the monomer conversion versus reaction time by using the solvent as internal standard.

MALDI-TOF analyses were performed at "Service Central d'Analyse du CNRS" (Solaize, France) in reflectron mode (accelerating potential of 20 kV) on a Perkin-Elmer VOYAGER DE SR apparatus equipped with a nitrogen laser (337 nm). Pentafluorocinnamic acid (PFCA) was used as the matrix, and sodium iodide (NaI) was used as cationizing 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. The mixture (1 μL) was deposited on a stainless steel target, air-dried, and introduced in the spectrometer under vacuum.

3. Synthesis of Poly(methyl methacrylate) Oligomers with $M_{n,targeted}$ = 10 200 g mol^{-1} by Reverse Iodine Transfer Polymerization (RITP) ([MMA]/[AIBN]/[I_2] = 200/2/1). MMA (10.000 g, 1.0 × 10^{-1} mol), iodine (I_2) (0.127 g, 5.0 × 10^{-4} mol), AIBN (0.164 g, 1.0 × 10^{-3} mol), and toluene (10 mL) were placed in a 50 mL round-bottom Schlenk flask protected with an aluminum film. The reaction medium was purged with argon for 15 min at 0 °C to remove oxygen, then sealed with a septum and plunged in an oil bath at 80 °C under magnetic stirring. Samples were withdrawn periodically, cooled in an ice bath, and inhibited with MEHQ, and analyzed by SEC, ^{1}H NMR and GC analyses to determine the molecular weights and monomer conversion, respectively. When the monomer conversion was close to 90%, the reaction was stopped. Toluene was removed by rotary evaporation and replaced by THF. Then the polymer was precipitated twice in pentane. The precipitated polymer was analyzed by ^{1}H and ^{13}C NMR and SEC analyses. The yield of polymerization was determined by gravimetry (eq 1)

$$\text{Yield} = (m_p/(m_{MMA} + m_{I_2})) \times 100 \quad (1)$$

in which m_P, m_{MMA}, and m_{I_2} are the weight of polymer recovered after precipitation and the initial weight of MMA and iodine in the reaction medium, respectively. Results: polymerization time = 320 min, monomer conversion = 91%, $M_{n,SEC}$ = 9800 g mol^{-1}, and PDI = 1.5.

4. Kinetics of Poly(methyl methacrylate) Oligomers with $M_{n,targeted}$ = 10 200 g mol^{-1} by Reverse Iodine Transfer Polymerization (RITP) Followed by ^{1}H NMR ([MMA]/[AIBN]/[I_2] = 200/2.5/1). The kinetics were followed by ^{1}H NMR, in a 5-mm-diameter NMR tube with a Bruker 400 MHz spectrometer. Mixtures were prepared as follows: MMA (5.000 g, 5.0 × 10^{-2} mol), iodine (0.064 g, 2.5 × 10^{-4} mol), and AIBN (0.103 g, 6.2 × 10^{-4} mol) were introduced in a one-neck round-bottom flask. The mixture was stirred until iodine was dissolved. An aliquot of this solution (0.300 g) was withdrawn with a syringe and introduced in the NMR tube with deuterated toluene (0.200 g). The tube was degassed with argon for 30 s and introduced in the spectrometer that was equilibrated at 80 °C. The temperature of the spectrometer was checked with DMSO by measuring the coupling constant of the two methyl groups, knowing the coupling constant is a function of temperature.

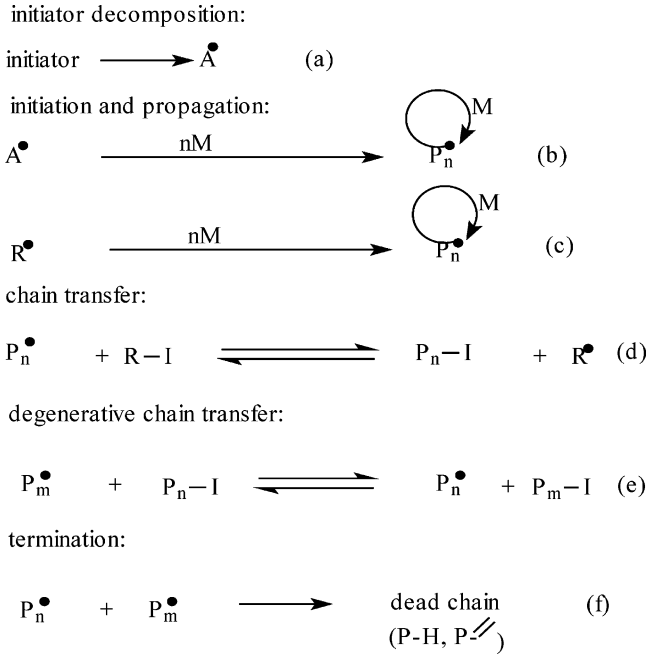
5. Synthesis and Characterization of a Macrotransfer Agent P−I with $M_{n,targeted}$ = 3200 g mol^{-1} ([MMA]/[AIBN]/[I_2] = 60/1.7/1). MMA (20.00 g, 2.0 × 10^{-1} mol), AIBN (0.93 g, 5.6 × 10^{-3} mol), iodine (0.84 g, 3.3 × 10^{-3} mol), and toluene (20.00 g) were introduced in a 100 mL two-necked round-bottom flask covered with aluminum film and equipped with a condenser. After degassing the mixture with argon for 10 min at 0 °C, the flask was sealed with a septum and placed in an oil bath at 80 °C under magnetic stirring. The reaction was stopped when monomer conversion reached 70% (measured by GC). The polymer was recovered by precipitation in pentane at 0 °C (to avoid the degradation of the polymer), filtrated, washed with pentane (25 mL), and dried under vacuum in the dark. A white powder was obtained with a yield of 65% (14.00 g). The polymer was stored in the dark at 0 °C, and characterized by NMR, SEC, and MALDI-TOF analyses. The amount of free iodine was determined by titration with thiol and by liquid-phase chromatography. Results: polymerization time = 360 min, monomer conversion = 70%, $M_{n,SEC}$ = 2300 g mol^{-1} and PDI = 1.4, $DP_{n,SEC}$ = 21, $DP_{n,H-NMR}$ = 20, $DP_{n,C-NMR}$ = 20, free iodine < 0.1 wt %, iodine functionality = 95%, ^{1}H NMR and ^{13}C NMR (given in the sections Results and Discussion and Supporting Information), and MALDI (Supporting Information).

6. Determination of the Amount of Free Iodine by Titration with Thiol. This titration was used to follow the consumption of free iodine during reverse iodine transfer polymerization (RITP) and to determine the amount of free iodine in the sample of macrotransfer agent (eq 2). A typical example of titration for the sample of macrotransfer agent is as follows: thioglycolic acid (0.092 g, 1.0 × 10^{-3} mol) is introduced in a 100 mL graduated flask completed with toluene. The macrotransfer agent (1 g) is dissolved in toluene (10 mL) and titrated with the solution of thioglycolic acid at 0.01 mol L^{-1}. In our case, we have found that the amount of free iodine is very small (lower than 0.1 wt %)

$$2RSH + I_2 \rightarrow RSSR + 2HI \quad (2)$$

A typical titration of a sample during reverse iodine transfer polymerization (RITP) is described here: thioglycolic acid (0.626 g, 6.8 × 10^{-3} mol) is introduced in a 1 L graduated flask completed

Scheme 1. Mechanism of Iodine Transfer Polymerization (ITP)



(M: monomer, $P_n^{\bullet}$: propagating radicals, n = number average degree of polymerization, R−I: alkyl iodide).

with toluene to obtain a solution 6.8×10^{-3} mol L^{-1}. An aliquot (1 mL) from the reaction medium was dissolved in toluene (5 mL) and then titrated with the solution of thioglycolic acid. The discoloration of the solution (from orange to uncolored) permits determination of the equivalent volume during the titration.

Results and Discussion

1. Introduction on Reverse Iodine Transfer Polymerization (RITP) of Methyl Methacrylate. ITP is a process involving a iodinated transfer agent (R−I), a monomer (e.g., MMA), and a radical initiator (e.g., AIBN), the ratio [AIBN]/[R−I] being lower than unity. The initiating radicals, A•, are generated by thermal decomposition of a conventional initiator in step (a), (Scheme 1). Then, A• radicals can initiate the polymerization of the monomer (M), as shown in step (b). The exchange of iodine from the transfer agent, R−I, to the propagating radical, P_n•, results in the formation of the polymeric alkyl iodide, P_n-I, and a new initiating radical, R•, as shown in step (d). The expelled radical R• has to be able to initiate the polymerization of the monomer (step (c)). Large differences in the stability of the reactants and products involved in step (d) could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of R• closely resembles the structure of the propagating radical, resulting in a thermodynamically neutral transfer step. The exchange process described in step (e) is thermodynamically neutral because P_n• and P_m• propagating chains as well as P_n-I and P_m-I dormant chains have the same structure (degenerative chain transfer). The two equilibria (steps (d) and (e)) involving dormant and propagating species are crucial[61] for the controlled/living behavior of the polymerization. As in any radical process, termination still occurs in ITP (step (f)), but the number of dead chains is kept low compared to the number of iodine-capped polymer chains (living chains).

The mechanism of RITP is different: the transfer agent is synthesized in situ in the reaction medium by reaction of radicals with iodine I_2 (Scheme 2). In RITP, the amount of initiator must be higher than the amount of iodine ([initiator]/$[I_2] > 1$) because the latter is known to be a good inhibitor for radical polymerization of methyl methacrylate.[62,63] It is possible to propose the mechanism in Scheme 2 with a first inhibition period when the radicals A• react preferentially with iodine to give A−I or propagate with very few monomer units before reacting with iodine to give very short telomers A−M_n−I, and a second period where the radicals initiate a polymerization governed by degenerative chain transfer.[56] To confirm this hypothesis, several reactions were performed at various initiator-to-iodine ratios, $[AIBN]_0/[I_2]_0$. All of these reactions were performed in the dark because iodocompounds are UV light sensitive.

2. Study of the RITP Mechanism with MMA. From Table 1, the ratio $[AIBN]_0/[I_2]_0$ must be higher than 1.5 to obtain a high yield of polymerization. Below 1.5, the polymerization yield is very low and the reaction medium remains colored (reddish). This is because the efficiency (f) of AIBN is lower than unity ($f < 1$). The efficiency of the initiator can be evaluated by using eq 3 and replacing the value of the theoretical inhibition time by the experimental value: it gives $f \approx 0.7$, which is close to the value reported in the literature.[64,65] The inhibition time, corresponding to the rise of monomer conversion, has been experimentally evaluated by GC or by the discoloration time of the reaction medium. These two values give close results. The theoretical inhibition time is given by eq 3, where $[I_2]_0$ is the initial concentration of iodine, $[AIBN]_0$ is the initial concentration of initiator, k_d is the decomposition rate constant of the initiator ($k_d = 3.660 \times 10^{-5}$ s^{-1} at 70 °C and $k_d = 1.331 \times 10^{-4}$ s^{-1} at 80 °C for AIBN),[66] and f is the initiator efficiency ($f = 0.7$ for AIBN).[64,65]

$$\text{time}^{\text{inhibition}}\,(\text{theoretical}) = -\ln(1 - [I_2]_0/(f \times [AIBN]_0))/k_d \quad (3)$$

The experimental and theoretical inhibition times agree well for RITP of MMA at 70 °C and 80 °C (Table 1 and Table 2). The inhibition time is independent of the targeted molecular weight (i.e., independent of the $[M]_0/(2 \times [I_2]_0)$ ratio). This behavior is different from the case of styrene, where the inhibition period is influenced by the concentrations of monomer and iodine because of the formation of a styrene−iodine complex.[67] The iodine is an acceptor able to form weak complexes with donor compounds,[68] such as benzene, ethers, and esters, or stronger complexes with amino compounds, such as triethylamine.[69,70] In the case of RITP of MMA in toluene, it seems that the possible complex formation with iodine does not alter the inhibition time (i.e., the neat process is well described in Scheme 2, although complexes with iodine might take part in intermediate reactions).

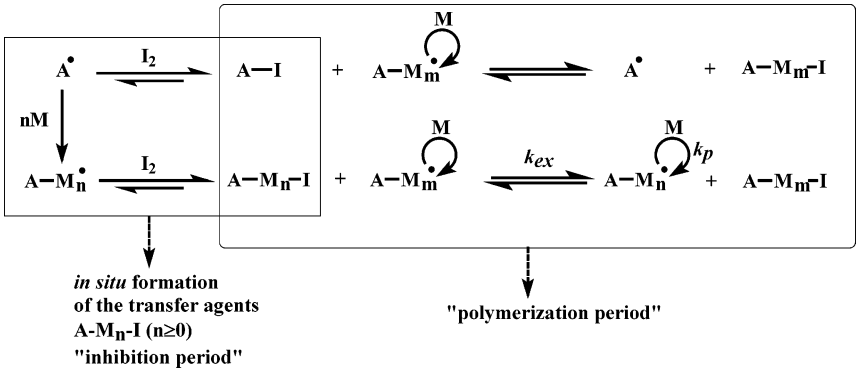
In the case of ITP, the molecular weight (M_n) of the polymer is controlled by the quantity of transfer agent and its transfer constant value $C_{tr,R-I}$.[32] For RITP, the molar ratio of monomer over iodine controls the targeted mean degree of polymerization ($DP_{n,targeted}$) (eq 4a) and thus the targeted molecular weight (eq 4b). These equations hold for a monomer conversion close to 100%. In these equations, dead chains generated from the excess amount of initiator used to initiate and propagate the polymerization are neglected.[56]

$$DP_{n,targeted} = [MMA]_0/(2 \times [I_2]_0) \quad (4a)$$

$$M_{n,targeted} = [MMA]_0 \times M^{MMA}/(2 \times [I_2]_0) + M^{A-I} \quad (4b)$$

in which $[MMA]_0$ is the initial concentration of MMA, $[I_2]_0$ the initial concentration of iodine, M^{MMA} the molecular weight of MMA ($M^{MMA} = 100$ g mol^{-1}), and M^{A-I} the molecular weight of the polymer chain ends (i.e., the molecular weight of

Scheme 2. Simplified Mechanism of Reverse Iodine Transfer Polymerization (RITP)



(A• = radical from the initiator; I_2 = molecular iodine; M = monomer unit (methyl methacrylate); n = number average degree of polymerization; k_{ex} degenerative chain transfer rate constant; k_p = propagation rate constant).

Table 1. Influence of the Molar Ratio Initiator/Iodine on the Inhibition Time, Molecular Weight, and Polydispersity Index for Reverse Iodine Transfer Polymerization of Methyl Methacrylate (MMA) at T = 70 °C in Toluene in the Presence of 2,2′-Azobis(isobutyronitrile) (AIBN) as Initiator

				time^{inhibition}				
run	$M_{n,targeted}$[a] (g mol^{-1})	conversion[b] (%)	ratio $[AIBN]_0/[I_2]_0$	theoretical[c] (h)	experimental[b] (h)	$M_{n,theoretical}$[d] (g mol^{-1})	$M_{n,experimental}$[e] (g mol^{-1})	PDI[e]
1	5200	5	1.5	22.9	∞[f]	400	400	1.2
2	10200	3	1.5	22.9	∞[f]	500	500	1.2
3	20200	3	1.5	22.9	∞[f]	800	400	1.2
4	5200	90	1.7	13.8	14	4700	4600	1.7
5	11200	80	1.7	13.8	14.1	9000	9000	1.8
6	20200	90	1.7	13.8	14	18200	18200	1.8
7	5200	90	2.0	9.4	10	4700	4400	1.8
8a	10200	94	2.0	9.4	10.1	9600	9500	1.8
8b		95	no iodine				60000	2.1
9	5200	96	2.5	6.4	7	5000	4700	1.8
10	10200	98	2.5	6.4	7	10000	9600	1.8

[a] Calculated by $M_{n,targeted} = [MMA]_0 \times M^{MMA}/(2 \times [I_2]_0) + M^{A-I}$, where $M^{MMA} = 100$ g mol^{-1}, $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}. [b] Determined by gas chromatography. [c] Calculated by time^{inhibition} (theoretical) $= -\ln(1 - [I_2]_0/(f \times [AIBN]_0))/k_d$ with $k_d = 3.660 \times 10^{-5}$ s^{-1} and $f = 0.7$. [d] Calculated by $M_{n,theoretical} = [MMA]_0 \times M^{MMA} \times$ conversion$/(2 \times [I_2]_0) + M^{A-I}$, where $M^{MMA} = 100$ g mol^{-1}, and $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}. [e] Determined by size exclusion chromatography (PMMA calibration in THF). [f] ∞ No polymerization observed.

Table 2. Influence of the Molar Ratio Initiator/Iodine on the Inhibition Time, Molecular Weight, and Polydispersity Index for Reverse Iodine Transfer Polymerization of Methyl Methacrylate (MMA) at T = 80 °C in Toluene in the Presence of 2,2′-Azobis(isobutyronitrile) (AIBN) as Initiator

				time^{inhibition}				
run	$M_{n,targeted}$[a] (g mol^{-1})	conversion[b] (%)	ratio $[AIBN]_0/[I_2]_0$	theoretical[c] (h)	experimental[b] (h)	$M_{n,theoretical}$[d] (g mol^{-1})	$M_{n,experimental}$[e] (g mol^{-1})	PDI[e]
11	4200	5	1.5	6.4	∞[f]	400	300	1.2
12	10200	3	1.5	6.4	∞[f]	500	400	1.2
13	20200	2	1.5	6.4	∞[f]	600	400	1.2
14	5200	90	1.7	3.8	4	4700	4600	1.6
15	10200	88	1.7	3.8	4.1	9000	9600	1.6
16	20200	91	1.7	3.8	4	18400	19200	1.5
17	5200	90	2.0	2.6	2.7	4700	4400	1.5
18	10200	91	2.0	2.6	2.8	9300	9800	1.5
19	5200	96	2.5	1.8	1.5	5000	4700	1.5
20	10200	98	2.5	1.8	1.5	10000	9600	1.6

[a] Calculated by $M_{n,targeted} = [MMA]_0 \times M^{MMA}/(2 \times [I_2]_0) + M^{A-I}$, where $M^{MMA} = 100$ g mol^{-1}, $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}. [b] Determined by gas chromatography. [c] Calculated by time^{inhibition} (theoretical) $= -\ln(1 - [I_2]_0/(f \times [AIBN]_0))/k_d$ with $k_d = 1.331 \times 10^{-4}$ s^{-1} and $f = 0.7$. [d] Calculated by $M_{n,theoretical} = [MMA]_0 \times M^{MMA} \times$ conversion$/(2 \times [I_2]_0) + M^{A-I}$, where $M^{MMA} = 100$ g mol^{-1}, and $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}. [e] Determined by size exclusion chromatography (PMMA calibration in THF). [f] ∞ No polymerization observed.

the adduct A−I formed during the inhibition period, $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}).

Table 1 shows that the molecular weight of the polymer can be effectively tuned by varying the concentration of iodine. As a comparison, when the polymerization is performed in the absence of iodine (run 8b, Table 1), a polymer of much higher molecular weight is obtained (conversion = 95%, M_n = 60 000 g mol^{-1}, PDI = 2.1). When the temperature is increased to 80 °C to diminish the inhibition time, the control of the molecular weight is still good (Table 2). Furthermore, the polydispersity index decreases slightly from about 1.8 (at 70 °C) to 1.5 (at 80 °C).

3. Study of the Inhibition Period in RITP of MMA. To confirm that the inhibition period is correlated with the presence of free iodine in the reaction medium, the concentration of iodine was followed by titration for a reaction performed at 80 °C with a molar ratio $[AIBN]_0/[I_2]_0 = 2.5$. High values for the temperature and the quantity of initiator allow decrease of the theoretical inhibition time to 1 h 47 min and thus to facilitate the analysis of the reaction medium (significant evolution of

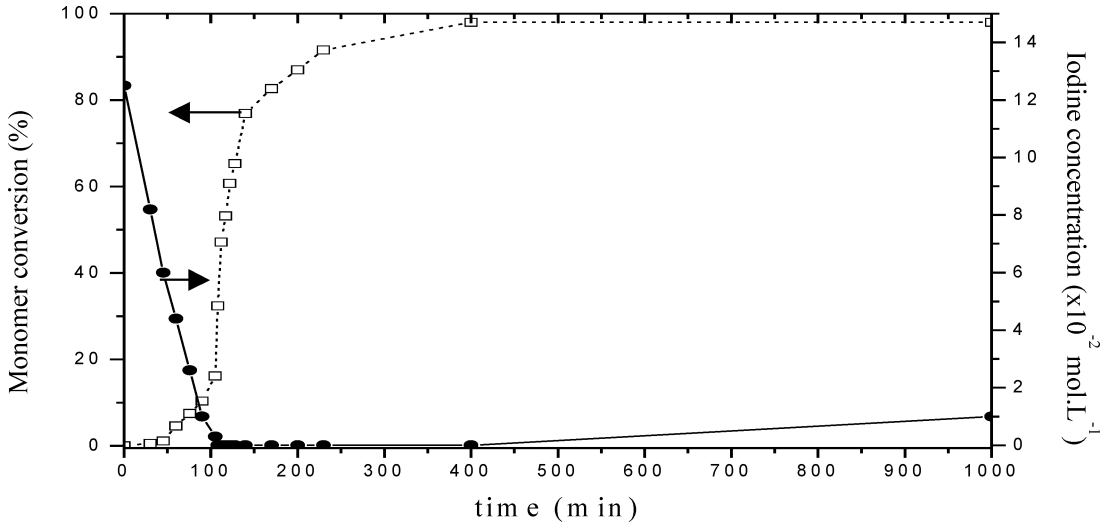


Figure 1. Evolution of monomer conversion (□) and iodine concentration (●) vs time (min) in reverse iodine transfer polymerization of methyl methacrylate (MMA) at 80 °C. Experimental conditions: 31.00 g (3.10×10^{-1} mol) of MMA, 2.56 g (1.56×10^{-2} mol) of 2,2′-azobis(isobutyronitrile), 1.58 g (6.22×10^{-3} mol) of iodine, 25 mL of toluene at 80 °C.

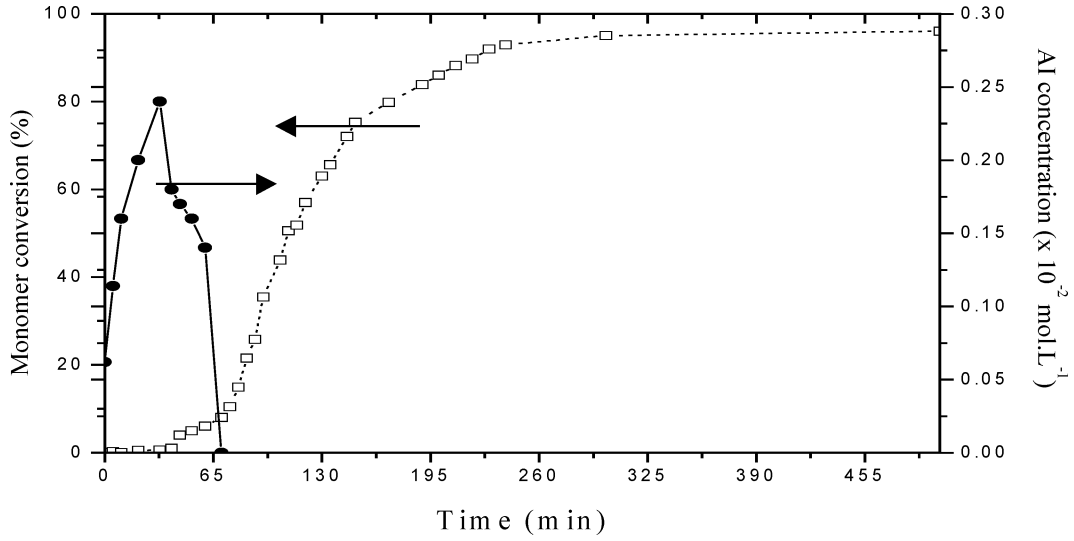


Figure 2. Evolution of monomer conversion (□) and concentration of A−I (●) vs time (min) during reverse iodine transfer polymerization of methyl methacrylate (MMA) at 80 °C. Experimental conditions [MMA]/[AIBN]/[I_2] = 200/2.5/1: 5.000 g (5.00×10^{-2} mol) of MMA, 0.103 g (6.20×10^{-4} mol) of 2,2′-azobis(isobutyronitrile) (AIBN), 0.064 g (2.50×10^{-4} mol) of iodine (I_2). This solution (0.300 g) was added with 0.20 g of deuterated toluene in the NMR tube.

the concentrations) over a relatively short period of time (4 h of reaction). Because iodine (I_2) is a strong oxidizer, it can be reduced by several reactants such as thiols or thiosulfates (eq 2). Thiols are simple molecules, miscible with organic solvents, and able to titrate I_2 solution. Iodine reacts with thiols to give hydriodic acid (HI) and disulfides (RSSR). The discoloration of the solution (from orange to uncolored) permits determination of the equivalent volume during the titration. This type of titration is often used to determine the transfer constants of thiols in telomerization.[71] This method was applied in our case by using a solution of thioglycolic acid in toluene at 6.8×10^{-3} mol L^{-1}. The equivalent volume is around 20 mL at the beginning of the reaction. Figure 1 depicts the evolution of monomer conversion and iodine concentration versus time. The consumption of the monomer is very low until the concentration of iodine becomes negligible. This result indicates that the rate of reaction between radicals and iodine R_c is much higher than the propagation rate R_p.[56] Thus, all the iodine is consumed, whereas only a few percent of monomer has been consumed during this period. It must be noticed that this result agrees well with those obtained in the literature: iodine is an excellent inhibitor of radical polymerization.[63]

Therefore, the inhibition period is correlated with the presence of free iodine in the reaction medium, whereas the concentration of iodine is negligible (not detected by thiol titration) during the polymerization period. However, it is worth mentioning that, in contrast to the observations on RITP of methyl acrylate,[56] if the reaction is left for a long time at 80 °C, free iodine reappears in the reaction medium and this is also confirmed by a visual observation (slight yellow coloration of the reaction medium). This result is presumably due to the thermal homolytic cleavage of P−I (more labile tertiary −C−I bond in PMMA-I than the secondary −C−I bond in poly(methyl acrylate)-I) to give I$^\bullet$ that can recombine with P$^\bullet$ to give P−I or react with another I$^\bullet$ to give I_2, the latter reaction being responsible for the slight yellow recoloration. The extent of this cleavage reaction will be reported in more depth in a separate paper.

To have a more precise knowledge of what happens during the inhibition period between the different species, the reaction was directly performed in a spectrometer and followed on line

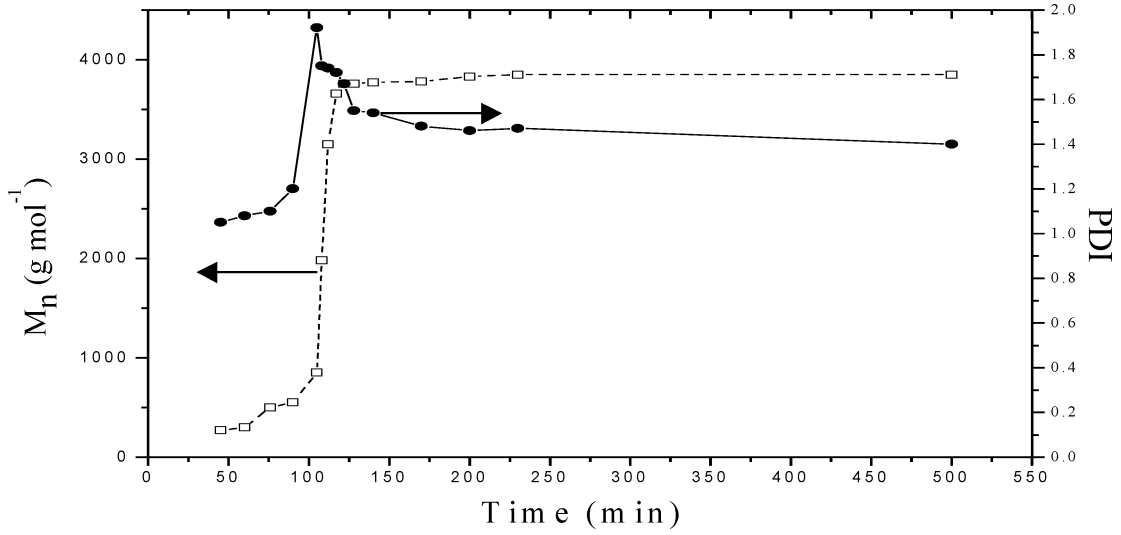


Figure 3. Evolution of number-average molecular weight M_n (□) and polydispersity index PDI = M_w/M_n (●) vs time for reverse iodine transfer polymerization of methyl methacrylate (MMA) at 80 °C in toluene as solvent. Experimental conditions: 25.00 g (2.5×10^{-1} mol) of MMA, 1.28 g (7.8×10^{-3} mol) of 2,2′-azobis(isobutyronitrile) (AIBN), 0.79 g (3.11×10^{-3} mol) of iodine (I_2), and 25 mL of toluene.

by ^{1}H NMR. It allowed us to determine the evolution of the monomer conversion (α) (eq 5) and the concentration of the A−I adduct (eq 6) versus time (Supporting Information)

$$\alpha = 1 - ([MMA]_t/[MMA]_0) = 1 - ((\int^{5.30\&5.95ppm} CH_2{=}C/2)/(\int^{3.5ppm} - OCH_3/3)) \quad (5)$$

in which $[MMA]_t$ and $[MMA]_0$ are the monomer concentrations at a given time t and at $t = 0$, respectively.

$$[A{-}I]_t = [MMA]_0 \times (\int^{1.97ppm} IC(CN)(CH_3)_2/6)/(\int^{3.5ppm} - OCH_3/3) \quad (6)$$

As in the case of RITP of methyl acrylate,[56] two stages can be distinguished during the inhibition period (Figure 2): appearance and disappearance of the A−I adduct.

RITP was also followed by SEC analyses. Aliquots were prepared by dilution in THF at a fixed concentration. Figure 3 represents the evolution of M_n and polydispersity index (PDI) versus time. Two periods are observed. The first period is accompanied by the formation of low-molecular-weight oligomers of low PDI. After this inhibition period, a second period appears where the molecular weight increases quickly. The PDI is maximum between these two periods where two distributions coexist (oligomers and polymers) (Figure 3). During the first stage of the inhibition period (increase of $[A{-}I]_t$), oligomers are not formed (or in very small quantity, undetected by SEC). The oligomer formation only occurs during the second stage of the inhibition period (when $[A{-}I]_t$ decreases) and is correlated with the low consumption of monomer.

Figure 4 shows several SEC chromatograms for RITP of MMA, each plot corresponding to a given monomer conversion. The first chromatogram (A) shows the formation of oligomers during the inhibition period. Such oligomers were also observed in RITP of styrene.[55,67] On the chromatogram (B), it is possible to observe the coexistence of oligomers and polymers. For higher monomer conversions (C, D), the population of oligomers decreases, whereas the population of polymers increases.

In conclusion of this part, the inhibition period correlates with the presence of free iodine in the reaction medium (Figure 1). Moreover, this inhibition period can be divided into two stages

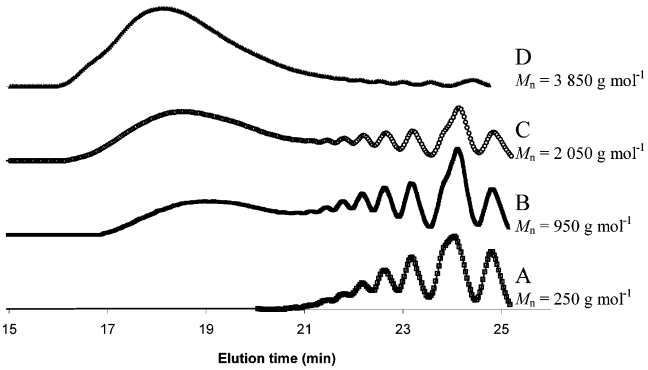


Figure 4. SEC chromatograms for reverse iodine transfer polymerization of methyl methacrylate (MMA) at 80 °C at (A: □) 5%, (B: ◆) 10%, (C: ○) 20%, and (D: ▲) 50% monomer conversion. Experimental conditions: 25.00 g (2.5×10^{-1} mol) of MMA, 1.28 g (7.8×10^{-3} mol) of 2,2′-azobis(isobutyronitrile) (AIBN), 0.79 g (3.11×10^{-3} mol) of iodine (I_2), 25 mL of toluene.

(Figure 2): a first stage where the concentration of the A−I adduct builds up, and a second stage corresponding to the formation of very short A−M_n−I oligomers to the detriment of A−I.

4. Study of the Polymerization Period in RITP of MMA. First, we checked that the assumption of the quasistationary state is applicable to RITP of MMA. For this purpose, we plotted $\ln([M]_0/[M]_t)$ versus time (Figure 5): a linear trend is observed after the inhibition period confirming that the quasistationary state is reached. Thus, the relation of Tolbosky[72] (eq 7) can be used to assess the value of $k_p/(k_t)^{1/2}$. To carry out this calculation, we took into account only the points located after the inhibition period: $\tau = (t - t^{inh})$, where t^{inh} is the time of the inhibition period and t is the reaction time

$$\ln([M]_0/[M]_t) = 2\,k_p \times (f \times [AIBN]_{t,inh})^{1/2}/(k_d \times k_t)^{1/2} \times (1 - \exp(-k_d \times \tau/2)) \quad (7)$$

in which f is the initiator efficiency, k_p the propagation rate constant, $[AIBN]_{t,inh}$ the initiator concentration at the end of the inhibition period, k_d the initiator decomposition rate constant, and k_t the termination rate constant.

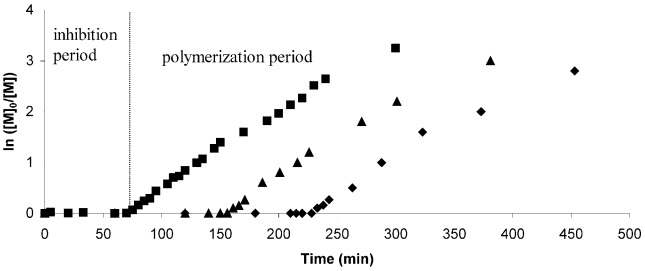


Figure 5. Evolution of $\ln([M]_0/[M]_t)$ vs time for reverse iodine transfer polymerization of methyl methacrylate (MMA) at 80 °C performed with different initial 2,2′-azobis(isobutyronitrile) (AIBN) concentrations: ■ [AIBN] = 0.25 M ([MMA]/[AIBN]/[I_2] = 50/2.6/1), ▲ [AIBN] = 0.20 M ([MMA]/[AIBN]/[I_2] = 50/2/1), ◆ [AIBN] = 0.17 M ([MMA]/[AIBN]/[I_2] = 50/1.75/1). Experimental conditions: 25.00 g (2.5×10^{-1} mol) of MMA, 1.27 g (5.0×10^{-3} mol) of iodine (I_2), and 25 mL of toluene.

The concentration of the initiator in the reaction medium at the end of the inhibition period $[AIBN]_{t,inh}$ is given by eq 8

$$[AIBN]_{t,inh} = [AIBN]_0 \times \exp(-k_d \times t_{inh}) \qquad (8)$$

The obtained value of $k_p/(k_t)^{1/2} = 0.165$ $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ (see Supporting Information) is close to the value given in the literature in the case of the polymerization of MMA[73−76] (at 80 °C, $k_p/(k_t)^{1/2} = 0.177$ $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ according to IUPAC[74,75] values of k_p and k_t at ambient pressure for bulk polymerization of MMA, and $k_p/(k_t)^{1/2} = 0.190$ $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ according to Boutevin[73] et al. in telomerization of MMA in benzene). So, the consumption of the monomer in RITP of MMA (after the inhibition period) follows the traditional laws of radical polymerization.

Last, we decided to follow the evolution of molecular weight (M_n) and polydispersity index (PDI) versus time for three different targeted molecular weights (4200, 10 200 and 20 200 g mol^{-1}). The evolution of molecular weights versus monomer conversion is represented in Figure 6. At low monomer conversion, the upward deviation of $M_{n,experimental}$ (measured by SEC analysis) compared to $M_{n,theoretical}$ (calculated by $M_{n,theoretical} = [MMA]_0 \times M^{MMA} \times$ conversion/$(2 \times [I_2]_0) + M^{A-I}$, in which $M^{MMA} = 100$ g mol^{-1}, and $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}) accounts for a low degenerative chain transfer constant $C_{ex} = k_{ex}/k_p$. Indeed, the iodinated species at the end of the inhibition period are very small iodotelomers (essentially $n < 6$ according to the results of Figure 4). These small telomers, i.e., A−M_n−I, are gradually consumed by degenerative chain transfer during the polymerization period to form a distinctive population of polymers of higher molecular weights. The molecular weights increase with conversion and approach the theoretical values at high conversion (90%). Such a behavior corresponds to a degenerative chain transfer constant C_{ex} slightly higher than unity. Furthermore, the decrease of the polydispersity index (PDI) versus monomer conversion confirms that C_{ex} is higher than unity.[77−79] The value of C_{ex} can further be assessed by the approximation $C_{ex} \cong [MMA]_0/(2\nu_0[I_2]_0)$ with $\nu_0 = (M_{n,x=0} - M^{A-I})/M^{MMA}$ where $M_{n,x=0}$ is the $M_{n,SEC}$ extrapolated at zero conversion.[56] Thus, in the case of $[MMA]_0/[I_2]_0 = 400$ ($M_{n,targeted}$ = 20 200 g mol^{-1}), extrapolation from Figure 6 gives $\nu_0 = (8000 - 195)/100 = 78$, leading to a degenerative chain transfer constant $C_{ex} = 2.6$ for PMMA-I at 80 °C. In an ideal case (i.e., in the absence of any side reactions), the minimal polydispersity index that can be obtained for the PMMA chains prepared by this process can be estimated by PDI = $1 + (1/C_{ex}) = 1.38$,[77] which is consistent with the experimental values indicated in Table 2 (PDI in the range of 1.5−1.6 at high monomer conversion). According to this result, it is possible to establish the order of reactivity: poly(styrene)-I ($C_{ex} = 3.6$ at 80 °C)[36] > PMMA-I ($C_{ex} = 2.6$ at 80 °C) > poly(methyl acrylate)-I ($C_{ex} = 2.2$ at 70 °C).[56]

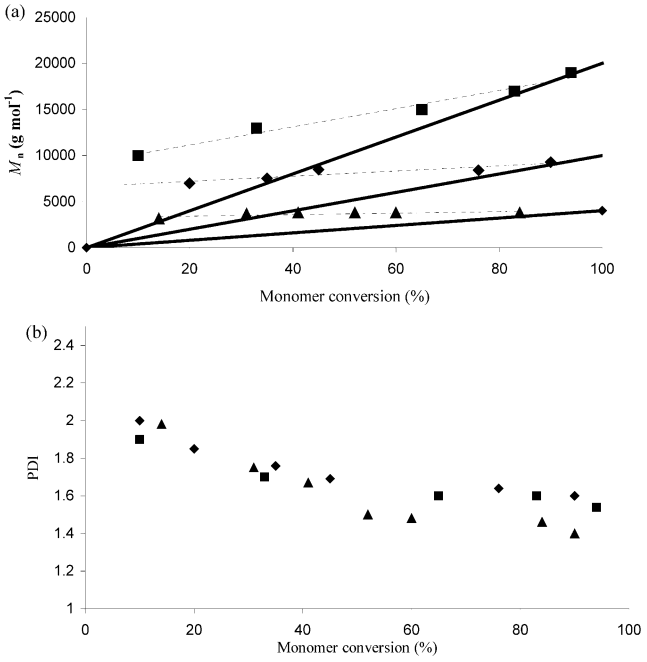


Figure 6. Polymerization of methyl methacrylate (MMA) by reverse iodine transfer polymerization at 80 °C: (a) Evolution of number-average molecular weight (M_n) and (b) evolution of polydispersity index (PDI = M_w/M_n) vs monomer conversion for different targeted molecular weights (▲ $M_{n,targeted}$ = 4200 g mol^{-1}, ◆ $M_{n,targeted}$ = 10 200 g mol^{-1}, ■ $M_{n,targeted}$ = 20 200 g mol^{-1}). Experimental values determined by SEC analysis (PMMA calibration). Theoretical line (bold line) calculated by $M_{n,theoretical} = [MMA]_0 \times M^{MMA} \times$ conversion/$(2 \times [I_2]_0) + M^{A-I}$, in which $[I_2]_0$ is the initial concentration of iodine, $M^{MMA} = 100$ g mol^{-1}, and $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}.

5. Confirmation of the Structure of PMMA Polymer Chains Prepared by RITP. After the study of the RITP mechanism, the synthesis of a polymer of low molecular weight has been performed at 80 °C in toluene with AIBN as initiator. This polymer, after precipitation in pentane, was characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF, and elemental analyses. The aim of this part is to confirm the structure of the polymer according to the mechanism previously described, i.e., A−M_n−I structure (Scheme 2). The presence of the iodide ω-chain end is confirmed by the methylene (−CH_2−C(CH_3)(CO_2CH_3)-I) in the β position of iodine (e) at 2.80 ppm, which is consistent with chemical shifts of −CH_2−C(CH_3)(CO_2CH_3)-X (X═Cl, Br) given in the literature.[80,81] The two methyl groups of the radical initiator moiety (−C(CN)(CH_3)$_2$) appear at 1.20 ppm (a), and the other signals centered at 0.80, 1.80, and 3.50 ppm are assigned to the methyl −CH_3 (b), the methylene −CH_2− (c), and the methoxy −OCH_3 (d) groups of the monomer units in the PMMA chain (Figure 7). Thus, it is possible to calculate the mean number degree of polymerization DP_n by ^{1}H NMR (eq 9) and to evaluate the iodine functionality of the chains F^{iodine} (i.e., the proportion of chains end-capped with iodine) (eq 10)

$$DP_n = \int(-OCH_3^{(d)}/3)/\int(-C(CN)(CH_3)_2{}^{(a)}/6) \qquad (9)$$

$$F^{iodine} = \int(-CH_2-^{(e)}/2)/\int(-C(CN)(CH_3)_2{}^{(a)}/6) \qquad (10)$$

^{13}C NMR analysis confirms the presence of the initiator moiety at the α-chain end: the signal of the cyano group −CN

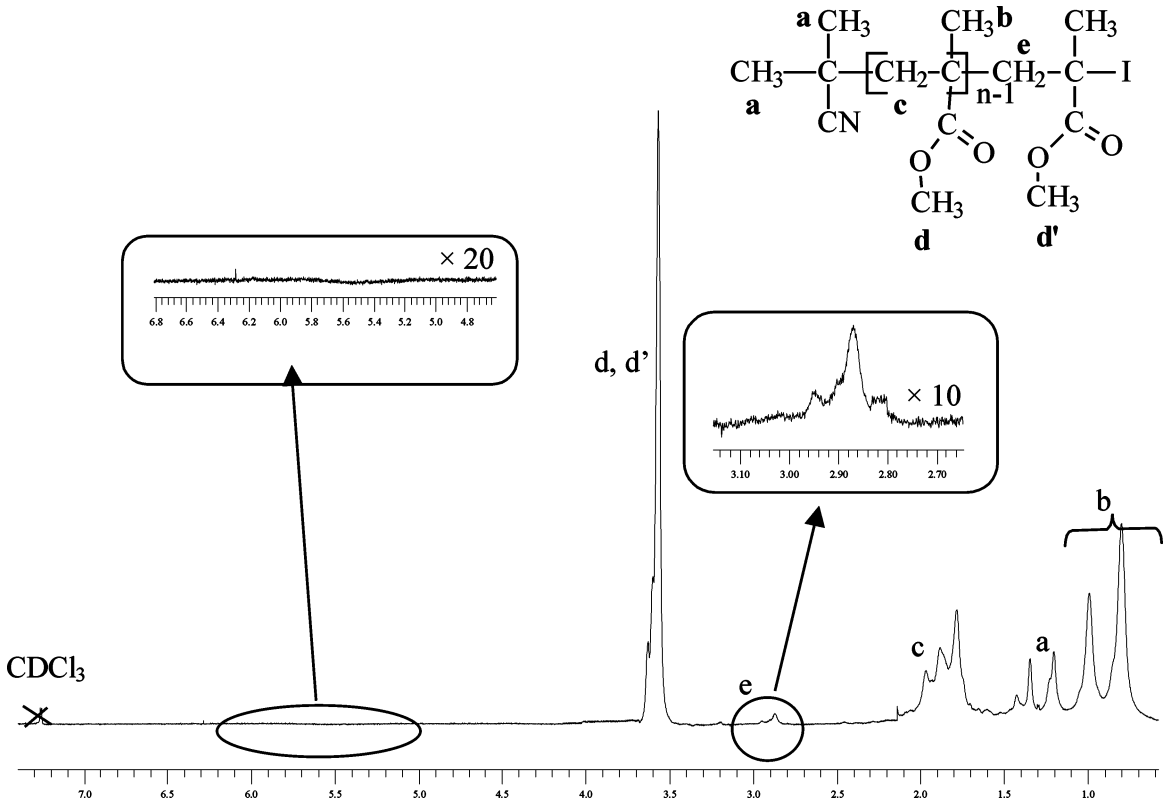


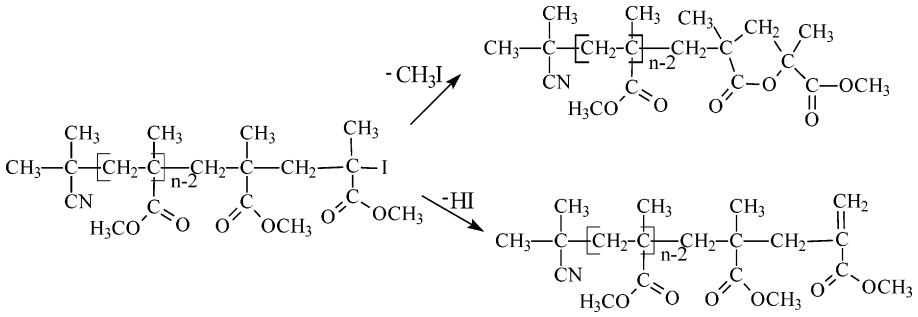
Figure 7. ^{1}H NMR spectrum of a low-molecular-weight poly(methyl methacrylate)-I (M_n = 2300 g mol^{-1}, M_w/M_n = 1.4) in $CDCl_3$.

Table 3. Determination of the Iodine Functionality (F^{iodine}) of a Poly(methyl methacrylate) Oligomer Obtained by Reverse Iodine Transfer Polymerization[a]

						iodine functionality, F^{iodine} (%)		
$M_{n,targeted}$[b] (g mol^{-1})	ratio $[AIBN]_0/[I_2]_0$	conversion[c] (%)	$M_{n,SEC}$[d] ($DP_{n,SEC}$)	PDI[d]	DP_n (^{1}H and ^{13}C NMR)	theoretical[e]	by NMR (^{1}H and ^{13}C)	by elemental analysis
3 200	1.7	70	2 300 (*21*)	1.4	20 (*20*)	94	95 (*96*)	95

[a] Polymerization of methyl methacrylate (MMA) in toluene at 80 °C in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator and iodine (I_2). [b] Calculated by $M_{n,targeted} = [MMA]_0 \times M^{MMA}/(2 \times [I_2]_0) + M^{A-I}$, where M^{MMA} = 100 g mol^{-1}, and $M^{A-I} = M^{chain-ends}$ = 195 g mol^{-1}. [c] Monomer conversion determined by gas chromatography. [d] $M_{n,experimental}$ and PDI measured by size exclusion chromatography analysis (PMMA calibration). [e] Evaluated by F^{iodine}(theoretical) = $2 \times [I_2]_0/(2 \times [I_2]_0 + 2f \times \Delta AIBN)$.

Scheme 3. Reactions of Degradation of Poly(methyl methacrylate)-I Polymer Chains Observed during Mass-Assisted Laser Desorption Ionization Time-of-Flight Analysis (MALDI-TOF)



appears toward 126 ppm, and the signals of the two methyl groups $-(CH_3)_2(CN)C-$ appear at 15 ppm. The methylene $-CH_2-$ of the monomer units in PMMA appears at 44 ppm. The presence of the iodide ω-chain end is confirmed by the signal at 38 ppm.[82] The absence of the carbon−carbon double bond ($C{=}C$) is confirmed by the absence of signal toward 130 ppm in ^{13}C NMR and the absence of the signals around 5.4 and 6.1 ppm in ^{1}H NMR.[83] From this analysis, the DP_n can also be assessed (eq 11), and the iodine functionality F^{iodine} can be assessed too (eq 12) (in ^{13}C NMR, a long relaxation time of 10 s was chosen to allow quantitative analysis). The experimental values are reported in Table 3

$$DP_n = \int -CH_2-^{44ppm} / \int -CN^{126ppm} \qquad (11)$$

$$F^{iodine} = \int -C-I^{38ppm} / \int -CN^{126ppm} \qquad (12)$$

F^{iodine} could also be assessed by a mass balance based on the results of elemental analyses (eq 13) and titration of free iodine

by ionic chromatography in liquid phase (Supporting Information)

$$F^{\text{iodine}} = (\text{wt \%}_{\text{iodine,total}} - \text{wt \%}_{\text{iodine,free}})/(\text{wt \%}_{\text{iodine,theoretical}}) \quad (13)$$

in which wt $\%_{\text{iodine,total}}$ is the total percentage of iodine in the sample, wt $\%_{\text{iodine,free}}$ is the percentage of free iodine in the sample (traces of HI and I_2), and wt $\%_{\text{iodine,theoretical}}$ is the theoretical percentage of iodine in the sample, calculated by wt $\%_{\text{iodine,theoretical}} = M^{\text{iodine atom}} \times 100/M_n$, in which $M^{\text{iodine atom}} = 127$ g mol^{-1} and M_n is the number-average molecular weight of the sample.

The experimental values of F^{iodine} should be compared to the theoretical iodine functionality, F^{iodine} (theoretical), given by eq 14

$$F^{\text{iodine}}(\text{theoretical}) = 2 \times [I_2]_0/(2 \times [I_2]_0 + 2f \times \Delta\text{AIBN}) \quad (14)$$

in which ΔAIBN is the excess amount of AIBN used to initiate and propagate the polymerization during the polymerization period (τ_{polym}) (after the inhibition period) (Supporting Information).

The experimental values of F^{iodine} (about 95%) determined by the different methods (^{1}H NMR, ^{13}C NMR, and elemental analysis) are in good agreement with the calculated theoretical value (94%) (Table 3).

The structure of the polymers was further studied by MALDI-TOF analysis performed in reflectron mode (Supporting Information). However, in contrast to poly(methyl acrylate)-I,[56] PMMA-I chains undergo very significant modifications during the analysis (elimination of CH_3I, elimination of HI) (Scheme 3), and therefore, the A−M_n−I structure could not be directly checked by this method.

In conclusion, by coupling various analyses such as ^{1}H and ^{13}C NMR, elemental analysis, and titration of free iodine by thiols, it was demonstrated that the main structure is as expected, i.e., A−M_n−I.

Conclusions

The mechanism of the RITP of MMA involves two distinct periods: (i) an inhibition period that corresponds to the consumption of free iodine (I_2) in the reaction medium to give A−I adduct in a first stage and very short A−M_n−I oligomers in a second stage; (ii) after the disappearance of free iodine (I_2), a second period takes place to give A−M_n−I polymers. In RITP, two parameters are very important: first, the quantity of iodine introduced in the medium allows to control the molecular weight of the polymers (various polymers from 2000 to 20 000 g mol^{-1} were synthesized); second, the amount of initiator determines the overall duration of the process (inhibition time and kinetics of polymerization). In the second part of this study, the structure of the polymers has been confirmed by various analyses (NMR spectroscopy, elemental analyses, and titration of iodine). The structure obtained by this polymerization method agrees with the theoretical A−M_n−I structure, and so, this process permits easy synthesizing of functional PMMA-I polymers of controlled molecular weights. In a forthcoming work, this process will be used for the synthesis of block copolymers.

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Supporting Information Available: Kinetics of polymerization, i.e., evolution of $[A-I]_t$ and $[A-M_n-I]_t$ vs time, evolution of functionality in iodine vs conversion, evolution of $\ln(M_0/M)$ vs $(1 - \exp(-k_d \times \tau/2))$ for RITP of MMA performed with [AIBN] = 0.25, 0.20, and 0.17 M at 80 °C and summary of values $k_p/k_{te}^{1/2}$ ($L^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$), ^{13}C NMR spectrum, and elemental analyses of oligomers PMMA-I, calculation of the theoretical functionality in iodine of oligomers PMMA-I, MALDI-TOF spectrum, peak assignments, and simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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