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Aqueous RAFT Polymerization of Acrylamide: A Convenient Method for Polyacrylamide with Narrow Molecular Weight Distribution

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Abstract Controlled and homogeneous free-radical polymerization of acrylamide (AM) in aqueous phase was realized by using *S*,*S*′-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate as a reversible addition-fragmentation transfer (RAFT) agent. Linear increases in molecular weight with conversion and narrow molecular weight distribution were observed for polyacrylamide (PAM) throughout the polymerization. By this method, PAMs with controlled molecular weight (up to 1.0×10^6) and narrow molecular weight distribution ($M_w/M_n < 1.2$) were prepared. This study provides an effective method for synthesis of PAMs with narrow molecular weight distribution under environmentally friendly conditions.

Keywords Homogeneous aqueous RAFT polymerization; Polyacrylamide; Controlled molecular weight; Narrow molecular weight distribution

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INTRODUCTION

Polyacrylamide (PAM) is one of the most widely-used water-soluble polymers. As an efficient flocculant and thickener, high-molecular-weight PAM has been used for oil displacement in oil industry and also in the fields of geology, textile and water purification[1].

PAM is conventionally synthesized by homogeneous aqueous free-radical polymerization with simple operation process and less environmental pollution. High monomer conversion and high molecular weight can be easily achieved. However, the heat of reaction is difficult to be removed and the kinetics of jelly-like polymerization cannot be well controlled, resulting in the PAM with wide molecular weight distribution. Part of low-molecular-weight PAMs in this product shows poor performance when used for flocculant and thickener, which limits the application of homogeneous aqueous solution polymerization.

In recent years, controlled radical polymerization (CRP) techniques[2], including atom transfer radical polymerization (ATRP)[3–5], nitroxide-mediated polymerization[6–8], and reversible addition-fragmentation transfer (RAFT) polymerization[9–11] have shown to be robust for synthesizing polymers with defined chemical structure and controlled molecular weight. RAFT polymerization has been used for controlled polymerization of a wide range of functional and non-functional monomers under different conditions in a variety of solvents (including water) to attain polymers with pre-determined molecular weights, narrow molecular weight distributions, and complex macromolecular architectures[12–17]. Polymerization of acrylamide (AM) by other CRP techniques usually requires toxic organic solvents and metal catalysts[18–20]. Thus, synthesis of PAMs with well-controlled molecular weights and narrow molecular weight distributions by RAFT is of considerable

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interest.

PAMs with precisely controlled molecular weights by CRP techniques have been rarely reported in contrast with other polymers like poly(methyl acrylate) and poly(methyl methacrylate), which have been polymerized to high molecular weight (typically > 10^5 g·mol^{-1}) by using high pressures, metal catalysts, or toxic organic solvents[21−29]. Millard *et al.*[30] have reported RAFT polymerization of AM in water at 20 °C by γ-initiation, in which the limited molecular weight of 10^5 g·mol^{-1} was attained. Recently, ATRP was used for polymerization of AM using the copper(I) chloride and tris(2-dimethylaminoethyl)amine (CuCl/Me_6-TREN) as metal/ligand pair at ambient temperature[31], and PAMs with molecular weight below 4 × 10^5 g·mol^{-1} were synthesized. PAM with molecular weight up to 1.0 × 10^6 g·mol^{-1} and narrow molecular weight distribution was achieved by Read *et al.*[32] using aqueous macromolecular design *via* an interchange of xanthates (MADIX)/RAFT polymerization. However, in this MADIX/RAFT polymerization, in order to perform polymerization of AM in a purely aqueous medium, low molecular weight hydrophilic macro-MADIX/RAFT agents were synthesized from the hydrophobic *O*-ethyl-*S*-(1-methoxycarbonyl)ethyl dithiocarbonate agent and used as mediating agents. This indispensable step made the method complicated.

In this paper, a dicarboxyl-terminated trithiocarbonate was synthesized and used as a water-soluble chain transfer agent (CTA) for the homogeneous aqueous solution free-radical polymerization of AM. By changing the polymerization conditions, such as initial monomer concentration ($[M]_0$), monomer/CTA feed ratio ($[M]_0/[CTA]_0$), CTA/initiator feed ratio ($[CTA]_0/[I]_0$), and the purging time with argon prior to polymerization, a controlled aqueous, homogeneous free-radical AM polymerization was realized. PAMs were synthesized in a short induction period at different $[M]_0/[CTA]_0$. The linear pseudo first order kinetics and the subsequent chain extension of the macro chain transfer agent (macro-CTA) validated the controlled and “living” characteristics of these polymerizations. By using these polymerization conditions, PAMs with controlled molecular weight (M_n = 1.0 × 10^6 g·mol^{-1}) and narrow molecular weight distribution ($M_w/M_n < 1.2$) were synthesized.

EXPERIMENTAL

Materials

AM was purchased from Acros Organics and dried in vacuo at 45 °C before use. Carbon disulfide, chloroform, acetone, petroleum ether, sodium hydroxide, hydrochloric acid (HCl), toluene, potassium bromate, potassium bromide, potassium iodide, sodium thiosulfate, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was provided by Qingdao Runxing Photoelectric Material Co., Ltd. Tetrabutylammonium hydrogen sulfate (TBAHS) was purchased from J&K Chemical. All these reagents were of analytical-grade and used as received unless otherwise specified. Deionized water was used in this work.

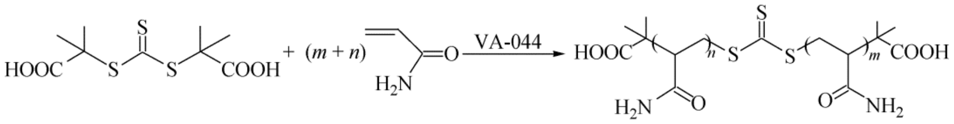
Synthesis of RAFT Agent

RAFT agent, *S*,*S*'-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate, was synthesized according to the literature[33]. The synthetic process is shown in Scheme 1. Carbon disulfide (13.7 g, 0.18 mol), chloroform (53.75 g, 0.45 mol), acetone (26.15 g, 0.45 mol), and TBAHS (phase transfer catalyst, 1.21 g, 3.55 mmol) were mixed with 60 mL of petroleum ether in a 1.0 L jacketed reactor. Sodium hydroxide (50%) (100.8 g, 1.26 mol) was added dropwise over 90 min. The synthetic process was done under nitrogen atmosphere. The reaction was stirred at 10 °C for 24 h. 450 mL of water was then added to dissolve the solid, followed by addition of 60 mL of concentrated HCl to acidify the aqueous layer. The resulting solution was stirred for 30 min with nitrogen purge to precipitate. The precipitated solid was filtered and rinsed thoroughly with water. The khaki product was further purified by dispersing in toluene/acetone (4/1, *V*/*V*) and stirring to get a yellow crystalline solid (11.9 g).

Scheme 1 Synthetic process of *S*,*S*'-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate

RAFT Polymerization of AM

The synthesis process of PAM by RAFT polymerization is shown in Scheme 2. RAFT polymerization of AM was conducted at 45 °C using VA-044 as the primary radical source and *S,S'*-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate synthesized above as the RAFT agent. All the polymerizations were performed in deionized water with different monomer feed concentrations in 500 mL flask, respectively. The flask was purged with argon and the aqueous solution of initiator was introduced to start the polymerization. Different $[\mathrm{M}]_0/[\mathrm{CTA}]_0$ and $[\mathrm{CTA}]_0/[\mathrm{I}]_0$ were used in the synthesis. The polymerization kinetics and molecular weights were determined from samples (5.0 mL) taken at pre-determined time intervals.



Scheme 2 Synthesis of PAM by RAFT polymerization

AM conversion was determined by the modified bromination method[34]

$$C=\left[1-\frac{(V_0-V)\times c\times M}{2000\times m\times w}\right]\times 100\% \tag{1}$$

where, C is the conversion of AM; V_0 and V are consumption volumes of sodium thiosulfate solution titrated into blank and experimental groups, respectively; c is the concentration of sodium thiosulfate solution; M is the molecular weight of AM (71.08 $\mathrm{g\cdot mol^{-1}}$); m is the weight of sample and w is the mass fraction of AM in the original reactants.

The theoretical molecular weight of PAM was calculated by

$$M_{\mathrm{n,th}}=\frac{M\times[\mathrm{M}]_0\times c}{[\mathrm{CTA}]_0+2\times[\mathrm{I}]_0\times\left[1-\exp\left(-k_{\mathrm{d}}t\right)\right]}+\mathrm{CTA}_{\mathrm{MW}} \tag{2}$$

where $M_{\mathrm{n,th}}$ is the theoretical molecular weight of PAM, k_{d} means the decomposition rate constant of initiator ($4.05\times10^{-5}\ \mathrm{s^{-1}}$), t is the reaction time, and $\mathrm{CTA_{MW}}$ is the molecular weight of RAFT agent (282 $\mathrm{g\cdot mol^{-1}}$).

Size Exclusion Chromatography

The polymerization mixtures were analyzed by aqueous size exclusion chromatography (SEC) using PL GPC 50 plus (Polymer Laboratory Co., UK) equipped with three columns, Waters Ultrahydrogel 2000, Waters Ultrahydrogel linear, and PL aquagel-OH 20. The eluent was 0.1 $\mathrm{mol\cdot L^{-1}}$ sodium nitrate aqueous solution, the flow rate was 0.8 $\mathrm{mL\cdot min^{-1}}$, and the column temperature was set at 30 °C. Differential refractive index detector was used and PEOs with narrow molecular weight distributions were used as the standard.

^{1}H-NMR Spectroscopy

Spectra were recorded on a BRUKER 500 MHz spectrometer using DMSO-d_6 as the solvent.

RESULTS AND DISCUSSION

Characterization of S,S'-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate

For RAFT polymerization of AM in homogeneous aqueous solution, a water-soluble RAFT agent is necessary. With two terminal carboxyl groups, *S,S'*-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate is easy for dissolution in water and further reaction. On the other hand, *S,S'*-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate is symmetrical, which is suitable to synthesize triblock copolymers. *S,S'*-bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate was synthesized and characterized by ^{1}H-NMR spectroscopy (shown in Fig. S1). The peak at $\delta = 1.59$ is assigned to the methyl protons from the segment—$\mathrm{C(CH_3)_2}$— and the peak at $\delta = 12.93$ is attributed to the carboxyl protons. The ratio of peak areas at $\delta = 12.93$ and 1.59 is about 1:6, indicating that the target product is obtained.

Aqueous RAFT Polymerization of AM

Polymerization conditions, AM conversion, and molecular weights of prepared PAM are shown in Table 1. It is obvious that the use of trithiocarbonate allows for the controlled polymerization of AM because of good agreement between the theoretical and experimental molecular weights and corresponding narrow molecular weight distributions shown under the conditions described from entries 1 to 6.

Table 1 Polymerization conditions, conversion, molecular weight, and molecular weight distribution data for the aqueous polymerization of AM

Entry	$[M]_0$ (mol·L^{-1})	$[M]_0/[CTA]_0$	$[CTA]_0/[I]_0$	Purging time (min)	Time (min)	Conversion (%)	$M_{n,exp}$ (g·mol^{-1})	$M_{n,th}$ (g·mol^{-1})	M_w/M_n
1	0.7	300	10	30	450	78	13800	14100	1.21
2	2.0	300	10	30	427	87	15400	15700	1.20
3	2.0	300	5	30	310	97	14400	15000	1.20
4	2.0	300	5	60	250	96	15500	14900	1.17
5	2.0	500	5	60	185	98	24300	25100	1.19
6	2.0	800	5	60	175	97	37300	39500	1.22

Figure 1 shows the SEC traces of PAM at different polymerization times and AM conversions for the polymerization under the conditions given in entry 3. The SEC peak shifts toward shorter retention time, indicating the gradual increase of molecular weight with polymerization time. This is characteristic for a controlled and “living” polymerization. At high monomer conversions (96.8%), no high molecular weight peak or shoulder is observed in the SEC traces, which is different from the homogeneous aqueous solution free-radical polymerization of AM[35].

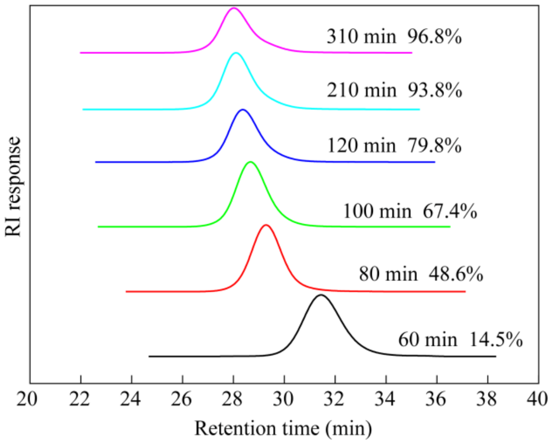


Fig. 1 SEC traces of PAM at different polymerization time and AM conversions: $[M]_0/[CTA]_0 = 300$, $[CTA]_0/[I]_0 = 5$

The kinetic plots for the RAFT polymerization of AM are shown in Fig. 2. The linear pseudo first order kinetics is observed for the polymerizations of entries 4, 5, 6. None of the three polymerizations have significant inhibition periods. Figure 3 shows the plots of M_n and M_w/M_n against conversion for the polymerization of entries 4, 5, 6. As shown from this figure, the molecular weight of PAM increases linearly with conversion and the measured molecular weight agrees well with the theoretically predicted values. The M_w/M_n values of PAM remain small (< 1.25) at all conversions.

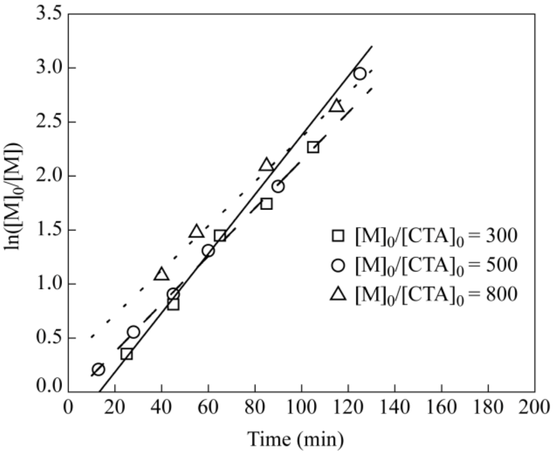


Fig. 2 Kinetics plots for AM polymerization at different $[M]_0/[CTA]_0$ ratio

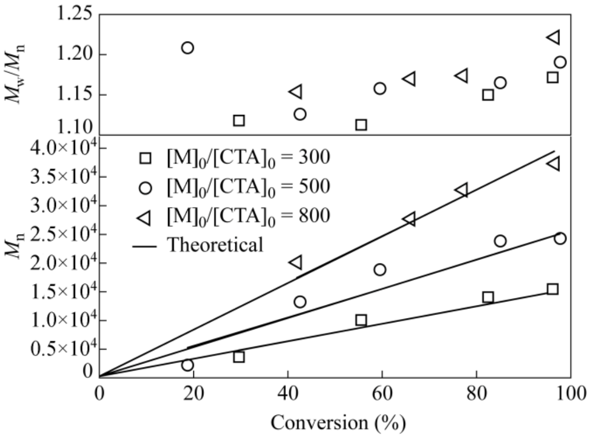


Fig. 3 Plots of M_w/M_n and M_n versus AM conversion in polymerization with different $[M]_0/[CTA]_0$ ratio

Figure 4 shows the conversion versus time plots for the polymerizations of entries 1–6. It is obvious that the polymerization rate of AM tends to increase with increasing $[M]_0$. Similarly, when $[CTA]_0/[I]_0$ is individually altered under the conditions described in entries 2 and 3, the slope of conversion curve and the polymerization rate of AM increases with decreasing $[CTA]_0/[I]_0$, as verified by Ni *et al.*[36] that the polymerization rate of AM is strongly correlated with the concentration of initiator. In addition, with changing the polymerization conditions, the polymerizations of entries 4, 5, 6 show faster reaction rates, higher monomer conversions, and shorter inhibition periods. Thus, the optimum conditions for the RAFT polymerization of AM are that $[M]_0 = 2.0$ mol·L^{-1}, $[CTA]_0/[I]_0 = 5$ and sufficient time for the contents to be purged with argon prior to reaction. By changing $[M]_0/[CTA]_0$, PAMs with controlled molecular weight and narrow molecular weight distribution could be synthesized in the homogeneous aqueous solution free-radical polymerization.

Chain Extension of Living PAM in Aqueous Polymerization

To further demonstrate the trithiocarbonate end-functionality and the controlled nature of these polymerizations, the PAM synthesized under the conditions described in entry 3 is used as a macro-CTA in the further chain extension polymerization of AM ($[M]_0 = 1.0$ mol·L^{-1}). The monomer conversion of chain extension AM is about 97%. As shown in SEC chromatograms (Fig. 5), the SEC peak of PAM shifts toward the shorter retention time side after chain extension. The molecular weight of the chain-extended PAM increases to 47100 g·mol^{-1} ($M_w/M_n = 1.71$) from that of PAM macro-CTA ($M_{n,exp} = 14100$ g·mol^{-1}, $M_w/M_n = 1.22$); the M_n of chain-extended PAM is similar to the theoretically predicted value ($M_{n,th} = 53600$ g·mol^{-1}). The chain-extended PAM does not show the detectable shoulder on the SEC curves, suggesting that most of the macro-CTA has the trithiocarbonate end-functionality and is effective for the subsequent chain extension polymerization.

PAM with Narrow Molecular Weight Distribution

Using the optimum polymerization conditions established above, a series of PAMs with controlled molecular weights and narrow molecular weight distribution are prepared by changing the parameter $[M]_0/[CTA]_0$. Figure 6 shows the SEC chromatograms of synthesized PAMs ($[M]_0/[CTA]_0$ = 6000, 9000, 15000, 25000, respectively). In all the experiments, the conversion of AM is larger than 90% after polymerization for 10 h. The chromatograms are nearly monomodal and symmetrical regardless of the targeted molecule weights. The molecular weight distributions of all the synthesized PAMs are relatively narrow ($M_w/M_n < 1.30$).

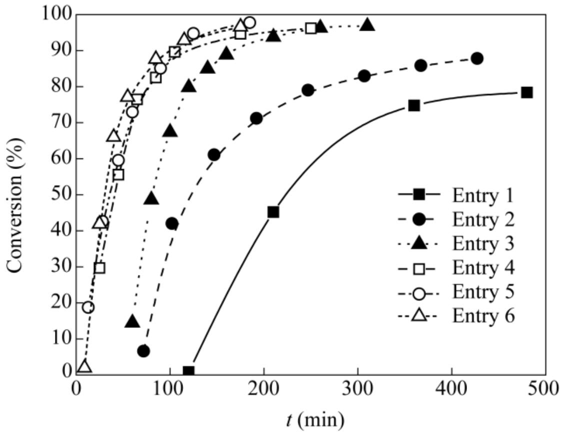


Fig. 4 AM conversion versus time under the polymerization conditions described in Table 1

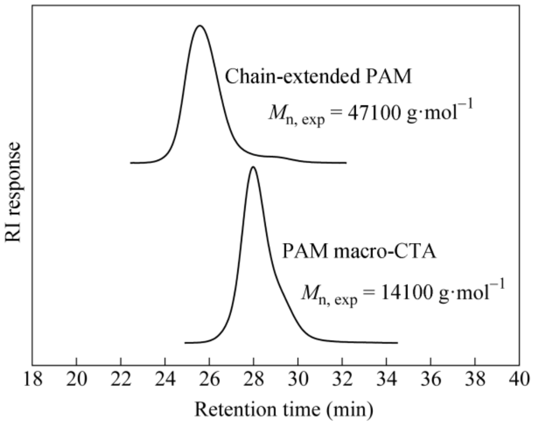


Fig. 5 SEC traces of PAM macro-CTA and chain-extended PAM

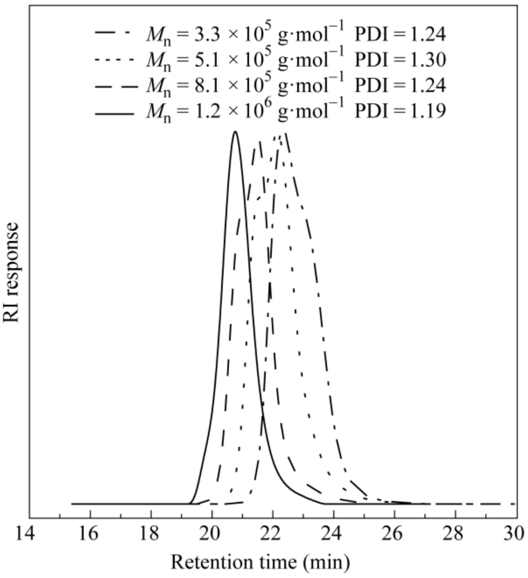


Fig. 6 SEC chromatograms of synthesized PAMs

CONCLUSIONS

The optimum conditions were established for homogeneous aqueous solution RAFT polymerization of AM using dicarboxyl-terminated trithiocarbonate as water-soluble CTA. In these RAFT polymerizations, AM was polymerized to high conversion and the synthesized PAMs showed controllable molecular weight and narrow molecular weight distribution, demonstrating the controlled/“living” characteristics of these polymerizations. PAMs (molecular weight up to 1.0×10^6 g·mol^{-1}) with controlled molecular weights and narrow molecular weight distribution ($M_w/M_n < 1.30$) were synthesized *via* RAFT polymerization.

Considering the economic and environmental-friendly benefits for the aqueous polymerizations and the wide application of PAMs, the results reported in this paper would be highly helpful for the preparation of controlled molecular weight PAMs in an environmentally-friendly method.

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