Efficient Synthesis of Poly(acrylic acid) in Aqueous Solution via a RAFT Process

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The direct polymerization of acrylic acid (AA) in aqueous solution for high molecular weight by means of living radical polymerization is still difficult. Here, AA was polymerized homogeneously in water by a reversible addition-fragmentation transfer polymerization (RAFT) in the presence of a water-soluble trithiocarbonate as a RAFT agent. Various ratios [AA]:[RAFT agent] were investigated to aim at different molecular weights. The polymerization exhibited living free-radical polymerization characteristics at different ratios [AA]: [RAFT agent]: controlled molecular weight, low polydispersity and well-suited linear growth of the number-average molecular weight, M_n with conversion. The chain transfer to solvent or polymer was suppressed during the polymerization process, thus high linear PAA with high molecular weight and low PDI can be obtained. Moreover, using the generated PAA as a macro RAFT agent, the chain extension polymerization of PAA with fresh AA displayed controlled behavior, demonstrated the ability of PAA to reinitiate sequential polymerization.

Keywords: RAFT polymerization, acrylic acid, trithiocarbonate, aqueous phase

1 Introduction

Poly(acrylic acid), a well-known pH responsive polymer (1), has usually worked as a hydrophilic segment for amphiphilic or amphipathic block copolymers with different novel properties (2–6), and its quality of the dispersion is influenced strongly by the molecular weight and the polydispersity (7, 8). However, the polymerization of acrylic acid is not easy to perform directly in a controlled fashion. In the past decades, most of these homopolymer or block copolymers of AA with well-defined structures were synthesized by sequentially anionic polymerization or controlled radical polymerization of acrylate, followed by a hydrolysis and purification (2–6, 9).

With the advent of controlled radical polymerization (CRP), a wide variety of well-defined homopolymers and copolymers have been synthesized successfully (10–12). Several methods are available including nitroxide medicated polymerization (NMP), (13, 14) atom transfer radical polymerization (ATRP) (15, 16) and reversible addition-fragmentation transfer polymerization (RAFT) (17–19).

AA is one of the monomers which can only be polymerized via radical polymerization due to its functional groups. Therefore, recently the direct synthesis of acrylic acid via controlled radical polymerization is an attractive topic.

ATRP of PAA was considered to be problematic since the acrylic acid can react with the metal complexes (20). Using NMP, Couvreur et al. first synthesized the PAA homopolymers by direct polymerization of AA in dioxane at 120°C (21). RAFT was the most successful method used in the controlled polymerization of AA. The first direct polymerization of AA was reported by Chiefari. et al. in DMF at low conversion (17, 18). Various RAFT agents were tested in controlled radical polymerization of AA in protic media and phenoxyxanthates and dibenzyl trithiocarbonates were concluded to be the most suitable RAFT agent (22). Subsequently, more detailed and thorough research was reported and the polymerization could be controlled at low conversion (23).

Nevertheless, the radical polymerization of acrylic monomers suffers from the side reactions, mainly including chain transfer to solvent which limits the achievement of high molecular weight, and the chain transfer to polymer which leads to the branched structures. Avoiding the chain transfer is not easy for both RAFT and NMP, thus the preparation of PAA with high molecular weight and low PDI via CRP is still a challenge. Recently, Peng et al. (24) applied cobalt porphyrin derivatives in mediating the

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controlled radical polymerization of AA to produce PAA with high molecular weight and low polydispersity in a very short reaction time. However, the cost of organic metal catalyst is high, and the method may also lead to residual metal remaining in the final product.

Considering both environmental and economic reasons, we have focused our research efforts on polymerization in aqueous media (25–27). Besides the environmental advantage, the polymerization rate of AA is much larger in water than in other solvents (28), and Loiseau et al. also suggested that the polymerization in water utilizing a water-soluble RAFT agent may reduce the chain transfer to solvent, but not experimental data was reported to support the suggestion (23). Recently, the RAFT agent-mediated polymerizations of acrylic acid in aqueous phase and bulk were performed separately under γ-irradiation (29,30). Also, UV radiation has been used in the RAFT polymerization of acrylic acid in aqueous phase at ambient temperature (31). However, either γ-irradiation or UV-irradiation needs additional equipment, e.g., the former needs a ^{60}Co source and the latter needs UV lamps. Here, a facile and simple method in direct synthesis of PAA with high molecular weight and low PDI via RAFT polymerization in aqueous solution is presented.

In a typical RAFT process, the living characteristic of polymerization will be strongly influenced by the structures of the RAFT agents (32,33). The studies on the polymerization of AA and other polar monomers via RAFT reveal that trithiocarbonate is the best choice as RAFT agent, whose intermediate radical is less stable than that of dithioester (34,35). In this work, an asymmetric trithiocarbonate RAFT agent was synthesized which can be readily dissolved in water when the carboxylic group was neutralized at the neutral pH. The direct polymerization of AA in the presence of this trithiocarbonate RAFT agent was carried out.

2 Experimental

2.1 Materials

All compounds, except as noted, were brought from Shanghai Chemical Reagents Company. Acrylic acid was distilled under reduced pressure before use. 4,4′-Azobis(4-cyanopentanoic acid) (radical initiator, V-501, Acros Organics Company) was used as received. Ultra-pure water (18 MΩ) was produced by a Millipore System (Millipore Q, USA). D$_2$O and CDCl$_3$ as the solvents for NMR measurement were used as received.

2.2 Sample Preparation

2.2.1. *Synthesis of RAFT agent*
The synthesis and characterization of the RAFT agent 2-{[(ethylsulfanyl)carbonothioyl] sulfanyl}butyric acid has
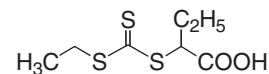
Sch. 1. Structure of the RAFT agent.

been described in our previous work.(27) The structure of the RAFT agent is shown in Scheme 1.

^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) 1.0 (-CH-CH$_2$-CH$_3$), 1.3 (-CH$_2$-CH$_3$), 2.1 (-CH-C*H*$_2$-CH$_3$), 3.3 (-C*H*$_2$-CH$_3$), 4.8 (-CH-CH$_2$-CH$_3$), 9.3 (-COOH).

2.2.2. *Aqueous solution polymerization of acrylic acid*
All the polymerizations were carried out at a 2.0 M monomer concentration and the [AA]/[RAFT] ratios were varied by changing the RAFT agent concentration. In a typical procedure, RAFT agent was first dissolved fully in aqueous phase containing an equivalent molar amount of NaOH. Then, AA and V-501 were added into the mixture and the polymerization solution was added into a septa capped round-bottom flask. The polymerization recipe is shown in Table 1. The flask was deoxygenated by bubbling nitrogen through the solution for 30 min. Then it was immersed into water bath at 65°C and the polymerization was allowed to proceed for a predetermined time under magnetic stir. Samples with the same volume were taken at regular time intervals under a nitrogen flow and immediately quenched by cooling in an ice-water bath. Polymers were recovered by freeze drying for 2 days. The same procedure was applied to the chain extension of AA except the purified PAA macro RAFT agent was used instead of the RAFT agent.

2.3 Characterization of the Polymers

The monomer conversions were obtained using gravimetry. Molecular weight and molecular weight distribution (M_w/M_n) were determined on Waters Gel-Permeating chromatography (GPC) (Waters Co., USA). Series of Ultrahydrogel 250, 500, and 2000 columns thermostated at 40°C was used, with aqueous buffer (0.05 M NaHCO$_3$, 0.1 M NaNO$_3$, 0.02 M triethanolamine, and 0.03% of NaN$_3$) as eluent at a flow rate of 1.0 mL/min. The detection was carried out at 35°C with a diode array UV detector at 254 nm and simultaneously with a refractive index detector. The samples were filtered with a 0.45 μm hydrophilic filtration membrane prior to injection (100 μL). Calibration was relative to low polydispersity poly(ethylene oxide) standards. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker spectrometer (Avance 300, 300MHz) with D$_2$O as solvent. For ^{13}C-NMR spectrum, additional acetone was added as calibration ($\delta_0 = 30.8$ ppm).

Table 1. Influence of the Monomer/RAFT agent ratio in the RAFT polymerization of AA in water using V-501 as initiator at 65°C, [AA]=2 mol/L, [RAFT agent]/[initiator]=10

Experiment	$[AA]_0/[RAFT\ agent]_0$	reaction time (h)	$Conv^a$ (%)	$M_n(exp)^b$ (g/mol)	$M_n(theo)^c$ (g/mol)	PDI
1	100	6 h	97%	11000	7100	1.18
2	411	6 h	84%	34000	25000	1.15
3	804	6 h	79 %	76600	46000	1.13
4	2000	6 h	58 %	151967	84000	1.13
5[d]	2000	3 h	97 %	230572	144000	1.14

[a]Monomer conversions were determined by gravimetry.
[b]Molecular weight and molecular weight distribution were determined by GPC using aqueous buffer solution as eluent with PEO standards.
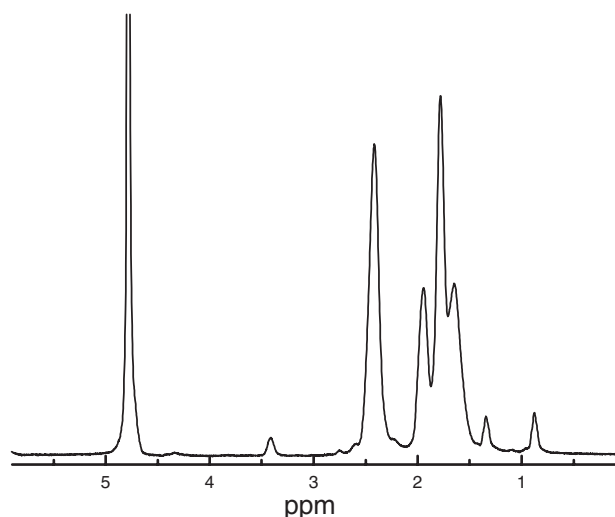[c]Theoretical molecular weight was calculated from the monomer conversion.
[d][RAFT agent]/[initiator]= 4.

3 Results and Discussion

Figure 1 shows the ^{1}H-MR spectrum of PAA (D$_2$O solvent). The signal at 1.6 ppm-1.9 ppm arises from the two methylene protons of the PAA main chain, and the methyne proton appears at 2.4 ppm. The signals at 1.3 ppm and 0.9 ppm are attributed to the two methyl protons originated from the RAFT agent and this provides good evidence that the polymer chains have ends that are derived from the original RAFT agent.

The free radical polymerization of acrylic acid in the presence of trithiocarbonate RAFT agent in aqueous solution was carried out at different [AA]/[RAFT] ratios. All results are listed in Table 1 and Figure 2. It clearly shows an increase of the [AA]/[RAFT] ratio leads (at a comparable conversion) to an increase of the molecular weight. The GPC curves exhibit unimodal and narrow peaks in all conducted polymerization, and the PDI remains low even at high conversion and high [AA]/[RAFT agent], indicating that the RAFT polymerization of AA is well-controlled under the reaction conditions mentioned earlier.

The samples were withdrawn at regular times to monitor the molecular weight and conversion. Figure 3 shows the variations of $\ln([M]_0/[M]_t)$ vs. time, for the polymerizations where [AA]:[RAFT] are 411, 804 and 2000 (experiment 2, 3, 4 in Table 1), respectively. All of the polymerizations exhibit the slight inhibition period at the beginning, which is often observed in the RAFT process. This induction period in the initial phase of polymerization is assigned to the inherent stability of the RAFT intermediate radicals and the pre-equilibrium, which involves the initial RAFT agent and the initialization of the living process (shown in Scheme 2, which is a typical mechanism of the RAFT process (17)). After the inhibition period of about 1 h, a linear relationship is depicted in Figure 2, which demonstrates that the polymerization in the presence of RAFT agent is linear first-order kinetics and the concentration of growing chain radical remains constant throughout the polymerization. A distinct effect of [AA]/[RAFT] ratio on the reaction rate can be observed. From a fast to slow rate, ratios can be rated in the following order: 411:1 > 804:1 > 2000:1, indicating the polymerization rate decreases with increasing [AA]:[RAFT]. It also can be seen in Table 1, at the same reaction time (6 h), the monomer conversions

Fig. 1. ^{1}H-NMR spectrum of PAA.
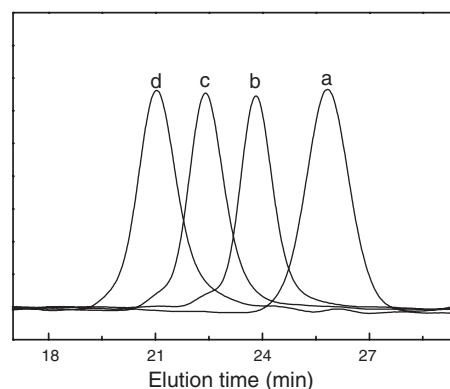
Fig. 2. GPC curves of PAA at different ratios [AA]/[RAFT agent], [AA] = 2 M, reaction time = 6 h, T = 65°C, in water, a) 100:1; b) 411:1; c) 804:1; d) 2000:1.
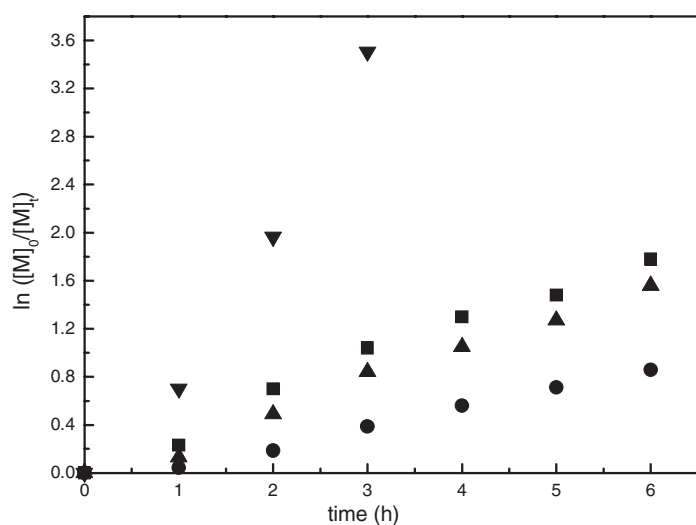
Fig. 3. Pseudo-first-order kinetic plot for the RAFT polymerization of AA in water: experiment 2 (■):[AA]:[RAFT agent]:[Init] = 411:1:0.1; experiment 3 (▲):[AA]:[RAFT agent]:[Init] = 804:1:0.1; experiment 4 (●):[AA]:[RAFT agent]:[Init] = 2000:1:0.1; experiment 5 (▼):[AA]:[RAFT agent]:[Init] = 2000:1:0.4.

decrease with the [AA]/[RAFT] ratio. These can be attributed to the decrease of the concentration of initiator as the increase of [AA]:[RAFT], which leads to the decrease of the initial free radical concentration. To further testify this suggestion, the concentration of the initiator in experiment 4 was increased by a factor of 2.5 (experiment 5 in Table 1). It can be seen that the conversion arrives at 97% at 3 h and the propagation rate increases sharply, which confirms our suggestion. In addition, due to the increased conversion in experiment 5, the experimental molecular weight arrives at 2.3×10^5 g/mol and the PDI still keeps low.

The M_n and the PDI evolutions with the conversion at different [AA]/[RAFT] ratios are shown in Figure 4. All of them obviously exhibit linear evolution of the molecular weight with conversion, along with low PDIs less than 1.3 except at the early stage of the experiment 4. The PDI first decreases with conversion and then remains at low values (PDI = 1.1). These results indicate that the controlled fashion of the polymerization.

It has been reported that for high [AA]/[RAFT] (larger than 100, high target M_n), the downward deviation of M_n with increasing conversion along with broad PDI occurs during the RAFT polymerization process of AA in protic
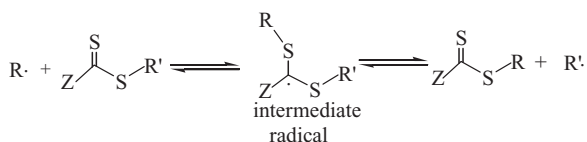
Sch. 2. Addition-fragmentation equilibrium in RAFR process.
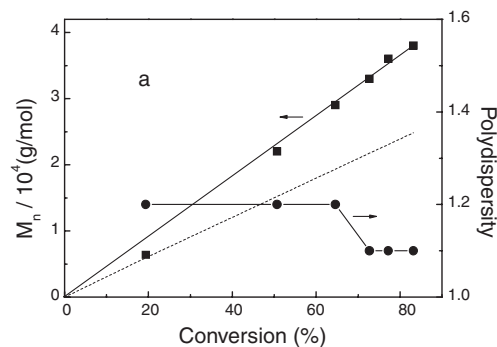

Fig. 4. M_n and PDI vs. conversion: a) [AA]:[RAFT agent]:[Init] = 400:1:0.1; b) [AA]:[RAFT agent]:[Init] = 804:1:0.1; c) [AA]:[RAFT agent]:[Init] = 2000:1:0.1. The dash straight line corresponds to the theoretical molecular weight.

media, which is attributed to the chain transfer to solution (22,23,36). The same conclusion is also drawn in the controlled radical polymerization of AA via NMP technique when the alkoxyamine concentration is low (21). Thus, only low molecular weight PAA can be obtained. Using the experimental values of M_n and conversion x, the chain transfer constant to solvent can be calculated from Equation 1. In this equation, the concentration of polymer chains is calculated by [polymer chains] = $x[AA]_0/DP_n$, in which the DP_n is the number average degree of polymerization, can be estimated from GPC analysis. A nonlinear optimization of the evolution of -ln(1-[polymer chains]/[solvent]$_0$) to $-\ln(1-x)$ gives the C_{tr} value.

$$C_{tr} = \frac{\ln(1 - [\text{polymer chains}]/[\text{solvent}]_0)}{\ln(1 - x)} \qquad (1)$$

The profile of -ln(1-[polymer chains]/[solvent]$_0$) vs. $-\ln(1-x)$ in these experiments is shown in Figure 5, which was calculated from the experimental values in Figure 4. However, the evolution <u>cannot</u> be optimized as y = xC_{tr} since the C_{tr} value decreases as the increase of conversion. Thus the influence of chain transfer to water on the molecular weight of PAA at high conversion in the experiment is insignificant. This can be assigned to the use of aqueous solution, which would reduce or quench the chain transfer to solvent. It also can be seen in Figure 4, the polymerization occurs in a controlled fashion at high conversion when [AA]/[RAFT] is high and the PDI is low even at high molecular weight (8.0×10^4 g/mol at [AA]/[RAFT] = 804 and 1.8×10^5 g/mol at [AA]/[RAFT] = 2000). This indicates that high molar mass polymers with narrow molecular distribution can be simply prepared according to the proposed recipe.

To illustrate, we present the GPC curves of PAA ([AA]/[RAFT] = 804) at different reaction times and conversions. As can be seen from Figure 6, the GPC curves are unimodal and symmetric and no bimodalities are observed
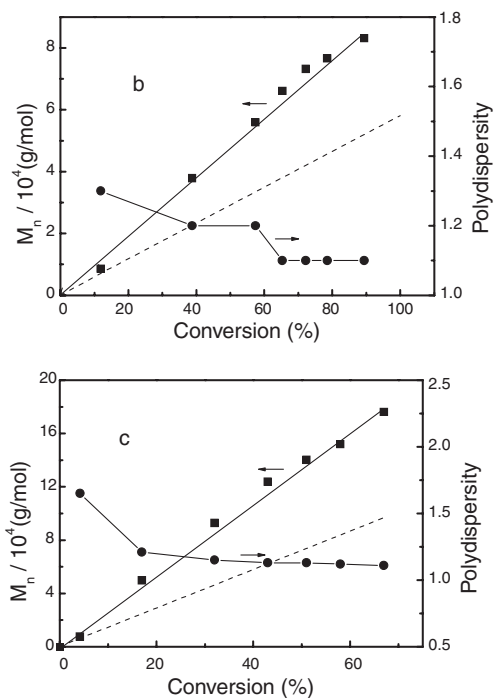
Fig. 5. $-\ln(1-[\text{polymer chains}]/[\text{solvent}]_0)$ vs $-\ln(1-x)$ for experiment 2 (■); experiment 3 (▲) and experiment 4 (●).

at all conversions, which again demonstrates the living characteristic of the whole process.

With the acrylate monomers and acrylic acid, chain transfer to polymer during radical polymerization, which leads to the formation of highly branched structures, has also been investigated intensively (37–41). ^{13}C-NMR spectroscopy is an efficient technique to inspect the branch

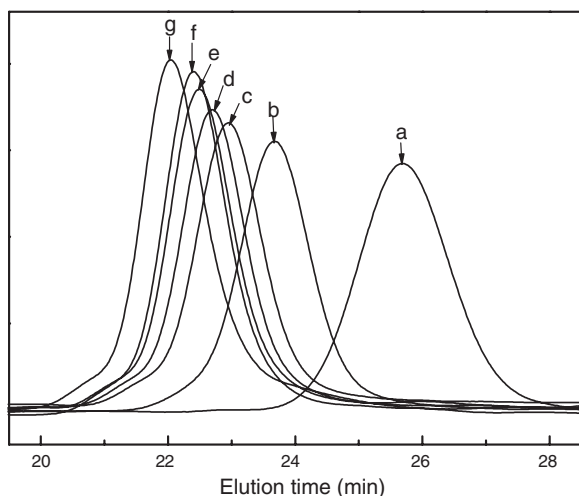**Fig. 6.** A typical GPC curves of PAA with times and conversions: [AA] = 2.0 M, [AA]:[RAFT agent]:[Init] = 804:1:0.1, T= 65°C, in water, a) 1 h, 12%; b) 2 h, 39%; c) 3 h, 57%; d)4 h, 65%; e) 5 h, 72%; f) 6 h, 79%; g) 8.5 h, 90%.
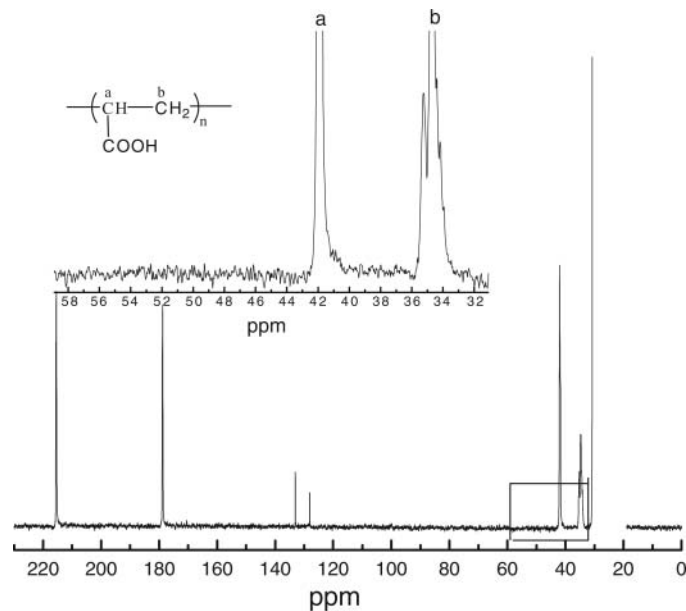

Fig. 7. ^{13}C-NMR spectrum for the final PAA product from experiment 3, at 90% conversion. The inset is the expanded spectrum between 32 and 59 ppm.

structures of PAA and polyacrylate and the peak assignment has been presented in detail by these groups (21,23,37–41). Figure 7 shows the ^{13}C-NMR spectrum for the final PAA from experiment 3 ([AA]/[RAFT]=804 at 90% conversion). The inset is the expanded spectrum between 32 and 58 ppm. It is amazing that resonance peaks in the range of 36–40 ppm and 47–50 ppm that are characteristic of acrylate branching are not detected. (^{13}C-NMR: Acetone: $\delta = 30.8$ ppm (-CH$_3$), $\delta = 215.1$ ppm (C=O); Residual monomer: $\delta = 127.7.5$ ppm (-CH= CH$_2$), $\delta = 135.5$ ppm (-CH=CH$_2$); Poly(acrylic acid): $\delta = 34.6$ ppm (-CH-CH$_2$-), $\delta = 41.4$ ppm (-CH-CH2-), $\delta = 178.4$ ppm (-COOH)).The other samples with different molecular weights obtained at different conversions were also examined by ^{13}C-NMR spectroscopy and the same results were exhibited. It is the evidence that the generated PAA is highly linear and the chain transfer to polymer is limited in the experiment. The transfer reaction to polymer may proceeds via intramolecular hydrogen abstraction process or intermolecular pathway. Recently Thomas et al. (34) demonstrated that an added chain transfer agent is able to suppress the side reactions of mainchain radicals, which are formed via chain transfer to polymer. However, its consequences on branching levels in acrylate polymerization have not yet been researched, but it can be speculated that the extent of branching is also related to the structure of the added chain transfer agent.

The NMR results reveal that the as-prepared PAA by a RAFT process has the trithiocarbonate group at the end of the chain, which makes the obtained PAA can work as a macro-RAFT agent.
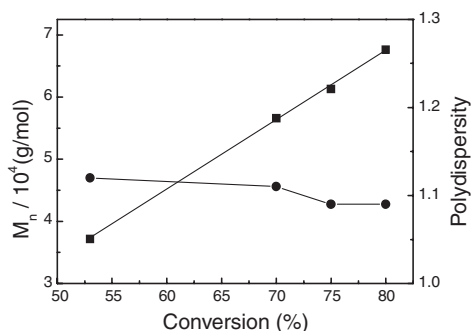
Fig. 8. M_n and PDI vs. conversion for extended PAA.

4 Conclusions

Poly(acrylic acid) was synthesized directly in aqueous phase in the presence of trithiocarbonate RAFT agent. Linear increase of molecular weight with conversion and low PDIs were obtained at different [AA]:[RAFT] ratios, indicating well-controlled RAFT polymerization of AA was achieved. Chain transfer to solvent water and polymer were limited to a large extend and low polydispersity and linear PAA with different chain lengths from short to long can be prepared easily. The living character of the PAA macro-RAFT agent was confirmed in the subsequent chain extension experiment. The use of these polymers as macro-RAFT agents initiate the polymerization of AA monomer leading to well-defined PAA.

To further demonstrate the existence of the trithiocarbonate functionality and the livingness, the chain extension of PAA ($M_n = 11000$, PDI $= 1.18$) as macro-RAFT agent with AA was carried out in aqueous phase. In this way, acrylic acid was polymerized in the same conditions and the [AA]/[macro RAFT] ratio was 600: 1. The overall conversion as estimated by gravimetry reached 80% within 6 h. Figure 8 shows the M_n of extended PAAs with low PDIs increases linearly with conversion, indicating the polymerization of the added AA was also well controlled. The GPC curves of extended PAAs are shown in Figure 9, which displays a continuous shift to higher molecular weight as the increase of fresh AA conversion. However, GPC curves appear to have the slight tailing at low molecular weight position to all extended PAAs. These can be attributed to the residual PAA macro RAFT agent and the tailing trends to disappear as the curve shift toward high molecular weight position. Therefore, PAA prepared via RAFT polymerization is able to be used as macroinitiator to initiate another polymerization in a controlled fashion, producing well-defined block copolymers.
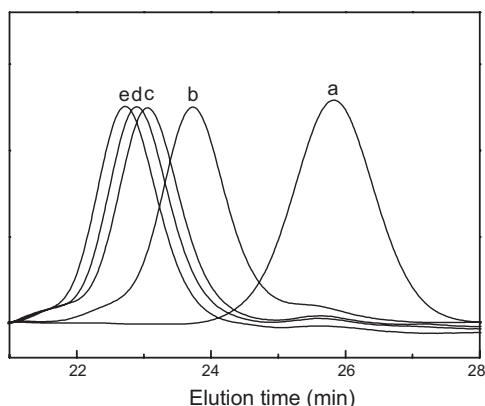
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Fig. 9. GPC curves of chain extension polymerization: a). PAA macro RAFT agent (experiment 1 in Table1); b, c, d and e for four extended PAAs, respectively.

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