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Stereospecific preparation of polyacrylamide with low polydispersity by ATRP in the presence of Lewis acid

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Abstract

The stereospecific atom transfer radical polymerizations of acrylamide were achieved in the presence of the Lewis acid $Y(OTf)_3$ or $AlCl_3$ as stereospecific catalyst using chloroacetic acid/CuCl/*N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA) as initiating system. The addition of Lewis acid $Y(OTf)_3$ in the ATRP of acrylamide led to an increased polymerization rate and an improved tacticity of polyacrylamide ($m \sim 71\%$) at the expense of controllability of the molecular weight distribution. In the case of $AlCl_3$, the polymerizations were committed to afford the resultant polyacrylamide with lower polydispersity index ranging from 1.03 to 1.42 and well-controlled tacticity with *meso* content ranging from 57 to 76% depending on the different reaction conditions used. Lower temperature or higher concentration of the feeding Lewis acid helped to obtain the polyacrylamide with increased tacticity which revealed a decreased glass transition temperature (T_g).

Keywords: Polyacrylamide; Tacticity; ATRP

1. Introduction

For years an increasing attention has been paid to simultaneously control the molecular weight and tacticity in synthesizing polymers, as the primary structures of polymers represented by tacticity, molecular weight and polydispersity substantially decide the mechanical and chemical properties of polymers and consequently determine the expansion of their applications. By far the control of either of them has become possible in various addition polymerizations by a design of the initiating system. However, the simultaneous control of both via radical polymerization is still one of the focused issues in polymer syntheses.

At the aspects of synthesizing the polymers with determined molecular weight and narrow polydispersity, some living/controlled radical polymerizations (CRP) such as nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) have proved to be the very efficient approaches [1–4]. Among them, ATRP is probably the most promising process in terms of the controllability, facility and versatility. ATRP not only allows the CRP of a wide variety of vinyl monomers such as styrenes, (meth)acrylates, acrylonitrile, (meth)acrylamides and vinyl pyridines with a diverse range of initiator molecules and catalysts but also provides the opportunity of synthesizing various homopolymers and copolymers with desired molecular weight, low polydispersities and functionalities. However, as a result of the radical nature of the propagation step in the polymerization that the

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growing radical species with a planar-like sp^2-carbon structure could induce a non-stereospecific propagation, ATRP has also been much less successful in controlling chain microstructure in terms of sequence distribution and tacticity.

On the other hand, several approaches have been reported to contribute to a significant control over tacticity in polymerization. The first one is to choose the monomers with either extremely bulky substituents or a chiral auxiliary in order to control the addition direction of the monomers [5–7]. The second one is to apply polar solvents such as bulky fluoroalcohols in the polymerization to achieve the stereospecific polymerization by forming hydrogen bonding between the alcohols and monomers as well as growing species [8–11]. The third one is to introduce Lewis acids as a chelating agent in free radical polymerization via their probable interaction with the pendent groups of the polymer terminal or the monomer to accomplish the purpose of increasing tacticity of polymers [12–14,24].

Recently, we have witnessed the progress in controlling both microstructures and macromolecular architectures by combination of using either of Lewis acids or fluoroalcohols with living radical polymerization. For instance, Matyjaszewski et al. reported preparation of well-defined alternating copolymers of styrene and (meth)acrylates using Lewis acids such as $AlClEt_2$ and $AlCl_{1.5}Et_{1.5}$ in RAFT and subsequent extension of this system to butyl methacrylate and methyl acrylate afforded the corresponding block copolymers [15,16]. Moreover, they employed ATRP and RAFT for the polymerization of acrylamide derivatives such as *N*,*N*-dimethylacrylamide (DMAA) and *N*-methyl methacrylamide using Lewis acid $Y(OTf)_3$ or $Yb(OTf)_3$ as stereospecific catalyst to enhance tacticity, affording isotactic rich poly(DMAA) and poly(*N*-methyl methacrylamide) with controlled molecular weights and low polydispersity [17,18]. Okamoto et al. reported the synthesis of molecular weight controlled isotactic poly(NIPAM) (*N*-isopropylacrylamide) by RAFT in the presence of a Lewis acid $Y(OTf)_3$ [19,20], and developed the stereospecific living radical polymerizations of *N*-vinylpyrrolidone(NVP) and methyl methacrylate (MMA) in fluoroalcohols [20–23]. Furthermore, they applied a series of Lewis acids such as $Yb(OTf)_3$ and $Yb(NTf_2)_3$ in the iron(I)-catalyzed *N*,*N*-dimethylacrylamide (DMAM) polymerization, giving the polymers with high isotacticity ($m > 80\%$) and the large polydispersities ($d > 1.87$) [20,24].

Apparently, most of the mentioned stereospecific preparations via ATRP polymerization are not dealing with the monomer acrylamide but the acrylamide derivatives such as *N*-methyl methacrylamide, DMAA, NIPAM and DMAM. This is because the ATRP of acrylamide is more challenging and difficult to be satisfactory owing to the existence of intrinsic hydrogen protons in primary amines and easier occurrence of inactivation of the catalyst, slow activation and cyclization side reactions [25,26]. Up to now, the only report concerning the ATRP of acrylamide was made by Jewrajka and Mandal, which revealed that the polyacrylamide with a relatively high polydispersity index ($M_w/M_n = 1.51$) was obtained using ATRP in aqueous-based medium [27]. Meanwhile, when the combined polymerization system of CRP and the addition of Lewis acid are conducted to achieve the simultaneous control of molecular weight and tacticity, ATRP seems not so applicable as RAFT due to the fact that the ATRP ligand could be transferred to the Lewis acid and then influence the complexation with the transition metal ATRP catalysts [16]. Therefore, the stereospecific ATRP of acrylamide for simultaneous control of polydispersity of molecular weight and tacticity of polyacrylamide is never reported.

We have currently developed a new ATRP system for polymerization of acrylamide using chloroacetic acid as a functional initiator, affording the carboxyl-end polyacrylamide with lower polydispersities ranging from 1.03 to 1.44 [28]. In this paper, we introduced Lewis acids $Y(OTf)_3$ and $AlCl_3$ as stereospecific catalyst in our ATRP of acrylamide together with chloroacetic acid/CuCl/*N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine(TMEDA) as initiating system. It is expected that the acidic polymerization condition due to the addition of the initiator chloroacetic acid could not only effectively protect the ATRP of acrylamide from the unexpected complexation and cyclization by-reactions but also beneficial in blocking the ATRP ligand from transferring to the Lewis acid and obtaining polyacrylamide with high tacticity and low polydispersity at the same time.

2. Experimental

2.1. Materials

Acrylamide (chemically pure, Shanghai Chemical Reagent Co., Ltd., China) was recrystallized before use. $Y(OTf)_3$ (98%) was purchased from Aldrich and used without further purification. TMEDA (biochemical reagent, Shanghai Qianjing Chemical Reagent Plant, China), methanol and glycerol (analytical reagent, Hangzhou Chemical Reagent Co., Ltd., China), chloroacetic acid, $AlCl_3 \cdot 6H_2O$ and KCl (analytical reagent, Shanghai Linfeng Chemical Reagent Co., Ltd., China) were used as received. CuCl was synthesized from $CuCl_2$ (98%, Shanghai Chemical Reagent Co., Ltd., China) and purified according to the literature [29].

2.2. Polymerizations

2.2.1. Single-point experiments

A typical polymerization procedure was as follows: 1 mmol CuCl (0.0995 g), 2 mmol TMEDA (0.2324 g), 50 mmol acrylamide (3.6 g), 2.5 mmol Lewis acid, 50 mmol solvent and 1 mmol chloroacetic acid (0.0945 g) were added to a dry glass tube in turn. The tube was sealed under nitrogen after three freeze-vacuum cycles and then placed in an oil bath held at the desired temperature by a thermostat. After the specified reaction time the polymerization was terminated by taking out the tube, opening the flask and exposing the catalyst to air. The polymerization product was dissolved in water and precipitated in methanol. Separated by centrifugation, the precipitated polymer was re-dissolved in water and treated with cation-exchange resin to remove the copper complex. Finally, the product was reprecipitated in methanol and dried under vacuum at 40 °C for 24 h.

2.2.2. Kinetic experiments

CuCl, TMEDA, acrylamide, solvent, Lewis acid, initiator and other additives in appropriate ratios were added to a tube. Sealed with a rubber septum, the tube was cycled three times between vacuum and nitrogen to remove oxygen and then placed in an oil bath kept at the desired temperature. After certain time intervals, samples were withdrawn from the reaction mixture using degassed syringes and processed with the procedures mentioned above.

2.2.3. Characterization

The conversion of the polymerization was determined gravimetrically. The ^{1}H NMR spectra were obtained with a 500-MHz INOVA instrument with DMSO-d_6 as a solvent. The chemical shifts were reported in parts per million with tetramethylsilane as an internal standard. The molecular weights and molecular weight distributions of the polymers were determined on a Wyatt gel permeation chromatograph (GPC) equipped with TRI STAR MINIDAWN light scattering detector and SHOWA DENKOK.K. shodex R1-71 differential refractometer, using two Shodex OHpak SB-806M HQ columns. Poly(ethyleneglycol) and poly(ethylene oxide), obtained from Wyatt, were used to calibrate the columns. A 0.1 mol/dm^3 solution of $NaNO_3/CH_3CN$ (v/v = 3:1) was used as an eluant at a flow rate of 0.5 ml/min. To free the polymer from copper salts, the polymer solutions were treated with the cation-exchange resin before injecting into the GPC system and then filtered through a prefilter–filter combination system. All samples were run at 25 °C. Differential scanning calorimetry (DSC) runs were made on samples of about 5 mg in a stream of nitrogen (flow rate 20 mL/min) on a Perkin–Elmer Model DSC-2C system with a data station. The samples were heated at the flow rate of 20 °C/min to 210 °C and maintained at this temperature for 2 min to destroy the thermal history. Then the samples were cooled down at constant cooling rate of 20 °C/min to 50 °C and held for 2 min. Finally, reheated the samples from 50 to 210 °C to obtain the glass transition temperature of the samples. Data processing was carried out with the software furnished by the instrument manufacture.

3. Results and discussion

As is well known, the acidity of a Lewis acid depends on the central metals and the ligands, and it increases as the ionic radius of the metal decreases or as the more electron-withdrawing ligands the Lewis acid has. The rare earth trifluoromethanesulfonates such as $Y(OTf)_3$ are known as unique Lewis acids characterized by strong Lewis acidity, high coordinate numbers, and tolerance toward protic solvents and water [24], and have been commonly looked upon as the most effective stereospecific catalyst in achieving desired tacticity during polymerizations. Typically, with their participation as stereospecific catalyst in the stereospecific living radical polymerization of the acrylamide derivatives such as DMAA, NIPAM, DMAM and *N*-methyl methacrylamide, the corresponding polymers were successfully prepared with expected tacticity and low polydispersity. Therefore, we tried our stereospecific ATRP polymerization of acrylamide firstly in the presence of different amounts of the Lewis acid $Y(OTf)_3$ to probe the effect of this Lewis acid on the properties of resulting polyacrylamide.

Table 1 showed the results of the ATRP of acrylamide using chloroacetic acid/CuCl/*N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA) as initiating system under different reaction conditions. The data in entries 1–4 presented the information of the polymerization carried out in water at 80 °C with or without the addition of Lewis acid $Y(OTf)_3$. It could be seen that when the amount of the added Lewis acid $Y(OTf)_3$ accounted to 0.05 equiv (relative to monomer), the polymerization rate was accelerated greatly, with the conversion within 48 reaction hours rising up to 66.4% from 7.6%, compared with the situation without the Lewis acid. This

Table 1

The results of the ATRP of acrylamide under different reaction conditions[e]

Entry	$[Y(OTf)_3]_0/[\text{acrylamide}]_0$	$[AlCl_3]_0/[\text{acrylamide}]_0$	Solvent[f]	Temp. (°C)	Time (h)	Conv.[a] (%)	$M_{n,GPC}$[b] (g mol^{-1})	$M_{n,th}$ (g mol^{-1})	M_w/M_n[b]	m[c]	T_g[d] (°C)
1	0	0	H_2O	80	48	7.6	122,800	364	1.19	0.49	178
2	0.01	0	H_2O	80	48	9.2	46,470	430	1.31	0.49	177
3	0.03	0	H_2O	80	48	16.9	48,690	711	1.26	0.56	175
4	0.05	0	H_2O	80	48	66.4	123,000	2485	1.58	0.71	144
5	0	0.05	H_2O	80	48	2.1	34,620	102	1.24	0.63	165
6	0	0.1	H_2O	80	48	1.7	52,280	100	1.03	0.76	138
7	0	0.05	CH_3OH	80	48	1.9	33,740	101	1.27	0.65	156
8	0	0.1	CH_3OH	80	48	1.6	39,250	100	1.42	0.71	145
9	0	0.05	Mixture	130	12	16.7	139,200	696	1.34	0.57	172
10	0	0.1	Mixture	130	12	15.3	137,600	644	1.23	0.66	154

[a] Measured gravimetrically.

[b] Determined on a Wyatt gel permeation chromatograph (GPC).

[c] *meso* content, measured by ^{1}H NMR spectra with a 500-MHz INOVA.

[d] Measured by differential scanning calorimetry (DSC) run at 25 °C on a Perkin–Elmer Model DSC-2C system.

[e] ATRP with a $[\text{acrylamide}]_0/[\text{chloroacetic acid}]_0/[CuCl]_0/[TMEDA]_0$ ratio of 50:1:1:2 at 80 or 130 °C.

[f] Mixture solvent: glycerol–water (1:1 v/v).

observation was consistent with the polymerization results of acrylamide derivatives reported by Matyjaszewski et al. [17]. The enhanced rate with $Y(OTf)_3$ was possibly because of the coordination of the Lewis acid $Y(OTf)_3$ to the amide group of the monomer acrylamide as well as the propagating radical species [14,30,31]. However, the molecular weight of the obtained polyacrylamide in presence of the Lewis acid $Y(OTf)_3$ tended to be smaller than that of the polymer obtained in the absence of the acid. This behavior had also been observed for the stereospecific ATRP of DMAA by Matyjaszewski et al [18], which could be a consequence of a faster initiation process compared with propagation in the case of the ATRP polymerization with Lewis acid.

Moreover, it is noteworthy that the ATRP of acrylamide in the presence of Lewis acid $Y(OTf)_3$ tended to be less controllable. When 0.05 equiv Lewis acid $Y(OTf)_3$ (relative to monomer) was added in the polymerization, the polydispersity index of the resultant polyacrylamide reached 1.58, demonstrating the worse controllability of the polymerization. This deteriorated controllability was most probably caused by the enhanced polymerization rate. The markedly increased rate due to the addition of $Y(OTf)_3$ would make it difficult to maintain the dynamic equilibrium between the initiation and propagation, and consequently lead to a poor controlling of the polymerization.

The microstructure of the polyacrylamide prepared by such ATRP was investigated by ^1H NMR spectroscopy. The proportion of *meso* dyads was determined from the signals of the main-chain methylene protons of polyacrylamide (Fig. 1) [32]. In the absence of Lewis acids, the polymer formed was almost atactic ($m = 49\%$), which was caused by the nearly equal probability of *meso* and *racemo* addition of the monomer during the radical polymerization. Also, the Lewis acid at low concentration (e.g. 0.01 equiv of $Y(OTf)_3$) laid less effect on the tacticity of polyacrylamide. When a larger amount of the Lewis acid $Y(OTf)_3$ (0.05 equiv of $Y(OTf)_3$ relative to monomer) was introduced in the polymerizations, the resultant polymers showed an increased *meso* content ($m \sim 71\%$). This indicated that the tacticity of polyacrylamide depended on the Lewis acid concentration applied in the polymerization system.

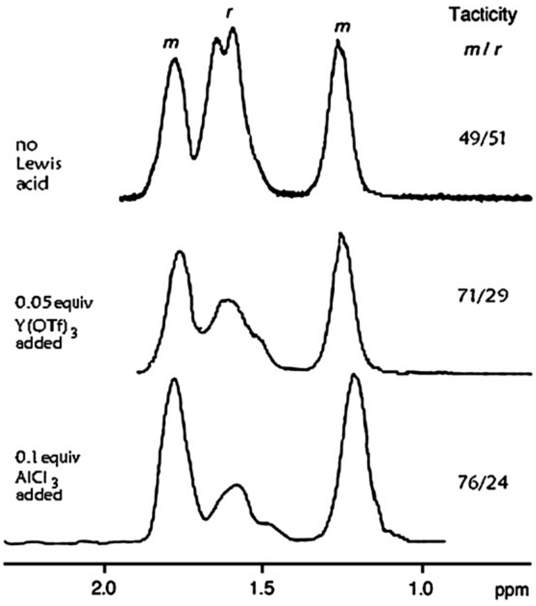


Fig. 1. ^1H NMR (500 MHz) of polyacrylamide prepared by ATRP with or without Lewis acid. $[Y(OTf)_3]_0/[\text{acrylamide}]_0 = 0.05$, $[AlCl_3]_0/[\text{acrylamide}]_0 = 0.1$.

From the description above, although the Lewis acid $Y(OTf)_3$ could make for stereocontrolling in the ATRP of acrylamide, it also brought broad molecular weight distribution of polyacrylamide due to its accelerating effect on polymerization. Thus, how to choose a good stereospecific catalyst for achieving simultaneous control of both tacticity and polydispersity in the ATRP of acrylamide is very important.

Compared with the rare earth metal trifluoromethanesulfonates, the Lewis acid $AlCl_3$ is considered as a candidate of effective stereospecific catalyst because of its intermediate acidity, easy availability and low-cost. According to its reactivity and properties, when conducted in the polymerization system, it might partially hydrolyze in the solvent water, generating HCl to further increase the acidity of the medium, and thus make the polymerization rate moderate in the ATRP of acrylamide [28]. Also, if methanol is used as the polymerization medium, the Lewis acid $AlCl_3$ would be possibly decomposed by the solvent into corresponding alkoxide [24]. These hydrolyzation or decomposition reactions would consume some amount of the added Lewis acid and restrict its coordination to the amide group of the monomer as well as the propagating radical species. Furthermore, the possible deactivation of the catalytic system of ATRP due to the addition of the Lewis acid would also devote to the polymerization rate adjustment. Therefore, we suggested that the application of Lewis acid $AlCl_3$ in the ATRP of acrylamide would to some extent lower the polymerization rate to achieve a better ATRP process.

Just as we had expected, Table 1 showed that when Lewis acid $AlCl_3$ was introduced in the polymerizations of acrylamide either in water under homogeneous condition or in methanol suspension system, the polymerization rate was decreased. In contrast with the results in the presence of Lewis acid $Y(OTf)_3$, when the Lewis acid $AlCl_3$ was added in the polymerization system the polydispersities of the polymers remained low ranging from 1.03 to 1.42 depending on the different reaction conditions, which showed the living nature of the polymerization.

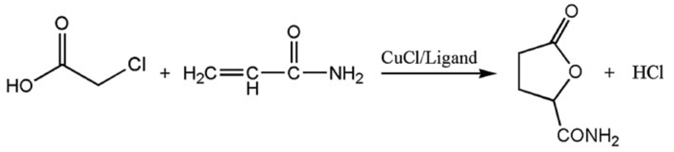
It is also worthwhile to notice that the Lewis acid $AlCl_3$ was of the comparable influence on improving the tacticities of the polyacrylamide in our polymerizations with $Y(OTf)_3$. When 0.05 or 0.1 equiv of Lewis acid $AlCl_3$ (relative to monomer) was applied in the polymerization performed in water at 80 °C, the resultant polyacrylamide had increased *meso* contents of 63 and 76%, respectively.

Several possible reactions related to the Lewis acid $AlCl_3$ were suggested when the ATRP of acrylamide was conducted in its presence. (1) The Lewis acid could be consumed partially as the ligand could be transferred to the Lewis acid besides its complexation with the transition metal ATRP catalyst.

(2) The Lewis acid $AlCl_3$ would undertake the hydrolyzation or decomposition reactions to some extent and thus bated its complexation with the amide group of the monomer acrylamide as well as the propagating radical species when it was introduced in the polymerizations of acrylamide either in water or in methanol. (3) The Lewis acid $AlCl_3$ might also coordinate with the pendent groups of the polymer terminal and the monomer and force them into the *meso* configuration during monomer addition propagation, leading to a stereocontrol polymerization, as demonstrated in Scheme 1. (4) The Lewis acid $AlCl_3$ could also form complexes with alkene containing electron-withdrawing groups, thus enhancing the coordination with the segments of the growing polymer chain and the monomer. In the case of a small amount of the Lewis acid introduced in the polymerization, the first two reactions might predominate and consume most of the acid. When the added Lewis acid was summed up to a certain concentration in the system, the aftereffects of the reactions 3 and 4 could become important, which brought about the improved stereocontrol in the polymerization.

Several reports claimed that for ensuring stereocontrol of polymerization, the polar solvent methanol was more efficient than others in the solvents cooperated with Lewis acid [31,33]. However, we did not reproduce such results in our polymerizations. This might be subjected to the fact that the monomer acrylamide is well soluble in water and water is an intrinsically polar solvent, which is of great benefit to stereocontrol in our ATRP of acrylamide as methanol did in the polymerizations of other monomers.

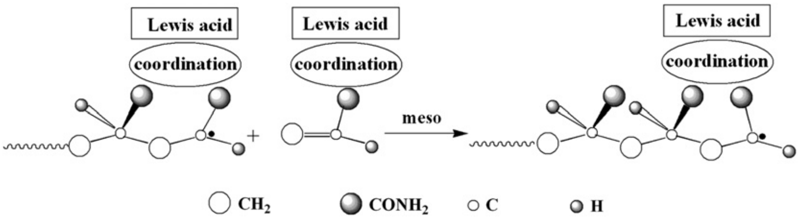
The ATRP of acrylamide with different feeding ratios of $[AlCl_3]_0/[acrylamide]_0$ at different temperatures, 80 and 130 °C, was also performed. The relevant results in Table 1 showed that an increased polymerization temperature (130 °C) led to a raised polymerization rate, which might attribute to the following factors: (1) the higher temperature did benefit improving the radical polymerization rate in the initiating system. (2) The elevated reaction temperature 130 °C, for the glycerol–water mixture solvent system, could effectively diminish undesirable side reactions which might easily occur in only water as the solvent. And it was this raised polymerization rate that consequently resulted in the loss of tacticity of the resultant polymer. The combination of both lower temperature (80 °C) and higher feeding ratio 0.1 of [Lewis acid]$_0$/[acrylamide]$_0$ afforded the best stereocontrol of the resultant polymer ($m \sim 76\%$).



Scheme 2. Possible intermolecular cyclization between chloroacetic acid and acrylamide.

However, we also noticed that there existed another striking occasion in our experiments that the experimental molecular weights from gel permeation chromatograph (GPC) were much higher than the predicted $M_{n,th}$ ($M_{n,th} = [(\text{Conversion} \times M_{\text{Monomer}} \times [\text{Monomer}]_0)/[\text{Initiator}]_0] + M_{\text{Initiator}}$, where M_{Monomer} and $M_{\text{Initiator}}$ are the molecular weight of acrylamide and chloroacetic acid, respectively). We think that the unexpected molecular weights were quite likely subjected to lower initiation efficiency of the initiator employed during the reactions due to some possible undesirable side reactions of the initiator [34–36]. To begin with, in the aqueous medium, the radicals produced by the redox reaction of CuCl/TMETA with chloroacetic acid in the initiation process might be easily affected by the coupling termination or the aquation of the water molecules. Secondly, under the polymerization condition, an intermolecular cyclization between the chloroacetic acid and the monomer would probably take place, forming γ-butyrolactone in high yield as showed in Scheme 2 [37–39]. Thirdly, the initiator might also react with the amide group of the ligand TMEDA to some extent. These extra consumptions of the initiator would induce the loss of the initiator efficiency.

We further measured the glass transition temperature (T_g) of the samples by differential scanning calorimetry (DSC), so as to reveal the possible influences of the tacticities on heat behavior of the resultant polyacrylamide. Interestingly, the glass transition temperature of polyacrylamide showed a decreased tendency with an increased tacticity of polyacrylamide. As a property of the polymer, the glass transition temperature generally depends upon several factors such as the free volume of the polymer, the attractive forces between molecules, the internal mobility of the chains (their freedom to rotate about bonds), the chain stiffness, the geometry of the polymer chain, molecular weight and polydispersity as well as measure conditions (heat history, heating rate, etc.). Whereas, the glass transition temperature is predominately determined by the microstructure of the polymer. Most probably, we could ascribe the above tendency as the aftermath of a smaller number of intermolecular hydrogen bonds between the O/N and H atom in polyacrylamide in the case of the high tacticity obtained.



Scheme 1. Radical propagation in the presence of Lewis acid.

In order to know more about the polymerization system, the kinetic polymerization of acrylamide proceeded with an [acrylamide]$_0$/[chloroacetic acid]$_0$/[CuCl]$_0$/[TMEDA]$_0$ ratio of 50:1:1:2 in the absence/presence of the Lewis acid $AlCl_3$ at 130 °C. Fig. 2 showed that the monomer conversion increased with the time and a linear relationship between the $\ln([M]_0/[M])$ and time was observed. The results showed that the kinetics was first order and the concentration of the propagating radicals remained constant during the polymerization process. The apparent rate constant obtained from the slope of Fig. 2a was $2.16 \times 10^{-2}\ \mathrm{min}^{-1}$, while that from Fig. 2b turned out to be $2.56 \times 10^{-4}\ \mathrm{min}^{-1}$, indicating a rather slower polymerization rate in the presence of Lewis acid $AlCl_3$. However, we noticed from Fig. 2a that the polymer yield after the first 10 min of polymerization reached 31.5%, while the yield after another 10 min was only increased to 35.1%. In other words, the increased value of conversion at the first interval of 10 min was relatively higher than those at other intervals. This might be due to the relatively greater activity of the ATRP catalyst arising from the lower viscosity at the beginning of the polymerization. With the increase of polymerization time, the polymerization system became viscous and would lead to a sluggish formation of the radical as well as the slow movement of the propagating chains. In Fig. 3, the number-average molecular weights (M_n) of the polymers measured by the GPC increased linearly with conversion, and the polydispersity index (M_w/M_n) remained lower, ranging from 1.09 to 1.39 and 1.07 to 1.38 in the absence/presence of the Lewis acid $AlCl_3$, respectively. These results indicated that the polymerizations proceeded by the normal ATRP with a living nature and the polydispersities of the polymers were well controlled with or without the addition of the Lewis acid $AlCl_3$.

4. Conclusion

To sum up, we succeeded in carrying out the stereospecific atom transfer radical polymerizations of acrylamide in the presence of Lewis acid $Y(OTf)_3$ or $AlCl_3$ as stereospecific catalyst using chloroacetic acid/CuCl/*N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA) as initiating system. The addition of

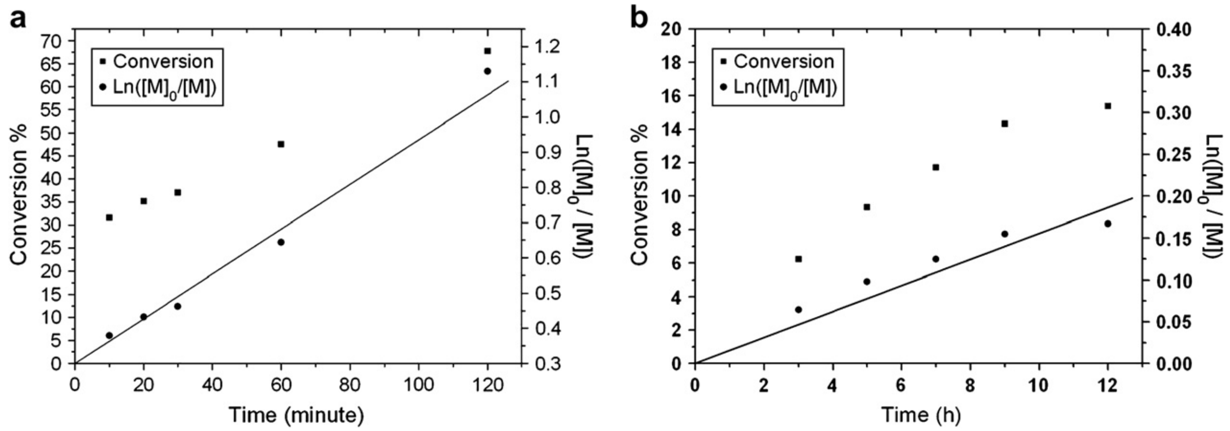


Fig. 2. Plots of conversion (%) and $\ln([M]_0/[M])$ versus the reaction time for the polymerization of acrylamide proceeded in glycerol–water (1:1 v/v) medium at 130 °C with an [acrylamide]$_0$/[chloroacetic acid]$_0$/[CuCl]$_0$/[TMEDA]$_0$ ratio of 50:1:1:2. (a) Without the addition of Lewis acid $AlCl_3$. (b) With the addition of Lewis acid $AlCl_3$: [Lewis acid]$_0$/[acrylamide]$_0$ = 0.1.

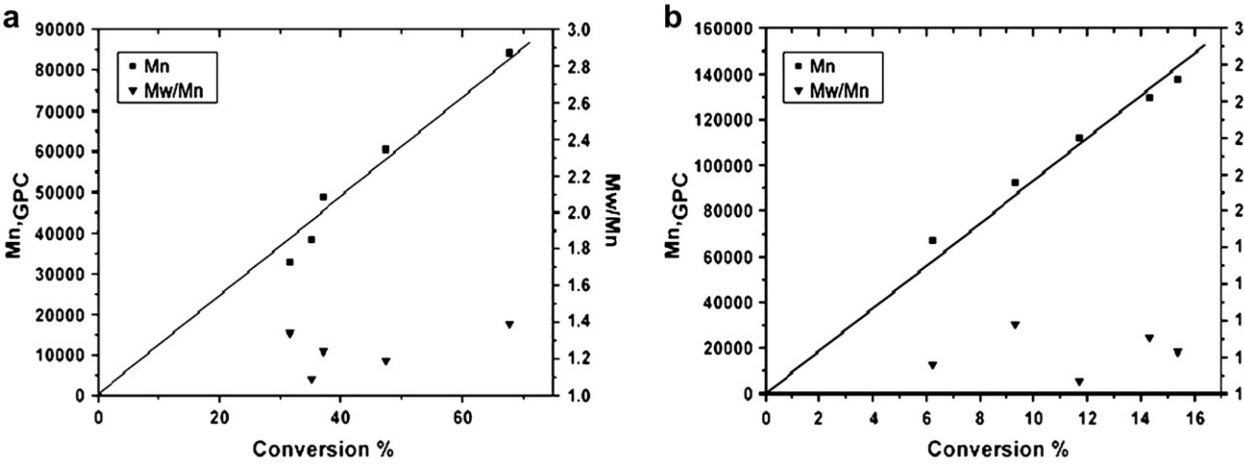


Fig. 3. The relationship between the number-average molecular weight (M_n) and polydispersity (M_w/M_n) with conversion (%) for the polymerization of acrylamide in glycerol–water (1:1 v/v) medium at 130 °C with a [acrylamide]$_0$/[chloroacetic acid]$_0$/[CuCl]$_0$/[TMEDA]$_0$ ratio of 50:1:1:2. (a) Without the addition of Lewis acid $AlCl_3$. (b) With the addition of Lewis acid $AlCl_3$: [Lewis acid]$_0$/[acrylamide]$_0$ = 0.1.

Lewis acid $Y(OTf)_3$ in the ATRP of acrylamide led to an increased polymerization rate, an improved tacticity of polyacrylamide and a deteriorated controllability of the polymerizations, namely, a broad molecular weight distribution. In the presence of the Lewis acid $AlCl_3$, the polymerization of acrylamide was well controlled in both aspects of tacticity and polydispersity. The resultant polyacrylamide showed low polydispersity index of 1.03 and high tacticity with *meso* content up to 76% at the optimal reaction condition. Lower temperature or higher feeding ratio of $[\text{Lewis acid}]_0/[\text{acrylamide}]_0$ helped to achieve the increased stereocontrol of the polymerization and the glass transition temperature of resultant polyacrylamide tended to decrease with its increased tacticity.

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