A Novel “Stable” Radical Initiator Based on the Oxidation Adducts of Alkyl-9-BBN

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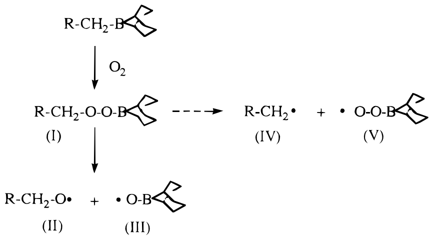
Received August 14, 1995

Living polymerization, with fast initiation and no self-termination, provides polymer chemists control in tailor-making polymers with desirable molecular weights and narrow molecular weight distributions. The development of “living” radical polymerization presents an excellent opportunity to prepare well-defined functional polymers[1] which are usually very difficult to obtain by other polymerization processes, namely Ziegler−Natta, anionic, and cationic reactions. Unfortunately, only a very few living radical polymerization systems[1,2] with relatively complicated stabilization mechanisms have been reported. The “iniferter” [3] and “atom transfer radical polymerization” [4] concepts, with the formation of a reversible bond between the growing chain end radical and a “dormant” species, have been used to explain the stability and long life of radicals during the polymerization.

This paper describes a new “stable” radical species which can be produced under a relatively simple reaction condition and can initiate radical polymerizable monomers at ambient temperature to produce polymers with well-controlled molecular structures. The active site formation is based on the oxidation adducts of alkyl-9-BBN, such as 1-octyl-9-borabicyclononane. At ambient temperature, the oxidation reaction occurs upon mixing 1-octyl-9-borabicyclononane with oxygen. Due to the unfavorable ring strain increase upon inserting oxygen into the C−B bonds in the bicyclic ring, which destroys the stable double chair-form structure, the oxidation reaction preferentially takes place at the C−B bond in the linear alkyl group to produce peroxyborane (C−O−O−B, **I**), as shown in eq 1. The oxidative selectivity of the linear alkyl group was usually between 90 and 70%[5] at ambient temperature, which was very dependent on the oxygen administration. The best results were realized when the O_2 was introduced slowly, so that $O \ll B$ at any time. Excess O_2 on the solution surface leads to overoxidation of boranes to boronates and borates,[6] both of which are also poor initiators for polymerizations.

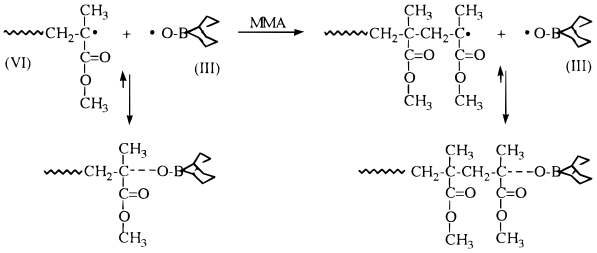


(1)

The peroxyborane **I** behaves very differently from regular benzoyl peroxides and consequently decomposes by itself, even at ambient temperature. The decomposition reaction follows the homolytical cleavage of peroxide to generate an alkoxy radical ($C-O^\bullet$, **II**) and a borinate radical ($B-O^\bullet$, **III**) which is relatively stable due to the back-donating of electron density to the empty p-orbital of boron, as illustrated below:

It is interesting to compare borinate and nitroxide radicals,[2] such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical, which have opposite stabilization mechanisms by electron-donating of the lone-pair electrons in the p-orbital of nitrogen to the free radical. The alternative reaction could involve an asymmetric cleavage of peroxide to produce alkyl radical ($C^\bullet$, **IV**) and peroxyborane radical **V**, both of which are very unstable. This unfavorable reaction may only occur at high temperature. The *in situ* formation of a stable borinate radical (**III**) is very interesting, as it not only promotes the selective peroxy cleavage at ambient temperature but also forms the dormant radical species which are essential for the stable radical polymerization (will be discussed later).

The alkoxyl radical **II**, produced by the homolytical cleave of peroxyborane, is very reactive. With the coexistence of free radical-polymerizable monomers, such as methacrylates, vinyl acetate, acrylonitrile, etc., the alkoxyl radical **II** initiates radical polymerization at ambient temperature. On the other hand, the borinate radical **III** is too stable to react with monomer. However, the borinate radical **III** may form a weak and reversible bond with the growing chain end (**VI**) during the polymerization reaction, as illustrated in eq 2. Upon the dissociation of the electron pair, the growing chain end (**VI**) can then react with monomer, such as methyl methacrylate (MMA), to extend the polymer chain. The resulting new chain end radical immediately forms a week bond with the borinate radical **III**, such a process minimizes the undesirable chain transfer and termination (coupling and disproportional) reactions between two growing chain ends.



(2)

In a typical example, 1-octyl-9-BBN (0.042 g) was mixed with ethyl methacrylate (7 g) monomer and 25 mL of THF or benzene solvent in a septum-capped 250 mL flask equipped with a high-vacuum stopcock. The reaction was initiated by injecting O_2 into the reaction flask at room temperature. To assure the formation of stable initiator, only 50% of oxygen (vs borane) was added, and the unreacted oxygen was vacuum-removed within 1 h. Under this reaction condition, only a few percent of borane was oxidized. The slow reaction is mainly due to the inhomogeneous mixing between two very dilute reagents, borane reagent in solution and oxygen gas. However, the resulting initiators were sufficient to initiate the polymerization, and poly(ethyl methacrylate) (PEMA) was periodically removed. Figure 1 shows the GPC curves of PEMA polymers with various reaction times. The first sample was removed after

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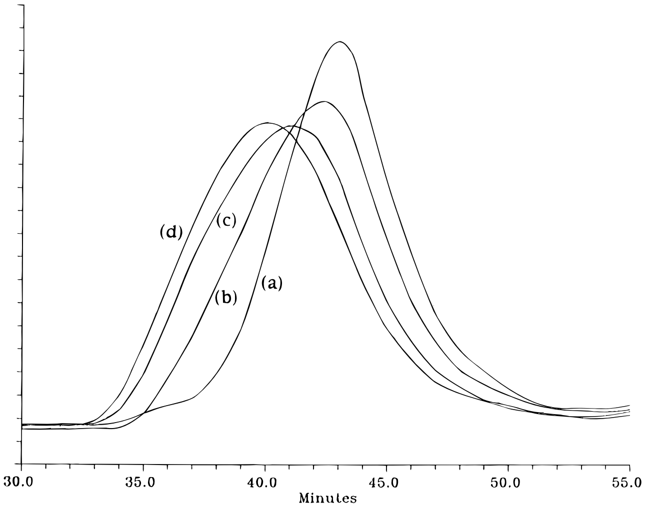

Figure 1. Comparison of GPC curves between PEMA homopolymers with various reaction times: (a) 1 h (PDI = 2.2), (b) 3 h (PDI = 2.5), (c) 5 h (PDI = 2.6), and (d) 24 h (PDI = 2.5).

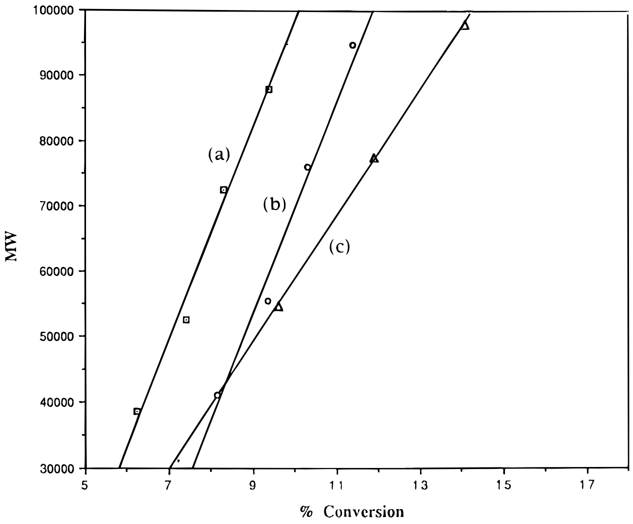

Figure 2. Plots of molecular weight and yield of (a) PMMA (⊡), (b) PEMA (○), and (c) P-*t*-BMA (△) polymers.

1 h of reaction, which was under alkyl-9-BBN and O_2 conditions. In other words, the propogating chain ends increased with the polymerization time. After removal of oxygen, the propogating chain ends became constant, and the consective samples were produced under a constant number of active sites. It clearly shows that polymer continuously increases its molecular weight during the entire polymerization process. The molecular weight distribution remains very constant, with the polydispersity index (PDI = M_w/M_n) about 2.5. The relatively broad molecular weight distribution, compared with those in living anionic polymerization cases, may be attributed to the slow initiation in the first hour (as discussed above). In other words, the initiation of each polymer chain took place at different times. Figure 2 compares the yields and molecular weights of poly(methyl methacrylate) (PMMA), PEMA, and poly(*tert*-butyl methacrylate) (P-*t*-BMA) during the similar radical polymerization conditions. The molecular weight was determined by GPC measurement using polystyrene as the calibration standard. The linear increase of molecular weight versus the yield of polymer indicates a constant polymer chain number after the oxidation reaction, which also implies the stable propogating chain end without significant termination and chain transfer reactions. In fact, high molecular weight (more than 1 million) polymers of PMMA and PEMA with relatively narrow PDIs (<3) have also been prepared. Such polymer structures would be very difficult to achieve by traditional free radical polymerization.

It is remarkable to think of the simplicity of this stable radical polymerization process, which occurs at ambient temperature with the injection of oxygen (or air) to alkyl-9-BBN. The lack of chain transfer and termination, both disproportional and coupling reactions, must be associated with the existence of dormant species, produced *in situ* during the formation of initiator. This radical polymerization route has also been applied to the preparation of graft and block copolymers[7] with the use of borane-containing polymers.

Acknowledgment. The authors are grateful for financial support from the Polymer Program of the National Science Foundation.

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