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# Reversible Nitroxide Trapping of the Mid-Chain Radical in *n*-Butyl Acrylate Polymerization

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Ⓢ *Supporting Information*

## INTRODUCTION

Chain transfer to polymer is a significant process in the polymerization of acrylate-type monomers.[1−4] It is well accepted that intramolecular chain transfer to polymer (so-called backbiting) is favored over intermolecular chain transfer to polymer. It has been reported that chain transfer to polymer occurs primarily via a 1,5-hydrogen shift (Scheme S1, Supporting Information).[5−7] It is important to note that intramolecular chain transfer to remote positions is also possible, though not favored. The result of chain transfer to polymer is an interesting situation in which two distinct transient radicals coexist in the system. The complexity and challenges posed by the coexistence of two distinct transient radicals in *n*-butyl acrylate (BA) polymerization becomes apparent in the kinetic description of its controlled radical polymerization.

The prime focus of this Communication is to probe the kinetics of BA polymerization mediated by nitroxides, especially the implications on kinetics of the reversible deactivation of the tertiary mid-chain radicals (MCRs).

## RESULTS AND DISCUSSION

For BA polymerization, the equilibrium constant ($K$) describing this reaction has been expressed in the literature by eq 1, where $k_d$ and $k_c$ are rate coefficients of dissociation and combination, respectively.

$$K = \frac{k_d}{k_c} \tag{1}$$

Equation 1 falls short in the description of the equilibrium reaction(s) in BA polymerization, as it assumes only a single type of transient radical. The intramolecular chain transfer to polymer results in coexistence of secondary propagating radicals (SPRs) and tertiary MCRs. Based on structural differences, the reactivity of the two transient radicals toward the nitroxide/mediator is expected to differ. As a result, no single set of $k_c$ and $k_d$ can hold true in describing both the reversible deactivation−activation involving the SPRs and the MCRs. To find an equivalent expression for the description of the equilibrium in BA type polymerization systems, Scheme S2 is considered. This alternative expression should in general hold for systems in which two distinct transient radicals ($P^{\bullet}$ and $Q^{\bullet}$) coexist, both with the capability to undergo reversible deactivation. Differential equations derived from Scheme S2 are illustrated by eqs 2−5.

$$\frac{d[P_0]}{dt} = k_d[P_0{-}Y] - k_c[P_0][Y] - k_{p,i}[P_0][M] \tag{2}$$

$$\frac{d[P_1]}{dt} = k_i[P_0][M] - k_p[P_1][M] + k_d[P_1{-}Y] - k_c[P_1][Y] - (k_t[P_i] + k_t^t[Q_i])[P_1] \tag{3}$$

$$\frac{d[P_i]}{dt} = k_p[M][P_{i-1}] - k_p[M][P_i] - k_{bb}[P_i] + k_p^t[M][Q_{i-1}] + k_d[P_i{-}Y] - k_c[P_i][Y] + k_\beta[Q_i] - (k_t[P_i] + k_t^t[Q_i])[P_i] \tag{4}$$

$$\frac{d[Q_i]}{dt} = k_{bb}[P_i] - k_p^t[M][Q_i] - (k_t^{tt}[Q_i] + k_t^t[P_i])[Q_i] + k_d^t[Q_i{-}Y] - k_c^t[Q_i][Y] - k_\beta[Q_i] \tag{5}$$

Because of the smooth molecular weight distribution, concentration of chains of length $i$ and $i - 1$ can be considered identical such that one can write $[P_{i-1}] = [P_i]$ and $[Q_{i-1}] = [Q_i]$. Furthermore, $[P] = \Sigma_{i=1}^{\infty} P_i$ and $[Q] = \Sigma_{i=1}^{\infty} Q_i$. Assuming steady-state conditions, the change with time of the total concentration of transient radicals ($[P] + [Q]$) is expressed by eq 6. From eqs 4−6, the expression governing the equilibrium in nitroxide-mediated BA polymerization can be derived (eq 7).

$$\frac{d([P] + [Q])}{dt} = 0 \tag{6}$$

$$k_d[P{-}Y] + k_d^t[Q{-}Y] = k_c[P][Y] + k_c^t[Q][Y] \tag{7}$$

For systems with a single type of transient radical, the equivalent of eq 7 is $k_d[P{-}Y] = k_c[P][Y]$, from which eq 1 is derived. However, for a system with two distinct transient radicals, the equilibrium constant is dependent on four rate coefficients instead of two. In the literature, several sets of $K$, $k_d$, and $k_c$ have been reported for BA with different nitroxides.[8−10] Values of $K$ and $k_d$ are determined experimentally, from which values of $k_c$ are then calculated using eq 1. For an acrylate type system, the values of $K$ and $k_d$ obtained experimentally are, in a

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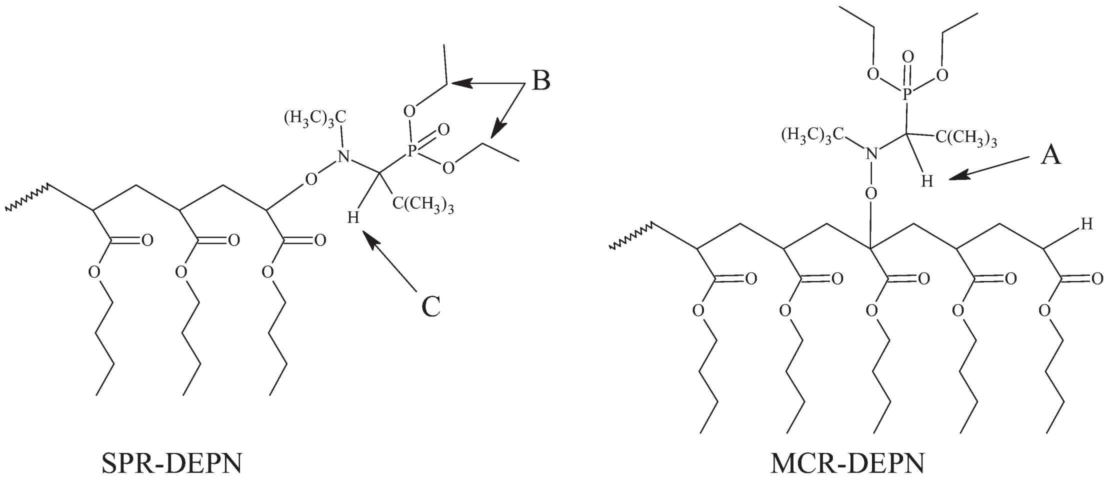
**Scheme 1. Possible Dormant Structures of Poly(*n*-butyl acrylate) (PBA) Illustrating the Adducts of the SPR and the MCR with the Nitroxide DEPN**



way, composite values that contain contributions of both reversible reactions of the SPRs and MCRs. Since the value of $k_c$ is obtained from $K$ and $k_d$, the value of $k_c$ is also directly influenced by the coexistence of SPRs and MCRs. To the best of our knowledge, the effects of MCRs on the equilibrium description in CRP systems have not been addressed to date. A concise description of the equilibrium in BA polymerization mediated by persistent radical species is illustrated by eq 8.

$$K^{app} = \frac{k_d^{app}}{k_c^{app}} = \frac{([P] + [Q])[Y]}{[P-Y] + [Q-Y]} \qquad (8)$$

The consequence of neglecting eq 8 in favor of the simpler expression (eq 1) is addressed, considering homo- and copolymerization of BA. First, in the case of nitroxide-mediated BA homopolymerization the respective equilibria are illustrated in Scheme S3 . As mentioned earlier, it can be argued that the equilibrium constant reported in the literature represents a weighted average of both equilibria.

Second, in a copolymerization system (Scheme S4), intramolecular chain transfer to polymer is reduced by the presence of the comonomer (such as styrene (S)). The extent to which the reduction occurs depends on the initial feed composition of the monomers. In BA homopolymerizations, two types of active chains are present (namely SPR and MCR) illustrated by Scheme S1. However, in the presence of a comonomer such as styrene, the likelihood of the backbiting reaction, transforming SPRs into MCRs, is greatly minimized if not completely eliminated. Therefore, if one was to consider a copolymerization system of BA and styrene, the active chains with BA as the terminal unit can be illustrated as shown in Scheme S4, showing the penultimate unit.

The reversible deactivation involving chain end radicals with BA as the terminal unit only involves the reaction between a nitroxide and the SPR of BA (Scheme S5). The effects of the penultimate unit on the activation/deactivation processes are not taken into account in the description of the equilibria illustrated in Scheme S5. In a copolymerization system, eq 8 reduces to the simpler form, eq 1. It can be hypothesized that the equilibrium constant obtained from BA homopolymerization will not be suitable for the description of the equilibrium of a terminal BA radical in a S/BA copolymerization.

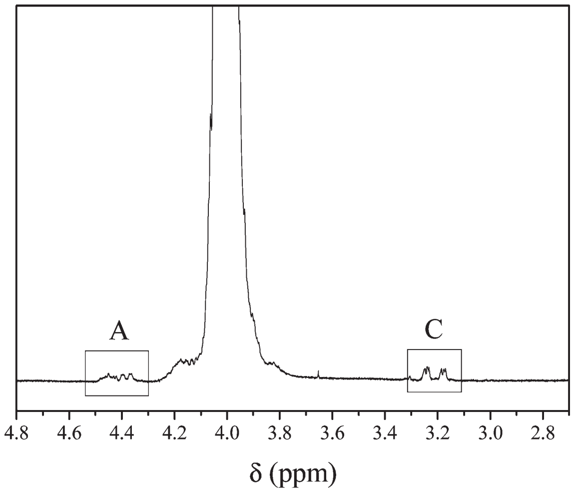


**Figure 1.** $^1$H NMR spectrum of PBA in the region 4.7−2.8 ppm with the peaks labeled A and C assigned to signals of the protons labeled in Scheme 1.

Support for validity of the approach in this contribution is obtained by experimentally showing the existence of the dormant species of SPRs and the MCRs (Scheme 1) with *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN). Special attention is given to MCR-DEPN since it has been largely overlooked in the literature and because of its implication on the description of the reaction kinetics.

A $^1$H NMR spectrum of poly(*n*-butyl acrylate) (PBA) prepared using the alkoxyamine 2-methyl-2[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethoxypropyl)aminoxy]propionic acid (MAMA-DEPN) as the initiator is shown in Figure 1. The signal peaks at $\delta \sim 3.2$ ppm are due to the α-proton (labeled C in Scheme 1) of DEPN attached to an SPR. However, the prime region of interest in Figure 1 is that of peaks labeled A. This signal has been assigned to the α-proton (labeled A in Scheme 1) of DEPN in a dormant structure in which the MCR is reversibly terminated by DEPN. The assignment of peaks in Figure 1 was aided by prediction of $^1$H and $^{13}$C NMR spectra of the species of interest (Scheme 1). The predictions of NMR spectra of the

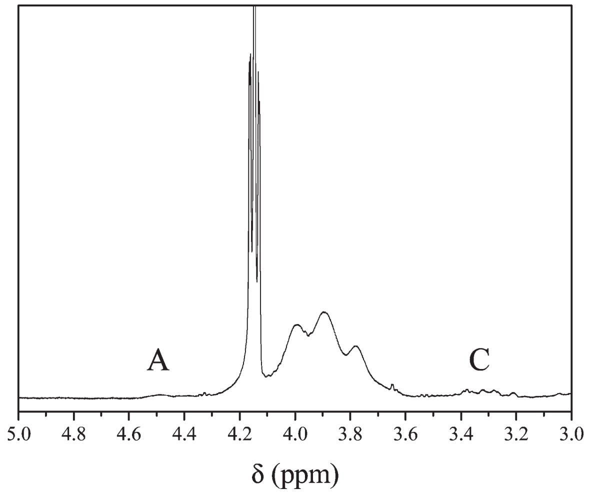


**Figure 2.** $^1$H NMR spectrum of styrene/BA copolymerization mixture in the region 5.0−3.0 ppm with the peaks labeled A and C assigned to signals of the protons labeled in Scheme 1 ($f_S$ = 0.4).

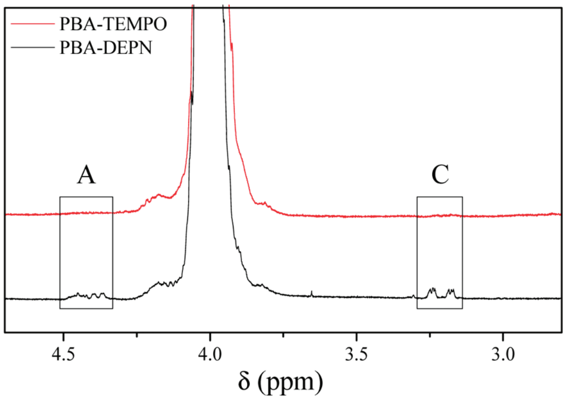


**Figure 3.** $^1$H NMR spectra of PBA end-capped with DEPN (black solid line) and TEMPO (red solid line). The PBA-DEPN was transformed to PBA-TEMPO via a nitroxide exchange reaction.

DEPN end-capped chains were carried out with ACD/Laboratories NMR predictor (version 7.07). In the predicted $^1$H NMR spectra of the SPR-DEPN adduct (not shown), the proton labeled C was observed in its expected region (3.2−3.4 ppm). With reference to the proton labeled C, the expected chemical shift for the peaks due to the proton labeled A could be predicted.

If the formation of MCRs is suppressed, the peak due to the α-proton of DEPN attached to MCRs would be expected to disappear in Figure 1. Elimination or significant minimization of chain transfer to polymer by introduction of styrene as comonomer resulted in the disappearance of the signal due to proton A (Figure 2).

An increase in the content of styrene in the feed resulted in the reduction of peak region A due to the (virtual) absence of the MCR-DEPN adducts. The peak labeled C remained as dormant species of DEPN with the SPRs still existed, albeit significantly reduced in size due to the large fraction of styrene terminal monomer units.[11]

If, on the other hand, the nitroxide DEPN was to be replaced by a different moiety, then both peaks labeled A and C (Figure 1) would be expected to disappear. The nitroxide DEPN in PBA-DEPN was exchanged with TEMPO. Upon nitroxide exchange of DEPN with TEMPO in PBA chains, signals due to protons A and C disappeared (Figure 3). The work of Farcet et al.[6] reported on PBA chains with multiple nitroxides illustrating multiple growth points as a result of chain transfer to polymer. The study provided no direct evidence of the MCR-DEPN adduct but illustrated that chain transfer to polymer in BA polymerization was predominantly via the intramolecular process.

## ■ CONCLUSIONS

In this Communication, the coexistence of two transient radicals in the nitroxide-mediated polymerization of BA was proven. The expected effect of the coexisting radicals on the kinetics of the polymerization was discussed. The validity was questioned of the commonly used expression (eq 1) in the description of the equilibrium in systems such as BA polymerization. An equivalent of eq 1 is proposed (eq 8) for a two-transient-radical system, as derived from eq 7. With knowledge of the fraction of MCRs in BA polymerization,[12,13] one can comprehend the contribution of such species toward the evaluated equilibrium constant in a homopolymerization system. This work is considered highly relevant, in relation to the common misconception of the description of acrylate copolymerization on the basis of rate coefficients derived from homopolymerization studies.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Polymerization and postpolymerization modification procedures; list of schemes; simulation of styrene/BA copolymerization with PREDICI. This material is available free of charge via the Internet at http://pubs.acs.org.

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