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AGET ATRP of Acrylamide in Aqueous Media

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Abstract: The recently developed initiation system, the activator generated by electron transfer (AGET) was used in atom transfer radical polymerization (ATRP) to synthesize well-controlled polyacrylamide in aqueous media at 25 ºC. The different reducing agents involved ascorbic acid and glucosa; well-controlled polymers were obtained when ascorbic acid was used as water-soluble reducing agent. The polymerizations targeted at degrees of polymerization in the range of 400 resulted in polymers with low polydispersity indices. Moreover, first order plots were linear.

Introduction

Atom transfer radical polymerization (ATRP) [1-3] have attracted increasing interest as a methods of controlled/living radical polymerization (CRP) in polymer science, since it allows the synthesis of polymers with predetermined molecular weight, narrow molecular weight distribution, as well as desired composition and molecular architecture. Importantly, the polymers prepared by ATRP are highly chain end-functionalized and could therefore participate in various post-polymerization modifications and served as macroinitiators in the synthesis of block copolymers.

ATRP has been applied in a wide range of monomers under varied conditions [4-6]. However, ATRP is especially sensitive to oxygen, which can inhibit polymerization not only by the formation of unreactive peroxy radicals but also by the irreversible oxidation of transition metal catalysts. For this reason, in order to obtain consistent kinetics, special deoxygenation procedures are required, such as a freeze-pump-thaw process. So, creating an oxygen-free environment is especially challenging when ATRP is carried out in water. In the latter case, it is much simpler to prepare a reaction mixture by starting with air-stable Cu (II) species and then, after homogenization and deoxygenation, reduced it to the Cu (I) state in order to start the polymerization. This has been accomplished by using simultaneous reverse and normal initiation (SR&NI) [7] and activators generated by electron transfer (AGET) processes [8]. The limitation of the former was that radicals produced from organic initiators (such as diazo compounds) reduced Cu (II) species and block copolymerization is always accompanied by the formation of small amounts of homopolymers. The AGET process overcomes this problem because reducing agents do not generate initiating radicals but are exclusively used for the reduction of Cu (II) to Cu (I) activating species [9].

Polyacrylamide and its derivatives are widely used in industry, agriculture and medicine due to their remarkable properties including biocompatibility, lack of toxicity, water solubility, and so on [10]. The successful synthesis of well-defined homopolymer or copolymer containing acrylamide-based monomers will be an important contribution to the field of controlled free-radical polymerization, serving to expand the scope of the ATRP processes in terms of applicable monomers.

During the past few years, most of the water-soluble polymers were successfully prepared by aqueous ATRP with relatively narrow molecular weight distribution and targeted degrees of polymerization [11-12]. It has been observed that ATRP in aqueous homogeneous media is fast and yields polymers of relatively high polydispersity index, indicating loss of control [13]. The well-controlled ATRP in aqueous media is challenging due to the occurrence of several side reactions. In water, the Cu (I)-based ATRP activator may disproportionate, the Cu (II)-based ATRP deactivator was likely to lose its halide ligand, and the alkyl halide initiator may hydrolyze or react with the monomer if it contained basic or nuclephilic groups.

In this work, the different reducing agents involved ascorbic acid and glucose was scanned, and ascorbic acid was used as the appropriate reducing agent; 2-Cl-PA/$CuCl_2$/Me_6TREN was used as the initiator and catalyst system. AGET ATRP of acrylamide was successfully carried out in aqueous solution at 25 ^{0}C. The polymerization with higher targeted degrees of polymerization in the range of 400 reached definite monomer conversion, and the polymers had narrow PDI level. Moreover, the molecular weight increased with the conversion, and the first-order kinetic plots were linear.

Results and Discussion

The catalytic activity increases generally in the order: bipyridine [14] < multidentate amines (e.g., *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA)) [15] < tripodalamines (e.g. Me_6TREN) < some cyclic amines (Me_4Cyclam) . Low values of ATRP equilibrium constants may be enhanced by using more reducing and more powerful catalyst, The choice of the Me_6TREN as the ligand follows from the fac. that it is sufficiently dynamic in order to enable efficient exchange reactions [16]; and, Me_6TREN is attempted to maintain lower polydispersities level. Furthermore, C-X bond at the chain end will be easily displaced by intra- or intermolecular nucleophilic amide group [17]. Thus, alkyl chlorides rather than bromides are used at relatively low temperatures and low polar solvents, which would reduce relative rates of S_N2 reactions in comparison with the ATRP process.

AGET ATRP with different reducing agents

Ascorbic acid and glucose are chosen as reducing agents to conduct AGET ATRP of acrylamide in water media. The result is shown in Table 1; well-controlled polymer is obtained with ascorbic acid in lower temperature, which maintains narrow molecular weight distribution (Table 1, entry 1). However, the polymerization cannot proceed with the aldehyde group reducing agent of glucose at the lower temperature, which may be due to its higher activation temperature (Table 1, entry 3). Furthermore, the higher temperature leads to a faster reaction rate and self-polymerization of portion of monomers, resulting in uncontrolled target polymers or gel (Table 1, entry 2, 4).

Thus, ascorbic acid is used as the appropriate reducing agent in following experiment. However, a fact will be noted that the molecular weights from the GPC

analyses deviates from the precise values due to differences of the hydrodynamic volume between polymers and the PNaAA standards used for calibration.

Tab. 1. AGET ATRP of AM in aqueous solution; initiating and catalytic system: 2-Cl-PA/$CuCl_2$/Me_6TREN.

Entry	Reducing agent	$[M]_0/[I]_0/[CuCl_2]_0/[L]_0/[R]_0$ [a]	Tempera-ture (ºC)	$[M]_0$	Time (min)	Conv. (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
1	Ascor-bic acid	100/1/1/1/0.5	25	1M	210	50%	1170	3160	1.11
2	Ascorbic acid	100/1/1/1/0.5	70	1M	40	40%	uncontrolled		
3	Glucose	100/1/1/1/0.5	25	1M			No polymer		
4	Glucose	100/1/1/1/0.5	70	1M	10		gel		

[a] $[M]_0$ = initial monomer concentration; $[I]_0$ = initial initiator concentration;$[L]_0$ = initial ligand concentration; $[R]_0$ = initial reducing agent concentration.

AGET ATRP in water media

Ascorbic acid is a strong reducing agent, and it can quickly convert Cu(II) to Cu(I) species [18]. This observation is different from other workers' discovery [19], which is more likely to be due to the dissociation of Cu(II) species in water and loss of catalysts. So AGET ATRP of PAM with lower ascorbic acid dosage has been performed in the initiator and catalyst system 2-Cl-PA/$CuCl_2$/Me_6TREN at 25 ^{0}C in aqueous media, but the polymerization is uncontrolled (Table 2, entry 1).

Tab. 2. AGET ATRP of AM carried on at 25 ºC in aqueous solution; initiating system: 2-Cl-PA/$CuCl_2$/Me_6TREN with ascorbic acid.

entry	$[M]_0/[I]_0/[CuCl_2]_0/[L]_0/[R]_0$ [a]	$[M]_0$	Time (min)	Conv. (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
1	100/1/0.01/0.1/0.005	1M	350	75%	18700	5330	3.95
2	100/1/0.8/1/0.4	1M	300	80%	2380	5690	1.27
3	100/0.5/1/1/0.5	1M	260	60%	2800	8530	1.24
4	100/0.5/0.8/1/0.4	1M	120	75%	5990	10660	1.54
5	100/0.5/2/2/1	1M	300	41%	2200	5830	1.25
6	100/0.5/1/1/0.5	2M	140	73%	3690	10380	1.26
7	100/0.25/1/1/0.5	1M	220	33%	3700	9380	1.31

[a] $[M]_0$ = initial monomer concentration; $[I]_0$ = initial initiator concentration;$[L]_0$ = initial ligand concentration; $[R]_0$ = initial reducing agent concentration..

As is shown in Table 2, good control of polymerization of acrylamide with various degrees of polymerization is achieved when the concentration of $CuCl_2$ increases to an appropriate level. Moreover, the polymerization reaches a limited conversion in definite times, and increasing the value of target degrees of polymerization will lead to a partial loss of control of ATRP and a severe limitation in the conversion. This can be attributed to the decrease in the radical concentrations as a result of termination reactions (Table 1, entry 1 and Table 2, entry 3, 7).

On the other hand, the concentration of Cu (II) in the catalyst system is a factor of great urgency. The polymerization will loss control when the deactivator is decreased a little, and the conversion of polymerization will be sacrificed with some additions of Cu(II) (Table 1, entry 1 and Table 2, entry 2; Table 2, entry 3, 4,5). Furthermore, the conversion increases with the increase of monomer concentration. This probably is due to decrease in the concentration of the deactivating species during the course of polymerization as a result of Cu (II) complexing with polyacrylamide [20]. Thus, the concentration increasing of polyAM leads to a competitive complexation of Cu (II) with respect to Me_6TREN, reducing the concentration of the deactivating species and leading to an increase in the radical concentration (Table 2, entry 3, 6).

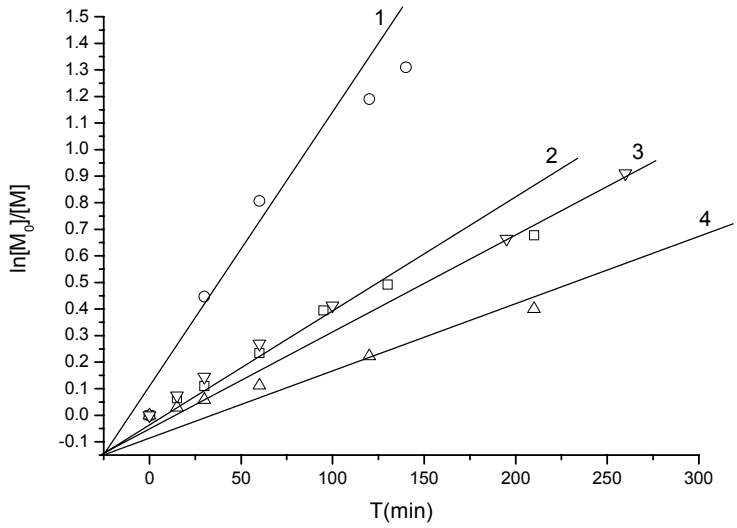

Fig. 1. ln[M_0]/[M] versus t for AGET ATRP of acrylamide with 2-Cl-PA/$CuCl_2$/Me_6TREN/Ascorbic acid initiator and catalyst system at 25 ºC in aqueous solution. (1)$[M]_0/[I]_0/[CuCl_2]_0/[L]_0/[R]_0$=100/0.5/1/1/0.5,$[M]_0$=2M(○);(2) $[M]_0/[I]_0/[CuCl_2]_0/[L]_0/[R]_0$=100/1/1/1/0.5, $[M]_0$=1M(□); (3)$[M]_0/[I]_0/[CuCl_2]_0/[L]_0/$ $[R]_0$=100/0.5/1/1/0.5, $[M]_0$=1M(∇); (4) $[M]_0/[I]_0/[CuCl_2]_0/[L]_0/[R]_0$=100/0.25/1/1/0.5, $[M]_0$=1M(Δ).

Figure 1 shows a typical linear variation of conversion with time in semilogarithmic coordinates, indicating that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. Moreover, the rate of polymerization decreases with increasing of degrees of polymerization (Figure 1, entry 2, 3, 4) and decreasing of monomer concentration (Figure 1, entry 1, 3).

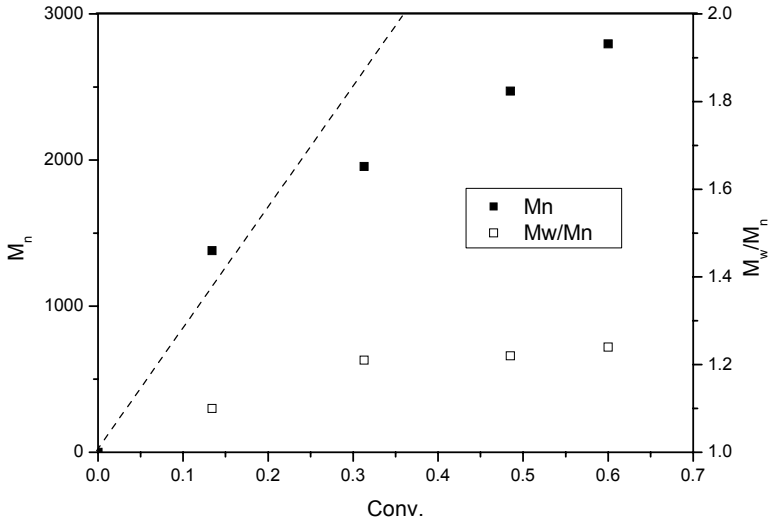

Fig. 2. Dependence of the molecular weights and the polydispersities on conversion. The dash line represents the theoretical molecular weight calculated on the basis of the [AM]/[2-Cl-PA] ratio. Conditions: AM/2-Cl-PA/$CuCl_2$/Me_6TREN/ Ascorbic acid = 100/0.5/1/1/0.5, $[M]_0$=1M, solvent = water, T = 25 ºC.

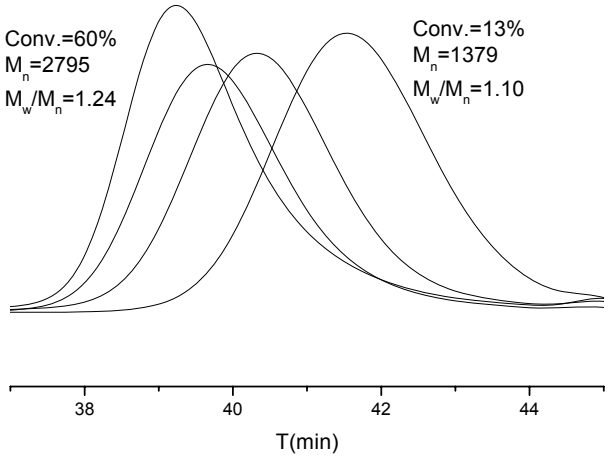

Fig. 3. GPC traces of PAM. Conditions: AM/2-Cl-PA/ $CuCl_2$/Me_6TREN/Ascorbic acid = 100/0.5/1/1/0.5, $[M]_0$=1M, solvent = water, T = 25 ºC.

As is shown in Figure 2, the PDI of target polymer maintains a lower values, and the molecular weight increases with the conversion, but the molecular weights from the GPC analyses deviates from the designed values due to differences of the hydrodynamic volumes between polymers and the PNaAA standards used for calibration. Furthermore, some tailing can be seen in the GPC spectra (Figure 3), suggesting small amounts of dead chains. Nevertheless, The GPC traces of the

polymers almost remain monomodal and symmetrical, indicating negligible amount of dead chains and insignificant termination [21].

Conclusions

This study showed that ascorbic acid was an appropriate reducing agent for the AGET ATRP of acrylamide in aqueous medium, which helped to obtain linear plots of $\ln[M]_0/[M]$ versus t when 2-Cl-PA/$CuCl_2$/Me_6TREN was used as the initiator/catalyst system. The molecular weight increased with increase of conversion, and the polydispersity (PDI) of the polymers was low.

Experimental part

Materials

Acrylamide (AM) was purified by recrystallization from acetone two times. 2-Chloropropionamide (2-Cl-PA, Aldrich, 98%), $CuCl_2$ (Aldrich, 99.999%), *L(+)*-ascorbic acid (Aldrich, 99%), glucose (Shanghai Chemicals Inc., 99%) were used as received without further purification. Tris(2-dimethyl/aminoethyl) amine (Me_6TREN) was prepared as described in the literature [22].

Characterization

Monomer conversion was measured by bromating method [23]. The number-average molecular weight (M_n) and molecular weight polydispersity (PDI) of polymers were measured using Gel Permeation Chromatography (GPC). The GPC system comprised of a Waters 515 HPLC pump, two columns (a guard column and Ultrahydrogel-2000 and Ultrahydrogel-1000 column from Waters) connected in series, and Waters 2414 refractive index detector. All the analyses were conducted at 30 ^oC. Poly (sodium acrylate) standards (M_p 900~1100000 g/mol) were used with a mobile phase of 0.1M $NaNO_3$ aqueous solution.

General Polymerization

Polymerization was conducted in a 50 mL Schlenk flask, which was secured by rubber septum. Before polymerization the reaction mixture was purged with oxygen-free argon for 30 min, the ascorbic acid was added to start the polymerization; samples were withdrawn using gastight syringes, and then the polymer was precipitated by anhydrous acetone. Finally, the polymer was dried in a vacuum oven at 50 ^0C for 24 h.

An example for polymerization is as follows, the mixture containing $CuCl_2$ (27.0 mg, 0.2 mmol), Me_6TREN (46.1 mg, 0.2 mmol), AM (1421.6 mg, 20 mmol), 2-Cl-PA (21.5 mg, 0.2 mmol) and water (20 mL) were added into the above-mentioned schlenk flask, and then was purged with argon and placed in a 25 ºC thermostated bath for 30 min. Finally, a gas-free ascorbic acid (17.6 mg, 0.1 mmol) solution was added to start the reaction. Simples were taken from the flask after appropriate interval via degassed syringe; then the conversion was measured. Opening the flask and exposing the catalyst to air stopped the polymerization. The reaction mixture was then passed through a column filled with silica gel to remove the copper complex. The polymer was recovered by precipitation in excess of cold acetone; filtered and dried to a constant weight; the sample was analyzed by GPC.

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