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Abstract

Iodo-terminated polystyrene and poly(methyl acrylate) (PMA-I) were synthesized by reverse iodine transfer polymerization. The resulting polymers were coupled by atom transfer radical coupling using Cu(I)/linear amino-ligand catalysts in the presence of reducing Cu(0). The efficiency of the coupling reaction is discussed as a function of various factors, namely, the Cu(0) particle sizes, the number of nitrogen present in the ligand structure, the type of halogen associated with Cu(I) (CuX, X = I, Br, Cl), the nature of the polymer and the nature of the chain ends. In particular, a quantitative coupling (100%) was obtained with a CuBr/HMTETA system in the presence of nanosized Cu(0) for PMA-I, thus opening for the first time a facile route to telechelic and multiblock poly(acrylate)-based structures.

Keywords: Reverse iodine transfer polymerization (RITP); Atom transfer radical coupling (ATRC); Poly(acrylate)

1. Introduction

Atom transfer radical coupling (ATRC) is a recent method for coupling polymers having at least one halide functionalized chain end. Such reactions have raised recent interest as a consequence of the strong development of the controlled radical polymerization (CRP) field and more specifically the atom transfer radical polymerization (ATRP) technique leading to polymers bearing bromine functionalities as terminal groups. Many groups have investigated the possibility to use ATRC with various bromo-polymers for chain extension purposes or telechelic polymer synthesis. Studies have mainly been carried out with polystyrene. Initially, α,ω-dibromo-polystyrene and ω-bromo-polystyrene ATRC reactions were studied by Yoshikawa et al. [1] before being further investigated by others groups [2−4]. Radical coupling of poly(butyl α-fluoroacrylate) and poly(alkyl acrylate) type polymers has also been reported by Otazaghine et al. [5,6] and Sarbu et al. [7] with more or less success depending on the nature of the polymer. In particular, it was necessary to activate the chain end by adjunction of styrene as final monomer units in the case of poly(methyl acrylate). ATRC technique is also a powerful tool giving potentially access to diblock and multiblock architectures containing blocks of controlled length. This way was recently investigated by Nagelsdiek et al. [8] onto poly(phenylene oxide)-*b*-polystyrene (PPO-*b*-PS) diblock and (PS-*b*-PPO-*b*-PS) triblock in order to obtain tri- and multiblock copolymers, respectively.

The ATRC process relies on the *in situ* formation of macroradicals by an atom transfer radical equilibrium and the subsequent termination reaction of these species by coupling in the presence of a reducing agent. Indeed, most ATRC techniques described so far are based on the use of copper in zero oxidation state as a reducing agent. The presence of Cu(0) in an ATRC system leads to the displacement of the equilibrium by the reduction of Cu(II) species into Cu(I) species. Thus, the equilibrium is strongly shifted toward the formation of active macroradicals whose higher concentration favors irreversible termination reaction by coupling (Scheme 1). As

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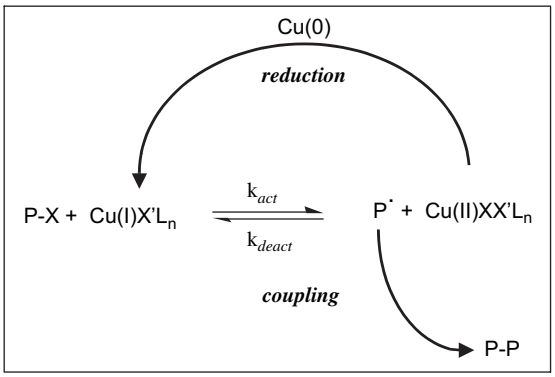


Scheme 1. General reaction scheme for copper-mediated atom transfer radical coupling (ATRC) (X and X′ are halide atoms, P is a polymer and L_n is a ligand).

shown in Scheme 1, the presence of the Cu(I) species is necessary to achieve activation of the carbon−halide bond although some authors did report successful ATRC with Cu(0) alone [3,5,6].

The growing importance of the iodine transfer polymerization (ITP) technique [9−18] and of its counterpart the reverse iodine transfer polymerization (RITP) technique, recently developed in our group [19−23] for the CRP of various monomers, leads to the synthesis of iodine-functionalized polymers. It appears interesting to apply the ATRC method to iodo-polymers. Indeed coupling reactions between two low molecular weight molecules containing iodine are well known. These coupling reactions can be achieved through UV [24,25] or electrochemical activation [26], but mostly through the use of metals. Among them, copper has been mainly used initially for the coupling between iodo-aromatic molecules (Ullmann coupling) or between iodo-aromatic molecules and perfluoroalkyl iodides [27−29]. Recently, some authors also used copper with iodo-alkyl compounds [30,31]. Other metals, most of them being transition metals, have also been reported for the coupling of perfluoroalkyl iodides or alkyl iodides: Mg [32], Zn [33−35], Mn [36], V [37], Fe [37], Ni [37], In [38], La [39], Sa [40] and Yb [40]. As mentioned above, all these reactions take place between low molecular weight iodine-containing molecules but, to the best of our knowledge, this approach has never been investigated on iodo-polymers. Since successful copper-mediated ATRC has been described for bromo-polymers, we focused on the use of this metal. One can expect that the replacement of bromine by iodine at the chain end should help coupling by ATRC in some cases, such as for poly(methyl acrylate), because of the weakest bond energy of the carbon−iodine bond compared to that of the carbon−bromine bond [41] (Table 1) which should favor the active radical species formation.

Table 1
Bond energy and bond length for carbon−halide bonds (C sp^3)

Bond type	Bond energy (kJ/mol)	Bond length (Å)
C—Cl	330	1.79
C—Br	275	1.97
C—I	220	2.16

In this article, we wish to report the first successful use of ATRC technique for the coupling of ω-iodo-polystyrene and ω-iodo-poly(methyl acrylate) previously synthesized by RITP which gives potential access to new telechelic polymers or multiblock architectures starting from iodo-functionalized polymers.

2. Experimental section

2.1. Materials

Styrene (Sty, Aldrich, 99%), methyl acrylate (MA, Aldrich, 99%) and toluene (Carlo Erba) were distilled under reduced pressure prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was recrystallized from methanol prior to use. Iodine (I_2, Aldrich, 99.8%), tetrahydrofuran (THF, Riedel-de Haën), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%), 2,2′-bipyridyl (Bipy, Aldrich, 99%), copper powder dendritic 3 μm (Cu(0) 3 μm, Aldrich, 99.7%), copper nanopowder (Cu(0) nano, Aldrich, 99.8%) and activated neutral aluminum oxide (Al_2O_3 50−200 μm, Acros) were used as received. Copper(I) iodide (CuI, Aldrich, 98%), copper(I) bromide (CuBr, Aldrich, 98%) and copper(I) chloride (CuCl, Aldrich, ≥98%) were purified according to the procedure previously described in the literature [42] prior to use and were stored under argon.

2.2. Reverse iodine transfer polymerization

In a typical procedure of styrene polymerization by RITP process, Sty (6 g, 57.6 mmol), toluene (7.5 ml), AIBN (335 mg, 2.04 mmol) and iodine (304 mg, 1.20 mmol) were introduced in a Schlenk flask. After three freeze−thaw pump cycles, the flask was heated at 70 °C in an oil bath. The polymerization was conducted in the dark, under argon atmosphere with magnetic stirring for 24 h. 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 $CDCl_3$ by using the integrals of the resonance signals of the monomer and the polymer, respectively. The polymer was recovered by precipitation in cold methanol and dried under vacuum (10^{-2} mbar) at 25 °C. Molecular weights were determined by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy by using the integral of the methine proton (Fig. 1, I_1) at the iodine chain end (4.5−4.8 ppm) [12] and the integral of the resonance signal of aromatic protons in the polymer chain (Fig. 1, I_2). Results: styrene conversion = 54%, $M_{n,theoretical}$ = 1520 g mol^{-1}, $M_{n,SEC}$ = 1750 g mol^{-1}, $M_{w,SEC}/M_{n,SEC}$ = 1.23 and $M_{n,NMR}$ = 1600 g mol^{-1}.

The procedure for the reverse iodine transfer polymerization of methyl acrylate was similar to that of styrene except for the calculation of the molecular weights determined by ^{1}H NMR spectroscopy that was based on the integral of the methine proton at the iodine chain end (4.5 ppm) [20] (Fig. 2, I_3) and the integral of the resonance signal of methyl

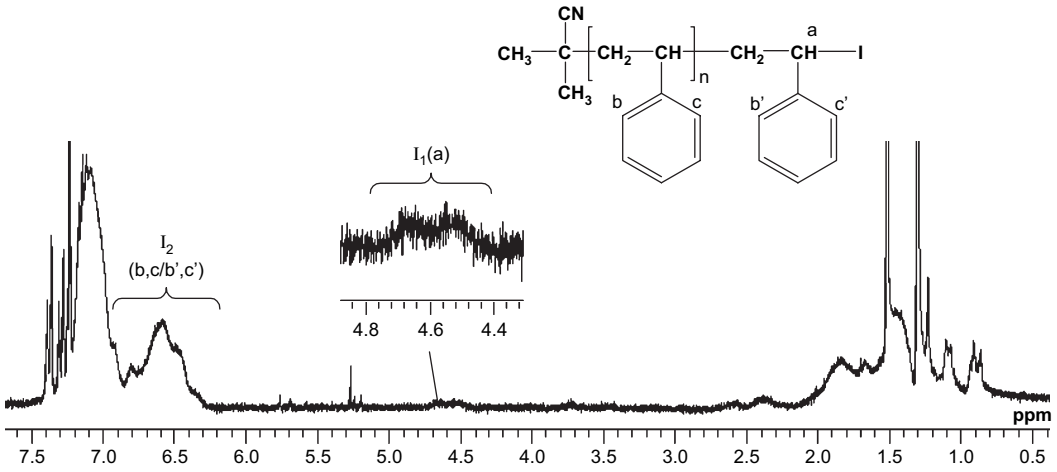


Fig. 1. ^{1}H NMR spectrum in $CDCl_3$ of a polystyrene sample synthesized by RITP process in toluene and precipitated in cold MeOH ([styrene] = 4 M, [AIBN] = 0.14 M, $[I_2] = 8.5 \times 10^{-2}$ M, 70 °C, 24 h, monomer conversion 54%, $M_{n,theoretical} = [(m_{styrene} \times \text{conversion})/(2 \times n_{I2}) + M_{chain\ ends}] = 1520$ g mol^{-1} with $M_{chain\ ends} = 195$ g mol^{-1}, $M_{n,SEC} = 1750$ g mol^{-1}, $M_{n,NMR} = [(I_2 \times M_{styrene})/(2I_1) + M_{chain\ ends}] = 1600$ g mol^{-1}).

protons in the polymer chain (Fig. 2, I_2). The crude poly(methyl acrylate) solution (monomer conversion >94%) was used for ATRC without purification.

2.3. Atom transfer radical coupling

In a typical coupling procedure, ω-iodo-polystyrene, PSty-I ($M_{n,SEC} = 2300$ g mol^{-1}, $M_{p,SEC} = 3750$ g mol^{-1}, $M_{w,SEC}/M_{n,SEC} = 1.60$) (0.5 g, 0.22 mmol) synthesized by RITP as described above, CuBr (31 mg, 0.22 mmol), nanosized copper (56 mg, 0.88 mmol), HMTETA (101 mg, 0.44 mmol) and 5 ml of toluene were charged into a Schlenk flask. The flask was flushed under argon flow, placed on a magnetic stirrer plate and sealed with septum. When the polymer was completely dissolved, three freeze−thaw pump cycles were performed and the flask was placed under argon atmosphere in an oil bath with magnetic stirring at 75 °C overnight. An aliquot of the reaction medium was filtered through a column filled with aluminum oxide to remove the catalyst, evaporated under vacuum, diluted in THF and filtered through a 0.20 μm SEC filter prior to SEC injection; $M_{n,SEC} = 4340$ g mol^{-1}, $M_{p,SEC} = 7120$ g mol^{-1} and $M_{w,SEC}/M_{n,SEC} = 1.55$. The efficiency of coupling ($x_c = 0.94$) was calculated from the molecular weight of the polymeric precursor $M_{n,0}$ and the coupling

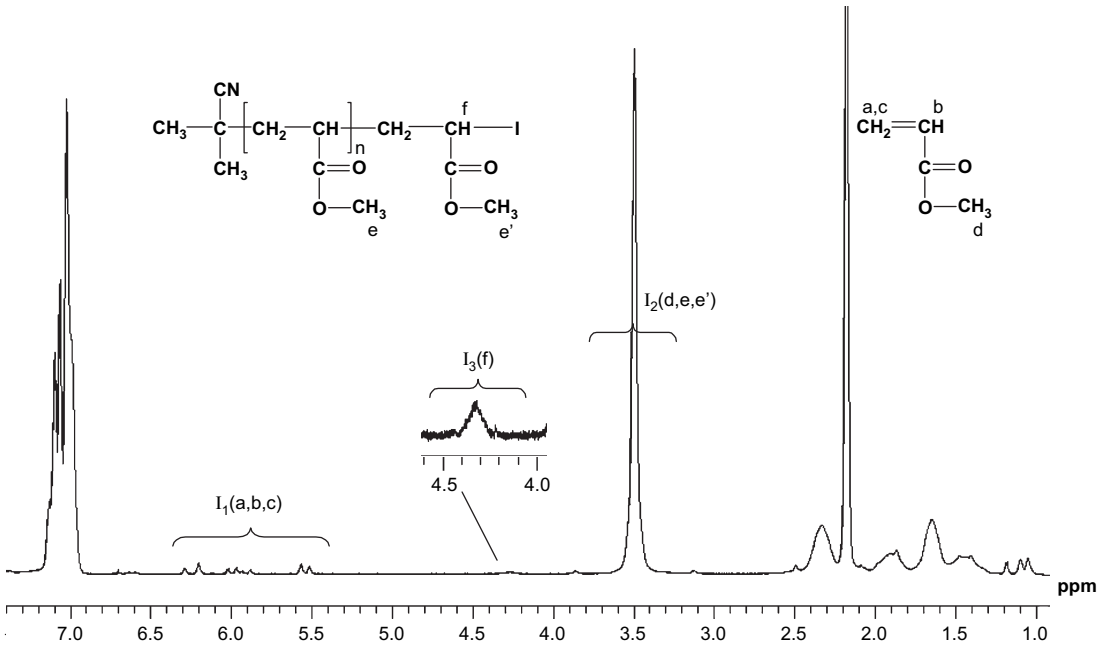


Fig. 2. ^{1}H NMR spectrum in $CDCl_3$ of a crude poly(methyl acrylate) sample synthesized by RITP process in toluene ([methyl acrylate] = 5 M, [AIBN] = 7.4×10^{-2} M, $[I_2] = 4.4 \times 10^{-2}$ M, 70 °C, 22 h, monomer conversion = $(1 - I_1/I_2) = 94\%$, $M_{n,theoretical} = [([\text{methyl acrylate}] \times \text{conversion} \times M_{methyl\ acrylate})/(2 \times n_{I2}) + M_{chain\ ends}] = 4790$ g mol^{-1} with $M_{chain\ ends} = 195$ g mol^{-1}, $M_{n,SEC} = 4450$ g mol^{-1}, $M_{n,NMR} = [(I_2 \times \text{conversion} \times M_{methyl\ acrylate})/(3 \times I_3) + M_{chain\ ends}] = 4220$ g mol^{-1}).

product M_n using Eq. (1) [4]. A value of $x_c = 0.95$ was obtained if M_p was used instead of M_n.

$$x_c = 2 \times \left(1 - \frac{M_{n,0}}{M_n}\right) \quad (1)$$

2.4. Characterizations

Size exclusion chromatography (SEC) was performed on samples diluted in tetrahydrofuran, with a Spectra Physics Instruments SP8810 pump equipped with a Shodex Rise-61 refractometer detector, and two 300 mm columns thermostated at 30 °C (columns mixed-C PL-gel 5 μm from Polymer Laboratories: 2×10^2–2×10^6 g mol^{-1} molecular weight range). Tetrahydrofuran was used as an eluent at a flow rate of 1.0 ml min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories and Mark Houwink coefficients for polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$) [43], for poly(methyl acrylate) ($K = 19.5 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.660$) [44] and for poly(*n*-butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.700$) [43] were used for the calculations. ^{1}H NMR analysis was performed on a Bruker AVANCE 250 (250 MHz) in $CDCl_3$.

3. Results and discussion

Atom transfer radical coupling (ATRC) reactions are based on ATRP systems with two main differences: the absence of monomer in the reaction medium since the coupling between two macroradical species is targeted, and the adjunction of reducing species to shift the equilibrium toward the formation of macroradicals. Like in ATRP, this equilibrium is strongly influenced by the choice of the ligand, transition metal and solvent polarity (Scheme 1). Some studies related to fundamental understanding of ATRP have been carried out, mainly by Matyjaszewski et al. [45–48] in order to express the activation (k_{act}) and deactivation (k_{deact}) rate constants and the corresponding equilibrium constant ($K_{ATRP} = k_{act}/k_{deact} \approx K_{ATRC}$ in our case) as a result of various contributions: electron transfer between metal complexes (Cu(I)X/$L_n \rightarrow$ [Cu(II)X/L_n]$^+ + e^-$), electron affinity of the halogen ($X^\bullet + e^- \rightarrow X^-$), dissociation energy of the carbon–halide bond and the halogenophilicity of the copper/ligand complex ($X^- +$ [Cu(II)X/L_n]$^+ \rightarrow$ Cu(II)X_2/L_n). As noted above, an increase of the macroradical concentration is desirable in ATRC reaction to improve the rate of coupling. Keeping this in mind, the conditions and reactants used should guaranty high k_{act} and concomitantly low k_{deact} values to favor the coupling reaction. In the following discussion, we will focus on some factors that can play a key role in the ATRC equilibrium and so determine the reaction efficiency.

3.1. Effect of the presence of Cu(I)X catalyst

Some authors have reported the possibility to couple bromine-terminated polymers synthesized via ATRP process without the use of the copper (I) activating agent [3,5,6].

Table 2
ATRC in the absence of added Cu(I)X catalyst

Expt	Ligand	Time (h)	T (°C)	$M_{n,0}$ (g mol^{-1})	x_c	Ref.
1[a]	PMDETA	2	90	8600	0.8	[3]
2[b]	PMDETA	25	70	12 800	0.0	This work
3[b]	Bipyridine	25	75	12 800	0.3	This work

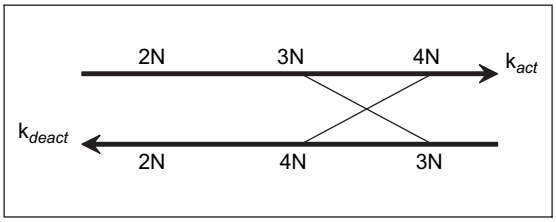
Each run was carried out in anisole with Cu(0) 3 μm and the following molar ratio.
[a] [PSty-Br]$_0$:[L]$_0$:[Cu(0)]$_0$ = 1:2:2.
[b] [PSty-I]$_0$:[L]$_0$:[Cu(0)]$_0$ = 1:2:4.

This appeared to be interesting as it would allow to work with a simplified and ''greener'' reaction system. We tried to couple a PSty-I using the described conditions: anisole as the solvent and PMDETA as the ligand. As can be seen in Table 2, despite similar conditions and molecular weight for the starting polymers, we could not get more than 0.3 as efficiency for the coupling of iodo-terminated polystyrene (runs 2 and 3) compared to the 0.8 for bromo-functionalized polystyrene (run 1). This difference is unexpected since the bond strength of the corresponding carbon–halide bond should favor the iodo-polymer coupling. Actually, this result might be attributed to the presence of residual Cu(I) in the PSty-Br synthesized by ATRP. Indeed, the amount of residual copper in the polymer was reported to range from 100 to 800 ppm depending on the catalytic system and treatment used [49]. The little coupling observed in run 3 could be due to *in situ* formation of traces of Cu(I) in the reaction medium as already assumed by Nagelsdiek et al. [8]. Since no or few coupling was obtained without Cu(I)X, the experiments that followed were all carried out in the presence of Cu(I)X catalysts.

3.2. Effect of the ligand

The nature and architecture of the ligand used in ATRC process do play an important role and is partially responsible for the K_{ATRC} value. Considering the literature [45–48], one expects that ligands containing more nitrogen atoms in their structure will activate the ATRC process more efficiently and that cyclic derivates will be more activating than linear ones. However, as was described by Matyjaszewski et al. [46] for ATRP reactions, the deactivation rate constant does not follow necessarily the inverse order since k_{deact} depends on the halogenophilicity of the copper/ligand complex. In the considered conditions and for linear aliphatic ligands, the authors discussed k_{act} and k_{deact} values as a function of the number of nitrogen (N) atoms [46]. This is roughly illustrated in Scheme 2. As a consequence, it can be seen that ligands exhibiting two nitrogens should be avoided for ATRC reaction since they have both the lowest activation rate constant and the highest deactivation one. It is also noteworthy that predictions are not possible for 3N and 4N containing ligands since their positions are inverted on the two scales and that their overall efficiency in ATRC will rely on the relative values of each constants.

We have used three linear ligands, namely, 2,2′-bipyridyl (2N), PMDETA (3N) and HMTETA (4N) with either PSty-I



Scheme 2. Ligands classification considering their k_{act} and k_{deact} values as a function of the number of nitrogen atoms (N) in the structure.

Table 3
Effect of the ligand

Expt	Ligand	Cu(0)	Cu(I)	Time (h)	T (°C)	$M_{n,0}$ (g mol^{-1})	x_c
1[a]	Bipyridine	3 μm	CuI	31	70	1750	0.2
2[a]	PMDETA	3 μm	CuI	31	70	1750	0.54
3[a]	PMDETA	Nano	CuBr	40	75	2300	0.69
4[a]	HMTETA	Nano	CuBr	1.5	75	2300	0.94
5[b]	PMDETA	Nano	CuBr	40	75	4450	0.68
6[b]	HMTETA	Nano	CuBr	4.5	75	4450	1

Each run was carried out in toluene with the following molar ratio.
[a] $[PSty\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)]_0 = 1:2:4:1$.
[b] $[PMA\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)]_0 = 1:2:4:1$.

or PMA-I polymers. Conditions and results are given in Table 3. The expected results were confirmed with an efficiency in the following order: 2,2′-bipyridyl < PMDETA < HMTETA. Quantitative coupling in short time was only achieved with HMTETA. It is interesting to note that both efficiency and reaction rate are higher for HMTETA instead of PMDETA with x_c between 0.9 and 1 in less than 5 h and x_c around 0.7 in 40 h, respectively (Table 3, runs 3−6). These observations are consistent with the coupling results obtained by other groups with bromo-terminated polymers [1,8]. The shift of the molecular weight distributions is shown in Fig. 3 in the case of PSty-I coupling (Table 3, run 4).

In order to assess more precisely the kinetic aspect of the coupling as a function of the ligand used, experiments have been achieved under the same conditions as those described for runs 3−6 in Table 3. Results are shown in Fig. 4. For PMA-I, it is confirmed that the coupling reaction is much faster with HMTETA (full circles) than with PMDETA (full triangles). The use of HMTETA leads to a very fast reaction since it appears that quantitative coupling is already obtained after 1.5 h with PSty-I (empty circles) and 4.5 h with PMA-I (full circles). The latter is a very short reaction time compared to those observed using bromo-poly(acrylates) as will be further discussed in Section 3.5.

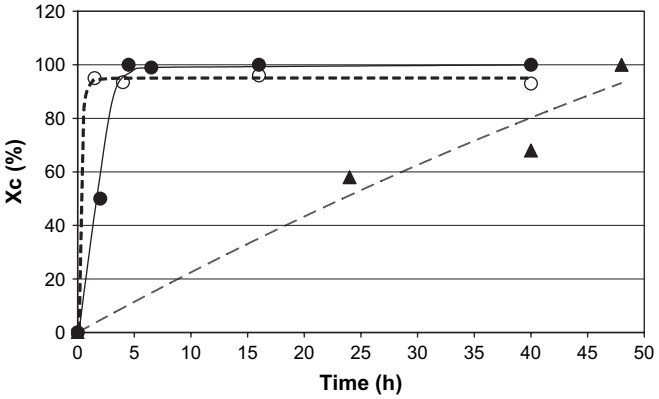


Fig. 4. Coupling kinetic study as a function of the ligand: PMA-I ($M_{n,SEC}$ = 4450 g mol^{-1}) with PMDETA (full triangles), PMA-I with HMTETA (full circles) and PSty-I ($M_{n,SEC}$ = 2300 g mol^{-1}) with HMTETA (empty circles). Experiments were carried out with Cu(0) nanosized and CuBr in toluene at 75 °C with the following molar ratio: $[PSty\text{-}I]_0$ or $[PMA\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)] = 1:2:4:1$.

3.3. Effect of the halogen X used in Cu(I)X catalyst

Experiments were conducted with Cu(I)X compounds with X = Cl, Br or I. The results are listed in Table 4. The halogen at the polymer chain end being iodine, one could expect that CuI is suitable. Runs 1 and 2 clearly show that it is not the case since starting from the same PSty-I (M_n = 1750 g mol^{-1}), x_c = 0.54 after 31 h with CuI compared to x_c = 0.90 after 22 h with CuBr. Other runs carried out with PMA-I confirm this trend with CuCl giving even a better efficiency and a faster reaction than CuBr. Thus, the Cu(I)X compounds for ATRC of iodo-functionalized polymers can be classified as follows: CuCl > CuBr > CuI. No comparative result was found in the literature since all the described ATRC reactions are made

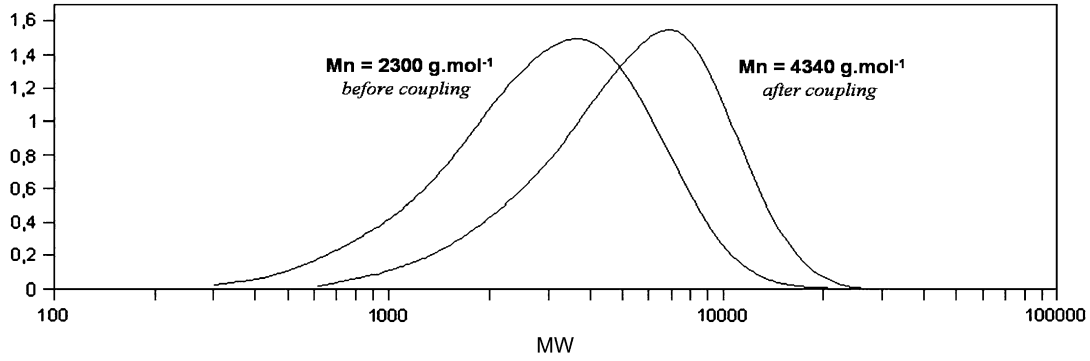


Fig. 3. Molecular weight distribution before ($M_{n,SEC}$ = 2300 g mol^{-1}, $M_{p,SEC}$ = 3750 g mol^{-1}) and after ($M_{n,SEC}$ = 4340 g mol^{-1}, $M_{p,SEC}$ = 7120 g mol^{-1}) coupling of an iodo-functionalized polystyrene, 1.5 h, at 75 °C, with HMTETA as a ligand, Cu(0) nanosized and CuBr in toluene with $[PSty\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)] = 1:2:4:1$, x_c = 0.94.

Table 4
Effect of the halogen used in Cu(I)X catalyst

Expt	P-I	Cu(I)	Time (h)	T (°C)	$M_{n,0}$ (g mol^{-1})	x_c
1	PSty-I	CuI	31	70	1750	0.54
2	PSty-I	CuBr	22	70	1750	0.90
3	PMA-I	CuBr	23	75	1800	0.57
4	PMA-I	CuCl	23	75	1800	0.95

Each run was carried out in toluene with PMDETA as the ligand, Cu(0) 3 μm and the following molar ratio $[P\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)]_0 = 1:2:4:1$.

on bromo-polymers coupled thanks to CuBr-based systems. As far as we know, the only comparison work done on the efficiency of copper−halide compounds is related to ATRP studies in which an inverse trend was found [46] with $K_{ATRP,CuBr} > K_{ATRP,CuCl}$. However, our trend (CuCl > CuBr > CuI) is consistent with the halogen exchange method used in ATRP where CuCl catalyst is used in conjunction with bromo-alkyl compounds to make the initiation step faster [50,51].

3.4. Effect of the Cu(0) particle size

Most authors achieved ATRC reaction using Cu(0) as a reducing zerovalent metal to reduce the Cu(II) species formed during the reaction. As noticed by Sarbu et al. [4], one could expect that the insoluble nature of the copper in the reaction medium forces to use ultrafine dispersed powders in order to increase the total surface area and to support the electron-transfer process. Actually, the size of the metal particles used in the literature ranges from 90 μm to nanosized particles. Results on the particle size effect for ω-iodo-poly(methyl acrylate) coupling are given in Table 5. Because of the decrease of the polydispersity index during the coupling reaction (from 2.00 to 1.40−1.20), it is easier to compare the evolution of M_p values rather than M_n values which lead to efficiencies superior to 1. It is shown that 3 μm Cu(0) is as effective as nanosized copper for the coupling of PMA-I with HMTETA. Therefore, the particle size of Cu(0) seems not critical.

3.5. Effect of the nature of the polymer chain

Studies carried out on model molecules [46], modeling calculations [52] as well as coupling experiments [7] have demonstrated that acrylate-type polymers are less reactive than styrenic ones under ATRP and ATRC conditions due to a much lower concentration of radicals formed in the equilibrium. Otazaghine et al. have shown that in the case of ATRP synthesized poly(acrylates), disproportionation and/or transfer might be the side reactions responsible for the limited coupling efficiency observed under their conditions. Depending on the number of transfer sites present in the polymer, namely CH in α-position of the carbonyl and/or CH_2 in α-position of the oxygen, they showed that the coupling efficiency was around 0.6 for poly(*n*-butyl acrylate) and increased to 0.7 without being ever quantitative for poly(*n*-butyl-α-fluoroacrylate), poly(*tert*-butyl acrylate) and poly(methyl acrylate) [5,6]. In order to circumvent this drawback, a described approach was to prepare bromo-functionalized polymers of poly(methyl acrylate) exhibiting few styrenic units at the chain end in order to enhance the homolytic cleavage of the C−Br bond [7]. This led to a highly efficient coupling reaction with an efficiency x_c of 0.94 in 5 h using PMDETA that can be compared with the low coupling efficiencies ($x_c < 0.30$ with over 24 h reaction time) obtained when coupling PMA−Br under the same conditions without styrenic unit [7]. This method has also been described with *n*-butyl acrylate-based polymers which were then coupled with an efficiency x_c of 0.75 [6].

One interest of the RITP [20] method for the synthesis of controlled polymer is the introduction of iodine chain end with a carbon−iodine bond whose homolytic cleavage energy is weaker than the carbon−bromide one [46]. As expected, in the case of poly(methyl acrylate) this allows for a better activation, an increased concentration of the formed macroradicals and so a higher extent of coupling in shorter reaction times. This improvement is clearly demonstrated in Table 6 (run 1) since in similar experimental conditions (except for temperature which is only 5 °C higher, and [PMDETA]/[Cu(I)X] which is 2:1 instead of 1:1), the efficiency of coupling rises from $x_c = 0.14$ after 61 h [7] to $x_c = 1$ after 48 h when working with HO−PMA−Br ($M_n = 1630$ g mol^{-1}) and PMA-I ($M_n = 4450$ g mol^{-1}), respectively. The same trend with even shorter reaction times is observed when using better

Table 6
Effect of the nature of the polymer chain

Expt	P-I	Ligand	Cu(I)	Time (h)	T (°C)	$M_{n,0}$ (g mol^{-1})	x_c
1	PMA-I	PMDETA	CuBr	48	75	4450	1.0
2	PMA-I	HMTETA	CuBr	4.5	75	4450	1.0[a]
3	PBuA-I	HMTETA	CuBr	120	75	4500	0.89

All experiments were carried out with nanosized Cu(0), in toluene, and in the following conditions: $[PMA\text{-}I]_0$ or $[PBuA\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)] = 1:2:4:1$.
[a] The efficiency is even superior to 1 (1.20) due to a refinement of M_w/M_n from ∼1.85 before coupling to ∼1.35 after coupling; considering M_p for the efficiency calculation gives $x_c = 0.99$.

Table 5
Effect of the Cu(0) particle size

Expt	P-I	Ligand	Cu(0)	Time (h)	$M_{n,f}$ (g mol^{-1})	$M_{w,f}/M_{n,f}$	$M_{p,f}$ (g mol^{-1})	x_{c,M_n}[a]	x_{c,M_p}[b]
1	PMA-I	HMTETA	3 μm	3	8000	1.39	11 800	1.25	1.00
2	PMA-I	HMTETA	Nano	3	10 100	1.20	11 700	1.41	0.99

Each run was carried out in toluene on ω-iodo-poly(methyl acrylate) ($M_{n,0} = 3000$ g mol^{-1}, $M_{p,0} = 5900$ g mol^{-1} and $M_{w,0}/M_{n,0} = 2.00$) with CuBr and the following molar ratio: $[PMA\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)]_0 = 1:2:4:1$.
[a] Coupling efficiency calculated with M_n values.
[b] Coupling efficiency calculated with M_p values.

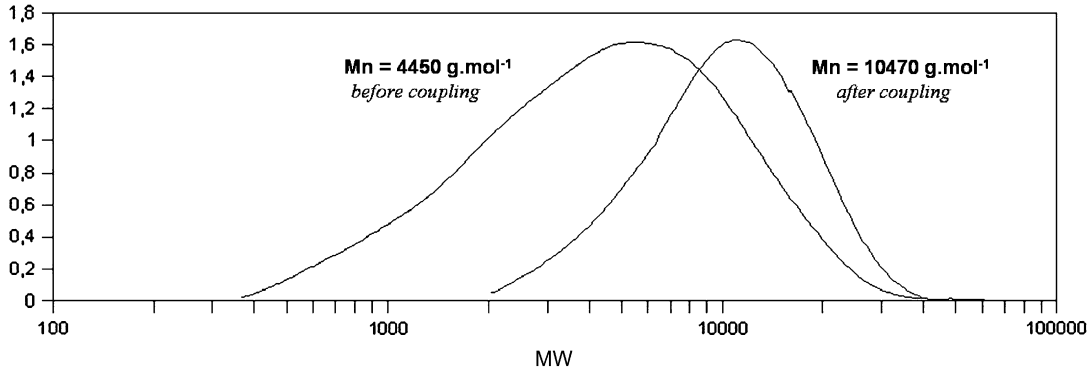


Fig. 5. Molecular weight distribution before ($M_{n,SEC} = 4450$ g mol^{-1}, $M_{p,SEC} = 8800$ g mol^{-1}) and after ($M_{n,SEC} = 10\,470$ g mol^{-1}, $M_{p,SEC} = 17\,400$ g mol^{-1}) coupling of an iodo-functionalized poly(methyl acrylate), 4.5 h, at 75 °C, with HMTETA, Cu(0) nanosized and CuBr in toluene with $[PMA\text{-}I]_0:[L]_0:[Cu(0)]_0:[Cu(I)] = 1:2:4:1$, $x_c = 1$.

ATRC ligands as can be seen in Table 6 (run 2) where the efficiency of coupling rises from $x_c = 0.27$ after 24 h for HO−PMA−Br with Me_6TREN [7] to $x_c = 1$ after only 4.5 h for PMA-I with HMTETA (Fig. 4 full circles and Fig. 5). It is noteworthy that, thanks to the iodo-functionalized chain end, HMTETA, which is known to be less effective than Me_6TREN in ATRC, leads to a quantitative and fast coupling (Fig. 5). Furthermore, considering the case of poly(*n*-butyl acrylate) (Table 6, run 3), it is remarkable that thanks to the iodo functionality, the coupling efficiency is also very good with $x_c = 0.89$ which is about 30% higher than the described ATRC attempts with ω-bromo-poly(*n*-butyl acrylate) [6]. The non-quantitative coupling could be due to side reactions (such as transfer reactions). These side reactions seem to be less important in this work compared to the 20% of occurrence observed by Otazaghine and Boutevin [5]. This could be explained by the lower temperature (75 °C instead of 90 °C) used during the coupling reaction of the ω-iodo-polymers.

These results tend to prove that, for bromo-functionalized polymers whose coupling is normally difficult to obtain, the efficiency of ATRC is greatly improved when the bromo chain end is replaced by an iodo chain end. Because AIBN, which gives relatively non-reactive terminal groups, was used for the synthesis of polymers by RITP, one could assume that the α-chain end resulting from the initiator decomposition has a strong influence onto the coupling efficiency and could explain the low x_c values obtained for hydroxyl groups functionalized polacrylates described in the literature [7]. This seems not to be the case if considering that high coupling efficiency has been described for both HO−PMA−Sty−Br and HO−PSty−Br [7], thus proving that the nature of the halide chain end is the only critical factor. This remark is confirmed considering the work of Otazaghine et al. [3]. They used ω-bromo-polystyrene synthesized by ATRP using various functional initiators leading to α-ketonic, α-hydroxylic and even α-carboxylic chain ends. In the described conditions, the coupling efficiencies were around 0.85−1, thus indicating that the ATRC efficiency improvement reported herein for ω-iodo-poly(methyl acrylate) is clearly linked with the iodine functionality.

4. Conclusion

ITP and more recently RITP developments offer a wide range of well-defined polymers exhibiting iodo-functionalized chain ends. In this paper, the use of such polymers in ATRC process has been described with special emphasis on two types of polymer chains, namely polystyrene and poly(methyl acrylate). Recent ATRC studies carried on ω-bromo-polymers had indeed pointed out that efficient coupling could only be obtained with polystyrene in acceptable reaction times and that poly(methyl acrylate) had to be activated through the adjunction of styrene units at the chain end in order to get an easier carbon−bromide homolytic bond cleavage. The results reported herein demonstrate that the ATRC equilibrium is strongly shifted toward macroradicals formation when using iodo-functionalized polymers. This is the first description of a one-step quantitative coupling of poly(methyl acrylate). The experiments that were carried out allowed us to study different parameters including the nature of the ligand, the Cu(0) particle size and the nature of the Cu(I)X compound (X = Cl, Br, I). Using the conditions described as being optimum in previous studies [7], we found that both PMDETA and HMTETA are efficient for coupling but that faster reactions are observed for the latter. Cu(0) particle size (3 μm or nanosized) was not found to be a critical parameter in our conditions. Cu(I)X catalysts' efficiency was found to follow the order CuCl > CuBr > CuI. Besides these observations, whereas polystyrene coupling is not changed, poly(methyl acrylate) coupling is dramatically improved by the presence of carbon−iodine bond at the chain end and reaches high level of efficiency (equal or close to 1) in the same short period of time (<5 h) than the ones described for ω-bromo- or ω-iodo-polystyrenes. Considering this high coupling efficiency, one prospect would be to study how low concentration of Cu(I)/L can be used to still get efficient ATRC with ω-iodo-polymers. Furthermore, using functional transfer agents or initiators, it is therefore expected that one could easily obtain telechelic poly(acrylates) using this ATRC process with polymers prepared by ITP or RITP, respectively. ATRC process could also be performed with iodo-derivatives obtained from

chloro- or bromo-polymers (prepared by ATRP) through substitution reaction with reactants such as sodium iodide. Finally, it is noteworthy that this easy coupling process also potentially gives access to other controlled architectures based on poly(acrylates) such as multiblock copolymers.

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