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Kinetic and Electron Spin Resonance Analysis of RAFT Polymerization of Styrene

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The reversible addition−fragmentation chain-transfer (RAFT) process[1−4] is an extremely versatile member of the class of controlled radical polymerization processes, and is capable of producing a wide variety of polymers of controlled molar mass[2] and molecular architecture[1,3,5,6] from many monomers.

The core reactions of RAFT are the addition−fragmentation equilibrium process (top half of Scheme 1).[1] This process allows the rapid redistribution of radical activity between growing chains, and thus control of their molar mass. There is currently debate in the literature regarding the fate of the intermediate radicals ($Y^•$), and the equilibrium between propagating ($P^•$) and intermediate radicals.[7−10] Barner-Kowollik et al.[7] initially argue that there has been no evidence of cross-termination between the intermediate and propagating radicals, whereas other authors[8,10−12] argue that such events can or do occur. The resulting estimations of the rate coefficients for the addition and fragmentation processes for the same RAFT/monomer combinations differ greatly as a consequence.[10−12] Understanding of this equilibrium between propagating and intermediate radicals is key to understanding the possibilities and limitations of RAFT.

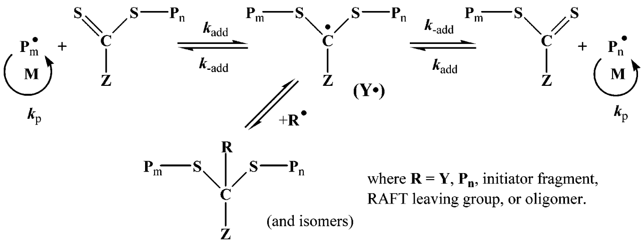
The central reactions in Scheme 1 imply equilibrium between intermediate and propagating radicals, with an equilibrium constant determined by the relative rates of addition of propagating radicals to RAFT-capped chains and fragmentation of the formed intermediate radicals.[10]

$$K_{\mathrm{eq}} = \left(\frac{c_{\mathrm{Y}}}{c_{\mathrm{P}}c_{\mathrm{PX}}}\right) = \left(\frac{k_{\mathrm{add}}}{k_{-\mathrm{add}}}\right) \qquad (1)$$

Here K_{eq} is the equilibrium constant, k_{add} and $k_{-\mathrm{add}}$ are the rate coefficients for addition and fragmentation, c_{Y} and c_{P} are the concentrations of the intermediate and propagating radicals, and c_{PX} is the concentration of RAFT-capped chains. K_{eq} should be constant for a particular RAFT/monomer combination at a particular temperature and independent of other conditions.

Electron spin resonance (ESR or EPR) spectroscopy provides valuable information regarding structure and environment of free radicals, which is extremely useful in free radical polymerization reactions.[13−22] Careful calibration enables measurement of accurate concentrations of all detectable radical species present, including the propagating radical. This technique has been used to obtain propagation rate coefficients for free radical polymerizations that are in excellent agreement with IUPAC-accepted values for some monomers,[23,24] thus establishing the quantitative reliability of measuring free radical concentrations.

Scheme 1. Currently Accepted Elementary Steps for the Central Equilibrium in the RAFT Process (Top Half),[1] plus a Suggested Reversible Radical Deactivation Step



The RAFT process would also appear to be an ideal candidate for ESR studies, since c_{P} is usually very low, and c_{Y} is expected to be high. Few studies to date have carefully examined the RAFT process by ESR. Hawthorne et al.[25] proved the existence of the intermediate radical species, and gave a rough indication of its concentration; also implying that c_{P} is much lower than c_{Y}. Laus et al.[26] and Du et al.[27] also used ESR to detect and identify the intermediate radical species in novel RAFT systems. Kwak et al.[10] have carefully examined RAFT polymerization by ESR spectroscopy, utilizing both the intermediate concentration and kinetic data to model the process.

In this study, c_{Y} and c_{P} (and their ratio) were examined by ESR spectroscopy and kinetics for styrene polymerization in the presence of cumyl dithiobenzoate (CDB, the RAFT agent). The system showed strong chain length effects in kinetics, that were very well predicted by classical (diffusion-controlled termination rate) kinetics assuming all chains were of mass $\bar{M}_{\mathrm{n}}$. However, unusual behavior with respect to existing mechanistic knowledge was observed in other aspects of the system.

ESR measurements were performed on sealed ESR tubes containing degassed solutions[28] of monomer, benzene, RAFT agent, and azobis(isobutyronitrile) (AIBN), in a preheated ESR cavity, under various ESR conditions.[29] The ESR system was calibrated with a series of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) standards (10^{-5}−10^{-8} M) in benzene, under the reaction conditions given in ref 24. Careful integration of the intermediate radical spectra, using the techniques of a previous quantitative ESR study,[24] was used to calculate the intermediate radical concentrations.

Reactions were run at 70 and 90 °C for various concentrations of AIBN and CDB, with constant $c_{\mathrm{initiator}}/c_{\mathrm{RAFT}}$ (=0.45). To maximize ESR signals, high initiator (and RAFT) concentrations were used, resulting in low $\bar{M}_{\mathrm{n}}$ chains. The concentration of the intermediate radical (which includes the contribution due to the signal of any underlying propagating radicals in this region) was measured by double integration of the background-corrected signal of the intermediate radical, and comparison with the TEMPO calibration.

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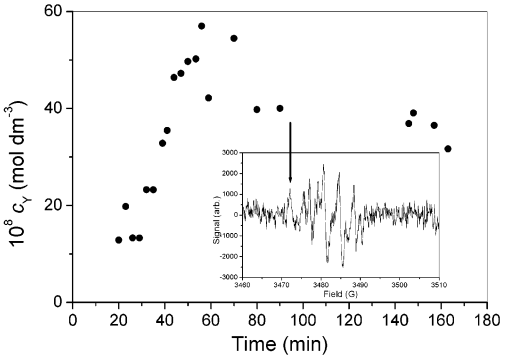

Figure 1. Typical intermediate radical concentration−time profile for styrene polymerization in the presence of CDB. Inset: ESR spectrum of intermediate radical species, with extra peak at low field side (indicated by arrow).

Kinetic reactions were run for the CDB systems, and sampled for gravimetric (conversion and w_p) and SEC analysis ($\bar{M}_n$).

In all styrene/CDB reactions, c_Y was initially too low for direct observation in the ESR spectra (but could be detected and measured when examining integrals of the spectra in the appropriate region), and increased (to observable concentrations) with time to a maximum ($<10^{-6}$ M), followed by a very slow decrease. The observed signal was similar to those observed in previous studies,[10,25] with the same g-factor and hyperfine splittings as those of Hawthorne et al.[25] A typical concentration−time profile (with inset ESR spectrum) is shown in Figure 1. The propagating radical concentration under all tested conditions was too low to be directly observed with the current equipment. Wider sweeps (up to 200 mT width) at a wide range of modulation amplitudes and power levels showed no significant broad or narrow signals other than the observed intermediate radical. Similar behavior was observed when n-butyl acrylate was used as monomer.

No difference in c_Y with time was observed when oxygen was rigorously removed by multiple freeze−pump−thaw cycles (rather than the usual nitrogen flushing). Thus, the slower than expected increase of c_Y early (i.e., much slower relative rate of increase than that of c_P) in the reaction was unlikely to be due to dissolved oxygen.

The ratio of the intermediate to propagating radical concentrations (c_Y/c_P) was determined by combining ESR and rate data. The observed ratios (see Figure 2a) always started very low, increased with time (showing initial correlations with $\bar{M}_n$), and appeared to be roughly independent of the concentration of the RAFT agent at 90 °C. The ratios at later times were roughly consistent with those of Kwak et al. The ratios predicted by the rate coefficients of Barner-Kowollik et al.[7] give predicted c_Y (from c_P) values that are much higher (several orders of magnitude) than observed; those rate coefficients are clearly not applicable to the current system.

The variation in c_Y/c_P implied a varying equilibrium constant (see eq 1, Figure 2b) with time and/or $\bar{M}_n$, and is inconsistent with both the standard model and the data of Kwak et al. The reason for this variation is under investigation, but the very short chains in the systems studied (usually $\bar{M}_n < 2000$), and the time dependence suggests that both initiator concentration and chain lengths play important roles here.

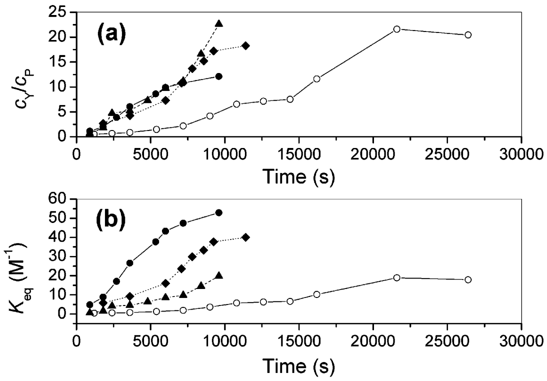

Figure 2. (a) Ratio of intermediate to propagating radicals, and (b) calculated equilibrium constant (K_{eq}) as a function of time for styrene polymerization in the presence of CDB. Key: circles, 90 °C, $c_{RAFT} = 0.23$ M; diamonds, 90 °C, $c_{RAFT} = 0.46$ M; triangles, 90 °C, $c_{RAFT} = 1.14$ M; open circles, 70 °C, $c_{RAFT} = 1.14$ M.

Without inferring major changes to the mechanism, a simple explanation for the variation is that both k_{add} and k_{-add} are chain-length dependent for very short chains, as exist in the current systems. This is consistent with observations of the chain length dependence of the propagation reaction.[30,31] Moreover, an inverse relationship exists between the "goodness" of a leaving group (radical stabilization) and its subsequent rate of radical addition, such that reduction in k_{add} may give a corresponding increase in k_{-add}, leading to enhanced ratio changes. Other possibilities include reactions that consume intermediate radicals, such as reversible or irreversible termination reactions involving the intermediate. The most likely reactions of the intermediate radical would be with primary radicals or other short-chain species, due to increasing steric congestion at the radical site with increasing chain lengths of nearby P_n, P_m, or Z or approaching chains. Either case will show a strong correlation with time and $\bar{M}_n$. The approximately constant $\bar{K}_{eq}$ of Kwak et al. (starting with macro-RAFT agent, $\bar{M}_n = 2000$) suggests that the current system might eventually reach a "pseudo-plateau" at sufficiently long chain lengths and times.

Propagating and intermediate radical concentrations were predicted for the styrene/CDB system by assuming that the c_P was determined by the balance of initiation and termination (by combination of propagating radicals only) events, and assuming steady-state solution (in propagating radical concentration) of the classical differential equation in eq 2.

$$\frac{\mathrm{d}c_P}{\mathrm{d}t} = 2fk_d\, c_I - \langle k_t(w_p)\rangle\, c_P^{\,2} \tag{2}$$

Here, c_I is the initiator concentration, $\langle k_t(w_p)\rangle$ is the average termination rate coefficient (strongly dependent on w_p, the weight fraction polymer, for a RAFT system), k_d is the initiator decomposition rate coefficient, and f is the initiator efficiency.

The average termination rate coefficient was calculated by assuming that all growing chains are of the same (number-average) degree of polymerization. The value of $\langle k_t(w_p)\rangle$ was then calculated in the usual manner from the diffusion coefficients of the terminating species.[32−34] Ignoring the chain-length distribution of radicals makes little difference to predicted c_P values under current conditions. Conversion (and w_p) and c_P (for c_Y calculation) were taken from conversion−time

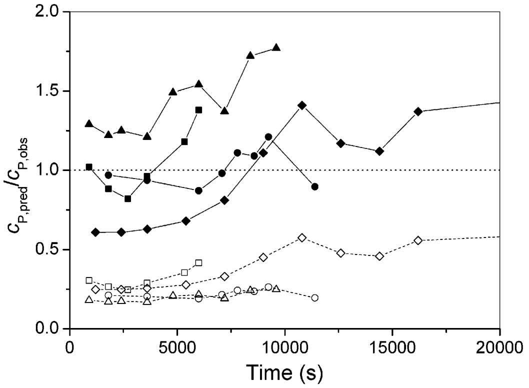

Figure 3. Ratio of predicted to observed propagating radical concentrations for styrene solution polymerizations in CDB. Parameters for predicted values: $k_d = 3.9 \times 10^{-5}$, 4.9×10^{-4} s^{-1} at 70, 90 °C;[30] $f = 0.7$;[30] oligomer diffusion coefficients (and thus $\langle k_t(w_p)\rangle$) calculated from the theory of Russell et al.,[32] w_p dependence of styrene diffusion coefficient of Scheren et al.;[33] scaling measurements of Griffiths et al.[34] Key: squares, 90 °C, $c_{RAFT} = 0.23$ M; circles, 90 °C, $c_{RAFT} = 0.46$ M; triangles, 90 °C, $c_{RAFT} = 1.14$ M; diamonds, 70 °C, $c_{RAFT} = 1.14$ M. The corresponding dotted lines and open symbols are the predictions after applying the retardation factor of Kwak et al.

data, c_I was estimated from k_d and time, and the number-average degree of polymerization was determined from $\bar{M}_n$ as measured by SEC.

The intermediate radical concentration was calculated from c_P by assuming the widely differing equilibrium constants given by Kwak et al.[10] (without the retardation factor) and Barner-Kowollik et al.,[7] and using eq 1.

The predicted values of c_Y were compared with those measured by ESR spectroscopy. The predicted values of c_P were compared with those inferred from experiment. The agreement of the predicted (using this very simple modeling scheme) and observed propagating radical concentrations was very good at 70 and 90 °C, and at low and high initiator concentrations, with the exception of the system with the highest initiator concentrations (see Figure 3). When the proposed retardation factor due to termination of intermediate radicals of Kwak et al.[10] was used, the predicted rates were always too low, suggesting that intermediate termination occurs to a significantly smaller extent. This discrepancy could not be compensated by reasonable adjustment of input parameters. However, c_Y (and the resulting c_Y/c_P ratios) was always predicted to be much higher than observed, with the closest prediction being for system with the lowest initiator concentration at 90 °C.

Similar experiments were attempted with two other RAFT agents: 2-phenylprop2-yl phenyldithioacetate (PPPDTA) and a trithiocarbonate in styrene/benzene solution at 90 °C. The intermediate radical concentration was undetectable with the current ESR equipment for PPPDTA (presumably due to a lower c_Y/c_P ratio[12]). For the trithiocarbonate system, the signal was too low for reliable integration, but c_Y could be (by examination) seen to show an immediate maximum, and rapidly decreased, presumably in accordance with the rapidly decreasing initiator concentration, without the complicating factors observed for the CDB system. The effectively immediate maximum c_Y supports the hypothesis that the slow increase in c_Y for the CDB system is not due to dissolved oxygen.

An extra signal (not corresponding to propagating radicals, see the inset in Figure 1) appeared at intermediate conversions during most reactions using CDB, increasing with time, and with concentration independent of c_Y. RAFT color intensity decreased as this signal increased, suggesting that this signal may be due to a RAFT degradation product. This is under further investigation.

An unexpected observation was that detectable concentrations of the RAFT intermediate species were present at very long reaction times at 90 °C. In one case, c_Y was observed to be slightly less than 10^{-7} M after 19 h at 90 (±0.5) °C. Given the literature values of k_d, almost no initiator would be expected to remain, and the predicted c_Y by the classical model used here was below 10^{-12} M (undetectable). This huge discrepancy cannot be explained by experimental uncertainties in reaction temperature or concentrations.

Assuming that there is no large change (at least 3 orders of magnitude being necessary) in the equilibrium between propagating and intermediate radicals at long reaction times (as implied by the data of Kwak et al.), the detectable intermediate concentration implies the presence of propagating radicals, which is consistent with recent observations of significant controlled RAFT polymerization of a system at 60 °C containing no initiator, after removal from a γ-ray source.[8] The required propagating radical concentrations to produce the observed signal using the observed maximum c_Y/c_P ratio is between 5×10^{-9} and 10^{-8} M. Using the observed rates of thermal polymerization of Barner-Kowollik et al.[8] gives an average c_P of significantly less than 5×10^{-10} M at 60 °C. Thermal radical production in the current system would be expected to be much slower due to the very low monomer concentration at the nearly terminal conversions (the rate of thermal initiation being dependent on the third power of the monomer concentration[30]) under such conditions, and is incapable of producing sufficient radicals to give the observed intermediate radical concentration. Note that radical trapping due to vitrification could not produce the observed radical signal (since final $w_p = 0.65$), and in analogous reactions where the samples were preheated in the water bath, and inserted into a room temperature cavity, the signal was observed to decrease very rapidly after insertion into the cavity. The presence of radicals in the virtual absence of initiator and their disappearance upon cooling implies very long-lived (nonintermediate radical) species that may act as a thermally activated radical source, which is consistent with a significant fraction of radicals being "protected" from termination events, possibly through reversible coupling mechanisms (see lower half of Scheme 1). Preliminary evidence for the presence of such species has been detected, and will be the topic of a future publication.

This apparently anomalous long time concentration cannot be explained by alternative models for radical fates. Any irreversible termination of intermediate species will further decrease the propagating and intermediate radical concentrations. Even if intermediate−intermediate radical termination is impossible, the intermediate species must still be in (relatively rapid) equilibrium with the propagating radicals, which may still undergo termination. Thus, any assumed model based on mechanisms including only irreversible termination predicts that no (extremely little) intermediate or propagating radical species remain. The observed intermediate radical concentration thus implies that additional events are occurring either to protect radicals from irreversible termination, or that there is a thermal radical source in the system.

Another example of unusual behavior is the apparently low sensitivity of the RAFT system to oxygen. Deliberate exposure of the reaction mixture to the atmosphere for more than 30 min at 90 °C showed little change in rate, concentration, or nature of radicals present, although a small amount of an underlying peroxy peak may have been present. The lack of retardation is probably due to the extremely high radical flux in this specifically chosen system, and similar results were observed for an analogous reaction in which no RAFT agent was included. This and the apparent insensitivity of the observed time evolution of c_Y to degassing procedures indicate that the RAFT agent and process are not particularly sensitive to oxygen up to 90 °C and imply that handling in the presence of oxygen, even at elevated temperatures, will not be extremely detrimental to RAFT performance.

The current work is part of an extensive investigation into the RAFT process, and the results presented show that much is still to be learned regarding the basic mechanism and possibilities of the RAFT process and that no currently accepted theory is capable of explaining all observations. The key observations for the current system were as follows:

- The central equilibrium “constant” is dependent on both temperature and starting concentrations. Intermediate radical concentrations were not consistent with the predictions based on existing literature models.[10−12]
- The time dependence of the intermediate radical concentration varies significantly with the type of RAFT agent.
- Intermediate radicals were detected at very long reaction times in the virtual absence of initiator.
- The propagating radical concentrations are predictable using classical kinetics using chain-length dependent termination rate coefficients. The retardation factor of Kwak et al.[10] could not fit the observed data.
- An extra radical (nonpropagating or intermediate) species was observed to form during reaction; its concentration increased with time.
- The RAFT process is not particularly sensitive to oxygen.

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(28) A typical reaction was as follows. Cumyl dithiobenzoate (0.28 g, 1.02 mmol) and AIBN (0.078 g, 0.47 mmol) were dissolved in a benzene (5.0 g) and styrene (5.0 g, 48 mmol) solution. An aliquot (0.2 g) of the solution was transferred to an ESR tube and oxygen removed by flushing with ultrahigh purity nitrogen for 10 min. The tube was sealed and transferred to the ESR cavity, which had been preheated to 90 °C.

(29) The ESR spectra (including standards) were recorded on a Bruker EMX spectrometer in the X-band region, with the ER4102 cavity preheated to the reaction temperature. The magnetic field was modulated at 100 kHz, with amplitude between 0.1 and 0.5 mT, and a microwave power of 2 mW (well below saturation) was used. Spectra were recorded as single 1 or 5 min scans, and adjusted by subtraction of cavity scans under identical conditions.

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