Stable Free Radical Polymerization of Acrylates Promoted by α-Hydroxycarbonyl Compounds

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ABSTRACT: The living-radical polymerization of *n*-butyl acrylate, moderated with TEMPO, is shown to proceed in a controlled fashion in the presence of a series of α-hydroxycarbonyl compounds with different organic bases. The best results were obtained with glyceraldehyde dimer in the presence of pyridine. These results further support the suggestion that the difficulty of polymerizing acrylate monomers in the presence of TEMPO is related to the excess buildup of TEMPO due to a small amount of polymer chain termination and to a lesser extent on the higher bond dissociation energy of the TEMPO acrylate bond relative to the TEMPO styrene bond at the chain's terminus.

Introduction

The difficulty of polymerizing acrylates by the stable free radical polymerization (SFRP) with TEMPO as the moderating nitroxide has been the subject of a number of published papers to date.[1] It has been suggested that for the polymerization of *n*-butyl acrylate mediated by TEMPO the equilibrium constant K is unfavorably small because of a low dissociation rate constant k_d and a high recombination rate constant k_c.[2] As a result, 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 too fast. This prevents linear increases in molecular weight vs increasing conversion and narrow final molecular weight distributions (MWDs).

It can also be argued that the inhibition of acrylate polymerization is due to a buildup of TEMPO in the reaction mixture due to a small amount of unavoidable chain termination. Electron spin resonance results showing a buildup of TEMPO levels in an acrylate polymerization reaction have been reported.[3] In the case of styrene polymerization, autoinitiation generates enough new polymer chains to consume the excess nitroxide. However, a lack of an autoinitiation mechanism for acrylates results in an accumulation of free nitroxide, forcing the equilibrium of the dormant TEMPO-capped polymer chains and the free radical propagating chain to the dormant state.

We recently demonstrated the successful polymerization of *n*-butyl acrylate by the SFRP process in the presence of TEMPO with the controlled addition of ascorbic acid.[4] It was argued that the ascorbic acid, known to react quickly and efficiently with nitroxides,[5] served to reduce the amount of the excess TEMPO allowing the polymerization to proceed unrestricted. The amount of ascorbic acid added to the reaction mixture was critical to the success of the polymerization. Adding too much ascorbic acid at the beginning of the polymerization resulted in an exotherm and an excessive rate of polymerization. The resulting polymer product had a very high molecular weight and a broad MWD. Adding too little ascorbic acid prevented the polymerization from proceeding at a reasonable rate. The best results were obtained with a slow continuous addition of ascorbic acid to the reaction mixture via syringe. While this approach worked very well to demonstrate that the polymerization of *n*-butyl acrylate could be polymerized in a controlled manner with TEMPO as the moderating nitroxide, as noted in the publication, the process was impractical. Even more troublesome was the fact that a larger amount of ascorbic acid had to be added each hour as the reaction progressed, a feature of the process that to date is still not understood.

Since it is the ene-diol moiety of ascorbic acid that reacts with TEMPO, we were interested in determining whether we could find a way of generating the ene-diol functionality in situ in such a way that only a small amount would be present at any given time, but more could be generated as it is consumed in its reaction with TEMPO, thus ensuring a low continuous source of the nitroxide destroyer. Earlier work in our laboratory demonstrated that a simple sugar, such as dextrose, in the presence of sodium bicarbonate would enable the polymerization of *n*-butyl acrylate in the presence of TEMPO, although relatively high temperatures (145 °C) were required and the MWDs of the products were generally broad (1.6−1.7).[6] In the same paper acetol was also demonstrated to give similar results to dextrose. One of the main problems with these reagents was their lack of solubility in the reaction mixture, typically resulting in a two-phase system.

On the basis of these examples, we initiated a study to determine whether other simple α-hydroxycarbonyl compounds could be used to form ene−diols in situ to allow the controlled polymerization of *n*-butyl acrylate. In this paper we report on the results of this study and show that dramatic improvements can be achieved with the appropriate choice of α-hydroxycarbonyl compound and base combination. Significantly, it is shown that polymer products with predictable molar masses and narrow MWDs can be achieved at much lower reaction temperatures than previously reported. It is further demonstrated that the choice of base is dependent on the ease of enolization of the α-hydroxycarbonyl. As will be demonstrated, the best results were obtained using glyceraldehyde with pyridine.

Experimental Section

(a) Materials and Equipment. 4-Oxo-TEMPO-stabilized *n*-butyl acrylate was prepared by passing *n*-butyl acrylate (Aldrich) through a 4-methoxyphenol inhibitor removal column (Aldrich) and adding 4-oxo-TEMPO at a concentration of 1 mg per 40 mL of *n*-butyl acrylate. The alkoxyamine unimer, 1-(benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST), **1**, was syn-

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thesized according to an as yet unpublished procedure developed in our laboratory and recrystallized from 2-propanol. TEMPO (Chemipan, Russia) was purified by sublimation. The following chemicals were all purchased from Aldrich and used as received: acetol, 2-hydroxy-2-phenylacetophenone (benzoin), 4,4′-dimethoxybenzoin (anisoin), 3-hydroxy-2-butanone, α-hydroxy-γ-butyrolactone, glyceraldehyde dimer, glycolaldehyde dimer, 4-(dimethylamino)-pyridine (DMAP), pyridine, and imidazole. Polymer molecular weights and MWDs were estimated by gel permeation chromatography (GPC) using a Waters 2690 separations module with Ultrastyragel columns HR1, HR3, and HR4 and a Waters model 410 differential refractometer (RI). Polystyrene standards were used for calibration.[7] THF was used as the eluent at a flow rate of 0.35 mL min^{-1}, and the operating temperature of the GPC was 40 °C. GPC was performed on samples taken directly from the reaction mixture without any prior precipitation that may remove low molecular weight chains. Excess monomer was removed by evaporation with a stream of air before GPC analysis. Percentage conversions were determined gravimetrically.

(b) General *n*-Butyl Acrylate Polymerization Procedure. Polymerizations were performed in a 50 mL three-necked round-bottom flask equipped with a septum, through which argon was introduced and samples were removed via syringe, a thermometer, and a condenser equipped at the top with a gas outlet adapter. Generally, experiments were conducted with *n*-butyl acrylate (20 mL, 1.4×10^{-1} mol) and BST (0.200 g, 5.2×10^{-4} mol) unless otherwise noted. An α-hydroxycarbonyl compound and a base were added at room temperature, and the solution was purged with argon gas for 10 min. The reaction mixture was heated under argon to 131−133 °C, and samples were removed at the times indicated in the tables to monitor the course of the polymerization.

(c) Polymerizations of *n*-Butyl Acrylate with Either Glyceraldehyde Dimer, 3-Hydroxy-2-butanone, α-Hydroxy-γ-butyrolactone, or Glycolaldehyde Dimer in the Absence of Base. Reactions were performed according to procedure b with each of the aforementioned α-hydroxycarbonyl compounds at two different concentrations of the α-hydroxycarbonyl compound, 1×10^{-4} and 3.5×10^{-4} mol, with no added base. No conversion beyond 8% was observed in any of these experiments after 3 h.

(d) Block Copolymer Formation. Heating poly(*n*-butyl acrylate) (M_n = 13 100 g mol^{-1}, PDI = 1.39) (6 g) in a solution of styrene (6 mL) and dimethyl sulfoxide (3 mL) under argon for 2 h at 130 °C resulted in a chain extension to provide a copolymer with M_n = 20 900 g mol^{-1} and PDI = 1.30.

(e) *n*-Butyl Acrylate−co-*tert*-Butyl Acrylate Random Copolymer Synthesis. A solution of BST (0.200 g, 5.2×10^{-4} mol), glyceraldehyde dimer (0.020 g, 1.1×10^{-4} mol), and pyridine (0.024 g, 2.9×10^{-4}) in *n*-butyl acrylate (15 mL, 1.1×10^{-1} mol) and *tert*-butyl acrylate (10 mL, 7.0×10^{-2} mol) was heated at 130 °C for 5 h under argon to give a polymer with M_n = 11 211 g mol^{-1} and PDI = 1.39.

Results and Discussion

Polymerizations of *n*-butyl acrylate with BST as the initiator, in the presence of 1×10^{-4} and 3.5×10^{-4} mol of either 3-hydroxy-2-butanone, α-hydroxy-γ-butyrolactone, glycolaldehyde dimer, or glyceraldehyde dimer (Figure 1), at 133 °C, typically proceeded to 4−8% monomer conversion in the first hour, providing polymers with M_n's of ∼2500 and 4000 g mol^{-1}. No further increases in monomer conversions were observed after 2 and 3 h. This is the same behavior found for the polymerization of *n*-butyl acrylate under SFRP conditions with TEMPO as the moderating nitroxide in the absence of any α-hydroxycarbonyl compound, thus showing that these α-hydroxycarbonyl reagents by themselves are ineffective at enabling the polymerization of *n*-butyl acrylate. These results suggest that the amount of ene−diol derived from these α-hydroxycarbonyl reagents is too little to effectively control the excess TEMPO that is inhibiting the polymerization.

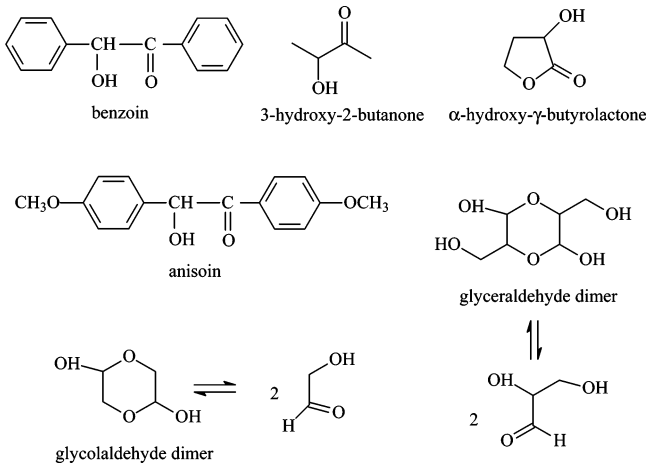


Figure 1. α-Hydroxycarbonyl compounds used in this study.

Polymerizations in the presence of benzoin or anisoin (Figure 1) behaved differently in that monomer conversions would continue to increase very slowly over time. However, the MWDs of the polymer chains would start off broad and remain broad. A typical result for a polymerization in the presence of benzoin is given in Table 1, entry 1. Monomer conversion after 1 h is 5%, and it continues to increase over the next 5.5 h to 15%. The molecular weight of the resulting polymers is low and the MWD is broad. When a 50% higher concentration of benzoin was used, a vigorous exotherm resulted as soon as the reaction mixture reached 130 °C. This prompted us to wonder whether benzoin by itself was generating radicals that caused the polymerization to go out of control. However, this did not seem to be the case. Heating *n*-butyl acrylate at 130 °C for 1 h with a concentration of benzoin 2.5 times higher than that used in the experiment outlined in Table 1, entry 1, in the absence of BST produced no exotherm. The monomer conversion was ∼4% after 1 h.

It is known that ketones and aldehydes undergo tautomerization between their keto and enol forms, with the equilibrium in the case of ketones greatly favoring the keto form. In the case of simple sugars, a similar relationship exists, but because the sugars are effectively α-hydroxycarbonyl compounds, the tautomerization results in the formation of ene−diols (Scheme 1). While the addition of base does not affect the equilibrium concentrations of the tautomers, it does increase the rate at which the keto tautomer is converted into the enol tautomer. With that as the background, polymerizations of *n*-butyl acrylate with the aforementioned α-hydroxyketones were performed in the presence of a series of organic bases. Three bases with different base strengths, pyridine (pK_a ammonium ion 5.25), imidazole (pK_a 7.0), and DMAP (pK_a 9.7), soluble in *n*-butyl acrylate, were chosen for investigation.

Polymerizations of *n*-butyl acrylate in the presence of benzoin and anisoin with the various bases were typically poor. Some representative results are provided in Table 1, entries 2 and 3. While the rates of polymerizations were high and conversions of up to 70% could be achieved in 3−5 h, the MWDs were typically broad, suggesting a lack of control in the polymerizations.

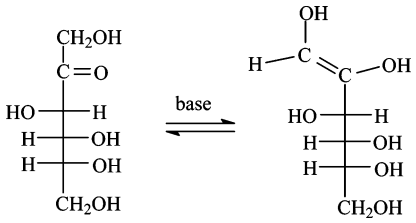
The results obtained for the polymerizations with 3-hydroxy-2-butanone in the presence of pyridine and imidazole were no different than those obtained when no base was added. Polymerizations would proceed in the first hour to between 5 and 8% conversion and then stop. Increasing the amounts of both the 3-hydroxy-2-butanone and bases afforded no improvement. While DMAP allowed an increase in monomer conver-

Table 1. Results for the Polymerization of *n*-Butyl Acrylate in the Presence of Benzoin or Anisoin and Pyridine Initiated with BST

entry	benzoin (10^{-4} mol)	anisoin (10^{-4} mol)	pyridine (10^{-4} mol)	rxn time (h)	M_n (10^{-3}) g mol^{-1}	PDI	conv (%)
1[a]	6.7			1	1.2	1.6	5
				3	2.6	1.5	10
				6.5	4.0	1.5	15
2[b]	2.2		6.5	1	6.7	2.6	24
				2	12.7	2.2	45
				3	18.2	1.9	73
3[b]		2.2	6.5	1	2.1	1.6	8
				3.5	15.7	1.8	55
				5	19.7	1.7	70

[a] Polymerization performed with a solution of 0.6 g (1.6×10^{-3} mol) of BST in 60 mL (4.2×10^{-1} mol) of *n*-butyl acrylate. [b] Polymerizations performed with a solution of 0.2 g (5.2×10^{-4} mol) of BST in 20 mL (1.4×10^{-1} mol) of *n*-butyl acrylate.

Scheme 1. Tautomerization of a Sugar



sions, the rates of polymerization were still quite slow. Some typical results are summarized in Table 2. Initial polymerizations with low amounts of 3-hydroxy-2-butanone and DMAP were typically slow (Table 2, entries 1 and 2) with only a slight improvement in rate with an increase in the amount of 3-hydroxy-2-butanone (Table 2, entry 3). Using a larger amount of DMAP with the increased concentration of 3-hydroxy-2-butanone again showed limited improvement (Table 2, entry 4).[8] In one case when the amounts of 3-hydroxy-2-butanone and DMAP were increased to 6.8×10^{-4} and 4.9×10^{-4} mol, respectively, a vigorous exotherm occurred when the reaction temperature reached 130 °C.

Using α-hydroxy-γ-butyrolactone in combination with DMAP gave results similar to those obtained with 3-hydroxy-2-butanone and DMAP. Monomer conversions of about 20−25% could be obtained after 7 h, after which the rates of conversion slowed down to less than 1% per hour. The addition of more α-hydroxy-γ-butyrolactone or DMAP to the reaction mixtures after the reaction had slowed down did not result in any significant change in conversion or molecular weight.

We took the opportunity to also revisit acetol with the various organic bases. The best results were obtained with DMAP, and some typical experiments are summarized in Table 3. Entry 1 shows the effect of acetol itself on the course of *n*-butyl acrylate polymerization with BST as the initiator. While a 20% conversion can be achieved in 5.5 h to give a polymer with a narrow MWD and a predictable molecular weight, the rate of polymerization slows with time. Repeating the polymerization with the addition of a small amount of DMAP (entry 2) had little effect on the rate of polymerization. Doubling the amount of both acetol and DMAP (entry 3) enabled a dramatic increase in the rate of polymerization to provide a 52% monomer conversion after 4 h, but the MWDs of early samples were quite broad. A further increase in acetol and DMAP (entry 4) provides a further increase in the rate of polymerization, but there was also a concomitant increase in the MWD. Also of concern with these last two polymerizations is the increase in deviation of the actual M_n from the theoretical M_n.

Results from some typical polymerizations in the presence of glyceraldehyde dimer and DMAP are summarized in Table 4. Only a small amount of DMAP was required to obtain reasonable rates of polymerization. While it can be seen that increasing the amount of glyceraldehyde dimer and DMAP leads to increase rates of polymerization, the MWDs of the resulting polymers were typically quite broad. Manipulation of the ratio between glyceraldehyde dimer and DMAP was ineffective at providing better control over the polymerization. Also, while not evident in the table, the results summarized in Table 4 were difficult to reproduce on a consistent basis, which was attributed to the sensitivity of the polymerization to the small amounts of DMAP needed to affect the course of the polymerization. In addition, the GPC plots of these polymerizations showed significant tailing at low molecular weights, one reason why the MWDs were so broad.

Repeating the polymerizations with glyceraldehyde dimer in the presence of pyridine provided the best results we obtained in this study. While a low concentration of glyceraldehyde dimer with a large amount of pyridine (Table 5, entry 1) gave a 21% monomer conversion in 5 h, the rate of polymerization after the first hour was relatively slow, allowing only an increase in conversion in the final 2 h of 6%. Doubling the amount of glyceraldehyde while reducing the amount of pyridine to half (Table 5, entry 2) gave significant improvements in the rate of polymerization, enabling the monomer conversion to go to 50% in 7 h. A further slight increase in the amount of glyceraldehyde dimer, even with a further reduction in pyridine (Table 5, entry 3), provided an additional increase in the rate of polymerization, enabling a monomer conversion of 58% in 5 h. Roughly the same rate of polymerization was obtained with a further slight increase in the amount of both glyceraldehyde and pyridine (entry 4). However, there was a noticeable increase in the MWDs of the samples removed from the reaction flask over the course of the polymerization. A further increase in the rate of polymerization could be achieved with higher amounts of glyceraldehyde (entry 5), but there was also a significant increase in the deviation of the actual M_n from the theoretical value.

The polymerization summarized in Table 5, entry 2, proceeds in a controlled fashion as indicated by the linear relationship between molecular and conversion (Figure 2) and L_n ($[M]_0/[M]$) vs time (Figure 3), as expected for a living-radical polymerization. Furthermore, as illustrated in Figure 2, molar masses can be varied by altering the *n*-butyl acrylate/BST ratio. In contrast to the reactions conditions required to achieve these results with ascorbic acid, in which the ascorbic acid had to be added over time via syringe, all the reagents for these reactions are added at the beginning of the polymerization, thus greatly simplifying the procedure.

Two further sets of results in this study were rather surprising. Considering the good results that were obtained with glyceraldehyde dimer, we were subsequently quite surprised to find that the glycolaldehyde dimer had no effect on the polymerization of *n*-butyl acrylate in the presence of either pyridine or DMAP. This would suggest that the glycolaldehyde dimer is very stable

Table 2. Results for the Polymerization of *n*-Butyl Acrylate (20 mL, 1.4×10^{-1} mol) in the Presence of 3-Hydroxy-2-butanone and DMAP Initiated with BST (0.2 g, 5.2×10^{-4} mol)

entry	butanone (10^{-4} mol)	DMAP (10^{-4} mol)	rxn time (h)	M_n (10^{-3}) g mol^{-1}	M_{nth} (10^{-3}) g mol^{-1}	PDI	conv (%)
1	2.4	2.7	3	5.6	4.8	1.3	14
2	2.4	1.6	6	5.4	5.1	1.3	15
3	5.7	1.6	7	8.0	10.2	1.3	30
4	5.7	4.1	4	9.2	8.9	1.4	26

Table 3. Results for the Polymerization of *n*-Butyl Acrylate (20 mL, 1.4×10^{-1} mol) in the Presence of Acetol and DMAP Initiated with BST (0.2 g, 5.2×10^{-4} mol)

entry	acetol (10^{-4} mol)	DMAP (10^{-4} mol)	rxn time (h)	M_n (10^{-3}) g mol^{-1}	M_{nth} (10^{-3}) g mol^{-1}	PDI	conv (%)
1	2.7	0	1.5	4.2	4.1	1.4	12
			3.5	6.0	5.8	1.3	17
			5.5	7.3	6.9	1.3	20
2	2.7	0.5	1.5	4.4	3.8	1.5	11
			4.0	5.6	5.1	1.4	15
3	5.4	1.0	1.0	10.2	9.6	1.8	28
			1.5	14.4	12.0	1.6	35
			4.0	20.0	17.8	1.4	52
4	6.8	2.5	1.5	17.6	20.6	1.6	60

Table 4. Results for the Polymerization of *n*-Butyl Acrylate (20 mL, 1.4×10^{-1} mol) in the Presence of Glyceraldehyde Dimer and DMAP Initiated with BST (0.2 g, 5.2×10^{-4} mol)

entry	glyceraldehyde dimer (10^{-4} mol)	DMAP (10^{-5} mol)	rxn time (h)	M_n (10^{-3}) g mol^{-1}	PDI	conv (%)
1	1.1	1.6	1	4.0	1.8	13
			3	11.9	1.5	31
			5	15.9	1.5	46
2	1.7	3.3	1	6.2	2.6	20
			2	12.6	1.8	37
3	1.9	7.4	1	9.5	1.9	26
			2	14.7	1.4	43

Table 5. Results for the Polymerization of *n*-Butyl Acrylate (20 mL, 1.4×10^{-1} mol) in the Presence of Glyceraldehyde Dimer and Pyridine Initiated with BST (0.2 g, 5.2×10^{-4} mol)

entry	glyceraldehyde dimer (10^{-4} mol)	Py (10^{-4} mol)	rxn time (h)	M_n (10^{-3}) g mol^{-1}	M_{nth} (10^{-3}) g mol^{-1}	PDI	conv (%)
1	0.55	12.7	1	3.5	3.4	1.4	10
			2	4.1	5.1	1.3	15
			5	7.2	7.2	1.4	21
2	1.1	6.3	2	5.8	7.2	1.5	21
			4	11.3	12.3	1.4	36
			6	15.0	16.5	1.35	48
			8	17.0	18.5	1.35	54
3	1.7	3.2	1	5.7	5.5	1.6	16
			2	11.1	10.6	1.5	31
			3	15.3	14.1	1.4	41
			4	18.6	17.1	1.4	50
			5	21.0	19.9	1.4	58
4	2.2	3.8	1	4.6	4.4	1.7	13
			2	11.2	10.6	1.6	31
			3	15.4	14.7	1.5	43
			4	18.1	17.5	1.4	51
5	2.2	11.4	1	16.0	12.0	1.5	35
			2	23.0	16.8	1.4	49
			3	26.4	21.6	1.4	63

in the dimeric form, certainly more so than the glyceraldehyde dimer.

To demonstrate that the poly(*n*-butyl acrylate) in the presence of glyceraldehyde and pyridine can be used to form block copolymers chain extensions were performed with styrene. As an illustrative example, heating a poly(*n*-butyl acrylate) (M_n = 13 100 g mol^{-1}, PDI = 1.39) in the presence of styrene and DMSO gave a new polymer with M_n = 20 900 g mol^{-1} and PDI = 1.30.

The ability to make random copolymers with another acrylate monomer was demonstrated by heating a solution of *n*-butyl acrylate and *tert*-butyl acrylate in the presence of BST, glyceraldehyde, and pyridine to provide a conversion after 5 h of 43% and a copolymer with M_n = 11 200 g mol^{-1} and PDI = 1.40. Integration of the terminal broad triplet methyl peak of the *n*-butyl acrylate monomer unit with the broad singlet peak of the *tert*-butyl group of the *tert*-butyl acrylate monomer unit in the ^{1}H NMR spectrum of the resulting copolymer demonstrates that the two monomers were incorporated into the copolymer in roughly the same proportion as the starting molar ratios of the two monomers.

Finally, we were surprised to find that if 20 mL of *n*-butyl acrylate is heated in the presence of 100 mg of glyceraldehyde dimer and 100 mg of pyridine and 0.5 mg of TEMPO, in the absence of BST, a mild exotherm results about 1 h after the reaction temperature reaches 130 °C. If the heating is stopped right after this point and the reaction mixture is cooled, an *n*-butyl acrylate polymer is obtained with a M_n of about 80 000 g mol^{-1} and a MWD of 1.17. The polymerizations are quite reproducible with conversion typically in the 25−30% range. While the MWD is narrow, the system is not living. If the reaction is allowed to continue for an additional 15 min, the

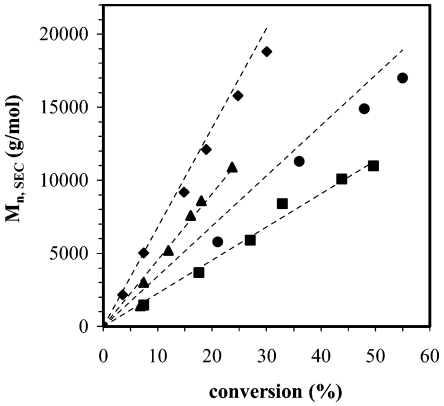


Figure 2. Dependence of molar mass on monomer conversion for the *n*-BuA polymerization in the presence of glyceraldehyde dimer and pyridine with different monomer/initiator at 133 °C. [*n*-BuA]/[BST]/[glyceraldehyde dimer]/[pyridine]: (◆) $1.4 \times 10^{-1}/2.6 \times 10^{-4}/1.1 \times 10^{-4}/6.3 \times 10^{-4}$; (▲) $1.4 \times 10^{-1}/3.9 \times 10^{-4}/1.1 \times 10^{-4}/6.3 \times 10^{-4}$; (●) $1.4 \times 10^{-1}/5.2 \times 10^{-4}/1.1 \times 10^{-4}/6.3 \times 10^{-4}$ (Table 5, entry 2); (■) $1.4 \times 10^{-1}/7.9 \times 10^{-4}/1.4 \times 10^{-4}/7.6 \times 10^{-4}$. The dotted lines show theoretical dependences.

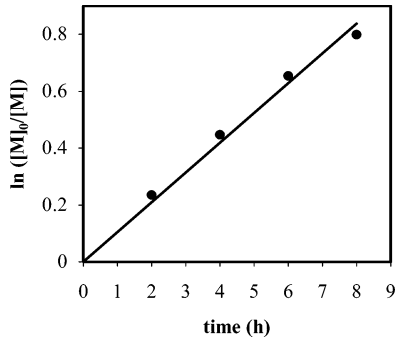


Figure 3. Plot of $\ln([M]_0/[M])$ vs time for *n*-butyl acrylate polymerization initiated by BST at 133 °C in the presence glyceraldehyde and pyridine. [*n*-BuA]/[BST]/[glyceraldehyde dimer]/[pyridine]: $1.4 \times 10^{-1}/5.2 \times 10^{-4}/1.1 \times 10^{-4}/6.3 \times 10^{-4}$ (Table 5, entry 2).

molecular weight of the polymer decreases and the polydispersity broadens. No shifting of the MWD plots to higher molecular weight is observed. Samples taken just before the exotherm contained only oligomers as indicated by GPC.

In summary, the ability to polymerize *n*-butyl acrylate under SFRP conditions using TEMPO as the moderating nitroxide has been shown to be possible at typical temperatures for the SFRP process using different combinations of α-hydroxycarbonyl compounds and organic bases. In the case of glyceraldehyde dimer and pyridine, the combination that gave the best results produces a linear relationship between the molecular masses and conversion and $L_n([M]_0/[M])$ vs time, suggesting that these polymerizations are proceeding under controlled conditions. The results in this paper further support the argument that the ability to polymerize *n*-butyl acrylate in the presence of TEMPO is primarily predicated on the ability to control excess free nitroxide accumulated in the reaction mixture due to inevitable chain termination. While the active species in these reactions is assumed to be the ene−diol, formed from the reaction of an α-hydroxyketone with an organic base, the advantage of this method over the use of ascorbic acid is that all the reagents are added at the beginning of the polymerization, eliminating the necessity of adding incremental amounts of a reagent over the course of the polymerization as was the case for ascorbic acid.

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Supporting Information Available: A table of reaction times, M_n's, PDI's, and conversions for samples analyzed for the random copolymerization of *n*-butyl acrylate and *tert*-butyl acrylate; a GPC overlay plot for these samples; a 500 MHz ^{1}H NMR spectrum in $CDCl_3$ (Varian Unity INOVA-500 spectrometer) for the final copolymer sample obtained in the polymerization described in experiment e; a GPC plot for the chain extension reaction of *n*-butyl acrylate with styrene, experiment d. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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