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Controlled Polymerization of Methyl Methacrylate and Styrene *via* Cu(0)-Mediated RDRP by Selecting the Optimal Reaction Conditions

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Electronic Supplementary Information

Abstract Cu(0)-mediated reversible deactivation radical polymerization (Cu(0)-mediated RDRP) has been demonstrated as an excellent technique to control the polymerization of multiple vinyl monomers (*e.g.*, acrylates, methacrylates, and styrene). However, the complexity of the reaction mechanism and multi-component system nature make it challenging to choose the appropriate conditions and consider the factors of achieving controllable polymerization when switching from one monomer to others with different reactivities. Herein, by polymerizing two examplary monomers: methyl methacrylate (MMA) and styrene *via* Cu(0)-mediated RDRP under different conditions, we have found that the reaction parameters (*e.g.*, initiator, ligand, solvent, and deactivator) play a crucial role in regulating two equilibriums: (i) mutual conversion of different copper species which determines the relative concentration of Cu(I) and Cu(II), and (ii) polymerization equilibrium which is the combination of activation/deactivation, propagation and termination processes. We have demonstrated that by taking both the mutual conversion of different copper species and the polymerization equilibrium into account, the optimal reaction conditions could be selected, and the well-controlled Cu(0)-mediated RDRPs of methyl methacrylate and styrene were achieved with narrow molecular weight distributions and predicted molecular weight.

Keywords Cu(0)-mediated RDRP; Reaction parameters; Polymerization equilibrium; Mutual conversion of copper species

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INTRODUCTION

The past decades have witnessed the significant progress of radical polymerization, in particular, the emergence of reversible deactivation radical polymerization (RDRP)[1,2] (also known as controlled/'living' radical polymerization (CLRP)). Based on a dynamic equilibrium in RDRP, the lifetime of growing chains is significantly extended by inserting a dormant period between short active stages. The three most commonly used RDRP techniques are nitroxide-mediated polymerization (NMP),[3,4] atom transfer radical polymerization (ATRP),[5,6] and reversible addition-fragmentation chain transfer polymerization (RAFT).[7] Besides, Cu(0)-mediated RDRP (commonly referred as supplemental activation and reducing agents (SARA) ATRP[8] or single-electron transfer living radical polymerization (SET-LRP))[9] has attracted intense attention owning to its great potential.[10−12]

Metallic copper (Cu(0)) was first introduced to ATRP system in 1997.[13] In the classic ATRP system, a dormant species (P_n-X, X is typically Br or Cl) can be activated by a transition metal complex in lower oxidation state, typically Cu(I)X/L, to generate a radical ($P_n\cdot$) and a transition metal complex (Cu(II)X_2/L) in higher oxidation state. The active radical is subsequently subjected to monomer addition and then deactivated by Cu(II)X_2/L to give dormant species (P_n-X). However, Cu(0)-mediated RDRP has an unaccounted-for polymerization mechanism due to the inherent complexity, *i.e.* the coexistence of three valence copper species—Cu(0), Cu(I), and Cu(II). SARA ATRP and SET-LRP are the two main mechanisms of Cu(0)-mediated RDRP, which are contradictory to each other. In SARA ATRP,[14−18] the activation of alkyl halides is achieved mainly by Cu(I) rather than Cu(0) in a so-called inner-sphere electron transfer (ISET) manner, while in SET-LRP,[9,12] Cu(0) is proposed to be the major activator that activates the alkyl halides by outer-sphere electron transfer (OSET), and the generated Cu(I) species instantaneously disproportionate to Cu(0) and Cu(II). Besides these two distinct mechanisms, some intermediate explanations were also proposed. For instance, Harrisson *et al.*[19−21] concluded that in Cu(0)-mediated RDRP system, initiators are activated by both Cu(0) and Cu(I) species; moreover, significant levels of comproportionation were observed even in polar solvents, which led to auto acceleration

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of the reaction and uncontrolled polymerization at the early stage. Wang *et al*.[22,23] investigated the mechanism and in particular the origins of the induction period of Cu(0)-mediated RDRP by employing various catalyst systems (Cu(0), Cu(I) and Cu(0)&Cu(II)) with different ligands. They demonstrated that the polymerization mechanism of Cu(0)-mediated RDRP is the equilibrium and competition of these two main mechanisms.

Cu-based reversible deactivation radical polymerization (RDRP) usually requires the optimized selection of various parameters (*e.g.*, the type of initiator, ligand, and solvent, and the amount of deactivator) to obtain polymers with well controlled molecular weight and molecular weight distribution. A suitable combination (initiator, ligand, and solvent) for a certain monomer is crucial for the successful polymerization, as their reactivity can vastly influence the polymerization rates and thus compromise overall control.[2,9,24,25] In traditional ATRP reaction catalyzed only by Cu(I), the effect of different initiators,[26,27] ligands,[28,29] and solvents[30,31] on the ATRP equilibrium constant (K_{ATRP}) can be accurately measured. Therefore, in general, the appropriate reaction conditions in ATRP system can be selected by considering the influence of different parameters on K_{ATRP}. Based on these studies in Cu(I)-mediated system, initiators are commonly selected when their structures resemble that of the monomers (*e.g.*, methyl 2-bromopropionate (MBrP) for methyl acrylate (MA), ethyl *α*-bromoisobutyrate (EBriB) for methyl methacrylate (MMA), and 1-phenylethyl bromide (PEBr) for styrene, *etc.*) or their activity is slightly higher than that of the monomers. As such, the initiators can be rapidly converted to primary radicals at the beginning of the polymerization so as to ensure the concurrent growth of all polymer chains.[6,32] Besides, the ligand and solvent are also important parameters which have effects on the ATRP equilibrium constant (K_{ATRP}) and the controllability of polymerization.[28−31] In general, more active ligands are more capable of providing better control when reacting with monomers with high propagation rate constant (k_{p}), *e.g.*, acrylates, and less active ligands are more suitable for monomers with low k_{p}, *e.g.*, methacrylates and styrenes.[33−35]

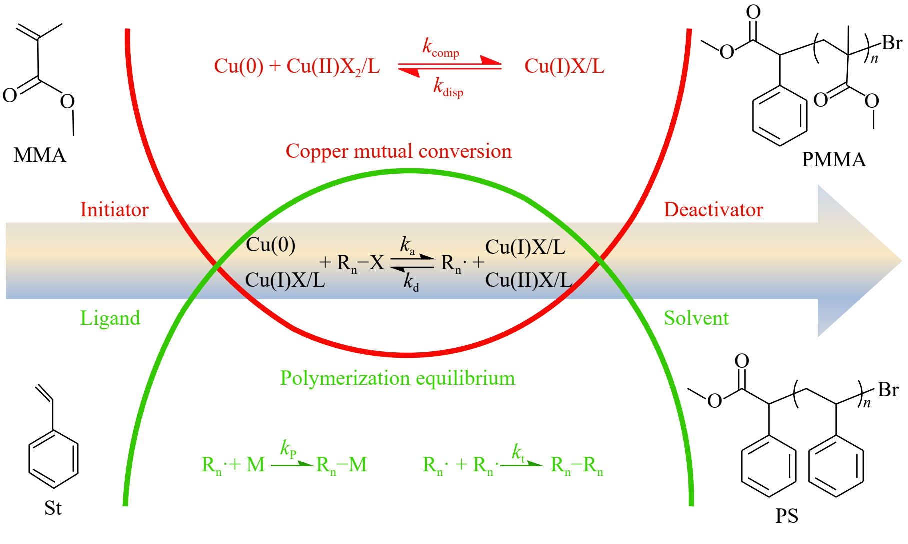
However, in Cu(0)-mediated RDRP systems, given the role of different copper species (*i.e.* the activation of Cu(0) and Cu(I)) and their conversion dependency on various parameters (*e.g.* polarity of the solvent, coordination of the ligand, activity of the initiator), it is challenging to accurately measure the effect of a certain parameter on the K_{ATRP} value. Although many researchers have achieved the controlled polymerizations of a variety of vinyl monomers,[36−40] for example, polymerizations of methyl methacrylate and styrene controlled by the initiator type,[36,37] as the polymerization system described above is extremely complex, it remains difficult to choose the suitable parameters and consider the factors of achieving controllable polymerization when switching from one monomer to others with different reactivities yet. Therefore, to understand and predict the Cu(0)-mediated RDRP process, the effects of different parameters on both the equilibrium between different copper species (disproportionation and comproportionation) and the equilibrium among activation/deactivation, propagation, and termination processes (polymerization equilibrium) should be considered together (Scheme 1).

In this work, we investigated the Cu(0)-mediated RDRP of MMA and styrene by considering the synergetic effect of mutual conversion equilibrium between copper species (Cu(0), Cu(I), and Cu(II)) and polymerization equilibrium under different conditions (changing the amount of deactivator Cu(II) and the type of initiator, ligand, and solvent). Through analysing and understanding the effects of different conditions on these two equilibriums, conditions for the Cu(0)-mediated RDRP of MMA and styrene were optimized and the polymers with narrow molecular weight distributions (MWDs) and predicted molecular weight (MW) were obtained.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, 99%, Aldrich), styrene (99.9%,



Scheme 1 Schematic representation of Cu(0)-mediated RDRP based on two kinds of equilibriums: the mutual conversion of different copper species and the polymerization equilibrium

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Aldrich), ethyl α-bromoisobutyrate (EBriB, 98%, Aldrich), methyl α-bromophenylacetate (MBPA, 97%, Aldrich), copper(I) bromide (CuBr, 99.9%, Aldrich), copper(II) bromide ($CuBr_2$, 99%, Aldrich), dimethyl sulfoxide (DMSO, 99.5%, Aldrich), *N*,*N*-dimethylformamide (DMF, 99.8%, Aldrich), toluene (99.8%, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), and tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 97%, Aldrich) were used as received unless otherwise stated. Cu(0)-wire (diameter 1 mm) was purchased from Sigma-Aldrich and was treated by immersion in conc. HCl prior to use. Solvents were purchased from Fisher Scientific and used as received.

Characterization

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) were obtained by SEC (Agilent GPC/SEC 50) equipped with RI and LS detectors. The columns (30 cm PLgel Mixed-C, two in series) were eluted using *N*,*N*-dimethylformamide (DMF) and calibrated using a series of 12 near-monodisperse PMMA standards (M_p from 690 g/mol to 1.944×10^6 g/mol). The polymers were analyzed in DMF at a concentration of 5.0 mg/mL. All calibrations and analyses were performed at 40 °C and a flow rate of 1 mL/min. ^{1}H-NMR analysis was carried out on a Varian NMR system 400 MHz spectrometer with MestRenova 6.1 processing software and reported in parts per million (ppm) relative to the response of $CDCl_3$ (7.26 ppm) and tetramethylsilane (0.00 ppm).

Synthesis of PMMA *via* Cu(0)-mediated RDRP

MMA (10 mL, 94.4 mmol, 100 equiv.), EBriB (138 μL, 0.944 mmol, 1 equiv.)/MBPA (149 μL, 0.944 mmol, 1 equiv.), Me_6TREN (46 μL, 0.17 mmol, 0.18 equiv.), and DMSO/DMF (10 mL) were added into the two-neck flask and bubbled with argon to remove oxygen for 15 min. A stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl and then thoroughly rinsed with acetone and water. After the pre-treated Cu(0)-wire was dried, it was added to the flask quickly under a positive pressure of argon. The reaction was stirred at 600 r/min in an oil bath at 25 °C, and polymerization was conducted for a desired period of reaction time.

Synthesis of Polystyrene *via* Cu(0)-mediated RDRP

Styrene (10 mL, 97.4 mmol, 100 equiv.), MBPA (138 μL, 0.87 mmol, 1 equiv.), Me_6TREN (43 μL, 0.16 mmol, 0.18 equiv.)/PMDETA (33 μL, 0.16 mmol, 0.18 equiv.), and DMSO/DMF/toluene (10 mL) were added into the two-neck flask and bubbled with argon to remove oxygen for 15 min. A stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl and then thoroughly rinsed with acetone and water. After the pre-treated Cu(0)-wire was dried, it was added to the flask quickly under a positive pressure of argon. The reaction was stirred at 600 r/min in an oil bath at the required temperature, and polymerization was conducted for a desired period of reaction time.

RESULTS AND DISCUSSION

Cu(0)-mediated RDRP of MMA

Successful Cu(0)-mediated RDRP of acrylates (*e.g.*, MA) can be carried out at ambient temperature using ethyl α-bromoisobutyrate (EBriB), tris[2-(dimethylamino)ethyl] amine (Me_6TREN), and dimethyl sulfoxide (DMSO) as initiator, ligand, and solvent, respectively. In this work, by maintaining the same conditions (DMSO as solvent, Me_6TREN as ligand, Cu(0)-wire as catalyst, and EBriB as initiator), the polymerization of MMA (whose k_p is relatively low compared to MA), however, led to broad MWDs ($Đ > 1.6$) with a much slower polymerization rate—the monomer conversion reached 78.7% after 20 h (entries 1–3 in Table 1) and obvious tails in GPC peaks (Fig. 1a) which normally is the sign of poor control. Furthermore, unlike in the acrylates system, where adding 5% Cu(II) (to initiator) can significantly improve the polymerization behavior,[22] the polymerization process was still poorly controlled with $Đ > 1.5$ after adding the same amount of Cu(II) (entries 4–6 in Table 1, Fig. 1b). We reason that such difference between the acylate and methacrylate monomers could be attributed

Table 1 ^{1}H-NMR and SEC analysis of the polymerization of MMA with DMSO as solvent at 25 °C [a]

Entry	Initiator	Catalyst [b]	Time (h)	$M_{n,th}$ [c]	$M_{n,SEC}$ [d]	$Đ$ [d]	Conv. [e] (%)
1	EBriB	Cu(0)	2	1230	3130	1.63	10.4
2			6	1970	4510	1.64	17.8
3			20	8070	12640	1.64	78.7
4		Cu(0)&Cu(II) (5%)	2	1260	2860	1.51	10.7
5			6	2730	4710	1.61	25.4
6			20	8840	12610	1.51	86.5
7		Cu(0)&Cu(II) (50%)	2	–	–	–	–
8			6	3120	5850	1.27	29.3
9			20	9310	10470	1.28	91.2
10	MBPA	Cu(0)	2	1130	1710	1.34	9.10
11			6	5080	7210	1.24	48.5
12			20	8660	11840	1.32	84.4
13		Cu(0)&Cu(II) (5%)	2	880	1760	1.27	6.50
14			6	4880	7230	1.21	46.5
15			20	8110	12790	1.21	78.8

[a] Reaction conditions: [M]:[I]:[L] = 100:1:0.18; L = Me_6TREN, Solvent = DMSO (10 mL), $T = 25$ °C; [b] Cu(0) = pretreated Cu(0)-wire ($l = 5$ cm, $d = 1$ mm), Cu(II) = $CuBr_2$; [c] $M_{n,th} = ([M]_0/[I]_0) \times \text{conversion} \times \text{MW}$; [d] Number-average molecular weights ($M_{n,SEC}$) and polydispersity ($Đ$) characterized using size exclusion chromatography (SEC) equipped with an RI detector; [e] Monomer conversion measured by ^{1}H-NMR (Fig. S6 in electronic supplementary information, ESI); "–" No polymer generated

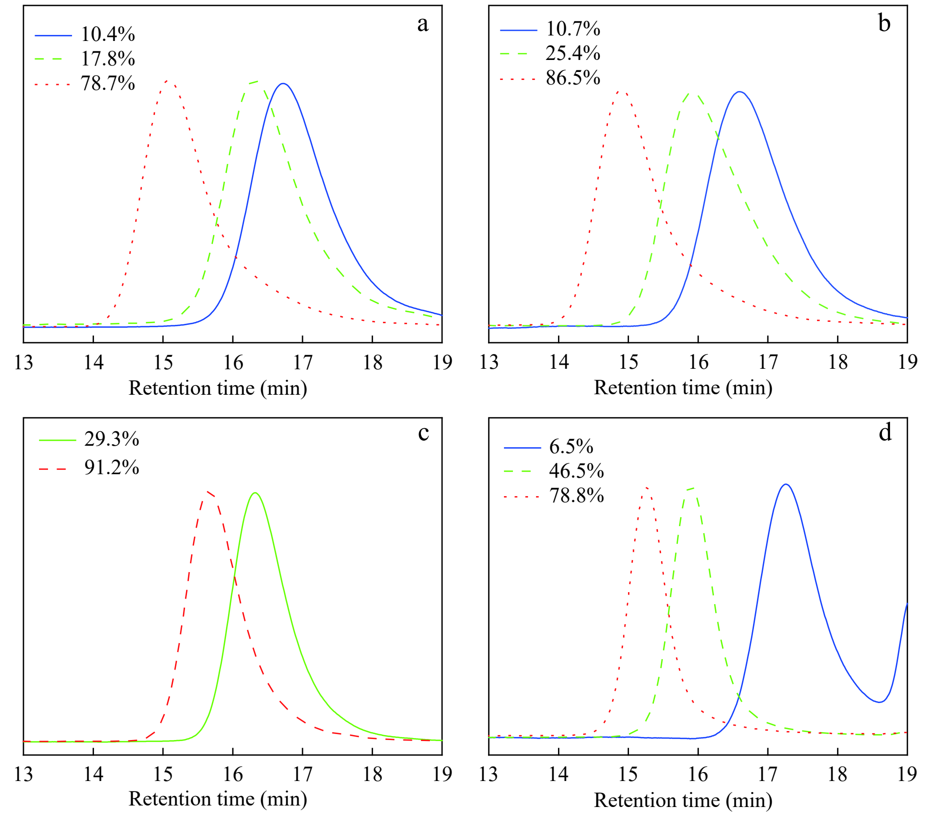

Fig. 1 The evolution of MW monitored by SEC: (a) Cu(0)/Me_6TREN-mediated RDRP of MMA with EBriB as initiator in DMSO; (b) Cu(0)&Cu(II)/Me_6TREN-mediated RDRP of MMA with EBriB as initiator in DMSO, Cu(II) = $CuBr_2$ (5% to initiator); (c) Cu(0)&Cu(II)/Me_6TREN-mediated RDRP of MMA with EBriB as initiator in DMSO, Cu(II) = $CuBr_2$ (50% to initiator); (d) Cu(0)&Cu(II)/Me_6TREN-mediated RDRP of MMA with MBPA as initiator and DMSO as solvent, Cu(II) = $CuBr_2$ (5% to initiator)

to the influence of monomer reactivity on copper mutual conversion. For Cu(0)-mediated RDRP of MMA, the lower k_p results in a slower polymerization equilibrium and longer time for copper mutual conversion at the early stage of polymerization. In this case, the small amount of Cu(II) extra added is mostly consumed in the comproportionation process rather than acting as extra deactivator contributing to the kinetic control. Meanwhile, the structure of EBriB is similar to that of the monomer—MMA, meaning that the monomer adduct structure resembles the initiators, as such the favor of initiation reaction over activation of dormant species cannot be maintained, which is critical for RDRP reaction.

Based on this, we speculate that at the early stage of MMA polymerization, a higher concentration of Cu(II) would be beneficial to achieving well-controlled polymerization. Thus, 50% equiv. (to initiator) of Cu(II) was added. Indeed, the controlled polymerization process was successfully obtained with predicted MW ($M_{n,th}$ = 9310, $M_{n,SEC}$ = 10470 at 20 h) and narrow MWDs ($Đ$ < 1.28) (entries 7–9 in Table 1). Moreover, from the GPC results (Fig. 1c), it can be seen that the tailing phenomenon is also diminished. All these suggest that strong deactivation is required to achieve the well-controlled polymerization of MMA *via* Cu(0)-mediated RDRP. However, the large amount of Cu(II) added resulted in a long induction period (no polymer obtained, entry 7 in Table 1) due to the longer period of mutual conversion of different copper species (comproportionation/disproportionation). Moreover, the high concentration of soluble copper species made the post polymerization purification more difficult.

As mentioned above, the tailing phenomenon from GPC peaks could also be attributed to the similar structure of initiator to monomer, making the fast initiation process impossible. Therefore, to find a controlled reaction system with fewer copper species involved, we switched the initiator EBriB to methyl α-bromophenylacetate (MBPA), which has higher activity,[37] while keeping the other conditions exactly the same. From the GPC traces in Fig. S1 (in ESI), obvious parallel shifts with minimal tailing drift can be observed, indicating an improved controllability of the polymerization process (entries 10–12 in Table 1). These results demonstrate that when an initiator with high activity, such as MBPA, is used in the polymerization system of MMA, the activation rate and addition rate of the initiator to monomer would be high; in this way, a low amount of Cu(II) would be required at the early stage to achieve a controlled polymerization. Under this condition, the addition of a small amount of Cu(II) (5% to initiator) can slightly improve the controllability ($Đ$ = 1.21 at 20 h, entry 15 in Table 1, Fig. 1d).

Therefore, for Cu(0)-mediated RDRP of MMA, the controllability can be improved by using highly active initiator and excessive extra Cu(II). This confirms that the degree of deactivation (*i.e.*, the amount of Cu(II) which can be influenced by the equilibrium between different copper species and the activity of initiator) and the relative rate of initiation and propagation (polymerization equilibrium) should be considered when switching a monomer in Cu(0)-mediated RDRP systems. The general trends are: for Cu(0)-mediated RDRP of MMA, either a relatively lowly reactive initiator combined with a higher amount of Cu(II) or a more highly reactive initiator and lower amount of Cu(II) are needed to achieve the controlled polymerization. The mechanism could be attributed to that the lower k_p results in a slower establishment of polymerization equilibrium and longer time for copper mutual conversion at the early stage of polymerization and thus the small amount of Cu(II) extra added is mostly consumed in the comproportionation process rather than acting as extra deactivator contributing to the kinetic control.

In addition, to further improve the controllability of the polymerization process, DMF was chosen as solvent to investigate the only Cu(0)-mediated RDRP of MMA, since the K_{ATRP} value in DMF is smaller than that in DMSO.[31] The monomer conversion was only 18.9% at 6 h ($Đ$ = 1.28, entry 2 in Table S1, Fig. S2 in ESI), which is much lower than that in DMSO system, where 48.5% of monomer conversion was achieved (entry 11 in Table 1, Fig. S1 in ESI). This indicates that the polymerization in DMF is also in a controlled manner although is much slower. The controllability of the polymerization can be slightly improved ($Đ$ = 1.25 in DMF, entry 3 in Table S1 in ESI, $Đ$ = 1.32 in DMSO, entry 12 in Table 1).

Cu(0)-mediated RDRP of Styrene

Based on these results, we further explored the Cu(0)-mediated RDRP of styrene. Styrene has an even lower k_p compared to MMA. According to the above conclusion (the Cu(0)-mediated polymerization of MMA), this could lead to a slower polymerization equilibrium, and the system could have more time for the mutual conversion to proceed between different copper species (*e.g.*, comproportionation/disproportionation). It means that adding only a small amount of Cu(II) is not an effective way to control the polymerization process, and therefore, the selection of a proper initiator can make the amount of Cu(II) desired at the early stage for a controlled polymerization.

Based on these considerations, for Cu(0)-mediated RDRP of styrene, we first chose MBPA as initiator, DMF as solvent (the solubility of polystyrene is extremely low in DMSO) and Cu(0)/Me$_6$TREN as catalyst to investigate its polymerization behaviour at 25 °C. It can be found that the polymerization rate was very slow—the monomer conversion was 32.4% at 45 h (entry 2 in Table 2, Fig S3 in ESI). In order to monitor the polymerization process in a faster manner, we increased the reaction temperature (40 and 60 °C) to investigate the polymerization behaviour of styrene under the same conditions. These results (entries 3−7 in Table 2) show that narrow MWDs can be obtained at lower monomer conversion (Conv. = 15.8%, $Đ$ = 1.21 at 25 °C, Conv. = 33.8%, $Đ$ = 1.17 at 40 °C, and Conv. = 28.3%, $Đ$ =1.18 at 60 °C), and the GPC curves show parallel shifts at the early stage (Fig. 2a, Figs. S3 and S4 in ESI). This further confirms that under a slow polymerization equilibrium, the initiator with high activation rate constant (k_{act}) can ensure the fast initiation process and accumulate sufficient Cu(II) required for a controlled polymerization system at the early stage of the reaction. However, when monomer conversion further increased, MWDs became broad (Conv. = 32.4%, $Đ$ = 1.37 at 25 °C, Conv. = 51.2%, $Đ$ = 1.36 at 40 °C, and Conv. = 61.0%, $Đ$ = 2.09 at 60 °C) (changing temperature can only speed up the polymerization rate but cannot improve the polymerization controllability). This could be attributed to the enhanced radical termination reactions, because as the reaction progresses, the monomer concentration decreases, which makes the free radical termination reactions occur more easily and the reaction more uncontrollable.

Regarding the uncontrollable polymerization caused by insufficient deactivation in the polymerization equilibrium at the late stage of the reaction, we further changed the ligand to *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), which can reduce K_{ATRP} of the polymerization system.[29] However, the controllability at the late stages of the reaction was not improved, as shown by $Đ$ of 1.61 at monomer conversion of 63.1% (entry 9 in Table 2, Fig. S5 in ESI), even when a small amount of Cu(II) (5% to initiator) was added ($Đ$ = 1.79, monomer conversion is 60.6%, entry 10 in Table 2). This proves again that for a system with a slow polymerization equilibrium, adding a small amount of Cu(II)

Table 2 ^{1}H-NMR and SEC analysis of the polymerization of styrene with MBPA as initiator [a]

Entry	Solvent	Catalyst [b]	Ligand	Temp. (°C)	Time (h)	$M_{n,th}$ [c]	$M_{n,SEC}$ [d]	$Đ$ [d]	Conv. [e] (%)
1	DMF	Cu(0)	Me$_6$TREN	25	20	1870	2440	1.21	15.8
2					45	3600	6240	1.37	32.4
3				40	20	3450	3490	1.15	31.0
4					30	3740	4200	1.17	33.8
5					45	5550	6360	1.36	51.2
6				60	6	3170	2910	1.18	28.3
7					20	6570	7460	2.09	61.0
8	DMF	Cu(0)	PMDETA	60	6	4080	2760	1.16	37.1
9					20	6790	8480	1.61	63.1
10	DMF	Cu(0)&Cu(II) (5%)	PMDETA	60	20	6530	6460	1.79	60.6
11	Toluene	Cu(0)	PMDETA	60	25	4780	3970	1.13	43.8
12					40	6410	5670	1.12	59.5
13					65	7610	6610	1.12	70.1

[a] Reaction conditions: [M]:[I]:[L] = 100:1:0.18, Solvent 10 mL; [b] Cu(0) = pretreated Cu(0)-wire (l = 5 cm, d = 1 mm), Cu(II) = CuBr$_2$; [c] $M_{n,th}$ = ([M]$_0$/[I]$_0$) × conversion × MW; [d] Number-average molecular weights ($M_{n,SEC}$) and polydispersity ($Đ$) characterized using size exclusion chromatography (SEC) equipped with an RI detector; [e] Monomer conversion measured by ^{1}H-NMR (Fig. S7 in ESI)

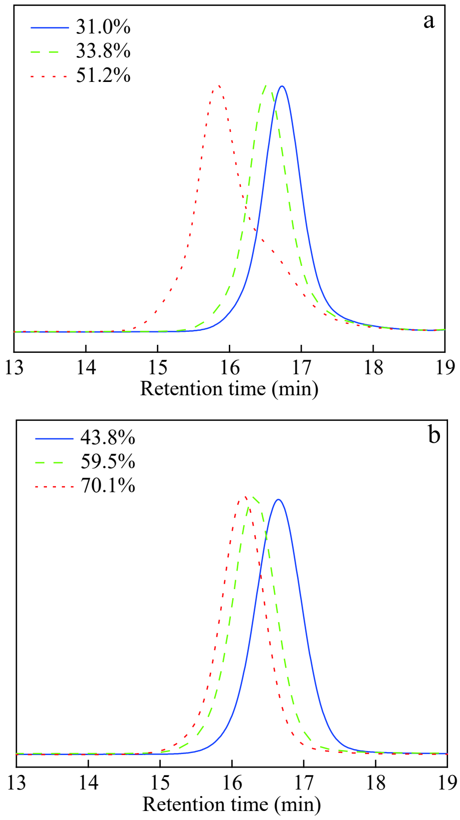

Fig. 2 The evolution of MW monitored by SEC: (a) Cu(0)-mediated RDRP of styrene with MBPA as initiator, Me_6TREN as ligand, and DMF as solvent; (b) Cu(0)-mediated RDRP of styrene with MBPA as initiator, PMDETA as ligand, and toluene as solvent

does not improve the controllability in the later stage of polymerization because of the mutual conversion of copper species. These results indicate that even if we reduce the K_{ATRP} value of polymerization system, the degree of deactivation is still insufficient at the late stage of polymerization. Therefore, to further enhance the degree of deactivation in the system, we chose toluene as the solvent (maintaining MBPA, PMDETA and Cu(0)-wire unchanged) which can lead to a much small K_{ATRP}.[31] In this situation, it can be seen from entry 13 in Table 2 that MWD was narrow ($Đ$ = 1.12) when the monomer conversion rate reached 70.1%. In addition, it can be observed from Fig. 2(b) that the GPC curves present obvious parallel shifts. Therefore, for the problem of uncontrollable polymerization in the late stage of reaction, we can enhance the degree of deactivation in the reaction system by selecting suitable solvents and ligands to improve the controllability.

CONCLUSIONS

For the complex system of Cu(0)-mediated RDRP, we collectively considered the effects of mutual conversion of different copper species (Cu(0), Cu(I), and Cu(II)) and the polymerization equilibrium to select appropriate reaction conditions for the controlled polymerization of MMA and styrene. It has been demonstrated that the activity of the initiator and the mutual conversion of the soluble copper species (Cu(0), Cu(I), and Cu(II)) are the main factors that affect the controllability of polymerization in the early stage, and the impact of the initiator activity is more significant (when k_p is low, the excessive amount of Cu(II) would be mainly consumed by the comproportionation). Moreover, it is found that activities of the solvent and ligand can affect K_{ATRP} and determine the controllability at the late stage of the reaction. To conclude, different polymerization parameters (initiator, ligand, solvent, and the amount of deactivator *i.e.*, Cu(II)) can influence the controllability throughout the entire polymerization process by influencing two equilibriums—mutual conversion of different copper species and polymerization equilibrium, which should be comprehensively considered to achieve a controlled polymerization system.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-019-2236-x.

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