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Reduced Branching in Poly(butyl acrylate) via Solution Radical Polymerization in *n*-Butanol

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INTRODUCTION

Acrylate polymerization kinetics deviate from the expected free-radical polymerization behavior due to the occurrence of an intramolecular chain transfer (backbiting) reaction that converts a chain-end radical to a less reactive midchain radical (MCR).[1] Because of the slower addition of monomer to the MCR (with rate coefficient k_p^{MCR}), the observed rate of acrylate polymerization is significantly lower[2−4] than would be expected from the chain-end propagation rate coefficient (k_p) measured by pulsed laser polymerization (PLP).[5] The backbiting rate coefficient (k_{bb}) and its temperature dependence have been evaluated for *n*-butyl acrylate (BA) by various techniques, including analysis of short-chain branching (SCB) frequency,[3,6] and by specialized pulsed-laser techniques that also provide an estimate of k_p^{MCR}.[7] MCR formation occurs at mild conditions, even at 0 °C,[6,8] and leads to significant SCB levels (>5 branches per 100 repeat units) in poly(BA) produced under starved-feed high-temperature (>100 °C) semibatch reaction conditions often used to produce acrylic polymers for coatings applications.[3,9,10] At these higher temperatures, the MCR formed by backbiting not only propagates and terminates but can also undergo β-scission to produce a chain-end radical and a terminally unsaturated polymer chain (a macromonomer)[9,11] detectable by proton NMR.[3,11,12]

Detailed models of high-temperature BA solution polymerization (including reaction of the macromonomer produced by β-scission) have been formulated to describe experimental results over a range of operating conditions.[10,13] It is also useful to examine analytical expressions for the averaged propagation rate coefficient (k_p^{av}, eq 1) and branching level (BL, eq 2) derived under the assumption that the majority of midchain radicals formed by backbiting result in formation of a branch point.[2,4]

$$k_p^{av} = \frac{k_p}{1 + \dfrac{k_{bb}}{k_p^{MCR}[M]}} \tag{1}$$

$$BL = \frac{k_{bb}}{k_p[M] + k_{bb}} \tag{2}$$

BL increases with reduced monomer concentration [M] and with increased temperature due to the higher activation energy of k_{bb} compared to k_p.[7,8,10] As branching increases, polymerization rate (proportional to k_p^{av}) decreases, as does average polymer chain length.[4,10]

It is possible to produce BA with low SCB levels by polymerizing at low temperatures, high monomer concentrations, and low conversions.[14] BL can also be reduced by adding a powerful chain-transfer agent to the system; however, such a reduction is accompanied by a drastic decrease in polymer molecular weight (MW).[15] Recently, we have shown that backbiting in acrylates is also affected by intermolecular H-bonding; addition of *n*-butanol (BuOH) to BA at 50 °C in a PLP experiment reduced BL from 0.3% to a level not detectable by ^{13}C NMR.[16] As both MW and SCB impact poly(BA) rheology,[14] it would be beneficial to independently control these properties under industrially relevant synthesis conditions. In this work, we demonstrate that the branching level in poly(BA) produced via starved-feed semibatch solution free-radical polymerization is reduced 5-fold through introduction of a solvent capable of H-bonding to the acrylate carbonyl group, such as BuOH. In addition, direct evidence of a reduced rate of backbiting in the BA/BuOH system is found via the single pulse−pulsed laser polymerization−electron paramagnetic resonance (SP-PLP-EPR) technique, which consists of highly time-resolved online monitoring of radical concentration after production of an intense burst of radicals by pulsed-laser-induced decomposition of a photoinitiator at $t = 0$.[8]

EXPERIMENTAL SECTION

Starved-feed semibatch solution experiments were carried out in a 1 L LabMax reactor system with an agitator, reflux condenser, and automatic temperature control. The reactor was charged with 243 g of xylene (isomeric mixture with boiling point between 136 and 140 °C, Sigma-Aldrich Co.) and heated to the reaction temperature of 110 °C. 104 g of BA (purity >99.5% containing 45−55 ppm of hydroquinone monomethyl ether inhibitor) and 0.88 g of benzoyl peroxide (BPO) initiator (0.5 mol% relative to BA added, dissolved in 20 g of acetone) were continuously fed over 3 h such that the final system contained 70 wt% solvent. Samples of approximately 1−2 mL were drawn from the reactor at specified times into an ice-cold solution of 4-methoxyphenol (1 g L^{-1}) in xylene to terminate the reaction. The same procedure was repeated for a second experiment, replacing xylene solvent with *n*-butanol (BuOH).

Residual monomer concentrations were determined by gas chromatography, and polymer molar mass distribution (MMD) was measured by size exclusion chromatography, as detailed previously,[12] with a light scattering detector used to verify the

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Table 1. Properties of Poly(butyl acrylate) Produced by Semibatch Solution Polymerization at 110 °C[a]

	M_n (g mol^{-1})	M_w (g mol^{-1})	MM%	BL%
BA in xylene[10]	4960	10700	0.60	6.55
BA in xylene	4750	11300	0.65	6.02
BA in BuOH	26900	55700	0.13	1.14

[a] Properties of final polymer sample (t = 3 h). M_n: number-average MW; M_w: weight-average MW; MM%: number of terminal unsaturations per 100 BA repeat units; BL%: number of branch points per 100 BA repeat units.

MW averages calculated from the refractive index detector and universal calibration. Proton NMR was used to determine the macromonomer content (MM%, reported per 100 BA repeat units in the polymer) of the final sample, and ^{13}C NMR was used to measure the branching level (BL%), using previously developed procedures.[12,16]

Backbiting rate coefficients, k_{bb}, were determined for 1.50 M BA solutions in *n*-butanol at 0 and 30 °C using the SP-PLP-EPR technique to measure the concentrations of secondary chain-end radicals and of midchain radicals, following the procedures described for BA polymerization in toluene solution.[8] EPR tubes of smaller inner diameter were required for measurements in *n*-butanol to compensate for the increased solvent polarity.

RESULTS AND DISCUSSION

The experimental conditions and operating procedure chosen at 110 °C are similar to those used in an extensive study of high-temperature BA semibatch solution polymerization,[10] with the following differences: xylene was used instead of a mixed xylene/ethylbenzene solvent; BPO (half-life of 8.1 min at 110 °C) was used as initiator instead of *tert*-butyl peroxyoctoate (half-life of 11.8 min); BA and initiator were fed over 3 h instead of a 1 h feed period followed by 1 h hold. Despite these operational differences, the properties—MW averages, MM%, and BL%—of the poly(BA) produced with xylene in this study are very similar to those reported in ref 10 for the same solvent and initiator levels, as summarized in Table 1.

Figure 1 plots the free monomer levels and MW averages over the course of the experiment. Monomer concentrations remain low (<0.3 M) throughout the course of both experiments, a general feature of the starved-feed semibatch process[3,9,10] and one that promotes SCB formation. Despite the lower [M] in BuOH relative to xylene, however, the MW of the poly(BA) formed in BuOH is significantly higher. The data summarized in Table 1 indicate that replacing the xylene solvent with BuOH has a remarkable effect on polymer properties: BL and MM levels decrease by a factor of 5, and the polymer weight-average MW increases by a similar factor. In addition, the polydispersity index of the polymer decreases from 2.4 (produced in xylene) to 2.1 (in BuOH).

Equations 1 and 2 provide a rough measure of the dramatic effect that H-bonding has on the values of k_{bb} and k_p^{av}. Using the values for k_p (80 200 L mol^{-1} s^{-1}) and k_p^{MCR} (150 L mol^{-1} s^{-1}) at 110 °C taken from the literature as summarized in the previous modeling study,[10] and using a rough estimate for [M] of 0.28 M in xylene and 0.18 M in BuOH (approximate average over last 2 h of reaction, see Figure 1), the estimated value for k_{bb} in BuOH is a factor of 8 lower than the value estimated for the experiment in xylene; the actual difference may be smaller, as there are indications that the value of k_p for BA in BuOH is higher than in bulk.[16] With reduced backbiting, the formation of macromonomer is also lowered, and the polymer chain length is dramatically increased as the estimated value of k_p^{av} (from eq 1) increases by a factor of 4–5 in BuOH compared to xylene.

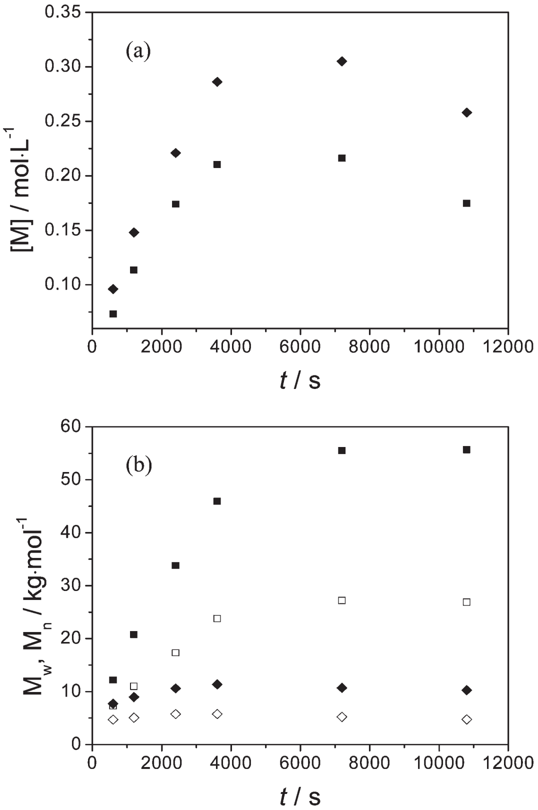

Figure 1. (a) Butyl acrylate concentration ([M]) and (b) polymer number-average (M_n, open symbols) and weight-average (M_w, closed symbols) molecular weight profiles for semibatch starved-feed solution polymerizations at 110 °C in xylene (◆) and *n*-butanol (■).

An independent estimate of k_{bb} has been obtained at lower temperatures by measuring the concentrations of secondary chain-end radicals (SPRs) and of midchain radicals (MCRs, from backbiting) using the SP-PLP-EPR technique. At polymerization temperatures up to 60 °C, side reactions such as β-scission of MCRs may be ignored. Data treatment of the concentration vs time profiles for SPRs and MCRs during BA polymerization in BuOH has been carried out the same way as used for the BA SP-PLP-EPR data obtained in toluene solution.[8] Presented in Figure 2 are experimental data for 30 °C.

Listed in Table 2 is the rate coefficient for backbiting, k_{bb}, for two temperatures as obtained by Predici fitting using a model which takes chain-length-dependent termination into account.[8] For comparison, the associated values for BA polymerization in either bulk or in toluene solution have been tabulated. For the fitting, the k_p value for chain-end radicals has been identified with the one measured for BA in toluene; however, it has been checked that modest variation of k_p has no major impact on the resulting k_{bb} estimate. In addition to k_{bb}, the fitting procedure yields the rate coefficient for propagation of MCRs, k_p^{MCR}, and three termination rate coefficients referring to reaction between secondary and tertiary radicals, $k_t^{\mathrm{s,s}}$, $k_t^{\mathrm{s,t}}$, and $k_t^{\mathrm{t,t}}$. The numbers

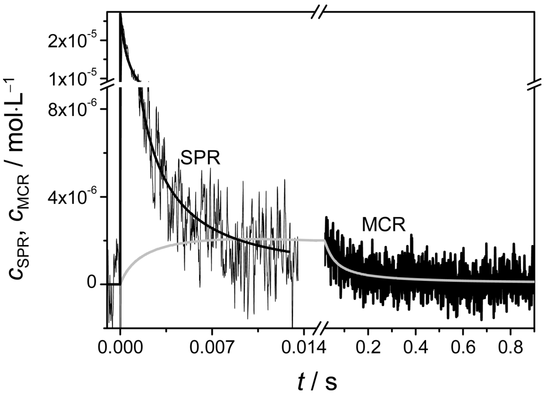

Figure 2. Measured SPR and MCR concentrations for polymerization of BA (1.50 M in *n*-butanol) at 30 °C plotted as a function of time t after applying the laser pulse at $t = 0$. The black line represents the fit of SPR concentration, whereas the gray lines refer to the concentration vs t correlation of MCRs.

Table 2. Rate Coefficient k_{bb} Obtained for BA Polymerization in Toluene (or in Bulk)[7,8] and in 1.5 M *n*-Butanol Solution As Obtained in the Present Work

T/°C	0	30
k_{bb}/s^{-1} (1.5 M in toluene)[8]	37	168
k_{bb}/s^{-1} (1.5 M in *n*-butanol)	11 ± 2	58 ± 12

found for these rate coefficients are more or less identical to the ones reported for BA in solution of toluene.[8] The backbiting rate coefficient of BA is significantly reduced, by about a factor of 3, in passing from BA polymerization in toluene (or in bulk) to polymerization in BuOH. While consistent with the lower branching levels of poly(BA) produced by semibatch polymerization in BuOH, the decrease in the backbiting rate coefficient is less pronounced. This difference may result from the lower monomer concentration of 0.18 M in the semibatch experiments as compared to 1.5 M in the SP-PLP-EPR measurement.

CONCLUSION

The SP-PLP-EPR technique is used to determine that there is a significant reduction in the fraction of midchain radicals formed during BA polymerization in the presence of the H-bonding solvent BuOH, compared to polymerization in toluene or in bulk. BuOH inhibits the intramolecular chain transfer to polymer reaction that causes a reduced reaction rate and the formation of branchpoints along the polymer backbone, in agreement with the conclusions inferred from the previous PLP study.[16] While the exact nature of the H-bonding interaction is yet to be determined, it is shown that the reduced backbiting leads to a significant decrease in poly(butyl acrylate) branching levels for solution polymerization in BuOH compared to xylene at higher temperature industrially relevant conditions. An important result of the reduced branching levels in BuOH is the production of higher MW polymer at identical synthesis conditions. Additional work is underway to investigate the ability to control branching levels through solvent choice as well as to study the role that employing monomers with hydroxyl functionality (e.g., 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate) has on copolymerization behavior.[16,17]

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