

Pyrrolidin-2-one Structure Derivatives as Novel Ligands for Copper-based Atom Transfer Radical Polymerization (ATRP)

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(N-R)₃TEDP, 1,1'-(2,2'-(2,2'-(alkylazanediyl)bis(ethane-2,1-diyl)bis(alkylazanediyl))bis(ethane-2,1-diyl)dipyrrolidin-2-one, with central alkyl amine and peripheral pyrrolidin-2-one structure was successfully employed as ligand in copper-based ATRP. The polymerization followed the first order kinetic and the molecular weights of PMMA increased linearly with monomer conversion. Although the M_n of products obtained by SEC was higher than the theoretic ones, the distribution of molecular weight was narrow (<1.4). By introducing deactivator CuBr₂, the polymerization rate of the ATRP catalyzed by CuBr/(N-butyl)₃TEDP decreased dramatically, but the control was improved ($M_w/M_n = 1.22$). Using mixed halide initiation system (CuCl/EBiB), the M_n of synthesized PMMA was more close to the calculated value with much lower molecular weight distribution ($M_w/M_n = 1.15$). The effect of temperature was investigated and the low ΔH_{eq}^θ value (21.38 kJ·mol⁻¹) was derived from the Arrhenius plot. The alkyl substitute of (N-R)₃TEDP had profound effect on the CuBr-catalyzed ATRP of MMA, due to the steric effect introduced by their bulky size. The activity of these ligands in the ATRP showed the following order: C12 \ll C4 \sim C6 \sim C8, in the abbreviate form of (N-R)₃TEDP.

KEY WORDS: Copper-based ATRP / Novel Ligand / Pyrrolidin-2-one Structure / Alkyl Substitute / Polymerization Kinetics /

Reported first in the mid-1990s,¹⁻³ Atom transfer radical polymerization (ATRP) is a catalytic process in which, a transition metal complex reversibly activates the dormant polymer chains *via* a halogen atom transfer reaction (Scheme 1).^{4,5} As one of the most versatile techniques to synthesize well-defined polymers with narrow molecular weight distributions,⁶ ATRP has been utilized successfully to prepare block,⁷⁻⁹ graft,¹⁰⁻¹² comb,¹³ star,¹⁴ hyperbranched copolymers,¹⁵ inorganic/organic hybrids (co)polymers¹⁶ and liquid-crystalline polymers¹⁷ in the past decades. Considerable research has been conducted in order to develop these well-defined polymers for wide applications from the coatings industry¹⁸ to the drug delivery¹⁹ and biotechnology.²⁰

Nowadays, there are a variety of transition metal complexes, including the Cu,¹ Ru,² Pd,²¹ Rh,²² Re,²³ Fe,²⁴ Ni,²⁵ have been found to be the effective catalysts in ATRP. Among these, Cu complex catalysts have attracted much attention because of their versatility and low cost.²⁶ Nitrogen-containing compounds, such as 2,2'-bipyridine¹ and its derivatives,²⁷ linear and branched aliphatic amine,^{28,29} terpyridy³⁰ and picolyl³¹ *et al.*, have been used as ligands for copper-based ATRP. And the results have shown that the structural, and electronic properties of a ligand have a significant influence on the catalytic activity and the control of the polymerization.^{32,33}

Matyjaszewski *et al.* demonstrated that the lower the redox potential is, the higher the activity of copper complex in ATRP is.³⁴ And the activation rate depends on the nature of the nitrogen-binding site of the ligands.^{33,35} They also found that the activities of complexes with tridentate ligands decrease in the following order: alkylamine \approx pyridine $>$ alkylimine \gg

arylimine $>$ arylamine.³³ Subsequently, Tang *et al.* reported that the activities of Cu complexes demonstrate the following order: tetradentate (cyclic-bridged) $>$ tetradentate (branched) $>$ tetradentate (cyclic) $>$ tridentate $>$ tetradentate (linear) $>$ bidentate ligands.³⁵ Some research revealed that ethylene is a better linkage for N atoms in the ligand than propylene.⁴ However, to our knowledge, there has been no report of copper-based ATRP using pyrrolidin-2-one derivatives as ligands.

Recently, we have developed a series of easily synthesized N-containing compounds (N-R)₃TEDP,³⁶ 1,1'-(2,2'-(2,2'-(alkylazanediyl)bis(ethane-2,1-diyl)bis(alkylazanediyl))bis(ethane-2,1-diyl)dipyrrolidin-2-one (see Scheme 2), used as ligand for copper-mediated ATRP. Compared with *N,N,N',N',N'*-penta-methyldiethylenetriamine (PMDETA), a widely used ligand, these compounds have peripheral pyrrolidin-2-one structure, in which the carbonyl group could coordinate with the copper atom too.³⁷ However, the acylamino group of the ligands might be inactive for Cu-based ATRP.³⁴ To better understand the structure-property relationship of these new compounds, we conducted copper mediated ATRP by using these dipyrrolidin-2-one derivatives as new ligands. The influence of several factors, such as halide exchanges, the dosage of deactivator CuBr₂ and the alkyl substitute of the ligands, on the control of the polymerization was reported herein in this paper.

EXPERIMENTAL

Materials

All chemicals were purchased from commercial sources. Methyl methacrylate was washed with 5% solution of sodium

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Table I. Copper-based ATRP of MMA with (*N*-butyl)₃TEDP as ligands

Entry	[M] ₀ : [I] ₀ : [Cu] ₀ : [L] ₀ ^a	Catalyst	T (°C)	t (h)	Conv. (%)	M _{n,Th} ^b	M _{n,SEC}	PDI
1	100:1:1:0.5	CuBr	70	7.5	36.4	3830	9630	1.39
2	100:1:1:1	CuBr	70	9.5	71.2	7315	14500	1.38
3	100:1:1:2	CuBr	70	10	87.8	8970	16240	1.33
4	100:1:2:2	CuBr	70	8	82.0	8395	12400	1.38
5	100:1:0.5:0.5	CuBr	70	10	42.1	4405	13070	1.39

^aThe polymerizations were performed in DMF (50 wt.-%) with EB*i*B as initiator (I), (*N*-butyl)₃TEDP as ligand (L), MMA as monomer (M), [M]₀ = 4.7 M. [Cu]₀ were the initiation concentration of CuBr. ^bM_{n,Th} was calculated by M_{n,Th} = M_w(initiator) + M_w(monomer) × [M]₀/[I]₀ × conv.

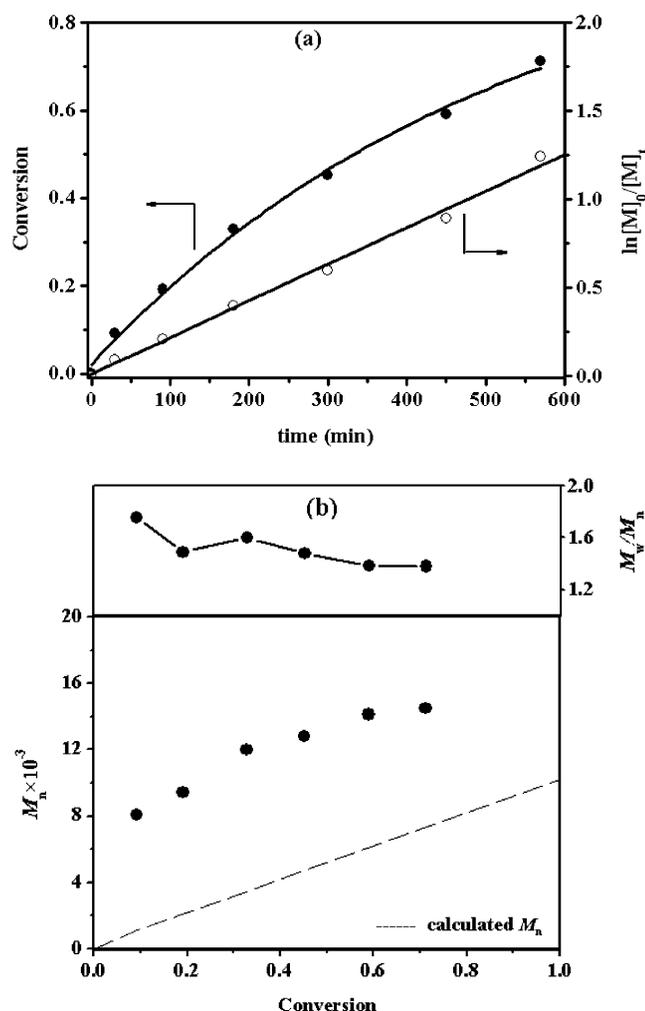


Figure 1. (a) Dependence of conversion and ln[M]₀/[M]_t on time, (b) Evolution of the molecular weights and polydispersity for the ATRP of MMA using (*N*-butyl)₃TEDP as ligand in the DMF at 70 °C, [MMA]₀ = 4.7 M, [MMA]₀: [EB*i*B]₀: [CuBr]₀: [L]₀ = 100:1:1:1.

system in this study k_i^{app} may be smaller than the observed propagation rate constant k_p^{app} . EB*i*B, though structurally similar to propagating species of methacrylates, is some less active in our polymerization system. The reason of the slow initiation may be ascribed to the steric bulky ligand used in polymerization system.

To get better understanding on the ATRP of MMA catalyzed by CuX/(*N*-R)₃TEDP, which may lead to get well-controlled polymerization, the influence of deactivator CuBr₂,

halide exchange, temperature and alkyl substitute of ligands were studied. The polymerizations were performed with a 100:1:1:1 stoichiometry of [M]₀: [I]₀: [Cu]₀: [L]₀ as the most ATRP processes.

Influence of Deactivator CuBr₂

To investigate the effect of the deactivator CuBr₂ on the control of polymerization, a series of polymerizations were carried out by changing the amount of CuBr₂. The results were collected in Table II. The polymerization behavior (Figure 2) were found to proceed the similar ATRP manner, affording first-order kinetics with respect to monomer concentration and a linear increase in molecular weight with conversion. But, as the concentration of CuBr₂ increased, the polymerization became well-controlled ($M_w/M_n = 1.38$ decrease to 1.22).

The results revealed that initial addition of Cu(II) affected the kinetics of the ATRP. The apparent rate constant of polymerization (k_p^{app} , Table II) is in the same magnitude as the most ATRP processes, and decreases with the dosage of CuBr₂ in the system. This result is slightly different from the literature,⁴¹ which concluded that there is an inverse first-order relationship between the polymerization rate and [Cu(II)]₀. The relationship between k_p^{app} and Cu(II) concentration in this work was not inverse first-order but showed a decay behavior, and the decreasing rate of k_p^{app} became slow when the molar ratio of Cu(II) to the total copper concentration increased from 0.1 to 0.2. This might be attributed to spontaneous formation of Cu(II), due to low levels of termination at the early stage of the polymerization, resulting in a higher concentration of Cu(II) in the system than predicted by the amount of added Cu(II).

Effect of Halide Exchange

The polymerization of MMA using mixed halide initiation system (CuCl/EB*i*B) was also investigated, and the results are summarized in Table II. The similar ATRP behavior was observed as above, affording first-order kinetics with respect to monomer concentration and a linear increase in molecular weight with conversion (Figure 3a and 3b). Meanwhile, the use of the mixed halide initiating system gave a better control of the molecular weight, the experimental values ($M_{n,SEC}$) were more close to theoretical values ($M_{n,Th}$), and the distribution of molecular weight was narrow ($M_w/M_n = 1.15$). This is attributed to the preferential end-capping of the activated polymer chains by chloride over bromide which increases the relative rate of initiation to that of propagation, because the C-Cl bond is stronger than C-Br.⁴² As described before, a

Table II. The effect of deactivator CuBr₂ and halide exchange on the ATRP of MMA with (*N*-butyl)₃TEDP as ligand

Entry ^a	Catalyst [Cu]	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%)	k_p^{app} ($\times 10^{-5} \text{ s}^{-1}$) ^c	<i>M</i> _{n,Th}	<i>M</i> _{n,SEC}	<i>PDI</i>
1	CuBr	70	9.5	71.2	3.45	7315	14500	1.38
2	90%CuBr + 10%CuBr ₂ ^b	70	10	50.1	1.83	5205	10540	1.25
3	80%CuBr + 20%CuBr ₂ ^b	70	10	41.7	1.44	4365	9700	1.22
4	CuCl	70	10	60.2	2.45	6215	8290	1.15

^aThe polymerizations were performed in DMF (50 wt.-% w/w) with EB/B as initiator (I), (*N*-butyl)₃TEDP as ligand (L) and MMA as monomer (M), [M]₀ = 4.7 M, [M]₀:[I]₀: [Cu]₀: [L]₀ = 100:1:1:1, [Cu]₀ were the initiation total concentration of copper salts including cuprous and cupric salt. ^bThe total concentration of copper salts ([Cu]₀ = [CuBr]₀ + [CuBr₂]₀) kept constant, just changed the relative concentration [CuBr₂]₀/[Cu]₀ (molar percentage). ^cThe apparent rate constant of polymerization (k_p^{app}), calculated by the slopes of kinetic plots of ln([M]₀/[M]_t) vs reaction time.

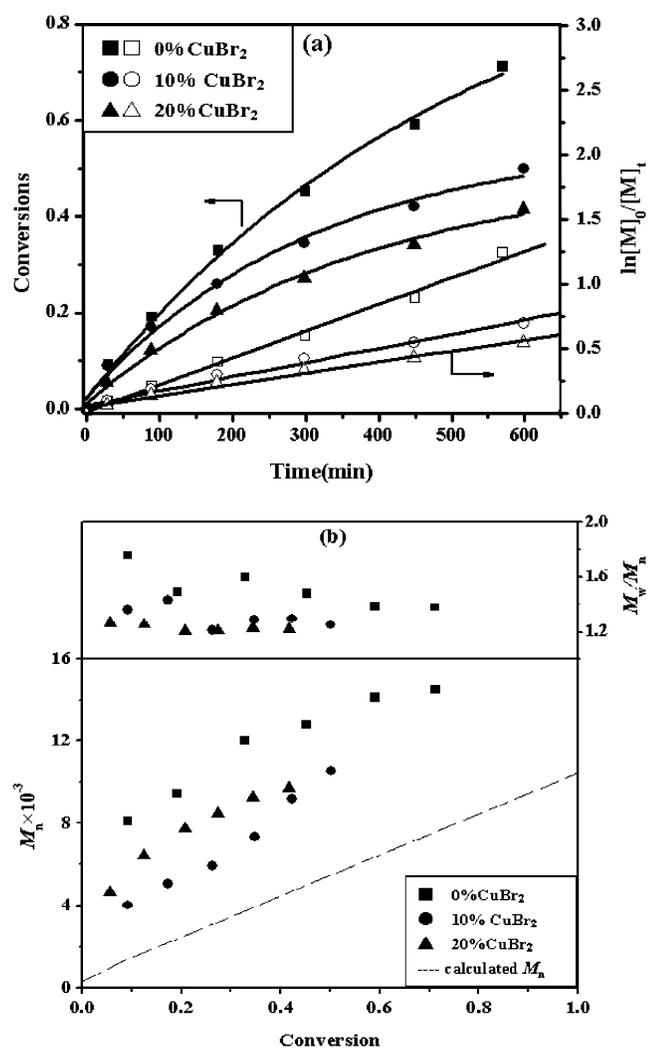


Figure 2. (a) Dependence of conversion and ln[M]₀/[M]_t on time, (b) Evolution of the molecular weights and polydispersity for the ATRP of MMA using (*N*-butyl)₃TEDP as ligand with different concentration of CuBr₂ in the DMF at 70 °C, [MMA]₀ = 4.7 M, [MMA]₀: [EB]/[B]₀: [Cu]₀: [L]₀ = 100:1:1:1; [Cu]₀ = [CuBr]₀ + [CuBr₂]₀, [CuBr₂]₀/[Cu]₀ = 0 (■□), 10% (●○), 20% (▲△).

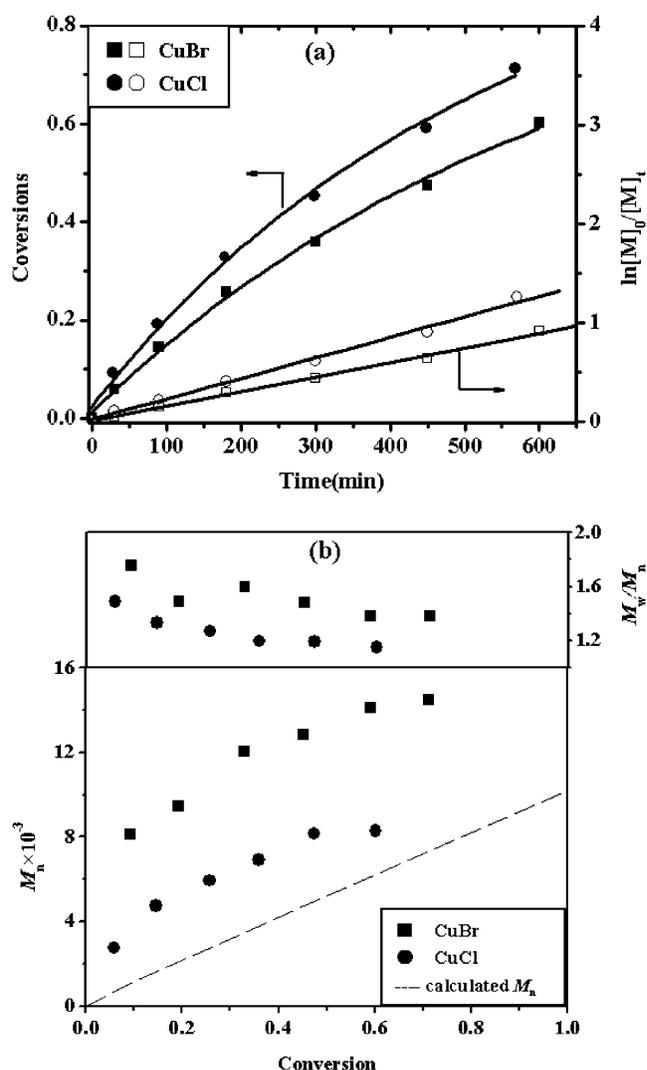


Figure 3. (a) Dependence of conversion and ln[M]₀/[M]_t on time, (b) Evolution of the molecular weights and polydispersity for the ATRP of MMA using (*N*-butyl)₃TEDP as ligand with different catalyst in the DMF at 70 °C, [MMA]₀ = 4.7 M, [MMA]₀: [EB]/[B]₀: [Cu]₀: [L]₀ = 100:1:1:1; CuBr (■□), CuCl (●○) as catalyst respectively.

successful ATRP system requires $k_i^{app} > k_p^{app}$. Thus, the lower apparent rate constants of polymerization (k_p^{app}) of CuCl indicate that halide exchange should be well-suited to this

ATRP catalysis. So halide exchange effectively improved the control of the ATRP of MMA with CuCl/(*N*-butyl)₃TEDP as catalyst complex.

Table III. The effect of temperature on the ATRP of MMA with (*N*-butyl)₃TEDP as ligands

Entry ^a	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%)	k_p^{app} ($\times 10^{-5} \text{ S}^{-1}$) ^b	k_p ($\times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{S}^{-1}$) ^c	$[P^*]^d$ ($\times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$)	$M_{n,Th}$	$M_{n,SEC}$	<i>PDI</i>
1	60	10	55.7	2.10	0.83	2.53	5765	10200	1.18
2	70	9.5	71.2	3.45	1.05	3.29	7315	14500	1.38
3	80	8	79.0	5.13	1.31	3.92	8090	13170	1.42

^aThe polymerizations were performed in DMF (50 wt.-%) at different temperature with EB/B as initiator (I), (*N*-butyl)₃TEDP as ligand (L) and MMA as monomer (M), $[M]_0 = 4.7 \text{ M}$, $[M]_0:[I]_0:[Cu]_0:[L]_0 = 100:1:1:1$. ^b k_p^{app} calculated by the slopes of kinetic plots of $\ln([M]_0/[M]_t)$ vs reaction time. ^c k_p Calculated according to eq. 1. ^d $[P^*] = k_p^{app}/k_p$.

Effect of Temperature

The effect of reaction temperature on the polymerization of MMA was studied in DMF (50 wt.-%) at 60 °C, 70 °C and 80 °C (See Table III). All of the polymerizations at different temperature showed good linear relationship between $\ln([M]_0/[M]_t)$ and polymerization time as shown in Figure 4a. The polymerization rate increased with increasing temperature. According to the literature,⁴³ eq 1 and eq 2 can be utilized to calculate the rate constant of radical propagation k_p , and the stationary concentration of the propagating radicals ($[P^*]$) respectively. The data at different temperature were listed in Table III.

$$k_p = 10^{6.423} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp\left(\frac{-22.34 \text{ kJ mol}^{-1}}{RT}\right) \quad (1)$$

$$R_p = -d[M]/dt = k_p[P^*][M] = k_p^{app}[M] \quad (2)$$

The apparent activation energy ($\Delta E_{app}^\ddagger = 43.72 \text{ kJ} \cdot \text{mol}^{-1}$) can be derived from the slope of Arrhenius plot of $\ln k_p^{app}$ versus $1/T$ for the polymerizations (Figure 5). According to $\Delta H_{eq}^\ddagger = \Delta E_{app}^\ddagger - \Delta E_{prop}^\ddagger$ and $\Delta E_{prop}^\ddagger = 22.34 \text{ kJ} \cdot \text{mol}^{-1}$ for MMA,⁴³ an enthalpy change ΔH_{eq}^\ddagger of $21.38 \text{ kJ} \cdot \text{mol}^{-1}$ was obtained for the ATRP of MMA catalyzed by CuBr/(*N*-butyl)₃TEDP. This ΔH_{eq}^\ddagger value is smaller than $\Delta H_{eq}^\ddagger = 40.74 \text{ kJ} \cdot \text{mol}^{-1}$ for *p*-TsCl/CuCl-initiated ATRP of MMA with dNbpy as ligand in biphenyl ether,⁴⁴ and $\Delta H_{eq}^\ddagger = 28.8 \text{ kJ} \cdot \text{mol}^{-1}$ for the CuBr/BPIEP catalyzed ATRP of MMA initiated by EBiB.⁴⁵ This is because the C-Cl bond was stronger than C-Br, and the lower activity of alkyl imine structure of BPIEP than the alkyl amine.³³ The apparent polymerization rate constant, $k_p^{app} = 7.83 \times 10^{-5} \text{ S}^{-1}$, for ATRP of MMA catalyzed by CuBr/(*N*-butyl)₃TEDP at 90 °C were calculated from the Arrhenius plot, which was some lower than the value ($k_p^{app} = 1.13 \times 10^{-4} \text{ S}^{-1}$ at 90 °C) for ATRP of MMA catalyzed by CuBr/PMDETA.⁴⁶

According to the above result, a conclusion could be deduced that the activity of (*N*-butyl)₃TEDP as ligand was more or less lower as the ones of PMDETA as ligand for Cu-based ATRP. This phenomenon can be possibly ascribed to the bulk alkyl substitute and pyrrolidinone structure of (*N*-butyl)₃TEDP. Ligands with phenyl-substituted imine and amine units formed inactive ATRP catalysts due to the strong electron-withdrawing effect of phenyl group.⁴⁵ So the acyl-amino group in the pyrrolidinone unit of (*N*-butyl)₃TEDP might not be active for ligand of Cu-based ATRP. The steric effect of bulk alkyl substitute led to the equilibrium between active and dormant species more slow to build and the catalyst more

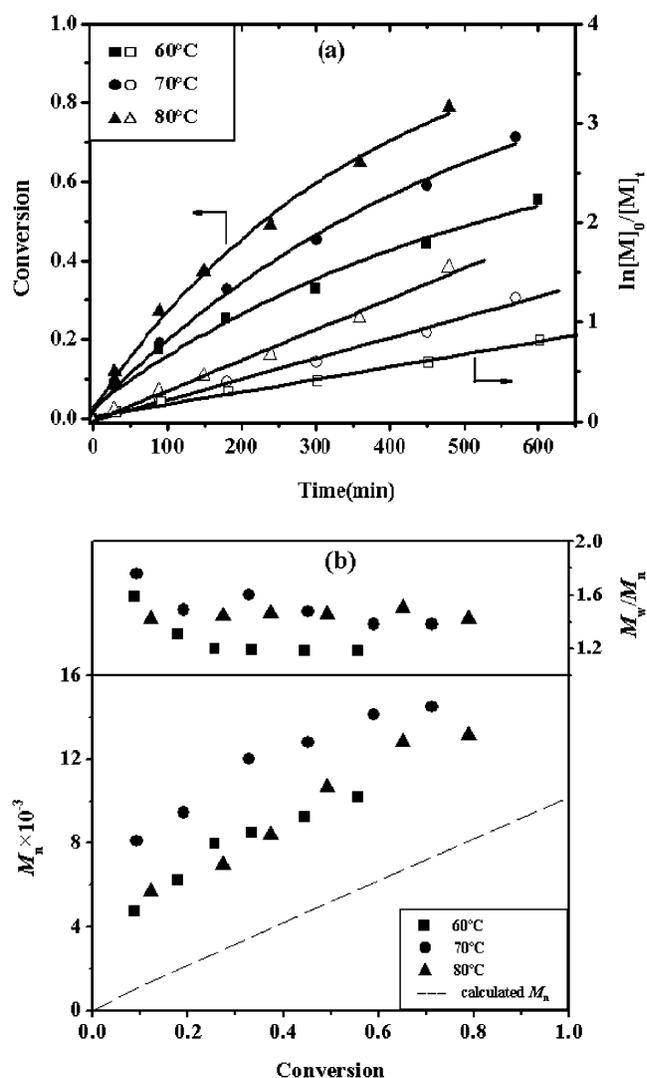


Figure 4. (a) Dependence of conversion and $\ln([M]_0/[M]_t)$ on time, (b) Evolution of the molecular weights and polydispersity for the ATRP of MMA using (*N*-butyl)₃TEDP as ligand in the DMF at different temperature: $[MMA]_0 = 4.7 \text{ M}$, $[MMA]_0:[EBiB]_0:[CuBr]_0:[L]_0 = 100:1:1:1$; $T = 60 \text{ }^\circ\text{C}$ (■□), $70 \text{ }^\circ\text{C}$ (●○), $80 \text{ }^\circ\text{C}$ (▲△).

difficult to contact with initiator and propagation radicals. The effect of alkyl substitute would be discussed below in detail.

Although higher temperature led to a faster rate of polymerization as expected (Figure 4b), the control of molecular weights distribution were sacrificed. On the other hand, the polydispersities of the PMMAs increased with the rising

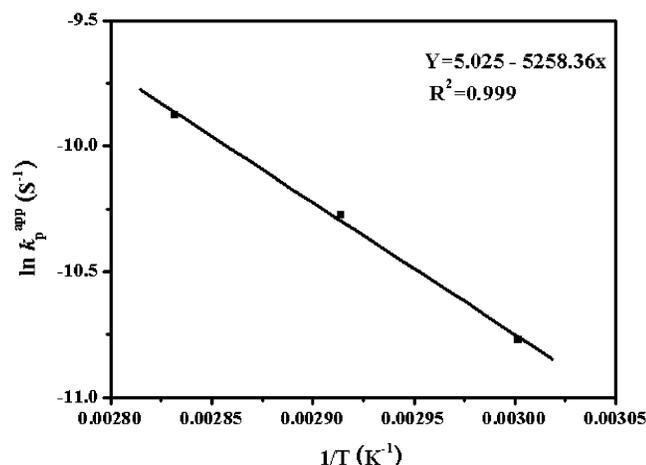


Figure 5. Plot of $\ln k_p^{\text{app}}$ versus $1/T$ for ATRP of MMA initiated by EB/B with $\text{CuBr}/(\text{N-butyl})_3\text{TEDP}$ as catalyst in DMF: $[\text{MMA}]_0 = 4.7 \text{ M}$, $[\text{MMA}]_0:[\text{EB/B}]_0:[\text{CuBr}]_0:[(\text{N-butyl})_3\text{TEDP}]_0 = 100:1:1:1$.

temperature. This could be due to more pronounced termination and transfer reactions with higher concentration propagation radicals at higher temperature.

Effect of Alkyl Substitute of Ligands

Ligands **1**, **2**, **3** and **4** (Scheme 2) were used in the polymerizations of MMA, under the same conditions as described above. Because the monomer conversion just reached about 5% for 30 h, the polymerization with **4** as ligand was considered nearly not occurred at 70°C and all data of **4** were collected at 90°C . The results were presented in Table IV. The similar ATRP manners were observed for different ligands (Figure 6a and 6b). The polymerization rate (k_p^{app}) seemed to be constant along with the increasing chain length of the alkyl substitute from C4 to C8 and then dramatically declined when C12 used. On the other hand, the polymerizations using ligands **2** and **3** are of a little but not obvious better-control of molecular weights compared with **1**. However, the controllability of the polymerization was severely destroyed by using **4** as ligand, where the $M_{n,\text{SEC}}$ was greatly deviated the theoretic values and the distribution of molecular weight was broad.

The results showed that the bulk alkyl substitute of $(\text{N-R})_3\text{TEDP}$ had profound effect on the CuBr-catalyzed ATRP of MMA, and the activity of these ligands in the ATRP showed the following order: $\text{C12} \ll \text{C4} \sim \text{C6} \sim \text{C8}$, in the abbreviate form of $(\text{N-R})_3\text{TEDP}$. The probable reason is the steric

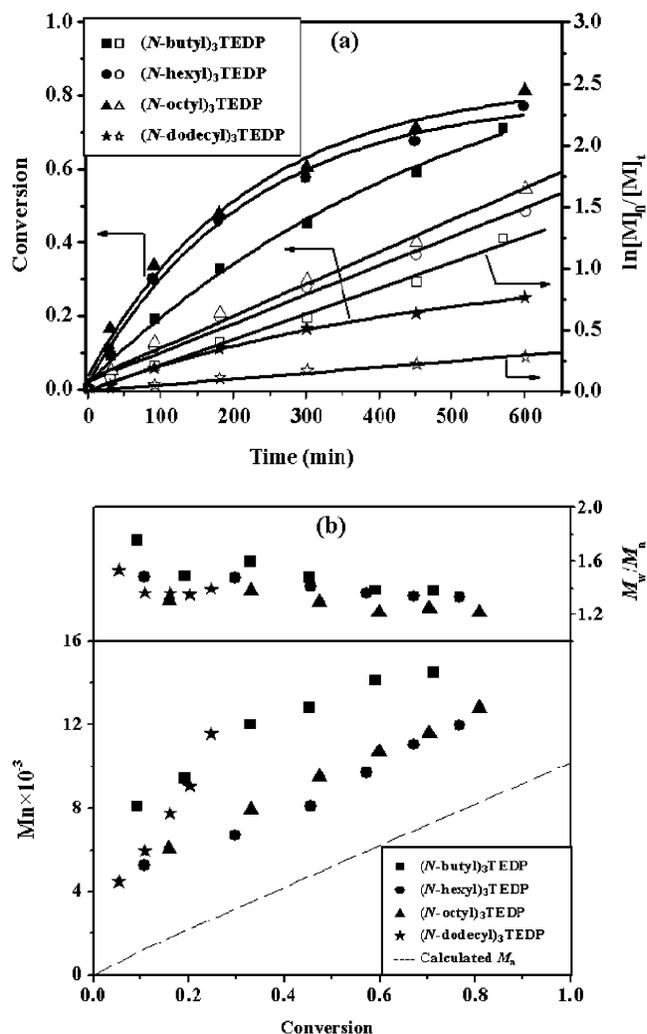


Figure 6. (a) Dependence of conversion and $\ln[\text{M}]_0/[\text{M}]_t$ on time, (b) Evolution of the molecular weights and polydispersity for the ATRP of MMA with different ligands. All polymerization were performed in DMF at 70°C except $(\text{N-dodecyl})_3\text{TEDP}$ as ligand at 90°C , $[\text{MMA}]_0 = 4.7 \text{ M}$, $[\text{MMA}]_0:[\text{EB/B}]_0:[\text{CuBr}]_0:[\text{L}]_0 = 100:1:1:1$; $(\text{N-butyl})_3\text{TEDP}$ (\blacksquare), $(\text{N-hexyl})_3\text{TEDP}$ (\bullet), $(\text{N-octyl})_3\text{TEDP}$ (\blacktriangle), $(\text{N-dodecyl})_3\text{TEDP}$ (\star) as ligand respectively.

hindrance effect of the alkyl substitute as mentioned above. When the alkyl chain length of $(\text{N-R})_3\text{TEDP}$ was not great (≤ 8 in this study), the steric effect was not distinct enough to impair the activity of catalyst complex. And there was a little improving the control of the polymerization by using ligand with long alkyl substitute as shown in Table IV, possibly due to the more bulky of ligand with longer alkyl substitute, the more

Table IV. The influence of alkyl substitute of $(\text{N-R})_3\text{TEDP}$ for Cu-based ATRP of MMA

Entry ^a	Ligands	T ($^\circ\text{C}$)	t (h)	Conv. (%)	k_p^{app} ($\times 10^{-5} \text{ S}^{-1}$) ^b	$M_{n,\text{Th}}$	$M_{n,\text{SEC}}$	PDI
1	$(\text{N-butyl})_3\text{TEDP}$	70	9.5	71.2	3.45	7315	14500	1.38
2	$(\text{N-hexyl})_3\text{TEDP}$	70	10	76.8	3.92	7870	11950	1.33
3	$(\text{N-octyl})_3\text{TEDP}$	70	10	80.8	4.32	8275	12810	1.21
4	$(\text{N-dodecyl})_3\text{TEDP}$	90°	10	24.7	0.8	2665	11560	1.39

^aThe polymerizations were performed in DMF (50 wt.-%) with EB/B as initiator (I), MMA as monomer (M) using different ligands, $[\text{M}]_0 = 4.7 \text{ M}$, $[\text{M}]_0:[\text{I}]_0:[\text{Cu}]_0:[\text{L}]_0 = 100:1:1:1$. ^b k_p^{app} calculated by the slopes of kinetic plots of $\ln([\text{M}]_0/[\text{M}]_t)$ vs reaction time. ^cDue to the monomer conversion just reached about 5% for 30 h, so polymerization with **4** as ligand was considered nearly not occurred at 70°C and all data of ligand **4** were collected at 90°C .

feasible to trap the propagation radicals by the catalyst complex. The steric effect became pronounced to destroy the activity of catalyst when using (*N*-dodecyl)₃TEDP as ligand. There seem to be a threshold value of the length of alkyl substitute. The activity of ligand decreased dramatically just when the length of alkyl substitute was above the threshold value by our study.

CONCLUSION

The derivatives of pyrrolidin-2-one, (N-R)₃TEDP as ligands were successfully employed in copper-based ATRP of MMA. The polymerization followed the first order kinetic and the molecular weights of PMMAs increased linearly with monomer conversion. Although the obtained M_n by SEC of products was higher than the theoretical ones, the distribution of molecular weight was narrow ($M_w/M_n < 1.4$). The polymerization rate for the ATRP of MMA with (N-R)₃TEDP as ligand at $[M]_0:[I]_0:[Cu]_0:[L]_0 = 100:1:1:1$, decreased dramatically by introducing CuBr₂, but the control of molecular weight was improved. Under halide exchange conditions with CuCl as catalyst for ATRP, the synthesized PMMA is more close to the calculated $M_{n,Th}$ with narrow molecular weight distribution of 1.15. The effect of temperature was investigated and the low ΔH_{eq}^θ value (21.38 kJ·mol⁻¹) for ATRP of MMA catalyzed by CuBr/(*N*-butyl)₃TEDP was calculated from the Arrhenius plot. The alkyl substitute structure of ligands (N-R)₃TEDP had strong influence on the control of ATRP, and the activity of these ligands in the ATRP demonstrated the following order: C12 \ll C4 \sim C6 \sim C8, in the abbreviate form of (N-R)₃TEDP. This result could be ascribed to the steric effect of ligands caused by the alkyl substitute with different length.

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