

# Preparation of Polyacrylamide with Improved Tacticity and Low Molecular Weight Distribution

Jianguo Jiang<sup>1,\*</sup>, Weifeng Chen<sup>2</sup>, Aimin Cheng<sup>1</sup>, Jin Guo<sup>1</sup>, Yueshu Liu<sup>1</sup>

<sup>1</sup> School of Biochemistry and Engineering, Yangzhou Polytechnic University, Yangzhou 225009, People's Republic of China.

<sup>2</sup> Yangzhou Institute of Product Quality Supervision and Inspection, Yangzhou 225001, People's Republic of China.

**Abstract:** Polyacrylamide with improved tacticity and low molecular weight distribution was obtained via stereospecific atom transfer radical polymerization (ATRP) using the mixture of Lewis acids Y(OTf)<sub>3</sub> and AlCl<sub>3</sub> in a certain ratio as stereospecific catalyst and chloroacetic acid/ Cu<sub>2</sub>O / N,N,N',N'-tetramethylethylenediamine(TMEDA) as initiating system. The initiating system afforded persistently controlled ATRP of acrylamide with lower polydispersity index ranging from 1.12 to 1.35 as well as a moderate polymerization process. The participation of the mixture of Lewis acids Y(OTf)<sub>3</sub> and AlCl<sub>3</sub> as stereospecific catalyst in the stereospecific ATRP of acrylamide contributed optimal stereospecific PAM with the meso content 80%~83%. Polymerization kinetics displayed a living/controlled nature of the present polymerizations.

**Keywords:** Polyacrylamide; Tacticity; ATRP; Polydispersity

## 1. Introduction

In recent years the preparation of acrylamide-based polymers with low polydispersities, defined molecular weights and tacticity has drawn increasing attention to further expand their typical applications[1,2] from the theoretical point of view that polymers' structure recounted by tacticity, molecular weight and polydispersity would predominantly decide the thermomechanical and chemical properties of polymers and consequently determine the expansion of their applications[3,4].

However, synthesizing these polymers seems difficult to be accomplished via the anionic polymerization as the result of the easy occurrence of hydrogen proton transfer in the polymerization but on the technique of the "living"/controlled radical polymerization (CRP)[5-12].

Several reports revealed the combination of using Lewis acids or fluoroalcohols with CRP could control both macromolecular architectures and microstructures of acrylamide-based polymers. Yue Sun et al. recently attained poly(N-hydroxyethyl acrylamide)(HEAA) with meso content (m) increased from 42% to 80% in a homopolymer with a dispersity PDI = 1.22 via ATRP in the presence of Y(OTf)<sub>3</sub>[13]. Matyjaszewski et al. introduced Lewis acid Y(OTf)<sub>3</sub> or Yb(OTf)<sub>3</sub> as stereospecific agent in their ATRP and RAFT of N-methyl methacrylamide and N,N-dimethylacrylamide (DMAA), achieving isotactic rich poly-(N-methyl methacrylamide) and poly(DMAA) with controlled molecular weights and low polydispersity[14,15]. The isotactic poly-(NIPAM) (N-isopropylacrylamide) with

controlled molecular weight was obtained by Okamoto group using Lewis acid in their RAFT polymerization [16,17], and they consequently synthesized poly-(N,N-dimethylacrylamide) with high isotacticity (m>80%) and the large polydispersities (PDI>1.87) by adding Lewis acid Yb(OTf)<sub>3</sub> and Yb(NTf<sub>2</sub>)<sub>3</sub> in their iron(I)-catalyzed ATRP [17,18].

These stereospecific preparations via ATRP mentioned above do not involve the monomer acrylamide but the acrylamide derivatives in that the ATRP of acrylamide turns to be more challenging due to the existence of intrinsic hydrogen protons in primary amines[19,20] as well as the possible transfer of ATRP ligand to the Lewis acid which subsequently impacted the complexation with the transition metal ATRP catalysts in case of the Lewis acid used as stereospecific catalyst in the stereospecific ATRP of acrylamide [14,21].

In our previous work, we introduced chloroacetic acid as initiator and CuCl/N,N,N',N'-tetramethylethylenediamine(TMEDA) as catalyst in the ATRP of acrylamide, affording polyacrylamide with lower polydispersity, and revealed the acidic polymerization condition provided by the initiator chloroacetic acid considerably prevented the ATRP of acrylamide from the unexpected side-reactions including complexation and cyclization[22]. Additively, we employed Lewis acids Y(OTf)<sub>3</sub> and AlCl<sub>3</sub>, respectively, as stereospecific catalyst in our ATRP of acrylamide and achieved stereospecific ATRP of acrylamide in the presence of the Lewis acid Y(OTf)<sub>3</sub> or AlCl<sub>3</sub>[23]. The addition of Lewis acid Y(OTf)<sub>3</sub> in the ATRP of acrylamide not only caused an increased polymerization rate but an improved tacticity

\* Corresponding author: [njujianguo@126.com](mailto:njujianguo@126.com)

of polyacrylamide ( $m \sim 71\%$ ), negatively brought about the worse controllability of the molecular weight distribution. On the other hand, the participation of Lewis acid  $\text{AlCl}_3$  in the polymerization afforded the obtained polyacrylamide with lower polydispersity (1.03-1.42) and well-controlled tacticity (meso content rising up to 76%), while the polymerization manifested a sluggish polymerization process.

In this paper, we showed that the use of  $\text{Cu}_2\text{O}$  as catalyst instead of  $\text{CuCl}$  which was used in our previous work, and the mixture of Lewis acids  $\text{Y}(\text{OTf})_3$  and  $\text{AlCl}_3$  in a certain ratio as stereospecific reagent in the stereospecific ATRP of acrylamide, led to a significant improvement in the control of the stereospecific ATRP of acrylamide. Not only were polymers with a lower polydispersity index ( $\text{PDI} = 1.18-1.26$ ) as well as higher meso content ( $m = 80\%-83\%$ ) obtained, but the polymerizations displayed a moderate process. Besides, the kinetic polymerization of acrylamide proceeded in presence of  $\text{Cu}_2\text{O}$  as catalyst and the mixture of Lewis acids  $\text{Y}(\text{OTf})_3$  and  $\text{AlCl}_3$  in a certain ratio as stereospecific reagent was carried out, testifying the present polymerization proceeded with a living/controlled nature.

## 2. Experimental

### 2.1 Materials

Acrylamide (chemically pure) was kindly provided by Shanghai Chemical Reagent Co., Ltd., China) and recrystallized before use. Methanol (analytical reagent, Hangzhou Chemical Reagent Co., Ltd., China), TMEDA (biochemical reagent, Shanghai Qianjing Chemical Reagent Plant, China), chloroacetic acid,  $\text{AlCl}_3$  (analytical reagent, Shanghai Linfeng Chemical Reagent Co., Ltd., China) were used as received.  $\text{Y}(\text{OTf})_3$  (98%) was purchased from Aldrich and directly put into use.  $\text{Cu}_2\text{O}$  was synthesized according to the published literature[24].

### 2.2 Stereospecific preparations of PAM

A typical stereospecific preparation procedure was as follows: Add in turn the reagents including  $\text{Cu}_2\text{O}$ , TMEDA, acrylamide, Lewis acid  $\text{Y}(\text{OTf})_3 / \text{AlCl}_3$  or  $\text{Y}(\text{OTf})_3 + \text{AlCl}_3$ , solvent(water) and chloroacetic acid in a certain ratio to a dry glass tube. The tube was then sealed under nitrogen after three freeze-vacuum cycles and then heated in an oil bath which was controlled at the desired temperature by a thermostat. The polymerization could be terminated by simply taking out the tube, opening the flask and exposing the reagents in the tube to air if the specified reaction time was up. Dissolve the polymerization product in water and then get it precipitated in methanol. Separated by centrifugation, the product was then re-dissolved with water and treated with cation-exchange resin in order to remove the copper complex. Re-precipitated in methanol again, and dried under vacuum at 40 °C for 24h, the final product was achieved.

### 2.3 Kinetic experiments

Add in turn the reagents including  $\text{Cu}_2\text{O}$ , TMEDA, acrylamide, Lewis acids, solvent and chloroacetic acid in appropriate ratios into a tube. The tube was then sealed under nitrogen after three freeze-vacuum cycles and then heated in an oil bath controlled at the desired temperature by a thermostat. After certain time intervals, withdraw the samples from polymerization using degassed syringes and process the samples with the similar procedures to what was mentioned above.

### 2.4 Characterization

A Wyatt gel permeation chromatograph (GPC) was introduced to determine molecular weights and molecular weight distributions (PDI) of the polymers. The  $^1\text{H}$  NMR spectra were achieved in a 500-MHz INOVA instrument with  $\text{DMSO-d}_6$  as a solvent. The conversion of the polymerization was determined gravimetrically.

## 3. Results and discussion

We developed a feasible polymerization system for ATRP of acrylamide in our previous work, in which chloroacetic acid was used as initiator and  $\text{CuCl} / \text{TMEDA}$  as catalyst, affording polyacrylamide with lower polydispersity ranging from 1.03 to 1.44, and revealed the acidic polymerization condition provided by the initiator chloroacetic acid considerably prevented the ATRP of acrylamide from the unexpected side-reactions including complexation and cyclization<sup>[22]</sup>. Successively, we employed Lewis acids  $\text{Y}(\text{OTf})_3$  and  $\text{AlCl}_3$ , respectively, as stereospecific catalyst in our ATRP of acrylamide and achieved stereospecific ATRP of acrylamide in the presence of the Lewis acid  $\text{Y}(\text{OTf})_3$  or  $\text{AlCl}_3$ <sup>[23]</sup>. In that case, the addition of Lewis acid  $\text{Y}(\text{OTf})_3$  in the ATRP of acrylamide contributed an increased polymerization rate as well as improved tacticity of polyacrylamide ( $m \sim 71\%$ ) at the expense of controllability of the molecular weight distribution. On the other hand, the participation of Lewis acid  $\text{AlCl}_3$  in the polymerization afforded the obtained polyacrylamide with lower polydispersity (1.03-1.42) and well-controlled tacticity (meso content rising up to 76%), however, the polymerization with the participation of  $\text{AlCl}_3$  manifested a sluggish polymerization process.

The choice of  $\text{Cu}_2\text{O}$  as catalyst followed from the screening experiments in our work, manifested that  $\text{Cu}_2\text{O}$  was more productive insofar as our ATRP of acrylamide was concerned. We employed  $\text{Cu}_2\text{O}$  as catalyst instead of  $\text{CuCl}$  which was used in our previous work, and subsequently carried out the stereospecific ATRP of acrylamide in presence of Lewis acids  $\text{Y}(\text{OTf})_3$  and  $\text{AlCl}_3$  as stereospecific reagent.

The results of stereospecific ATRP of acrylamide using chloroacetic acid/  $\text{Cu}_2\text{O} / \text{TMEDA}$  as initiating system and Lewis acid  $\text{Y}(\text{OTf})_3 / \text{AlCl}_3$  or  $\text{Y}(\text{OTf})_3 + \text{AlCl}_3$  in a certain ratio as stereospecific reagent were summarized in Table 1. The data in entries 2-5 depicted the participation of  $\text{Y}(\text{OTf})_3$  in the polymerization led to an increasing polymerization progress, and the molecular weight of the resultant polyacrylamide in presence of the  $\text{Y}(\text{OTf})_3$

tended to be smaller than that of the polymer obtained in the absence of the acid. These observations were consistent with the polymerization results we obtained in our previous work when we used chloroacetic acid/ CuCl/TMEDA as initiating system and Y(OTf)<sub>3</sub> as stereospecific reagent, and the similar observation was also reported by Matyjaszewski et al with their stereospecific ATRP of DMAA [15].

**Table 1.** Results of stereospecific ATRP of acrylamide in presence of Y(OTf)<sub>3</sub> or AlCl<sub>3</sub><sup>a</sup>

N o.	[Y(OTf) <sub>3</sub> ] <sub>0</sub> / [AM] <sub>0</sub>	[AlCl <sub>3</sub> ] <sub>0</sub> / [AM] <sub>0</sub>	Con v. %	Mn <sub>PC</sub> , g mol <sup>-1</sup>	Mw/ Mn	M <sub>b</sub>
1	0	0	35.6	136,800	1.18	0.49
2	0.01	0	41.2	62,320	1.24	0.51
3	0.03	0	60.4	68,750	1.26	0.63
4	0.05	0	72.8	125,400	1.35	0.72
5	0.07	0	86.7	131,560	1.33	0.70
6	0	0.05	26.7	41,520	1.21	0.64
7	0	0.1	21.6	62,260	1.12	0.78
8	0	0.15	18.2	53,420	1.12	0.76

<sup>a</sup> ATRP with a [acrylamide]<sub>0</sub>/[chloroacetic acid]<sub>0</sub>/[Cu<sub>2</sub>O]<sub>0</sub>/[TMEDA]<sub>0</sub> ratio of 50:1:1:2 at 80°C for 48h.

<sup>b</sup> meso content, measured by <sup>1</sup>H NMR spectra with a 500-MHz INOVA.

However, it is noteworthy that the ATRP of acrylamide with chloroacetic acid/ Cu<sub>2</sub>O / TMEDA as initiating system brought about more satisfactory polymerization progress compared with that using CuCl as catalyst. The polymerization catalyzed with Cu<sub>2</sub>O seemed to be beneficial to both accelerating the ATRP of acrylamide and maintaining the controllability of the polymerization. The conversion of ATRP of this initiating system at 80°C for 48h in the absence / presence of Lewis acid Y(OTf)<sub>3</sub> ranged from 35.6% to 86.7%, which was a lot higher than what we have reported with the former initiating system. Besides, the PDI of the resultant polymers remained low ranging from 1.18 to 1.35 depending on the different amount of the added Y(OTf)<sub>3</sub>, displaying the persistent living nature of the polymerization, which was also superior to the result we obtained before.

To the best of our knowledge, an applicable catalyst system cooperation with the given initiator is also a vital factor in a successful ATRP. Compared with the catalyst CuCl applied in our former ATRP system, Cu<sub>2</sub>O has shown a higher catalytic activity in the ATRP of several monomer including AN, methacrylates and styrene than CuBr and CuCl[25-31]. Moreover, the ligand TMEDA in our polymerization system was assumed to be more

efficacious for improving the solubility of Cu<sub>2</sub>O because of its linear structure similar to the monomer acrylamide. The solubility as well as catalytic activity of the catalyst increased and more radicals were generated, leading to the accelerating rate of the polymerization. Additionally, it was the improved the solubility of the catalyst that made it possible to maintain the dynamic equilibrium between the initiation and propagation, and consequently led to a persistent controlling of the polymerization in the whole polymerization process.

The <sup>1</sup>H NMR spectroscopy was applied to investigate the microstructure of the polyacrylamide prepared by the stereospecific ATRP of acrylamide. The proportion of meso dyads was determined from the signals of the main-chain methylene protons of polyacrylamide[32]. The low concentration of Lewis acid Y(OTf)<sub>3</sub> in the polymerization (e.g. 0.01 equiv of Y(OTf)<sub>3</sub>) had less impact on the tacticity of polyacrylamide. When 0.05-0.07 equiv of Y(OTf)<sub>3</sub> was applied in the polymerizations, the obtained polymers displayed an improved meso content (m~70-72%).

The Lewis acid AlCl<sub>3</sub> turned out to be an effective stereospecific catalyst in our stereospecific PAM preparation[23], affording the resultant PAM with well-controlled tacticity ( meso content ~ 76%), though the addition of this acid to the polymerization system unfavourably led to a tardy polymerization rate. In case of the current stereospecific ATRP of acrylamide using chloroacetic acid/ Cu<sub>2</sub>O / TMEDA as initiating system, the participation of AlCl<sub>3</sub> as stereospecific reagent in the polymerization brought about results paralleled to what we had obtained before. The data in entries 6-8 of Table 1 showed that the participation of Lewis acid AlCl<sub>3</sub> in the polymerizations of acrylamide rendered a decreased polymerization rate. And the more amount of the added AlCl<sub>3</sub>, the slower the polymerization rate. Nevertheless, the conversion of ATRP of this initiating system at 80°C for 48h in presence of Lewis acid AlCl<sub>3</sub> ranged from 18.2% to 26.7%, which was also far higher than that of the former ATRP system. As always, the polydispersities of the resultant PAM remained low ranging from 1.12 to 1.21 depending on the different amount of the added AlCl<sub>3</sub>, demonstrating the intrinsic living nature of the polymerization.

As we had proposed, the Lewis acid AlCl<sub>3</sub> in current polymerization system had identically favorable effect on improving the tacticities of the polyacrylamide in our polymerizations. When 0.1 or 0.15 equiv of Lewis acid AlCl<sub>3</sub> (relative to monomer) was applied in the polymerization, the resultant PAM enjoyed increased meso contents of 76~78%.

Subsequently, we performed the stereospecific ATRP of acrylamide in water at 80°C for 48h using the mixture of Lewis acids Y(OTf)<sub>3</sub> and AlCl<sub>3</sub> in a certain ratio as stereospecific catalyst and chloroacetic acid/ Cu<sub>2</sub>O / TMEDA as initiating system. As the information in Table 2 depicted, the introduction of the mixture of Lewis acids Y(OTf)<sub>3</sub> and AlCl<sub>3</sub> of appropriate ratio as stereospecific catalyst in the ATRP of acrylamide took responsibility for affording optimal stereospecific PAM: When 0.1 equiv of Lewis acid AlCl<sub>3</sub> (relative to monomer) combined with

0.01-0.05 equiv of Lewis acid  $Y(OTf)_3$  was applied, the meso content of the resultant PAM reached 80%~83%, which was higher than that of the polymers obtained by using either Lewis acid  $Y(OTf)_3$  or  $AlCl_3$  individually. Besides, the addition of mixed Lewis acids  $Y(OTf)_3$  and  $AlCl_3$  was beneficial to reconciling the ATRP process and resultantly generated a moderate polymerization. Meanwhile, the polymerizations in presence of the mixed Lewis acids  $Y(OTf)_3$  and  $AlCl_3$  were well controlled with the polydispersities of the resultant PAM ranging from 1.18 and 1.26, which manifested the characteristics of controlled radical polymerization.

**Table 2.** Results of stereospecific ATRP of acrylamide in presence of mixture of Lewis acids  $Y(OTf)_3$  and  $AlCl_3$

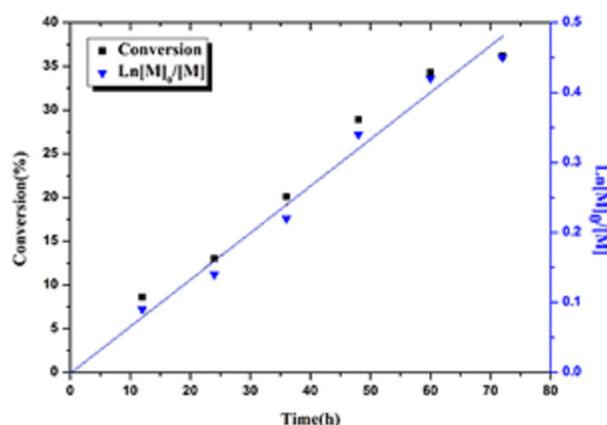
N <sub>o.</sub>	$[Y(OTf)_3]_0/[AM]_0$	$[AlCl_3]_0/[AM]_0$	Con v. %	$Mn_{GPC}$ gmol <sup>-1</sup>	Mw/Mn	m <sup>b</sup>
1	0.01	0.05	36.8	73,300	1.21	0.63
2	0.01	0.1	28.9	67,760	1.18	0.83
3	0.03	0.05	44.6	89,400	1.24	0.65
4	0.03	0.1	32.7	72,540	1.16	0.80
5	0.05	0.05	50.4	82,370	1.21	0.72
6	0.05	0.1	46.1	74,280	1.26	0.80

<sup>a</sup> ATRP with a  $[acrylamide]_0/[chloroacetic\ acid]_0/[Cu_2O]_0/[TMEDA]_0$  ratio of 50:1:1:2 at 80°C for 48h.

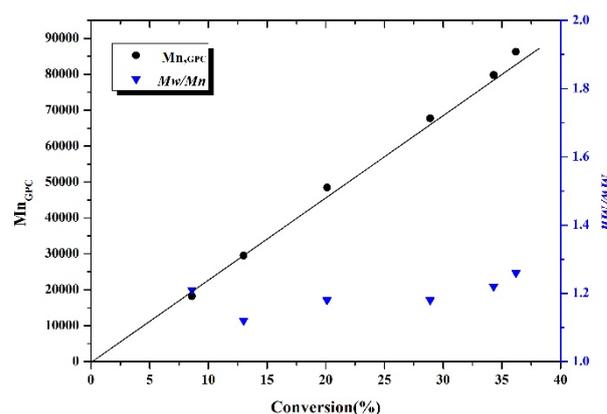
<sup>b</sup> meso content, measured by <sup>1</sup>H NMR spectra with a 500-MHz INOVA.

The kinetic polymerization of acrylamide was insuccession studied with an  $[acrylamide]_0/[chloroacetic\ acid]_0/[Cu_2O]_0/[TMEDA]_0$  ratio of 50:1:1:2 in presence of 0.1equiv of Lewis acid  $AlCl_3$  mixed with 0.01 equiv of  $Y(OTf)_3$  as stereospecific catalyst in water at 80°C. As Figure 1 depicted, a linear relationship between the  $Ln([M]_0/[M])$  and time was observed and the monomer conversion increased with the time, which recounted first order of the kinetics as well as the constant concentration of the propagating radicals during the whole course of polymerization. The apparent rate constant  $1.18 \times 10^{-4} \text{ min}^{-1}$

which was acquired from the slope implied an elevated polymerization rate compared with the former polymerization system. Besides, the number-average molecular weights of the polymers obtained from GPC ascended linearly with conversion, and the PDI of the polymers remained lower, ranging from 1.12 to 1.26, as was displayed in Figure 2. These information manifested a living nature of the polymerizations and the polydispersities of the polymers were well controlled with the addition of the mixed Lewis acid  $AlCl_3$  and  $Y(OTf)_3$ .



**Fig. 1.** Plots of conversion (%) and  $ln([M]_0/[M])$  versus the reaction time for the polymerization of acrylamide proceeded in water at 80°C with an  $[acrylamide]_0/[chloroacetic\ acid]_0/[Cu_2O]_0/[TMEDA]_0$  ratio of 50:1:1:2 in presence of 0.1equiv of Lewis acid  $AlCl_3$  mixed with 0.01 equiv of  $Y(OTf)_3$  as stereospecific catalyst.



**Fig. 2.** The relationship between the number-average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) with conversion (%) for the polymerization of acrylamide proceeded in water at 80°C with an  $[acrylamide]_0/[chloroacetic\ acid]_0/[Cu_2O]_0/[TMEDA]_0$  ratio of 50:1:1:2 in presence of 0.1equiv of Lewis acid  $AlCl_3$  mixed with 0.01 equiv of  $Y(OTf)_3$  as stereospecific catalyst.

#### 4. Conclusion

Polyacrylamide with improved tacticity and low molecular weight distribution was obtained via stereospecific ATRP using the mixture of Lewis acids  $Y(OTf)_3$  and  $AlCl_3$  in a certain ratio as stereospecific catalyst and chloroacetic acid/  $Cu_2O$  /  $N,N,N',N'$ -tetramethyl-ethylenediamine(TMEDA) as initiating system. In comparison with the previously reported approaches to the ATRP of acrylamide, our stereospecific ATRP of acrylamide displayed at least three merits: (1) Persistently controlled ATRP of acrylamide could be achieved with lower PDI ranging from 1.12 to 1.35; (2)

The introduction of the mixture of Lewis acids  $Y(OTf)_3$  and  $AlCl_3$  of appropriate ratio as stereospecific catalyst in the ATRP of acrylamide afforded optimal stereospecific PAM with the meso content 80%~83%; (3)The increased solubility as well as catalytic activity of the catalyst  $Cu_2O$  / TMEDA in our polymerization system was responsible for the accelerating rate of the polymerization, leading to a moderate polymerization process.

## Acknowledgements

We are grateful for the support from Yangzhou Science and Technology Plan Project (YZ2019046) and Scientific Research Project of Yangzhou Polytechnic University (2018ZR02) as well as the Jiangsu Qing Lan Project.

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