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ORIGINAL PAPER

A novel ligand for atom transfer radical polymerization

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Abstract A ligand is a crucial element for atom transfer radical polymerization (ATRP). A new nitrogen-containing compound, 1,1'-(2,2'-(ethane-1,2-diylbis(butyl azanediyl)) -bis(ethane-2,1-diyl)) dipyrrolidin-2-one (DBBD), was synthesized and utilized as the ligand of copper halide for ATRP of methyl methacrylate (MMA) and methyl acrylate (MA). It was found that the CuBr/DBBD and Ethyl 2-bromoisobutyrate (EBIB) system could mediate the polymerization of MMA and the reaction was first-order kinetics, although the control of molecular weights was not perfect. When CuCl was used to replace CuBr, the molecular weights of obtained polymers were well controlled, which indicated the halide exchange could improve the controllability. In the polymerization of MA using Methyl 2-bromopropronate (MBP) or EBIB as initiator and CuCl/DBBD as catalyst, good control of the polymerization could be achieved and the molecular weights were very close to the predicted value.

Keywords Atom transfer radical polymerization · Ligand · Electrochemistry

Introduction

Transition-metal-mediated living radical polymerization, also named atom transfer radical polymerization (ATRP), has been developed as a versatile tool for the synthesis of (co)polymers with well-controlled molecular weights and low

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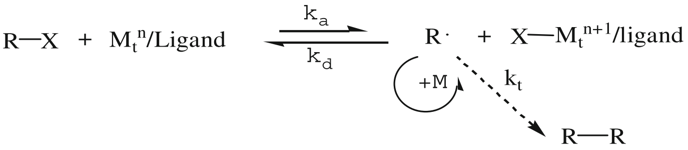


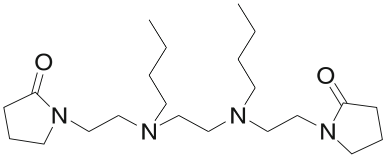
Scheme 1 Atom Transfer Radical Polymerization (ATRP)

polydispersity as well as various functionalities and architectures [1–4]. For example, ATRP has been used to synthesize block [5–7], star [8], graft [9, 10], comb [11], hyperbranched (co)polymers [12–14], inorganic/organic hybrid polymers [15], liquid-crystalline polymers [16]. Moreover, it has been used as a tool in many fields such as surface functionalization [17, 18], click chemistry [19, 20], separation science [21, 22] and so on.

To reach the aim of obtaining well-controlled polymers by ATRP, a proper catalyst should be selected and is generally composed of a transition-metal halide and a ligand, which can form complexes with the metal during the polymerization. So the catalytic activity and its controlling of the polymerization depend strongly on the types of ligands and the metal halides, and a proper redox potentials and halogenophilicity of the transition-metal complexes should be important to ATRP [23] (shown in Scheme 1). Among the various metal compounds developed for ATRP, Cu system was found to be the most versatile and active for various monomers. So numerous ligands for copper halide were synthesized to obtain a proper catalyst for ATRP such as 2,2-bispyridine and its derivative, bidentate and multidentate amines, picolylamine, and pyridylmethanimines. The structure, solubility and electronic character of ligand have significant influence on the catalytic activity and control of the polymerization. Therefore, one of the active research areas in ATRP is to design ligands that can form highly active catalysts, and to correlate their molecular structure and other characters with the catalyst activity and control of the polymerization.

Our objective in the present work is to develop a new useful ATRP ligand. In this paper, we reported a nitrogen bidentate compound having 2-dipyrrolidone structure, which was first used as ligand for copper (I) halide in ATRP process (Scheme 1). The behavior of this new catalytic system (Cu(I)X/DBBD) were studied in the polymerization of methyl methacrylate and methyl acrylate. Besides, the effect of the substituents to the controllability and reactivity of ATRP was also studied (Scheme 2).

Scheme 2 Structure of 1,1’-(2,2’-(ethane-1,2-diylbis(butylazanediyl))bis(ethane -2,1-diyl))-dipyrrolidin-2-one



Experimental

Materials

Methyl methacrylate,methyl acrylate were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC), and purified by distillation under vacuum. CuBr and CuCl (SCRC) were purified according to the literature [24]. Ethyl 2-bromoisobutyrate (EBIB) was purchased from Aldrich, Methyl 2-bromopropronate (MBP) was purchased from Wuhan Shengshi Chemical company and was distilled prior to use (143–145 °C). Triethylenetetraamine, Dihydro-furan-2-one, 1-Bromo-butane were obtained from SCRC. The other reagents were all purchased from SCRC and used as received. *N*-butyl-*N*-methyl morpholinium tetroflurobortate ($Mor_{1,6}BF_4$) was synthesized as our previous work [25].

Synthesis of DBBD

DBBD was synthesized according to the literature [26] and the detailed procedure is shown in supporting information 1.2.

Polymerizations

CuBr and a stirring bar were put into a reaction tube. The tube was tightly sealed with a rubber septum and three cycles of evacuating and backfilling with nitrogen were conducted. Then the degassed monomer (with anisole as internal standard and the ratio to monomer was 1:10 w/w), solvent and DBBD ligand mixture was added via a degassed syringe. The tube was immersed in oil bath which was set at desired temperature. Then the initiator EBIB was added to the mixture until the solution was homogenized. At different time intervals, samples were withdrawn from the tube with a nitrogen-purged syringe, and dissolved in THF. For MMA and MA, the conversion was measured with GC-MS by the ratio of monomer peak area to the internal standard. The molecular weights and polydispersities of the polymers were measured by gel permeation chromatography (GPC).

Characterization

Conversion measurements were conducted on a Thermo Finnigan GC-MS equipped with a fused silica capillary column (DB-5, 30 m × 0.25 mm × 0.25 μm) threaded into the ion source region of a Trace DSQ mass spectrometer (anisole as an internal standard). Molecular weights and molecular weight distributions were measured on a GPC system consisting of a Waters 515 pump, Wyatt Technology Optilab DSP and DAWN® EOS™. The columns were consisted of MZ gel SDplus linear 5 μm column and 500Å column and PSt with molecular weights 30,000 and 200,000 were used to calibrated the GPC.

Cyclic voltammetric measurements

Electrochemical experiments were performed in a three-electrode cell under argon constituted of a glass carbon (diameter 4 mm) as working electrode, a platinum wire as counter electrode. The reference electrode was Ag/AgCl (saturated KCl solution) separated from KCl solution by a salt bridge filled with 0.1 M $Mor_{1,6}BF_4$ solution in DMF. The scan rate was 100 mV s^{-1}. The concentrations of the copper complexes were kept at 0.01 M in all measurements.

Results and discussions

Polymerization of MMA using Cu(I)X/DBBD as the catalyst

To study the catalytic behavior of this new ligand in the ATRP of MMA, we launched the polymerization at 60 °C, using CuBr/DBBD as catalyst, EBIB as initiator and DMF as solvent. Figure 1 showed The relationship between $\ln([M]_0/[M])$ and conversion versus reaction time. The data revealed that the polymerization kinetics using DBBD ligand is first-order, because the number of propagating species remained constant during the polymerization process (Fig. 1). [P·] the concentration of steady state propagating species, can be calculated from $[P\cdot] = k_p^{app}/k_p = (d\ln[M]/dt)/k_p$ (Eq. 1), where dln[M]/dt is the slope of the plot of $\ln([M]_0/[M]_t)$ versus time (t) and the rate constant of radical propagation for MMA ($k_p = 8.31 \times 10^2\ M^{-1}S^{-1}$ at 60 °C) can be calculated from Eq. 2 [27]. The calculated concentration of propagating radicals appeared to be 8.2×10^{-8} M in 1/1 (w/w) MMA/DMF solution, which is similar to the value of some tridentate ligand [28].

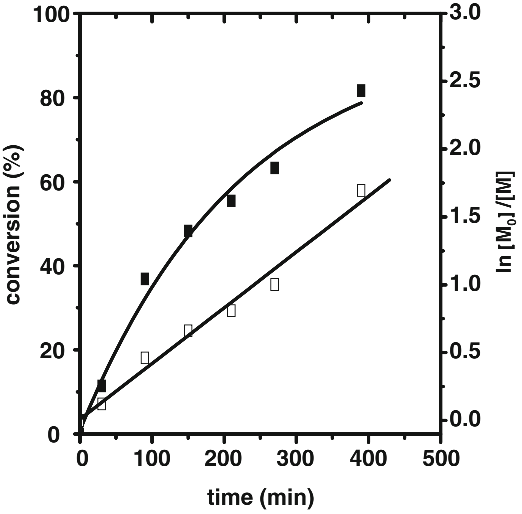
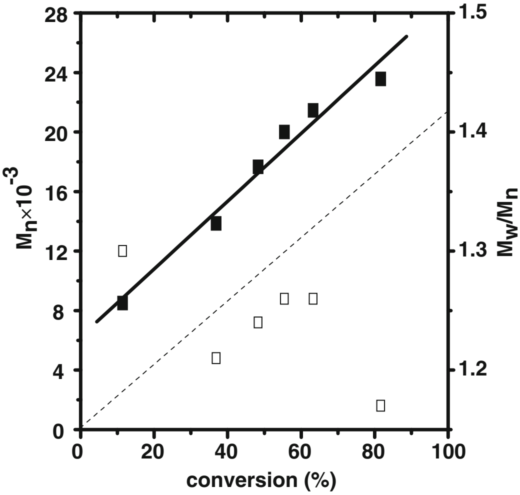


Fig. 1 The relationship between $\ln([M]_0/[M])$ and conversion versus reaction time. The polymerization conditions:M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:0.5:1:2 (molar ratio), $T = 60$ °C

Fig. 2 Plot of molecular weight and polydispersity versus conversion of MMA at 60 °C in DMF. Conditions:M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:0.5:1:2 (molar ratio)



$$R_p = -d[\mathrm{M}]/dt = k_p[\mathrm{P_n}\cdot][\mathrm{M}] = k_p^{\mathrm{app}}[\mathrm{M}]$$

$$d\ln[\mathrm{M}]/dt = k_p[\mathrm{P_n}\cdot] = k_p^{\mathrm{app}} \tag{1}$$

$$k_p = 10^{6.427}\mathrm{L\,mol^{-1}\,s^{-1}}\exp(-22.36\,\mathrm{kJ\,mol/RT})[27] \tag{2}$$

The changes of number-average molecular weight (M_n) of the obtained PMMA with conversion were listed in Fig. 2. The result indicated that M_n increases linearly when the monomer conversion increases, and the molecular weight distribution (M_w/M_n) of the polymers is in the range of 1.17–1.30. However, the plot of M_n versus conversion does not pass through the origin, and this should be due to a slow initiating process. The initiating efficiency estimated by M_{th} and M_{GPC} increased from 0.4 to 0.7 which also confirmed that the initiating rate was relatively slower than the propagation rate. This may be attributed to the back strain effect [29] and the steric bulky ligand. Matyjaszewski et al. [30] had reported similar results in the polymerization of MMA using EBIB/CuBr/dNbpy complex system. In their opinion, the substituent groups of the propagating radicals play a major role in the reactivity of the radicals, which should be lowered when the β-carbon of the radical was replaced by the substituent groups during the polymerization. This may lead to the observed deviation from the theoretical molecular weight at lower conversion as our experiments has showed. The higher reactivity of radical with shorter chains should correlate with the lower equilibrium constant and lower overall initiator efficiency. However, the molecular weight distribution were relatively narrow (<1.5), and this may be attributed to the low propagation radical concentration, and the radical termination could be neglected at this moment. The other explanation of the much higher M_n(GPC) value than predicted, was the poor solubility of Cu(II) complex in the reaction systems. The propagating radicals were difficult to become dormant species indicating a slow atom transfer process, which was confirmed by the little tail of the GPC curves (Fig. 3).

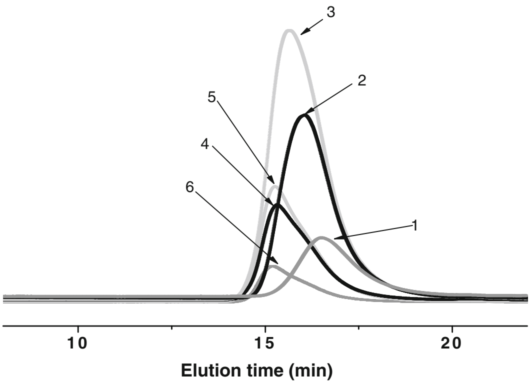


Fig. 3 GPC curves of the polymers synthesized after different reaction time. *1* 30 min, *2* 90 min, *3* 150 min, *4* 210 min, *5* 270 min, *6* 390 min

Effect of temperature and $CuBr_2$ on the polymerization

To investigate the effect of temperature on the polymerization, the reaction temperature was increased to 70 °C using CuBr/DBBD/EBIB system in DMF. This study showed that not only the polymerization rate but also the relative catalyst activity depends on the temperature. As shown in Fig. 4, the $\ln([M]_0/[M]_t)$ versus time (t) at different temperatures are linear. Higher k_{app} was obtained at higher temperature.

Moreover, the initiating efficiency of polymerization at 70 °C was increased compared to that at 60 °C, indicating that the k_i was increased faster than k_p when the temperature was increased. The M_n increased linearly with conversion and the molecular weight distributions were narrow (Fig. 5).

$CuBr_2$ was added at the beginning of ATRP process to study its effect on the reaction kinetics at 70 °C. The kinetic plots of $\ln([M]_0/[M])$ versus time (t) for the ATRP are shown in Fig. 3. When there was no Cu(II) added to the reaction initially, the curve did not pass through the origin. When $[Cu(II)]_0/[Cu]_0 = 20\%$, the curve of

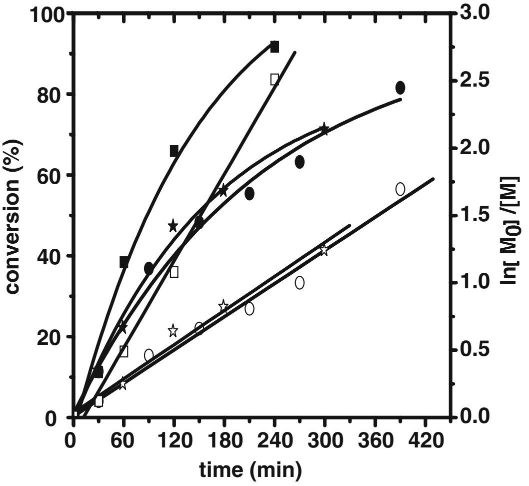


Fig. 4 The relationship between $\ln([M]_0/[M])$ and conversion versus reaction time. The polymerization conditions:M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:0.5:1:2 (molar ratio), $T = 60$ °C (*closed circle*, *open circle*); $T = 70$ °C (*closed square*, *open square*); $T = 70$ °C and 20% $CuBr_2$ (molar ratio to total Cu) (*closed star*, *open star*)

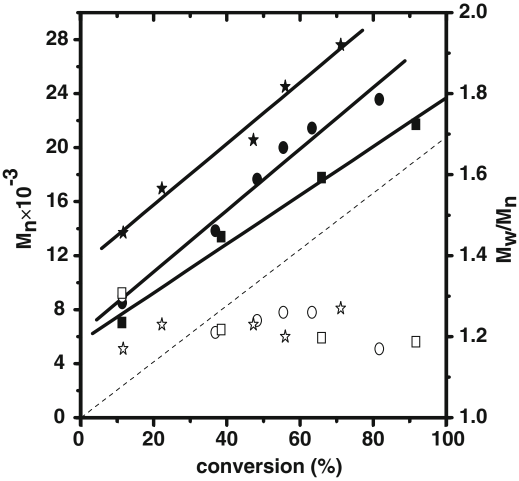


Fig. 5 Plot of molecular weight and polydispersity versus conversion of MMA at different temperature in DMF. Conditions: M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:0.5:1:2, $T = 60$ °C (*closed circle*, *open circle*); $T = 70$ °C (*closed square*, *open square*); $T = 70$ °C and 20% $CuBr_2$ (molar ratio to total Cu) (*closed star*, *open star*)

the ATRP system passed the origin indicating the steady-state concentrations of initiator and Cu(I) will be close to their initial concentrations ($[RX]_0$ and $[Cu(I)]_0$). The k_{app} decreased significantly indicating the 20% $CuBr_2$ was more than the threshold concentration and the 'self-regulation' may happen without $CuBr_2$ at 70 °C.

The polymerization with 20% $CuBr_2$ (mol/mol) showed a little big slope of molecular weight versus conversion indicating the molecular weight controllability was not significantly improved (Fig. 5) and the molecular weight of the final product was much higher than that without the initial Cu(II) addition indicating the lower initiating efficiency. The k_p^{app} decreased significantly and the intercept of the molecular weight was higher than that without $CuBr_2$. This indicates that the initial $CuBr_2$ may lead the initiating more difficult and the [P·] was lower than the reaction without initial $CuBr_2$. Moreover the small peak of EBIB in the final mixture was observed in GC-MS showing slow initiating process (As showed in supporting information 1.3).

Effect of halide exchange on the polymerization

To improve the polymerization control in the aspect of the molecular weight, CuCl was used to slow down the propagation rate and increase the initiation rate relatively. CuBr was replaced by CuCl on the same conditions except the temperature was elevated to 80 °C. Moreover the molar ratio of DBBD to CuCl were fixed at 2/1 and 1/1. The plot of $\ln([M]_0/[M]_t)$ versus time (t) was linear indicating the kinetics was first-order in monomer for both ligand concentration (Fig. 6). 1:1 molar ratio was faster, which was different from the CuBr/DBBD systems (Supporting information 1.4). The *M*n of obtained PMMA increased linearly with the increase of conversion and the molecular weights of obtained PMMA were similar to the predicted value (Fig. 7). This illustrated that the

Fig. 6 The relationship between $\ln([M]_0/[M])$ and conversion versus reaction time with different ligand ratio. The polymerization conditions: M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:1:1:x (molar ratio), T = 80 °C. $x = 1$ (*closed circle*, *open circle*); $x = 2$ (*closed square*, *open square*)

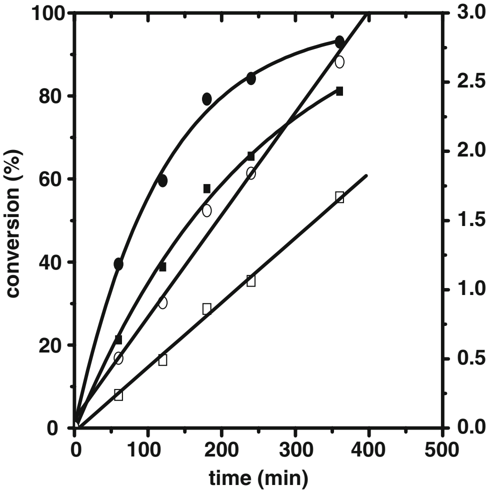
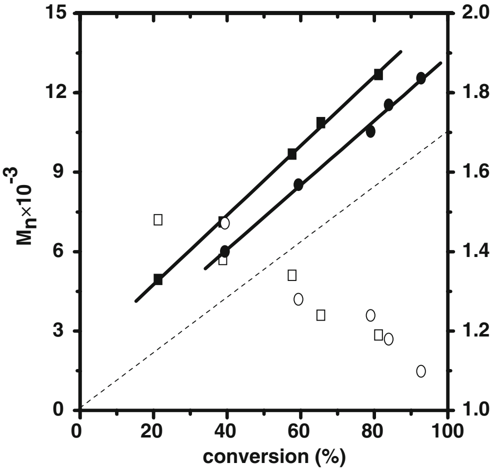


Fig. 7 Plot of molecular weight and polydispersity versus conversion of MMA with different ligand ratio at 80 °C. The polymerization conditions: M/DMF = 1:1 (w/w) and [M]/[I]/[CuBr]/[L] = 100:1:1:x (molar ratio), T = 80 °C. $x = 1$ (*closed circle*, *open circle*); $x = 2$ (*closed square*, *open square*)



controlling of molecular weight was improved by halide exchange. The peak of EBIB on GC-MS decreased quickly and disappeared after a 60 min polymerization time (Show in supporting information 1.5) also confirmed a relatively faster initiating process in this experiment, especially the better control when then ligand concentration decreased. The possible explanation is that the 1:1 ratio of DBBD to CuCl could give an optimum ratio of activator to deactivator concentration under these conditions as reported.

To study the solvent effect, anisole was used to compare with DMF and the result was show in supporting information (Supporting information 1.6).

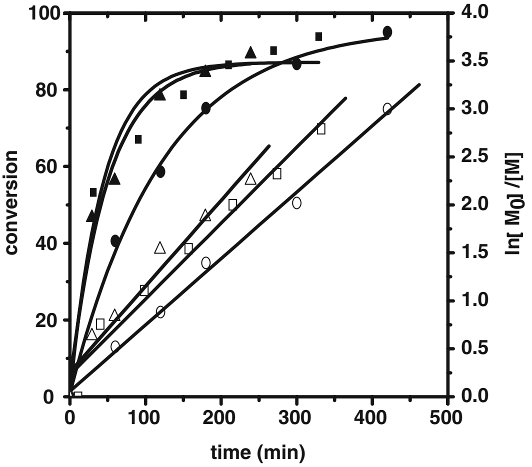


Fig. 8 The relationships between ln($[M]_0$/[M]) and reaction time. The polymerization conditions:[M]/[I]/[CuX]/[L] = 100:0.5:1:2 (molar ratio), DMF:MA = 1:1 (weight), $T = 80$ °C except for (1) EBIB, CuBr; (*closed and open triangle*); (2) MBP and CuBr (*closed circle*, *open circle*); (3) [M]/[MBP]/[CuBr]/[L] = 100:1:1:1 (molar ratio) (*closed square*, *open square*)

Polymerization of MA using DBBD as ligand

Different initiator

Polymerization of MA was first examined by using CuBr complexed with DBBD as catalysts using MBP or EBIB as the initiators in DMF solution (1:1 w/w). The solutions were pale green and homogeneous while the solution became slightly yellow and also homogeneous after the addition of initiator. Figure 8 shows the kinetic plot of ln($[M]_0$/[M]) and conversion versus time with different initiators. The data indicated that both of the plots were linear, except the plot using EBIB as initiator, which had a significant jump in the initial step. The molecular weight increased linearly with the conversion for MBP initiator, and the measured molecular weights of obtained polymers were close to the predicted (Fig. 9). The

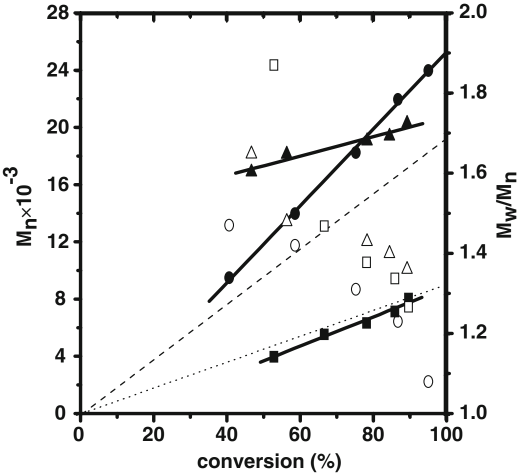


Fig. 9 Plot of molecular weight and polydispersity versus conversion of MA. The polymerization conditions: [M]/[I]/[CuX]/[L] = 100:0.5:1:2 (molar ratio), DMF:MA = 1:1 (weight), $T = 80$ °except for (1) EBIB, CuBr; (*closed triangle*, *open square*); (2) MBP and CuBr (*closed circle*, *open circle*); (3) [M]/[MBP]/[CuBr]/[L] = 100:1:1:1 (molar ratio) (*closed square*, *open square*). Dash and dot linear were the theory molecular weight linear

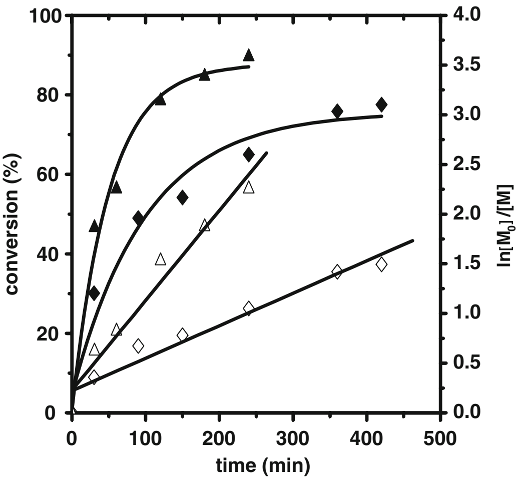


Fig. 10 The relationships between $\ln([M]_0/[M])$ and reaction time. The polymerization conditions: all the $[M]/[I]/[CuX]/[L] = 100:0.5:1:2$ (molar ratio), DMF:MA = 1:1 (weight), $T = 80$ °C except for (1) EBIB, CuBr (*closed triangle*, *open triangle*); (2) EBIB, CuCl (*closed square*, *open square*)

polydispersity decreased with the polymerization process and was kept relatively narrow. However, when using EBIB as initiator, the molecular weights arrived at a ‘plateau’ quickly and nearly have no increase with the conversion, this may be because the very fast propagation under the conditions without enough accumulating Cu(II) species [31].

The experiment using the 1:1 ratio of CuBr to ligand was also conducted to study the ligand effect. The kinetic plot of $\ln([M]_0/[M])$ versus time was linear indicating the constant radical concentration. The measured molecular weights were a little lower than the predicted. A possible explanation was the chain transfer to monomer, solvent or ligand at higher initiator concentration. The molecular weights polydispersities of PMMA obtained with high initiator concentration were relatively broad (around 1.4), and even arrived 1.9 in the initial step confirming the chain transfer.

Halide exchange

Polymerization of MA was also conducted by using CuCl complexed with DBBD as catalysts and EBIB as the initiators in DMF solution (1:1 w/w). Both CuCl/DBBD/EBIB and CuBr/DBBD/EBIB solutions of MA were pale green and homogeneous, but the former systems were blue after EBIB was added while the latter became slight yellow after the addition of initiator. This phenomenon show that the Cu(I) complex in latter systems domains throughout the polymerization indicating the catalyst equilibrium was kept in the left and the equilibrium constant were small. Figure 10 showed the kinetics of the solution polymerization of MA for the two systems. The CuBr system showed very high activity, but a little jump still existed at the initial stage and the line deviated downwards in high conversion. This suggested that at the beginning of the polymerization, the activation step was too fast and produced more radicals, and this led to more radical termination, which resulted in the deviation in high conversion [1]. As well as CuCl system, a slower

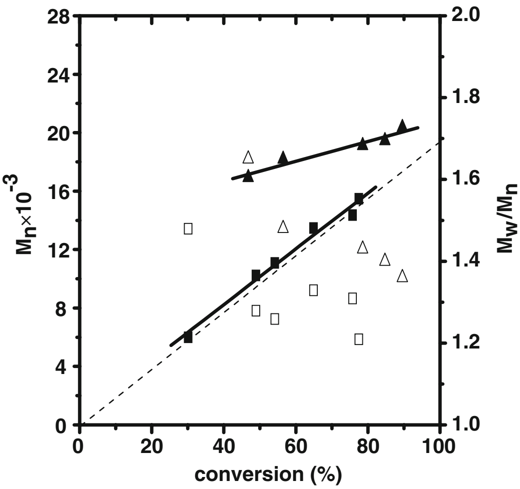


Fig. 11 Plot of molecular weight and polydispersity versus conversion of MA. The polymerization conditions: all the [M]/[I]/[CuX]/[L] = 100:0.5:1:2 (molar ratio), DMF:MA = 1:1 (weight), $T = 80$ °C except for (1) EBIB, CuBr (*closed triangle*, *open triangle*); (2) EBIB, CuCl (*closed square*, *open square*). Dash linear was the theory molecular weight linear

polymerization rate was observed. Their molecular weights of PMA synthesized in this system increased linearly with the conversion and agreed well with the theoretical values (Fig. 11), and the polydispersity is in the range of 1.2–1.4.

Cyclic voltammetric measurements

From the above analysis, we can draw the conclusion that when using DBBD ligand, the ATRP of MMA is fast but the control of molecular weight is not satisfied. But for MA, the polymerization can be better controllable. In order to understand the copper/DBBD complex behavior in ATRP process, electrochemical study was performed with copper bromide complexed with DBBD or PMDETA in DMF.

Cyclic voltammetric (CV) measurements were performed on the copper complexes in order to obtain some insight into the behavior of the complexes in DMF solution. Both CuBr/DBBD and $CuBr_2$/DBBD were conducted in the ratio 1:2. From Table 1 and Fig. 12 it can be seen that the anodic-cathodic peak potential separations ($E = 240$ mv for both CuBr-2L and $CuBr_2$-2L complexes) exceed the value (58.5 mv), theoretically expected for a one-electron redox process, and indicated a quasi-reversible one-electron transfer behavior.

Data in Table 1 show that PMDETA/$CuBr_2$ have a ΔE value of 160 mV in this system, and the ΔE was 240 mv for both CuBr and $CuBr_2$ complexes with DBBD. The redox potentials was about 0.54 v (vs. NHE) and between −0.3 and 0.6 V, in which the ATRP catalysts become useful in polymerization of styrene and (meth)acrylates [32]. But the relatively high redox potentials showed the Cu(I) complex was a weak reducing agent and hard to be oxidized. The high oxidation potential of Cu(II)Br_2/DBBD ($E_{ox} = 460$ mV for DBBD/CuBr and 470 mv for DBBD/CuBr) indicates a relatively poor stabilization of the redox state (II) of the copper center complexed by DBBD may be leading to the big substituents. This

Table 1 Redox potentials of several copper (I) bromide complexed with different nitrogen ligands measured by cyclic voltammetry at 100 mV/s in DMF at room temperature (*E* vs. Ag/AgCl)

No	Ligand: Copper halide	E^{a}_{red} (mV)	E^{a}_{ox} (mV)	$E^{b}_{1/2}$ (mV)	ΔE^{c} (mV)
1	2:1 (DBBD: $CuBr_2$)	230	470	350	240
2	2:1 (DBBD: CuBr)	220	460	340	240
3	1:1 (PMDETA: $CuBr_2$)	−94	66	−14	150

[a] E_{red} and E_{ox} are the peak potentials of the reduction and oxidation waves, respectively

[b] $E_{1/2} = 1/2\ (E_{\mathrm{red}} + E_{\mathrm{ox}})$

[c] $\Delta E = E_{\mathrm{ox}} - E_{\mathrm{red}}$

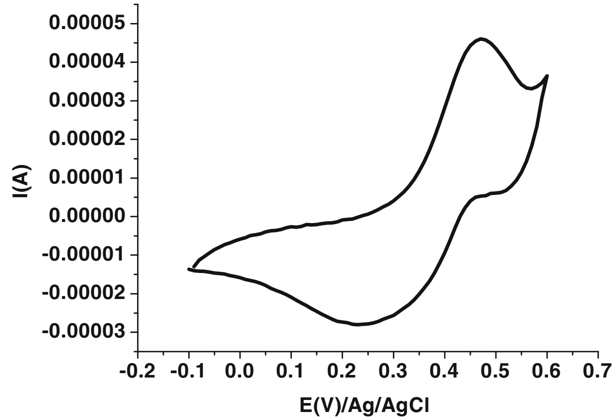


Fig. 12 Cyclic voltammogram in DMF of Cu(I)Br/DBBD. Scan rate: 100 mV/s, $[\mathrm{Mor}_{1,6}\mathrm{BF}_4] = 0.1$ M, [Cu(I)Br] = 0.01 M, [BDED] = 0.02 M, *E* versus Ag/AgCl

showed that the CuBr complex was difficult to be oxidized to CuBr(II) complex and the activation was relatively slower than other systems. As a result, a slow activation and fast reduction (with a proper equilibrium $\Delta E = 240$ mv) is not fit for ATRP of MMA but optimal to ATRP of MA using Cu(I)Br/DBBD complex.

Conclusions

Using DBBD new ligand, the catalytic systems based on Cu(I)X were used for the ATRP of MMA, MA. The kinetic plots of the studied systems for MMA were linear and the obtained PMMA were of low polydispersities (PDI = 1.12–1.3), though the measured molecular weights are higher than the theoretical value for the Cu(I)Br/DBBD systems. Halide exchange using CuCl could improve the controlling of molecular weight. For the polymerization of MA, the kinetic plots of $\ln([M]_0/[M])$ versus reaction time were also linear, and the experimental and theoretical molecular weights were in a good agreement though the polydispersity indexes of obtained polymers were a little high (in the range of about 1.2–1.4), which also can be accepted for ATRP. Electrochemical study has allowed to understand the behavior of the Cu(I)Br/DBBD complex. Because of its high value of $E_{1/2}$ and the average ΔE, the equilibrium between Cu(II) and Cu(I) complexed with DBBD is quite fast but the k_a and k_{deact} are slow, so this catalyst is more effective to polymerize MA than MMA.

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