



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 ($M_w/M_n \sim 1.5$).

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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*-

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