Communications to the Editor

Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents

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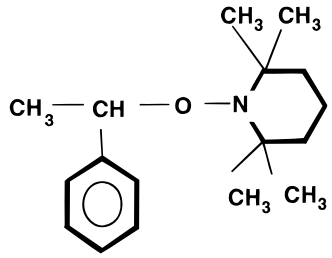
Introduction. The free radical polymerization area has undergone a revival in recent years as evidenced by the ever increasing number of publications since 1993 when it was demonstrated that narrow polydispersity polystyrene could be prepared by a stable free radical polymerization (SFRP) process. While the SFRP process has been demonstrated to work extremely well for styrene and its derivatives,[1a−e] extension to acrylates and dienes has proven troublesome. The polymerizations with the latter two monomers start off well, but as they continue, the rates of polymerization decrease and the polymerizations eventually stop due to a buildup of excess free nitroxide. The mechanism[2] of the SFRP process involves an equilibrium between nitroxide-capped polymer chains and uncapped polymer chains. The success of the SFRP process relies on having just the right amount of free nitroxide in the reaction mixture to keep the propagating polymer radical chains at a concentration where the probability of termination by coupling is low but enough are present to allow the polymerization to proceed at an appreciable rate. An excess of free nitroxide shifts the equilibrium to the capped form, resulting in very little to no monomer addition. Monitoring of the excess free nitroxide levels by ESR has shown that in nonstyrenic systems there is a gradual increase in free nitroxide levels over time to levels where polymerization is inhibited.[3] While the increase in free nitroxide levels can occur for a number of reasons, for the purpose of this paper, the discussion will focus on how to manage or reduce the excess free nitroxide concentration by the use of an additive. Recent work has shown that the trapping rate of nitroxide by an acrylate is faster than that for a styrene radical, rendering acrylate polymerizations more sensitive to excess free nitroxide than the corresponding styrene polymerizations.[4] Therefore, to successfully polymerize acrylates by the SFRP process, a method of reducing the amount of free nitroxide was necessary. Since some free nitroxide is probably generated by polymer chain termination by molecular oxygen, a known radical scavenger,[5] attempts were made to remove all oxygen from the reaction mixture by the use of reducing sugars, well-known oxygen scavengers.[6] Since reducing sugars are also relatively strong reducing agents,[7] it was anticipated that they might also react with the excess nitroxide to further reduce the nitroxide level to a point where propagation could proceed unimpeded.

Results. When *n*-butyl acrylate is heated to 145 °C in the presence of benzoyl peroxide (BPO) and a nitroxide, such as tetramethylpyridinyloxy radical (TEMPO), monomer initially adds to the polymer chains in a living manner. However, as the reaction proceeds, the rate of polymerization decreases to the point where after 1−2 h the polymerization has effectively stopped. The molecular weight of the acrylate polymer at this point is typically low, generally below 4000, and the conversions are generally about 5%. If the polymerizations are run under conditions where careful control of the amount of oxygen is exercised, the polymerizations continue to higher conversions, but rarely exceeding 20%. Similar results are obtained when initiator/nitroxide adducts, such as (1),[8] are used to control the



(1)

initial amount of excess free nitroxide. In contrast, when acrylate polymerizations are performed with *n*-butyl acrylate, (1), and glucose as a reducing sugar, in the presence of sodium bicarbonate, the polymerization proceeds in a living fashion to over 60% conversion in 6.5 h (Figure 1). In a typical sugar-controlled polymerization, BPO, 4-hydroxy-TEMPO, *n*-butyl acrylate, and glucose are heated at 125 °C for 15 min to initiate the polymerization. After initiation is complete, sodium bicarbonate, which reduces the initiation efficiency if added prior to initiation, is added and the reaction mixture is heated to 145 °C (Figure 2). The marked effect glucose has on the course of an acrylate polymerization is illustrated in Figure 3. A polymerization without added sugar proceeds slowly to low molecular weight over the first 2 h and then shows very little change over the next 4 h. In contrast, a similar polymerization with added sugar shows a dramatic increase in molecular weight at the beginning of the polymerization and slows only slightly as the monomer concentration is reduced. The living character of the poly(*n*-butyl acrylate) prepared in this manner can be further demonstrated by chain extension with styrene to form a block copolymer that, by GPC analysis in

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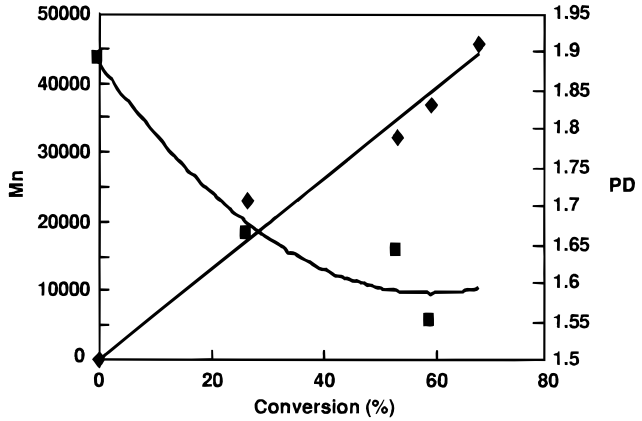
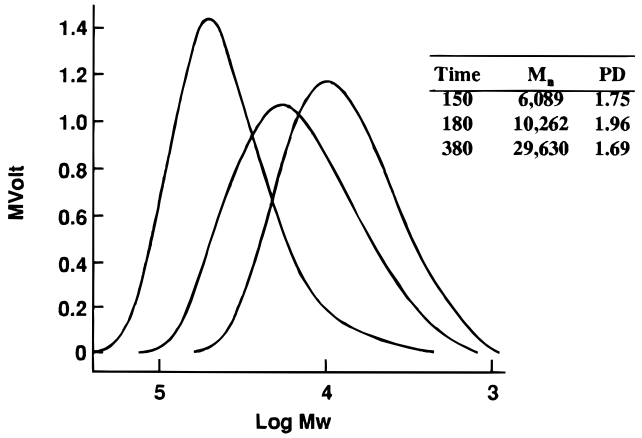


Figure 1. M_n vs conversion vs PD for an SFR polymerization of *n*-butyl acrylate from adduct, (1), with glucose as an additive.



Time	M_n	PD
150	6,089	1.75
180	10,262	1.96
380	29,630	1.69

Figure 2. Molecular weight increase vs time for an *n*-butyl acrylate polymerization from initiator (BPO) with glucose as an additive.

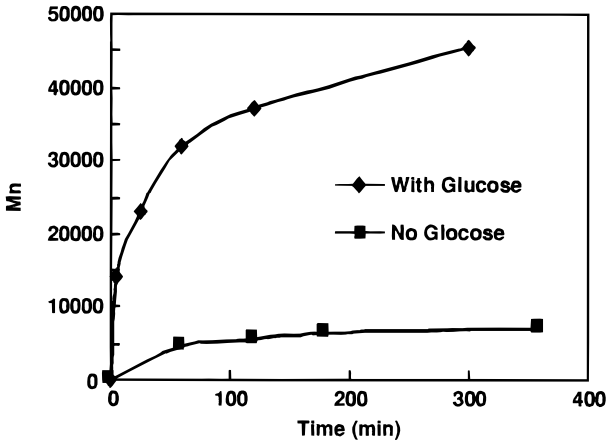


Figure 3. Number average molecular weight change vs time for a BPO initiated polymerization of *n*-butyl acrylate with and without added glucose.

o-xylene, is free of poly(*n*-butyl acrylate) (Figure 4; the presence of poly(*n*-butyl acrlyate) would show up as a negative peak in the block copolymer chromatogram[9]). One issue in using sugars in bulk polymerizations is the relative insolubility of the reducing agent in acrylates. Since it was believed that the active species in these reactions was the ene-diol derived from the base-catalyzed equilibrium with the aldehyde or ketone in equilibrium with the sugar,[7] α-hydroxy ketones and aldehydes, capable of forming ene-diols, were investi-

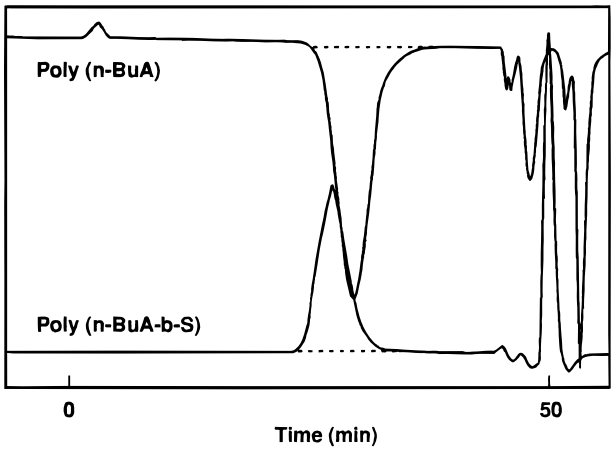
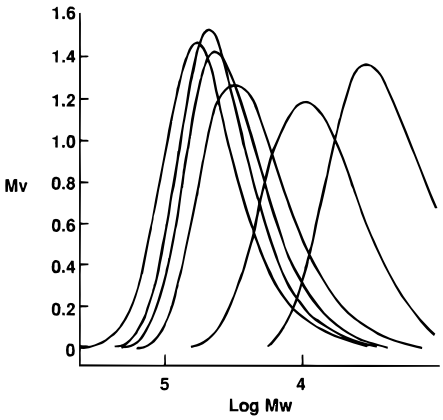


Figure 4. GPC of an *n*-butyl acrylate-*b*-styrene block copolymer in *o*-xylene.



Time	Mn	PD
70	2700	1.4
120	6075	1.72
190	16688	1.77
255	24296	1.61
360	29811	1.56
510	63297	1.62

Figure 5. Molecular weight increase vs time for an *n*-butyl acrylate polymerization in the presence of hydroxyacetone.

gated as substitutes for glucose. When hydroxyacetone was used in the polymerizations of *n*-butyl acrylate, with BPO and hydroxy-TEMPO, the polymerizations proceeded to yields of 60−70% in a living manner, as indicated by the incremental increase in molecular weight with time (Figure 5).

To gain some insight into the role of the reducing agents in these polymerizations, ESR experiments were conducted to monitor nitroxide levels in *n*-butyl acrylate polymerizations initiated with (1), with and without added hydroxyacetone. In the reaction without the added reducing agent, the free nitroxide levels are seen to increase with time (Figure 6) to levels where the polymerization is expected to be inhibited. In contrast, the polymerization with the added reducing agent initially shows an increase in the free nitroxide level but the amount then slowly decreases to a level where polymerization can proceed unimpeded.

Extending the use of reducing sugars to dienes, which up to this point also suffered from poor yields, proved quite successful. Illustrated in Figure 7 is the SFR polymerization of isoprene in the presence of hydroxyacetone. Incremental increases in the molecular weight with time are evident with the polydispersities decreasing as the polymerization proceeds to 50% conversion. This result is significant in view of the fact that even under conventional free radical polymerization conditions the polymerization of isoprene gives low yields.[10]

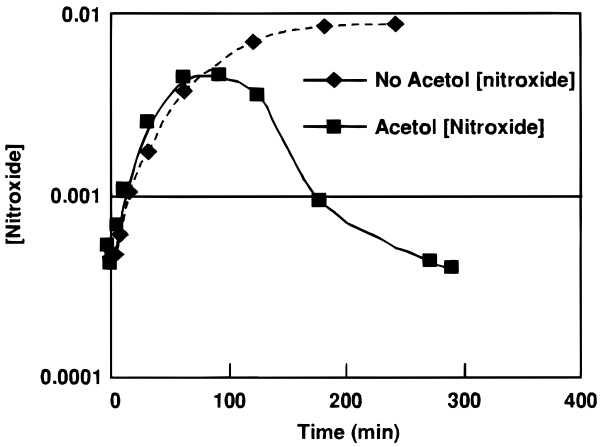


Figure 6. Change in nitroxide concentration vs time for an *n*-butyl acrylate polymerization with adduct (1) with and without hydroxyacetone.

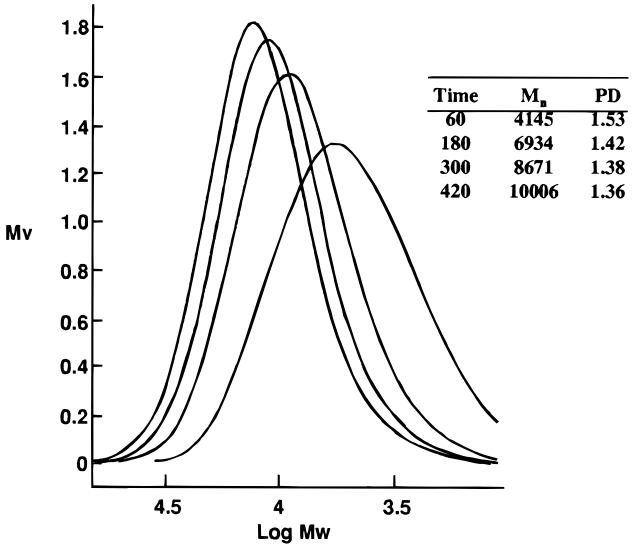


Figure 7. Molecular weight increase vs time for an isoprene polymerization in the presence of hydroxyacetone.

Experimental Section. *Experiment 1.* In a 100 mL three-necked round-bottom flask equipped with a condenser, gas inlet, and rubber septum was added *N*-[(1-methylbenzyl)oxy]-2,2,6,6-tetramethyl-1-piperidine (MB-TMP) (0.072 g, 0.0271 mmol), dextrose (0.16 g) as a reducing agent, $NaHCO_3$ (0.16 g) as a basic buffer, and *n*-butylacrylate (25 mL) monomer. The resulting mixture was then deoxygenated by bubbling argon through the suspension followed by heating with a preheated oil bath (to 145 °C). The reaction was stirred for 5 h, resulting in poly(*n*-butyl acrylate)−TEMPO terminated of M_n = 45 537 with polydispersity (PD) 1.55 and conversion 65%.

Experiment 2. The poly(*n*-butyl acrylate)−TEMPO (2.2 g) of experiment 1 was dissolved in styrene monomer (35 mL) in a 100 mL three-necked round-bottomed flask equipped with a condenser, gas inlet, and rubber septum. The resulting mixture was then deoxygenated by bubbling argon through the mixture and heated by immersion into a preheated oil bath of 135 °C. The reaction was stirred for 2.5 h and then precipitated into methanol (500 mL). The resulting polymer of poly(*n*-butyl acrylate-*b*-styrene) had a M_n = 104 900 with PD = 1.71.

Experiment 3. In a PARR reactor was discharged isoprene (75 mL), *N*-[(1-methylbenzyl)oxy]2,2,6,6-tetramethyl-1-piperidine (MB-TMP) (0.079 g), glucose (0.12 g), and $NaHCO_3$ (0.14 g). The reactor was purged with argon through the solution for 15 min and then heated to 145 °C over a 20 min interval. This temperature was maintained for 4 h, after which it was cooled and monomer evaporated to yield polyisoprene of M_n = 20 573, with a PD = 1.33 and conversion of 25%.

Experiment 4. To a round-bottomed flask equipped with a reflux condenser, thermometer, and gas inlet tube was added BPO (0.1 g, 0.413 mmol), stable free radical agent 4-HO-TEMPO (0.097 g, 0.563 mol), acetol (0.2 mL, 2.69 mmol) as a reducing agent, and *n*-butyl acrylate (25 mL) monomer. This solution was deoxygenated for 10 min by bubbling argon through the solution and then heated by immersion into a hot oil bath (145 °C). The reaction was stirred for 8.5 h to yield 4-HO-TEMPO terminated poly(*n*-butyl acrylate) of M_n = 36 297 with a polydispersity of 1.65 and conversion of 56%.

Conclusion. An efficient and practical solution to the low conversion problem of acrylate polymerization by the SFRP process has been presented. Ene-diols have been shown to control excess free nitroxide levels to enable the polymerizations to proceed unimpeded to high molecular weights and high yields. The living character of the acrylates is demonstrated by the efficient chain extension of these resins with styrene to block copolymers. Extension of this work to dienes resulted in improved yields. The detailed mechanism of the role of the reducing agents and the extension to methyacrylates is currently under investigation.

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