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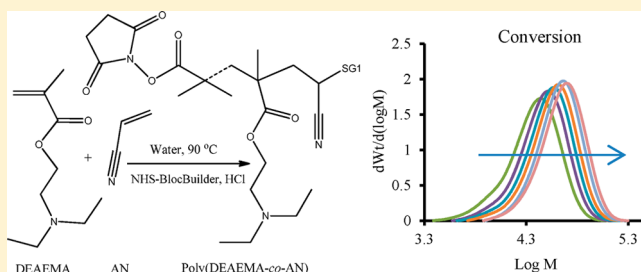
# Nitroxide-Mediated Polymerization of 2-(Diethylamino)ethyl Methacrylate (DEAEMA) in Water

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## S Supporting Information

**ABSTRACT:** Nitroxide-mediated polymerization (NMP) of 2-(diethylamino)ethyl methacrylate (DEAEMA) with a small amount of acrylonitrile (AN) as a comonomer was performed for the first time in water at 90 °C and atmospheric pressure using *n*-hydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system composed of 2,2'-azobis[2-(2-imidazolin-2-yl)propane]-dihydrochloride (VA-044) as initiator and *N*-tert-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as nitroxide. Both polymerization reactions were well-controlled and exhibited excellent livingness as evidenced by low molar dispersity and evolution of the molar mass distribution. The hydrolytic stability of DEAEMA at the polymerization conditions and the effects of several parameters including initiating system, temperature, ratio of nitroxide to initiator, initiator and monomer concentrations, and comonomer type were investigated. Chain extension of the synthesized macroinitiator with methyl methacrylate (MMA) and styrene (S) in a one-pot process led to the *in situ* formation of poly(DEAEMA-*co*-S)-*b*-poly(MMA-*co*-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.



## INTRODUCTION

Development of controlled/living radical polymerization (LRP) has had a major impact on polymer science.<sup>1–3</sup> (The new terminology of reversible deactivation radical polymerization (RDRP) has been proposed by IUPAC for LRP.<sup>4</sup>) Polymeric architectures with different composition, structures, and functionalities can be prepared in relatively mild conditions by LRP techniques. Of the three main types of LRP, nitroxide-mediated polymerization (NMP) and atom-transfer radical polymerization (ATRP) are based on reversible activation–deactivation cycles of growing polymer chains while reversible addition–fragmentation transfer (RAFT) polymerization is based on reversible chain transfer.<sup>3</sup> NMP is a powerful technique with arguably the simplest mechanisms among all LRP techniques for preparing polymers with a narrow molecular weight distribution (MWD) and low molar dispersity ( $\bar{D}$ ).<sup>5</sup> Furthermore, there is no concern of residual catalyst, color, or toxicity in the final polymer. LRP can be applied for the preparation of well-defined polymeric architectures in aqueous media which is not possible in ionic polymerization.<sup>1</sup> However, applying LRP in aqueous media (homogeneous or dispersed) is often quite difficult due to problems such as hydrolysis and aminolysis reactions in RAFT polymerization or other side reactions in the case of ATRP.<sup>6,7</sup> There are a very limited number of reports related to NMP in homogeneous aqueous solution. A further difficulty for NMP is the high temperature (>100 °C) traditionally required which necessitates using pressurized vessels. However, performing NMP at lower temperatures now is possible with some nitroxide/

monomer combinations. The first example of NMP conducted in homogeneous aqueous solution was with of sodium 4-styrenesulfonate in water using a 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO)-based carboxy-functionalized nitroxide.<sup>7</sup> The alkoxyamine was synthesized by a multistep process and was water-soluble in its basic form. NMP of the same monomer was performed at 120 °C using a bicomponent initiating system consisting of the water-soluble nitroxide (synthesized beforehand through a multistep process) and VA-044 and V-50 initiators.<sup>8</sup> NMP of *N,N*-dimethylacrylamide, sodium 4-styrenesulfonate, and 2-(acryloyloxy)ethyl benzyltrimethylammonium chloride was carried out in water using an SG1-based alkoxyamine containing a carboxylic acid group (MAMA-SG1) and free excess SG1.<sup>6</sup> The alkoxyamine was converted to the water-soluble state by addition of sodium hydroxide before the start of the reaction, and the blocking efficiency of the synthesized polymers was assessed by chain extension experiments. Grassl et al.<sup>9</sup> conducted the NMP of acrylamide in water at 120 °C using a bicomponent initiating system composed of SG1 as the nitroxide and 2,2'-azobis(2-methylpropionamide) dihydrochloride (VAZO56WSP) as the initiator. The polymerization proceeded (without significant monomer hydrolysis), yielding star-like polymer chains. The same group polymerized acrylamide in water employing a similar initiating system in microwave-assisted NMP.<sup>10</sup>

Received: October 24, 2014

Revised: December 11, 2014

**Table 1.** Experimental Conditions for the NMP of DEAEMA in Water

exp	DEAEMA (mol L <sup>-1</sup> )	initiator	<i>s</i> <sup>a</sup>	comonomer	<i>f</i> <sub>x,0</sub> <sup>b</sup>	<i>r</i> <sup>c</sup>	<i>M</i> <sub>n,SEC</sub> (g mol <sup>-1</sup> )	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	time (min)	<i>χ</i> <sup>d</sup> (%)	temp (°C)
1	0.5	VA-044	0.005	styrene	0.09	1.5	19300	1.61	60	84.0	90
2	0.5	VA-044	0.005	styrene	0.09	2	18000	1.36	60	66.0	90
3	0.5	VA-044	0.005	acrylonitrile	0.09	2	15600	1.43	90	75.8	90
4	0.5	NHS-BB	0.005	acrylonitrile	0.09	0	49400	1.30	120	82.0	90
5	0.5	NHS-BB	0.005	acrylonitrile	0.09	0.1	45500	1.34	120	58.0	90
6	1.0	NHS-BB	0.005	acrylonitrile	0.09	0.1	54000	1.22	120	80.0	90
7	0.5	NHS-BB	0.005	acrylonitrile	0.09	0.2	39500	1.27	120	40.7	90
8	0.5	NHS-BB	0.01	acrylonitrile	0.09	0.2	21600	1.34	120	60.4	90
9	0.5	NHS-BB	0.005	acrylonitrile	0.09	0.2	42100	1.40	90	30.0	80
10	0.5	VA-044	0.005	acrylonitrile	0.09	1.5	22400	1.35	300	90.0	80

<sup>a</sup>Molar ratio of initiator to monomers ( $s = [\text{initiator}]_0 / ([\text{DEAEMA}]_0 + [\text{comonomer}]_0)$ ). <sup>b</sup>Initial molar fraction of comonomer in the monomer mixture ( $f_{x,0} = [\text{comonomer}]_0 / ([\text{DEAEMA}]_0 + [\text{comonomer}]_0)$ ). <sup>c</sup>Ratio of free nitroxide to initiator ( $r = [\text{SG1}]_0 / [\text{initiator}]_0$ ). <sup>d</sup>Conversions were calculated by <sup>1</sup>H NMR.

Charleux's group<sup>11</sup> performed nitroxide-mediated copolymerization of methacrylic acid (MA) and sodium 4-styrenesulfonate in acidic conditions (pH = 3.5) in water using the BlocBuilder alkoxyamine and SG1 at a comparatively low temperature (76 °C). The short polymerization time and low temperature were considered important parameters in enabling the successful NMP even at low pH. Chain extension experiments were then conducted in the emulsion copolymerization of methyl methacrylate (MMA) and styrene at 90 °C in the same pot.

(Diethylamino)ethyl methacrylate (DEAEMA) and (dimethylamino)ethyl methacrylate (DMAEMA) are two typical examples of tertiary amine methacrylate-based monomers. The *pK<sub>a</sub>* of DEAEMA and DMAEMA monomers are 8.8 and 8.3 while the *pK<sub>a</sub>* of their corresponding homopolymers are 7.5 and 7.4, respectively.<sup>12</sup> Recently, DEAEMA and DMAEMA have received considerable attention because of their CO<sub>2</sub> switchability.<sup>13–24</sup> For example, CO<sub>2</sub>-switchable latex,<sup>25</sup> surfactant,<sup>26</sup> and hydrogel<sup>17,27</sup> have been prepared using DEAEMA and DMAEMA as CO<sub>2</sub>-switchable components in the structure of the final polymers. In most of these publications, DEAEMA and/or DMAEMA were polymerized via RAFT or ATRP. There are few reports related to the NMP of functional monomers bearing a tertiary amine group. Polystyrene macroinitiator was employed for the NMP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in bulk.<sup>28</sup> The effect of different parameters such as solvent polarity, temperature, excess nitroxide, and chain transfer to polymer on the NMP of DMAEA was reported by Cunningham.<sup>29</sup> A copolymer of DMAEMA and styrene was synthesized by NMP in bulk at 80 °C employing *n*-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder) alkoxyamine.<sup>30</sup> The chain extension experiment with a DMAEMA/styrene mixture was performed to assess the livingness of the poly(DMAEMA-*co*-S).

In our previous publication<sup>31</sup> we synthesized poly(DEAEMA-*co*-S) in bulk and then employed it in the protonated form as a macroalkoxyamine for the preparation of PMMA latexes. To the best of our knowledge there is no report of NMP of methacrylate monomers containing a tertiary amine group in water. In this paper we report for the first time the NMP of DEAEMA in water using different initiating system at temperatures below the boiling point of water. The effect of several parameters including temperature, comonomer type, excess nitroxide, monomer concentration, and initiator concentration on the control and livingness of the polymerization reaction are studied in detail. The livingness of the

poly(DEAEMA-*co*-S) is demonstrated by chain extension in a one-pot process using polymerization-induced self-assembly (PISA).<sup>32</sup>

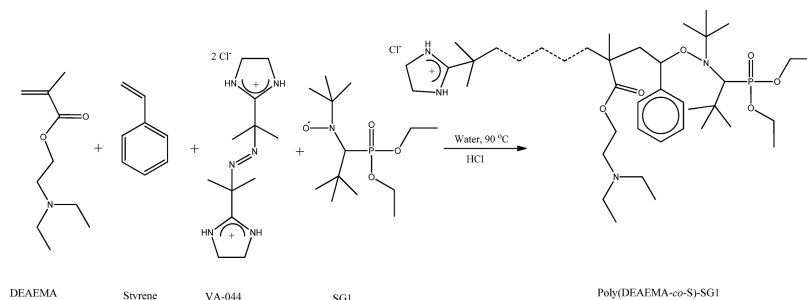
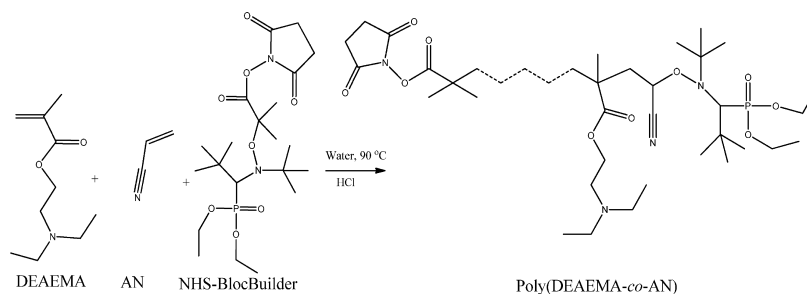
## EXPERIMENTAL SECTION

**Materials.** All chemicals, monomers, and inhibitor removal columns were purchased from Aldrich unless otherwise stated. 2-(Diethylamino)ethyl methacrylate (DEAEMA, 99%) was passed through a column of basic aluminum oxide (mesh ~150) prior to use. Styrene (S, >99%) and methyl methacrylate (MMA, 99%) were purified by passing through columns packed with inhibitor remover. The 2-((*tert*-butyl-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)-amino)oxy)-2-methylpropanoic acid initiator (BlocBuilder) and *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 85%) were supplied by Arkema. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was purchased from Wako Pure Chemical Industries and used without further purification. Sodium hydroxide (NaOH, >97%), tetrahydrofuran (THF, >99%), hydrochloric acid (38 wt %), and nitrogen (N<sub>2</sub>, Praxair, medical grade) were used as received. All aqueous solutions were prepared with deionized water (DIW). *N*-Hydroxysuccinimide BlocBuilder (NHS-BB) was synthesized according to the reported procedure.<sup>33</sup>

### Copolymerization of DEAEMA with AN or Styrene in Water.

In a typical experiment (exp 5, Table 1), DEAEMA (5.0 g, 27.0 mmol) and deionized water (48 mL) were mixed in a 100 mL three-neck round-bottom flask. The flask was immediately immersed in an ice-water bath, and the pH of the solution adjusted to 6 by dropwise addition of concentrated hydrochloric acid (HCl, 38 wt %). Then, AN (0.14 g, 2.7 mmol) (initial molar fraction of AN in the monomer mixture:  $f_{s,0} = 0.09$ ), NHS-BB (0.07 g, 0.15 mmol), and SG1 (8.0 mg, 0.03 mmol) were introduced into the flask, and the mixture was deoxygenated with a nitrogen stream for 20 min. The mixture was then introduced into a preheated oil bath at 90 °C and fitted with a reflux condenser, a nitrogen inlet, and a thermometer. Time zero of the polymerization was taken when the flask was immersed in the oil bath. The reaction mixture, while remaining under N<sub>2</sub>, was stirred at a speed of 300 rpm and allowed to react for 2 h with samples withdrawn periodically for kinetic studies and raw polymer analysis. Samples were quenched by immersion in ice-water bath. A portion of each sample was used for NMR analysis, and the remainder was neutralized with NaOH (1 M) and then dried under air for 24 h for SEC analysis. Copolymerization of DEAEMA and S was performed in a similar way. The only difference is using S instead of AN.

**Chain Extension Experiment.** DEAEMA (0.5 g, 0.53 mol L<sup>-1</sup>), styrene (28 mg, 0.053 mol L<sup>-1</sup>), SG1 (23 mg, 11 mmol L<sup>-1</sup>), VA-044 (17 mg, 7.5 mmol L<sup>-1</sup>), and DIW were mixed in a round-bottom flask, and the pH was adjusted to 6 by dropwise addition of concentrated HCl. The contents of the flask were then deoxygenized by bubbling nitrogen for 20 min while immersing in an ice-water bath. Then flask was inserted into a preheated oil bath at 90 °C. After 15 min of reaction, the contents of the flask were added to a second flask

**Scheme 1. Schematic Representation of the Polymerization of DEAEMA with 9 mol % Styrene in Water Initiated by VA-044****Scheme 2. Schematic Representation of the Polymerization of DEAEMA with 9 mol % Acrylonitrile in Water Initiated by NHS-BB**

containing hydrophobic monomers, and the reaction continued for 2 h. For the preparation of hydrophobic monomers, MMA (10.12 g, 0.09 mol L<sup>-1</sup>), S (1.04 g, 0.09 mol L<sup>-1</sup>), and deionized water were mixed in a separate flask and deoxygenized for 20 min by bubbling with nitrogen and then inserted into a preheated oil bath at 90 °C.

**Characterization.** The monomer conversion was determined by <sup>1</sup>H NMR (Bruker Advance-400) performed in 5 mm diameter tubes in D<sub>2</sub>O at room temperature. The monomer conversion was calculated by measuring the vinyl proton integrals at  $\delta = 6.11$  ppm and  $\delta = 5.82$  ppm using 1,3,5-trioxane as an internal reference ( $\delta = 5.26$  ppm). The chemical shift scale was calibrated based on tetramethylsilane. Size exclusion chromatography (SEC) was used to determine the molecular weight and polydispersity index (*D*) of the polymer samples. The SEC was equipped with a Waters 2960 separation module containing three Styragel columns coupled with the separation limits between 400 and  $1 \times 10^6$  g mol<sup>-1</sup>. THF was used as the eluent with a flow rate of 0.3 mL min<sup>-1</sup>. A differential refractive index detector (Waters 2960) was used, and the average molar masses (*M<sub>n</sub>* and *M<sub>w</sub>*) and molar mass dispersity (*D*) were derived from a calibration curve based on polystyrene (PS) standards from Polymer Standard Service. All the amine groups were neutralized with base (1 M sodium hydroxide) before running SEC.

## RESULTS AND DISCUSSION

Performing polymerizations in water is an attractive option, if possible. However, in the case of the NMP of methacrylate monomers there are challenges. Fast reaction rates of methacrylate monomers and side reactions between nitroxide and methacrylate-based monomers specifically in water cause poor control over the reaction.<sup>34,11</sup> Nitroxide interaction with water via intermolecular hydrogen bonding leads to the higher polymerization rate.<sup>35</sup> Tertiary amine methacrylate-based monomers also undergo hydrolysis in water.<sup>36</sup>

**Hydrolysis of DEAEMA.** Recently, we synthesized poly-(DEAEMA-co-S)-SG1 macroinitiator in bulk and then used it as a macroalkoxyamine in the preparation of PMMA latexes.<sup>31</sup> DEAEMA is a CO<sub>2</sub>-switchable monomer that becomes hydrophilic when protonated by purging CO<sub>2</sub> in its aqueous solution at room temperature. Our attempts at conducting

NMP of DEAEMA under CO<sub>2</sub> atmosphere in aqueous solutions were not successful, primarily because of the very low solubility of CO<sub>2</sub> in water at the higher temperatures required for NMP. In fact, the reaction medium was heterogeneous, and some small fraction of DEAEMA remained in the protonated form while the major part of that was deprotonated and became hydrophobic. In this work we decided to protonate DEAEMA using a strong acid (HCl) to ensure that all of the DEAEMA remains in the protonated form during reaction at high temperatures and the system is homogeneous at all times. In all of our experiments the pH was adjusted to 6.0, which is low enough to solubilize DEAEMA in water and prevent hydrolysis at elevated temperatures.

At pH 9 the rate of hydrolysis is very high (Figure S1); in 2 h more than 90% of the monomer is hydrolyzed at 90 °C, which is the reaction temperature used for the NMP of DEAEMA in this study. While decreasing temperature to 80 °C reduced the hydrolysis percentage to some extent, reduction of pH from 9 to 8 had a much more pronounced effect on decreasing the hydrolysis percentage. At pH 7, hydrolysis was negligible during the 2 h experiment although there was still some hydrolysis observed over a longer period of time (<10% after 5 h). All experiments in this study were performed at pH range between 6 and 6.5, and no hydrolysis was observed during the polymerization. Since SG1 decomposes at low pH,<sup>38</sup> this pH range is also high enough to be suitable for SG1 use and low enough to prevent hydrolysis of NHS-BlocBuilder.<sup>39</sup>

**Comonomer Type.** DEAEMA is a methacrylate monomer and therefore not effectively homopolymerized using SG1 since a high portion of propagating radicals will terminate irreversibly due to the high activation–deactivation equilibrium constant *K*. Hydrogen transfer between propagating radicals and the nitroxide is another concern.<sup>40</sup> Adding a few mole percent of a comonomer with small *K* in the monomer mixture can reduce the overall equilibrium constant and increase the control and livingness of the reaction.<sup>41</sup> Therefore, in all experiments in this



study 9 mol % of a comonomer such as styrene or acrylonitrile was added to the monomer mixture (Schemes 1 and 2). Table 1 shows experimental conditions for the NMP of DEAEMA in water.

In the first experiment (exp 1, Table 1), styrene was employed as a comonomer, VA-044 as initiator, and SG1 as nitroxide. At the start of the reaction, the mixture was not completely homogeneous because of the low solubility of the styrene, but after a few minutes it became homogeneous. The ratio of SG1 to VA-044 was adjusted to 1.5. Although the livingness of the reaction was reasonably good according to the shift in molecular weight distributions (MWD) to higher values, the  $\bar{D}$  of the final polymer was high ( $\bar{D} = 1.61$ ), indicating relatively poor control over the reaction. Adding more SG1 ( $[SG1]_0/[VA-044]_0 = 2.0$ ) increased the control of the reaction and lowered  $\bar{D}$  to 1.36 (exp 2, Table 1). The addition of more SG1 did have a significant effect on the rate of the polymerization, and conversion plateaued after 40 min at 66%, likely due to nitroxide accumulation in the reaction medium. At the start of the reaction, the polymerization medium had a yellowish color which disappeared quickly once the polymerization started, and after a few minutes the solution became completely colorless.

While DEAEMA is completely water-soluble at pH 6, styrene is a hydrophobic monomer, and its solubility in water is low. Therefore, a hydrophilic monomer such as acrylonitrile would be better choice as a comonomer (exp 3, Table 1). It was previously reported that acrylonitrile is an effective comonomer for the NMP of MMA.<sup>42</sup> Figure 1 shows kinetic plots of experiments 2 and 3 in Table 1. The  $\ln[1/(1 - \chi)]$  versus conversion plot is closer to linear in the case of acrylonitrile (Figure 1a), and the molar dispersities are lower when

acrylonitrile was used as a comonomer compared to styrene (Figure 1b).

When styrene is employed as a comonomer, the  $M_n$  versus conversion plot has a nonzero intercept. Therefore, it shows an initially high value of  $M_n$  and does not intercept the origin. This reflects the time required for establishing the activation–deactivation equilibrium.

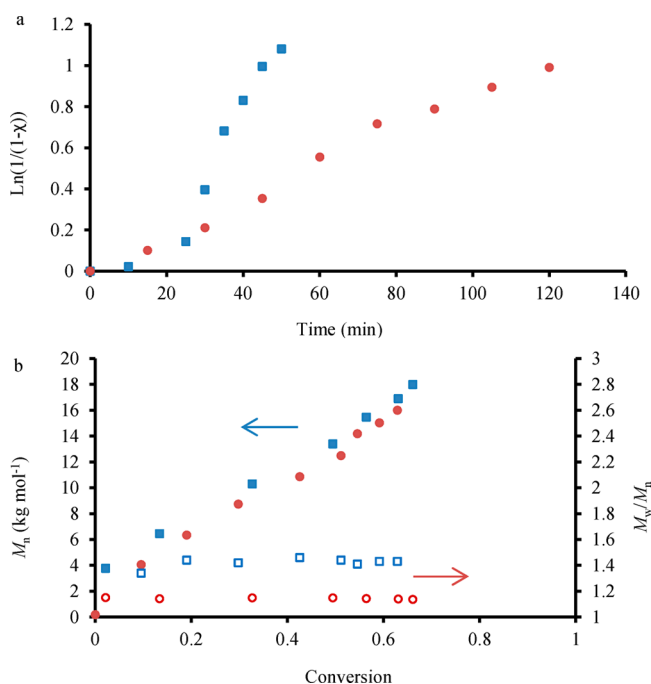
The linearity of the  $\ln[1/(1 - \chi)]$  versus time graph indicates a constant concentration of propagating radicals over the course of the polymerization. Also, the low molar mass dispersity ( $\bar{D} < 1.5$ ) and the linear increase of the number-average molecular weight ( $M_n$ ) versus conversion show good control of the reaction. The complete shift of the molecular weight distribution with increasing conversion (Figure 2) confirms the livingness of the polymer chains.

**Initiating System.** To investigate the effect of the initiating system (monocomponent versus bicomponent) on the kinetic of the polymerization, NHS-BB was used as alkoxyamine in the NMP of DEAEMA in water (exp 4, Table 1) using acrylonitrile as a comonomer. NHS-BlocBuilder has been applied previously in the NMP of DMAEMA in bulk using styrene as a comonomer at 80 °C.<sup>30</sup> To prevent hydrolysis of NHS-BlocBuilder and DEAEMA, the pH was adjusted to 6.<sup>35</sup> NHS-BB is not soluble in water at pH = 6, but when the reaction is started at elevated temperatures, it is decomposed by heat and becomes soluble after a few minutes. Figures 3 and 4 show the kinetic plots and SEC chromatograms of the reaction.

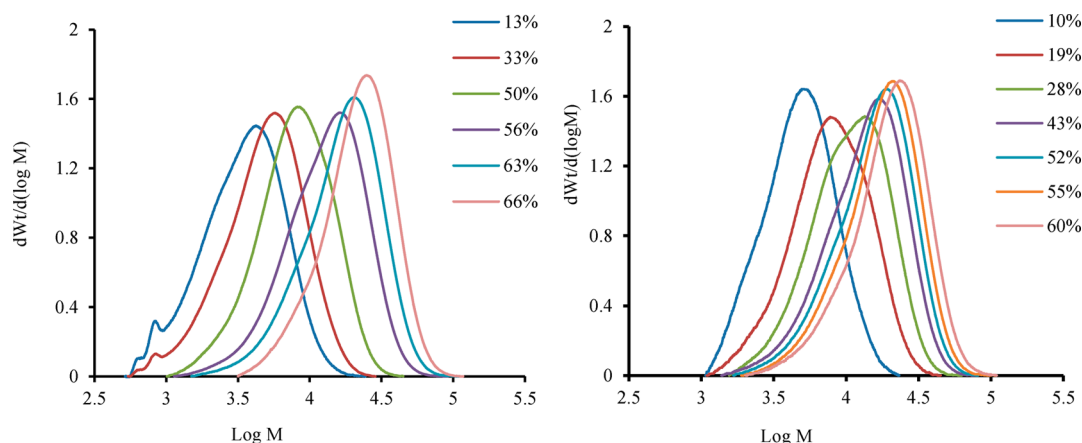
$M_n$  and  $\ln[1/(1 - \chi)]$  increased linearly with conversion and time, respectively, which show the concentration of growing chains has remained constant during the reaction. The final  $\bar{D}$  is 1.3, which confirms good control over the polymerization. The MWD plots show excellent livingness (Figure 4). Somewhat surprisingly, good control over the reaction has been achieved using NHS-BB despite not adding free nitroxide.

**Monomer Concentration.** To determine the effect of monomer concentration on the kinetics of the polymerization, two experiments were performed (exp 5 and 6 in Table 1) with DEAEMA concentration of 0.5 and 1.0 mol L<sup>-1</sup>, respectively, while the rest of the conditions such as comonomer concentration in the monomer mixture, the ratio of  $[SG1]_0/[NHS-BB]_0$ , and the temperature were kept constant (as a result, the target  $M_n$  increased). The polymerization rate was much faster for the higher concentration of DEAEMA (Figure 5). For ideal first-order kinetics, the conversion–time profile should be independent of monomer concentration. The presence of monomer concentration effects is not expected, but it likely attributable to conducting the polymerization in water. Both reactions had a linear trend in the  $\ln[1/(1 - \chi)]$  versus time graph, but when the DEAEMA concentration was increased, the control over the reaction improved remarkably and the final  $\bar{D}$  dropped from 1.34 to 1.22. Increasing the monomer concentration causes the polymerization medium to more closely resemble the bulk condition. The livingness of the reaction is also excellent, which can be seen in the shifts of the MWD to higher molecular weights in Figure 6.

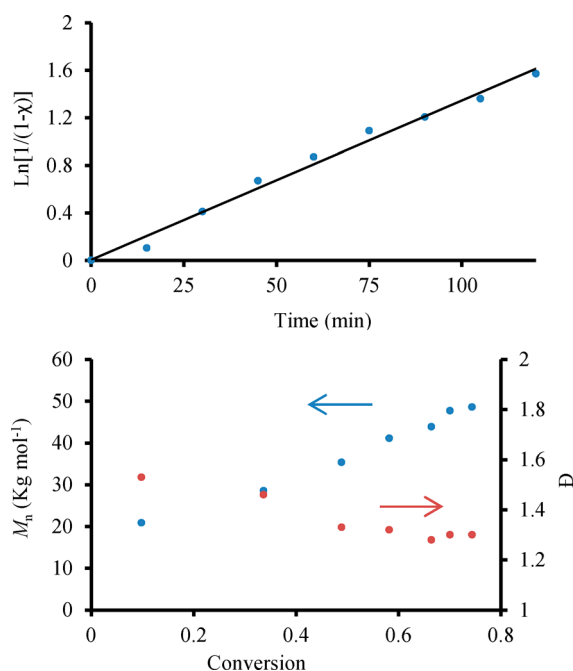
**Effect of SG1.** It is common in NMP to add a few percent of free excess nitroxide with respect to the alkoxyamine at the start of the reaction to facilitate the establishment of the reversible activation–deactivation cycles of the dormant polymer chains. Without having free nitroxide at the start of the reaction and before establishment of the activation–deactivation equilibrium, increased termination can occur early in the polymerization. To compare the results of different



**Figure 1.** Kinetic plots of the NMP of DEAEMA (initial molar fraction of the comonomer:  $f_{s0} = 0.1$ ) at 90 °C using VA-044 as the initiator and SG1 as the nitroxide ( $[SG1]_0/[VA-044]_0 = 2$ ): (a)  $\ln[1/(1 - \chi)]$  versus time, (b)  $M_n$  and  $M_w/M_n$  versus conversion. (■) Comonomer: styrene; (●) comonomer: acrylonitrile. Hollow symbols represent molar dispersities.



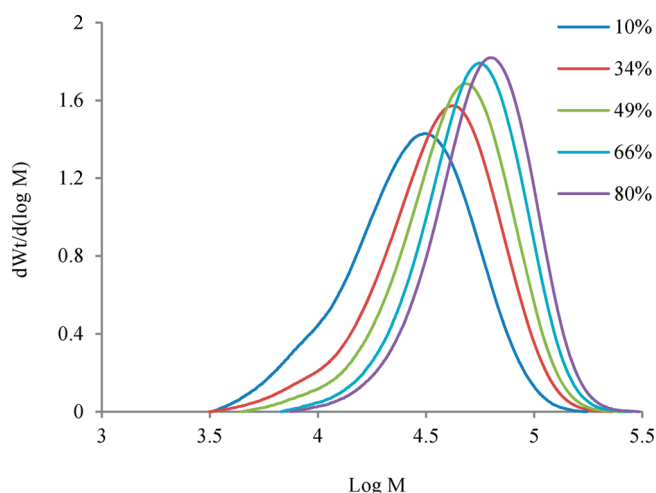
**Figure 2.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % styrene (left picture) or acrylonitrile (right picture) in water at 90 °C using VA-044 as the initiator and SG1 as the nitroxide.



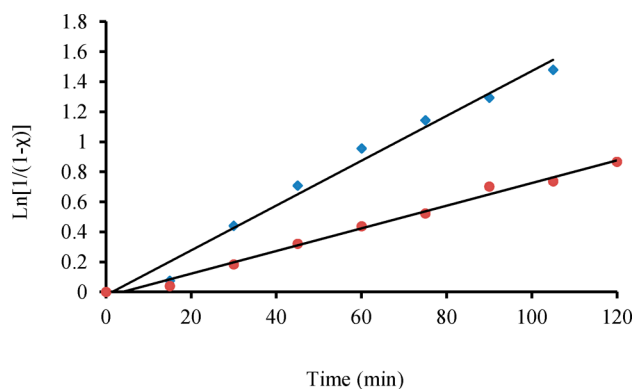
**Figure 3.** Kinetic plots of the copolymerization of DEAEMA and acrylonitrile (initial molar fraction of acrylonitrile:  $f_{x0} = 0.09$ ) in water at 90 °C using NHS-BB as alkoxyamine without adding free SG1: (a)  $\ln[1/(1-\chi)]$  versus time; (b)  $M_n$  and  $M_w/M_n$  versus conversion.

experiments with variable quantities of free SG1 in the polymerization reaction, experiments 4, 5, and 7 in Table 1 were designed with  $[SG1]_0/[NHS-BB]_0 = 0, 0.1$ , and 0.2, respectively. Figure 7 shows  $\ln[1/(1-\chi)]$  versus time.

Increasing the amount of free SG1 decreases the rate of reaction which can be observed in Figure 7. More SG1 in the polymerization medium increases the probability of growing radicals being deactivated by SG1 before termination with other polymer chains (thereby increasing livingness) but also reduces the propagating radical concentration and therefore the polymerization rate. As a result, the final conversion decreased from 82% in the experiment with  $[SG1]_0/[NHS-BB]_0 = 0$  to 41% in the experiment with  $[SG1]_0/[NHS-BB]_0 = 0.2$ . The livingness of the reaction for all three reactions is excellent, which can be observed in Figures 4 and 8.

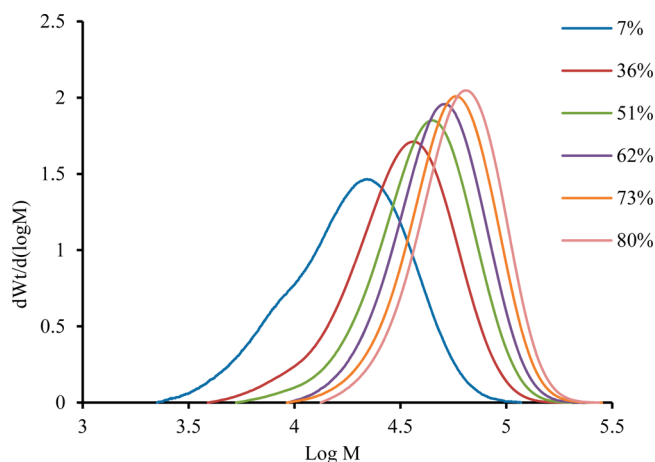


**Figure 4.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as alkoxyamine without adding free nitroxide.

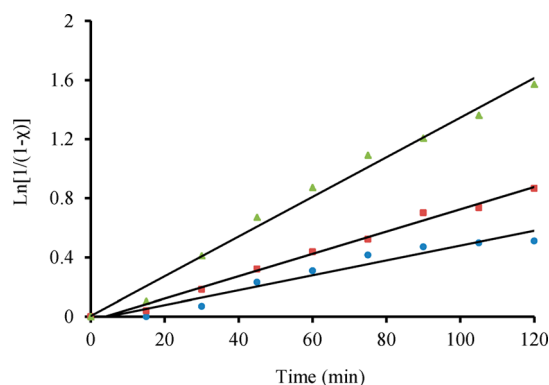


**Figure 5.** Kinetic plots of the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as an alkoxyamine and SG1 as a nitroxide ( $[SG1]_0/[NHS-BB]_0 = 0.1$ ); square:  $[DEAEMA]_0 = 1.0 \text{ mol L}^{-1}$ ; circle:  $[DEAEMA]_0 = 0.5 \text{ mol L}^{-1}$ .

**Initiator Concentration.** To increase the conversion in experiment 7 (Table 1), the concentration of NHS-BB was increased (exp 8, Table 1). The final conversion jumped from 40% to 60%, while linearity in the kinetic plots was preserved



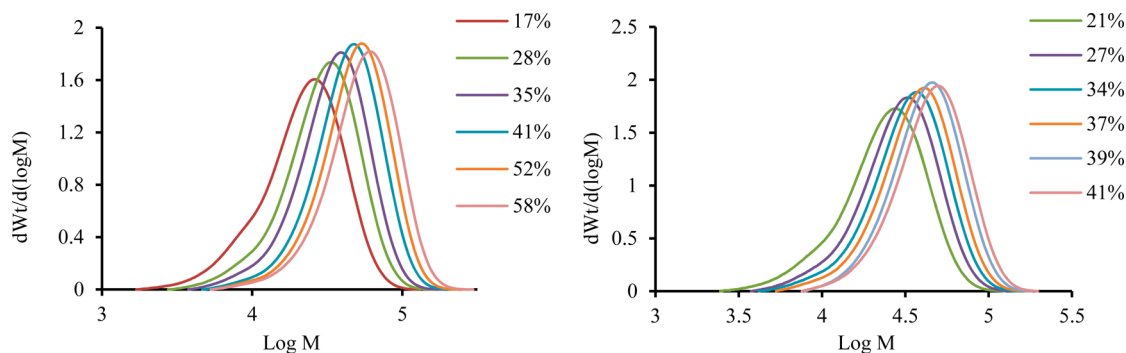
**Figure 6.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as an alkoxyamine and SG1 as a nitroxide ( $[SG1]_0/[NHS-BB]_0 = 0.1$ ) with  $[DEAEMA]_0 = 1.0 \text{ mol L}^{-1}$ .



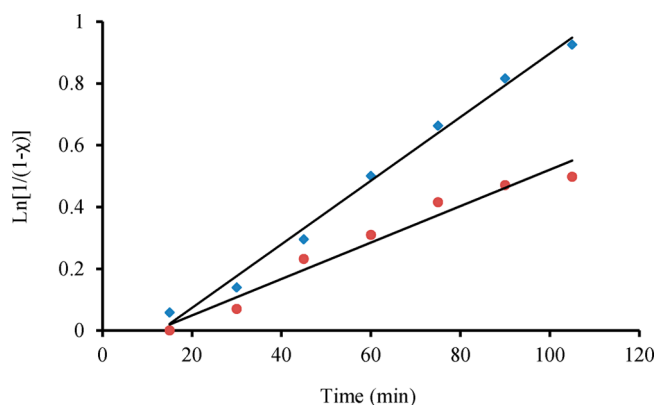
**Figure 7.** Plot of  $\ln[1/(1-\chi)]$  versus time for the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as an alkoxyamine and SG1 as the nitroxide: triangle:  $[SG1]_0/[NHS-BB]_0 = 0$ ; square:  $[SG1]_0/[NHS-BB]_0 = 0.1$ ; circle:  $[SG1]_0/[NHS-BB]_0 = 0.2$ .

and clean evolution of the MWDs was observed (Figures 9–11).

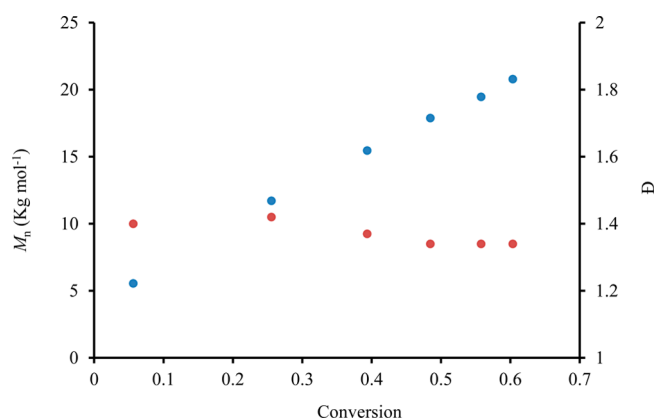
$M_n$  increased linearly with conversion while the  $\bar{D}$  remained around 1.35, demonstrating good control over the polymerization (Figure 10). The final molecular weight in experiment 8 (Table 1) is approximately half of the molecular weight in experiment 7—an expected result since the number of growing chains was doubled due to doubling of the amount of initiator.



**Figure 8.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as an alkoxyamine and SG1 as a nitroxide: left: ( $[SG1]_0/[NHS-BB]_0 = 0.1$ ); right: ( $[SG1]_0/[NHS-BB]_0 = 0.2$ ).



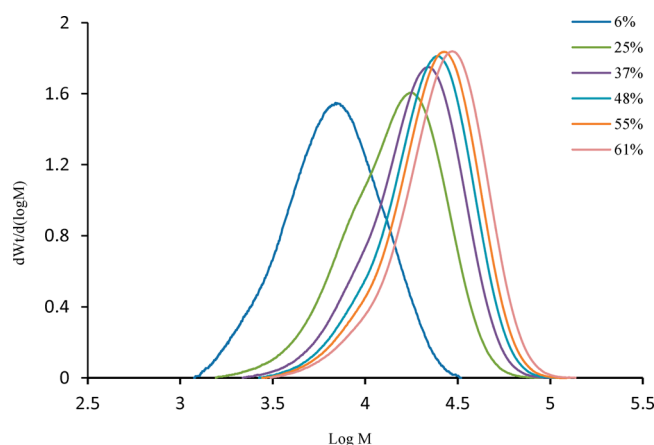
**Figure 9.** Plot  $\ln[1/(1-\chi)]$  versus time for the NMP of DEAEMA with 9 mol % acrylonitrile in water NHS-BB as an alkoxyamine and SG1 as a nitroxide ( $[SG1]_0/[NHS-BB]_0 = 0.2$ ): square:  $[NHS-BB]_0/[monomers]_0 = 0.01$ ; circle:  $[NHS-BB]_0/[monomers]_0 = 0.005$ .



**Figure 10.**  $M_n$  and  $M_w/M_n$  versus conversion in the NMP of DEAEMA and a small amount of AN at 90 °C using NHS-BB alkoxyamine and SG1 nitroxide ( $[SG1]_0/[VA-044]_0 = 2$ ) with  $[DEAEMA]_0 = 0.5 \text{ mol L}^{-1}$  and  $[NHS-BB]_0/[monomers]_0 = 0.01$ .

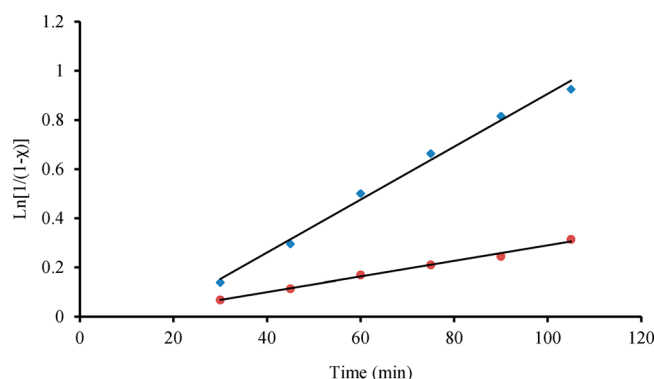
In Figure 11 a very small amount of tailing can be seen at low molecular weights, indicating a small population of dead chains. These dead chains probably form during the early stage of polymerization before the establishment of the reversible deactivation cycles of the dormant chains capped with the SG1. Another indicator of this phenomenon is the nonzero intercept of the  $M_n$  versus conversion graph.

**Temperature.** Temperature has a direct effect on the decomposition of the alkoxyamine, which can affect the rate of



**Figure 11.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 90 °C using NHS-BB as alkoxyamine and SG1 as nitroxide ( $[SG1]_0/[NHS-BB]_0 = 0.2$ ) with  $[DEAEMA]_0 = 0.5 \text{ mol L}^{-1}$  and  $[NHS-BB]_0/[monomers]_0 = 0.01$ .

polymerization. To assess the effect of temperature on the NMP of DEAEMA in water, experiment 8 in Table 1 was repeated at 80 °C (exp 9, Table 1). At lower temperature the decomposition of NHS-BB alkoxyamine is lower, and polymerization is therefore also slower compared to 90 °C (Figure 12).

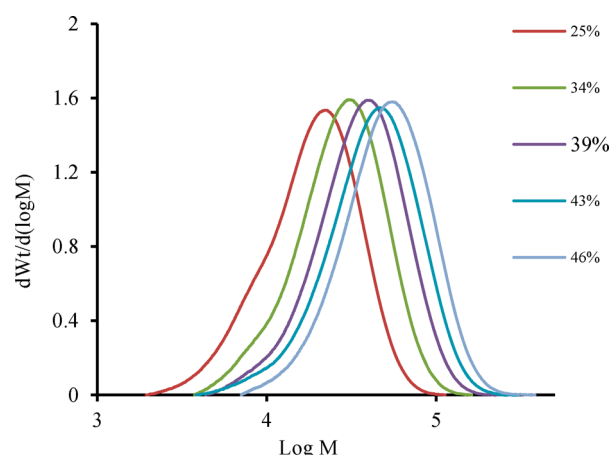


**Figure 12.** Plot of  $\ln[1/(1 - \chi)]$  versus time for the NMP of DEAEMA with 9 mol % acrylonitrile in water using NHS-BB as alkoxyamine and SG1 as nitroxide ( $[SG1]_0/[NHS-BB]_0 = 0.2$ ): square:  $T = 90 \text{ °C}$ ; circle:  $T = 80 \text{ °C}$ .

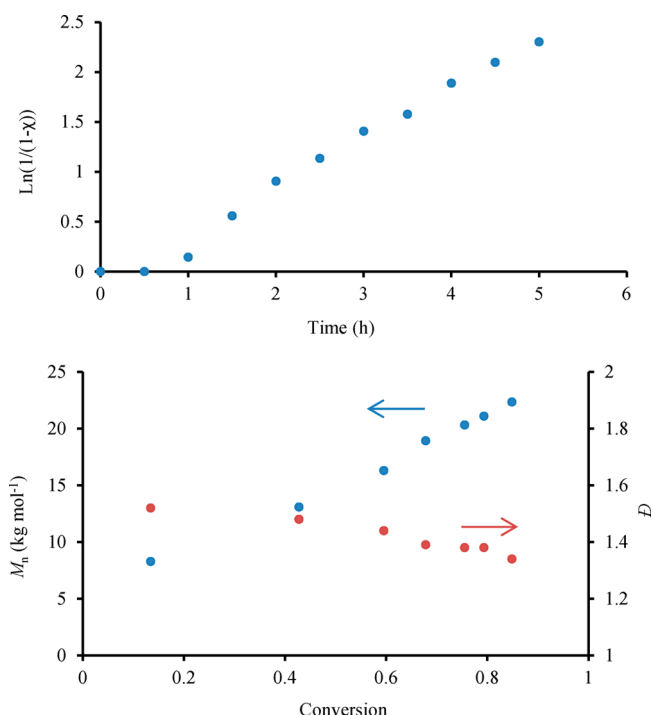
The final molar dispersity increased from 1.27 to 1.40 when lowering the temperature from 90 to 80 °C, but the livingness of the reaction remained very good (Figure 13). Lowering the temperature increases the time of activation–deactivation cycles of the dormant chains and as a result decreases the control over the polymerization.

Experiment 3 (Table 1) was repeated at 80 °C but with less SG1 to increase the conversion (exp 10, Table 1). Since the decomposition of VA-044 is slower at 80 °C compared to 90 °C, the polymerization should proceed more slowly but at the same time reducing the amount of SG1 will tend to increase the rate of polymerization. Again, excellent results indicating good control over the reaction and excellent livingness were obtained. Final conversion reached to 90% in 5 h (Figures 14 and 15).

**Chain Extension.** To check the ability of the poly-(DEAEMA-co-S)-SG1 macroalkoxyamine to be extended by a second block, a chain extension experiment was performed.



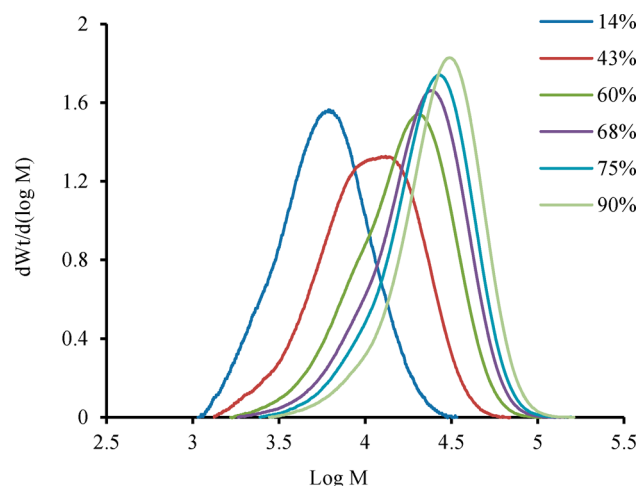
**Figure 13.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 80 °C using NHS-BB as alkoxyamine and SG1 as nitroxide with the ratio of  $[SG1]_0/[NHS-BB]_0 = 0.2$ .



**Figure 14.** Kinetic plots of the copolymerization of DEAEMA and acrylonitrile (initial molar fraction of acrylonitrile:  $f_{x0} = 0.09$ ) in water at 80 °C using VA-044 as initiator and SG1 as nitroxide ( $[SG1]_0/[VA-044]_0 = 1.5$  at 80 °C: (a)  $\ln[1/(1 - \chi)]$  versus time; (b)  $M_n$  and  $M_w/M_n$  versus conversion.

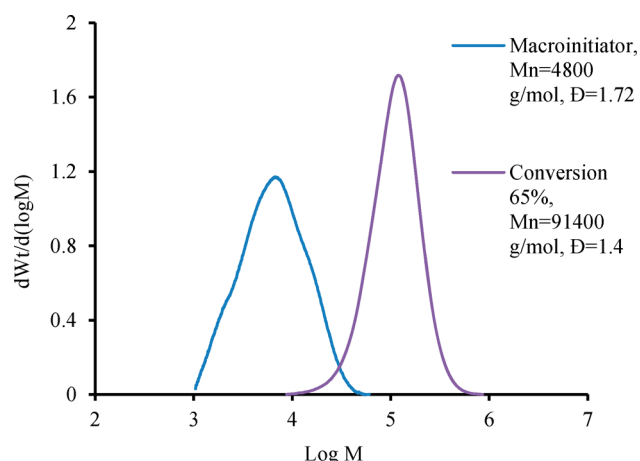
Experiment 1 in Table 1 was repeated but with a higher amount of initiator ( $[VA-044]_0/[monomers]_0 = 0.02$ ). VA-044 was chosen because it decomposes to radicals containing positively charged imidazole groups, which can help stabilize particles in emulsion. Then after 15 min (corresponding to 60% conversion based on  $^1H$  NMR observation) the contents of the reaction were added to the hydrophobic monomers (MMA and S). Styrene was used as a comonomer in both the first and second blocks. When the hydrophobic block attains a certain chain length which is no longer soluble in water, the diblock copolymer forms a particle based on a PISA process.<sup>32</sup> Here in our work the hydrophilic poly(DEAEMA-co-S) containing the





**Figure 15.** Evolution of MWDs with conversion during the NMP of DEAEMA with 9 mol % acrylonitrile in water at 80 °C using VA-044 as initiator and SG1 as nitroxide ( $[SG1]_0/[VA-044]_0 = 1.5$ ).

stabilizing moieties forms the shell of the particle and hydrophobic poly(MMA-*co*-S) forms the core of the particle. Unreacted monomers from the first step will be consumed at the start of the second step, and thus a gradient copolymer will be formed between the hydrophilic and hydrophobic blocks. Figure 16 shows the SEC chromatograms of the macroinitiator and latex. The complete shift of the MWD to the right confirms the livingness of the macroinitiator.



**Figure 16.** Evolution of MWDs with conversion during the chain extension experiment.

## CONCLUSION

Nitroxide-mediated polymerization of DEAEMA with a small amount of acrylonitrile was performed for the first time in water, an environmentally friendly and inexpensive solvent, using NHS-BB alkoxyamine without addition of free nitroxide. Results of the detailed kinetic study were presented, examining the effects of several parameters including initiating system, comonomer type, initiator concentration, DEAEMA concentration, temperature, and the ratio of free excess nitroxide to alkoxyamine. The polymerization reaction showed all the features of a well-controlled and living polymerization; linearity in the plots of  $\ln[1/(1 - \chi)]$  versus time, linear increase of  $M_n$  with conversion, and clear shifts of the MWD with conversion.

Successful chain extension of poly(DEAEMA-*co*-S) with MMA and S in water led to the *in situ* creation of poly(DEAEMA-*co*-S)-*b*-poly(MMA-*co*-S) diblock copolymer nanoparticles via the PISA process. Since the chain extension experiment in water showed promising results, we are currently working on a detailed study of the synthesis of PMMA latex by surfactant-free emulsion polymerization (SFEP) based on the PISA technique using poly(DEAEMA-*co*-AN) or poly(DEAEMA-*co*-S) macroalkoxyamine synthesized in water, followed chain extension with MMA in a one-pot process. This will be the subject of a forthcoming paper.

## ASSOCIATED CONTENT

### Supporting Information

Hydrolysis data at different pH and temperatures and  $^1H$  NMR of DEAEMA at 90 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada, the Ontario Research Chairs Program (Cunningham), and the Canada Research Chairs Program (Jessop) for financial support and Arkema Inc. for providing BlocBuilder and SG1.

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