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The Effect of Intramolecular Transfer to Polymer on Stationary Free Radical Polymerization of Alkyl Acrylates

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ABSTRACT: New expressions that account for the formation of acrylate midchain radicals by intramolecular transfer and their subsequent propagation, termination, and transfer events have been derived for polymerization rate, average chain-length, and chain-length distribution under stationary conditions. The nonidealities observed in previous kinetic studies are captured in a single lumped rate coefficient, θ, that controls the apparent order of rate on monomer concentration. Applied to rate data from the literature, the treatment yields consistent estimates for θ and $k_p/k_t^{0.5}$ for butyl acrylate polymerization at 50 °C. Combining these ratios with chain-end propagation values determined by pulsed-laser polymerization, intramolecular transfer rate coefficients estimated from ^{13}C NMR data, and/or radical concentrations measured by ESR provides a new means to estimate the individual rate coefficients for acrylate polymerization systems. It is also shown that estimates for butyl acrylate transfer to monomer rate coefficients obtained from chain-length distributions are valid even in the presence of acrylate backbiting events.

Introduction

Numerous studies[1−9] indicate that alkyl acrylate kinetics deviate considerably from the expected behavior for stationary free radical polymerization (eq 1).

$$R_p = -\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}}[M](\nu_{in})^{1/2} \tag{1}$$

While the expected ½ order dependence of polymerization rate R_p on initiation rate v_{in} is observed, the first-order proportionality between rate and monomer concentration [M] is not. Instead, the exponent m in the proportionality law $R_p \sim [M]^m$ is found to lie between 1.4 and 1.8 and to vary with monomer concentration. The ratio $k_p/k_t^{0.5}$ (k_p and k_t are propagation and termination rate coefficients, respectively) also apparently varies with [M]. For example, Madruga and Fernandez-Garcia[6] have shown that $k_p/k_t^{0.5}$ for *n*-butyl acrylate (BA) decreased from 1.54 to 1.4 at 50 °C as the monomer concentration in benzene decreased from 5 to 3 mol/L. The same experiment for methyl methacrylate did not show any change in the $k_p/k_t^{0.5}$ ratio. Kaszás et al.[5] have shown that the decrease of BA monomer concentration from 6.79 to 0.305 mol/L in benzene leads to an almost 5-fold decrease in $k_p/k_t^{0.5}$. Various hypotheses to explain this unexpected kinetic behavior for acrylates have been proposed, including primary radical termination and degradative chain transfer,[4] chain-length dependence of termination rate coefficients,[8] the hot radical theory,[5] and monomer/solvent complexation.[3] Among these explanations is also the influence of intramolecular transfer to polymer, put forth by Scott and Senogles.[3] However they came to the conclusion that "theoretical and experimental evidence is inconclusive for the occurrence of degradative radical backbiting process in acrylate polymerization".[3]

Since the pioneering work of Scott and Senogles, strong evidence has emerged to show that backbiting and slow reinitiation of the resulting midchain radical is indeed an important process for acrylate polymerization, even at low temperatures. The propagating chain-end radical wraps around to abstract a hydrogen-atom from an acrylate unit on its own backbone, most likely via the formation of a six-membered ring, as shown in Scheme 1 for BA. The presence of the midchain radical has been directly observed via ESR.[10−12] Indirect evidence is based upon ^{13}C NMR measurement of the quaternary carbons in the polymer that result from addition to the midchain radical to form a short-chain branch, following the work of Ahmad et al.[13] The intramolecular chain transfer reaction, sometimes referred to as backbiting, is well-known in high-temperature ethylene homopolymerization, and it has been observed in ethylene/BA copolymerization that the methine hydrogens on BA units in the polymer chain are much more susceptible to abstraction than hydrogens from a CH$_2$ unit in the backbone.[14] Quaternary carbons and midchain radicals are found under conditions of very low polymer concentration and low temperatures (for example, branching on poly(BA) samples resulting from backbiting has been detected even at −16 °C),[13,15] indicating that the intramolecular (backbiting) mechanism must be considered when examining the acrylate kinetic studies in the literature.

Pulsed-laser polymerization (PLP) studies demonstrate that addition of monomer to a chain-end radical (R) is very fast,[16,17] but observed rates of BA polymerization are significantly lower than would be expected from this estimate.[18,19] This result is in agreement with evidence suggesting that monomer addition to the midchain radical proceeds at a much slower rate than addition to the parent end-chain radical, including an ESR study of methyl acrylate trimer polymerization,[20] a monomer that forms a similar radical structure as that

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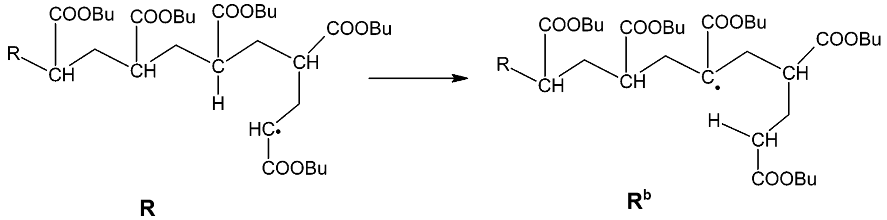
Scheme 1. Formation of a Midchain Radical (R^b) by Intramolecular Chain Transfer to Polymer by a Chain-End Radical (R)[a]



[a] Monomer addition to the new radical structure creates a short-chain branch in the polymer.

shown for the midchain radical in Scheme 1. After the first monomer addition to the midchain radical, the propagating radical assumes chain-end character and continues growth with the normal k_p value. Following recent experimental and modeling studies by Asua, Leiza and co-workers,[15,18,21−22] Nikitin et al.,[23,24] and Peck and Hutchinson,[19] a consensus has emerged that the intramolecular transfer event followed by slow reinitiation has a significant effect on acrylate polymerization rate, even at low temperatures.

In this work, we reconsider the basic expressions describing free radical polymerization rate, average chain-length, and chain-length distribution, taking into consideration the additional mechanisms important for acrylate systems. The resulting equations capture the nonidealities observed in the literature, and provide a new means to generalize the treatment of acrylate kinetics.

Model Development

A basic model of free radical polymerization takes into account the set of reactions denoted in Scheme 2. The subscript i denotes the number of monomeric units in growing polymer radicals (R_i) and dead polymer chains (P_i). The free radical initiator (I) unimolecularly decomposes (with rate coefficient k_d) to form two primary radicals (R_0) with efficiency f. Chain initiation occurs when the primary radical adds to monomer M, and chain growth continues via successive addition of monomer units to the chain-end radical center (chain propagation, with rate coefficient k_p). Bimolecular coupling of two growing chains results in the loss of two radicals from the system and the formation of either one (termination by combination, k_{tc}) or two (termination by disproportionation, k_{td}) dead polymer chains. Chain stoppage may also occur via a transfer mechanism, where the growing radical abstracts a weakly bonded atom (usually hydrogen) from monomer or other molecules (solvent or chain-transfer agent, denoted by S and A) in the system to generate a dead polymer chain as well as a new polymeric radical of length 1.

Scheme 2. Basic Free-Radical Polymerization Mechanisms

initiation $$I \xrightarrow{k_d} 2fR_0 \qquad (2a)$$

$$R_0 + M \xrightarrow{k_i} R_1 \qquad (2b)$$

propagation $$R_i + M \xrightarrow{k_p} R_{i+1} \qquad (2c)$$

chain transfer

to monomer $$R_i + M \xrightarrow{k_{tr,M}} P_i + R_1 \qquad (2d)$$

to solvent $$R_i + S \xrightarrow{k_{tr,S}} P_i + R_1 \qquad (2e)$$

to agent $$R_i + A \xrightarrow{k_{tr,A}} P_i + R_1 \qquad (2f)$$

termination by disproportionation

$$R_i + R_j \xrightarrow{k_{td}} P_i + P_j \qquad (2g)$$

termination by combination

$$R_i + R_j \xrightarrow{k_{tc}} P_{i+j} \qquad (2h)$$

For acrylate polymerization it is necessary to consider the generation of tertiary (or midchain) radicals via intramolecular transfer to polymer. The formation of these radicals (denoted as R_i^b) with rate coefficient k_{fp}, and their subsequent possible reactions are summarized in Scheme 3. After addition of a single monomer unit to R_i^b (reinitiation, with rate coefficient k_p^b to form a short-chain branch (SCB)) the propagating radical assumes secondary chain-end character and continues growth with the normal k_p value. The superscript b differentiates the associated rate coefficients from those reactions involving chain-end radicals.

Scheme 3. Additional Free-Radical Polymerization Mechanisms for Acrylates

backbiting

$$R_i \xrightarrow{k_{fp}} R_i^b \qquad (3a)$$

reinitiation $$R_i^b + M \xrightarrow{k_p^b} R_{i+1}(+SCB) \qquad (3b)$$

chain transfer

to monomer $$R_i^b + M \xrightarrow{k_{tr,M}^b} P_i + R_1 \qquad (3c)$$

to solvent $$R_i^b + S \xrightarrow{k_{tr,S}^b} P_i + R_1 \qquad (3d)$$

to agent $$R_i^b + A \xrightarrow{k_{tr,A}^b} P_i + R_1 \qquad (3e)$$

termination by disproportionation

$$R_i^b + R_j^b \xrightarrow{k_{td}^b} P_i + P_j \qquad (3f)$$

$$R_i + R_j^b \xrightarrow{\sqrt{k_{td}k_{td}^b}} P_i + P_j \qquad (3g)$$

termination by combination

$$R_i^b + R_j^b \xrightarrow{k_{tc}^b} P_{i+j} \qquad (3h)$$

$$R_i + R_j^b \xrightarrow{\sqrt{k_{tc}k_{tc}^b}} P_{i+j} \qquad (3i)$$

The set of mechanisms summarized by Schemes 2 and 3 provides a complete representation of lower temperature (<80 °C) acrylate polymerization. As the model is used to analyze low-conversion kinetic data, intermolecular chain-transfer need not be included. β-Scission of tertiary radicals is omitted from Scheme 3, since the mechanism has been found to be of negligible importance in this temperature regime.[18,25] The different reactivity of midchain and chain-end radicals in propagation, chain-transfer, and termination mechanisms is explicitly considered. While the slower reactivity of the midchain radical to monomer addition has received much attention, previous modeling works have not considered the difference in termination behavior. k_t^b will be bounded between the value for BA homopolymerization (10^7–10^8 L·mol^{-1}·s^{-1})[26] and values reported (10^5–10^6 L·mol^{-1}·s^{-1}) for polymerizations of methyl acrylate trimer (MAT)[20] and for dimethyl itaconate.[27] The latter monomer also forms a radical structure similar to the midchain radical of Scheme 1. Note that the mobility of these sterically hindered MAT and itaconate radicals, where every repeat unit on the chain contains a SCB, will be greatly reduced compared to R_i^b, for which most of the repeat units preceding the midchain radical will be flexible acrylate units. With little data available, the added complexity of chain-length dependent termination is not considered. The model assumes that the rate coefficient for termination of radicals from the two different populations R_i and R_i^b (reactions 3g and 3i) can be approximated as the geometric mean of k_t^b and k_t, and that secondary and tertiary radicals both have the same mode of termination ($\delta = k_{td}/k_t = k_{td}^b/k_t^b$, where $k_t = k_{td} + k_{tc}$ and $k_t^b = k_{td}^b + k_{tc}^b$). The geometric mean assumption is often used to describe cross-termination of unlike radicals, and also simplifies the derivation of analytical expressions for rate and average chain-length.

General Expressions for Free-Radical Polymerization with Intramolecular Transfer: Radical Concentrations and Polymerization Rate. The following equations for concentrations of secondary ([R]) and mid chain radicals ([R^b]) are derived from the sets of mechanisms given in Schemes 2 and 3

$$[\mathrm{R^b}] = \sqrt{\frac{v_{in}}{k_t}} \times \frac{k_{fp}}{k_{fp}\sqrt{\dfrac{k_t^b}{k_t}} + k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}} \tag{4}$$

$$[\mathrm{R}] = \sqrt{\frac{v_{in}}{k_t}} \times \frac{k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}}{k_{fp}\sqrt{\dfrac{k_t^b}{k_t}} + k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}} \tag{5}$$

where v_{in} is the initiation rate in the system. The derivation of these expressions, which assumes radical stationarity, is given in Appendix A. The ratio of midchain to end-chain radicals is thus:

$$\frac{[\mathrm{R}]}{[\mathrm{R^b}]} = \frac{k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}}{k_{fp}} = \omega_R \tag{6}$$

This ratio, denoted by ω_R, occurs frequently in the derivations below.

The relative radical concentrations have a significant effect on polymerization rate, defined according to eq 7.

$$R_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}][\mathrm{R}] + k_p^b[\mathrm{M}][\mathrm{R^b}] \tag{7}$$

This expression neglects monomer consumption by initiation and transfer reactions, as customary in treatment of polymerization. After substituting eqs 4 and 5 for radical concentrations and rearrangement, one can rewrite eq 7 as follows:

$$R_p = \gamma_b k_p[\mathrm{M}]\sqrt{\frac{v_{in}}{k_t}} \tag{8}$$

Here the factor γ_b, capturing the effect of intramolecular transfer to polymer and the reactions of the resulting midchain radical, is expressed as eq 9.

$$\gamma_b = \frac{k_{fp}\dfrac{k_p^b}{k_p} + k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}}{k_{fp}\sqrt{\dfrac{k_t^b}{k_t}} + k_p^b[\mathrm{M}] + k_{tr,M}^b[\mathrm{M}] + k_{tr,S}^b[\mathrm{S}] + k_{tr,A}^b[\mathrm{A}] + \sqrt{v_{in}k_t^b}} = \frac{\dfrac{k_p^b}{k_p} + \omega_R}{\sqrt{\dfrac{k_t^b}{k_t}} + \omega_R} \tag{9}$$

The polymerization rate is also used to define an average propagation rate coefficient, k_p^{av} for the acrylate system according to eq 10.

$$R_p = -\frac{d[\mathrm{M}]}{dt} = k_p^{av}[\mathrm{M}]([\mathrm{R}] + [\mathrm{R^b}]) \tag{10}$$

Comparison with eq 7 yields

$$k_p^{av} = \frac{k_p[\mathrm{R}] + k_p^b[\mathrm{R^b}]}{[\mathrm{R}] + [\mathrm{R^b}]} \tag{11}$$

and substitution for radical concentrations from eqs 4 and 5 gives the result

$$k_{\mathrm{p}}^{\mathrm{av}} = k_{\mathrm{p}} - \frac{k_{\mathrm{p}} - k_{\mathrm{p}}^{\mathrm{b}}}{1 + \dfrac{k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}] + \sqrt{v_{\mathrm{in}}k_{\mathrm{t}}^{\mathrm{b}}}}{k_{\mathrm{fp}}}} = k_{\mathrm{p}} - \frac{k_{\mathrm{p}} - k_{\mathrm{p}}^{\mathrm{b}}}{1 + \omega_{\mathrm{R}}} \quad (12)$$

or, in terms of γ_{b}, eq 13.

$$k_{\mathrm{p}}^{\mathrm{av}} = k_{\mathrm{p}}\gamma_{\mathrm{b}}\frac{\sqrt{\dfrac{k_{\mathrm{t}}^{\mathrm{b}}}{k_{\mathrm{t}}}} + \omega_{\mathrm{R}}}{1 + \omega_{\mathrm{R}}} \quad (13)$$

The relative rate of monomer addition to the midchain radical to the rate of monomer consumption also controls the level of short-chain branching in the polymer, expressed by eq 14.

$$BL = \frac{k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}][\mathrm{R}^{\mathrm{b}}]}{k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}] + k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}][\mathrm{R}^{\mathrm{b}}]} = \frac{1}{1 + \dfrac{k_{\mathrm{p}}}{k_{\mathrm{p}}^{\mathrm{b}}}\omega_{\mathrm{R}}} \quad (14)$$

Simplification of these full expressions for radical concentrations (eqs 4 and 5), rate of polymerization (eqs 8 and 9), branching level (eq 14), and $k_{\mathrm{p}}^{\mathrm{av}}$ (eqs 12 and 13) is deferred to the discussion section.

General Expressions for Free-Radical Polymerization with Intramolecular Transfer: Average Chain Length and Chain-Length Distribution. For the reactions given in Schemes 2 and 3, the Mayo dependence is expressed through eq 15 (the derivation is in Appendix B)

$$\frac{1}{\bar{P}_{\mathrm{n}}} = \frac{0.5(1+\delta)R_{\mathrm{p}}k_{\mathrm{t}}}{(k_{\mathrm{p}}[\mathrm{M}]\gamma_{\mathrm{b}})^2} + \frac{(k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])}{k_{\mathrm{p}}[\mathrm{M}]}\left(\frac{\omega_{\mathrm{R}}}{\omega_{\mathrm{R}} + \dfrac{k_{\mathrm{p}}^{\mathrm{b}}}{k_{\mathrm{p}}}}\right) + \frac{(k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}])}{k_{\mathrm{p}}[\mathrm{M}]}\left(\frac{1}{\omega_{\mathrm{R}} + \dfrac{k_{\mathrm{p}}^{\mathrm{b}}}{k_{\mathrm{p}}}}\right) \quad (15)$$

where $\bar{P}_{\mathrm{n}}$ is the number-average degree of polymerization.

An expression for the full chain-length distribution (CLD) can also be derived, as described in Appendix C. It takes the following form, where f_i represents the number fraction of polymer chains of length-i generated at an instant in time:

$$f_i = (a + b(i-1))\omega^{i-1} \quad (16a)$$

and

$$\omega = \frac{k_{\mathrm{p}}[\mathrm{M}] + \dfrac{k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}]}{\omega_{\mathrm{R}}}}{k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}] + k_{\mathrm{fp}} + \sqrt{k_{\mathrm{t}}v_{\mathrm{in}}}} \quad (16b)$$

$$a = \frac{a_{\mathrm{u}}(1-\omega)^2}{a_{\mathrm{u}} + (b_{\mathrm{u}} - a_{\mathrm{u}})\omega} \quad (16c)$$

$$b = \frac{b_{\mathrm{u}}(1-\omega)^2}{a_{\mathrm{u}} + (b_{\mathrm{u}} - a_{\mathrm{u}})\omega} \quad (16d)$$

$$a_{\mathrm{u}} = r(\delta\sqrt{k_{\mathrm{t}}v_{\mathrm{in}}} + k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}]) + \frac{r(\delta\sqrt{v_{\mathrm{in}}k_{\mathrm{t}}^{\mathrm{b}}} + k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}])}{\omega_{\mathrm{R}}} \quad (16e)$$

$$b_{\mathrm{u}} = \frac{1}{2}(1-\delta)\left(r\left(\sqrt{k_{\mathrm{t}}} + \frac{\sqrt{k_{\mathrm{t}}^{\mathrm{b}}}}{\omega_{\mathrm{R}}}\right)\right)^2 \quad (16f)$$

$$r = \{v_{\mathrm{in}} + (k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}] + (k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}])[\mathrm{R}^{\mathrm{b}}]\}/\left\{k_{\mathrm{p}}[\mathrm{M}] + \frac{k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}]}{\omega_{\mathrm{R}}}\right\} \quad (16g)$$

This CLD expression can then be transformed and differentiated to the $\mathrm{d}(\ln(f_i))/\mathrm{d}i$ form (Appendix D):

$$\frac{\mathrm{d}(\ln(f_i))}{\mathrm{d}i} = \frac{b}{a + b(i-1)} - \frac{\sqrt{v_{\mathrm{in}}k_{\mathrm{t}}}}{k_{\mathrm{p}}[\mathrm{M}]} - \frac{k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}]}{k_{\mathrm{p}}[\mathrm{M}]} - \frac{k_{\mathrm{fp}}}{k_{\mathrm{p}}[\mathrm{M}]}\omega_{\mathrm{d}} \quad (17a)$$

where

$$\omega_{\mathrm{d}} = \frac{k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}] + \sqrt{v_{\mathrm{in}}k_{\mathrm{t}}^{\mathrm{b}}}}{k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}] + \sqrt{v_{\mathrm{in}}k_{\mathrm{t}}^{\mathrm{b}}}} \quad (17b)$$

The $\mathrm{d}(\ln(f_{\mathrm{i}}))/\mathrm{d}i$ form of the CLD has been proposed as an alternative method of determining chain-transfer coefficients from experimental MWDs,[28] and has been applied to butyl acrylate to estimate chain transfer constants to monomer at different temperatures.[29] However, the influence of intramolecular transfer to polymer was not considered when analyzing the experimental MWDs. Equations 16 and 17, derived for the first time in this paper, explicitly consider the effect of midchain radicals on the CLD. The influence of these additional mechanisms on the experimental determination of chain-transfer rate coefficients is discussed below.

Results and Discussion

Application of these new equations to the analysis of alkyl acrylate polymerization data is simplified if the following inequality holds true:

$$k_{\mathrm{p}}^{\mathrm{b}}[\mathrm{M}] \gg k_{\mathrm{tr,M}}^{\mathrm{b}}[\mathrm{M}] + k_{\mathrm{tr,S}}^{\mathrm{b}}[\mathrm{S}] + k_{\mathrm{tr,A}}^{\mathrm{b}}[\mathrm{A}] + \sqrt{v_{\mathrm{in}}k_{\mathrm{t}}^{\mathrm{b}}} \quad (18)$$

i.e.; if the reinitiation of midchain radicals is much more probable then their transfer or termination. Estimates for k_p^b suggest that it is on the order of 10^2 L·mol^{-1}·s^{-1} at 50 °C,[18] which is significantly higher than expected rate coefficients for transfer to monomer and solvent. (Methacrylate-based radicals, also tertiary carbon centered, have k_{tr}/k_p ratios on the order of 10^{-5}.[30]) The $\sqrt{v_{in}k_t^b}$ term is also small since, as discussed previously, k_t^b is on the order of 10^5 to 10^7 L·mol^{-1}·s^{-1}, and typical radical generation rates (v_{in}) are on the order of 10^{-7} mol·L^{-1}·s^{-1}. Equation 18 is a variant of the long-chain approximation (LCA) often applied to free radical polymerization systems, and results in the following simplified expression for eq 6, the ratio of chain-end to midchain radicals in the system:

$$\omega_R = \frac{[R]}{[R^b]} = \frac{k_p^b[M]}{k_{fp}} \tag{19}$$

When substituted into eq 13, this yields the expression for k_p^{av} derived previously[18,24] (eq 20).

$$k_p^{av} = \frac{k_p}{1 + \dfrac{k_{fp}}{k_p^b[M]}} \tag{20}$$

Substitution into eq 9 yields the following for γ_b, the factor that captures the effect of intramolecular transfer to polymer on reaction rate (eq 21).

$$\gamma_b = \frac{\dfrac{k_p^b}{k_p} + \dfrac{k_p^b[M]}{k_{fp}}}{\sqrt{\dfrac{k_t^b}{k_t} + \dfrac{k_p^b[M]}{k_{fp}}}} \tag{21}$$

The reported levels of branching in acrylate polymerization are small enough to conclude that $k_p[M] \gg k_{fp}$, so that eq 21 may be further simplified (eq 22).

$$\gamma_b = \frac{[M]}{\theta + [M]};\ \theta = \frac{k_{fp}}{k_p^b}\sqrt{\frac{k_t^b}{k_t}} \tag{22}$$

Thus, the rate of polymerization (eq 8) may be rewritten as

$$R_p = \left(\frac{[M]}{\theta + [M]}\right) k_p[M]\sqrt{\frac{v_{in}}{k_t}} \tag{23}$$

and branching level (eq 14) as eq 24.

$$BL = \frac{k_{fp}}{k_p[M] + k_{fp}} \tag{24}$$

These equations can be used to analyze available acrylate kinetic data. For example, using known values for k_p,[16,17] eq 24 has been applied to estimate k_{fp} from SCB levels in poly(butyl acrylate) as determined by a measure of quaternary carbons via ^{13}C NMR. The values for k_{fp} range from 50 to 100 s^{-1} at 0 °C,[15] 900 to 1700 s^{-1} at 75 °C,[15,18] and 2500 to 4000 s^{-1} at 138 °C.[19]

Concentration of Radicals. As well as the simplified expression (eq 19) for the ratio of the two radical types in the system, application of LCA to the expressions for individual radical concentrations is possible. Equations 4 and 5 can be rewritten as eqs 25 and 26.

$$\frac{1}{[R^b]} = \sqrt{\frac{k_t^b}{v_{in}}}\frac{[M]}{\theta\gamma_b} = \sqrt{\frac{k_t^b}{v_{in}}}\left(1 + \frac{[M]}{\theta}\right) \tag{25}$$

$$\frac{1}{[R]} = \gamma_b\sqrt{\frac{k_t}{v_{in}}} = \sqrt{\frac{k_t}{v_{in}}}\left(1 + \frac{\theta}{[M]}\right) \tag{26}$$

Substituting eq 23 for polymerization rate into these equations yields eqs 27 and 28.

$$[R^b] = \frac{k_{fp}}{k_p^b}\frac{R_p}{k_p}\frac{1}{[M]^2} \tag{27}$$

$$[R] = \frac{R_p}{k_p[M]} \tag{28}$$

Equations 25–28 are applicable to the analysis of ESR measurements of radical concentrations during polymerization. For example, a plot of 1/[R^b] vs [M] could be used to determine $\sqrt{k_t^b/v_{in}}$ and θ according to eq 25, and a plot of 1/[R] vs 1/[M] could be used to determine $\sqrt{k_t/v_{in}}$ and θ using eq 26. If polymerization rate is measured simultaneously with [R^b], the ratio of k_{fp}/k_p^b could be determined using eq 27. ESR data could even be used to determine the k_p value according to eq 28, since monomer consumption is dominated by chain-end propagation. And with a measure of both radical populations ([R^b] and [R]) and R_p, it is possible to simultaneously estimate k_{fp} and k_p^b through a combination of eqs 10, 12, and 19. It is clear that the application of these equations to ESR data could provide valuable new insights to the kinetics of acrylate polymerization.

Rate of Polymerization. Equation 23 provides a new and powerful means to analyze rate data obtained in kinetic studies of acrylate polymerization. The derivation is general, making only the well-justified assumptions that radical stationarity is valid, that midchain radicals obey the long-chain hypothesis (eq 18), and that chain-end radicals are more likely to grow through monomer addition than to backbite ($k_p[M] \gg k_{fp}$). All unknown rate coefficients—those for backbiting (k_{fp}), reinitiation of (monomer addition to) the midchain radical (k_p^b), and the relative importance of midchain to chain-end termination ($\sqrt{k_t^b/k_t}$)—are lumped together in the single parameter θ that controls the apparent order of rate on monomer concentration. As shown below, consideration of this factor is essential in understanding the unusual polymerization behavior of acrylates observed in the literature.

According to eq 23, because of $v_{in} = 2fk_d[I]$ (where f is the initiation efficiency, k_d is the initiator decomposition rate coefficient, [I] is the initiator concentration) the rate of polymerization remains proportional to $[I]^{1/2}$, as observed experimentally.[3,5] Second, it is clearly seen how the observed dependence of polymerization rate on monomer concentration (R_p proportional to $[M]^m$) can vary between first and second order, with the value of m dependent on monomer concentration. This behavior is in distinct contrast from the prediction of the classical model of polymerization for which only the case $m = 1$ is expected. Consideration of θ helps to "normalize" the

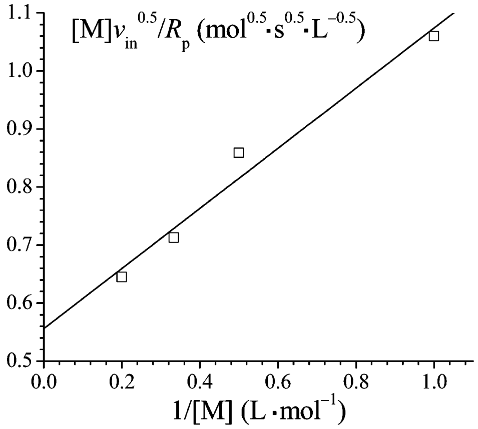


Figure 1. Result of fitting data points from ref 8 by eq 30 for polymerization of butyl acrylate in benzene solution at 50 °C.

polymerization kinetics of acrylates so that they become as predictable as those for methacrylates and styrene. The value of θ can be estimated by experimentally determining the dependence of rate of polymerization R_p on monomer concentration [M] according to the linearized form:

$$\frac{[\mathrm{M}]}{R_\mathrm{p}} = \frac{1}{B} + \frac{\theta}{B[\mathrm{M}]} \tag{29}$$

where $B = k_\mathrm{p}\sqrt{(\mathrm{v_{in}}/k_\mathrm{t})}$.

Scott and Senogles,[1-3] when considering intramolecular transfer to polymer, obtained a similar expression for polymerization rate, the only difference being that they did not consider the difference in termination rate coefficients for [R] and [R^b]. They noted that their expression could explain high monomer orders and initiator orders of 0.5. However in the end they discarded this explanation because of the lack of experimental evidence of midchain radicals at that time, and because of a single data point that disrupted the expected linear dependence between [M]/R_p and 1/[M] expressed by eq 29. In addition to the insightful work of Scott and Senogles, a number of other kinetic studies have documented the unusual polymerization behavior of acrylates. In this work, we apply eqs 23 and 29 to available experimental data to estimate values for θ and $k_p/k_t^{0.5}$.

The kinetic study of Madruga and co-workers[8] is particularly amenable for this analysis, since both polymerization and initiation rates are measured for the free radical polymerization of butyl acrylate in benzene solution at 50 °C, with [M] varied between 1 and 5 mol·L^{-1}. With known v_{in}, and definition of the variable $x = R_p/\sqrt{v_{in}}$, eq 29 can be modified to eq 30.

$$\frac{[\mathrm{M}]}{x} = \frac{\sqrt{k_\mathrm{t}}}{k_\mathrm{p}} + \frac{\sqrt{k_\mathrm{t}}}{k_\mathrm{p}}\frac{\theta}{[\mathrm{M}]} \tag{30}$$

The data from ref 8 have been plotted according to eq 30, as shown in Figure 1, with the best fit parameters determined as θ = 0.93 mol·L^{-1} and $k_p/k_t^{0.5}$ = 1.8 (L·mol^{-1}·s^{-1})$^{1/2}$. It is interesting to note that fitting of the rate data by eq 29 yields an estimate for θ of 1.9 mol·L^{-1}: the difference is due to the measured dependence of initiation rate on monomer concentration.[8]

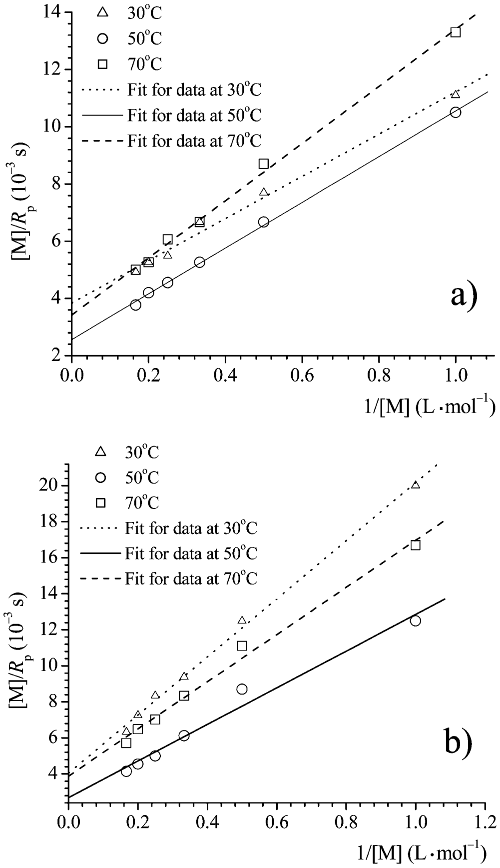


Figure 2. Data from ref 4 plotted according to eq 29 for butyl acrylate polymerization at 30, 50, and 70 °C in (a) benzene and (b) butyl propanoic acid solution.

Table 1. Values of θ and B Determined from the Fit of Eq 29 to Butyl Acrylate Polymerization Data from Ref 4

solvent	temp (°C)	θ (mol/L)	B (10^{-4} s^{-1})	R^a
benzene	30	1.9	2.6	0.9955
	50	3.1	3.9	0.9995
	70	2.9	2.9	0.9985
butylpropanoic acid	30	4.0	2.5	0.9984
	50	3.8	3.7	0.9891
	70	3.4	2.6	0.9960

[a] Correlation coefficient.

Wunderlich[4] tabulated R_p via [M] data for butyl acrylate free radical polymerization in benzene and butyl propanoic acid solutions at 30, 50, and 70 °C. The data, along with the fit according to eq 29, are plotted in Figure 2 and the resulting estimates for θ and B given in Table 1. With no independent measure of initiation rate, it is not possible to directly relate B to $k_p/k_t^{0.5}$. Although the data are very well fit by eq 29, as demonstrated by the tabulated correlation coefficients, there is no consistent trend between temperature and estimates for θ. Furthermore, the range of values ($1.9 < \theta < 4.0$ mol·L^{-1}) is significantly higher than the value of 0.93 estimated from the data in ref 8. It is beyond the scope of this work to resolve these discrepancies. Thus, we consider the region $0 \le \theta \le 4$ when applying this treatment to other literature data.

The $k_p/k_t^{0.5}$ ratios reported in previous kinetic studies are estimated from experimental measurements of acrylate polymerization rates without consideration of the effect of intramolecular transfer to polymer. As shown by eq 23, it is necessary to correct these values by the factor γ_b defined by eq 22. This correction has been applied to the 50 °C butyl acrylate in benzene solution data from refs 5 and 8. For both data sets, the

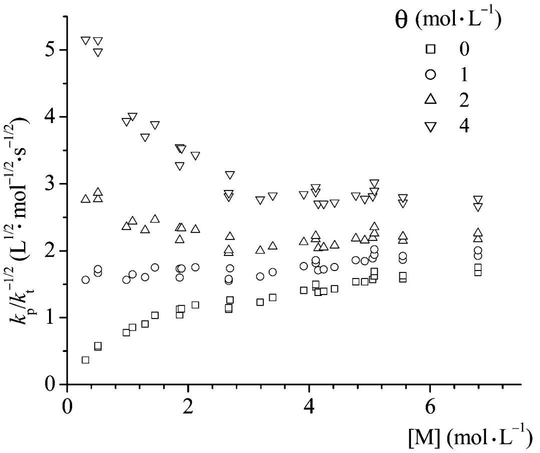


Figure 3. Reconsideration of kinetic data from ref 5 for butyl acrylate polymerization in benzene solution at 50 °C, calculating $k_p/k_t^{0.5}$ ratios for different values of θ.

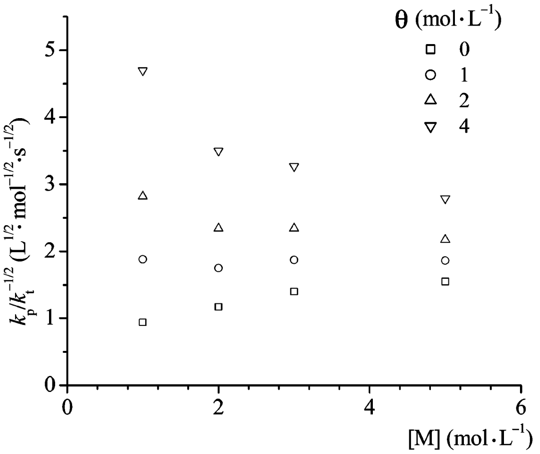


Figure 4. Reconsideration of kinetic data from ref 8 for butyl acrylate polymerization in benzene solution at 50 °C, calculating $k_p/k_t^{0.5}$ ratios for different values of θ.

$k_p/k_t^{0.5}$ ratios are recalculated assuming values for θ of 0 (no intramolecular transfer), 1, 2, and 4 mol·L^{-1}. Figures 3 and 4 show the resulting estimates for $k_p/k_t^{0.5}$ plotted against monomer concentration. For both data sets, an increase in $k_p/k_t^{0.5}$ with [M] is observed when intramolecular transfer is not considered ($\theta = 0$). This apparent dependence is removed by setting θ to 1 mol·L^{-1}, while a further increase of θ to 2 or 4 mol·L^{-1} creates an apparent decrease in $k_p/k_t^{0.5}$ with [M]. It is remarkable that the absolute values of $k_p/k_t^{0.5}$ from these two different groups are in perfect agreement with each other, with $k_p/k_t^{0.5}$ of 1.8 (L·mol^{-1}·s^{-1})$^{1/2}$ estimated with $\theta = 1$ mol·L^{-1}. Since both studies involve butyl acrylate polymerization in benzene, no conclusions can be made regarding possible solvent effects on these values.

McKenna et al.[7] have studied the stationary polymerization of butyl acrylate in toluene and in ethyl acetate at 60 °C, for [M] between 0.3 and 1.3 mol·L^{-1}. $k_p/k_t^{0.5}$ values are estimated experimentally under the assumption that the ratio does not change with conversion, and their dependence on [M] is captured by eq 31.[7]

$$\frac{k_p}{\sqrt{k_t}} = 0.15 + 0.4[\mathrm{M}]\ (L^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{s}^{-1/2}) \qquad (31)$$

Despite the difference in solvents, this result is in good agreement with the data from ref 5 shown in Figure 3: i.e.; apparent $k_p/k_t^{0.5}$ ($\theta = 0$) increases from 0.27 to 0.67 (L·mol^{-1}·s^{-1})$^{1/2}$ as [M] increases from 0.3 to 1.3 mol·L^{-1}. The data from Wunderlich[4] are in discrepancy to these other three sets, with a significantly higher value of 3.3 (L·mol^{-1}·s^{-1})$^{1/2}$ reported for $k_p/k_t^{0.5}$ for butyl acrylate polymerization at 50 °C.

From $k_p/k_t^{0.5} = 1.8$ (L·mol^{-1}·s^{-1})$^{1/2}$ we are able to evaluate k_t using the k_p value calculated from the known Arrhenius dependence for butyl acrylate.[17] With a 50 °C k_p value of 27390 L·mol^{-1}·s^{-1}, k_t is calculated as 2.3×10^8 L·mol^{-1}·s^{-1}. It is interesting to compare this result with the value of 1.2×10^8 L·mol^{-1}·s^{-1} estimated from the Arrhenius dependence reported from kinetic studies using the single-pulse PLP technique.[26] The agreement is good, with the small difference perhaps attributable to a changing population of midchain radicals not accounted for in the analysis of the SP–PLP data.

Kinetic information can also be gleaned from the estimate of 1 mol·L^{-1} for θ at 50 °C. With $k_t \approx 2 \times 10^8$ L·mol^{-1}·s^{-1} and $k_{fp} \approx 500$ s^{-1} (estimated from reported branching level according to eq 24), the calculated value for the ratio $\sqrt{k_t^b}/k_p^b$ is 28 (L·mol^{-1}·s^{-1})$^{-1/2}$. If it is assumed that values for k_t^b and k_t are identical, the resulting estimate for k_p^b is 500 L·mol^{-1}·s^{-1} at 50 °C. On the other hand, if k_t^b is significantly reduced, say to 2×10^6 L·mol^{-1}·s^{-1}, an estimate for k_p^b of 50 L·mol^{-1}·s^{-1} is obtained. Although it is clear that addition to the midchain radical is greatly reduced relative to chain-end propagation, further experimental work (such as ESR) is required to resolve the ratio of $\sqrt{k_t^b}/k_p^b$ into individual rate coefficients. In addition, the temperature dependence of the lumped parameter θ must be measured. The new equations and techniques for data analysis presented in this work should facilitate further experimental efforts in this area.

Average Chain-Length and Chain-Length Distribution. Substitution for ω_R from eq 19 and using the inequality $k_p[\mathrm{M}] \gg k_{fp}$ leads to the following simplification of eq 15, the Mayo relationship.

$$\frac{1}{\bar{P}_n} = \frac{0.5(1+\delta)R_p k_t}{(k_p[\mathrm{M}]\gamma_b)^2} + \frac{(k_{tr,M}[\mathrm{M}] + k_{tr,S}[\mathrm{S}] + k_{tr,A}[\mathrm{A}])}{k_p[\mathrm{M}]} + \frac{(k^b_{tr,M}[\mathrm{M}] + k^b_{tr,S}[\mathrm{S}] + k^b_{tr,A}[\mathrm{A}])}{k^b_p[\mathrm{M}]}\left(\frac{k_{fp}}{k_p[\mathrm{M}]}\right) \qquad (32)$$

Given that the final term in this expression is negligible ($k_p[\mathrm{M}] \gg k_{fp}$), it can be seen that the Mayo equation is the same as that of an ideal polymerization, except for the nonidealities in the rate term captured by γ_b. Even if radical–radical termination is the dominant chain-length controlling event, the value of $\bar{P}_n$ will be highly dependent on monomer concentration, as can be seen by transforming eq 32 to the following form, valid when $\bar{P}_n$ is controlled by termination:

$$\frac{[\mathrm{M}]}{\sqrt{R_p\bar{P}_n}} = \frac{1}{B_p} + \frac{\theta}{B_p[\mathrm{M}]} \qquad (33)$$

where $B_p = k_p/\sqrt{0.5(1+\delta)k_t}$. Note the similarities to eq 29 used to analyze acrylate rate data. In principle, the same methodology could be used to estimate θ from the combination of molecular weight and rate data, providing that transfer to solvent can be neglected.

In the case where transfer to small molecules (e.g., solvent) controls polymer molecular weight, eq 32 indicates that a standard plot of $1/\bar{P}_n$ vs [S]/[M] will yield a good estimate of $k_{\mathrm{tr,S}}/k_{\mathrm{p}}$. Despite the nonidealities in rate caused by intramolecular transfer, the Mayo method of determination of chain transfer constants is still valid for acrylates. Similarly, the chain-length distribution expressed by eq 16 is in fact the well-known Schultz–Flory most probable distribution,[31–33] indicating that the intramolecular transfer to polymer does not influence the polydispersity of polymer MWDs.

The chain transfer constant to butyl acrylate monomer has been experimentally determined under conditions where transfer to monomer is the dominant chain-stopping event.[29] The study used the derivative of the chain-length distribution to estimate $k_{\mathrm{tr,M}}/k_{\mathrm{p}}$, a methodology developed by Clay and Gilbert considering only the standard free-radical polymerization mechanisms of Scheme 2.[28] It is important to examine whether the technique is still valid when intramolecular transfer is considered. Under presence of intramolecular transfer to polymer the derivative $\mathrm{d}(\ln(f_i))/\mathrm{d}i$ is expressed by eq 17. The term $b/(a + b(i - 1))$ is equal to zero for termination by disproportionation and becomes negligible for large i, as discussed by Moad and Moad.[34] The terms $\sqrt{v_{\mathrm{in}}k_{\mathrm{t}}}/(k_{\mathrm{p}}[\mathrm{M}])$ and $(k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])/(k_{\mathrm{p}}[\mathrm{M}])$ are identical to the classical model of polymerization, and the fourth term $k_{\mathrm{fp}}\omega_{\mathrm{d}}/(k_{\mathrm{p}}[\mathrm{M}])$ arises from the intramolecular transfer to polymer. The Clay and Gilbert approach could be applied successfully for determination of chain transfer constants if the term $k_{\mathrm{fp}}\omega_{\mathrm{d}}/(k_{\mathrm{p}}[\mathrm{M}])$ is small compared with the term $(k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])/(k_{\mathrm{p}}[\mathrm{M}])$. In the absence of solvent and added transfer agent, this condition can be written as $(k_{\mathrm{tr,M}}/k_{\mathrm{p}}) \gg (k_{\mathrm{fp}}/(k_{\mathrm{p}}[\mathrm{M}]))(k^{\mathrm{b}}_{\mathrm{tr,M}}/k^{\mathrm{b}}_{\mathrm{p}})$ or $(k_{\mathrm{tr,M}}/k^{\mathrm{b}}_{\mathrm{tr,M}}) \gg (1/\omega_{\mathrm{R}})$. It is expected that this condition is easily fulfilled for acrylates, as the chain-end radicals are significantly more active than the midchain radicals. Thus, the estimates of $k_{\mathrm{tr,M}}/k_{\mathrm{p}}$ reported in ref 29 should be valid.

Conclusions

New expressions have been derived that account for the formation (by intramolecular transfer) and reaction of midchain radicals on acrylate polymerization rate, average chain-length and chain-length distribution under stationary conditions. The new equations are used to analyze literature data without explicit treatment of the midchain radical population. In particular, the nonidealities observed in previous kinetic studies are captured in a single lumped rate coefficient, θ, that controls the apparent order of rate on monomer concentration.

Applied to rate data from the literature, the new treatment yields consistent estimates for θ (~1 mol·L^{-1}) and $k_{\mathrm{p}}/k_{\mathrm{t}}^{0.5}$ (1.8 (L·mol^{-1}·s^{-1})$^{1/2}$) for butyl acrylate polymerization at 50 °C. Combining these ratios with chain-end propagation values determined by PLP–SEC, intramolecular transfer rate coefficients estimated from ^{13}C NMR data, and/or radical concentrations measured by ESR provides a new means to estimate the individual rate coefficients for acrylate polymerization systems. It is also shown that previous estimates for butyl acrylate $k_{\mathrm{tr,M}}/k_{\mathrm{p}}$ obtained from chain-length distributions are valid even in the presence of acrylate backbiting events.

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Appendix A

For the reactions in Schemes 1 and 2 the following rate equations can be written

$$\frac{\mathrm{d}[\mathrm{R}_0]}{\mathrm{d}t} = v_{\mathrm{in}} - k_i[\mathrm{M}][\mathrm{R}_0] \tag{A1}$$

$$\frac{\mathrm{d}[\mathrm{R}_1]}{\mathrm{d}t} = k_i[\mathrm{M}][\mathrm{R}_0] - k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}_1] - k_{\mathrm{fp}}[\mathrm{R}_1] + (k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}] + (k^{\mathrm{b}}_{\mathrm{tr,M}}[\mathrm{M}] + k^{\mathrm{b}}_{\mathrm{tr,S}}[\mathrm{S}] + k^{\mathrm{b}}_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}^{\mathrm{b}}] - (k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}_1] - ((k_{\mathrm{td}} + k_{\mathrm{tc}})[\mathrm{R}] + (\sqrt{k_{\mathrm{td}}k^{\mathrm{b}}_{\mathrm{td}}} + \sqrt{k_{\mathrm{tc}}k^{\mathrm{b}}_{\mathrm{tc}}})[\mathrm{R}^{\mathrm{b}}])[\mathrm{R}_1] \tag{A2}$$

$$\frac{\mathrm{d}[\mathrm{R}_i]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}_{i-1}] - k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}_i] - k_{\mathrm{fp}}[\mathrm{R}_i] + k^{\mathrm{b}}_{\mathrm{p}}[\mathrm{M}][\mathrm{R}^{\mathrm{b}}_{i-1}] - (k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + k_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}_i] - ((k_{\mathrm{td}} + k_{\mathrm{tc}})[\mathrm{R}] + (\sqrt{k_{\mathrm{td}}k^{\mathrm{b}}_{\mathrm{td}}} + \sqrt{k_{\mathrm{tc}}k^{\mathrm{b}}_{\mathrm{tc}}})[\mathrm{R}^{\mathrm{b}}])[\mathrm{R}_i] \tag{A3}$$

$$\frac{\mathrm{d}[\mathrm{R}^{\mathrm{b}}_i]}{\mathrm{d}t} = k_{\mathrm{fp}}[\mathrm{R}_i] - k^{\mathrm{b}}_{\mathrm{p}}[\mathrm{M}][\mathrm{R}^{\mathrm{b}}_i] - (k^{\mathrm{b}}_{\mathrm{tr,M}}[\mathrm{M}] + k^{\mathrm{b}}_{\mathrm{tr,S}}[\mathrm{S}] + k^{\mathrm{b}}_{\mathrm{tr,A}}[\mathrm{A}])[\mathrm{R}^{\mathrm{b}}_i] - ((k^{\mathrm{b}}_{\mathrm{td}} + k^{\mathrm{b}}_{\mathrm{tc}})[\mathrm{R}^{\mathrm{b}}] + (\sqrt{k_{\mathrm{td}}k^{\mathrm{b}}_{\mathrm{td}}} + \sqrt{k_{\mathrm{tc}}k^{\mathrm{b}}_{\mathrm{tc}}})[\mathrm{R}])[\mathrm{R}^{\mathrm{b}}_i] \tag{A4}$$

where

$$[\mathrm{R}] = \sum_{i=1}^{\infty}[\mathrm{R}_i] \text{ and } [\mathrm{R}^{\mathrm{b}}] = \sum_{i=1}^{\infty}[\mathrm{R}^{\mathrm{b}}_i]$$

The sum of the terms on the left sides of eqs A1–A4 gives $\mathrm{d}([\mathrm{R}] + [\mathrm{R}^{\mathrm{b}}])/\mathrm{d}t$ that is chosen to be equal to zero using the approximation of stationary polymerization. So the sum of the right sides of eqs A1–A4 should be equal to zero. This condition results in the following expression

$$[\mathrm{R}] + \sqrt{\frac{k^{\mathrm{b}}_{\mathrm{t}}}{k_{\mathrm{t}}}}[\mathrm{R}^{\mathrm{b}}] = \sqrt{\frac{v_{\mathrm{in}}}{k_{\mathrm{t}}}} \tag{A5}$$

Also the sum of the terms on the left sides of eqs A4, $\mathrm{d}[\mathrm{R}^{\mathrm{b}}]/\mathrm{d}t$, equals zero according to the approximation of stationary polymerization. Then the sum of the terms on the right sides of eqs A4 gives the dependence

$$k_{\mathrm{fp}}[\mathrm{R}] - (k^{\mathrm{b}}_{\mathrm{p}}[\mathrm{M}] + k^{\mathrm{b}}_{\mathrm{tr,M}}[\mathrm{M}] + k^{\mathrm{b}}_{\mathrm{tr,S}}[\mathrm{S}] + k^{\mathrm{b}}_{\mathrm{tr,A}}[\mathrm{A}] + k^{\mathrm{b}}_{\mathrm{t}}[\mathrm{R}^{\mathrm{b}}] + \sqrt{k_{\mathrm{t}}k^{\mathrm{b}}_{\mathrm{t}}}[\mathrm{R}])[\mathrm{R}^{\mathrm{b}}] = 0 \tag{A6}$$

Equations A5 and A6 are transformed into eqs 4 and 5.

Appendix B

The instantaneous number-average degree of polymerization can be calculated from the mechanisms in Schemes 2 and 3 according to eq B1.

$$\bar{P}_n = \frac{\text{total number of polymerized monomer units}}{\text{number of dead polymer molecules formed}} = \{k_p[M][R] + k_p^b[M][R^b]\}/\{0.5(1+\delta)v_{in} + (k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A])[R] + (k_{tr,M}^b[M] + k_{tr,S}^b[S] + k_{tr,A}^b[A])[R^b]\} \quad \text{(B1)}$$

Rearranging B1 into the Mayo form yields B2.

$$\frac{1}{\bar{P}_n} = \frac{0.5(1+\delta)v_{in}}{k_p[M][R] + k_p^b[M][R^b]} + \frac{(k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A])[R]}{k_p[M][R] + k_p^b[M][R^b]} + \frac{(k_{tr,M}^b[M] + k_{tr,S}^b[S] + k_{tr,A}^b[A])[R^b]}{k_p[M][R] + k_p^b[M][R^b]} \quad \text{(B2)}$$

Taking into account the expressions 4 and 5 for [R] and [R^b] and eqs 7 and 8 for rate of polymerization R_p, eq B2 is rewritten as eq 15.

Appendix C

The induction approach is used to derive analytical expressions for MWDs from eqs A1–A4. The condition of stationary polymerization $(d[R_i]/dt) = 0$ and $(d[R_i^b]/dt) = 0$ has been applied for each radical concentration $[R_i]$ and $[R_i^b]$ beginning from $i = 0$. Then the following expressions have been derived for stationary concentrations of radicals:

$$[R_0] = \frac{v_{in}}{k_i[M]} \quad \text{(C1)}$$

$$[R_i] = r\omega^i \quad \text{(C2)}$$

$$[R_i^b] = \frac{r\omega^i}{\omega_R} \quad \text{(C3)}$$

where the values of r, ω_R, and ω are expressed by eqs 16g, 6, and 16b. Using eqs C2, C3, 4, and 5 the expression for dead macromolecules

$$\frac{d[P_i]}{dt} = \delta(k_t[R_i][R] + k_t^b[R_i^b][R^b] + \sqrt{k_t k_t^b}([R_i][R^b] + [R_i^b][R])) + \frac{1}{2}(1-\delta)(k_t\sum_{j=1}^{i-1}[R_j][R_{i-j}] + 2\sqrt{k_t k_t^b}\sum_{j=1}^{i-1}[R_j][R_{i-j}^b] + k_t^b\sum_{j=1}^{i-1}[R_j^b][R_{i-j}^b]) + (k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A])[R_i] + (k_{tr,M}^b[M] + k_{tr,S}^b[S] + k_{tr,A}^b[A])[R_i^b] \quad \text{(C4)}$$

is transformed into:

$$\frac{d[P_i]}{dt} = (a_u + b_u(i-1))\omega^i \quad \text{(C5)}$$

where the values a_u and b_u are expressed by eqs 16e and 16f. The normalization of the expression resulting from the integration of eq C5 leads to eq 16.

Appendix D

In accordance with eq 16 we could write

$$\frac{d(\ln f_i)}{di} = \frac{b}{a + b(i-1)} + \ln\omega \quad \text{(D1)}$$

Taking into account the expression 16b for ω, we have

$$\ln\omega = \ln\left(\frac{k_p[M] + \dfrac{k_p^b[M]}{\omega_R}}{k_p[M] + k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}\right) = \ln\left(1 + \frac{k_p^b}{k_p\omega_R}\right) - \ln\left(1 + \frac{k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}{k_p[M]}\right) \quad \text{(D2)}$$

Considering only first-order values of Taylor expansion, we have

$$\ln\left(1 + \frac{\mathrm{k}_p^b}{\mathrm{k}_p\omega_R}\right) \approx \frac{\mathrm{k}_p^b}{\mathrm{k}_p\omega_R} \quad \text{(D3)}$$

$$\ln\left(1 + \frac{k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}{k_p[M]}\right) \approx \frac{k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}{k_p[M]} \quad \text{(D4)}$$

So

$$\ln\omega = \frac{k_p^b}{k_p\omega_R} - \frac{k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}{k_p[M]} \quad \text{(D5)}$$

Taking into account eq 6 for ω_R we have

$$\ln\omega = -\frac{k_{fp}}{k_p[M]} \times \frac{k_{tr,M}^b[M] + k_{tr,S}^b[S] + k_{tr,A}^b[A] + \sqrt{v_{in}k_t^b}}{k_p^b[M] + k_{tr,M}^b[M] + k_{tr,S}^b[S] + k_{tr,A}^b[A] + \sqrt{v_{in}k_t^b}} - \frac{k_{tr,M}[M] + k_{tr,S}[S] + k_{tr,A}[A] + k_{fp} + \sqrt{v_{in}k_t}}{k_p[M]} \quad \text{(D6)}$$

From D1 and D6 we have eq 17.

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