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Initialisation in RAFT-mediated polymerisation of methyl acrylate†

J. B. McLeary,[a] J. M. McKenzie,[b] M. P. Tonge,*[ac] R. D. Sanderson[a] and B. Klumperman*[ad]
[a] *UNESCO Centre for Macromolecules and Materials, Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa*
[b] *Nuclear Magnetic Resonance Laboratories, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa*
[c] *Key Centre for Polymer Colloids, Chemistry School F11, University of Sydney, NSW, 2006, Australia. E-mail: tonge_m@chem.usyd.edu.au; Fax: +61-2-93518651; Tel: +61-2-93513330*
[d] *Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: l.klumperman@tue.nl; Fax: +31 (40) 2463966; Tel: +31 (40) 2472339*

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Inhibition in Reversible Addition–Fragmentation chain Transfer (RAFT)-mediated polymerisations is currently a controversial issue; here we provide evidence that the slow "propagation" of the initiating and leaving group radicals during the early part (the period of consumption of the initial RAFT agent) of methyl acrylate RAFT-mediated polymerisation has characteristics similar to inhibition.

Inhibition is common in free radical polymerisation and can usually be ascribed to some species, such as dissolved oxygen, that inhibits the addition of radicals to monomer. In RAFT-mediated reactions that have been purified of common inhibiting materials, an "inhibition" period has often been observed. This effect is particularly strong in the case of methyl acrylate.[1] It has been suggested that this "inhibition" behaviour is due to slow fragmentation of formed intermediate radicals.[1]

Previously we have investigated the early polymerisation behaviour of styrene in RAFT-mediated polymerisations.[2] The period during which the initial RAFT agent was consumed was termed initialisation, and resulted in different reaction behaviour before and after this period. This was a result of extremely strong selectivity resulting in the formation of the single monomer adduct of the original RAFT agent. This was caused by a large difference in addition–fragmentation rate coefficients during this period. This resulted in a bias in the reaction favouring the formation and propagation of RAFT agent leaving group- and initiator-derived radicals, and the effective prevention of propagation of oligomeric (monomer-derived) radicals. This selectivity resulted in these radicals being the dominant type until almost all of the initial RAFT agent was consumed, after which oligomeric monomer-derived radicals could form in significant quantities. The length of the initialisation period is dependent on the RAFT agent concentration, the "propagating" radical concentrations, and the addition rate constants of the RAFT agent leaving group- and initiator-derived radical groups to monomer.[3,4] We have suggested that this behaviour could be the predominant cause of "inhibition" in RAFT-mediated acrylate polymerisations.[2]

Here, it is shown that the RAFT-mediated methyl acrylate (MA) polymerisations also show very strong fragmentation selectivity during the initialisation period, which leads to slow propagation during this period, which can have the appearance of inhibition.

Fig. 1 shows the relative concentrations of RAFT-derived species and monomer, as measured by ^{1}H NMR spectroscopy, during the early part of the RAFT-mediated polymerisation at 70 °C of MA, using RAFT agents that show both strong (cumyl dithiobenzoate (1)), and weak (cumyl phenyl dithioacetate (2)) rate retardation.‡ The rates of propagation and consumption of the initial RAFT agents are very similar during initialisation (before the concentration of the initial RAFT agent reaches zero). Very little formation of CM$_n$X (where C is the cumyl group, M is a monomer unit, n is the degree of polymerisation, and X is the RAFT "core", *i.e.*, the dithiobenzoate (D) or phenyl dithioacetate group (Dta)) for $n \geq 2$ occurs until initialisation is complete. Thus, these reactions show strong fragmentation selectivity during initialisation, as previously reported for styrene systems.[2] This also implies that the predominant propagating radicals during initialisation are cumyl (and cyanoisopropyl) radicals. This was confirmed by ESR spectroscopy.[5] The rate of propagation changed significantly at the end of initialisation for both systems, as the type of propagating radical changed. Very similar kinetic behaviour to that of the reaction with (1) was observed when cyanoisopropyl dithiobenzoate was used as RAFT agent.

The following relationship exists for addition and propagation rate coefficients for MA and styrene systems:[3,4,6]

$$\frac{k_{\mathrm{p,MA}}}{k_{\mathrm{p,A,MA}}} >> 1 >> \frac{k_{\mathrm{p,STY}}}{k_{\mathrm{p,A,STY}}} \qquad (1)$$

Here $k_{\mathrm{p,MA}}$ and $k_{\mathrm{p,STY}}$ refer to the long chain propagation rate coefficients for MA and styrene, and $k_{\mathrm{p,A,MA}}$ and $k_{\mathrm{p,A,STY}}$ to the rate coefficients for the addition of the cyanoisopropyl radical to MA and styrene. If there are similar propagating radical concentrations before and after initialisation, the relative reaction rates will be primarily dependent on the relevant k_p values. For MA, a lower rate of reaction is expected during initialisation than for the period afterwards, as $k_{\mathrm{p,MA}}$ is 13100 L mol^{-1} s^{-1} at 25 °C,[7] and $k_{\mathrm{p,A,MA}}$ is 367 L mol^{-1} s^{-1} at 42 °C.[4] The experimental data in Fig. 1 show

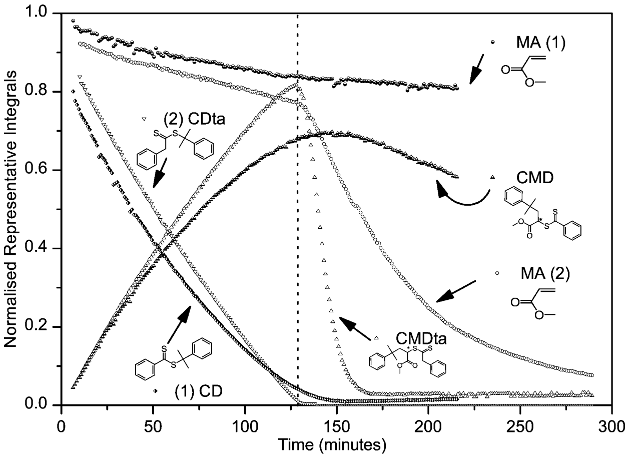

Fig. 1 The consumption of MA (2.90 × 10^{-3} mol) in the presence of (1) (3.79 × 10^{-4} mol) and (2) (4.02 × 10^{-4} mol) at 70 °C, in C_6D_6 (2.99 × 10^{-3} mol). The vertical line indicates the end of initialisation for (2).

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† Electronic Supplementary Information (ESI) available: chemical structures of all species. See http://www.rsc.org/suppdata/cc/b4/b404857a/

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large changes in the rate of reaction before and after initialisation. The difference in rate at the end of initialisation between reactions mediated by (1) and (2) is that the concentration of intermediate radicals (as observed by ESR spectroscopy)[5] rises rapidly (by a factor of at least 50) near the end of initialisation for (1), which leads to strong rate retardation. This is because in a RAFT system, high concentrations of the formed intermediate radicals result in rate retardation.[8–10] Termination of the intermediate radical (increasing the overall termination rate) occurs, although if this is the only cause of retardation is not yet known.[11] Significant concentrations of intermediate radicals do not form for (2). In the case of (2), the rate increases significantly (by more than a factor of 10) at the end of initialisation as the dominant type of propagating radical changes to the faster propagating monomer-derived oligomers. This rate increase is not observed for (1), since the drop in propagating radical concentration (causing retardation) is greater than the increase in k_p. The extent of retardation is dependent on the concentration of (1), and acceleration at the end of initialisation can also be seen for lower concentrations of (1). This behaviour also holds for other investigated dithiobenzoate RAFT agents.

During the early part of initialisation, the propagating radical concentrations are very similar, since the intermediate radical concentrations are small. Since the types of propagating radicals are the same during initialisation, the rates of monomer consumption are very similar, and, since the rate determining step for consumption of the initial RAFT agent is this addition (monomer consumption) step, the rates of consumption of (1) and (2) are very similar. Since addition to the RAFT agent is not rate determining, the rates of consumption are independent of the concentrations of the initial RAFT agents, which is very clear in the case of (2). The deviations later in the initialisation period are due to the slow increase in the intermediate radical concentration during initialisation for (1), leading to a decreasing propagating radical concentration, and slower rates of consumption of monomer and (1). There is very good correlation between the rate of monomer and (1) consumption until the last few minutes of initialisation, when the concentration of (1) becomes too low to prevent propagation to form CM_2X. The same holds for the reaction mediated by (2).

In typical RAFT-mediated polymerisations, monomer to RAFT agent concentration ratios are often of the order of a thousand to one,[1] *i.e.*, long chains are targeted, in which case a very small fraction of the monomer will be consumed during the initialisation period. In the case of MA, the rate of reaction will be much slower during initialisation than after. This would hold even in cases in which small amounts of dimeric oligomeric radicals can form, since the selectivity of fragmentation will ensure that most propagating radicals are the slower propagating initiator- and leaving group-derived species, and the total amount of monomer consumed during initialisation will still be minimal. Examples of systems in which total inhibition has been reported also show colour change,[12] which is consistent with polymerisation and consumption of the initial RAFT agent to form its monomeric or higher adducts in RAFT-mediated polymerisations. Similar behaviour was also observed when longer chain lengths were targeted (using lower RAFT agent and initiator concentrations as shown in Fig. 2), *i.e.*, this behaviour is not a result of unusual starting conditions.

Thus, the slow rate at the start of the reaction is due to low propagation rate coefficients during the initialisation period. The duration of this period is roughly proportional to the RAFT agent concentration (since the slow propagation lasts while the initial RAFT agent is present), after which the rate increases, due to a change to a faster propagating radical. This behaviour is capable of explaining previous reports of "inhibition" phenomena for long chain target lengths in RAFT-mediated polymerisation of MA. Such behaviour can lead to apparent inhibition in any such system, *e.g.*, vinyl acetate,[3,4] where the propagation rate coefficients of the radicals during initialisation are much slower than for long chain polymeric radicals.

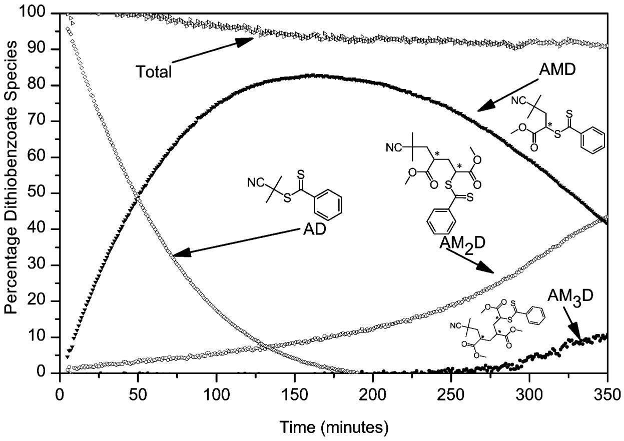

Fig. 2 The concentrations of RAFT-derived species during the reaction of MA in the presence of cyanoisopropyl (A) dithiobenzoate (D), initiated by AIBN at 60 °C, with a target degree of polymerisation of 50.

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Notes and references

‡ RAFT agents were synthesized according to established literature procedures.[5,13] The purity of cumyl dithiobenzoate was > 97% and that of the cumyl phenyl dithioacetate > 98%, as shown by ^1H NMR spectroscopy analysis. All impurities were tracked by NMR spectroscopy and none of the species present interfered with the reactions. Conditions for the NMR spectroscopy experiments have been discussed in detail previously.[2] Spectra were integrated both manually and automatically (ACD labs 7.0 ^1H processor®) to allow identification of species during formation.

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