Further Effects of Chain-Length-Dependent Reactivities on Radical Polymerization Kinetics

Johan P.A. Heuts,[A,C] *Gregory T. Russell,*[B,C] *Gregory B. Smith*[B]

[A] Laboratory for Polymer Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, THE NETHERLANDS

[B] Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, NEW ZEALAND

[C] Corresponding authors: j.p.a.heuts@tue.nl, greg.russell@canterbury.ac.nz

Abstract

In this paper we finalize some threads in our investigations into the effects of chain length-dependent propagation (CLDP) on radical polymerization kinetics, confirming all our previous conclusions. Additionally, and more significantly, we uncover some unexpected and striking effects of chain-length dependent chain transfer (CLDTr). It was found that the observed overall rate coefficients for propagation and termination (and therefore the rate of polymerization) are not affected by whether or not chain transfer is chain-length dependent. However this situation is different when considering the molecular weight distributions of the resulting polymers. In the case of chain-length independent chain transfer, CLDP results in a considerable narrowing of the distribution at the low molecular weight side of the distribution in a chain-transfer controlled system. On the other hand, the inclusion of both CLDP and CLDTr yielded identical results to classical kinetics – in these latter two cases the molecular weight distribution is governed by the same, chain-length independent chain transfer constant, whereas in the case of CLDP only it is governed by a chain-length dependent chain transfer constant which decreases with decreasing chain length, thus enhancing the probability of propagation for short radicals. Furthermore, it was shown that the inclusion of a very slow first addition step has tremendous effects on the observed kinetics, increasing the primary radical concentration and thereby the overall termination rate coefficient dramatically. However, including possible penultimate unit effects does not significantly affect the overall picture and can be ignored for the time-being. Lastly, we explore the prospects of using MWDs to probe the phenomena of CLDP and CLDTr. Again, some interesting insights follow.

Introduction

Recent years have seen a revival of research in free-radical polymerization kinetics, especially in regard to chain-length-dependent termination[1] and the determination of elementary rate coefficients in controlled radical polymerisation,[2-4] including both topics together.[5] While testing the performance of a simple, physically realistic, model for termination (i.e., the "composite termination model"[6]) at very low chain lengths (with number average degrees of polymerization, $DP_n \approx 12$ - 250), we discovered that for an adequate description of the kinetics in these systems the chain-length dependence of the propagation rate coefficient, k_p, cannot be ignored.[7] Up to that point in time, it had been known, especially as result of experiments with nitroxides[8,9] and catalytic chain transfer agents,[10] that k_p depends on the chain length of the propagating radical for the first few addition steps.[11] However it had not been realized that this chain-length dependence of k_p would also be affecting the observed macroscopic kinetics for a conventional free-radical polymerization in which polymers are produced with chain lengths longer than a few units. There was (and still is) some contention as to whether the chain-length dependence of k_p extends beyond small chain lengths.[12,13] Ignoring, for the time being, any chain-length dependence of k_p at higher chain lengths, we have explored theoretically how a short-chain chain-length dependence of k_p can affect the observed macroscopic kinetics in a conventional free-radical polymerisation, and our preliminary findings indicate that chain-length dependent propagation (CLDP) affects the observed value for k_p (i.e., $\langle k_p \rangle$) and the rate of polymerization (R_p) in systems with $DP_n < \sim100$.[7,14-16] For polymerizations in which the first addition step is not slower than long chain propagation,

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i.e., $k_p^1 \geq k_p$, it was found that for a given DP_n the macroscopic average termination rate coefficient ($\langle k_t \rangle$) is not significantly affected by CLDP, but in the case where $k_p^1 < k_p$, a significant increase in $\langle k_t \rangle$ is observed.[15] One of the objectives of the current study is to investigate the latter observation in more detail. Furthermore, we wish to address two important points that hitherto we have ignored in our kinetic modelling: (1) the effects of a chain-length dependent chain transfer reaction, and (2) the incorporation of possible penultimate unit effects in the modelling of a slow first addition step. Feeling that the (preliminary) model development is coming to maturation and that further development is not very sensible without new experimental data, we also investigate the possible effect of CLDP on the molecular weight distribution (MWD) in order to see whether it is possible to extract information regarding CLDP from experimental MWDs.

Model Description

Composite Termination Model

Although it has been known for quite some time that the termination rate coefficient depends on the length of the reacting radical and that the rate-determining processes for the termination reactions of small and long radicals are center-of-mass and segmental diffusion, respectively,[17] it has not been until recently that all available experimental observations have been included in a simple, physically realistic model for termination.[6] The most relevant of these observations are:

  a. Termination rate coefficients for small, "monomeric", radicals are of the order of $10^9 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$.[18]

b. The rate determining step for short radicals is center-of-mass diffusion. It is known that the diffusion coefficient for such a process scales with chain length as $\sim i^{-0.5}$ for styrene[19] and methacrylate[20,21] oligomers.

c. The rate determining step for long radicals is segmental diffusion, for which the diffusion coefficient is known to scale with chain length as $\sim i^{-0.16}$.[22,23]

Combining these observations into a single simple model may appear a trivial exercise, but until we proposed the "composite termination model" a few years ago,[6] it was common practice to ignore one or two of the above observations when modelling chain-length dependent termination. In the composite termination model, the termination rate coefficient between two i-meric radicals, $k_t^{i,i}$ is given by Eq. 1, where we assume a critical chain length i_{crit} of about 100 units as being where the rate determining process changes from center-of-mass diffusion ($i \leq i_{crit}$) to segmental diffusion ($i > i_{crit}$):

$$k_t^{i,i} = \begin{cases} k_t^{1,1} \times i^{-e_S} & \text{for } i \leq i_{crit} \\ k_t^{1,1} \times (i_{crit})^{-(e_S - e_L)} \times i^{-e_L} & \text{for } i > i_{crit} \end{cases} \tag{1}$$

The cross-termination rate coefficient between an i-meric and a j-meric radical can be specified in various ways, but it turns out that this choice has no significant effect on the kinetics.[24,25] Given this and that $k_t^{i,j} = (k_t^{i,i} \times k_t^{j,j})^{1/2}$ greatly simplifies calculations,[6,24,26] we use this so-called geometric mean model in this work.

In our proposal of the composite termination model, we suggested $e_S \approx 0.5$, $e_L = 0.16$ and $i_{crit} \approx 100$.[6] This picture has subsequently been confirmed for various methacrylates[27-29] and for an itaconate[30] through careful, sophisticated experiments by the groups of Barner-Kowollik[29] and Buback.[27,28,30] Notwithstanding that for acrylates a slightly different picture is emerging[31,32] (higher e_S and lower i_{crit}), in this work we

will use $k_t^{1,1} = 1{\times}10^9$ dm^3 mol^{-1} s^{-1}, $e_S = 0.5$, $e_L = 0.16$ and $i_{crit} = 100$ for calculations, as these were the values that have been found to describe MMA polymerization around 60 °C.[7,29]

Chain-Length Dependent Propagation Model

From the use of pulsed laser polymerization (PLP),[33-36] especially in the 1990s, many reliable propagation rate coefficients have become available.[37-41] From comparing the obtained values with those from small radical additions,[11,42,43] it was clear from the onset that small radical additions were faster than long-chain propagation. This observation clearly suggested a chain-length dependence of the propagation rate coefficient. In more recent PLP studies, a chain-length dependence of k_p has also been observed.[12,44,45] There is, however, still some contention about whether this chain-length dependence is only operative at short chain lengths or whether it continues indefinitely.[12,13,44,45] Since we believe that there is sufficient convincing proof for the existence of a short-chain chain-length dependence and that this is of a different nature to any possible long-chain effects, we have only focussed on short-chain CLDP until now. Analysis of the available experimental and theoretical data to date suggests that the short-chain chain length dependence of k_p can be described by the following (empirical) model:[16]

$$k_p^i = k_p \left[1 + C_1 \exp\left\{ -\frac{\ln 2}{i_{1/2}}(i-1) \right\} \right] \qquad (2)$$

In this equation, k_p is the long-chain propagation rate coefficient, $C_1 = (k_p^1 - k_p)/k_p$ is the factor by which k_p^1 exceeds k_p, and $i_{1/2}$ is the chain length range over which $k_p^i - k_p$ halves in value (*i.e.*, it is like a "half-life"). Available data thus far suggest $C_1 \approx 10\text{-}50$ and $i_{1/2} \approx$

0.5-1.5;[16] for MMA polymerization we found the values C_1 = 15.8 and $i_{1/2}$ = 1.12 describe both our own steady-state data[7] and the PLP results of Van Herk et al.[13]

Macroscopic Kinetics

The fact that both k_t and k_p are chain-length dependent has an effect on the rate of polymerization (R_p) and the instantaneous number-average degree of polymerization (DP_n). Instead of using a constant value for k_p and k_t for the calculation of these parameters, one needs to use their chain-length averaged values, which depend on the individual k_p^i and $k_t^{i,j}$ as in equations 3 and 4 respectively:

$$\langle k_p \rangle = \frac{\sum_{i=1}^{\infty} k_p^i [R_i]}{[R]} \tag{3}$$

$$\langle k_t \rangle = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_t^{i,j} [R_i][R_j]}{[R]^2} \tag{4}$$

In these expressions, R_i and R_j denote *i*-meric and *j*-meric radicals, respectively, and [R] $(= \sum_{i=1}^{\infty} R_i)$ is the overall radical concentration. It is important to note that in this work R_1 refers to a truly monomeric radical, whether it has been derived from initiator, chain transfer agent or chain transfer to monomer (so it does *not* refer to the radical after the first addition to monomer – this radical would be denoted as R_2 here).

Using the above definitions, the steady-state rate and Mayo equations are given by equations 5 and 6 respectively:

$$R_p = \langle k_p \rangle \sqrt{\frac{f k_d [I]}{\langle k_t \rangle}} [M] \tag{5}$$

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$$\frac{1}{DP_n} = (1+\lambda)\frac{\langle k_t \rangle [R]}{\langle k_p \rangle [M]} + \sum_X \frac{k_{tr,X} [X]}{\langle k_p \rangle [M]} \tag{6}$$

In these equations, f is the initiator efficiency, k_d the initiator decomposition rate coefficient, λ is the fraction of termination by disproportionation, $k_{tr,X}$ is the rate coefficient for chain transfer to any chain transfer agent X (including monomer), and [I], [M] and [X] are the concentrations of initiator, monomer and chain transfer agent (CTA) respectively. One has to be aware that equation 6 was derived using the long-chain approximation, which is strictly speaking not valid for the short chain lengths that are of our main interest here. However, this problem is easily remedied by adding 1 to the value of DP_n obtained by equation 6: $DP_n = DP_n$ (eq. 6) + 1. This is valid for those cases where dead chain formation is caused by chain transfer and/or disproportionation (as is the case here).

It should be noted here that in equation 6 we used a chain-length independent value for $k_{tr,X}$ and in all our simulations and modelling thus far we have made this assumption. One of the objectives of the current paper is to investigate the effect of including a chain-length dependent $k_{tr,X}$ on the generality of the results obtained thus far.

In Figure 1 we have summarized our most important findings thus far.[15] It can be seen that:

a.   A fairly general correlation exists between $\langle k_t \rangle$ and DP_n, and further, this correlation corresponds very closely to Eq. 1, i.e., $\langle k_t \rangle$ vs. DP_n almost exactly overlays $k_t^{i,i}$ vs. i.[25,46]. However it is stressed that this finding is not exact: as shown, where there is a chain-length dependence of k_p given by Eq. 2, $\langle k_t \rangle$ at a

given DP_n is slightly lower than in the absence of CLDP, while when the first addition step is really slow, there is a larger increase in $\langle k_t \rangle$.

b. The effect of CLDP on $\langle k_p \rangle$ is noticeable up to $DP_n \approx 100$, even though k_p^i reaches k_p by $i \approx 10$.

c. The effect of CLDP counteracts the effect of CLDT on the rate for short chain lengths, except for the case when $k_p^1 < k_p$, where a significant retardation is observed.

INSERT FIGURE 1

As stated before, the results in Figure 1 were obtained using two assumptions, viz. chain-length independent chain transfer and no penultimate unit effects for systems in which $k_p^1 < k_p$. The effects of these assumptions will be investigated in this paper.

Kinetic Modelling

The kinetic modelling in this paper was carried out by using an iterative procedure for solving the radical population, as outlined in previous publications.[6,15] DP_n was calculated either by using Equation 6 or by evaluating the required moments of the full dead-chain chain length distribution. The weight-average degree of polymerization, DP_w, was evaluated in the latter way.

Results and Discussion

The Effect of Chain-Length Dependent Chain Transfer

As stated before, in our simulations up to now we have ignored any possible chain-length dependence of the chain transfer reaction rate, which is in line with what has been generally assumed in kinetic modelling to date. Since our main interest was primarily directed at the DP_n-dependence of $\langle k_t \rangle$ and $\langle k_p \rangle$, we did not wish to complicate our modelling and the interpretation of the results any further by introducing an additional chain-length dependent rate coefficient. Considering that theory suggests that the chain transfer reaction may have a chain-length dependence which is very similar to propagation (the Arrhenius pre-exponential factors of both reactions appear to be determined by very similar physical parameters),[47] it is important that we investigate whether this simplification is indeed justified and thus whether our conclusions regarding the DP_n-dependence of $\langle k_t \rangle$ and $\langle k_p \rangle$ are valid. Furthermore, it is important to know whether the use of long-chain chain transfer constants (C_S^{long}) can be used for DP_n predictions at smaller chain lengths.

We investigated the effect of chain-length-dependent chain transfer (CLDTr) by considering three different situations:

(1)   CLDP (with k_p^i given by equation 2) in combination with chain-length-independent chain transfer (CLITr). This is what we used in our previously published simulations, and in this situation the chain transfer rate coefficient for an *i*-meric radical, k_{tr}^i, is given by (for simplicity we use the notation k_{tr} rather than $k_{tr,X}$ from now on)

$$k_{tr}^i = C_S^{long} \times k_p \tag{7}$$

It is noted that such polymerization is thus characterized by a *chain-length-dependent chain transfer constant*, $C_S^i = k_{tr}^i/k_p^i$, that decreases with decreasing chain length of the *i*-meric radical.

(2)   CLDP (with k_p^i given by equation 2) in combination with CLDTr. Here we assume that the chain-length dependence of chain transfer is the same as the chain-length dependence of propagation. In this case k_{tr}^i is defined by:

$$k_{tr}^i = C_S^{long} \times k_p^i \tag{8}$$

Thus in effect the polymerization is characterized by a *chain-length independent chain transfer constant*, $C_S^i = k_{tr}^i/k_p^i = C_S^{long}$, that is constant for all chain lengths.

(3)   CLIP in combination with CLITr. Here we only assume chain-length dependent termination and classical kinetics in terms of propagation and chain transfer. In this case, the polymerization is also characterized by a chain-length independent chain transfer constant, C_S^{long}.

Note that in the event of CLDTr, $k_{tr,X}$ in Equation 6 must be replaced by $\langle k_{tr,X} \rangle$, which is defined as in Equation 3, except that k_{tr}^i replaces k_p^i.

The results of our simulations, in which parameters were chosen to ensure that the MWDs are controlled by chain transfer, are shown in Figure 2 in terms of DP_n and in Figure 3 in terms of chain transfer agent concentration, [CTA]. It is immediately clear from Figure 2 that there is no significant effect of CLDTr on the dependence of $\langle k_t \rangle$ and $\langle k_p \rangle$ (and hence also the rate) on DP_n. This validates our earlier conclusions regarding the effect of CLDP on the observed macroscopic kinetics.

INSERT FIGURES 2 AND 3

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An interesting observation is made, however, when we compare the polydispersity indices (*PDI*) from the simulations. For high [CTA] (Figure 3d), and thus low DP_n (Figure 2d), we observe a significant decrease in *PDI* for the simulations in which we combine CLDP with CLITr. This effect of CLDP has previously been noted by us,[14] including that it seems to be observed in our experimental data,[7] not to mention other experimental data involving very short chains.[48] What is new to this work and is especially interesting is that the effect disappears in the situations where $C_S^{i} = C_S^{long}$, for which one obtains identical results, regardless of whether or not CLDP (and CLDTr) are operative. In these situations one has $PDI \approx 2$, i.e., the classical limit for chain-transfer controlled polymerisations; values slightly greater than 2 are obtained at high DP_n because of the effect of CLDT, which acts to broaden the MWD,[49] while at very low DP_n this effect is overridden by the breakdown of the long-chain approximation, which acts to reduce *PDI*.

In view of the above results we were stimulated to look at the entire (dead-chain) MWDs from our simulations. The narrowing of the molecular weight distribution for the case of CLDP with CLITr is clearly evident in Figure 4a, where it can be seen that there are many more low-molecular-weight chains in the systems with a constant C_S than in the system with CLDP+CLITr. This is caused by the fact that in the latter system the probability of chain growth for small chains is higher than in the case of CLIP, and thus small chains are 'protected' from becoming dead chains, resulting in a narrowing of MWD and thus a lowering of *PDI*. On the other hand, for larger chains there should be no difference in propagation probability, and that is indeed what is observed: the high

molecular weight parts of the distributions are identical. This is also why the peak molecular weights for all three systems are the same.

INSERT FIGURE 4

The surprising result from Figure 4a is that the MWD is identical for the two cases of CLDP+CLDTr and CLIP+CLITr. This is a surprise because the values of k_{tr}^i are different in each case (see Equation 8), meaning that one would expect different rates of production of dead chains of length i in each case. The explanation for this riddle lies in the fact that this rate of production depends also on [R_i]. In fact one can show (derivation presented later) for the case of transfer control that the increase in k_{tr}^i due to CLDTr is exactly counterbalanced by a decrease in [R_i], with the result that the product of these two terms is the same as in the absence CLDP and CLDTr (i.e., classical polymerization). Thus the results of Figure 4a should not be interpreted as meaning that CLDP+CLDTr has no effect on the radical chain-length distribution: it does, with CLDP reducing values of [R_i] at small i. But, in contrast to the case of CLDP+CLITr, this effect is not expressed in the dead-chain MWD.

The above results quite naturally prompt one to wonder how Mayo plots are affected: do they yield the long-chain value of C_S? To investigate this we constructed Mayo plots from our results; these are presented in Figure 4b. From Equation 6 it is evident that for classical kinetics a plot of $1/DP_n$ vs. [CTA]/[M] will have slope of C_S (= 1 in our simulations) while $1/DP_w$ vs. [CTA]/[M] will have slope of $C_S/2$ (= 0.5 here). It is evident from Figure 4b that only for the case of CLDP+CLITr is there a significant

deviation in the slope from the long-chain value of C_S. Of practical significance is that this deviation is much smaller for DP_w than for DP_n.[50] It should also be noticed that the DP at the peak of the $w(\log M)$ distribution corresponds in almost all cases to DP_w, and that for all three systems these values lie on the same straight line. All these results are as would be expected given the findings already discussed above.

To summarize the above, we can conclude that inclusion of CLDTr does not affect the overall rate of polymerization but it does affect the molecular weight distribution. In terms of rate we find that: R_p(CLIP+CLITr) < R_p(CLDP+CLDTr) ≈ R_p(CLDP+CLITr). In terms of PDI we find that PDI(CLIP+CLITr) = PDI(CLDP+CLDTr) > PDI(CLDP+CLITr).

It is now interesting to consider the available experimental data. As already mentioned, our published data on methyl methacrylate polymerizations in the presence of large amounts of dodecane thiol (DDM) indeed show a decrease in PDI with increasing [CTA][7], and this trend was quantitatively reproduced by our modelling with CLDP and CLITr.[14] Our present work indicates that this trend should largely be absent if CLDTr is operative. Taken together these results suggest that chain transfer to DDM has a much weaker chain length dependence than propagation. This might reflect that DDM is a relatively large CTA, meaning that the variation of transition state mass with oligomer chain length i is relatively small, such mass variations largely being the origin of chain-length-dependent variations of propagation and transfer rates.[16,47] An interesting test of this suggestion would be to carry out experiments with a smaller CTA, for example butyl mercaptan: does it give rates and MWDs more in line with those predicted here for the case of CLDP+CLDTr? In carrying out such investigations, it is important to be aware

that standard SEC analyses of very low molecular weight polymers is fraught with uncertainties; polymer properties which are constant for high molecular weight polymers, such as the differential refractive index increment (dn/dc) and the UV absorption, depend on the chain length for short chains.[51] For this reason we feel that more careful experimental studies are required that especially focus on the molecular weight distributions of very short polymers.

The Effect of Incorporating the Penultimate Unit Effect in Propagation

In previous studies we also investigated the impact of using $k_p^1 \neq (C_1+1)k_p$, a situation which is of practical relevance as initiator- or transfer-derived primary radicals are seldom the same as a truly monomeric radical. In these previous studies we assumed that the dimeric radical resulting from all first addition steps to monomer has the same reactivity as a dimeric radical resulting from the addition of a truly monomeric radical; in other words, we ignored any possible penultimate unit effect (PUE) in the reactivity of the radical, and regardless of the value of k_p^1 we used k_p^i given by Equation 2 for $i \geq 2$. Since we know that PUEs are operative in copolymerization,[52] there is no *a priori* reason to assume that they are negligible in CLDP. Therefore we will here examine the effect on kinetics of a PUE in CLDP, even though this introduces greater complexity into our simulations and we must somewhat guess at the quantitative nature of such PUEs, given the absence of definite information about them.

In our previous modelling we observed the largest effects of k_p^1 on the DP_n-dependences of $\langle k_p \rangle$, $\langle k_t \rangle$ and the rate when $k_p^1 < k_p$.[15,16] For this reason we chose this situation of retardation to investigate how a possible PUE would affect kinetics. For a

system in which we varied DP_n by changing [I], we treated the initiator-derived radicals to have an addition rate coefficient of $k_p^1 = k_p/10$. We then compared the situations where only the first addition (k_p^1) was slower than given by Equation 2, with the situations where the first two additions (k_p^1 and k_p^2), then the first three and finally the first four additions were slower (see Figure 5). It is important to note here that using a value of k_p^1 that is ten times smaller than the long-chain value is by no means fiction. For example, the addition of cyanoisopropyl radical (i.e., the radical derived from AIBN decomposition) is roughly 150 and 50 times slower than long chain propagation at 42 °C for vinyl acetate and methyl acrylate, respectively.[16,36,53]

INSERT FIGURES 5 AND 6

The results of these simulations are presented in Figure 6. From Figure 6a it is clear that the behaviour of $\langle k_t \rangle$ is not significantly affected by inclusion of PUEs, as the data lie on virtually the same curve. It is, however, important to note that all these $\langle k_t \rangle$ values are observably higher than those obtained in systems with CLIP or with CLDP without retardation (i.e., $k_p^1 \geq k_p$). We will study this effect in more detail in the following section. The effect of including PUEs on $\langle k_p \rangle$ seems to be more pronounced (Figure 6b): the more i for which k_p^i is less than its Equation-2 value, the smaller is $\langle k_p \rangle$ for a given DP_n. However, the effect does not seem to be larger than about 10%. Hence, the combined effect of $\langle k_p \rangle$ and $\langle k_t \rangle$ in the rate seems to be negligible (see Figure 6c). Since we are currently mainly interested in the effects of CLDP on the macroscopic kinetics and MWDs, we conclude that until there is specific information regarding PUEs,

it is probably safe to ignore them in seeking to model and understand data: the dominant effect is that of retardation (k_p^1 significantly less than k_p), and any associated PUE has only a small additional effect in comparison.

From a general point of view the results in Figure 6 are very interesting. What is shown is that a slow primary radical addition has a tremendous retardative effect on the observed kinetics and that this effect is a combination of slower propagation and faster termination. Especially the latter is interesting as we found that the DP_n-dependence of $\langle k_t \rangle$ was not significantly affected by the parameter values of C_1 and $i_{1/2}$, with all data being only slightly below the data obtained for CLIP.[15] The fact that the inclusion of only one slow first addition causes the $\langle k_t \rangle$-values to increase dramatically is the subject of following section.

The Origin of Retardation in Systems with Slow Initiation or Retardative Chain Transfer
In a previous work[16] we considered the situation of re-initiation from transfer occurring with a different rate coefficient (k_p^B) to that for addition of primary radicals from initiator (k_p^A), where these rate coefficients replace what up until now has all been lumped under the umbrella of k_p^1. Where k_p^B is significantly less than k_p one has the situation commonly referred to as 'degradative chain transfer', i.e., transfer tends to result also in termination because of the creation of a long-lived, highly mobile radical, and thus there is significant rate retardation. Quite obviously this is because of elevation of $\langle k_t \rangle$, and in our previous work we showed that kinetically there is no distinction between this effect being caused either by slow initiation ($k_p^A \ll k_p$) or slow re-initiation ($k_p^B \ll k_p$).[16] However, what is slightly surprising is that even for systems with the same value of DP_n,

the value of $\langle k_t \rangle$ is observably larger for the case of retardation. This is shown clearly in the results of Figure 7, which presents simulation output for variation of [CTA], one set of calculations having k_p^A and k_p^B both equal to k_p^1 of Equation 2, the other being identical except for having $k_p^B = k_p/10$.

INSERT FIGURE 7

In an effort to understand why retardation elevates $\langle k_t \rangle$ even where DP_n is identical, we had a look at the radical chain-length distribution, $[R_i]$, from two such simulations: see Figure 8. It is evident that the distributions are quite different in each case, even though both result in the same value of DP_n. Although both DP_n and $\langle k_t \rangle$ are functions of the $[R_i]$, they are so in different ways, and thus it is plausible that two different $[R_i]$ distributions can result in identical DP_n but different $\langle k_t \rangle$, as here. In particular attention is drawn to the value of $[R_1] = [R_A] + [R_B]$ for the case of retardation: due to the very low value of k_p^B, it is two orders of magnitude higher than it would otherwise be. Due to the high value of $k_t^{1,1}$ this gives an enormous boost to the value of $\langle k_t \rangle$ (see Equation 4), one that evidently even overrides the fact that for $2 \leq i \leq 40$ the value of $[R_i]$ is less than in the absence of retardation. So it would seem that it is this outstandingly high value of $[R_1]$ that gives undue elevation of $\langle k_t \rangle$ in the case of retardation.

INSERT FIGURE 8

Obtaining Information on CLDP from Molecular Weight Distributions

In the final section of this paper we would like to anticipate further necessary studies. Clearly the field of RP kinetics has advanced in recent times through an interplay of experiment and theory: the composite termination model[6] was proposed on the basis of hints in experimental data, and subsequently it has found spectacular confirmation via improved experiments;[27-30] similarly, transition state theory[54] was used to probe CLDP on the basis of insinuations in experimental data, and since then a variety of experiments[7,12,13,44,45] have added considerable weight to this theoretical picture.[16] Now we have introduced CLDTr into considerations. Especially with regard to CLDP and, even more so, CLDTr, it is evident that modelling is now well ahead of what is experimentally known with confidence. Therefore the need for further experimental input is currently the rate-determining step for further progress.

Because CLDP and CLDTr are phenomena involving very small chains, an obvious suggestion for learning more about them is to carry out kinetic studies at low DP_n, and in particular the idea arises of carrying out careful analysis of the resulting molecular weight distributions: intuition is that CLDP and CLDTr might impact upon MWD in a distinctive way at very small chain lengths, and thus provide an avenue for learning about these phenomena. Therefore it is of interest to carry out some simulations to see whether there is substance to this idea.

First of all we present results for two different systems with very low and identical DP_n: Figure 9a gives the MWD as $w(\log M)$, as would be obtained from size exclusion chromatography, while Figure 9b shows the same results as the natural logarithm of the number distribution, $\ln P(M)$, vs. M. The two different systems are

CLDP+CLITr and CLIP+CLITr (the latter being the same as CLDP+CLDTr, as already discussed).   This comparison enables the pure effect of chain-length-dependent propagation on MWD to be seen.

INSERT FIGURE 9

Perhaps the most remarkable result of Figure 9a is that these two MWDs have the same DP_n, even though they are differently positioned. The reason for this becomes clear from Figure 9b: the concentrations of monomeric, dimeric and trimeric chains are much lower for the case of CLDP, which acts to increase DP_n and counterbalances the effect of lower numbers of long chains, an effect that acts to reduce DP_n. This latter effect is emphasized in $w(\log M)$ because of the nature of this form of the MWD, but such differences in $w(\log M)$ at high M have only a relatively weak effect on DP_n. On the other hand, they have a much greater effect on DP_w, and indeed, this quantity is much less for the case of CLDP than CLIP (22.5 vs. 28.4 in our example).

The above discussion highlights several important things about CLDP: (1) It has a spectacular effect on $P(M)$ at very low M, as is clearly evident in Figure 9b. The origin of this effect is that fast propagation reduces the probability of dead-chain formation, and thus low numbers of oligomers are formed when CLDP is operative. (2) While CLDP has a large effect on $P(M)$ at low M, this effect is not visible in $w(\log M)$ – compare Figures 9a and 9b – because of the nature of the latter distribution. Further, the effect of CLDP is a negative one, i.e., it results in something less measurable rather than more measurable. We therefore conclude that CLDP would be very difficult to detect using

size exclusion chromatography (SEC) to look at oligomers, not just because the signal differences would be small (see Figure 9a), but even more so because they would be very difficult to distinguish from baseline noise and uncertainty. Curvature of $\ln P(M)$ plots is common,[50] and it is almost always impossible to say with confidence whether it is mechanistic in origin or whether it is instrumental artefact − if in practice one converted SEC data to $\ln P(M)$ and obtained the strongly concave-down shape of the CLDP results of Figure 9b, how could one be sure that these results were genuine or whether they were an artefact of calibration errors, baseline selection, and so on? (3) Insofar as CLDP does have an observable effect on $w(\log M)$, in fact it is in the broadness of the distribution, as discussed earlier (lowering of PDI) and as shown clearly in Figure 9a (narrower MWD). So somewhat unexpectedly, we conclude that the best prospects for seeing CLDP in SEC results is to look at the bulk of the distribution and not at what is obtained for oligomers.

The above conclusions have been made on the basis of results for DP_n = 15, which is indeed very low. The impact of CLDP on the shape of $P(M)$ at very low M will always be present regardless of the value of DP_n, so an experimental method that, in contrast to SEC, can measure $P(M)$ directly for oligomers should always have good prospects for detecting CLDP. Therefore the emergence of a reliable such method would be a major boost for the investigation of CLDP. On the other hand, the effect of CLDP on distribution broadness becomes less and less as DP_n increases, with Figure 2d showing that it is virtually absent by $DP_n \approx 100$. So for SEC studies one can only hope to see CLDP effects where the average chain size is very short; as already mentioned, it is not straightforward to obtain reliable results under such circumstances.[51]

Clay and Gilbert[55] urged the plotting of MWD data as $\ln P(M)$ vs. M because the slope of such plots, given the symbol Λ_M, tells a clear mechanistic story.[50,55] It is already obvious that this idea has merit in terms of detecting CLDP, so we decided to pursue this further in the present context. What is perhaps confusing about the results of Figure 9b is that once they reach a constant slope, it is different in each case. This is because it was necessary to use a different value of [CTA] in each calculation in order to get the same DP_n. Therefore we decided to analyze results with the same [CTA]; those of Figure 4a meet this criterion, and so they are re-presented in Figure 10a in the form of $\ln P(M)$ vs. M. From these distributions one may calculate $\Lambda_M = d(\ln P(M))/dM$, which is plotted in Figure 10b. It is clear that, as desired, both distributions now have the same slope (Λ_M) once beyond low M.

INSERT FIGURE 10

The most important conclusion from Figure 10 is that in the absence of CLDTr, the phenomenon of CLDP leaves a very clear imprint on $\ln P(M)$ at very low M: not only is Λ_M positive rather than negative, but it is very strongly positive. However, if there is concomitant CLDTr, then this effect entirely disappears, and Λ_M is a constant and negative value for all M, exactly as is also the case when both propagation and transfer are chain-length independent. Thus in the case of an invariant Λ_M it is not possible to distinguish between models, however the case of a positive Λ_M at low M can unambiguously be taken as evidence for CLDP. In this respect it is interesting that some experimental results of ours from nearly a decade ago – again for methyl methacrylate

(MMA) with dodecyl mercaptan – do in fact look just like the 'CLDP only' results of Figure 10a (see Figure 4 of ref. [50]). Of course given the caveats already discussed about SEC, one needs to be wary of over-interpreting experimental results such as these. Nevertheless it is interesting that CLDP provides a framework for explaining experimental results that otherwise have to be (and were) dismissed as artefactual, exactly as also the low *PDI* values – of order 1.5 for low-DP_n PMMA – obtained by Zammit et al.[48]

Finally, it is of interest to see whether the convergence in Figure 10b of all results to the same constant value of Λ_M is consistent with theory. For the case of dominant dead-chain formation by transfer, one can show that

$$P(i) \sim k_{tr}^i[\text{CTA}][\text{R}_i] \sim \frac{k_{tr}^i[\text{CTA}]}{k_p^i[\text{M}]} \prod_{j=1}^{i}\left(1 + \frac{k_{tr}^i[\text{CTA}]}{k_p^i[\text{M}]}\right)^{-1} \tag{9}$$

This result assumes only steady-state and negligible dead-chain formation by termination, otherwise it is general, e.g. it allows for both CLDP and CLDTr. Evident from Equation (9) is that [R_i] is markedly different for the cases of CLDP+CLDTr and CLIP+CLITr, even though these end up giving the same $P(M)$, something that is now very easy to show. This is because both these cases have $k_{tr}^i/k_p^i = C_S$, independent of i. In this event Equation (9) simplifies to

$$P(i) \sim \prod_{j=1}^{i}\left(1 + C_S\frac{[\text{CTA}]}{[\text{M}]}\right)^{-1} = \left(1 + C_S\frac{[\text{CTA}]}{[\text{M}]}\right)^{-i} \tag{10}$$

For this situation one has

$$\frac{d(\ln P(i))}{di} = \ln\left(1 + C_S\frac{[\text{CTA}]}{[\text{M}]}\right)^{-1} \approx -C_S\frac{[\text{CTA}]}{[\text{M}]} \tag{11}$$

Since $di = dM/M_o$, where M_o is the molar mass of monomer, Equation 11 can be transformed to

$$\Lambda_M = \frac{d(\ln P(M))}{dM} = \frac{1}{M_o} \ln\left(1 + C_S \frac{[CTA]}{[M]}\right)^{-1} \approx -\frac{C_S}{M_o} \frac{[CTA]}{[M]} \tag{12}$$

We note that Gilbert and Clay[55] only ever derive and present results for Λ_M in the long-chain limit (last entries of Equations 11 and 12), but as shown by our derivation above, there is absolutely no need to make this approximation for the situation of transfer control.

Equation 12 provides a framework for understanding the results of Figure 10b: (1) It is immediately clear why Λ_M is independent of M for the two cases with chain-length-independent C_S. (2) It is also clear from this derivation that the case of chain-length-dependent C_S must also give this same constant value of Λ_M once the effects of the chain-length dependencies have died out. (3) Equation 12 predicts this value to be (see Figure 10 for parameter values) $\Lambda_M = -9.5 \times 10^{-4}$ mol g^{-1} (exact), -1.0×10^{-3} mol g^{-1} (approximate). It is evident from Figure 10b that this is indeed what was found in our simulations. (4) Clearly Equation 9 must quantitatively describe variations of Λ_M with M – e.g. that of Figure 10b – that occur as a result of CLDP.

In summary, in the event of CLDP the quantity Λ_M remains a powerful guide to mechanism and a useful index for quantitative determination of rate coefficients.

Conclusion

It can be exasperating that so many complexities enter into the kinetics of radical polymerization. For a long time it was vigorously debated whether termination is chain-length dependent. By the time it had become clear that it definitely is, suggestions began to emerge that propagation is also chain-length dependent. It may be said that this is no longer disputed, even if there is still conjecture about the nature of this variation. Now we have introduced the possibility of transfer being chain-length dependent, something that really must be expected given that propagation, a reaction similar in nature, is chain-length dependent. All this may give a feeling of hopelessness in the face of overwhelming complexity. And yet it should not, for it is really just a challenge to understand things that have never really been understood properly and are of real-world importance. What makes this challenge especially fascinating is that sometimes these effects are there but hidden. This is implicit in the fact that for so long the simple classical model of RP kinetics held sway, even though it may now be seen to be deficient in so many ways. What this points to is that sometimes effects cancel out, as has been illustrated in this paper. For example, CLDP+CLDTr results in the same MWDs as CLIP+CLITr. Or CLDP+CLDT results in rates that at low chain lengths look like those of CLIP+CLIT. We continue to be stimulated by the challenge of trying to understand all these nuances, and we hope that in some small way our work both inspires others to take up this challenge – one that is both experimental and theoretical – and helps them in doing so.

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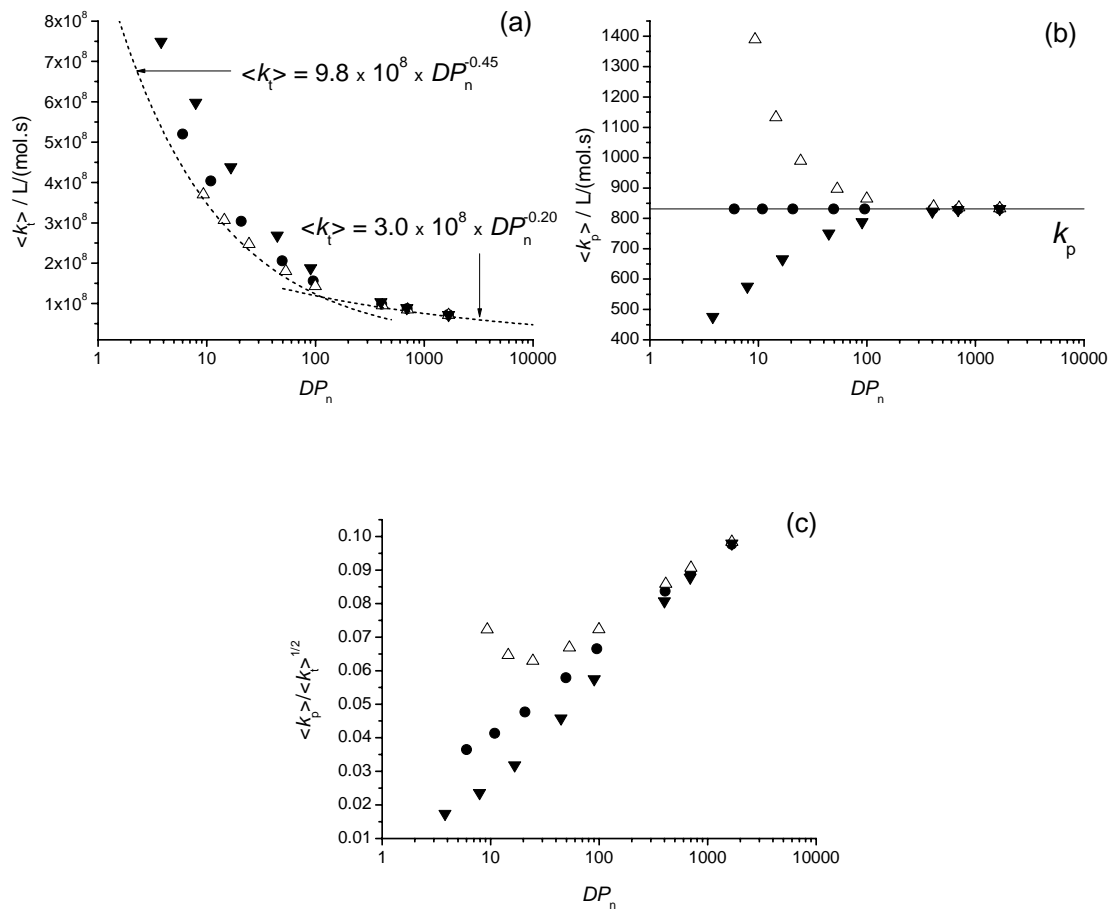
Fig. 1. Dependence of (a) $\langle k_t \rangle$, (b) $\langle k_p \rangle$ and (c) $\langle k_p \rangle / \langle k_t \rangle^{1/2}$ on DP_n. For all figures $k_p = 831$ dm^3 mol^{-1} s^{-1} and CLDT is according to the composite termination model using the parameter values given in the text. Filled circles ($\bullet$): chain length independent propagation; empty triangles ($\triangle$): CLDP with $C_1 = 10$ and $i_{1/2} = 1$; filled triangles ($\blacktriangledown$): CLDP with $k_p^1 = 0.1 \times k_p$ and k_p^i according to Eq. (2) with $C_1 = 10$ and $i_{1/2} = 1$ for all $i \geq 2$. The dashed lines in (a) are the overall fits for CLDP described by $C_1 = 10 - 50$ and $i_{1/2} = 0.5 - 5$.[12]
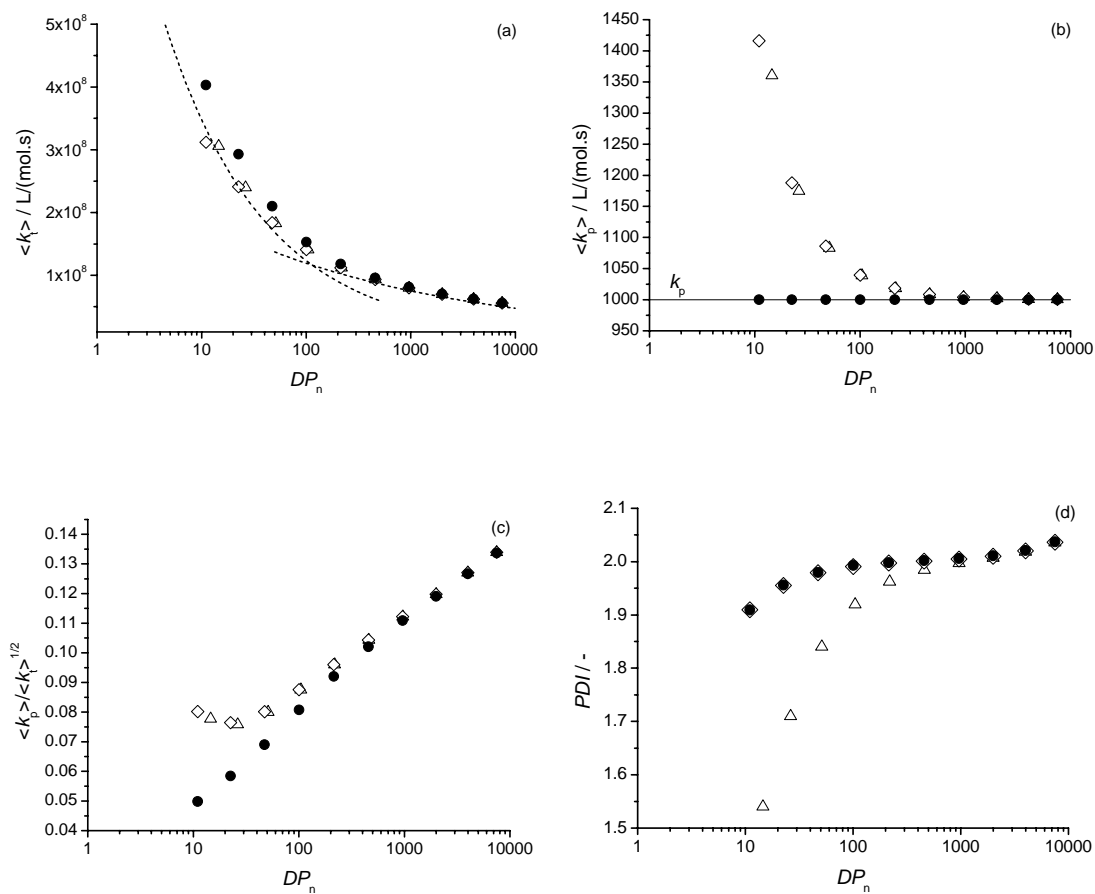
Fig. 2. Dependence of (a) $\langle k_t \rangle$, (b) $\langle k_p \rangle$, (c) $\langle k_p \rangle / \langle k_t \rangle^{1/2}$ and (d) *PDI* on DP_n. For all figures $2fk_d[\text{I}] = 1 \times 10^{-9}$ mol dm^{-3} s^{-1}, $k_p = 1000$ dm^3 mol^{-1} s^{-1}, [M] = 10 mol dm^{-3}, $C_1 = 10$, $i_{1/2} = 1.0$, $C_S^{\text{long}} = 1$ and CLDT is according to the composite termination model using the parameter values given in the text. Empty triangles ($\triangle$): CLDP + CLITr; empty diamonds ($\lozenge$): CLDP + CLDTr; filled circles ($\bullet$): CLIP + CLITr.
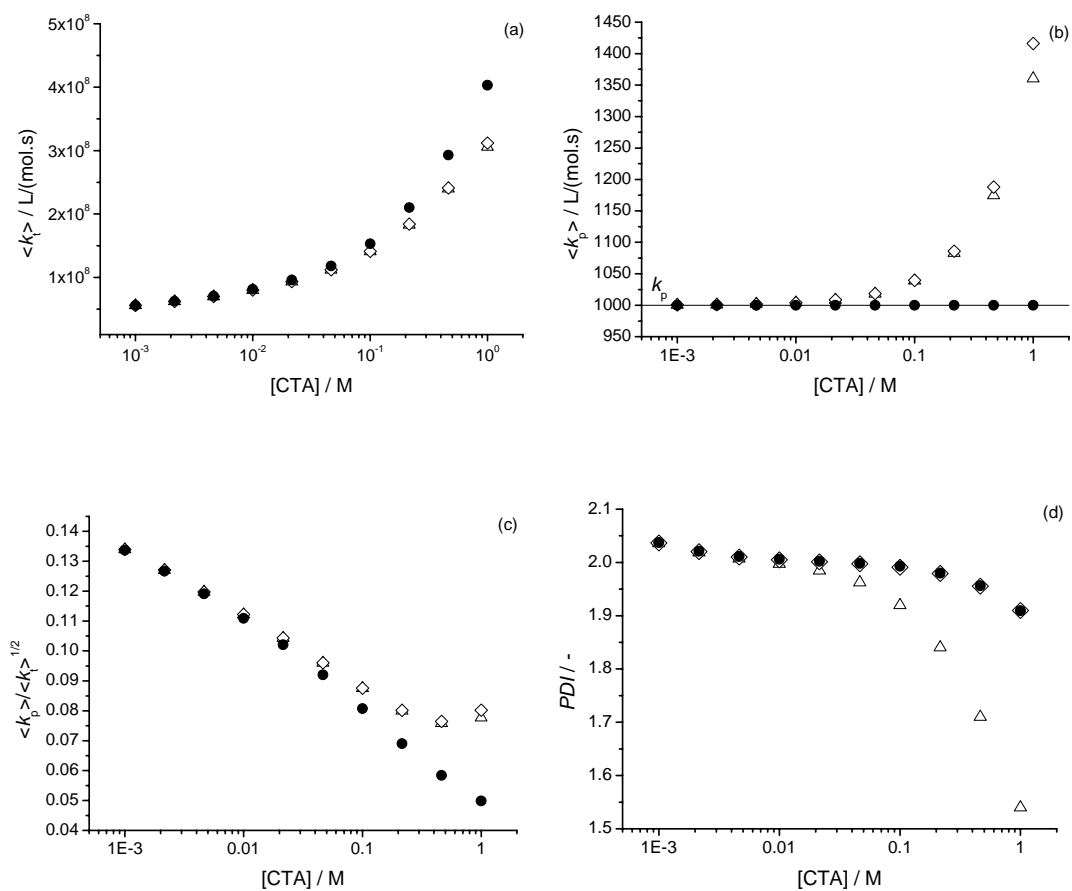
Fig. 3. Dependence of (a) $\langle k_t \rangle$, (b) $\langle k_p \rangle$, (c) $\langle k_p \rangle / \langle k_t \rangle^{1/2}$ and (d) *PDI* on [CTA]. All parameter values and symbols are exactly as for Figure 2.
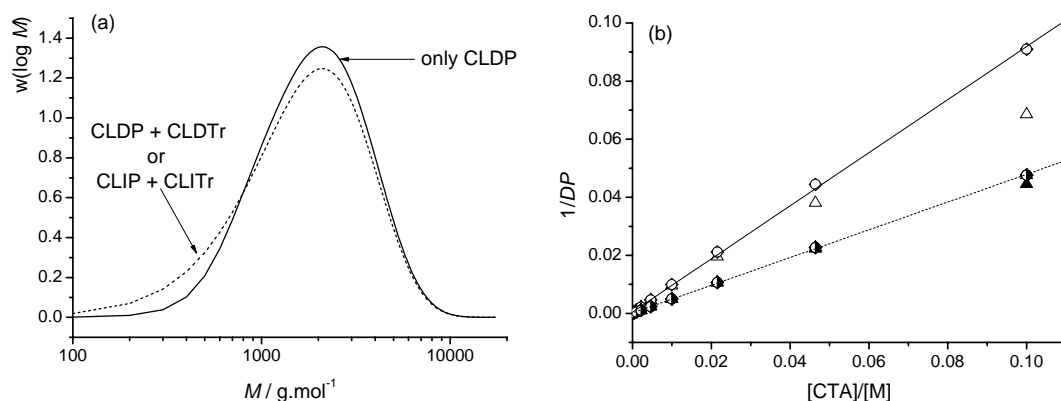
Fig. 4. (a) Normalized instantaneous molecular weight distributions (using $M = i \times$ 100.12 g mol^{-1}) from the results of Figures 2 and 3 for [CTA] = 1 mol dm^{-3}. Dashed line: CLDP+CLDTr and CLIP+CLITr; full line: CLDP+CLITr. (b) Mayo-plots for degrees of polymerization, DP, from the results of Figures 2 and 3. Open symbols: DP_n; filled symbols: DP_w; half-filled symbols: DP of peak of the $w(\log i)$ distribution. Triangles: results for CLDP+CLITr; squares and circles: CLDP+CLDTr and CLIP+CLITr (identical results).
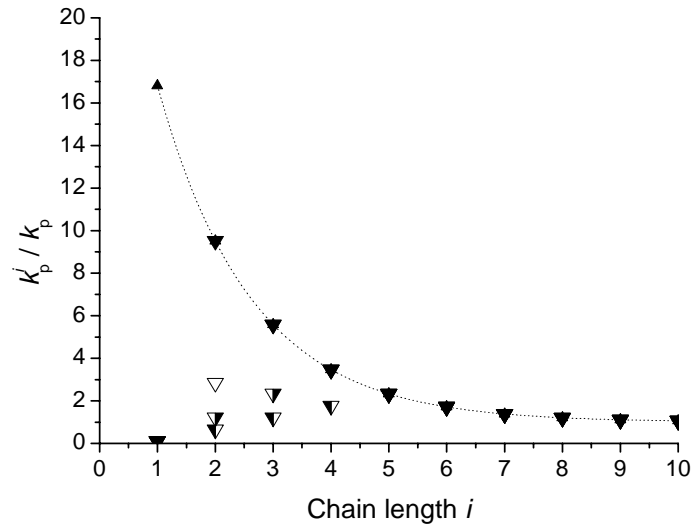
Fig. 5. Chain-length dependence of k_p^i used in simulations investigating the effect of PUEs in k_p^i. In all cases the general chain-length dependence is given by Equation 2 with $C_1 = 15.8$ and $i_{1/2} = 1.12$ (dotted line). (▲): k_p^1 according to Eq. 2 with $C_1 = 15.8$ and $i_{1/2} = 1.12$; (▼): CLDP with $k_p^1 = 0.1k_p$; empty triangles: CLDP with $k_p^1 = 0.1k_p$ and $k_p^2 <$ Eq. 2; triangles with filled right half: CLDP with $k_p^1 = 0.1k_p$ and $k_p^2 < k_p^3 <$ Eq. 2; triangles with filled left-half: CLDP with $k_p^1 = 0.1k_p$ and $k_p^2 < k_p^3 < k_p^4 <$ Eq. 2.
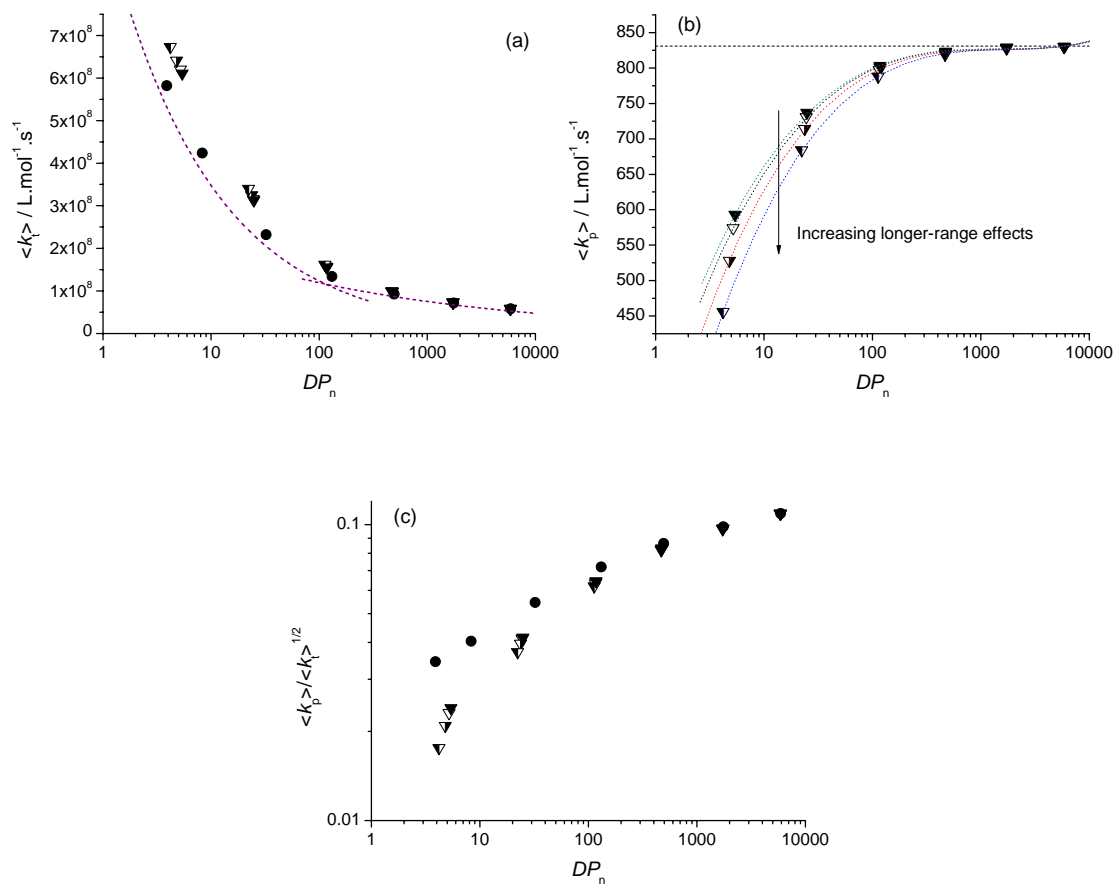
Fig. 6. Dependence of (a) $\langle k_t \rangle$, (b) $\langle k_p \rangle$ and (c) $\langle k_p \rangle / \langle k_t \rangle^{1/2}$ on DP_n. CLDT is according to the composite termination model using the parameter values given in the text. Filled circles (λ): CLIP; all other symbols: $k_p{}^i$ as in Figure 5. Dashed line in (a): best fit from using Equation 2 for $k_p{}^i$.[12]
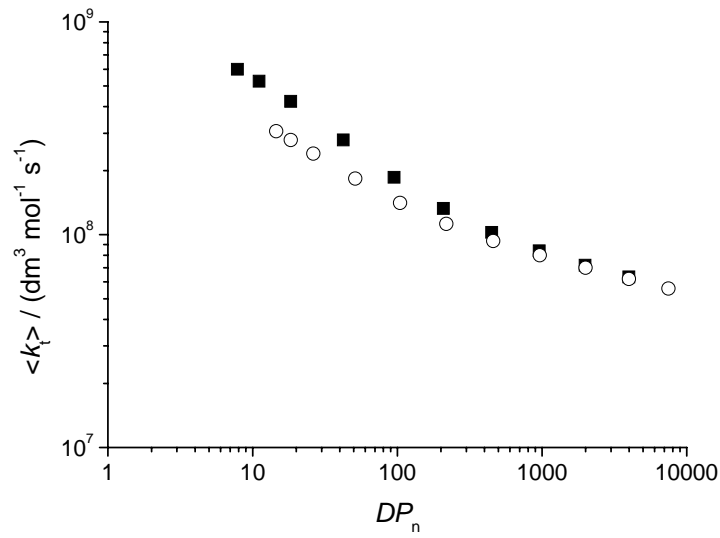
Fig. 7. Dependence of $\langle k_t \rangle$ on DP_n for $2fk_d[I] = 1 \times 10^{-9}$ mol dm^{-3} s^{-1}, $k_p = 1000$ dm^3 mol^{-1} s^{-1}, [M] = 10 mol dm^{-3}, $C_1 = 10$, $i_{1/2} = 1.0$, k_p^A given by Equation 2, $C_S^{long} = 1$ and CLDT according to the composite termination model using the parameter values given in the text. Empty circles (O): $k_p^B = k_p^A$ (fast re-initiation after transfer); filled squares (■): $k_p^B = k_p/10$ (slow re-initiation).
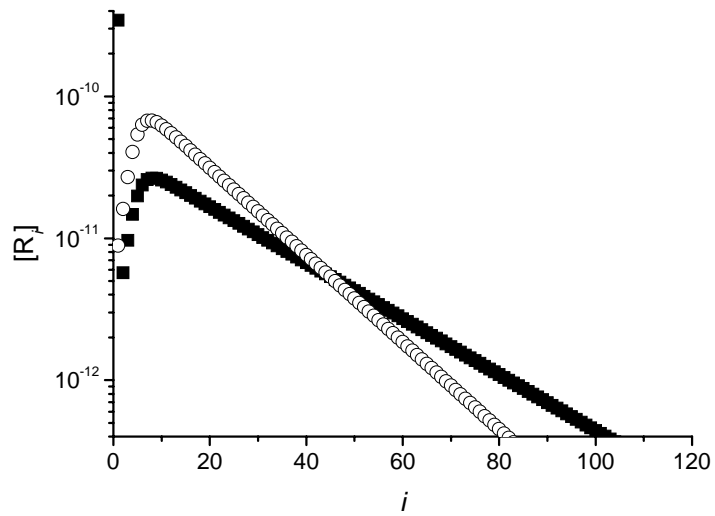
Fig. 8. Radical chain-length distributions from the results of Figure 7 for DP_n = 18.33. Empty circles (O): $k_p^B = k_p^A$ (fast re-initiation after transfer); filled squares (■): $k_p^B = k_p/10$ (slow re-initiation; note the outstandingly high value for $i = 1$).
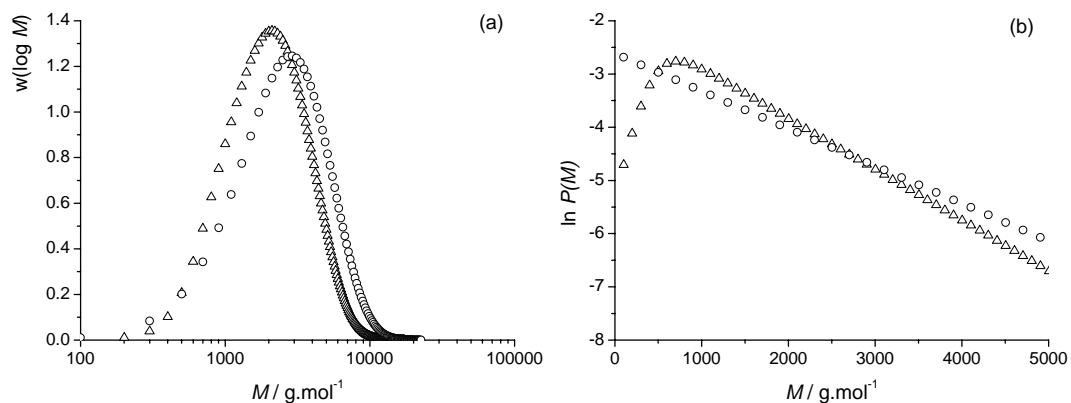
Fig. 9. Normalized instantaneous molecular weight distributions (using $M = i \times 100.12$ g mol^{-1}) for $2fk_d[I] = 1 \times 10^{-9}$ mol dm^{-3} s^{-1}, $k_p = 1000$ dm^3 mol^{-1} s^{-1}, [M] = 10 mol dm^{-3}, C_S = 1 and CLDT according to the composite termination model using the parameter values given in the text. Circles (O): CLIP and [CTA] = 0.73 mol dm^{-3}, giving DP_n = 14.7; triangles ($\triangle$): CLDP with $C_1 = 10$, $i_{1/2} = 1.0$, and [CTA] = 1 mol dm^{-3}, giving DP_n = 14.6. MWDs as (a) $w(\log M)$, (b) $\ln P(M)$.
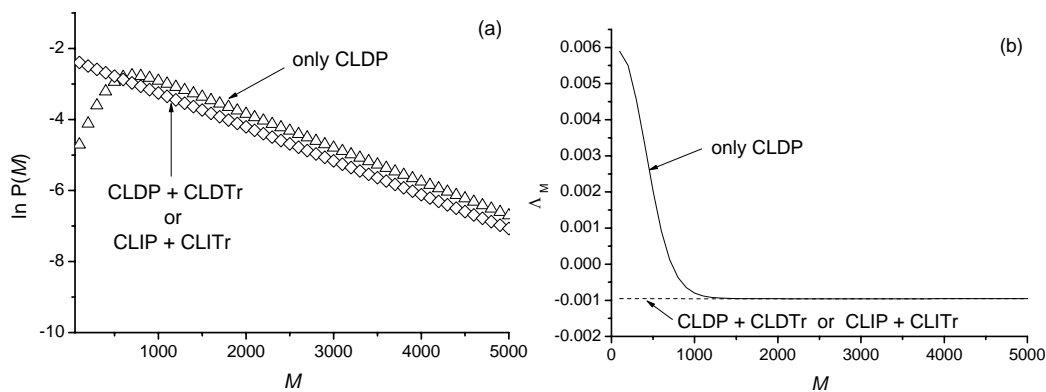
Fig. 10. Instantaneous molecular weight distributions from Figure 4a plotted as (a) $\ln P(M)$ vs. M, and (b) its first derivative, Λ_M. Results are as indicated for CLDP (and CLDITr), giving $DP_n = 14.6$, and CLDP+CLDTr and CLIP+CLITr (same), giving $DP_n = 11.0$. Important parameter values: $M = i \times 100.12$ g mol^{-1}, [CTA] = 1 mol dm^{-3}, [M] = 10 mol dm^{-3} and $C_S = 1$.