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# Stable free radical polymerization of *n*-butyl acrylate in the presence of high-temperature initiators

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ABSTRACT

Living radical polymerizations of acrylate are known to be difficult to achieve using TEMPO as a mediator. The stable free radical polymerization (SFRP) of acrylate tends to stop at low monomer conversion due to the accumulation of TEMPO in the medium as a result of unavoidable bimolecular termination. Rather than solving this problem by destroying the excess nitroxide using ascorbic acid or glyceraldehyde associated with pyridine as reported recently, high temperature initiators were used to slowly and continuously generate new radicals throughout the polymerization to consume the excess TEMPO molecules. Polymerizations of *n*-butyl acrylate initiated by the alkoxyamine unimer (1-benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST) were performed between 130 °C and 134 °C in the presence of a series of high temperature peroxide and azo initiators. The best results in this study were obtained by the continuous addition of small amounts of di-*tert*-amyl peroxide throughout the polymerization. Under these conditions, the acrylate polymerizations fulfilled the criteria of a controlled polymerization process although the molecular weight distributions were slightly broad ($M_w/M_n \sim 1.5$).

## 1. Introduction

It is now well established that living radical polymerizations, such as the stable free radical polymerization (SFRP) [1–4], atom transfer radical polymerization (ATRP) [5–8], reversible addition-fragmentation chain transfer (RAFT) polymerization [9] and degenerative transfer polymerization using iodine exchange [10], lead to well-defined polymers with predictable molecular weights and narrow molecular weight distributions (MWDs). Our main focus has been the SFRP process and, as is the case with other research groups, we are interested in studying and understanding why this process has had difficulty in enabling the polymerization of acrylates as a class of monomers. Much has been written on this subject and it remains an intriguing issue.

Early attempts at polymerizing *n*-butyl acrylate in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) resulted in conversions of less than 10% in the first hour with no further increase upon continued heating. These results prompted one author to comment that TEMPO would be relegated “to a niche role for select styrenic polymerizations” [4]. It was subsequently suggested that the inability to polymerize *n*-butyl acrylate in the presence of TEMPO is due to a low equilibrium constant $K$, in turn attributed primarily to a low rate constant, $k_d$, for the dissociation of TEMPO from the polymer chain end, and a high recombination rate constant, $k_c$ [11]. These conclusions prompted the development and use of different nitroxides for acrylate polymerization, an approach that has proven to be quite successful. The first of these nitroxides, a phosphorus containing acyclic nitroxide, N-*tert*-butyl-N-

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[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1), was reported by Gnanou and coworkers [12,13]. A typical polymerization of *n*-butyl acrylate performed at 120 °C in the presence of SG1 and 1,1′-azobis(isobutyronitrile) (AIBN) with a [SG1]/[AIBN] ratio of 5/1 gave a poly(*n*-butyl acrylate) having a molecular weight of 17000 g mol$^{-1}$ and a polydispersity index of 1.09. Hawker subsequently used N-*tert*-butyl-isopropylphenylmethyl nitroxide (TIPNO) to prepare *n*-butyl acrylate polymers with molecular weights up to 76,500 g mol$^{-1}$ while keeping the polydispersity index below 1.1 [14,15]. In addition to a lower C–ON bond dissociation energy, a certain intrinsic instability of these acyclic nitroxides [16] is also a factor for their success as moderating agents for acrylate polymerizations. Recently, sterically hindered TEMPO-substituted alkoxyamines, such as the *trans*-2,6-diethyl-2,6-bis(1-trimethylsilanoxyethyl)-1-(1-phenylethoxy)piperidine, were synthesized by Studer and shown to promote high conversion (up to 89%) of styrene and *n*-butyl acrylate at temperatures between 70 and 105 °C while maintaining polydispersity indexes around 1.2 [17,18].

Our laboratory [19] took a different approach and continued to focus on TEMPO as the moderating nitroxide primarily based on the fact that solutions of styrene and *n*-butyl acrylate readily polymerize to high conversions to yield random copolymers with narrow MWDs [20]. On the basis of this result we were not convinced that a low $k_d$ and high $k_c$ were the only culprits in the inability of TEMPO to enable the successful polymerization of acrylates. We surmised instead that a larger problem was the inhibition of the polymerization caused by excess free nitroxide generated by unavoidable premature bimolecular termination of some of the propagating chains. In the case of styrene polymerization, autoinitiation generates enough new radicals to consume this excess nitroxide [21,22]. A corresponding mechanism does not exist for acrylates resulting in the accumulation of excess nitroxide, which inhibits the polymerization. The change in concentration of free nitroxide in the reaction mixture for a TEMPO-mediated SFRP process was studied by electron paramagnetic resonance (EPR) [23,24]. Whereas, during the polymerization of styrene a slow decay of the concentration of TEMPO was observed [23], the concentration of TEMPO increased when the polymerization of *n*-butyl acrylate was performed under similar conditions [24]. These results suggested that an additive that would consume the excess nitroxide should enable the polymerization of acrylates to proceed unencumbered. The key would be to find an additive that would just destroy the excess nitroxide that is formed as a result of bimolecular termination and destroy it at the same rate at which it is formed; not a trivial task.

Over the years, we have tried a number of different additives to control the excess nitroxide. The first approach involved the use of glucose as a reducing agent in the presence of sodium bicarbonate [25]. It was shown that the polymerization of *n*-butyl acrylate at 145 °C could reach conversions up to 60% in 6.5 h, however, the molecular weight distributions were consistently broad ($M_w/M_n$ above 1.6). A more successful approach involved a continuous slow addition of a dilute solution of ascorbic acid to a polymerization of *n*-butyl acrylate initiated with (1-benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST), a TEMPO-based alkoxyamine unimer [19]. Ascorbic acid reacts quickly and quantitatively with TEMPO reducing the nitroxide to the corresponding hydroxylamine [26]. An improvement to this strategy was recently reported by taking advantage of the tautomerization that exists between an α-hydroxyketone or aldehyde and its corresponding ene-diol in the presence of a base [27]. The best example of this approach was the use of glyceraldehyde in the presence of pyridine, added at the beginning of the polymerization. High conversions (above 50%) of *n*-butyl acrylate were achieved while maintaining narrow molecular weight distributions.

One can also imagine reducing the amount of the excess nitroxide with a second initiator which upon heating would generate new radicals that would react with the excess TEMPO. Matyjaszewski and Greszta [28] showed that the addition of dicumyl peroxide could enhance the rate of polymerization of styrene mediated by TEMPO while maintaining the livingness of the process. In a similar manner, Goto and Fukuda [29] used *tert*-butyl hydroperoxide (BHP) without adversely affecting the livingness of the system. The addition of a small amount of 1,1′-azobis-(cyclohexane-1-carbonitrile) (Vazo® 88) was used to increase the rate of polymerization for a styrene polymerization conducted at low temperatures (70–110 °C) using a spiro nitroxide [30].

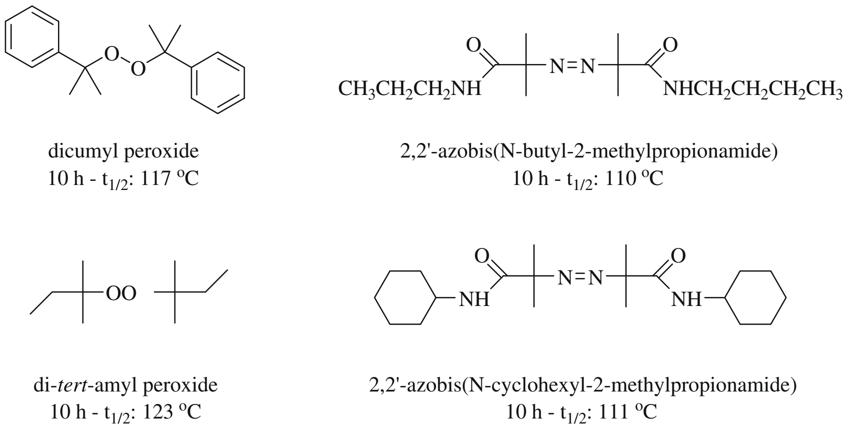
The addition of a second initiator was also used for the polymerization of acrylate monomers. For example, the polymerization of *tert*-butyl acrylate was studied using di-*tert*-butyl nitroxide and a small amount of dicumyl peroxide. The polymerization rate was increased due to the presence of the peroxide initiator, while no significant broadening of the molecular weight distribution was observed [31]. Vazo® 88 has been used in a similar manner with some success [19]. However, the instantaneous decomposition of the Vazo® 88 at the polymerization temperature of 130 °C required a continuous addition of tiny amounts of initiator throughout the polymerization rendering the process impractical.

With this background, and mindful that TEMPO is one of the least expensive nitroxides and readily available in very large quantities, we were interested in determining whether the autopolymerization of styrene could be mimicked in acrylate polymerizations by using high temperature initiators that would slowly, and continuously, generate new radicals that would consume any excess TEMPO that would be generated by bimolecular chain termination. Both high temperature peroxide and azo initiators were investigated (Fig. 1). The work presented in this paper was performed in parallel with the work conducted using α-hydroxyketones and aldehydes in the presence of a base [27].

## 2. Experimental

### 2.1. Materials

The inhibitor was removed from *n*-butyl acrylate (99+%) by passing it through an inhibitor removal column. Di-*tert*-


dicumyl peroxide
10 h - $t_{1/2}$: 117 °C

2,2'-azobis(N-butyl-2-methylpropionamide)
10 h - $t_{1/2}$: 110 °C

di-*tert*-amyl peroxide
10 h - $t_{1/2}$: 123 °C

2,2'-azobis(N-cyclohexyl-2-methylpropionamide)
10 h - $t_{1/2}$: 111 °C

**Fig. 1.** High-temperature initiators used in the study and their 10 h half-life (10 h–$t_{1/2}$).

amyl peroxide (Luperox® DTA, 97%), dicumyl peroxide (Luperox® DCP, ⩾99%), dimethyl sulfoxide (anhydrous, 99.9+%), 2,2′-azobis(N-butyl-2-methylpropionamide) (VAm-110), 2,2′-azobis(N-cyclohexyl-2-methylpropioamide) (VAm-111) were used as received. All the reagents were purchased from Sigma–Aldrich except the non-commercial VAm-110 and VAm-111 compounds, which were obtained from Wako. The alkoxyamine unimer (1-benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST) was synthesized according to a procedure developed in our laboratory [32].

### 2.2. General polymerization procedure

*n*-Butyl acrylate (20 mL, 140 mmol) was added to BST (381 mg, 1 mmol) in a round-bottom flask equipped with a reflux condenser, a septum and a thermometer. The system was degassed with argon gas. The reaction mixture was heated to 134 °C, except where otherwise noted, in an oil bath.

A stock solution of a high temperature initiator in monomer was prepared by dissolving it in *n*-butyl acrylate at a concentration of 0.5 mg per drop (9 mg) of *n*-butyl acrylate. The weight of initiator corresponded to 2.9 µmol of dicumyl peroxide, 1.8 µmol of di-*tert*-amyl peroxide and 1.6 µmol of 2,2′-azobis(N-butyl-2-methylpropionamide) per drop of *n*-butyl acrylate. The amount and the rate of addition of the high temperature initiator are specified under the tables of results.

### 2.3. Characterization

Polymer molecular weights and polydispersity indexes ($M_w/M_n$) were estimated by gel permeation chromatography (GPC) using a Waters/Millipore liquid chromatograph equipped with a Waters model 510 pump, Ultrastyragel© columns HR1, HR2 and HR4, and a Waters model 410 differential refractometer (RI). Polystyrene standards were used for calibration. THF was used as the eluent at a flow rate of 0.35 mL min$^{-1}$. GPC was performed on samples after removal of unreacted monomer by evaporation with a stream of air. Percentage conversions were determined gravimetrically.

## 3. Results and discussion

This study began with dicumyl peroxide as the high temperature initiator, which has a 10 h half-life of 117 °C in decane. A small amount of the initiator was introduced at the beginning of a polymerization of *n*-butyl acrylate initiated with BST (Table 1, entry 2). However, virtually no improvement in the rate of polymerization was observed for this polymerization when compared to a polymerization with no additive (Table 1, entry 1). On the other hand, the continuous addition of dicumyl peroxide in small amounts throughout the polymerization enabled the polymerization to proceed to relatively high conversion, i.e. 45% (Table 1, entry 3). Unfortunately, all the polymerizations attempted under these conditions gave *n*-butyl acrylate polymers with broad molecular weight distributions suggesting that the concentration of radicals

**Table 1**
*n*-Butyl acrylate polymerization in the presence of the dicumyl peroxide initiator at 130 °C.

| Entry | Time (h) | $M_{n,GPC}$ | $M_w/M_n$ | Conv. (%) | $M_{n,th}$ |
|---|---|---|---|---|---|
| 1[a] | 1 | 1000 | 1.53 | 7 | 1300 |
| | 3 | 1200 | 1.43 | 8 | 1400 |
| | 5 | 1400 | 1.36 | 9 | 1600 |
| | 7 | 1500 | 1.34 | 9 | 1600 |
| | 9 | 1600 | 1.29 | 9 | 1600 |
| | 22 | 1800 | 1.31 | 9 | 1600 |
| 2[b] | 1 | 1800 | 1.72 | 12 | 2100 |
| | 3 | 2100 | 1.57 | 12 | 2100 |
| | 5 | 2200 | 1.54 | 13 | 2300 |
| | 7 | 2200 | 1.52 | 13 | 2300 |
| | 9 | 2200 | 1.52 | 13 | 2300 |
| | 22 | 2300 | 1.49 | 14 | 2500 |
| 3[c] | 1 | 900 | 1.78 | 7 | 1300 |
| | 3 | 1600 | 1.36 | 9 | 1600 |
| | 5 | 2200 | 1.38 | 13 | 2300 |
| | 7 | 5000 | 2.00 | 30 | 5400 |
| | 9 | 7700 | 1.85 | 45 | 8100 |

[a] No addition of dicumyl peroxide.

[b] 7.4 µmol of dicumyl peroxide added at the beginning of the polymerization.

[c] 7.4 µmol of dicumyl peroxide added at the beginning of the polymerization and then 7.4 µmol of dicumyl peroxide added each subsequent hour.

in the reaction medium was too high. While the purpose of the radicals generated by the added high temperature initiator was to initiate new polymer chains which would react with the excess free nitroxide in the reaction medium, the amount of radicals produced is critical: if the concentration of produced radicals is too high, not only will they initiate new chains during the polymerization, but they will also increase the actual concentration of propagating chains thereby increasing the probability of bimolecular termination reactions leading to a broad molecular weight distribution of the polymer chains.

To lower the amount of radicals generated per unit of time we replaced dicumyl peroxide (10 h half-life of 117 °C) with di-*tert*-amyl peroxide initiator, which has a 10 h half-life of 123 °C in dodecane. Since the rate of decomposition of this initiator relative to dicumyl peroxide is slower, the release of new radicals into the reaction medium should similarly be slower. However, this particular initiator did not perform as intended. The addition of a relatively large amount of di-*tert*-amyl peroxide (23.0 μmol, Table 2, entry 2) led to high conversion (67%) in only 2 h, but the livingness of the process was not particularly good as assessed by the very broad molecular weight distribution ($M_w/M_n \sim 2$) that resulted. Decreasing the amount of di-*tert*-amyl peroxide by half (11.5 μmol, Table 2, entry 3) showed some improvement providing polymer that increased in molecular weight over time while the molecular weight distribution remained somewhat narrow ($M_w/M_n \sim 1.4$). However, the final conversion after 22 h was a disappointing 28%, with only an 8% increase in conversion over the last 18 h. We were puzzled by this reduction in rate of polymerization and wonder whether it might have been due to an increase in the reaction mixture viscosity. It has been reported that the viscosity of a reaction solution can reduce the rate of decomposition of an initiating species by increasing the lifetime of the initially formed "reaction cage" [33–35]. This is especially true for radicals formed by a one-bond homolysis reaction. Pryor and Smith demonstrated that the initiators that decompose by a one-bond homolysis reaction, as for example, peroxides, are more prone to radical recombination due to cage return, which in turn is viscosity dependent, i.e. the rate of decomposition of the initiator decreases within creasing viscosity [36]. In the event that this was occurring we used DMSO as a diluent to reduce the solution viscosity. Before performing the polymerization of *n*-butyl acrylate in the presence of the high temperature initiator and DMSO, we first compared the polymerization reactions without any additives in the presence (Table 2, entry 5) and absence (Table 2, entry 1) of DMSO. The similar results obtained demonstrated that DMSO does not affect the polymerization. To our dismay, polymerizations of *n*-butyl acrylate with di-*tert*-amyl peroxide in the absence (Table 2, entry 3) or presence (Table 2, entry 4) of DMSO gave polymers with comparable molecular weights while monomer conversion was slow in both cases.

**Table 2**
*n*-Butyl acrylate polymerization at 134 °C in presence of di-*tert*-amyl peroxide.

| Entry | Time (h) | $M_{n,GPC}$ | $M_w/M_n$ | Conv. (%) | $M_{n,th}$ |
|---|---|---|---|---|---|
| 1[a] | 1 | 1800 | 1.43 | 11 | 2000 |
| | 2 | 2000 | 1.36 | 12 | 2100 |
| | 4 | 2100 | 1.34 | 13 | 2300 |
| | 6 | 2200 | 1.32 | 13 | 2300 |
| | 23 | 2300 | 1.29 | 15 | 2700 |
| 2[b] | 0.5 | 1800 | 3.23 | 14 | 2500 |
| | 1 | 6900 | 2.60 | 51 | 9000 |
| 3[c] | 1 | 2000 | 1.41 | 11 | 2000 |
| | 2 | 2100 | 1.64 | 12 | 2100 |
| | 4 | 3400 | 1.37 | 20 | 3600 |
| | 6 | 3700 | 1.34 | 22 | 3900 |
| | 22 | 4500 | 1.36 | 28 | 5000 |
| 4[d] | 1 | 2600 | 1.48 | 15 | 2700 |
| | 2 | 2900 | 1.41 | 16 | 2900 |
| | 4 | 3200 | 1.34 | 18 | 3200 |
| | 6 | 3500 | 1.32 | 20 | 3600 |
| | 23 | 4400 | 1.50 | 25 | 4500 |
| 5[e] | 1 | 1700 | 1.42 | 9 | 1600 |
| | 2 | 1800 | 1.36 | 10 | 1800 |
| | 4 | 1900 | 1.35 | 11 | 2000 |
| | 6 | 1900 | 1.33 | 11 | 2000 |
| | 23 | 2300 | 1.49 | 19 | 3400 |
| 6[f] | 1 | 1300 | 1.77 | 10 | 1800 |
| | 2 | 3400 | 1.51 | 22 | 3900 |
| | 3 | 5500 | 1.44 | 32 | 5700 |
| | 4 | 6900 | 1.45 | 43 | 7700 |
| | 5 | 8200 | 1.47 | 51 | 9000 |
| | 6 | 9200 | 1.47 | 59 | 10600 |
| | 7 | 9400 | 1.57 | 65 | 11600 |

[a] No addition of di-*tert*-amyl peroxide initiator.

[b] 23.0 μmol of di-*tert*-amyl peroxide initiator added at the beginning.

[c] 11.5 μmol of di-*tert*-amyl peroxide initiator added at the beginning.

[d] 11.5 μmol di-*tert*-amyl peroxide initiator and 3 mL of DMSO added at the beginning.

[e] 3 mL of DMSO added at the beginning.

[f] Addition of an incremental amount of di-*tert*-amyl peroxide initiator, i.e. 2.9 μmol after 30 min, 5.7 μmol after 1 h, 8.6 μmol after 2 h, 11.5 μmol after 3 h, 14.3 μmol after 4 h, 20.1 μmol after 5 h, 25.8 μmol after 6 h.

The addition of di-*tert*-amyl peroxide in incremental amounts over time (Table 2, entry 6) instead of adding it all at once at the beginning of the polymerization (Table 2, entries 2 and 3) was also investigated providing some reasonable results. The GPC chromatograms of the polymer samples removed from the reaction mixture over time (Fig. 2) clearly shift to shorter elution times signifying an increase in molecular weight, while the molecular weight increased in a linear fashion with the monomer conversion (Fig. 3a). Moreover, the plot of $\ln([M]_0/[M])$ versus time (Fig. 3b) was linear indicating the steady state assumption holds. In addition, there was a good correlation between the actual and theoretical molecular weight [37]. Under these conditions, the polymerization showed fairly good living character considering that the molecular weight distribution at the beginning of the polymerization started off very broad. However, the process was impractical since it required a continuous addition of the high temperature initiator throughout the polymerization and failed at what we were attempting to do, that being to have an initiator that could be simply added at the beginning of the polymerization and slowly dissociate in a manner that continuously produced radicals at a rate that mimicked the autopolymerization of styrene.

Pryor and Smith also reported that the rate of decomposition of an initiator is independent of the solution

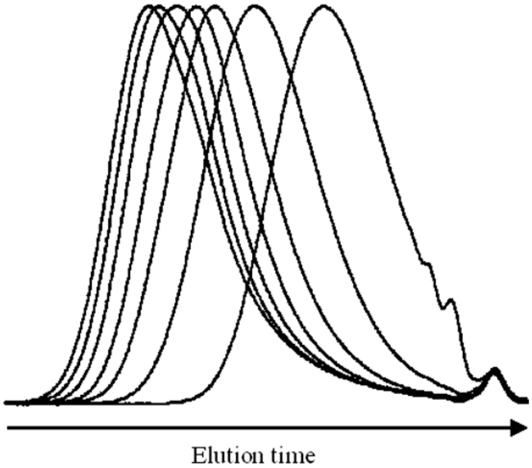


**Fig. 2.** GPC chromatogram of the *n*-butyl acrylate polymerization with an incremental addition of di-*tert*-amyl peroxide (Table 2, entry 6).

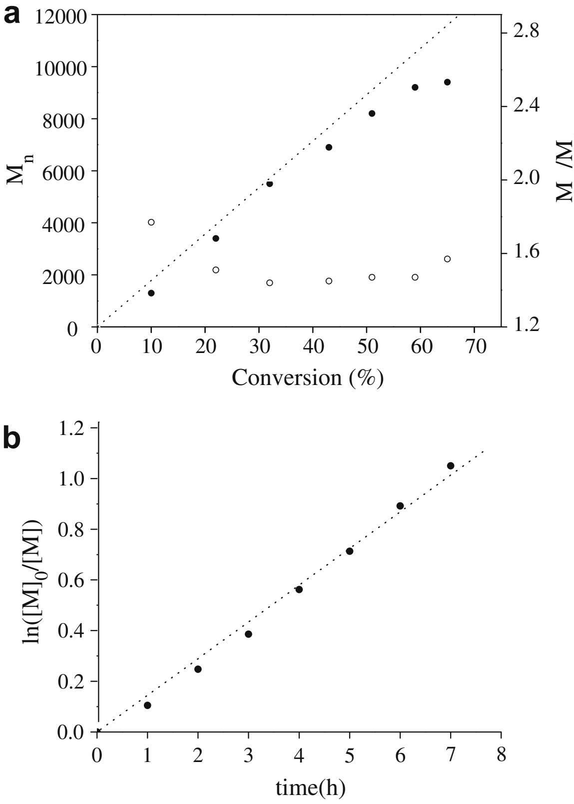


**Fig. 3.** *n*-Butyl acrylate polymerization at 134 °C with an incremental addition of di-*tert*-amyl peroxide (Table 2, entry 6): (a) dependence of the molecular weight (●) and the molecular weight distributions (○) with the conversion and (b) first-order kinetic plot.

viscosity if it decomposes by a simultaneous scission of more than one bond. Azo initiators are examples of these types of initiators. To see if azo initiators would be better than peroxide initiators in our attempts to polymerize *n*-butyl acrylate in the presence of TEMPO, we investigated the use of 2,2′-azobis(N-butyl-2-methylpropionamide), a high temperature initiator with a 10 h half-life of 110 °C. The addition of a small amount (6.4 μmol, Table 3, entry 2) of this azo initiator at the beginning of the polymerization resulted in only a conversion of 9% after 24 h, very similar to the conversion obtained without any additive. Incremental additions of 2,2′-azobis(N-butyl-2-methylpropionamide) showed no improvement (Table 3, entry 3). However, the regular addition of the high temperature initiator at short time intervals in the early stage of the polymerizations enabled higher conversions (Table 3, entries 4 and 5). For entry 5, where the first addition occurred 30 min after the beginning of the polymerization, the molecular weight of the polymer increased with the monomer conversion as expected for a living polymerization process. Although the results were an improvement compared to the results obtained with dicumyl peroxide, the molecular weight distributions remained relatively broad ($M_w/M_n \sim 1.4$–$1.5$). This is probably due to the production of too large an amount of radicals by the high temperature initiator at the polymerization temperature of 130 °C. Further attempts to control the excess production of radicals by adjusting the amount and rate of addition of 2,2′-azobis(N-butyl-2-methylpropionamide) were not successful. The polymerizations were typically very slow or when they did go at reasonable rates control over the the MWD was poor.

**Table 3**
*n*-Butyl acrylate polymerization in the presence of the 2,2′-azobis(N-butyl-2-methylpropionamide) initiator at 130 °C.

| Entry | Time (h) | $M_{n,GPC}$ | $M_w/M_n$ | Conv. (%) | $M_{n,th}$ |
|---|---|---|---|---|---|
| 1[a] | 1 | 1000 | 1.53 | 7 | 1300 |
| | 3 | 1200 | 1.43 | 8 | 1400 |
| | 5 | 1400 | 1.36 | 9 | 1600 |
| | 7 | 1500 | 1.34 | 9 | 1600 |
| | 9 | 1600 | 1.29 | 9 | 1600 |
| | 22 | 1800 | 1.31 | 9 | 1600 |
| 2[b] | 1 | 1100 | 1.79 | 8 | 1400 |
| | 3 | 1500 | 1.38 | 9 | 1600 |
| | 5 | 1600 | 1.35 | 9 | 1600 |
| | 7 | 1700 | 1.34 | 9 | 1600 |
| | 24.5 | 1800 | 1.34 | 9 | 1600 |
| 3[c] | 1 | 1100 | 1.50 | 7 | 1300 |
| | 3 | 1300 | 1.38 | 8 | 1400 |
| | 5 | 1400 | 1.34 | 8 | 1400 |
| | 7 | 1500 | 1.32 | 9 | 1600 |
| 4[d] | 1 | 1600 | 1.48 | 10 | 1800 |
| | 3 | 2500 | 1.31 | 14 | 2500 |
| | 5 | 3300 | 1.27 | 18 | 3200 |
| | 7 | 3800 | 1.29 | 20 | 3600 |
| 5[e] | 1 | 1900 | 1.49 | 11 | 2000 |
| | 2 | 4000 | 1.50 | 22 | 3900 |
| | 4 | 5900 | 1.35 | 30 | 5400 |
| | 6 | 6600 | 1.36 | 37 | 6600 |
| | 8 | 7200 | 1.37 | 40 | 7200 |
| | 23 | 8200 | 1.45 | 51 | 9100 |

[a] No addition of 2,2′-azobis(N-butyl-2-methylpropionamide).

[b] 6.4 μmol of 2,2′-azobis(N-butyl-2-methylpropionamide) added at the beginning.

[c] 6.4 μmol of 2,2′-azobis(N-butyl-2-methylpropionamide) each hour.

[d] 6.4 μmol of 2,2′-azobis(N-butyl-2-methylpropionamide) after 1 h, 1.5 h, 2 h, then each hour.

[e] 6.4 μmol of 2,2′-azobis(N-butyl-2-methylpropionamide) after 30 min, 1 h, then each hour until hour 6, then after 8 h.

A second high temperature azo initiator, 2,2′-azobis(N-cyclohexyl-2-methylpropioamide) (10 h half-life of 111 °C) was also investigated but the results were similar to the those obtained with 2,2′-azobis(N-butyl-2-methylpropionamide).

## 4. Conclusion

High temperature initiators were used as source of radicals to consume excess free TEMPO in *n*-butyl acrylate polymerizations. The study of these initiators was based on the assumption that the radicals slowly formed by these substrates would mimic the formation of benzylic radicals that consume the excess free nitroxide in styrene polymerizations. Although the addition of the high temperature initiator all at once at the beginning of the polymerization was not successful, reasonable monomer conversions were obtained by adding an incremental amount of the high-temperature initiator in a regular fashion over the course of the polymerization. The fact that we were able to get some of these polymerizations to behave in a living fashion confirms that the relatively high stability of the C–ON bond between TEMPO and the poly(*n*-butyl acrylate) chains is not the only reason for the low conversion observed in the absence of additives. Of the initiators investigated di-*tert*-amyl peroxide gave the best results, promoting a living system with a linear dependence of $\ln([M]_0/[M])$ with time and predictable molecular weights, even though the molecular weight distribution of the polymer formed were slightly broad (1.4–1.5).

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[37] This calibration remains appropriate for poly(*n* -butyl acrylate) samples as shown by the Mark-Houwink-Sakurada parameters which are similar for *n*-butyl acrylate and styrene. (a) Couvreur L, Lefay C, Belleney J, Charleux B, Guerret O, Magnet S. Macromolecules 2003; 36: 8260-8267. (b) Farcet C, Belleney J, Charleux B, Pirri R. Macromolecules 2002; 35: 4912-4918. Mark-Houwink-Sakurada parameter in THF at 30 °C $K_{PS} = 11.4 \times 10^{-5}$ dL $g^{-1}$, $\alpha_{PS} = 0.706$; $K_{PBA} = 12.2 \times 10^{-5}$ dL $g^{-1}$, $\alpha_{PBA} = 0.700$ from: Beuermann S, Paquet DA, McMinn JH, Hutchinson RA. Macromolecules 1996; 29: 4206-4215.