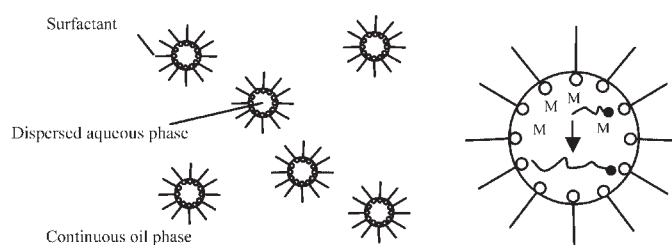


RAFT Inverse Miniemulsion Polymerization of Acrylamide

Genggeng Qi, Christopher W Jones,* F. Joseph Schork*

RAFT inverse miniemulsion polymerization is demonstrated for the first time as an alternate way to synthesize hydrophilic polymer latexes. The kinetic behavior of inverse RAFT miniemulsion polymerization of acrylamide is similar to that observed in aqueous RAFT solution polymerization. A water-soluble initiator provides better control than a lipophilic initiator in inverse RAFT miniemulsion polymerization under the conditions used here.



Introduction

A conventional miniemulsion is an aqueous dispersion of relatively stable oil droplets within a size range of 50–500 nm prepared by strong shearing of a system containing oil, water, surfactants, and costabilizers.^[1] Miniemulsion polymerizations are superior to emulsion polymerizations in their ability to produce latexes which are more colloidal stable, have better composition control, and are robust to contamination and operating errors in the polymerization. An inverse miniemulsion is a miniemulsion in which the continuous phase and dispersed phase of a conventional miniemulsion are inverted, i.e., an aqueous emulsion dispersed in a continuous oil phase.^[2] In the case of appropriately formulated inverse miniemulsions, the polymerization takes place in the aqueous droplets and

ideally, no mass transfer takes place between the droplets that act as individual batch reactors. Inverse miniemulsion polymerizations exhibit typical properties of conventional miniemulsions, for example, droplet nucleation, uniform particle size distributions, and excellent colloidal stability.^[2,3] Inverse miniemulsion polymerization has not been thoroughly investigated, although the commercial process for making high-molecular-weight water-soluble polymers, termed inverse emulsion polymerization, shares some of the features of inverse miniemulsion polymerization (e.g., droplet nucleation, application of high shear).^[3–9]

Controlled radical polymerizations, such as reversible addition fragmentation transfer (RAFT) polymerization, have been demonstrated to be potentially useful, and are important new approaches to the production of polymers with well-defined or special architectures in a controlled manner.^[10–14] Here we combine RAFT chemistry with inverse miniemulsion polymerization for the first time. By applying RAFT polymerization to inverse miniemulsion, we can in principle combine the advantages of both of these techniques and offer a convenient way to synthesize unique or well-defined structured polymer colloids such as hydrophilic nanogels or amphiphilic block copolymers.

Hydrophilic polymers, in particular poly(acrylamide)s, are widely used in industry. Poly(acrylamide) and its derivatives are used as flocculants in wastewater treatment

G. Qi, C. W. Jones
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr., Atlanta, Georgia 30332, USA
E-mail: chris.jones@chbe.gatech.edu
F. J. Schork
Department of Chemical and Biomolecular Engineering, 2113 Building 090, University of Maryland, College Park, MD 20742, USA
E-mail: fjschork@umd.edu

Table 1. Experimental set up for the RAFT inverse miniemulsion polymerizations of acrylamide at 60 °C.

Expt.	Polymerization type	Initiator	[B246]/[(CH ₂) ₆]	[monomer]/[RAFT]/[initiator]
			wt.-%	
1	RAFT solution	ABCP	0	600:3:1
2	RAFT radical mini	AIBN	2	600:3:1
3	RAFT radical mini	ABCP	2	600:3:1

applications,^[15] as drag reduction agents and drilling fluids in enhanced oil recovery,^[16,17] as additives in paper making,^[18] and as drug-delivery agents.^[19–21] The extremely high ratio of the propagation rate constant to the termination rate constant of acrylamide permits the synthesis of water-soluble polymers with molecular weights that exceed several million Daltons. The high heat of polymerization for acrylamide along with extreme solution viscosities generated by the high molecular weights leads to problems in large scale reactor operation including non-uniform mixing and heat transfer limitations.^[22] RAFT inverse miniemulsion polymerization is proposed here to provide a potential route to overcome these difficulties, facilitate process control of the homopolymerizations of acrylamide, and synthesize poly(acrylamide) copolymers.

Experimental Part

The inverse miniemulsion was prepared by adding a dispersed phase to a solution of the surfactant, B246SF (Uniqema), in cyclohexane. The dispersed phase was a degassed aqueous solution of acrylamide and the costabilizer, MgSO₄. The RAFT agent, 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid (RAFT), was synthesized according to literature procedures.^[23] Two types of initiators were used. The water-soluble initiator, 4,4'-azobis(4-cyanovaleric acid) (ABCP), was dissolved in the aqueous solution while AIBN, the lipophilic initiator, was

dissolved in cyclohexane. The emulsion was stirred under nitrogen at 7 °C using an ice-water bath for 90 min, purged with nitrogen, and then sonicated with a Fischer Model 30 sonic dismembrator operated at 70% power output for approximately 10 min under nitrogen while cooled in an ice bath.

Molecular weights of the polymers were determined by aqueous size exclusion chromatography (ASEC) at 30 °C. The ASEC system was comprised of a Shimadzu LC-20AD pump, a Shimadzu RID-10A RI detector, a Shimadzu SPD-20A UV detector, a Shimadzu CTO-20A column oven, and Viscotek TSK Viscogel PW_{XL} Guard, G3000, G4000, and G6000 columns mounted in series. The mobile phase consisted of 0.05 M Na₂SO₄ and the flow rate was maintained at 0.5 mL·min⁻¹. Poly(ethylene glycol) narrow standards were used to calibrate the ASEC by universal calibration method. Miniemulsion aliquots were removed and vacuum dried at 30 °C. The conversion of the monomer was determined with ASEC using a known method by comparing the area of the RI signals that corresponded to the monomer and the polymer.^[24]

Results and Discussion

All the experiments in this study were carried out at 60 °C and the ratio of monomer, RAFT agent, and initiator was fixed to 600:3:1, as outlined in Table 1. The typical recipe for RAFT inverse miniemulsion polymerization is shown in Table 2. The recipe for the RAFT solution polymerization (Table 1, Expt. 1) was the same as the dispersed phase of the inverse miniemulsion polymerization. The RAFT solution polymerization (Table 1, Expt. 1) was first performed

Table 2. Typical recipe for a RAFT inverse miniemulsion polymerization of acrylamide at 60 °C.

Component		Mass	Notes
Continuous phase	Dispersed phase	g	
B246		1.00	2 wt.-% of continuous phase
Cyclohexane		50.0	
	H ₂ O	7.5	1 wt.-% of dispersed phase [monomer]/[RAFT] = 200 [RAFT]/[ABCP] = 3
	Acrylamide	5.0	
	MgSO ₄	0.12	
	RAFT agent	0.089	
	ABCP (85 wt.-%)	0.039	

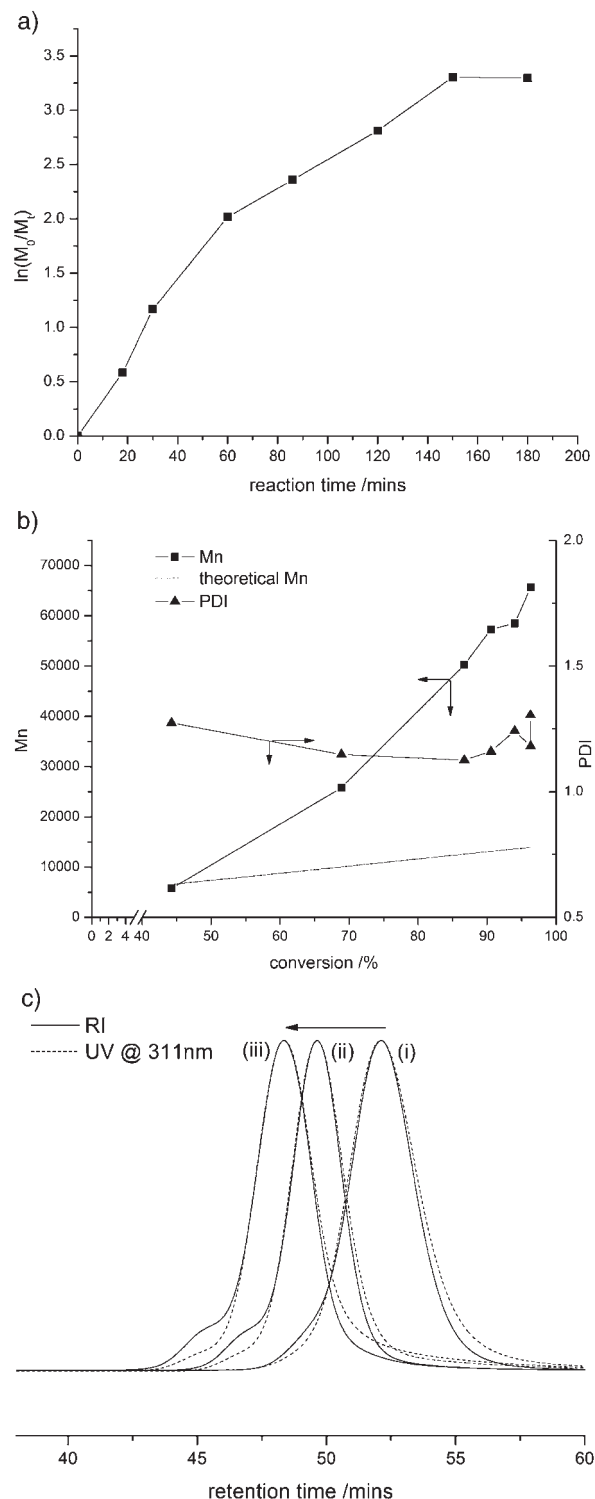


Figure 1. RAFT solution polymerization of acrylamide in Expt. 1: a) Evolution of the conversion as a function of reaction time. b) Evolution of \bar{M}_n and PDI as a function of conversion. c) ASEC chromatogram (RI and UV traces at 311 nm) evolution during the polymerization; i) 18 min, conversion = 44%, $\bar{M}_n = 5774$, PDI = 1.27, ii) 30 min, conversion = 69%, $\bar{M}_n = 25802$, PDI = 1.15, iii) 86 min, conversion = 91%, $\bar{M}_n = 57329$, PDI = 1.16).

to check the polymerization recipe since the appropriate selection of the RAFT agent is important for achieving well-controlled RAFT polymerizations, especially for RAFT polymerizations in an aqueous environment.^[25,26] As shown in Figure 1a, the polymerization initially followed pseudo first order kinetics, followed by a deviation with a lower polymerization rate after about 60 min. The molecular weight of poly(acrylamide), as shown in Figure 1b, falls on the theoretical line at first and then deviates from the predicted line with a higher value. The PDIs also show an increasing trend with the conversion up to 1.35, although it is still far below the typical PDI of about two for free radical polymerization of acrylamide with disproportionation termination. The reduced control at higher conversions could result from the hydrolysis and aminolysis of the RAFT agent, among other factors, which are common problems in aqueous RAFT polymerizations.^[25] McCormick and co-workers have reported very similar behavior in systems where RAFT agent hydrolysis and aminolysis were shown to be problematic.^[25,27] Albertin et al. also observed the above phenomena in the RAFT polymerization of methacrylic glycomonomer in the presence of added base. They claimed that hydrolysis of the free RAFT agent and the end-of-chain dithiobenzoyl groups was promoted by the high pH of the solution and the hydrolysis could lead to the deviation from a well-controlled RAFT process.^[28] Figure 1c shows the RI curve from the gel permeation chromatograph overlaid with the UV curve monitored at 311 nm. The UV curve monitored at 311 nm corresponds to the C=S bond in the RAFT agent. The absorption indicates that the polymer chains contain a RAFT agent functional group and that they could be 'living chains'.^[29] It is worth noting that there is a small shoulder in the RI curve with a shorter retention time in the GPC. This likely corresponds to the dead chains associated with the coupling termination of the polymeric radicals or terminated RAFT intermediates. The increase of this shoulder with prolonged reaction time suggests a loss of control, which might be attributable to hydrolysis or aminolysis of the RAFT agent and a higher content of terminated RAFT intermediates.^[27,28,30–32] The overall RI signal has a very good overlay with the UV curve throughout the RAFT solution polymerization of acrylamide in spite of the small shoulder, which suggests that a species with a C=S bond is associated with most polymer chains, even at long times where the kinetics and molecular weight deviate from the theoretical curve. Therefore, the same recipe was utilized as the dispersed phase of inverse miniemulsion polymerizations.

The results of RAFT inverse miniemulsion polymerizations of acrylamide with AIBN as initiator (Table 1, Expt. 2) and ABCP as initiator (Table 1, Expt. 3) are shown in Figure 2 and 3. The two systems behaved similarly in some aspects. As shown in Figure 2a and 2b, the

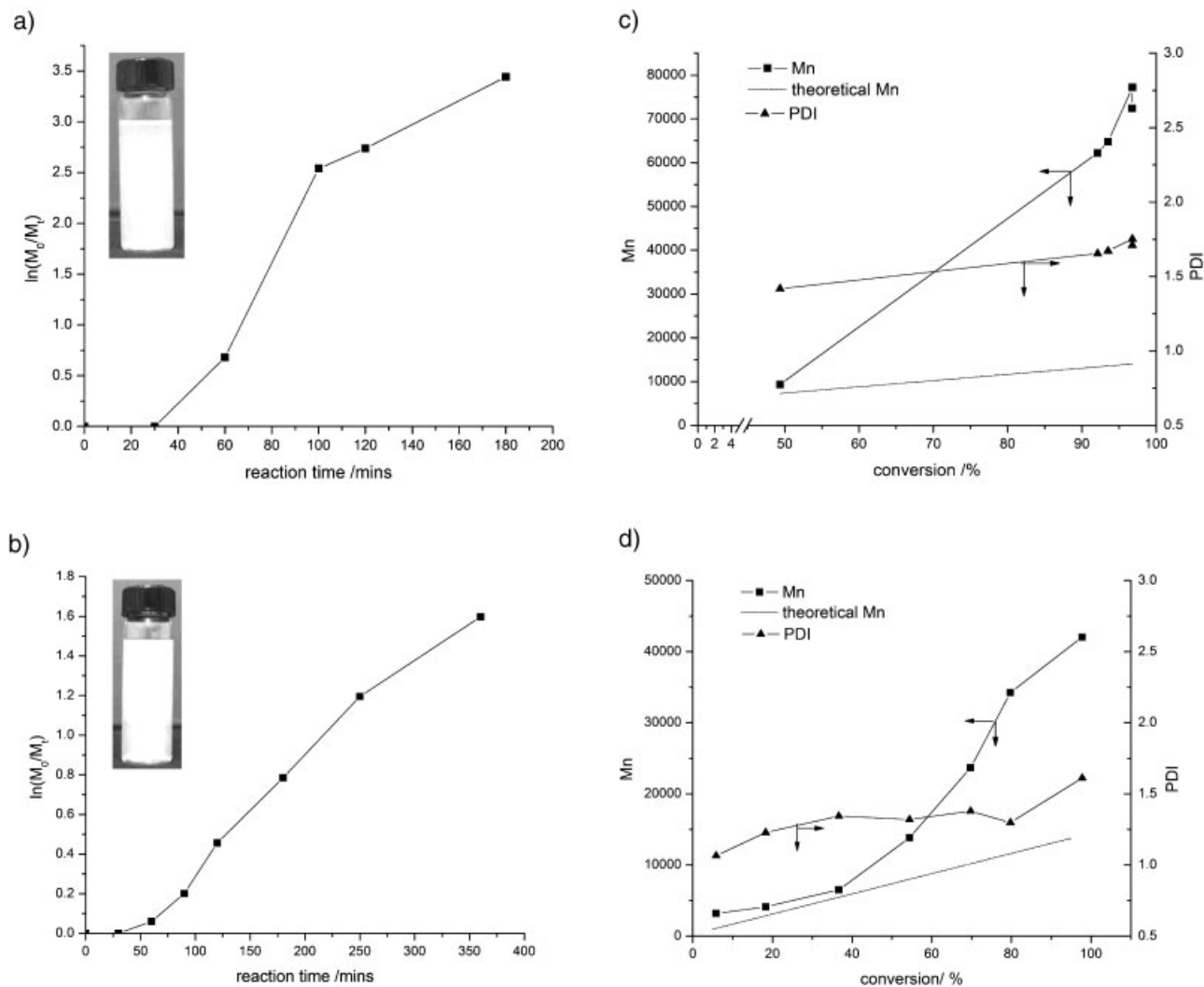


Figure 2. Evolution of the conversion as a function of reaction time for the RAFT inverse miniemulsion polymerization of acrylamide with a) AIBN as initiator (Expt. 2) and b) ABCP as initiator (Expt. 3). Evolution of M_n and PDI as a function of conversion for the RAFT inverse miniemulsion polymerization of acrylamide with c) AIBN as initiator (Expt. 2), and d) ABCP as initiator (Expt. 3).

poly(acrylamide) latexes produced in both experiments had good colloidal stability, with no phase separation observed after 5 d. In both inverse miniemulsion polymerizations, there was an induction time of around 30 min, probably caused by a small amount of O_2 or other impurities trapped in the aqueous phase.^{a[33]} The polymerization rates, as shown in Figure 2a and 2b, both decreased with reaction time. As in the solution polymerization, the molecular weights in both Expt. 2 and 3 showed a deviation from the predicted value after the

conversions reached $\sim 50\%$. However, despite these similarities, there were some significant differences between the two inverse miniemulsion polymerizations. The molecular weight of poly(acrylamide) in Expt. 2 was much higher than that of Expt. 3 at the same conversion. The PDIs in Expt. 2, as high as 1.7, were much broader than that of Expt. 3, which is indicative of less control in Expt. 2. Furthermore, the overlay of the RI and UV GPC curves from Expt. 2 and 3, as shown in Figure 3a and Figure 3b respectively, suggest a significant loss of control in Expt. 2. A bimodality in the RI signal and poor overlay of the RI and UV curves were observed in Expt. 2, which suggests AIBN, an oil-based initiator, leads to poor control in this system. In contrast, a good overlay of the curves was achieved in Expt. 3. Though the true cause of the observed differences

^a Inverse miniemulsions are very difficult to completely free of dissolved oxygen compared to conventional miniemulsions, as oxygen must be transferred from the aqueous droplets across an organic phase in which it has very low solubility.

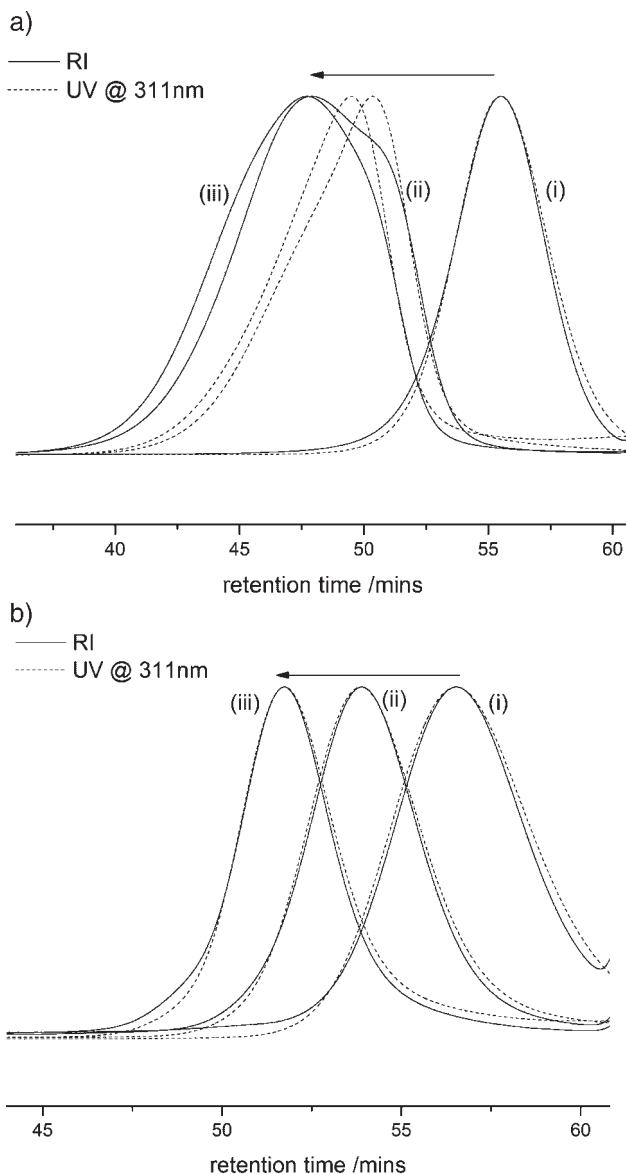


Figure 3. ASEC chromatograms (RI and UV traces at 311 nm) showing the evolution of the RAFT inverse miniemulsion polymerization of acrylamide with a) AIBN as initiator (Expt. 2) i) 60 min, conversion = 49%, $\bar{M}_n = 9320$, PDI = 1.42; ii) 100 min, conversion = 92%, $\bar{M}_n = 62218$, PDI = 1.65; iii) 186 min, conversion = 97%, $\bar{M}_n = 74235$, PDI = 1.70, and b) ABCP as initiator (Expt. 3): i) 120 min, conversion = 37%, $\bar{M}_n = 6530$, PDI = 1.34 (note: the RI curve deviated slightly from the baseline in this case because of a partial overlap of the salt peak at the retention time around 63 min); ii) 180 min, conversion = 54%, $\bar{M}_n = 13828$, PDI = 1.32; iii) 250 min, conversion = 70%, $\bar{M}_n = 23677$, PDI = 1.38.

with the two initiators is still under investigation, there are several potential phenomena that could contribute to them. The first that we considered is homogeneous nucleation in the continuous phase. The acrylamide radicals have a high diffusion rate out of the droplets.^[5] The different concentration ratio of RAFT agent and

acrylamide in the droplets and any homogeneous nucleated particles could lead to a different controlled behavior in each locale. The water-soluble initiator, ABCP, would greatly suppress the chance of homogeneous (organic phase) nucleation while the use of AIBN could result in an increase in this occurrence, and thus increased termination in the continuous phase where the primary radicals are generated. A second cause we considered was a hypothetical boundary layer barrier of the nonionic surfactant and poly(acrylamide) that forms with time between the cyclohexane continuous phase and the aqueous droplets. The boundary layer gets thicker and denser with the increasing conversion and thus greatly limits the diffusion rate of entry radicals.^[33,34] This could also lead to an increase in termination in the continuous phase if oil-soluble initiators are utilized.

The above data suggest that ABCP-initiated inverse miniemulsion RAFT polymerization of acrylamide produces polymer chains with kinetics and molecular weights that deviate from the theoretical line at high conversion but that still contain the C=S bond on most chains. To further probe this, the polymers from Expt. 2 and 3 were extended with another aliquot of acrylamide. The final polymer products of Expt. 2 and 3 were collected, precipitated with acetone, and dried in vacuum at 40 °C for 4 d. After fully dissolving the dried RAFT-bearing polymers in water, acrylamide and ABCP were added and the mixture polymerized at 60 °C. These chain extension experiments clearly showed a difference in the 'livingness' of the poly(acrylamide)s made in Expt. 2 and 3. As shown in Figure 4a, only the relatively low molecular weight

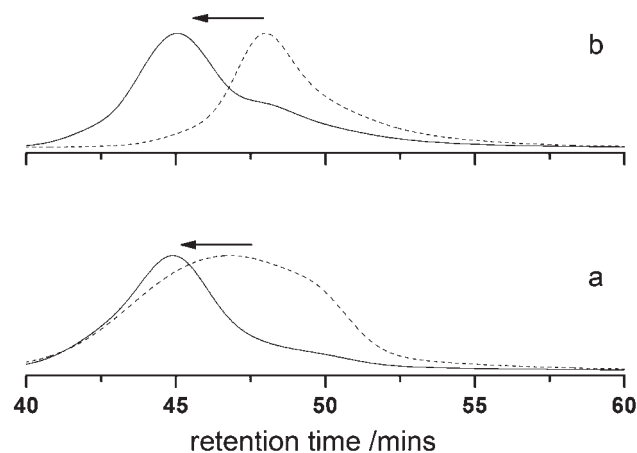


Figure 4. RI traces of ASEC chromatograms for the chain extension of poly(acrylamide) in solution at 60 °C. The poly(acrylamide)s made from the final products of Expt. 2 ($\bar{M}_n = 79975$, PDI = 1.66) and Expt. 3 ($\bar{M}_n = 49926$, PDI = 1.43) were used as the chain transfer agents. [Acrylamide]/[CTA] = 800 and [CTA]/[ABCP] = 0.5. a) Chain extension of the poly(acrylamide) from Expt. 2, and b) chain extension of the poly(acrylamide) from Expt. 3.

poly(acrylamide) chains were extended when using the samples prepared by AIBN initiation in Expt. 2, while nearly all the poly(acrylamide) chains prepared by ABCP initiation in Expt. 3 grew in Figure 4b. These data suggest that like the solution polymerization, the ABCP-initiated inverse miniemulsion polymerization proceeds in a controlled manner up to about 40% conversion, after which the polymerization proceeds in a pseudo-living manner.^b Thus, ABCP is a suitable initiator for RAFT inverse miniemulsion polymerization, which is demonstrated to proceed under pseudo-living conditions here for the first time.

Conclusion

RAFT inverse miniemulsion polymerization provides an alternate way to synthesize hydrophilic polymer latexes. It was found that the polymerization rate in RAFT solution polymerization and the inverse miniemulsion polymerizations decreased with reaction time. The loss of control is similar to what others have observed and have been attributable to RAFT agent hydrolysis.^[25–27] We show here that the nature of the initiator also has a great effect on the kinetics and controllability of the RAFT inverse miniemulsion of acrylamide. When the water-soluble initiator ABCP was used, the polymerization proceeded in a controlled/living manner at low conversion and pseudo-living manner at high conversion both in inverse miniemulsion and solution. When the oil-soluble initiator AIBN was utilized, however, a significant loss of control was observed with prolonged reaction time. It should be noted that the degree of livingness/control at low conversions is comparable to the only other report of inverse miniemulsion polymerization with a control agent present.^[35,36] In those works, good control was achieved up to a conversion of 65–80%. The RAFT polymerizations here appear well controlled at conversions up to 50% and only deviate at higher conversions. The use of a buffer solution in the aqueous phase to suppress the suspected RAFT agent hydrolysis or aminolysis may improve the control/livingness in the inverse miniemulsions.^[26]

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^b We describe the polymerizations that appear here as a typical 'living/controlled' RAFT polymerization at low conversion but that deviate from the theoretical line at high conversion while i) maintaining RAFT functional groups associated with most if not all polymer chains, and ii) where those chains can be extended, as 'pseudo-living'.

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