TEMPO-Mediated *n*-Butyl Acrylate Polymerizations

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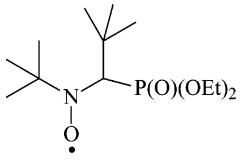
ABSTRACT: Polymerizations of *n*-butyl acrylate under stable free radical polymerization (SFRP) conditions, using TEMPO as the nitroxide mediator, are reported at reaction temperatures between 133 and 135 °C. The polymerizations proceed in a living manner under both bulk and miniemulsion conditions with polydispersities of around 1.3. Plots of number-average molecular weight vs conversion and $\ln([M]_0/[M])$ vs time are linear, indicating a controlled polymerization. It is argued that the ability of a particular nitroxide to control the polymerization of *n*-butyl acrylate is not only due to a favorable equilibrium constant (*K*) between the dormant and active polymeric species in the system but also due to the amount of excess nitroxide that is present. In these experiments excess TEMPO is controlled by the continuous addition of a dilute solution of ascorbic acid or an ascorbic acid derivative, leading to successful *n*-butyl acrylate polymerizations. Chain extension of a homopoly(*n*-butyl acrylate) prepared under miniemulsion conditions is demonstrated.

Introduction

A number of publications have shown that the polymerization of *n*-butyl acrylate is feasible by the stable free radical polymerization (SFRP) process with TEMPO and its derivatives as the nitroxide mediators, but only under unique conditions. For example, it has been shown that *n*-butyl acrylate can be polymerized in the presence of 4-oxo-TEMPO in a controlled manner, but the reaction temperature required was high, 155 °C, and polydispersities (>1.4) were broad.[1] Also, chain extension to high conversion of polystyrene terminated with TEMPO has been accomplished with *n*-butyl acrylate, but only under miniemulsion conditions.[2] Despite these results, it is still the general consensus that TEMPO is not an ideal mediator for acrylate polymerizations, thus relegating "the latter (TEMPO) to a niche role for select styrenic polymerizations".[3] To circumvent the perceived limitations of TEMPO to control the polymerization of acrylates, efforts were made to find other nitroxides that might be more successful. The work culminated in the discovery of a number of acyclic nitroxides that work very well for this purpose.[4,5]

Ananchenko et al.[6] reported that, for the polymerization of *n*-butyl acrylate mediated by TEMPO, the equilibrium constant *K* is unfavorably low when compared to the system in which DEPN **(1)** is the nitroxide



(1)

mediator. The low *K* value is attributed primarily to a lower dissociation rate constant k_d and a higher recombination rate constant k_c for TEMPO. The cleavage of the TEMPO/acrylate bond is not much faster than monomer conversion, and the rate of recombination of TEMPO with the active polymer chain end is fast as compared to the bulkier DEPN. As a result, it was concluded that linear increases in molecular weight vs increasing conversion and low final polydispersities cannot be obtained when TEMPO is the moderating nitroxide for *n*-butyl acrylate polymerizations.

However, in most cases, the polymerization of acrylates in the presence of TEMPO is not simply a case of an uncontrolled polymerization occurring. What actually happens is that polymerizations proceed to low conversions in the first hour and then stop.[7] While these results could certainly be used to conclude that once the acrylate/TEMPO bonds are formed they are too strong to break at a reasonable rate at typical SFRP reaction temperatures (130−135 °C) to allow the polymerizations to continue, this argument ignores the fact that random copolymers of styrene and *n*-butyl acrylate,[8] and styrene and *tert*-butyl acrylate,[9] can readily be prepared in the presence of TEMPO in high yield under similar conditions to those used for the polymerization of styrene. Acrylate/TEMPO bonds formed in these reactions must be sufficiently labile to allow these reactions to proceed. If not, there would be a continual buildup of acrylate/TEMPO bonds, causing the polymerization to slow down and eventually stop. This is not observed.

It is our contention that the difficulty associated with TEMPO-mediated polymerizations of *n*-butyl acrylate is directly related to the excess free nitroxide that builds up in the reaction mixture due to termination reactions that occur throughout the course of the polymerizations. The excess nitroxide shifts the equilibrium that exists between the TEMPO-capped dormant polymer chains and the uncapped propagating polymer chains in these living-radical polymerizations to the left, as depicted in Scheme 1, causing the polymer chains to exist almost exclusively in the dormant state. In this state the polymer chains cannot add monomer, and the polymerization is effectively inhibited.

We would submit that the reason random copolymerizations of styrene and acrylates are successful is because there is sufficient styrene present in these polymerizations to allow the autopolymerization[10] mechanism of styrene to consume enough of the excess nitroxide to shift the equilibrium in Scheme 1 to the right, allowing the polymerization to proceed. That being the case, it would suggest that if a reagent can

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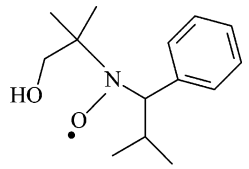
Scheme 1. Equilibrium between Active and Dormant Polymer Chains under SFRP Conditions Where P_n is a Polymer Chain with *n* Monomer Units and T is a Terminating Agent, in This Case TEMPO

$$P_n\text{—}T \rightleftharpoons P_n\bullet + \text{excess } T$$

be found to effectively reduce the excess nitroxide in the acrylate polymerizations, any nitroxide should be able to be used for these polymerizations. Keeping in mind that the acyclic nitroxides used at present to affect the polymerization of acrylates require multistep syntheses to prepare, some tend to be unstable and decompose upon storing, and most, if not all, are very expensive; the development of an acrylate polymerization process based on TEMPO becomes important both for practical and economic reasons.

In this paper we demonstrate in a clear and unequivocal manner that, contrary to accepted opinion, *n*-butyl acrylate can be polymerized in a living manner under SFRP conditions with TEMPO as the nitroxide mediator. A continuous addition to the reaction mixture of a dilute solution of ascorbic acid, or an ascorbic acid derivative, is the key to the success of these polymerizations. The polymerizations can be performed under either bulk or miniemulsion conditions at temperatures typically used for the polymerization of styrene. In the case of the miniemulsion polymerization, for which we have comparable data, the polydispersities of the resulting homopoly(*n*-butyl acrylates) are essentially the same as those we obtained with acyclic nitroxide **2**. Chain extension of these homopolymers provides further supporting evidence for the livingness of the homopolymers.



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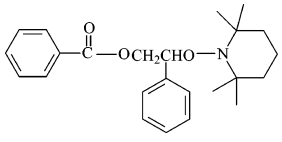
Experimental Section

(a) Materials and Equipment. The unimer, BST (**3**), was prepared as described[11] and recrystallized from 2-propanol. TEMPO was purified by sublimation. 4-Oxo-TEMPO was recrystallized from hexanes. Camphorsulfonic acid (CSA), ascorbic acid, ascorbic acid 6-palmitate, 1,1′-azobis(cyclohexanecarbonitrile) (Vazo 88), tetrahydrofuran (THF), *n*-butyl acrylate, *tert*-butyl acrylate, and styrene were used as received.



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Molecular weights and polydispersities were estimated by gel permeation chromatography (GPC) using a Waters/Millipore liquid chromatograph equipped with a Waters model 510 pump, Ultrastyragel columns HR3, HR1, and HR4E, and a Waters model 410 differential refractometer (RI). Polystyrene standards were used for calibration. Polymer molecular weights for poly(*n*-butyl acrylate) reported were calculated with the following Mark−Houwink coefficients: $K_{PS} = 11.4 \times 10^{-5}$ dL g^{-1} and $\alpha_{PS} = 0.706$; $K_{PBA} = 12.2 \times 10^{-5}$ dL g^{-1} and $\alpha_{PBA} = 0.700$.[12] THF was used as the eluent at a flow rate of 0.5 mL min^{-1}. GPC was performed on samples taken directly from the reaction mixture. In the case of bulk polymerizations, unreacted monomer was removed by evaporation with a stream of air before GPC analysis. For miniemulsion polymerizations, the reaction mixture was diluted with a 3-fold excess of a brine solution, and the polymer was extracted using ethyl acetate. The ethyl acetate was then evaporated with a stream of air. The miniemulsion reaction mixtures were prepared, and reactions were performed as reported previously.[13] A Harvard PHD 4400 programmable syringe pump was used for the addition of the ascorbic acid solutions. The rates that were used for the addition of the different solutions used in the various experiments were determined empirically.

Table 1. Bulk Polymerization of *n*-Butyl Acrylate Controlled by the Addition of a 2.3×10^{-3} M Solution of Vazo 88 in *n*-Butyl Acrylate

time (h)	M_n (g mol^{-1})	PD	% conversion
0.5	930		5
1.5	2889	1.73	11
3.0	8674	1.68	29
4.0	11799	1.56	36

(b) Typical Bulk *n*-Butyl Acrylate Polymerization. *n*-Butyl acrylate was added to a mixture of BST and 4-oxo-TEMPO in a three-necked round-bottom flask equipped with a reflux condenser, a septum, and a thermometer. Argon gas was introduced via a syringe needle through the septum to deoxygenate the reaction mixture. The reaction mixture was heated in an oil bath whose temperature was adjusted to maintain a reaction temperature of 133 °C. A solution of either ascorbic acid in THF or water, or ascorbic acid 6-palmitate in *n*-butyl acrylate, deoxygenated with argon, was added dropwise through the septum via a syringe needle attached to a syringe pump, at a rate determined by the particular solution used, as described below. Reactions were typically taken to 50% conversion and stopped. Samples were removed every hour to monitor monomer conversion. Monomer conversions were calculated from the ratio of the weight of polymer formed over the weight of the sample taken from the reaction solution, times 100.

(c) Bulk Polymerization of *n*-Butyl Acrylate with Vazo 88. *n*-Butyl acrylate (25 mL) was added to a mixture of BST (0.25 g, 6.6×10^{-4} mol) and 4-oxo-TEMPO (0.8 mg. 4.7×10^{-6} mol) and heated under argon. Once the solution had reached a temperature of 133 °C, a solution of Vazo 88 in *n*-butyl acrylate (2.3×10^{-3} M) was added at a rate of 1.25 mL/h. Samples were removed after 0.5, 1.5, 3, and 4 h and analyzed for conversion, molecular weight, and polydispersity (PD). The results are summarized in Table 1. The GPC molecular weight distributions are shown in Figure 1.

(d) Bulk Polymerization of *n*-Butyl Acrylate with Ascorbic Acid in Water. *n*-Butyl acrylate (20 mL) was added to a mixture of BST (0.15 g, 3.9×10^{-4} mol) and 4-oxo-TEMPO (0.4 mg, 2.3×10^{-6} mol) and heated under argon. Once the solution had reached reaction temperature, a solution of ascorbic acid in water (2.8×10^{-3} M) was added at a rate of 0.20 mL/h. After 4 h GPC analysis showed the polymer to have a number-average molecular weight (M_n) of 8316 g mol^{-1} and a PD of 1.4. The conversion was 26%. At this point approximately 0.8 mL of the aqueous ascorbic acid solution had been added, and the water in the reaction mixture caused the temperature of the reaction mixture to slowly drop to 117 °C; the polymerization stopped as indicated by no further increase in conversion with time.

(e) Bulk Polymerization of *n*-Butyl Acrylate with Ascorbic Acid in THF. *n*-Butyl acrylate (30 mL) was added to a mixture of BST (0.40 g, 1.05×10^{-3} mol) and 4-oxo-TEMPO (0.8 mg, 4.5×10^{-6} mol) and heated under argon. Once the solution had reached reaction temperature, a solution of ascorbic acid in THF (2.8×10^{-3} M) was added beginning at a rate of 0.25 mL/h and increased every half hour by 0.05 mL/h. Samples were removed after 1, 2, 3, 5, and 7 h and analyzed for conversion, molecular weight, and polydispersity. The results are summarized in Table 2. The GPC molecular weight distributions are shown in Figure 2.

(f) Bulk Polymerization of *n*-Butyl Acrylate with Ascorbic Acid 6-Palmitate in *n*-Butyl Acrylate. *n*-Butyl

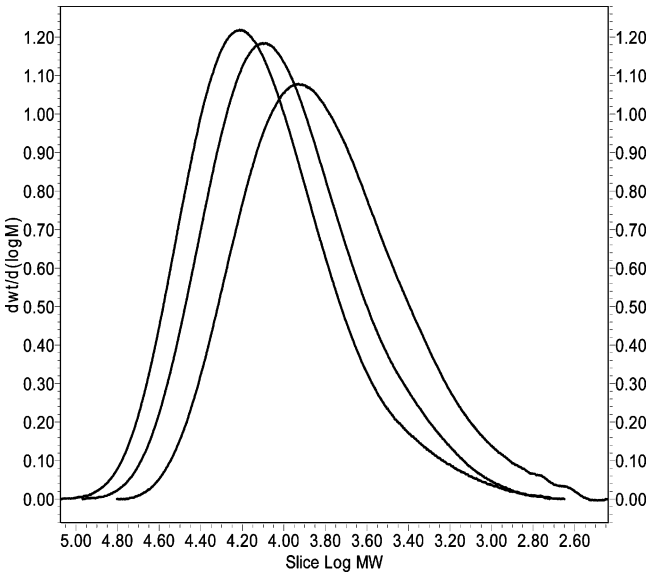

Figure 1. GPC molecular weight distribution plot for the bulk homopolymerization of *n*-butyl acrylate controlled by the addition of a 2.3×10^{-3} M solution of Vazo 88 in *n*-butyl acrylate.

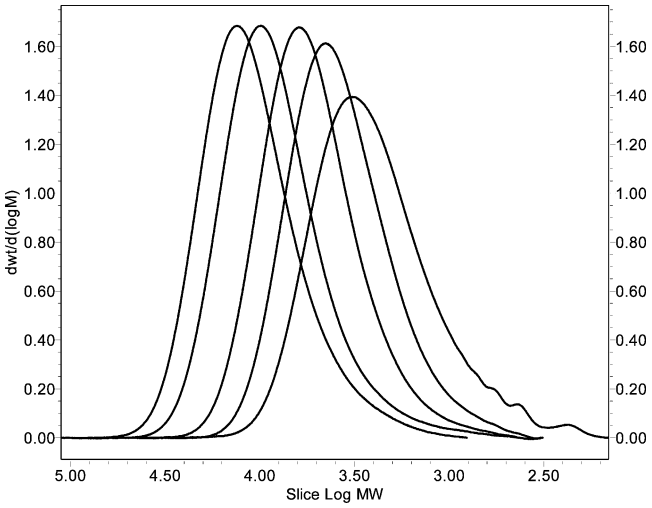

Figure 2. GPC molecular weight distribution plot for the bulk homopolymerization of *n*-butyl acrylate controlled by the addition of a 2.8×10^{-3} M solution of ascorbic acid in THF.

Table 2. Bulk Polymerization of *n*-Butyl Acrylate Controlled by the Addition of a 2.8×10^{-3} M Solution of Ascorbic Acid in THF

time (h)	M_n (g mol^{-1})	PD	% conversion
1	2164		10
2	3170	1.45	14
3	4930	1.34	24
5	8010	1.33	39
7	10426	1.33	51

acrylate (25 mL) was added to a mixture of BST (0.25 g, 6.6×10^{-4} mol) and 4-oxo-TEMPO (0.4 mg, 2.3×10^{-6} mol) and heated under argon. Once the solution had reached reaction temperature, a solution of ascorbic acid 6-palmitate in *n*-butyl acrylate (1.4×10^{-2} M) was added at a rate of 1.0 mL/h for the first hour. The rate was then increased to 1.2 mL/h and maintained at that rate throughout the rest of the reaction. Samples were removed after 0.5, 1.5, 2.5, 3.5, and 4.5 h and analyzed for conversion, molecular weight, and polydispersity. The results are summarized in Table 3. The GPC molecular weight distributions are shown in Figure 3.

The above reaction was repeated using a solution of ascorbic acid 6-palmitate in *n*-butyl acrylate (3.2×10^{-3} M) injected at a rate of 0.25 mL/h and increased every half hour by 0.1 mL/h. After 4.5 h the M_n of the polymer was 3651 g mol^{-1} with a PD of 1.31, and the conversion was 19%.

Table 3. Bulk Homopolymerization of *n*-Butyl Acrylate Controlled by the Addition of a 1.4×10^{-2} M Solution of Ascorbic Acid 6-Palmitate in *n*-Butyl Acrylate

time (h)	M_n (g mol^{-1})	PD	% conversion
0.5	3 105		10
1.5	6 460	1.50	18
2.5	10 033	1.44	30
3.5	12 951	1.40	37
4.5	16 156	1.35	45

(g) Miniemulsion Polymerization of *n*-Butyl Acrylate with Ascorbic Acid in Water. A miniemulsion mixture was prepared by emulsifying a solution of BST (400 mg; 1.05×10^{-3} mol), TEMPO (6 mg; 3.8×10^{-5} mol), and hexadecane (1.2 g) in *n*-butyl acrylate (30 mL) with a solution of sodium dodecylbenzenesulfonate (1.2 g) in distilled water (120 mL). The reaction was heated to 135 °C in a modified Parr bomb reactor under 6.9 bar of pressure for 6 h. A solution of ascorbic acid in water (3.2×10^{-2} M) was injected throughout the course of the reaction at the following rates:[14]

time (h)	addition rate (mL/h)
start	1.2
1	0.6
2	0.8
3	1.2
4	1.5
5	2.0

Samples were removed every hour and analyzed for conversion, molecular weight, and polydispersity. The results are summarized in Table 4. The GPC molecular weight distributions are shown in Figure 4.

(h) Block Copolymer Synthesis; Chain Extension of Poly(*n*-butyl acrylate). A 50 mL portion of the miniemulsion polymerization described in (g) was diluted with 150 mL of a brine solution, and the resulting aqueous mixture was extracted with ethyl acetate (50 mL). The ethyl acetate solution was washed with a fresh solution of brine, dried over sodium sulfate, filtered, and evaporated to dryness to provide a clear thick oil poly(*n*-butyl acrylate). Poly(*n*-butyl acrylate) (3 g), TEMPO (1 mg), and CSA (4 mg) were dissolved in 8 mL of a 1:1 (v/v) solution of *tert*-butyl acrylate and styrene, degassed with argon, and heated to 127 °C for 1.5 h. Samples were removed every half hour, and the resulting polymers were analyzed by GPC. The molecular weights and polydispersities for these samples are shown in Table 5. The GPC distributions are shown in Figure 5.

Results and Discussion

We have argued in the case of styrene that the rate of polymerization is controlled by excess nitroxide in the reaction mixture, where excess nitroxide is defined as nitroxide not associated with a polymer chain.[15] The excess nitroxide is produced by various termination reactions that occur throughout the polymerization. In the case of styrene, autopolymerization produces new radicals that can consume some of the excess nitroxide and additives, such as CSA,[16] 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS),[17] and acetic anhydride,[18] can be added to consume more, to enable the polymerizations to proceed at a reasonable rate. Published electron spin resonance (ESR) data for FMPTS show that the rate of styrene polymerizations increase as the concentration of nitroxide decreases and that the concentration of nitroxide deceases as the concentration of FMPTS increases.[7] Under bulk conditions, without these additives, the polymerization of styrene is slow, taking 70 h to achieve 90% conversion.[19] With these

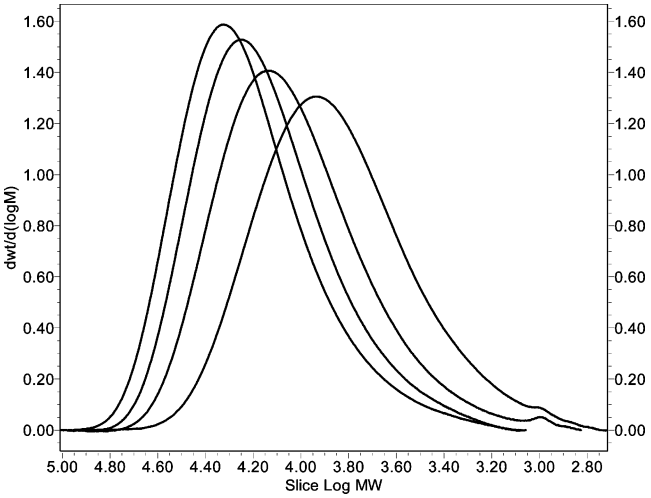

Figure 3. GPC molecular weight distribution plot for the bulk homopolymerization of *n*-butyl acrylate controlled by the addition of a 1.4×10^{-2} M solution of ascorbic acid 6-palmitate *n*-butyl acrylate.

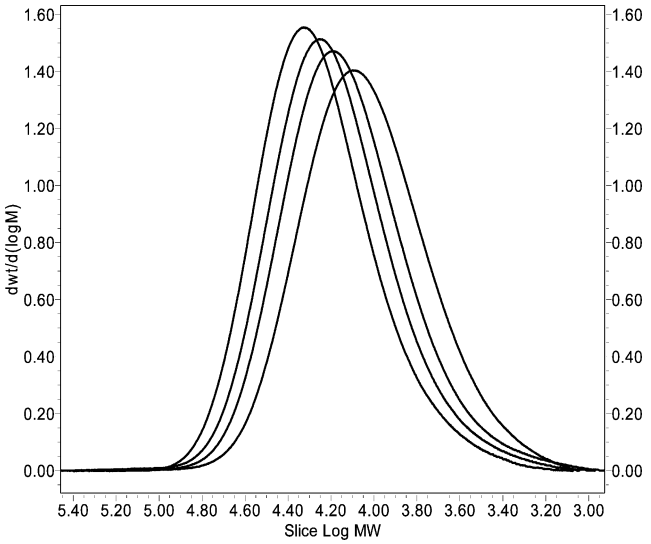

Figure 4. GPC molecular weight distribution plot for the miniemulsion homopolymerization of *n*-butyl acrylate controlled by the addition of a solution of ascorbic acid in water.

Table 4. Miniemulsion Polymerization of *n*-Butyl Acrylate Moderated by the Addition of a Solution of Ascorbic Acid in Water

time (h)	M_n (g mol^{-1})	PD	% conversion
2	6 755		
3	10 647	1.47	30
4	15 573	1.36	41
5	16 594	1.36	49
6	18 594	1.35	53

additives, polymerizations of styrene readily proceed to greater than 75% conversion in 6 h at a temperature of 135 °C.[16]

In stark contrast, TEMPO-mediated polymerizations of acrylates proceed to less than 10% conversion in the first 30−60 min and then stop. ESR data show that the concentration of nitroxide is relatively low at the beginning of these polymerizations but continues to increase over time.[7] We continue to believe that acrylate polymerizations are inhibited by this excess nitroxide. Acrylates do not display an autopolymerization mechanism that can generate new radicals to consume the excess nitroxide and the additives mentioned earlier,

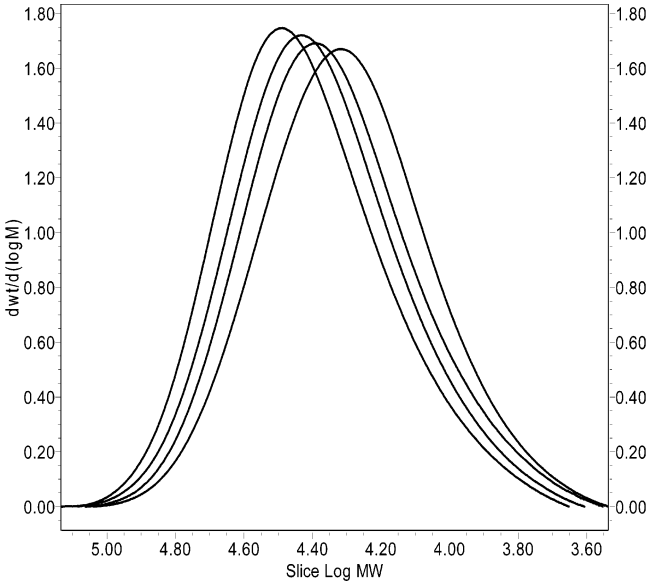

Figure 5. Chain extension of poly(*n*-butyl acrylate) prepared under miniemulsion conditions with a 1:1 solution by volume of *tert*-butyl acrylate and styrene. The distribution on the right corresponds to the starting poly(*n*-butyl acrylate).

Table 5. Chain Extension of Poly(*n*-butyl acrylate) Prepared under Miniemulsion Conditions with a 1:1 Solution by Volume of *tert*-Butyl Acrylate and Styrene

time (h)	M_n (g mol^{-1})	PD
0	17 874	1.34
0.5	19 729	1.33
1	21 730	1.33
1.5	24 025	1.33

which are so effective in increasing the rate of styrene polymerizations, are ineffective with *n*-butyl acrylate.

Therefore, a program was initiated to investigate other additives that would react with the excess TEMPO to see how they might affect the polymerization of *n*-butyl acrylate under SFRP conditions.

Some initial success was achieved by slowly adding the initiator molecule Vazo 88, dissolved in monomer, to the reaction mixture.[20] However, while the polymerization did appear living, and incremental increases in molecular weight were achieved, the polydispersities were typically broad (1.6 and greater) due to significant tailing at the low molecular weight end of the GPC distribution (Figure 1, Table 1). The primary radicals generated by the thermal dissociation of Vazo 88 can add to TEMPO to give an adduct that can initiate new polymer chains, or they can react with monomer first, followed by TEMPO, to give short oligomers that can react further to give new polymer chains. Either way, it would appear that enough new chains are generated throughout the polymerization to broaden the polydispersity. Attempts to minimize the formation of these new polymer chains, and thereby narrow the molecular weight distributions (MWDs) of the polymers, by either slower addition of the Vazo 88 solution or using less concentrated solutions, were unsuccessful.

We next turned our attention to ascorbic acid, which reacts quickly and quantitatively with nitroxides to form hydroxyamines.[21] In an earlier communication, we reported on some initial success using ascorbic acid to enable the polymerization of *n*-butyl acrylate under miniemulsion conditions.[2] In these new bulk polymerizations the ascorbic acid was added at the beginning

of the polymerization along with all the other reagents. While the polymer chains increased in molecular weight with time, the growth of the polymer chains was uneven. Relatively large increases in molecular weight were observed in the first hour of polymerization, but only modest increases occurred in the subsequent hours. In addition, MWDs were broad (1.7−1.8), suggesting an uncontrolled polymerization. It was speculated at the time that the broad MWDs might have been due to too much ascorbic acid being present early in the polymerization. Disproportionate amounts of ascorbic acid destroy not only the excess nitroxide but also the nitroxide that otherwise needs to be present to cap the propagating polymer chains. The uncapped polymer chains grow in an uncontrolled manner and eventually terminate, giving rise to dead polymer chains that contribute to a broadening in the MWD. Methods for the slow continuous addition of ascorbic acid to the reaction mixture were studied in an attempt to solve this problem.

The ideal scenario would have been to add the ascorbic acid as a solution in *n*-butyl acrylate. However, ascorbic acid was found to be too insoluble in *n*-butyl acrylate to attempt this approach. Addition of an aqueous solution of ascorbic acid to the *n*-butyl acrylate reaction mixture initially seemed to work in that molecular weights were seen to increase in a controlled fashion in the first 4 h. However, after this time, as the amount of water built up in the reaction mixture, the temperature of the reaction mixture dropped to 117 °C and the polymerization stopped.

The addition of a solution of ascorbic acid in THF proved more successful. The results of a typical *n*-butyl acrylate polymerization performed under these conditions are summarized in Table 2, with the corresponding GPC distributions shown in Figure 2. Molecular weights are seen to increase in an incremental fashion over time to high conversions while a narrow MWD is maintained. What remains puzzling about these reactions is that the rate of addition of the ascorbic acid solution must be increased as the reaction proceeds, or the reaction slows down to the point where conversions are less than 2% per hour. A control reaction in which no ascorbic acid was added proceeded to 6% conversion in the first hour and then stopped to give an oligomer with an M_n of 2000 g mol^{-1} and a PD of 1.6.

In an attempt to demonstrate that the rate of polymerization is controlled by the amount of ascorbic acid that is added, a 1.4×10^{-3} M solution of ascorbic acid in THF was prepared. However, attempts to add this concentrated solution to the reaction mixture resulted in the dispensing syringe needle becoming blocked. Because of the temperature at which the polymerizations are performed, the void volume in the reaction flask was sufficiently hot that some of the THF emerging from the syringe needle evaporated, causing the ascorbic acid to crystallize and block the needle. To circumvent this problem, ascorbic acid was replaced by ascorbic acid 6-palmitate, a derivative of ascorbic acid that has an appreciable solubility in organic solvents such as *n*-butyl acrylate. Besides being more compatible with the reaction mixture, the high boiling point of *n*-butyl acrylate ensures that it will not evaporate at the syringe tip as it is being added to the reaction mixture. With the addition of a 1.4×10^{-2} M solution of ascorbic acid 6-palmitate in *n*-butyl acrylate at a rate of 1.2 mL/h the polymerization of *n*-butyl acrylate proceeded in a controlled fashion to 45% conversion in 4.5 h. The results of this reaction are summarized in Figure 3 and Table 3. In comparison, the addition of a 3.2×10^{-3} M solution of ascorbic acid 6-palmitate in *n*-butyl acrylate at an average rate of 1.2 mL/h similarly resulted in a controlled polymerization, but the conversion was only 19% after 4.5 h. These results confirm that the rates of polymerization are directly affected by the amount of ascorbic acid or its derivatives added per unit time.

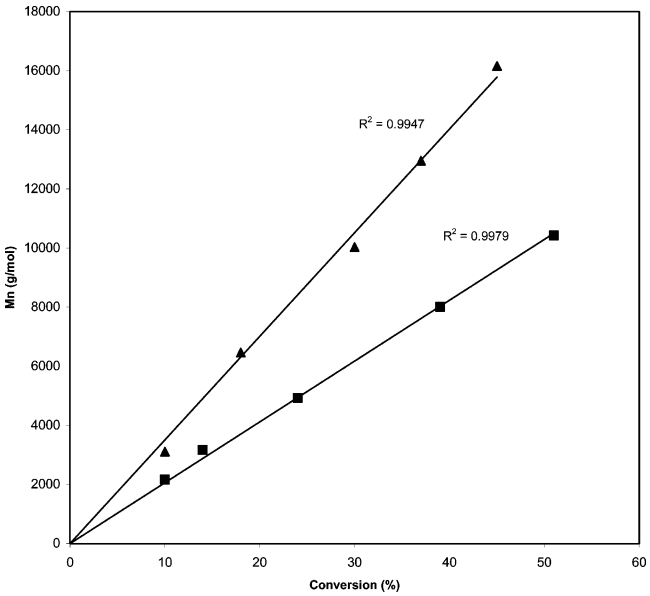

Figure 6. Number-average molecular weight vs conversion plot for the bulk polymerization of *n*-butyl acrylate under SFRP conditions: ■, 2.8×10^{-3} M ascorbic acid in THF; ▲, 1.4×10^{-2} M ascorbic acid 6-palmitate in *n*-butyl acrylate.

The use of ascorbic acid to enable TEMPO-mediated *n*-butyl acrylate polymerizations is also applicable to miniemulsion polymerizations. The slow continuous addition of a solution of ascorbic acid in water to a miniemulsion polymerization of *n*-butyl acrylate gives the results shown in Figure 4 and Table 4. As was the case for the bulk polymerization, the miniemulsion polymers increased in molecular weight in an incremental fashion while narrow MWDs were maintained. It should be noted that the PD of 1.35 obtained in this experiment is comparable to the PD of 1.27 we reported for the miniemulsion polymerization of *n*-butyl acrylate using the acyclic nitroxide (**2**)[2]. However, the rate of polymerization was higher with nitroxide (2) (87% conversion in 4 h) as compared to TEMPO (53% conversion in 5 h) under comparable miniemulsion conditions. The lower rate of polymerization with TEMPO may be due to a lower *K* for TEMPO as compared to (**2**) but could as likely be due to the rate of addition of ascorbic acid not being optimized.

Chain extension of the poly(*n*-butyl acrylate) product isolated from the miniemulsion polymerization, under bulk conditions using a solution of *tert*-butyl acrylate and styrene (1:1 v/v),[22] proceeded smoothly to give a block copolymer in which the original narrow polydispersity of the starting material was maintained (Table 5). Well-behaved incremental shifting of the molecular weight distributions is also observed (Figure 5).

As an indication of the livingness of the ascorbic acid and ascorbic acid 6-palmitate mediated polymerizations, straight-line relationships are obtained for plots of M_n vs conversion and $\ln([M]_0/[M])$ vs time for the bulk polymerizations as shown in Figures 6 and 7,

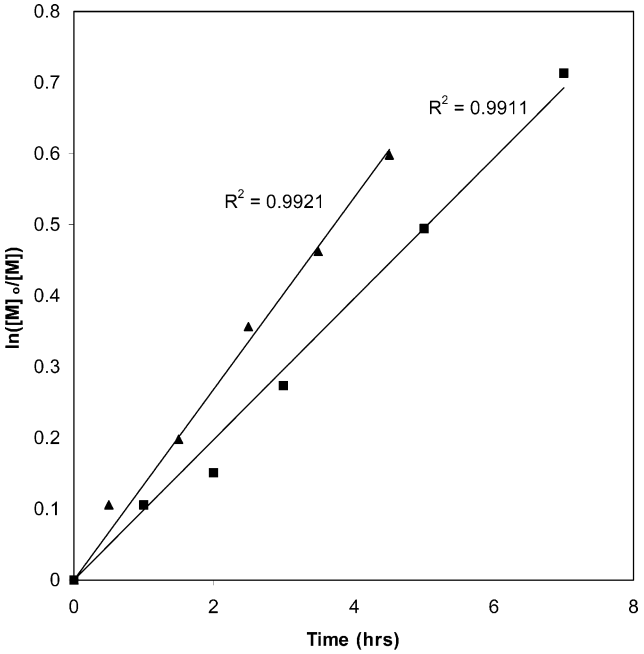

Figure 7. Plot of $\ln([M]_0/[M])$ vs time for the bulk polymerization of *n*-butyl acrylate under SFRP conditions: ■, 2.8×10^{-3} M ascorbic acid in THF; ▲, 1.4×10^{-2} M ascorbic acid 6-palmitate in *n*-butyl acrylate.

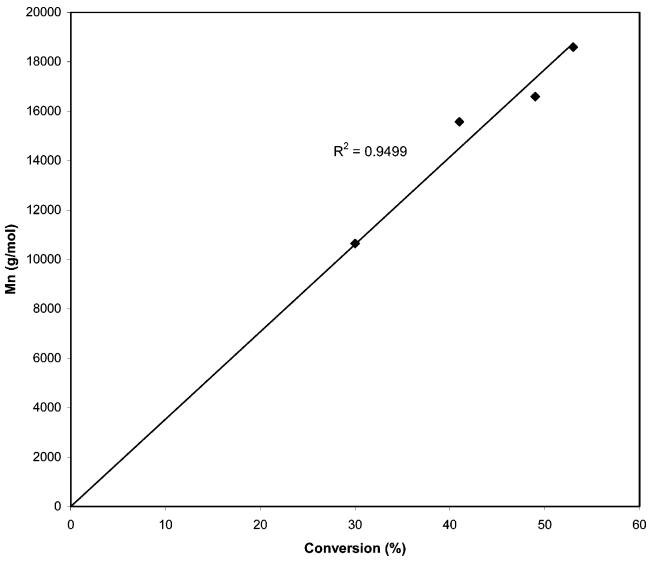

Figure 8. Number-average molecular weight vs conversion plot for the miniemulsion polymerization of *n*-butyl acrylate under SFRP conditions controlled by the addition of an aqueous solution of ascorbic acid.

respectively. Similar straight-line relationships are obtained for the miniemulsion polymerizations (Figures 8 and 9).

It is instructive to note that while the slow addition of ascorbic acid, or ascorbic acid 6-palmitate, to the reaction mixture is key to ensuring that a large excess of ascorbic acid is not present at any given time to destroy too much nitroxide, there is never a consistently even amount of ascorbic acid present. Each addition of a drop of the ascorbic acid solution causes an immediate rise in the ascorbic acid concentration, which drops over time as it reacts with TEMPO. Then there is another spike in the ascorbic acid concentration as the next drop is added. It would seem that if an in situ method can be found to control the excess nitroxide, the rates of the

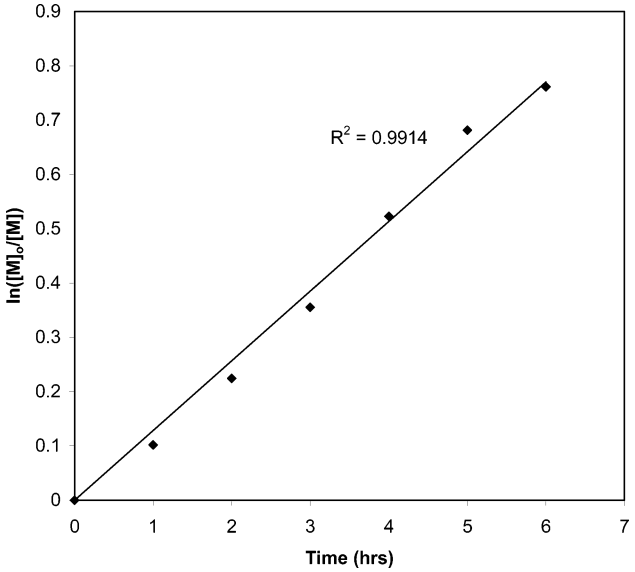

Figure 9. Plot of $\ln([M]_0/[M])$ vs time for the miniemulsion polymerization of *n*-butyl acrylate under SFRP conditions controlled by the addition of an aqueous solution of ascorbic acid.

polymerization and the polydispersities could be optimized further. Work is continuing in that direction.

While the ability of some acyclic nitroxides to enable acrylate polymerizations may be due, as reported, to their higher *K* values with acrylates, it is also distinctly possible that their success is due to their inherent instability at the elevated temperatures of the polymerization. This inherent instability provides an internal control over the excess nitroxide that would otherwise impede the polymerization. The argument about the instability of one of these acyclic nitroxides at high temperatures has been used to explain a deviation in a $\ln([M]_0/[M])$ vs time plot for the polymerization of *n*-butyl acrylate.[23]

In summary, we have demonstrated in a clear and unambiguous manner that acrylates can be polymerized under SFRP conditions with TEMPO as the mediating nitroxide. While the equilibrium constant *K* for a particular monomer with a particular nitroxide can be used to explain the success of some nitroxides to successfully polymerize acrylates, the results in this paper show that nitroxides with unfavorable *K* values can also be used if the excess nitroxide in the reaction medium is controlled. ESR studies have been initiated to look at the relationship between ascorbic acid addition, TEMPO concentrations, and rates of reaction. Studies are continuing to identify an additive that can be added in one step at the beginning of the polymerization and that will slowly react with the excess nitroxide in a more uniform and continuous manner.[24] It is anticipated that the success of this endeavor will lead to faster rates of reaction and improved control over polymer polydispersities.

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Note Added after ASAP Posting. This article was posted ASAP on 01/07/2004. Changes have been made to Table 1. The correct version was posted on 01/21/2004.

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