Electron Spin Resonance Studies of Reversible Addition-Fragmentation Transfer Polymerisation

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SUMMARY: The polymerisation of styrene in the presence of cumyl dithiobenzoate (RAFT agent) was studied. Electron spin resonance spectroscopy was used to determine the time-dependence of the concentrations of the intermediate radical species, as a function of temperature and relative initial amounts of reactants. The intermediate radical concentration was found to be much lower than predicted by the studies of Barner-Kowollik *et al.*[Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1353], but consistent with that observed by Hawthorne *et al.*[Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 5457] and Kwak *et al.*[Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026] Several observations that are not consistent with the current RAFT model were made. Intermediate radical signals were observed long after a significant amount of initiator remained and an extra signal appeared in the ESR spectrum at longer reaction times.

Introduction

Living free radical polymerisations allow the preparation of complex macromolecular architectures in a controlled manner. One such technique is the reversible addition-fragmentation chain transfer (RAFT) process.[1] This controlled radical polymerisation process is capable of producing a wide variety of polymers of controlled molar mass[2] from numerous monomers, under a wide range of experimental conditions. The control of molecular architecture[1,3-5] of the resulting polymers enables the synthesis of

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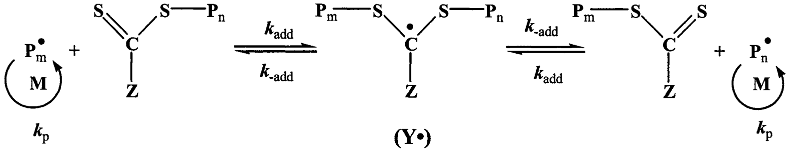
previously unavailable materials.

The accepted model for RAFT polymerisation[1] involves a chain transfer process in which a propagating radical $P_n^\bullet$ (of degree of poymerisation n) adds to the dormant species P_m-X (where X is the RAFT agent) to form an intermediate radical P_n-($X^\bullet$)-P_m (= $Y^\bullet$), followed by (relatively rapid) fragmentation to form $P_m^\bullet$ and P_n-X (Scheme 1). The concentrations of each species involved in this main equilibrium are dependent on the relative sizes of the rate coefficients for addition of a propagating radical to the RAFT agent (k_{add}) and fragmentation of the formed intermediate ($k_{\text{-add}}$). The relative concentrations of propagating and intermediate radicals, and the fates of intermediate radicals, hold the key to understanding the RAFT process, especially for reactions in aqueous dispersions, such as emulsion polymerisations.



Scheme 1: The currently accepted main equilibrium in the RAFT process.[1]

The main equilibrium in Scheme 1 allows the calculation of an equilibrium constant (K_{eq}) for this addition-fragmentation process, that can be expressed in terms of the addition and fragmentation rate coefficients.

$$K_{\text{eq}} = \left(\frac{[Y^\bullet]}{[P^\bullet]\,[PX]}\right) = \left(\frac{k_{\text{add}}}{k_{\text{-add}}}\right) \tag{1}$$

Here $[P^\bullet]$, $[Y^\bullet]$, and $[P_n\text{-X}]$, are the total concentrations (i.e. the summation over all chain lengths) of all $P_n^\bullet$, $Y^\bullet$, and P_n-X species, respectively. The equilibrium constant is expected to be invariant for any monomer/RAFT agent combination at a particular temperature. However, during the early part of the reaction, for some systems, this may not be the case.[6]

There is currently debate in the literature regarding the reactivity and related fate of intermediate radical species. There are two classes of model: those that only allow fragmentation reactions of the intermediate radicals (the original mechanism[1]), and those that allow reactions, such as cross-termination, between intermediate and other radicals.[7-9] The resulting estimations of the rate coefficients for the addition and fragmentation processes, and the resulting equilibrium between propagating and intermediate radicals, differ greatly as a consequence.[8-10]

Electron spin resonance (ESR (also known as EPR)) spectroscopy is an extremely useful tool for the study of free radical polymerisation reactions, especially those in which the concentrations of the radical species of interest are relatively high. ESR spectroscopy provides information regarding the structure, mobility, and environment of free radicals.[11-20] Moreover, with careful calibration it is possible to obtain accurate concentrations of all radical species present, including the propagating radical. This is evidenced by the use of ESR spectroscopy to obtain propagation rate coefficients for free radical polymerizations that are in excellent agreement with IUPAC-accepted values for some monomers.[21,22]If estimations of propagating and intermediate radical concentrations are made using the rate coefficients and model of Barner-Kowollik *et al.*[10] for the cumyl dithiobenzoate (CDB)/styrene system, it appears that the RAFT process is an ideal candidate for ESR studies, since the propagating radical concentration is predicted to be very low, and the concentration of the intermediate radical species is predicted to be very high. This would allow the concentrations of the two species to be studied relatively independently, by a combination of ESR and kinetic techniques.

There are currently few existing studies of the RAFT process by ESR. Hawthorne *et al.*[23] proved the existence of the intermediate radical species and implied its role in the RAFT process. Their data gave a rough indication of its concentration, and implied that in that system the propagating radical concentration was much lower than that of the intermediate species, since no signal due to the propagating radical signal was detected in their spectra. Laus *et al.*[24] and Du *et al.*[25] have also shown the structures of intermediate radicals in RAFT systems. The only detailed kinetic study to date is that of Kwak *et al.*,[9] who carefully examined RAFT polymerisation by ESR spectroscopy, and utilised both the intermediate concentration and kinetic data to model the RAFT process.

Experimental

Chemicals: Azobis(isobutyronitrile) (AIBN, Aldrich, 99 %) was recrystallised from methanol, benzene (Aldrich, 99 %) and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, Aldrich) were used as received, and styrene (Aldrich, 98%) was washed with KOH and distilled before use. Cumyl dithiobenzoate (CDB, > 99 % purity, ^{1}H NMR) was synthesised according to literature procedures.[26]

ESR Spectroscopy: A Bruker EMX spectrometer was used to record the ESR spectra in the X-band region, with a TE4102 cavity pre-heated to the reaction temperature. The magnetic field was modulated at 100 kHz, with amplitude between 0.1 and 0.5 mT. Spectra were recorded as single scans of 1024 points between approximately 1 and 5 min sweep times. Conversion times and time constants were chosen to avoid distortion of the spectra while maximising the signal:noise ratio. Background spectra were recorded prior to reaction, and subtracted from the experimental spectra for both the standards and the reaction samples. A microwave power of 2 mW was used in this study. Saturation effects were not visible below *ca.* 10 mW under these conditions.

ESR measurements were performed on sealed ESR tubes containing degassed solutions of monomer, benzene, CDB RAFT agent, and AIBN, in a pre-heated ESR cavity, under various ESR conditions. The ESR system was calibrated with a series of TEMPO standards (10^{-5} – 10^{-8} M) in benzene, recorded at various temperatures and modulation amplitudes, as appropriate to the range of experimental conditions.[21]

Reactions were run at 70 °C and 90 °C for various concentrations of AIBN and CDB, with a constant ratio of initiator to RAFT agent concentration (≈ 0.45). The concentration of the intermediate radical (and that of any underlying propagating radicals that may be present, since most organic radicals have similar *g*-factors and corresponding centre resonant magnetic field) was measured as a function of time by double integration of the background-corrected spectra. Note that correction of the calculated intermediate radical concentrations for underlying propagating radical signals was not made, since in most cases the difference was small, due to the fact that the ESR spectrum of the polystyryl radical is much broader than that of the RAFT intermediate species, it has a different *g*-factor (and thus different centre field in the spectrum), and the intermediate radical concentration was typically much greater than that of the propagating radical.

A typical reaction was as follows. CDB (0.28 g, 1.02 mmol) and AIBN (0.078 g, 0.47 mmol) were dissolved in a solution of benzene (5.0 g) and styrene (5.0 g, 48 mmol). An aliquot (0.2 g) of the solution was transferred to an ESR tube and oxygen removed by flushing with ultra-high purity nitrogen for 10 min. The tube was sealed and transferred to the ESR cavity, which had been pre-heated to the reaction temperature (90 °C). ESR spectra were recorded at frequent intervals.

Results and Discussion

An example of a typical observed ESR spectrum of the intermediate radical for the CDB/styrene system, which is essentially the same as the spectra of the intermediate radical reported elsewhere,[9,23] is given in Fig. 1. This signal is due to intermediate radicals of the form R_1-($X^\bullet$)-R_2 (as assigned by Hawthorne *et al.*,[23] radicals of this general form are denoted as $Y^\bullet$ here), where R_1, R_2 may be polystyrene oligomers (of degree of polymerisation ≥ 0) with terminal cumyl groups (RAFT-derived) or AIBN-derived fragments.

Typical intermediate radical concentration-time profiles are shown in Figs. 2 and 3, for reactions at 90 °C and 70 °C, respectively. In all reactions there was an initial inhibition period in which the intermediate radical concentration was too low to be directly observed (but could be detected by analysis of integrals in the region towards the end of this period) and increased (to observable concentrations) with time to a maximum, followed by a slow decrease. The rates of increase to the maximum concentration, and the slower decrease, were dependent on temperature, with the faster kinetics for the higher temperature. The relative rates and the maximum intermediate radical concentration were strongly coupled to the rate of initiator decomposition.

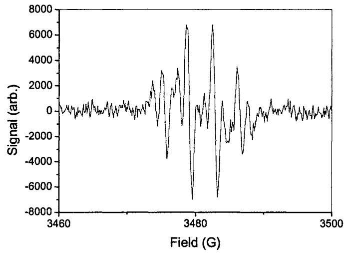


Fig. 1: A typical ESR spectrum of the intermediate radical obtained for the RAFT solution (50 % benzene) polymerisation of the styrene/AIBN/CDB system. T = 90 °C, [AIBN] = 5.10 x 10^{-1} M, [CDB] = 11.5 x 10^{-1} M.

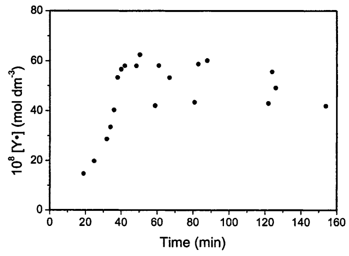


Fig. 2: The time evolution of the intermediate radical concentration for the solution polymerisation of styrene (in 50 % benzene) in the presence of CDB at 90 °C. [AIBN] = 5.10 x 10^{-1} M, [CDB] = 11.5 x 10^{-1} M.

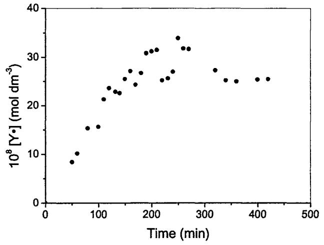


Fig. 3: The time evolution of the intermediate radical concentration for the solution polymerisation of styrene (in 50 % benzene) in the presence of CDB at 70 °C. [AIBN] = 5.10 x 10^{-1} M, [CDB] = 11.5 x 10^{-1} M.

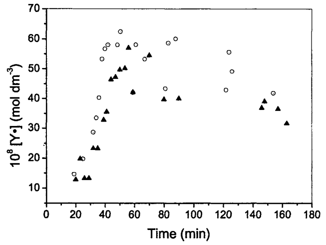


Fig. 4: The time evolution of the intermediate radical concentration at 90 °C with [CDB] = 2.3 x 10^{-1} M, [AIBN] = 1.02 x 10^{-1} M (triangles) and [CDB] = 11.5 x 10^{-1} M, [AIBN] = 5.10 x 10^{-1} M (open circles).

It was initially thought that dissolved oxygen might be the cause of the long inhibition times for the intermediate radical concentration. However, even with rigorous oxygen removal by multiple freeze-thaw cycles, no detectable difference was observed in the evolution of the intermediate radical concentrations with time. It was thus concluded that this inhibition of the intermediate radical concentration was unlikely to be due to dissolved oxygen, and that the normal procedure for elimination of dissolved oxygen was sufficient. This is consistent with the observations that RAFT polymerisation under these conditions is not particularly sensitive to oxygen,[6] different concentration-time profiles were observed when the RAFT agent was changed,[6] and that this inhibition period was observed for both lower and higher initiator concentrations. The reason for this inhibition period is currently unknown, but is likely to be due to reactions of the intermediate radical,[6] and is currently under investigation.

A maximum intermediate radical concentration of approximately 6 × 10^{-7} M (roughly consistent with the observed maximum of Hawthorne *et al.*[23]) was reached after 50 minutes of reaction time at 90 °C. The reaction at 70 °C showed a much slower rate of increase in the intermediate radical concentration, and only reached an approximate maximum concentration of 3 × 10^{-7} M after 200 min. This was as expected, since initiator decomposition is significantly faster at 90 °C than at 70 °C, and it has been shown that the reaction rate kinetics can be predicted with reasonable accuracy using classical kinetics, using appropriate rate coefficients for chain length dependent termination.[6]

The evolution of the intermediate radical concentration for two styrene/benzene solutions with CDB to AIBN concentrations of 2.30×10^{-1} M to 1.02×10^{-1} M, and 11.5×10^{-1} M to 5.10×10^{-1} M, respectively, are given in Fig. 4. For these reactions, with a difference of a factor of 5 in initiator concentration, little difference in the variation of the intermediate concentration with time was observed. In general, the rate of increase of the intermediate radical concentration and its maximum appear to be independent of the monomer to RAFT agent ratio, and only slightly dependent on the ratio of the initiator to RAFT agent concentrations. The same trends have been shown to hold for the rate of reaction, where the rate appears to be independent of the initator concentration, and appears to be primarily the result of the opposing effects of the faster termination of the shorter chains formed in the case of higher initiator/RAFT concentrations versus the lower termination rates for the lower initiator/RAFT concentrations.[6] However, the exact reason for the time of the maximum in the intermediate concentration versus time is unknown, but appears to be due again to opposing effects: the decreasing radical flux with the decrease in initiator concentration with time, and the decreasing rate of "consumption" of intermediate radicals, by currently unknown loss reaction processes, as suggested earlier.

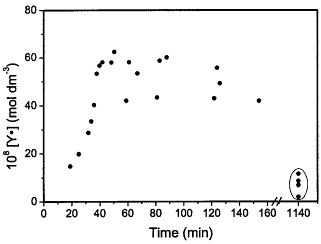


Fig. 5: The time evolution of the intermediate radical concentration for the solution polymerisation of styrene (in 50 vol% benzene) in the presence of CDB at 90 °C, with observations after 19 h reaction time. [AIBN] = 5.10 x 10^{-1} M, [CDB] = 11.5 x 10^{-1} M.

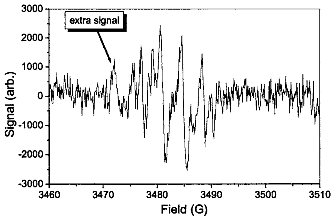


Fig. 6: A typical ESR spectrum at intermediate reaction time obtained for a styrene/AIBN/CDB system showing the extra signal. T = 90 °C, [AIBN] = 5.10 x 10^{-1} M, [CDB] = 11.5 x 10^{-1} M.

Fig. 5 illustrates an observation that was made at long reaction times that contradicts the "classical" RAFT mechanism. For the reaction of styrene/CDB at 90(±0.5) °C, detectable concentrations of the RAFT intermediate species were present after 19 h. The intermediate radical concentration was determined to be approximately 10^{-7} M. Given that the RAFT intermediate radical is assumed to be in fast equilibrium with propagating radicals and RAFT-capped chains, but with no other species (Scheme 1), and that this concentration can be determined by the equilibrium expression in eq 1, then the presence of a significant concentration of intermediate radicals implies both a significant concentration of propagating radicals, and a source of these radicals. Thus, at long reaction times for a rapidly decomposing thermal initiator (as is the case here, given the literature values of the initiator decomposition rate coefficient (k_d) for AIBN), no effective initiator-derived radical source is available. The predicted intermediate radical concentration in this case would be below 10^{-12} M. This extremely large difference between predicted and observed intermediate radical concentrations cannot be explained by experimental uncertainties in either reaction temperature or reactant concentrations, uncertainty in k_d, nor initiation by spontaneous thermal generation of radicals from styrene. Similar observations were also made for the butyl acrylate/CDB system under the same conditions. The presence of radicals in the virtual absence of a known radical source implies the existence of either very long-lived species (as suggested by the study of Barner-Kowollik *et al.*[7]), an unknown radical source, or a very large (several orders of magnitude) shift in the equilibrium constant for the reaction.

An extra signal (Fig. 6) appeared in the ESR spectra, towards a lower magnetic field than the spectrum of the intermediate radical, at intermediate reaction time during most reactions using CDB as RAFT agent. The signal (with apparent approximate $g = 2.01$, suggesting strong coupling to S nuclei) does not correspond to that of the propagating radicals, and does not have a symmetrical component on the other side of the intermediate radical signal. This signal increased with time, with concentration (signal intensity) independent of the intermediate radical concentration, *i.e.* it is not closely reactively coupled (such as by equilibrium) to the intermediate radical. RAFT colour intensity decreased as this signal increased, suggesting that this signal may be due to a RAFT degradation product, via a free radical mechanism. The clearly observable loss of colour in these intensely coloured samples suggests that the loss of RAFT agent under such conditions is significant. This is under further investigation.

In Fig. 7 the observed intermediate radical concentration at 70 °C is compared with those predicted using the observed propagating radical concentration (from rate data) and the equilibrium constants of the models of Kwak *et al.*[9] and Barner-Kowollik *et al.*[10] The predicted intermediate radical concentrations were calculated from the predicted propagating radical concentrations by assuming an equilibrium constant between these species that does not differ with time or temperature. Two widely differing values for this constant were used, those of Barner-Kowollik *et al.*[10] and Kwak *et al.*[9] This comparison was made at 70 and 90 °C, for the complete range of initiator/RAFT concentrations used, and the results for all systems showed the same trends. The large deviation (observable in Fig. 7) between predicted and observed intermediate concentrations at early times was present for all systems, and appears to be due to unexpectedly low concentrations of the intermediate radicals in the initial stages of all reactions tested here. The equilibrium constant in this early period would thus appear to be changing rapidly with time or conversion.

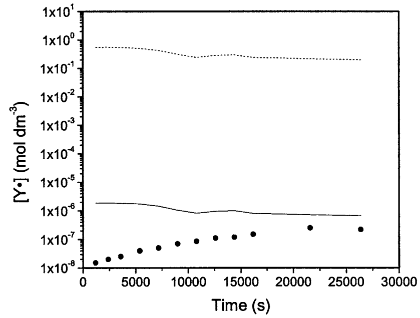


Fig. 7: Comparison of the observed (circles) intermediate radical concentrations and those predicted by the rate coefficients of Kwak *et al.*[9] (solid line) and Barner-Kowollik *et al.*[10] (dashed line) with time.

The observed intermediate radical concentrations were roughly consistent with those using the above approach, and the rate coefficients of Kwak *et al.*,[9] Under all conditions where this comparison was made, the predicted intermediate radical concentration using either model was always higher than the corresponding observed concentration, with the deviation being larger at higher temperature and lower initiator/RAFT concentration. Thus, ignoring the early time discrepancy, the rate coefficients of this model do not quantitatively describe the equilibrium. However, the temperatures in this study were higher than those of Kwak *et al.*,[9] and the discrepancy beyond the initial region is not large, although a possible initiator/RAFT concentration dependence suggests that other factors beyond the basic equilibrium may be important.

When the same calculations were performed using the equilibrium constant of Barner-Kowollik *et al.*,[10] the predictions for the intermediate radical concentrations were higher by more than 5 orders of magnitude than those observed. The rate coefficients that give this equilibrium constant are clearly not applicable to the current system.

Conclusions

Electron spin resonance spectroscopy was used to determine the nature and time evolution of the intermediate radicals in the RAFT polymerisation of styrene in the presence of CDB. Propagating radical concentrations were too low for direct detection using the current combination of experimental system and instrumentation.

The intermediate radicals were found to correspond to those reported by Hawthorne *et al.*,[23] and it was found that, in all studied cases, there was a strong initial retardation in the concentration of intermediate radicals, followed by an increase to a maximum concentration that was dependent on temperature and initiator concentration, and then a slow decrease. Detectable concentrations of intermediate radicals were observed at very long reaction times, under conditions under which no initiator would be expected to remain. Both the slow increase in the concentration of intermediate radicals, and their presence long after the presence of an initiator source, suggest that their concentration is somewhat decoupled from that of the initiator, and that the accepted RAFT equilibrium is quite variable, and/or that more events are occurring in addition to those described in the equilibrium in Scheme 1. Beyond the initial region where the intermediate radical concentrations were unexpectedly low, the intermediate radical concentrations were roughly (although not exactly) consistent with the predictions based on the equilibrium rate coefficients of Kwak *et al.*,[9] and those of Barner-Kowollik *et al.*[10] were not capable of accurately modeling the observed data.

The observation of an extra signal, corresponding to neither propagating nor intermediate radicals, at intermediate reaction times (with subsequent increasing concentration) during most reactions, suggests that further radical processes are occurring during the reaction. The coincidence of this signal and the loss of RAFT agent colour from the reaction medium suggests that this peak may be due a degradation reaction of the RAFT agent.

Acknowledgments

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