Simultaneous Reverse and Normal Initiation in Atom Transfer Radical Polymerization

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ABSTRACT: Atom transfer radical polymerization (ATRP) with concurrent reverse and normal initiation process was investigated. Bulk polymerizations of both *n*-butyl acrylate (BA) and styrene (St) were conducted using $CuBr_2$ complexed with 1 equiv of tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) as the catalytic system, initiated by 2,2′-azobis(isobutyronitrile) (AIBN) and an alkyl halide (RX). Polymerization of BA at 60 or 90 °C provided well-defined polymers with molecular weights up to 40 000 g/mol and low polydispersities ($M_w/M_n < 1.10$). Similar results were obtained for the polymerization of styrene at 110 °C. The effects of polymerization temperature and solubility were studied in order to moderate the high activity of the catalyst and the poor solubility of the Cu(II) complex in monomers. Additionally, other parameters influencing this ATRP process are discussed.

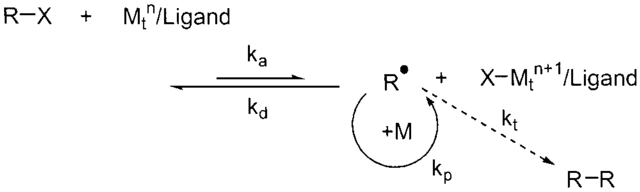
Introduction

Controlled/living radical polymerization is among the major fields of interest of polymer chemists in the past 5 years.[1,2] This interest can be attributed to the large range of monomers polymerizable by a radical process and to the simple adjustable experimental conditions (bulk, solution, suspension, and emulsion). In controlled/living polymerizations contributions of the inevitable and irreversible termination reactions observed in conventional radical processes are negligible. This allows well-defined polymers to be synthesized with narrow molecular weight distributions and controlled complex architectures. Among these controlled radical processes, ATRP is one of the most successful.[3−8] It is based on a dynamic equilibrium where a transition metal complex reversibly activates a dormant polymer chain via an atom transfer event (Scheme 1).

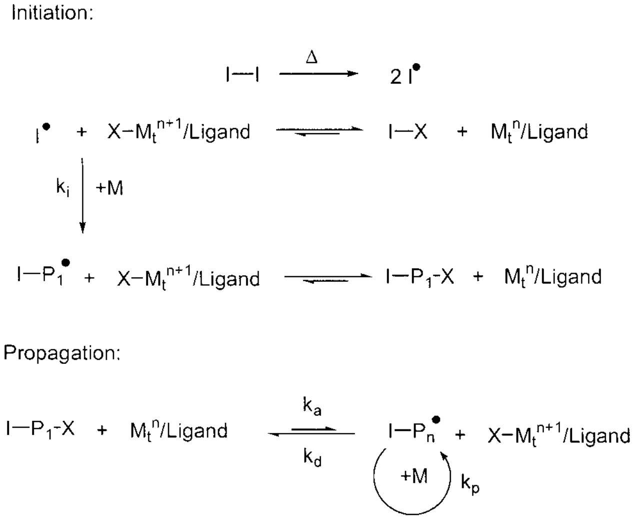
Two pathways can be followed to reach this dynamic equilibrium. In the first one, called normal ATRP, the transition metal catalyst (M_t^n/L, where M_t^n is the transition metal in the oxidation state *n* complexed with an appropriate ligand L) reacts reversibly with an alkyl halide initiator (RX) and generates an oxidized transition metal halide complex ($X{-}M_t^{n+1}/L$) and a radical ($R^\bullet$). This radical propagates, adding monomer (M), and is rapidly deactivated by reaction with the oxidized transition metal halide complex to re-form the initial transition metal catalyst and an oligomeric halogen-terminated chain ($P_1{-}X$). Then, this sequence can repeat itself, until the desired consumption of the monomer is reached, resulting in the synthesis of polymers with predetermined molecular weights ($DP_n = \Delta[M]/[RX]_0$) and low polydispersities ($M_w/M_n < 1.5$).

The second pathway, called reverse ATRP, differs from the normal ATRP in its initiation process. In this case, the initiation step does not proceed by activation of the alkyl halide with a M_t^n/L catalyst, but rather by deactivation reaction between radicals, $I^\bullet$ or $I{-}P_1^\bullet$, and $X{-}M_t^{n+1}/L$ (Scheme 2). A conventional radical initiator, such as AIBN, is used as a radical source.[9−12] Once radicals are thermally generated, either they react immediately with the higher oxidation state transition-metal complex to form the reduced transition-metal species and a dormant species (I−X) or they react with monomer to form a propagating radical, which can then be deactivated by reaction with $X{-}M_t^{n+1}/L$ to form M_t^n/L and a dormant species ($I{-}P_1{-}X$). In the subsequent step, the reduced transition-metal species, M_t^n/L, reacts with the newly formed halogenated chains, as in normal ATRP. A variety of monomers such as styrenes and (meth)acrylates have been polymerized in a well-controlled manner by using normal and reverse ATRP.[6−8]

Scheme 1



Scheme 2. Proposed Reverse ATRP Mechanism



In normal ATRP, much research was devoted to the development of new more active catalytic systems in

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order to reduce the amount of catalyst and polymerize less reactive monomers. The catalytic activity can be adjusted by changing either the ligand,[7] the counterion,[13−16] or the transition metal itself.[4,11,17−20] Selection of the ligand is an efficient way to modify, or tune, the reactivity of the catalyst since the ligand affects the ability of the metal to be oxidized. For Cu complexes, the higher the redox potential is, the higher the catalytic activity observed in ATRP.[21−23] In copper-mediated ATRP, various ligands have been studied (bipyridine derivatives,[24] terpyridyl,[25] pyridynimine,[26] picolyl ligands[27]).[28] Branched aliphatic polyamines presently form the most efficient catalysts.[29] These highly active catalysts not only allow but also require the polymerization to be performed with a lower catalyst concentration and at lower temperatures. Among this class of ligands, tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) associated with Cu(I) (1:1 ratio) provides the most active catalyst reported to date.[29] With this catalytic system, the polymerization of methyl acrylate, using 0.1 equiv of catalyst relative to the initiator, reached 40% conversion within 1 h at room temperature, resulting in a polymer with $M_n = 8200$ and $M_w/M_n = 1.09$. However, it is “too active” and inefficient for the polymerization of MMA.[30]

Since the more active catalytic systems are generated by less oxidatively stable Cu(I) complexes, reverse ATRP, using more stable initiating Cu(II) complexes, could be a convenient method to circumvent this problem. Additionally, Cu(II) is less expensive than Cu(I). Copper-mediated reverse ATRP of styrene with AIBN as initiator was initially achieved using 2,2′-bipyridine[9] and 4,4′-dinonyl-2,2′-bipyridine[10] ligands respectively under heterogeneous and homogeneous conditions. Reverse ATRP was also adapted for the emulsion polymerization of *n*-butyl methacrylate.[31,32] In addition, iron complexes have been used in reverse ATRP of MMA[12,33−35] and styrene.[36,37] The range of initiators useful for reverse ATRP is large and includes initiators as azo compounds,[9,10] peroxides,[38,39] and thermal iniferters.[34] The usual conditions for successful reverse ATRP are $[Cu(II)]_0/[AIBN]_0 \geq 1$ and rather high polymerization temperature (≥100 °C) for rapid decomposition of the initiator. However, it should be noticed that Cu(II) complexes are usually less soluble in organic media than the corresponding Cu(I) complexes, often leading to heterogeneous polymerizations. In normal ATRP, it was proved that for highly active catalysts $[Cu(I)]_0/[RX]_0 \leq 0.1$, and lower temperature (≤60 °C) are necessary to observe a “living” behavior.[30] These requirements, opposite to those employed in reverse ATRP, seem to prevent the use of very active catalyst in the reverse process. So, combining both initiation processes could enable controlled/living polymerizations with highly active catalysts, using more stable initiating Cu(II) complexes and higher polymerization temperatures.

This paper describes the simultaneous reverse and normal initiation in ATRP of *n*-butyl acrylate and styrene using the $CuBr_2/Me_6$−TREN catalytic system. Addition of an alkyl halide to the Cu(II) complex/AIBN initiating system allows controlled polymerization with this highly active complex providing well-defined polymers. The alkyl halide can initiate polymerization concurrently with the slow decomposition of the initiator and can tolerate a low solubility of the copper(II) complex. The effects of solvent and temperature on this type of ATRP are also reported.

Experimental Section

Materials. *n*-Butyl acrylate (BA, 99%) and styrene (St, 99%) from Aldrich were vacuum-distilled over CaH_2, stored under nitrogen atmosphere at −15 °C, and bubbled with dry nitrogen for at least 15 min immediately before polymerization. The ligand, Me_6−TREN, was prepared according to a reported procedure.[40] 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from diethyl ether and stored at −15 °C. Alkyl halides, 1-phenylethyl bromide (1-PEBr, Aldrich, 97%), and methyl 2-bromopropionate (MBP, Acros, 99%) were used as received without further purification. Copper(II) bromide (Aldrich, 98%) was used as received. Methanol (Fisher Scientific, 99%) was distilled over CaH_2 and stored under nitrogen. 1,4-Dimethoxybenzene (Acros, 98%) was used without purification prior to use.

Polymerization Procedure. All operations were carried out under a nitrogen atmosphere. In a typical polymerization, the Schlenk flask was charged with $CuBr_2$ (9.6 mg; 4.36×10^{-5} mol), AIBN (4.3 mg; 2.62×10^{-5} mol), and 1,4-dimethoxybenzene (1.1 g; 7.96×10^{-3} mol). The flask was sealed with a rubber septum and was degassed on vacuum line (three nitrogen/vacuum cycles). Then degassed monomer (*n*-butyl acrylate:12.5 mL; 8.72×10^{-2} mol or styrene: 10 mL; 8.72×10^{-2} mol) and Me_6−TREN (0.011 mL; 4.36×10^{-5} mol) were added using previously purged syringes. The solution was stirred for 5 min at 0 °C to form and partially dissolve the complex, leading to a heterogeneous solution. To get a homogeneous solution, methanol (0.6 mL; 1.48×10^{-2} mol) was optionally added to the solution. The alkyl halide (methyl 2-bromopropionate: 0.048 mL; 4.36×10^{-4} mol or 1-phenylethyl bromide: 0.059 mL; 4.36×10^{-4} mol) was added to the solution, and the flask was immersed in an oil bath at desired temperature for 7 h. At timed intervals, samples were withdrawn from the solution using a degassed syringe. After heating was stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was then passed over alumina to remove Cu complexes before analysis. In homogeneous *n*-butyl acrylate polymerization at 60 °C, the results are the following: conversion: 79%; GPC: $M_n = 17\,500$, $M_w/M_n = 1.11$. The same experiment performed with styrene at 110 °C led after 8 h to the following: conversion: 65%; GPC: $M_n = 10\,200$, $M_w/M_n = 1.11$.

Characterization. Monomer conversion was determined from the concentration of residual monomer by gas chromatography (GC) with 1,4-dimethoxybenzene as internal standard, using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Analysis conditions: injector temperature, 250 °C; detector temperature, 250 °C; temperature program, 3 min 50 °C, 40 °C/min until 170 °C, 2 min 170 °C. Molecular weights (relative to linear polystyrene standards) and molecular weight distributions were measured using a Waters 712 WISP autosampler equipped with three PSS columns (10^2, 10^3, and 10^5 Å) in series with a Waters 410 refractive index detector, using toluene as internal standard and THF as the eluent at 25 °C with the flow rate 1 mL/min.

Results and Discussion

Normal ATRP of Acrylates Using Cu(I)Br/Me_6-TREN as Catalyst. Among all the multidendate ligands used in Cu-mediated ATRP, Me_6-TREN produces one of the most active catalysts with CuBr that has been reported.[29] As shown in Table 1, the use of a small amount of catalyst, typically between 5 and 20 mol % catalyst relative to initiator (methyl 2-bromopropionate), either at room temperature or at 60 °C results in a fast polymerization and yields well-defined polymers with low polydispersities (M_w/M_n).[30] On the other hand, when methyl acrylate (MA) was polymerized using 1.0 equiv of catalyst relative to initiator at 23 °C,[29] the polymerization reached 85% conversion within 15 min, but the control was poor since the experimental

Table 1. Bulk Polymerization of Acrylates Using CuBr/Me$_6$-TREN as Catalyst

[catalyst]$_0$/[2-EBP]$_0$	temp (°C)	time (h)	conv (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
1.0[a]	23	0.50	66	13 200	17 900	1.24
0.2[b]	23	0.75	76	15 200	18 000	1.10
0.2[a]	23	1.00	57	11 400	12 600	1.10
0.1[b]	23	5.00	94	26 200	24 700	1.13
0.1[b]	60	3.00	90	23 500	23 050	1.15
0.05[b]	60	8.00	92	25 210	23 552	1.11

[a] [Methyl acrylate]$_0$/[ethyl 2-bromopropionate]$_0$ = 200. [b] [*n*-Butyl acrylate]$_0$/[ethyl 2-bromopropionate]$_0$ = 200, $M_{n,th} = (\Delta[M]/[2\text{-EBP}]_0)M_0$.

molecular weight ($M_{n,GPC}$) was 25% lower than expected. According to these results, the utilization of such highly active catalysts in reverse ATRP of acrylates seems to present a great challenge. The prerequisites for a controlled/living polymerization in normal ATRP are the opposite of those applied in reverse ATRP. A high [RX]$_0$/[Cu(I)]$_0$ ratio and low temperature of reaction are recommended for the normal initiation process, whereas [AIBN]$_0$/[Cu(II)]$_0$ $\approx$ 0.6 and high temperature (~100 °C needed for fast decomposition of the thermal initiator) are essential for reverse ATRP. The following study shows that the addition of alkyl halide to a reverse ATRP can lead to controlled/living polymerizations with very active catalysts.

Simultaneous Reverse and Normal Initiation in ATRP of *n*-Butyl Acrylate under Heterogeneous Conditions. To compare this new simultaneous method of initiation with the alkyl halide initiation process, it was necessary to carry out the polymerization under the same standard conditions; i.e., the optimized conditions employed in the alkyl halide process were used as a reference. Consequently, bulk polymerization was performed using [M]$_0$/[I]$_0$ = 200, 10 mol % catalyst relative to the initiator, and [AIBN]$_0$/[Cu(II)]$_0$ = 0.62. The latter ratio should lead to the complete reduction of the initial Cu(II) complex into Cu(I) species, based on the decomposition efficiency of AIBN of 0.8. This value of thermal decomposition efficiency of AIBN is the most common value reported for this initiator under these experimental conditions[41,42] and provided the best results for the reported reverse ATRP.[10]

First, the polymerization of BA was carried out under heterogeneous conditions because of the low solubility of CuBr$_2$/Me$_6$-TREN complex in nonpolar media. A reaction temperature of 90 °C resulted in a very fast polymerization. A conversion of 72% was reached within 15 min and a poly(*n*-butyl acrylate) (PBA) of $M_{n,GPC}$ = 15 100 and M_w/M_n = 1.35 was obtained. The polymerization temperature was reduced to 60 °C, and the molecular weight increased linearly with conversion. The polydispersities were much lower, as low as 1.10, suggesting adequate polymerization control (Figure 1). In both cases, the experimental degree of polymerization matched well with the theoretical values determined by Δ[M]/[RX]$_0$, even if a deviation from the theoretical line was observed at 90 °C. The better control of the polymerization at 60 °C, confirmed by lower polydispersities, can be attributed to the higher residual [Cu(II)] due to the slower decomposition rate of AIBN, which enables efficient deactivation. At this temperature, the contribution of AIBN initiated chains to the average-number molecular weight is negligible. At 90 °C, the azo initiator decomposition is faster, and new azo-initiated chains are generated throughout the polymerization, leading to a broadening of the molecular weight distribution. The semilogarithmic plots are depicted in Figure 2. There is initial induction, or inhibition period, at lower temperature because of the slow decomposition of the thermal initiator, while a fast polymerization took place at 90 °C. In agreement with earlier reports, this catalytic system is more efficient at lower temperature.[29] This is especially important when Cu(II) complex is poorly soluble and cannot dissolve fast enough to trap all radicals generated by AIBN.

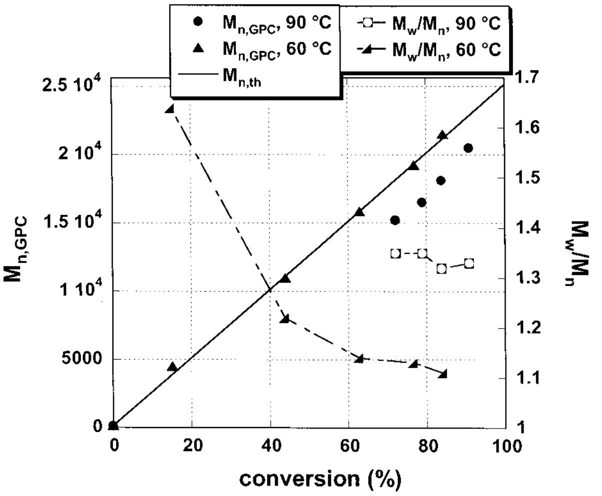

Figure 1. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA under heterogeneous conditions. [BA]$_0$ = 6.97 M; [CuBr$_2$/Me$_6$-TREN]$_0$ = 0.0035 M; [MBP]$_0$ = 0.035 M; [AIBN]$_0$ = 0.0021 M. $M_{n,th} = (\Delta[M]/[RX]_0)M_0$.

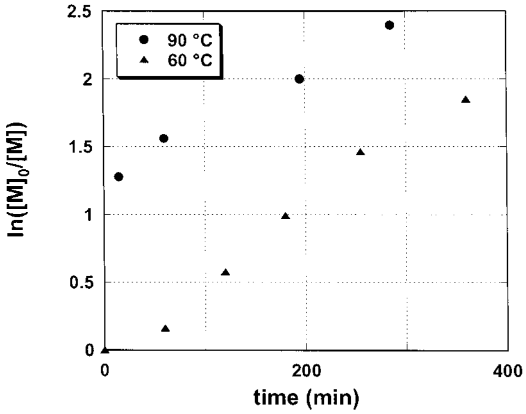

Figure 2. Effect of temperature on the first-order kinetic plot for the polymerization of BA under heterogeneous conditions. [BA]$_0$ = 6.97 M; [CuBr$_2$/Me$_6$-TREN]$_0$ = 0.0035 M; [MBP]$_0$ = 0.035 M; [AIBN]$_0$ = 0.0021 M.

Effect of [RX]$_0$. In the previous experiments, the molecular weight seems to be predominately controlled by the concentration of alkyl halide. To confirm this hypothesis, different concentrations of alkyl halide were employed at 60 °C ([M]$_0$/[RX]$_0$ = 200−400) as shown in Figure 3. The molecular weights increased linearly with conversion and were in good agreement with the theoretical values. The molecular weights were largely determined by the ratio Δ[M]/[RX]$_0$. To fit experimental and theoretical values, [AIBN]$_0$ and its thermal decomposition efficiency should be taken into account. Indeed, especially for low concentrations of alkyl halide, the number of chains initiated by the thermal initiator can no longer be neglected. Consequently, the theoretical

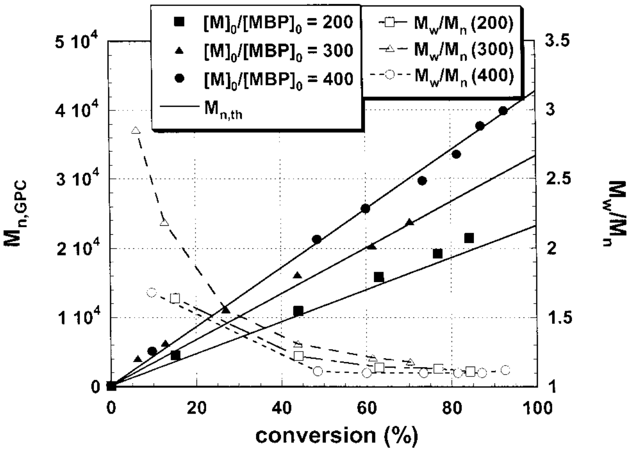

Figure 3. Dependence of molecular weights and polydispersities on conversion for the polymerization of BA using various amounts of MBP under heterogeneous conditions. $[BA]_0 = 6.97$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0035$ M; $[MBP]_0 = 0.017-0.035$ M; $[AIBN]_0 = 0.0021$ M; 60 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

degree of polymerization should be calculated from eq 1.

$$DP_n = \frac{\Delta[M]}{[RX]_0 + (2 \times 0.8[AIBN]_0)} \qquad (1)$$

Regardless of the initial alkyl halide concentration, the polydispersities remained very low (Figure 3), showing a good control of the polymerization with different $[RX]_0/[Cu(II)]_0$ ratios. In conclusion, the addition of alkyl halide to a reverse ATRP of *n*-butyl acrylate was successful and led to the formation of well-defined polymers having narrow molecular weight distributions. Even if, during this simultaneous normal and reverse initiation in ATRP, the majority of chains were initiated with a normal (alkyl halide) ATRP process, the initial catalytic system was different since a Cu(II) complex was employed. In addition, the reactions were fast and controlled, although performed under heterogeneous conditions.

Simultaneous Reverse and Normal Initiation in ATRP of *n*-Butyl Acrylate under Homogeneous Conditions. The previous results showed that a controlled/living polymerization of *n*-butyl acrylate could be achieved under heterogeneous conditions with $CuBr_2/Me_6$-TREN as a catalyst. However, it was not possible to define the concentration of Cu(II) species in solution needed for controlled ATRP. Therefore, we performed the same reaction using homogeneous conditions.

To solubilize the catalyst, a small amount of methanol was added. Typically, the amount of methanol was 5 vol % relative to the monomer. Under these homogeneous conditions, the polymerization of BA at 60 °C did not occur even after 480 min. The initial Cu(II) concentration was too high with regard to the slow radical formation at this lower temperature, resulting in a very long inhibition period. The results obtained at 90 °C were propitious as shown in Figure 4. The molecular weights were in a good agreement with those predicted by eq 1, and polydispersities remained very low. The higher initial concentration of Cu(II) in solution could efficiently trap more radicals, limiting termination reactions of primary radicals and thus improving the initiation efficiency of AIBN. The polydispersity increased slightly after 240 min of polymerization, from 1.08 to 1.11, as a possible result of termination reactions. This increase of the polydispersities was consistent with the decrease of the apparent rate of polymerization observed in the first-order kinetic plot (Figure 5). Termination can be ascribed to side reactions due to the presence of methanol or to the biradical process. Nevertheless, the homogenization of the reaction mixture allows the use of a higher polymerization temperature. In conclusion, the controlled/living polymerizations can be carried out either under heterogeneous or homogeneous conditions.

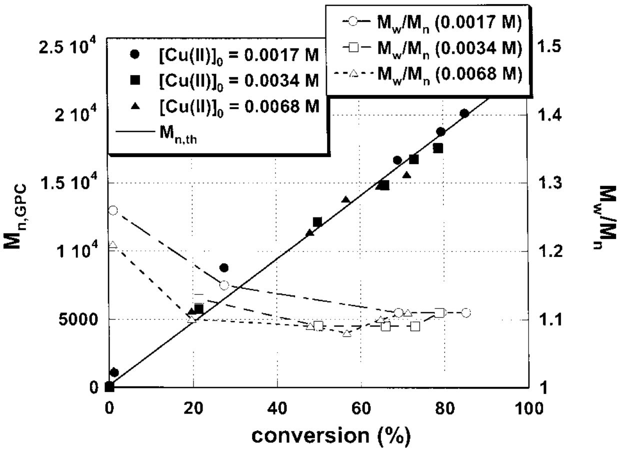

Figure 4. Effect of $[Cu(II)]_0$ on molecular weights and polydispersities for the polymerization of BA under homogeneous conditions. $[BA]_0 = 6.62$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0016-0.0064$ M; $[MBP]_0 = 0.033$ M; $[AIBN]_0 = 0.0020$ M; MeOH (5 vol %); 90 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

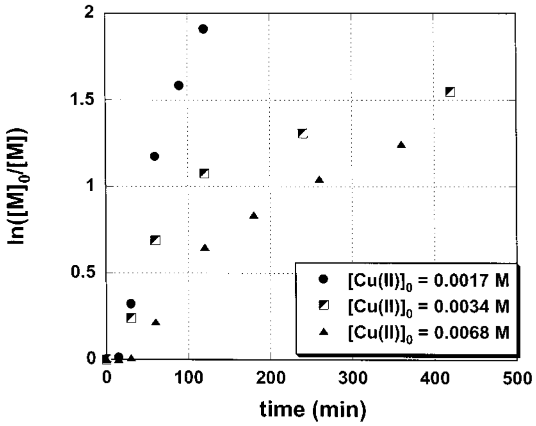

Figure 5. Effect of $[Cu(II)]_0$ on first-order kinetic plot for the polymerization of BA using homogeneous conditions. $[BA]_0 = 6.62$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0016-0.0064$ M; $[MBP]_0 = 0.033$ M; $[AIBN]_0 = 0.0020$ M; MeOH (5 vol %); 90 °C.

Effect of $[Cu(II)]_0$. For a better process understanding, the influence of each component on the polymerization was studied. First, the effect of $[Cu(II)]_0$ was investigated, keeping all the other parameters constant. Figure 4 shows that the number-average molecular weights were not affected by the initial concentration of Cu(II), as expected since Cu(II) is only a part of the catalytic system. However, it affects the apparent rates of polymerization, as observed in the semilogarithmic plots (Figure 5). A lower initial concentration of Cu(II) results in a higher apparent rate of polymerization. With the lowest amount of Cu(II) (0.05 equiv to RX), the first-order kinetic plot is quite linear, and the polymerization remained controlled despite the low

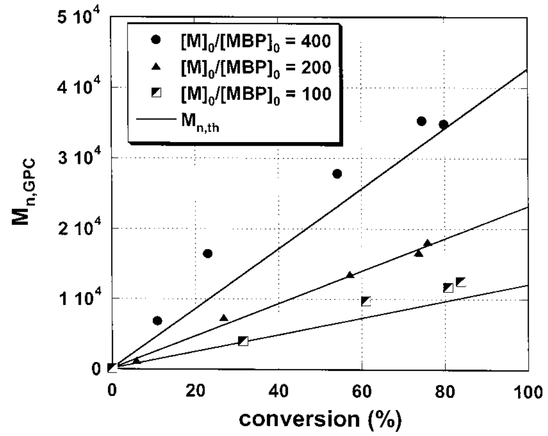

Figure 6. Evolution of the molecular weights with conversion using various amounts of MBP under homogeneous conditions. $[BA]_0 = 6.62$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0033$ M; $[MBP]_0 = 0.016-0.066$ M; $[AIBN]_0 = 0.0020$ M; MeOH (5 vol %); 90 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

deactivator concentration. The deviation observed for higher $[Cu(II)]_0$ could be explained by the deactivation of the halogen-terminated dormant chains by nucleophilic substitution with methanol, leading to terminated chains without a significant increase of either molecular weights or polydispersities. This was not observed with low $[Cu(II)]_0$ because of the higher polymerization rate. The experimental molecular weights matched the theoretical values and increased linearly with conversion. In addition, the polydispersities remained low (<1.15). With higher initial concentration of Cu(II) (0.0035−0.0070 M), the behavior in terms of molecular weight control and polydispersities was the same, but with an inhibition period. Contrary to the normal ATRP initiation process using CuBr/Me$_6$-TREN as catalyst, the low copper concentration did not impede control of the polymerization.[30] The polydispersities obtained with this simultaneous reverse and normal initiation process were lower than those obtained with the normal initiation process, even at lower temperature.[29] The usual values noticed with the normal process at 60 °C are $M_w/M_n \approx 1.20$, although lower values as $M_w/M_n = 1.09$ could be obtained at room temperature. Therefore, this method allows the use of a highly active catalyst, at higher temperature, and at low concentration, while preserving the controlled/living nature of the polymerization.

Effect of $[RX]_0$. The effect of the alkyl halide concentration was studied in the homogeneous systems. Figure 6 shows that the experimental average molecular weights, determined by eq 1, agreed well with the theoretical values, and the molecular weight increased linearly with conversion. Nevertheless, for low $[RX]_0$, a difference was observed between the experimental and predicted values.

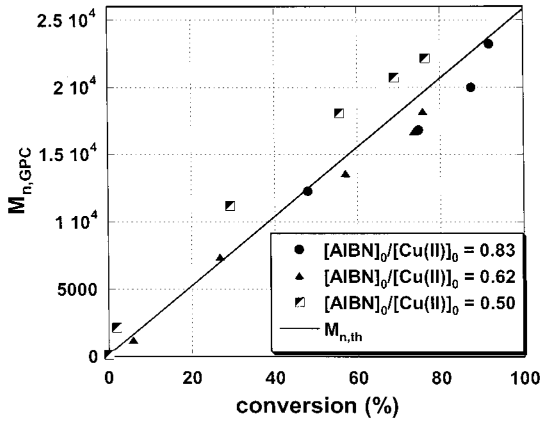

Figure 7. Effect of AIBN concentration on molecular weights for the polymerization of BA under homogeneous conditions. $[BA]_0 = 6.62$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0033$ M; $[MBP]_0 = 0.033$ M; $[AIBN]_0 = 0.0016-0.0034$ M; MeOH (5 vol %); 90 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

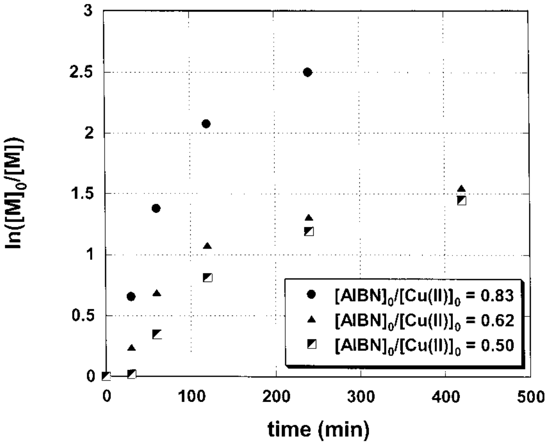

Figure 8. Effect of AIBN concentration on first-order kinetic plots for the polymerization of BA under homogeneous conditions. $[BA]_0 = 6.62$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0033$ M; $[MBP]_0 = 0.033$ M; $[AIBN]_0 = 0.0016-0.0034$ M; MeOH (5 vol %); 90 °C.

Effect of $[AIBN]_0$. Among the different components of polymerization system, AIBN has a particular role. AIBN participates in the determination of the average-number molecular weight and the molecular weight distribution by creation of initiating radicals and in the determination of the catalytic activity in changing the ratio Cu(II)/Cu(I). Figure 7 plots the molecular weights and polydispersities as a function of conversion. In the graph, an average line was used for the representation of the theoretical molecular weights corresponding to $[AIBN]_0/[Cu(II)]_0 = 0.65$, i.e., $[AIBN]_0 = 0.0028$ M. For all cases, the molecular weights increased linearly with conversion, and as expected, for $[AIBN]_0 = 0.0017$ M, the experimental M_n values were higher than the average theoretical line. For $[AIBN]_0 = 0.0036$ M, $M_{n,GPC}$ were lower than the predicted values. These results indicate that AIBN should be taken into account for the determination of the targeted molecular weights. Even with an excess of AIBN relative to Cu(II), the polydispersities remained low (<1.18). As anticipated, [AIBN] had a significant effect on the kinetics of polymerization (Figure 8). The highest $[AIBN]_0$ led to the highest polymerization rate, corresponding to the highest initial radicals concentration and fastest reduction of Cu(II). However, with the exception of using excess of AIBN relative to Cu(II), the apparent rate of polymerization decreased significantly, most probably due to termination. (The polydispersity increased slightly after 4 h of polymerization.) This phenomenon was not observed for $[AIBN]_0 = 0.0036$ M because of the fastest polymerization; 92% conversion was reached within 4 h, whereas 70% conversion was reached with lower [AIBN] at the same time. The inhibition period (45 min) for $[AIBN]_0/[Cu(II)]_0 = 0.50$ can be attributed to a significant residual [Cu(II)]. Using this ratio, the reduction of Cu(II) to Cu(I) could not be completed. The inhibition period was shorter for $[AIBN]_0/[Cu(II)]_0 = 0.62$.

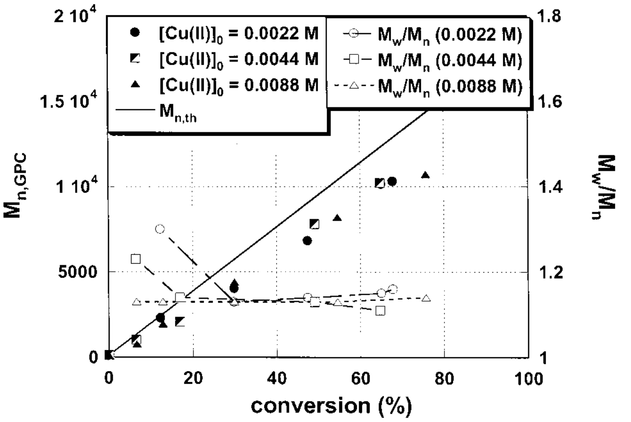

Figure 9. Evolution of molecular weights and polydispersities with conversion for the polymerization of styrene using different $[Cu(II)]_0$. $[St]_0 = 8.29$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0021-0.0084$ M; $[1\text{-}PEBr]_0 = 0.042$ M; $[AIBN]_0 = 0.0025$ M; MeOH (5 vol %); 110 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

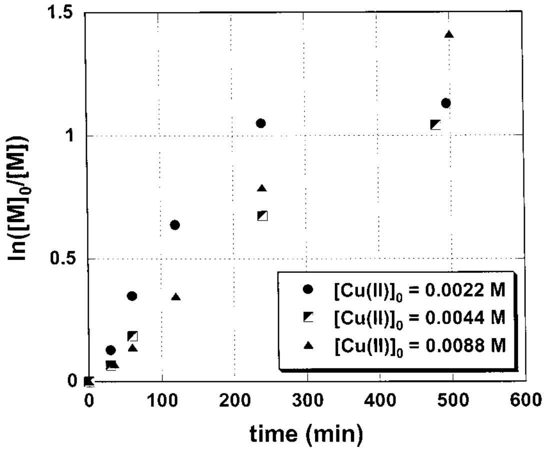

Figure 10. Effect of $[Cu(II)]_0$ on first-order kinetic plot for the polymerization of styrene. $[St]_0 = 8.29$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0021-0.0084$ M; $[1\text{-}PEBr]_0 = 0.042$ M; $[AIBN]_0 = 0.0025$ M; MeOH (5 vol %); 110 °C.

Simultaneous Reverse and Normal Initiation in ATRP of Styrene under Homogeneous Conditions. To gain a better insight about this simultaneous reverse and normal initiation process, the reverse ATRP of styrene in the presence of alkyl halide was also investigated. The polymerizations were performed using standard homogeneous conditions at 110 °C. As can be seen in Figure 9, for $[Cu(II)]_0 = 0.0044$ M, the $M_{n,GPC}$ values increased linearly with conversion, and the polydispersities were quite low, indicating a well-controlled polymerization process. The experimental molecular weights were somewhat lower than the predicted ones calculated by eq 1. Two effects may account for this observation. The first one could be transfer reactions, which were not noticed in the case of *n*-butyl acrylate. The second one, the most likely, could be the contribution of new chains generated by the thermal self-initiation of styrene. The production of radicals from this self-initiation process cannot be neglected at 110 °C, especially for a rather long reaction time and a low concentration of initiator. The first-order kinetic plot was nearly linear, indicating a constant radical concentration throughout the polymerization (Figure 10).

Effect of $[Cu(II)]_0$. The initial concentration of Cu(II) had no effect on the evolution of the molecular weights as shown in Figure 9. The experimental molecular weights increased linearly with conversion, and the molecular weight distributions were quite low (<1.20). The $M_{n,GPC}$ values were always slightly lower than the theoretical values. As shown in Figure 10, the kinetics was not significantly influenced by the initial concentration of Cu(II). At $[Cu(II)]_0 = 0.0022$ M, the apparent rate of polymerization was higher than at higher concentrations, but the difference was less noticeable than for *n*-butyl acrylate. Under these conditions, the initial copper concentration did not affect the kinetics. This behavior can be ascribed to the faster rate of AIBN decomposition and possible contribution of thermal self-initiation.

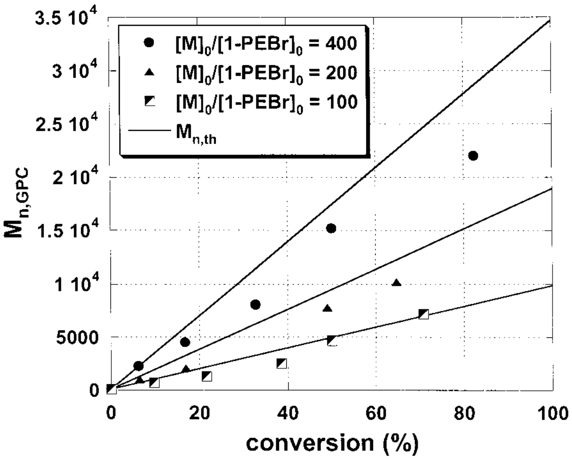

Figure 11. Evolution of molecular weights vs conversion for the polymerization of styrene using various $[RX]_0$. $[St]_0 = 8.29$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0042$ M; $[1\text{-}PEBr]_0 = 0.021-0.084$ M; $[AIBN]_0 = 0.0025$ M; MeOH (5 vol %); 110 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

Effect of $[RX]_0$. The effect of the initial concentration of alkyl halide was also studied. The different $[M]_0/[RX]_0$ ratios used in this study were the same as those examined for the polymerization of *n*-butyl acrylate, i.e., 400, 200, and 100. As shown in Figure 11, the evolution of molecular weight was strongly affected by the amount of alkyl halide introduced into the reaction medium. The theoretical molecular weights were calculated using eq 1. The experimental values were lower than the calculated ones. This deviation from the theoretical line was more significant at lower $[RX]_0$, i.e., higher $[M]_0/[RX]_0$. This would be expected from the contribution of self-initiation.

Effect of $[AIBN]_0$. Finally, the effect of $[AIBN]_0$ was examined. Figure 12 shows a good control of molecular weights, regardless of the initial AIBN concentration. The polydispersities remained low (Figure 12). Figure 13 shows the first-order kinetic plots corresponding to these experiments. At $[AIBN]_0/[Cu(II)]_0 = 0.50$, there is a long inhibition period (around 100 min), followed by slow acceleration in the rate of polymerization until a polymerization time of 200 min. This long induction period is because of the high concentration of Cu(II) at the early stage of the reactions and corresponds to the time required to reduce Cu(II) into Cu(I) to the appropriate concentration. This is accomplished not only by radicals generated from AIBN but also from the thermal self-initiation process.

Conclusions

The present study shows that reverse ATRP of both *n*-butyl acrylate and styrene using highly active cata-

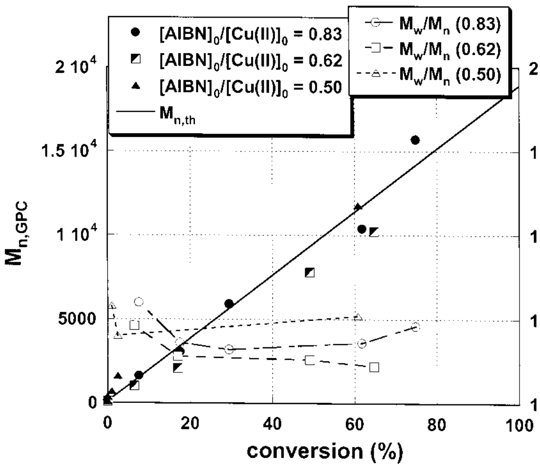

Figure 12. Effect of $[AIBN]_0$ on molecular weights and polydispersities for the polymerization of styrene. $[St]_0 = 8.29$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0042$ M; $[1\text{-}PEBr]_0 = 0.042$ M; $[AIBN]_0 = 0.0020-0.0034$ M; MeOH (5 vol %); 110 °C. $M_{n,th} = (\Delta[M]/([RX]_0 + (2 \times 0.8[AIBN]_0))M_0$.

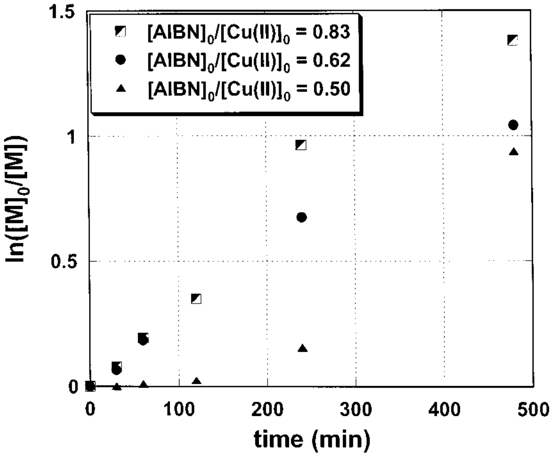

Figure 13. Effect of initial AIBN concentration on the first-order kinetic plot for the polymerization of styrene. $[St]_0 = 8.29$ M; $[CuBr_2/Me_6\text{-}TREN]_0 = 0.0042$ M; $[1\text{-}PEBr]_0 = 0.042$ M; $[AIBN]_0 = 0.0020-0.0034$ M; MeOH (5 vol %); 110 °C.

lyst, i.e., $CuBr_2/Me_6$-TREN, was successful by the means of a simultaneous reverse and normal initiation processes. The polymerization of BA was performed under both heterogeneous and homogeneous conditions, leading to controlled/living polymerizations. Well-defined poly(n-butyl acrylate) (M_n up to 40 000) with very low polydispersities, as low as 1.08, were obtained. The initial Cu(II) concentration influenced only the kinetics of the reaction, not the molecular weights. The targeted molecular weights were mainly determined by $[M]_0/[RX]_0$. The theoretical M_n values can be predicted by $\Delta[M]/[RX]_0$ ratio but could be calculated more precisely using eq 1, where the concentration and efficiency of decomposition of the standard free radical initiator should be also taken into account. The effect of $[AIBN]_0$ on the molecular weights was less important, except at low $[RX]_0$, but significant in terms of kinetics. The reverse ATRP of styrene was also carried out successfully; despite the thermal self-initiation of styrene, the experimental degrees of polymerization were principally defined by $\Delta[M]/[RX]_0$. Compared to the conventional reverse ATRP, the simultaneous reverse and normal initiation processes allowed higher [RX] relative to Cu(I). This may be a fundamental condition to reach controlled/living polymerizations with very active catalysts. In addition, a slow decomposition of the thermal initiator can be tolerated, enabling lower polymerization temperature. Finally, the most promising feature of this method is the possibility to use more reducing and more active complexes for ATRP. The simultaneous reverse and normal initiation processes therefore offer some opportunities for the development of new, highly active catalysts, especially catalysts that are unstable or difficult to handle when prepared from a lower oxidation state metal.

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