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Review

The nature of the chain-length dependence of the propagation rate coefficient and its effect on the kinetics of free-radical polymerization. 1. Small-molecule studies

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Abstract

In this paper we summarize and analyze the currently available small-molecule data, both experimental and theoretical, that is relevant to chain-length-dependent propagation in free-radical polymerization (FRP). We do this in order to appreciate the nature of chain-length-dependent propagation, because workers are becoming increasingly cognizant of its necessity in reaching a complete understanding of FRP kinetics. We show that studies of addition in small-molecule (model) systems support a chain-length dependence (at short chain lengths i) which is described by the following functional form, which therefore can be said to be physically realistic: $k_\mathrm{p}^i/k_\mathrm{p} = C_1 \exp[-\ln 2 \times (i-1)/i_{1/2}] + 1$, where the values of C_1 and $i_{1/2}$ are of the order of 10 and 1, respectively. These results are supported by transition state theory, which predicts a very similar behavior for the Arrhenius frequency factor. We illustrate that in systems with low number-average degree of polymerization ($\mathrm{DP_n}$), this chain-length dependence can dramatically affect the observed (chain-length-averaged) propagation rate coefficient $\langle k_\mathrm{p}\rangle$, which can be significantly higher than the long chain value, k_p. However, this effect is only observed if the activation energy for the first radical addition is similar to that for propagation. In the case that the former is significantly higher (e.g., when choosing a less than optimal initiator or in the case of retardative chain transfer), the chain-length-dependent propagation predicted by our model will not be observed, and in fact a significant lowering of $\langle k_\mathrm{p}\rangle$ can in cases be expected up to relatively high $\mathrm{DP_n}$.

Keywords: Chain-length-dependent propagation; Chain-length-dependent termination; Free-radical polymerization; Kinetics; Retardation

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Contents

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1. Introduction

The study of free-radical polymerization (FRP) kinetics has advanced markedly in recent decades due to the development of better experimental methodologies and the availability of more sophisticated instrumentation [1]. This has enabled workers to have more confidence in the rate parameters they have measured. Therefore researchers have been emboldened to accept unusual trends as genuine rather than worrying that they might just be experimental artifacts. This has led to deeper probing into the fundamental radical processes involved in FRP, something that is important not just from a scientific point of view, which demands an understanding of both conventional and living radical polymerizations, but also from a technological point of view, which seeks optimization of both process control and product properties. The greatest conceptual advance that has occurred has been the widespread acceptance that termination is chain-length dependent in rate [2]. This means that the rate of polymerization (R_p) in steady-state is given by

$$R_p = k_p[\mathrm{M}]\sqrt{\frac{fk_d[\mathrm{I}]}{\langle k_t \rangle}} \tag{1}$$

where k_p is the (long-chain) propagation rate coefficient, [M] the monomer concentration, f the initiator efficiency, k_d the initiator decomposition rate coefficient, [I] the initiator concentration and $\langle k_t \rangle$ the chain-length-averaged termination rate coefficient [3]. At first glance Eq. (1) looks identical to the ‘classical’ rate law of FRP kinetics. The subtle but highly significant difference is the introduction of $\langle k_t \rangle$ in place of k_t: the termination rate coefficient varies in value according to the chain-length regime of the system under study. To complicate matters further, $\langle k_t \rangle$ is also highly dependent on conversion, solvent, monomer, and so on [2,4–7].

Unfortunately the literature on $\langle k_t \rangle$ has not been easy to follow. In an attempt to ameliorate this situation, we recently proposed a simple but physically realistic model that adequately reproduces all experimental observations to date regarding the dependence of the termination rate coefficient on chain length i for low-conversion free-radical polymerization of monomers such as styrene and methyl methacrylate (MMA) [8]. Our model builds on the accepted picture of long-chain termination, which is one of control by segmental diffusion, by adding to this the idea of a stronger dependence of termination on chain length for short chains, probably as a result of control by centre-of-mass diffusion. The essential features of this model have found independent experimental confirmation in subsequent work by the Buback group [9,10].

It is appropriate in two ways that our termination model spotlights short chains. Firstly, and more generally, recent years have witnessed the placing of a greater emphasis on studying and modeling the kinetics of systems in which relatively short polymer chains are formed, for example catalytic chain transfer systems [11,12] and the early stages of living free-radical polymerization [13–17]. Secondly, and more specifically, workers have recently started to wonder about the propagation of short chains and whether chain-length-dependent propagation (CLDP) plays a role in FRP systems [18]. For systems of practical interest the assumption of chain-length-independent propagation is invariably made, even though several experimental studies in the late 1980s and early 1990s already indicated that the first few addition steps are much faster than is long-chain propagation [19]. Strictly this implies that any observed propagation rate coefficient is in fact a chain-length-averaged rate coefficient, as formally defined by Eq. (2), in which k_p^i is the rate coefficient of an i-meric radical (R_i) adding to a monomer molecule and [R] is the overall radical concentration:

$$\langle k_p \rangle = \sum_{i=1}^{\infty} k_p^i \frac{[R_i]}{[R]} \tag{2}$$

Further, CLDP requires that Eq. (1), the steady-state rate law, be re-written as

$$R_p = \langle k_p \rangle [M] \sqrt{\frac{f k_d [I]}{\langle k_t \rangle}} \tag{3}$$

As with termination, the change from k_p in Eq. (1) to $\langle k_p \rangle$ in Eq. (3) may seem trivial, but it will be seen in this paper that the effect can be profound.

An example of Eq. (3) being necessary is our recent investigation of the kinetics of MMA polymerization at 60 °C in the presence of large amounts of dodecyl mercaptan [20]. Our rate data could not be explained by chain-length-dependent termination alone and could only be rationalized by introducing also CLDP. Based upon consideration of the available experimental [21–26] and theoretical data [27–30] we proposed the following functional form for k_p^i:

$$k_p^i = k_p \left\{ 1 + C_1 \exp\left(\frac{-\ln 2}{i_{1/2}} (i-1) \right) \right\} \tag{4}$$

In this equation the parameter $C_1 = (k_p^1 - k_p)/k_p$ is the factor by which k_p^1 exceeds the long-chain propagation rate coefficient, k_p, while the parameter $i_{1/2}$ is a measure which dictates the chain-length dependence of k_p^i. Specifically, $i_{1/2}$ is analogous to the "half-life" of first-order kinetics: it is the change of chain length over which $k_p^i - k_p$ halves in value. For example, $1 + i_{1/2}$ is the chain length at which $k_p^i - k_p = (k_p^1 - k_p)/2$. Thus the larger is $i_{1/2}$, the higher the chain lengths to which the chain-length dependence of propagation persists. For our MMA experiments we found that $C_1 = 15.8$ and $i_{1/2} = 1.12$, derived from the data published by Van Herk and co-workers [25], reproduced our experimental data very well [20]. This suggests that k_p^i starts at an initially high value (i.e., the rate coefficient for the addition of a monomeric radical to monomer) that then exponentially decays over a relatively small range of chain length to its long-chain value (k_p).

Interestingly, an equation equivalent to Eq. (4) has been independently proposed and used by Olaj and co-workers [26]. As a point to keep in mind throughout this paper, we would like to stress that Eq. (4) is not based on any theory, and so we are not saying that it is exactly correct. Rather, we use Eq. (4) because we believe it is phenomenologically accurate in that it captures the most important features of CLDP that have been observed to date. In fact this is the primary motivation for this paper: to survey the literature on small-molecule investigations of propagation that are germane to FRP, and to summarize what these studies establish regarding CLDP in FRP; specifically, we would like to establish that Eq. (4) has a sound physical basis and that the phenomenological trends implicit in $C_1 = 15.8$ and $i_{1/2} = 1.12$ (see above) are real ones. We do this because even though FRP workers are starting to observe that CLDP often impacts upon the observed kinetics of FRP [18,20,25,26], there is only very limited awareness of what small-molecule studies reveal on this matter. Accordingly there is unchecked speculation regarding CLDP in FRP where really there should be none. This speculation can be damaging in that some readers undoubtedly interpret it as debate over the existence of CLDP, and consequently they resolve to ignore it. In fact there is no such debate: the findings summarized in this paper show that propagation is undoubtedly chain-length dependent, and the only issue is whether CLDP manifests itself in the kinetics of whichever particular FRP system is under study. In the subsequent paper in this series we will examine the extent to which recent FRP experiments probing CLDP [18,20,25,26]—all of which, importantly, are adamant in seeing a CLDP of some description—are consistent with the present findings.

Lastly, the reader is reminded that $\langle k_p \rangle$ is a pivotal parameter in both Eq. (3) and in any expression for the molecular weight of polymer produced in FRP. This is especially so for systems producing short chains, including most living FRP systems, as have been the subject of much recent attention. Thus it is unquestionably of importance to assess the significance of chain-length-dependent propagation in FRP.

2. General considerations and outline

Before discussing the addition of small radicals to alkenes, it is important to state that by k_p^i we denote the rate coefficient for

$$\mathrm{R}_i + \mathrm{M} \xrightarrow{k_\mathrm{p}^i} \mathrm{R}_{i+1} \tag{5}$$

Normally R_i would denote a polymerizing radical containing i monomer units. But because this paper is specifically concerned with small-radical propagation, we here adopt a slightly different definition, based on the desire that k_p^1 should refer to the very first addition step following radical formation:

$$\mathrm{R}_1 + \mathrm{M} \xrightarrow{k_\mathrm{p}^1} \mathrm{R}_2 \tag{6}$$

So R_1 is any radical derived directly from initiator dissociation, in which case R_1 is a primary radical, or from chain transfer to monomer, in which case R_1 corresponds truly to a monomeric radical, or from chain transfer to chain transfer agent, e.g., R_1 is $\mathrm{C}_{12}\mathrm{H}_{25}\mathrm{S}^{\bullet}$ in the case of dodecyl mercaptan. Thus the radical resulting from the addition of a primary radical to a monomer is a *dimeric* radical, R_2, where the '2' here is to be understood as meaning two units, including the endgroup, and analogously for R_i.

In what follows we will first of all discuss the kinetic results available in the literature on the addition of R_1 radicals—corresponding to "truly" monomeric and to primary radicals derived from initiator—to a variety of monomers and the effect that this may have on the chain-length-dependent behavior of $\langle k_\mathrm{p}\rangle$. We will show that differences between k_p^1 and k_p can dramatically affect the value of $\langle k_\mathrm{p}\rangle$, leading to values that can be either significantly larger or significantly smaller than the long-chain value. This will then be followed in Section 4 by a discussion of literature studies in which it has been attempted to measure the rate coefficients for the first few addition steps in a polymerizing system directly. It will be shown that the results obtained for k_p^1 in these studies are in accord with those obtained in the small-radical studies that will be discussed first in Section 3. Furthermore, we will show that the decrease in k_p^i for $i > 1$ indeed suggests the functional form of Eq. (4). Lastly, in Section 5 we present a brief review of some theoretical studies on radical addition reactions, showing that these support the experimental findings in Sections 3 and 4, including the functional form for the chain-length dependence of k_p^i.

Before commencing, it is appropriate to make clear the distinction we draw between studies involving non-polymerizing systems (Section 3) and polymerizing systems (Section 4). Of course strictly speaking no system in which a radical adds to monomer is non-polymerizing, because the product radical is obviously capable of adding to further monomer, and so on. However the small-molecule studies discussed in Sections 3.1 and 3.2 were all ones that were designed so that the measured kinetics pertained to one addition reaction only, with subsequent addition steps either being minimized or impacting only negligibly upon the measured kinetics. On the other hand, the studies of Section 4 involved a succession of propagation steps. However, these studies were planned so that chain growth was always terminated at very small chain lengths, meaning that the systems can be considered to be "small-molecule" investigations.

3. Monomeric-radical additions

3.1. Monomeric analogues of the propagating radical

Since the 1980s a large number of studies have been published on the direct measurement of rate coefficients of reactions involving (small) radicals. This is mainly due to the continuously increasing availability and accuracy of spectroscopic methods that can follow changes in radical concentrations. Several techniques have been developed to measure "genuine" k_p^1 values—i.e., the rate coefficients of monomeric radicals adding to the corresponding monomer. In general these methods are based on "instantaneous" radical generation, for example via a pulsed laser, and subsequently measuring either the decay in signal of the primary radical or the appearance of the signal of the product radical [31–37]. As such, these methods do not depend on the analysis of higher polymerization products and can yield reasonably accurate absolute rate coefficients for small radical additions. Because of well-known advances in our capacity to measure long-chain $\langle k_\mathrm{p}\rangle$ in FRP [38–43], it is now possible to compare these two types of propagation rate coefficient with some confidence for corresponding systems, and from this to draw mechanistic conclusions. Table 1 (Scheme 1), which was compiled by Fischer and Radom [21], presents such a comparison, in the form of the Arrhenius parameters. The parameters reveal that $\langle k_\mathrm{p}\rangle$ is about an order of

Table 1
Comparison of Arrhenius parameters for long-chain propagation rate coefficients of various monomers with those of small-radical model systems[a]

Monomer	$\log A$[b]	E_{act}[c]	Radical[d]	$\log A^{(1)}$[e]	$E_{\text{act}}^{(1)}$[f]	C_1[g]
Ethene	7.27	34.3	**1**	8.5	28.2	195[h]
Methacrylonitrile	6.43	29.7	**2**	7.5	26.4	43.1
Styrene	7.63	32.5	**3**	8.5	30.8	13.7
Methyl methacrylate	6.42	22.3	**4**	7.5	22.4	10.6
Methyl acrylate[i]	7.34	17.9	**5**	8.5	15.6	26.8

[a] All data, except for the calculated values of C_1, are taken from the review by Fischer and Radom [21].

[b] A is the Arrhenius frequency factor for (long-chain) $\langle k_p \rangle$ in L mol^{-1} s^{-1}.

[c] E_{act} is the Arrhenius activation energy for $\langle k_p \rangle$ in kJ mol^{-1}.

[d] The structures of the radicals are given in Scheme 1.

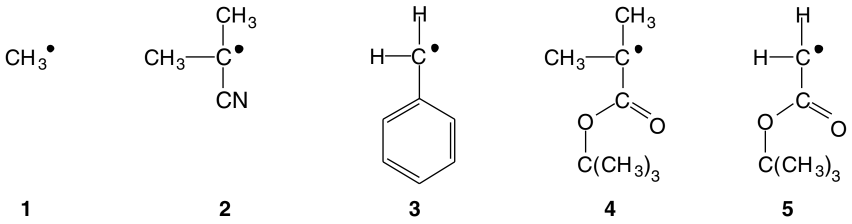
[e] $A^{(1)}$ is the Arrhenius frequency factor in L mol^{-1} s^{-1} for the addition rate coefficient (k_p^1) of the model radical to the monomer.

[f] $E_{\text{act}}^{(1)}$ is the Arrhenius activation energy for k_p^1 in kJ mol^{-1}.

[g] C_1 is here estimated as $(k_p^1 - \langle k_p \rangle)/\langle k_p \rangle$ at 60 °C.

[h] For the gas-phase addition of ethyl radical to ethylene for which $\log A^{(1)} = 8.3$ and $E_{\text{act}}^{(1)} = 30.5$ kJ mol^{-1} [83], a probably more realistic value of 48.3 for C_1 is obtained.

[i] The long-chain propagation data shown are those for butyl acrylate [40], which result in a value for k_p which is slightly higher than that for methyl acrylate [66]—however, the individual Arrhenius parameters should be representative of those for MA.



Scheme 1.

magnitude smaller than k_p^1 and that this can be largely attributed to frequency factor differences. This is most clearly evident from the entries for styrene and methyl methacrylate, the two systems for which, significantly, $\langle k_p \rangle$ has been most accurately established [38,39]. This finding is supported by transition state theory, which predicts a difference of about an order of magnitude between monomeric and polymeric radical additions, a difference which is basically "mechanical" in nature, i.e., mainly caused by differences in masses and sizes of the radicals [27–30] (see also Section 5).

Activation energies for propagation reactions appear to be similar or somewhat higher than those for the monomeric radical additions. To date there is insufficient data available to draw any general conclusions about this observation, but it appears that transition state theory predicts slightly higher activation energies for larger radicals adding to the same monomer, again partly due to "mechanical" reasons [28,30]. The presence of additional monomer units will also have a slight "chemical" effect on the activation energy, as shown by computational studies on the penultimate unit effect [44–46]. However, it is not expected that these differences are more than a few kJ mol^{-1}.

Thus in terms of Eq. (4) it is safe to conclude that C_1 is generally of the order of, or greater than, 10 for systems where R_1 is alike in electronic nature to the longer chain polymeric radical, and that this is primarily an effect of the frequency factor.

3.2. Initiator-derived radicals

A generalization similar to that made in the previous section cannot be made for the addition of initiator or chain transfer agent-derived "monomeric" radicals. As seen above, in the case of truly monomeric radical additions the activation energies for addition to monomer are similar to those for homopropagation (give or take a few kJ mol^{-1}). However, depending on the type of radical generated from the initiator or from chain transfer agent, the activation energy may dramatically change, and

Table 2
Rate coefficients for the addition of 2-cyano-2-propyl radical to a range of monomers and their homopropagation rate coefficients at 42 °C

Monomer	k^{ini} [a]	$\langle k_p \rangle$ [b]	$E_{\text{act}}^{\text{ini}}$ [c]	r_{MAN} [d]	Est. k^{ini} [e]
Vinyl acetate	41	6.2×10^3	35.5	21.7	49
Methyl acrylate	367	23.4×10^3 [f]	29.8	2.33	4.6×10^2
Methacrylonitrile	1060	32	27.0	1.00	1.1×10^3
Methyl methacrylate	1590	523	25.9	0.90	1.2×10^3
Styrene	2410	174	26.1 [g]	0.30	3.5×10^3

[a] k^{ini} is the rate coefficient for the addition of the 2-cyano-2-propyl radical to the indicated monomer in L mol^{-1} s^{-1}, taken from the study of Héberger and Fischer [31].

[b] $\langle k_p \rangle$ is the (long-chain) homopropagation rate coefficient of the indicated monomer in L mol^{-1} s^{-1}, taken from the review by Van Herk [47].

[c] $E_{\text{act}}^{\text{ini}}$ is the activation energy in kJ mol^{-1} for the addition of the 2-cyano-2-propyl radical to the indicated monomer, as estimated from k^{ini} using a ballpark figure of 7.5 for log A^{ini}, where A^{ini} is the Arrhenius frequency factor for the same reaction.

[d] r_{MAN} is the monomer reactivity ratio for the polymethacrylonitrile radical in a copolymerization of methacrylonitrile with the indicated monomer, as estimated from the *Q*,*e*-values listed in Table 6.3 of Ref. [19].

[e] The estimated value for k^{ini} in L mol^{-1} s^{-1} using Eq. (8) and $C_{1,\text{ MAN}} = 32.15$.

[f] This value is actually that for butyl acrylate, which should be a little larger than that for methyl acrylate.

[g] This value is actually the experimental value determined by Héberger and Fischer [31].

hence the rate coefficient will dramatically change. That this is the case is immediately clear from the data listed in Table 2, which shows results for the addition of 2-cyano-2-propyl radical (i.e., the radical generated from the decomposition of the commonly employed initiator 2,2′-azoisobutyronitrile [AIBN]) to several different monomers at 42 °C. These data are an extract from a more extensive study published by Héberger and Fischer [31], who measured the addition of 2-cyano-2-propyl radical to 26 alkenes in solution using time-resolved electron spin resonance spectroscopy. The activation energies for these addition reactions were estimated from the listed rate coefficients by assuming a constant average value of 7.5 for log*A*, as discussed in detail by Fischer and Radom [21].

The rate coefficients for addition to vinyl acetate (VAc) and methyl acrylate (MA) are clearly much smaller than the corresponding propagation rate coefficients, and this large discrepancy is mainly due to the very large activation energies for these reactions as compared with those for homopropagation, viz. 20.4 and ~17.4 kJ mol^{-1} for VAc and MA, respectively [47]. An estimated difference of 13 kJ mol^{-1} in activation energy (with a conceivable uncertainty of ±3 kJ mol^{-1}) leads to a 143-fold difference in rate coefficients at 42 °C, which is roughly the ratio $\langle k_p \rangle / k^{\text{ini}}$ for VAc and MA in Table 2. This result suggests that in the present case there is only a relatively small change in *A* caused by the change from small-radical (k^{ini}) to macroradical addition, as opposed to the factor-of-10 (or more) change of Section 3.1. This is consistent with the fact that tertiary radical additions in general have a lower *A* than secondary radical additions [21,29], meaning that the increase in *A* due to the small size of cyanoisopropyl is largely cancelled out by its tertiary nature, as opposed to the secondary radicals of MA and VAc propagation. In any event it is clear that primarily as a result of an elevated E_{act}, k_p^1 will be much lower than k_p when AIBN is used with VAc or MA, and thus the exponential decay behavior of Eq. (4) cannot be expected.

On the other hand, the situation is very different for the addition of 2-cyano-2-propyl radical to methacrylonitrile (MAN) (here the addition is of a truly *monomeric* radical), methyl methacrylate (MMA) and styrene (STY): for all these $k^{\text{ini}} \gg \langle k_p \rangle$. This behavior is in line with the fact that the activation energies for these addition reactions are similar to, or less than, those of the corresponding propagation reactions (see Table 1), and hence the situation is similar to the situation represented in Table 1: the initiator-derived radical now behaves more or less like a truly monomeric radical and a chain-length dependence of k_p^i with a value of C_1 of the order 10^0–10^1 can be expected (remembering that $C_1 = 1$ means that k_p^1 is double the value of k_p).

It is interesting to investigate whether the order of magnitude for all these addition reactions, and in particular the low addition rate coefficients for VAc and MA, could have been anticipated. For many decades the monomer reactivity ratios for a given (polymeric) radical with a range of monomers have been taken as a (relative) measure for the reactivity of this radical towards these monomers [48].

The monomer reactivity ratios of relevance for the present study are those of the polyMAN radical (r_{MAN}), as defined by Eq. (7), towards the monomers in Table 2:

$$r_{\mathrm{MAN}} = \frac{k_{\mathrm{p,MAN}}}{k_{12}} \tag{7}$$

In this equation, $k_{\mathrm{p,MAN}}$ is the (long-chain) homopropagation rate coefficient of MAN and k_{12} is the cross-propagation rate coefficient for the polyMAN radical with the other comonomer. The relevant values for r_{MAN} were estimated using the Q, e-scheme [19] and are listed in Table 2. Although it has been well established now that these terminal model reactivity ratios should not be treated as exact physical parameter values [49], they still serve as good (semi-)quantitative indications of the relative monomer reactivity towards a radical with a particular terminal unit, as is clearly proven by the elegant end-group studies by Bevington, Senogles and co-workers [50–54].

Referring to Eq. (7) and Table 2, it is clear that k_{12} for addition of polyMAN radical to VAc will be a small value because of both $r_{\mathrm{MAN}} \gg 1$—a polyMAN radical does not like adding to VAc—and $k_{\mathrm{p,MAN}} \ll k_{\mathrm{p,VAc}}$. And if the addition of polyMAN to VAc (k_{12}) is much slower than the addition of poly(VAc) to VAc ($k_{\mathrm{p,VAc}}$), then the addition of the 2-cyano-2-propyl radical to VAc can equally be expected to be much slower than the addition of a monomeric VAc radical to VAc.

In fact we can use the present information to (semi-quantitatively) estimate the value of k^{ini} for the addition of 2-cyano-2-propyl radical to a given monomer. Eq. (7) establishes that $k_{12} = k_{\mathrm{p,MAN}}/r_{\mathrm{MAN}}$. Of course this value is for polyMAN addition to monomer 2. To obtain k^{ini} it is reasonable to assume that $k^{\mathrm{ini}}/k_{12} \approx k_{\mathrm{p}}^{1}/k_{\mathrm{p}}$ for MAN propagation, because both ratios involve the same pair of radicals (monomeric MAN and polyMAN) adding to a particular monomer (monomer 2 and MAN). Remembering that $k_{\mathrm{p}}^{1}/k_{\mathrm{p}}$ for MAN is defined as ($C_{1,\mathrm{MAN}} + 1$), it is thus clear that

$$k^{\mathrm{ini}} \approx (C_{1,\mathrm{MAN}} + 1) \times \frac{k_{\mathrm{p,MAN}}}{r_{\mathrm{MAN}}} \tag{8}$$

gives an estimate of the rate coefficient for addition of 2-cyano-2-propyl radical to a given monomer. The estimated values for k^{ini} that are listed in Table 2 were obtained using $C_{1,\mathrm{MAN}} = 32.15$, which is the value obtained from the MAN values of k^{ini} and $\langle k_{\mathrm{p}} \rangle$ of Table 2. It can be seen that these estimated values are all within a factor of 1.5 of the measured values. This clearly suggests that even in our crude approximations we have considered the most important physics. At this stage, insufficient data are available to claim the general applicability of this equation and it is possible that we have just been fortuitous. However, it still may be useful to estimate the value of k^{ini} for a given initiator-monomer (or chain transfer agent-monomer) pair by this means if the experimental data are not available, because, as will now be shown, the effect of a very low k^{ini} can be a dramatic retardation of the polymerization (in fact this is exactly the classical meaning of ‘retardation’ in free-radical polymerization kinetics).

3.3. Influence of k_{p}^{1} on observed polymerization kinetics

At this point it is interesting to investigate the extent to which a particular value of k_{p}^{1} affects the overall chain-length-dependent propagation rate coefficient, $\langle k_{\mathrm{p}} \rangle$. Making the assumption that a dimeric radical initiated by an initiator or transfer-derived radical behaves similarly to a dimeric radical initiated by a truly monomeric radical, it is assumed that for $i > 1$ the exponential-decay behavior given by Eq. (4), with a “normal” value of C_1, is still applicable; on the other hand, an independently specified value of k_{p}^{1} will be used. The overall propagation rate coefficient will be evaluated using Eq. (2), and the overall termination rate coefficient using [3]

$$\langle k_{\mathrm{t}} \rangle = \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}_i][\mathrm{R}_j]}{[\mathrm{R}]^2} \tag{9}$$

In this equation $k_{\mathrm{t}}^{i,j}$ is the termination rate coefficient between an i-meric and a j-meric radical, for which we use the geometric mean model, Eq. (10), as this simplifies calculations without giving any significant alteration to the results obtained using more computationally-demanding models [3,8,55]:

$$k_{\mathrm{t}}^{i,j} = \sqrt{k_{\mathrm{t}}^{i,i} k_{\mathrm{t}}^{j,j}} \tag{10}$$

For the “self-termination” rate coefficients $k_{\mathrm{t}}^{i,i}$ we use Eq. (11), which is the “composite” termination model we recently proposed [8] and which explicitly allows for different termination mechanisms at short chain lengths (i.e., below a critical chain length i_{crit}) and long chain lengths ($i > i_{\mathrm{crit}}$)

$$k_{\mathrm{t}}^{i,i} = \begin{cases} k_{\mathrm{t}}^{1,1} \times i^{-e_{\mathrm{S}}}, & i \leqslant i_{\mathrm{crit}} \\ k_{\mathrm{t}}^{1,1} \times (i_{\mathrm{crit}})^{-(e_{\mathrm{S}}-e_{\mathrm{L}})} \times i^{-e_{\mathrm{L}}}, & i > i_{\mathrm{crit}} \end{cases} \tag{11}$$

The parameters in Eq. (11) and their respective values in our modeling for MMA at 60 °C [8,20] are the termination rate coefficient between two monomeric radicals ($k_t^{1,1} = 1 \times 10^9$ L mol^{-1} s^{-1}), the short-chain-length exponent ($e_S = 0.50$), the long-chain-length exponent ($e_L = 0.16$) and the critical chain length ($i_{crit} = 100$). As already mentioned, these values have been confirmed experimentally by Buback and co-workers [9]. However this is not essential; rather, the key point is that these parameters provide a good reflection of termination in these systems, and so the results of our model calculations must also reflect physical reality, even if termination turns out not to be exactly as here described.

It is clear that in order to evaluate $\langle k_p \rangle$ and $\langle k_t \rangle$ one needs to know the steady-state radical concentrations for all chain lengths. These can be determined by evaluation of Eq. (12) [56] for all i up to a very high value (we found 65,000 was sufficient for the current study)

$$[\mathrm{R}_i] = [\mathrm{R}_{i-1}] \frac{f_p^{i-1}}{f_p^i + f_t^i + f_{trX}} \tag{12}$$

In this equation $f_p^i = k_p^i[\mathrm{M}]$ is the frequency of propagation of an R_i species, $f_{trX} = k_{trX}[\mathrm{X}]$ is the frequency of chain transfer, $f_t^i = \sqrt{2k_t^{i,i}R_{init}}$ is the frequency of termination of an R_i species (note that this last result holds only because of the use of Eq. (10) [3,8]) and $R_{init} = 2fk_d[\mathrm{I}]$ is the rate of initiation.

Hence, when the concentration of R_1 radicals, $[\mathrm{R}_1]$, is known, the entire radical distribution can be evaluated.

For the present case it is useful to consider the case in which the R_1 population is made up of two different types of radicals, namely those that are derived from initiator decomposition ($\mathrm{R_A}$) and those derived from a chain transfer agent ($\mathrm{R_B}$), with k_p^A and k_p^B their respective addition rate coefficients. The overall monomeric radical concentration and average value for the monomeric radical addition rate coefficient ($\bar{k}_p^1$) are then given by Eqs. (13) and (14), respectively:

$$[\mathrm{R}_1] = [\mathrm{R_A}] + [\mathrm{R_B}] \tag{13}$$

$$\bar{k}_p^1 = \frac{k_p^A[\mathrm{R_A}] + k_p^B[\mathrm{R_B}]}{[\mathrm{R_A}] + [\mathrm{R_B}]} \tag{14}$$

The concentrations of $\mathrm{R_A}$ and $\mathrm{R_B}$ can be derived from their respective mass balances:

$$\frac{d[\mathrm{R_A}]}{dt} = R_{init} - [\mathrm{R_A}]\left\{k_p^A[\mathrm{M}] + k_{trX}[\mathrm{X}] + 2\sum_{j=1}^{\infty} k_t^{1,j}[\mathrm{R}_j]\right\} \tag{15}$$

$$\frac{d[\mathrm{R_B}]}{dt} = k_{trX}[\mathrm{X}][\mathrm{R}] - [\mathrm{R_B}]\left\{k_p^B[\mathrm{M}] + k_{trX}[\mathrm{X}] + 2\sum_{j=1}^{\infty} k_t^{1,j}[\mathrm{R}_j]\right\} \tag{16}$$

Here it has been assumed that both $\mathrm{R_A}$ and $\mathrm{R_B}$ have the same termination kinetics, which is reasonable on the grounds that termination is diffusion controlled, and thus will not vary greatly in rate for species of similar size (cf. propagation, which is chemically controlled). After making the steady-state approximation, and using the geometric mean model for the frequencies of termination, one obtains from the above equation that

$$[\mathrm{R_A}] = \frac{R_{init}}{k_p^A[\mathrm{M}] + k_{trX}[\mathrm{X}] + \sqrt{2k_t^{1,1}R_{init}}} \tag{17}$$

$$[\mathrm{R_B}] = \frac{k_{trX}[\mathrm{X}][\mathrm{R}]}{k_p^B[\mathrm{M}] + k_{trX}[\mathrm{X}] + \sqrt{2k_t^{1,1}R_{init}}} \tag{18}$$

With these concentrations both $\bar{k}_p^1$ and $[\mathrm{R}_1]$ can be evaluated, from which then in turn all other steady-state radical concentrations can be derived via Eq. (12), assuming that once the radicals have added to monomer, they behave like a dimeric radical, i.e., that $\mathrm{R_AM}$ and $\mathrm{R_BM}$ are kinetically the same, and hence are both denoted R_2.

Since Eq. (18) requires prior knowledge of the total radical concentration [R], which is a result of the calculations, the equations for all $[\mathrm{R}_i]$ need to be solved iteratively until convergence has been achieved between the guessed [R] and the calculated [R]. In the current study we evaluated the equations in a simple EXCEL spreadsheet. For a more detailed discussion on the used equations and calculations we refer to our previous [8,57] and upcoming [56] work. We note that this is the first time that calculations of the present nature have been carried out, i.e., this particular model and its utilization are new to this work.

Using the parameter values that adequately reproduced our experimental results for low conversion bulk polymerizations of MMA at low number-average degree of polymerization ($\mathrm{DP_n}$), i.e., $k_p = 831$ L mol^{-1} s^{-1}, $C_1 = 15.8$ and $i_{1/2} = 1.12$

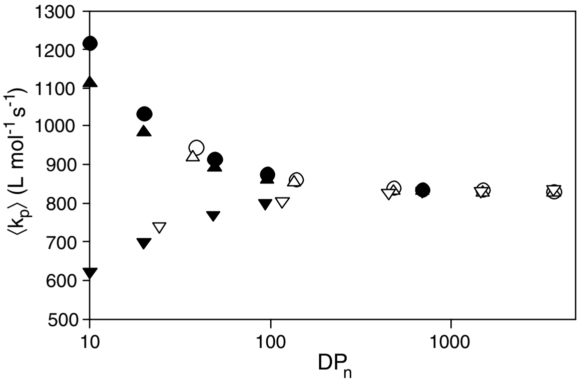


Fig. 1. The effect of the value of k_p^1 on the observed macroscopic propagation rate coefficient $\langle k_p \rangle$ as a function of the average chain length produced in the system. Filled symbols: $k_p^A = 13{,}960.8$ L mol^{-1} s^{-1} and DP$_n$ varied by different transfer frequencies (from highest DP$_n$ to lowest): $f_{trX} = 7.44$, 74.5, 148.9, 372.3 and 744.6 s^{-1}. k_p^B in L mol^{-1} s^{-1}: (●) 8310, (▲) 831, (▼) 83.1. Open symbols: $k_p^B = 13{,}960.8$ L mol^{-1} s^{-1} and DP$_n$ varied by different initiation rates (from highest DP$_n$ to lowest): $R_{init} = 1.22 \times 10^{-8}$, 1.22×10^{-7}, 1.22×10^{-6}, 1.22×10^{-5} and 1.22×10^{-4} mol L^{-1} s^{-1}. k_p^A in L mol^{-1} s^{-1}: (○) 8310, (△) 831, (▽) 83.1. In all calculations CLDP is characterized by $k_p = 831$ L mol^{-1} s^{-1}, $C_1 = 15.8$ and $i_{1/2} = 1.12$, termination is described by the "composite termination model" (see text) and $[M] = 8.96$ mol L^{-1}.

[20], we illustrate in Fig. 1 the effect of a changing k_p^1 on $\langle k_p \rangle$ in systems of different DP$_n$ (controlled by changing chain transfer or initiation rates). Values for DP$_n$ corresponding to a particular system were calculated using the Mayo equation given by Eq. (19), in combination with the $\langle k_t \rangle$ and $\langle k_p \rangle$ values obtained from the simulations

$$\frac{1}{\mathrm{DP_n}} = (1+\lambda)\frac{\langle k_t \rangle [\mathrm{R}]}{\langle k_p \rangle [\mathrm{M}]} + \frac{f_{trX}}{\langle k_p \rangle [\mathrm{M}]} \quad (19)$$

In this equation the fraction of termination by disproportionation, λ, was taken to be equal to 1 in our simulations.

In one series of calculations we varied DP$_n$ by varying f_{trX}, and investigated the effect of a varying k_p^B (with values of 83.1, 831 and 8310 L mol^{-1} s^{-1}) on $\langle k_p \rangle$ with k_p^A and R_{init} kept constant at values of $16.8 \times k_p$ and 6.1×10^{-8} mol L^{-1} s^{-1}, respectively. This of course simulates the effect of different reactivity of the radical from chain transfer. In another series of calculations we varied DP$_n$ by varying R_{init} and investigated the effect of a varying k_p^A (with values of 83.1, 831 and 8310 L mol^{-1} s^{-1}) on $\langle k_p \rangle$ with k_p^B and f_{trX} kept constant at values of $16.8 \times k_p$ and 0.745 s^{-1}, respectively. This investigates the effect of different primary radical reactivity.

A first important result from Fig. 1 is that variation of k_p^A has essentially the same effect on kinetics as variation of k_p^B. Thus it does not matter whether it is radicals from initiator or radicals from chain transfer agent that behave irregularly, the qualitative effect is the same. Hence in the following discussion we do not need to distinguish between these two possible origins of altered kinetics.

Turning now to the actual values of Fig. 1, they suggest that $\langle k_p \rangle$ observed in a system with $k_p^1 \geqslant k_p$ is higher than the value of k_p, but that this effect becomes insignificant in systems with DP$_n \approx 100$ (i.e., $M_n = 10^4$ g mol^{-1} for PMMA). Hence, in applications other than those in which very low molecular weight polymer is produced, this effect should not be noticeable. In the case of a slow addition of the monomeric radical, it is not immediately clear what to expect, because k_p^1 is lower than k_p but the following k_p^i are higher. Our calculations show that $k_p^1 \approx 0.1 \times k_p$ is sufficient to make the effect of k_p^1 the dominant one, and a $\langle k_p \rangle$ smaller than k_p is found. Of course as the average chain length becomes longer, this effect becomes less and less significant, with the results of Fig. 1 approaching the long-chain value by DP$_n \approx 100$. However, in further calculations we found that for a very low value of k_p^B ($\approx 0.01 \times k_p$), this effect is noticeable up to even DP$_n \approx 1000$. Specifically, using the same parameter set as for the calculations represented by the filled symbols in Fig. 1, a k_p^B of 8.31 L mol^{-1} s^{-1} results in values for $\langle k_p \rangle$ of 468 and 770 L mol^{-1} s^{-1} for systems with DP$_n$ of 100 and 1000, respectively. This situation is representative of the phenomenon known as retardative (or degradative) chain transfer.

The differences in propagation rates of monomeric radicals should also be reflected in the values of the observed termination rate coefficients, because a slowly propagating R$_1$ species is much more likely to terminate than a faster propagating one, and hence the contribution to termination by very short chains (with very high $k_t^{1,1}$!) in a system with low k_p^1 is much larger than in systems with a high k_p^1. So, one expects $\langle k_t \rangle$ to be higher in a system with low k_p^1, and that is indeed what is predicted in Fig. 2.

From the data obtained for $\langle k_p \rangle$ and $\langle k_t \rangle$ it is possible to investigate the possible effect on the observed rate of polymerization, which is proportional to $\langle k_p \rangle / \langle k_t \rangle^{1/2}$. These results are shown in Fig. 3, and the first thing we wish to point out from this Figure is the apparently odd behavior observed in the cases of higher k_p^1. This behavior, in which the

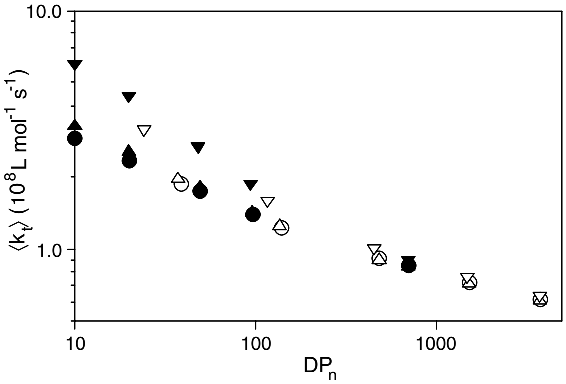


Fig. 2. The effect of the value of k_p^1 on the observed macroscopic termination rate coefficient $\langle k_t \rangle$ as a function of the average chain length produced in the system. Legend as in Fig. 1.

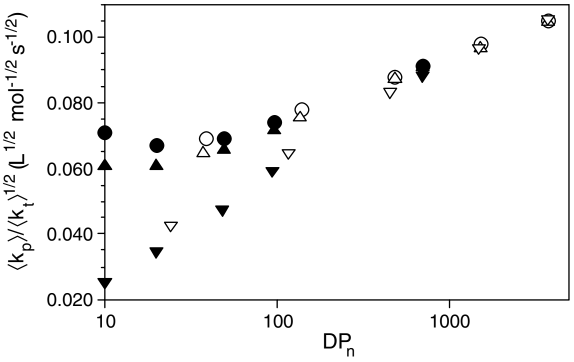


Fig. 3. The effect of the value of k_p^1 on the overall rate of polymerization, expressed here as $\langle k_p \rangle / \langle k_t \rangle^{1/2}$, as a function of the average chain length produced in the system. Legend as in Fig. 1.

rate first decreases and then increases with increasing $\mathrm{DP_n}$ of the system, is indeed what we observed experimentally [20], and in fact is what has stimulated this current line of research by us.

In the case of low k_p^1 values, the effect is immediately obvious: there should be a very strong retardation effect that is still noticeable in systems with a relatively high $\mathrm{DP_n}$. This is a good example of what happens in retardative chain transfer, and conceivably contributes to the retardation observed in reversible addition-fragmentation chain transfer polymerization (RAFT) when RAFT agents are used that contain a leaving group which is not an optimal initiator (this effect is in addition to any other possible retardation effects operative in RAFT [58]). Furthermore, the current results suggest that in experiments measuring chain-length-dependent k_t (e.g., single-pulse pulsed-laser polymerization (SP-PLP) and RAFT [9,10,59,60]) at low chain lengths, the appropriate selection of initiator and/or mediating agent is of utmost importance. In particular we note that the slow addition of cyanoisopropyl radicals to MA does not appear to have been taken into account in interpreting recent RAFT polymerizations of MA that were aimed at determining $k_t^{i,i}$, rendering as questionable the values for very low i [61]. In a subsequent paper dealing with dodecyl acrylate [62], the authors do include the correct value for k^{ini}, but do not include any further chain-length dependence of k_p in their analysis. On the basis of what has been discussed here, it is reasonable to suggest that the effect of a slow first propagation step (in conjunction with chain-length-dependent propagation) on these systems should be explored, perhaps by using different initiators and certainly by carrying out systematic kinetic simulations on well-behaved and well-characterized systems (for example, MMA or STY), taking full account of both chain-length-dependent propagation and termination.

To summarize this section, it can be concluded from small-radical studies that for small radicals that are sufficiently similar to the monomeric analogue of the propagating polymeric radical, the rate coefficient of addition to monomer is about an order of magnitude larger than k_p. For initiator or transfer-derived radicals that are very dissimilar to a truly monomeric radical, the situation can occur that $k_p^1 \ll k_p$, which results in a strong retardation, possibly even in systems with a relatively high $\mathrm{DP_n}$.

4. Direct measurements of the first few propagation steps

Several studies of chain-length-dependent propagation in polymerizing systems were published about a decade ago. Of particular interest is the study of Moad and co-workers on the first few propagation steps in MA polymerization at 60 °C [22]. Using a nitroxide radical scavenging technique and HPLC for product analysis, ratios of k_p^i / k_T were obtained, where k_T is the rate coefficient of the recombination reaction between the propagating radical and the nitroxide. In their analysis a chain-length-independent value of 3×10^8 L mol^{-1} s^{-1} for k_T was assumed. The assumption of chain-length independence is possibly justified as some experimental evidence suggests that nitroxide trapping experiments are not (completely) diffusion-controlled [63]. Even if they were, based on diffusion

Table 3
Summary of experimental chain-length-dependent rate coefficients for the first few propagation steps in free-radical polymerization

Monomer	k_p^1/k_p	k_p^2/k_p	k_p^3/k_p	C_1 [a]	$i_{1/2}$ [a]	E_{act} for k_p^1 [b]	Ref.
MA	10.7	1.8	0.5	9.7	0.27	$\approx E_{act}$ for k_p	[22]
MA [c]	21.4	3.6	1.0	20.4	0.33	$\approx E_{act}$ for k_p	[22]
MMA	16.8	4.3		15.8	0.44	$\approx E_{act}$ for k_p	[24]
MAN	6.3					$\approx E_{act}$ for k_p	[24]
STY	109.5	14	3	108.0	0.33	$\ll E_{act}$ for k_p [d]	[23]

[a] Parameter values obtained from fitting Eq. (4) to the experimental data.

[b] The values of the activation energies for the first addition step were estimated from Table 2 in Ref. [21].

[c] The experimentally reported values for k_p^1, k_p^2 and k_p^3 were multiplied by a factor of 2 (see text).

[d] This is the situation for azobis(methyl isobutyrate) as initiator; the activation energy for the benzoin-derived radical addition is unknown.

arguments, which suggest that $k_T \propto (1 + i^{-0.5})$ [64], the rate coefficients for a monomeric or a trimeric radical would not differ by more than 25%, which, given the difficulty of the experiments and the present purposes, is an acceptable error. The error in the absolute value used for k_T may be larger as its value is highly solvent and radical dependent [63,65], as the authors also point out in their paper [22]. However, this would introduce an uncertainty in the values of k_p^i by an *approximately constant factor* and hence the *ratios* of successive k_p^i values should still be fairly accurate. Given these assumptions, the addition of primary alkyl radicals was found to proceed with a rate coefficient—which, using the definition of this paper, is the same as k_p^1—of about 3×10^5 L mol^{-1} s^{-1}. Similarly, the rate coefficient for the addition of the resulting radical to monomer, i.e., k_p^2 (note that in the original paper this is designated as k_p^1 [22]), was found to be ~4–6 × 10^4 L mol^{-1} s^{-1}, while that for a trimeric radical to monomer was about 1.4×10^4 L mol^{-1} s^{-1}. These values correspond to a drop by a factor of about 5–8 in going from k_p^1 to k_p^2 and of about 3–4 in going from k_p^2 to k_p^3, suggesting a fairly rapidly declining chain-length dependence of k_p^i, which in terms of the model given by Eq. (4) corresponds to a situation described by a value of about 0.3 for $i_{1/2}$. Considering that the long chain propagation rate coefficient of MA should be about 2.8×10^4 L mol^{-1} s^{-1} (i.e., the k_p for butyl acrylate at 60 °C [40] corrected by a factor of about 0.82, which is k_p^{MA}/k_p^{BA} at 20 °C [66]) and that there are no obvious reasons why in the current system k_p^3 could be smaller than k_p, the most likely reason for this observation is that the value of k_T used in the data analysis was a little too low. Values of 1×10^9 L mol^{-1} s^{-1} and higher for k_T have been reported [63,65] and a factor of only 2 would rectify this apparent discrepancy. The data of this study, with corresponding C_1 and $i_{1/2}$ parameters from fitting of Eq. (4), are summarized in their uncorrected and their "corrected" (by a factor of 2) form in Table 3, and they are shown in Fig. 4.

A second study in which k_p^1 and k_p^2 were directly measured is that of Gridnev and Ittel, who studied the free-radical polymerization of MMA and MAN at 60 °C in the presence of very high amounts of catalytic chain transfer agent in order to limit the polymerization to very short chain lengths [24]. These workers determined from calorimetric rate measurements and product analysis the values of k_p^i, assuming a constant value for k_t in their analysis. Although k_t is clearly not a constant in this system, the effect on the derived values of k_p^1 and k_p^2 is not likely to be greater than about 20–25%, as explained

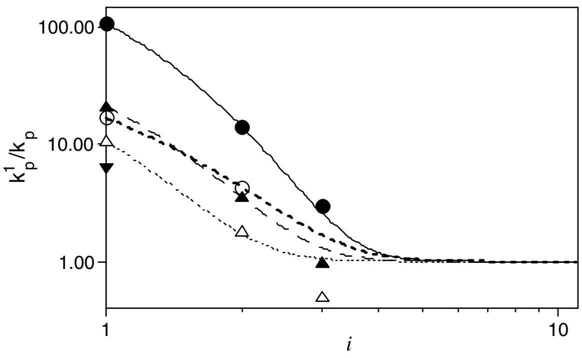


Fig. 4. The chain-length dependence of the rate coefficient for the first few addition steps in the free-radical polymerization of several different monomers, expressed as the ratio of k_p^i to the long-chain value, k_p. Points: experimental results of Table 3; lines: best fits of Eq. (4). Systems: styrene (●, solid line); methyl acrylate (△, dotted line); methyl acrylate multiplied by a factor of 2 (▲, broken line); methyl methacrylate (○, bold dotted line); methacrylonitrile (▼).

above. The results that were obtained in this study were $(14 \pm 1.5) \times 10^3$ and 3.6×10^3 L mol^{-1} s^{-1} for k_p^1 and k_p^2, respectively, for MMA and $k_p^1 = 340 \pm 40$ L mol^{-1} s^{-1} for MAN (k_p^2 was not determined). These results are also included in Table 3 and shown in Fig. 4.

Another study of relevance is the pulsed-laser polymerization (PLP) of styrene in the temperature range of 20–80 °C by Moad and co-workers [23]. In order to model the obtained molecular weight distributions in these studies, a chain-length dependence of k_p needed to be invoked. The following rate parameters (in our notation) were assumed and were found to reproduce the molecular weight distributions well: $k_p^1 = 3 \times 10^4$ L mol^{-1} s^{-1} for addition of primary radicals (derived from benzoin or azobis(methyl isobutyrate)) to styrene, followed by $k_p^2 \approx 14 \times k_p$, $k_p^3 \approx 3 \times k_p$ and $k_p^4 \approx k_p^5 \approx \cdots \approx k_p = 274$ L mol^{-1} s^{-1}. Even if this value of k_p^1 seems very high, it is indisputably clear that these data, which have also been included in Table 3 and are shown in Fig. 4, show the general trend of an initially high value for k_p^1 that exponentially decays to its long-chain value. That said, one recognizes that this was a modeling study rather than a direct measurement of k_p^i, and that other variations of k_p^i with i may also have reproduced the molecular weight data (no other variations were tried).

The results in Table 3 and Fig. 4 show that the data are adequately described by Eq. (4) and that for those cases where the first addition step corresponds closely to that of a truly monomeric radical, the value of C_1 is of the order of 10^1. In all cases the value of k_p^i decreases to its long-chain value within several addition steps, giving rise to a value of $i_{1/2}$ of about 0.3–0.4.

For completeness we should also mention work by Takács and co-workers [67–69] and by Zetterlund et al. The work by the former group using pulsed electron beam polymerization shows general potential for the investigation of propagation (and termination) rates of primary and oligomeric radicals, but these particular studies do not seem to yield any values of direct relevance to the present work. Zetterlund et al. studied the first few propagation steps in the free-radical polymerization of acrylonitrile [70], styrene [71] and methacrylonitrile [72] by means of the radical trapping technique (see above) with product analysis using electrospray-mass spectrometry (MS). All these studies show that $k_p^1 > k_p$, but the changes in k_p^i do not appear to follow a logical trend. For example, the acrylonitrile results (initiated by a 2-cyano-2-propyl radical) show an initial decrease in k_p^i until $i = 4$, after which an increase is observed [70]. These observations cannot reasonably be explained in terms of either changing activation energies or changing frequency factors (see the following section). The reported styrene data (again initiated by AIBN) suggest that k_p^i increases in going from $i = 1$ to 4, stays constant for a while and then decreases. Again, this behavior defies reasonable explanation. Specifically, the activation energy for the first addition is significantly smaller than that for propagation—see Tables 1 and 2—and converting the cyanoisopropyl radical into a dimeric radical with a styrenic terminal unit would increase the activation energy and hence lower the rate coefficient. Considering frequency factors, it will be shown in the following section that A for a dimeric addition is smaller than A for a monomeric addition. Given the kinetic assumptions in the analysis of the data and the uncertainties associated with the MS quantification of the product distribution, we feel that at present there remain some questions about this potentially elegant analysis technique, and that the reported kinetic parameters cannot be taken at face value.

A point of interest from the work of Zetterlund et al. [70–72] is that a serious attempt was made to measure k_p^i for $i > 3$. As is implicit in the results of Table 3, there is a gap in our knowledge concerning k_p^i for i in the range 4–10. It is our feeling, based on the results of transition state theory (see the next section) and the results of FRP experiments (see the next paper in this series), that there is probably a CLDP in the range $i = 4$–10 that has a significant effect on the kinetics. To put this in terms of Eq. (4), we believe that $i_{1/2}$ is more like 1 in value than the 0.3–0.4 deduced from the results of this section (see Table 3). The difference between a chain-length dependence characterized by $i_{1/2} = 0.44$ (i.e., the value corresponding to the MMA data obtained by Gridnev and Ittel [24]) and one by $i_{1/2} = 1.12$ (corresponding to the value obtained from steady-state free-radical polymerization [20] and PLP [25] at short chain lengths) is illustrated in Fig. 5. It can be seen from this figure that the experimental value for k_p^2 in Table 3 is about half that which is predicted from $i_{1/2} = 1.12$. Although an error of a factor 2 in the experimental data seems to be somewhat large, the very nature of the experiment and the assumptions used in the data analysis (e.g., a chain-length-independent k_t, the value of which can only be estimated) do introduce a significant

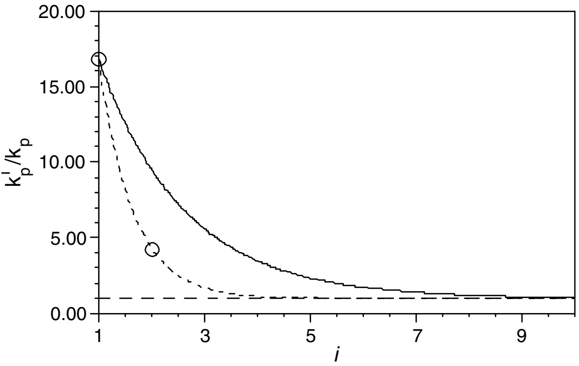


Fig. 5. Comparison of the different chain-length dependencies of the propagation rate coefficient for methyl methacrylate at 60 °C, as deduced from steady-state and PLP experiments (—: Eq. (4) with $i_{1/2} = 1.12$) and as measured in catalytic chain transfer studies at low chain length (○: experiment; - - -: Eq. (4) with $i_{1/2} = 0.44$).

uncertainty in the obtained values. Obviously, similar arguments can be made for the other mentioned experiments, where assumptions in the kinetic analysis lead to uncertainties which, given the difficulty of these experiments, are acceptable for many purposes, but which are still too large for obtaining the very detailed information that we are seeking. It is important to establish the chain-length dependence of the propagation rate coefficient for the first few addition steps (up to, at least, $i = 4$ or 5) in direct experiments, endeavors that we therefore encourage. We stress, though, that this is really an issue concerning the details of CLDP, not its fundamental nature, which is already established by the results of Table 3, viz. a strong initial effect that peters out over a short range of chain length.

5. Theoretical studies

In previous sections we referred several times to the fact that the observed chain-length dependence is consistent with what is predicted from transition state theory. Although this discussion has been described previously in detail [27,29,73], for the completeness of our argument it is useful to present some of the most relevant theoretical findings here, because these provide a rigorous justification for the k_p^i variation that we are espousing in this paper.

Within the formulation of transition state theory, the rate coefficient for a bimolecular reaction (k) can be expressed in terms of the statistical mechanical and electronic properties of the reactants and the transition state (Eq. (20)) [74,75]:

$$k = \frac{k_B \mathrm{T}}{h}\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\mathrm{e}^{-\frac{E_0}{k_B T}} \tag{20}$$

In this expression k_B is Boltzmann's constant, h is Planck's constant, T the temperature, E_0 the critical energy to reaction (which is determined by the electronic properties of the reactants and the transition state) and $Q^{\dagger}$, Q_{rad} and Q_{mon} are the molecular partition functions [76] of the transition state, radical and monomer, respectively. The link between the expression for the rate coefficient in Eq. (20) and the experimental Arrhenius parameters is given in Eqs. (21) and (22):

$$E_{\mathrm{act}} = -k_B\frac{\partial \ln k}{\partial T^{-1}} = E_0 - k_B\frac{\partial \ln\left(\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\right)}{\partial T^{-1}} + k_B T \tag{21}$$

$$\ln A = \ln\left(\frac{ek_B T}{h}\right) + \ln\left(\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\right) - \frac{1}{T}\frac{\partial \ln\left(\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\right)}{\partial T^{-1}} \tag{22}$$

As is probably expected from the expression in Eq. (20), the activation energy (Eq. (21)) is intimately linked with the critical energy of reaction (at 0 K) and contains a small temperature correction that depends partly on the molecular partition functions. As can be seen from Eq. (22), the Arrhenius frequency factor is more closely linked to the molecular partition functions, with any changes in the partition functions directly being reflected in the value of A.

It is clear that the molecular partition functions are pivotal to understanding the magnitude of A. In fact, it is from consideration of these partition functions that one can derive that $A^{(1)}/A \approx 10$ [27], which is consistent with the experimental data in Table 1. For the present purpose, these molecular partition functions can all be written as the product of translational (Q_{trans}), rotational (Q_{rot}) and internal (Q_{int}) contributions [76]:

$$Q = Q_{\mathrm{trans}} \times Q_{\mathrm{rot}} \times Q_{\mathrm{int}} \tag{23}$$

The translational partition function (Eq. (24)) arises from the three-dimensional motion of the molecule and depends on the mass (m) of the moving molecule:

$$Q_{\mathrm{trans}} \propto m^{3/2} \tag{24}$$

The rotational partition function (Eq. (25)) arises from the three-dimensional rotations of a molecule and depends on the three principal moments of inertia (I_a, I_b and I_c), each of which is defined as in Eq. (26), where m_i is the mass of atom i at a distance of r_i from the principal axis of rotation.

$$Q_{\mathrm{rot}} \propto (I_a I_b I_c)^{1/2} \tag{25}$$

$$I = \sum_i m_i r_i^2 \tag{26}$$

Hence, both the translational and rotational partition functions (and their contributions to the rate coefficients) can be considered as "mechanical" contributions in that they are solely governed by the masses and geometries of the reactants and the transition states. It is clear that with increasing chain length of the propagating radical, the differences in mass and geometry between the growing polymer chain and the transition state become increasingly smaller, and that in the long-chain limit, the contributions to k by the translational and rotational modes of the transition state and the radical cancel. Thus the only significant contributions arise from the monomer, as shown in Eq. (27) [27,29,73].

$$\left(\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\right)_{\mathrm{trans,rot—longchains}} \approx \frac{1}{Q_{\mathrm{mon,trans}}}\,\frac{1}{Q_{\mathrm{mon,rot}}} \tag{27}$$

To good approximation one can state that the most important chain-length effect on A is given by Eq. (27) (i.e., the loss of the contributions to A by the radical and the transition state for long chain lengths), and that this is a general effect independent of the monomer that is used.

A more subtle effect, one which determines the differences observed for different monomer systems, arises from the contribution of the internal modes (Q_{int}) to the molecular partition function (and hence to the rate coefficient). These arise from the vibrations and internal rotations (i.e., a total of $3N-6$ for an N-atomic non-linear molecule) within the molecule and depend on the frequencies of vibration or the barriers to rotation and their associated moments of inertia for internal rotors (Eq. (28)); of course these vibrations are those that are measured in infrared spectroscopy.

$$Q_{\mathrm{int}} = \prod_j Q_{\mathrm{int},j} \tag{28}$$

In this equation, the product is over $3M-6$ and $3N-6$ vibrations/rotations in the monomer and the radical, respectively, and over $3(N+M)-7$ in the transition state (see Fig. 6). As is shown in Fig. 6, the formation of the transition state from the two reactants is accompanied by a loss of 3 translational and 3 rotational modes and by a gain of 6 internal modes (i.e., the lost external modes have been converted into 6 internal modes), which are the so-called *transitional modes*. One of these transitional modes is the reaction coordinate, which in a radical addition reaction corresponds roughly to the C–C stretch vibration of the forming carbon–carbon bond; this vibration is omitted from the vibrational partition function of the transition state (hence the product over $3(N+M)$–7 modes). The other 5 are very important as they do not exist in the two reactants and hence are characteristic for the transition state and the reaction. For the sake of simplicity it can be said that the contributions from

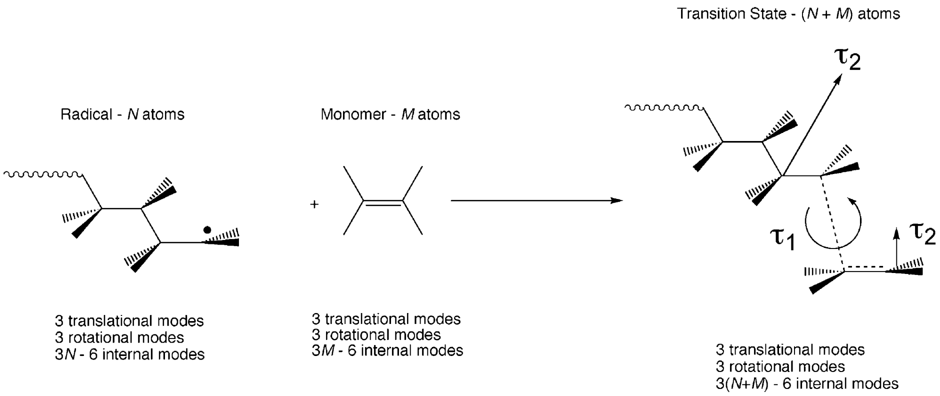


Fig. 6. Schematic representation of the formation of the transition state in a radical addition reaction and the corresponding changes in the external and internal modes [29]. τ_1 and τ_2 are the transitional modes that contribute most to $Q^{\dagger}$.

the non-transitional modes approximately cancel in the ratio of molecular partitions, and hence

$$\left(\frac{Q^{\dagger}}{Q_{\mathrm{rad}}Q_{\mathrm{mon}}}\right)_{\mathrm{int}} \approx \prod_{j}^{\substack{\text{transitional}\\ \text{modes}}} Q^{\dagger}_{\mathrm{int},j} \tag{29}$$

Two of the most important transitional modes for a radical addition [27,29,73,77,78] are shown in Fig. 6 and are indicated by τ_1 and τ_2. The former corresponds to a rotation of the monomer unit about the forming bond and the latter to a simultaneous bending of the two reactant fragments, with their hinges being the two carbon atoms at the forming bond. Since the structures of the transition states of radical additions of interest are sufficiently similar in those characteristics that determine the molecular partition functions [27,29,73,77,78], this observation and the following discussion can be considered generally applicable to the free-radical polymerization of most common monomers.

The transitional modes τ_1 and τ_2 obviously are affected by the nature (i.e., size) of the substituent group of the monomer. For example, theoretical studies show that changing the α substituent from an H to a CH_3 lowers the frequency factor by a factor of three when comparing methacrylonitrile with acrylonitrile [77], and this observation is backed up by the trends observed in experimental frequency factors for k_p (for a more detailed discussion, see Section 1.6.1.5 in Ref. [29]). What is important for the current discussion is that it is clear that the effect of an increasing chain length on the transitional modes will diminish until a constant value is reached, and it is likely that this is at $i \approx 3$–4. When comparing the frequency factors for a monomeric (A_{M}) and a dimeric (A_{MM}) addition, the presence of a penultimate monomer unit in the latter case will lower the frequency factor because of the additional hindrance to the transitional modes, i.e., $A_{\mathrm{MM}} < A_{\mathrm{M}}$. Making the chain any longer will not alter this situation very much, and hence the largest decrease in frequency factor (caused by a decreasing contribution of $Q^{\dagger}_{\mathrm{int}}$ to A) would be expected in going from a monomeric to a dimeric radical addition. An additional effect may be expected for the addition of a dimeric radical in the case of an initiating radical ($X^{\bullet}$) with very different substituents to the monomer, i.e., $A_{\mathrm{XM}} \neq A_{\mathrm{MM}}$ [79]. In the event that the substituents in X are significantly larger than those in the monomer, then $A_{\mathrm{XM}} < A_{\mathrm{MM}}$—an effect that is expected, for example, in the case of 2-cyano-2-propyl (X)-initiated VAc (M) (here, X contains two non-H α-substituents and M only one). In the event that the substituents in X are much smaller than in M, then $A_{\mathrm{XM}} > A_{\mathrm{MM}}$—a similar situation has been observed experimentally for polymeric radicals in the copolymerization of styrene with dimethyl itaconate [80]. As an additional note to the situation in which $A_{\mathrm{XM}} > A_{\mathrm{MM}}$, it should be mentioned that irrespective of this steric penultimate effect, the frequency factor for the first addition is still larger than that of the second addition (i.e., $A_{\mathrm{X}} > A_{\mathrm{XM}}$). Effects of the type that are described here would correspond to ones that are more familiarly termed 'steric 1,3-interactions' (in the transition state) by most polymer chemists.

To summarize the above, we can say that transition state theory predicts a decrease in the Arrhenius frequency factor upon increasing chain length of the propagating radical, and this is largely due to diminishing contributions of the rotational and translational contributions and to greater hindrances to the transitional modes. Further, this effect is largest when increasing the chain length from 1 to 2. The results for transition state theory calculations on the addition of n-alkyl radicals to ethylene [27], i.e., modeling the first few propagation steps in ethylene polymerization, are shown in Fig. 7, using both the lower (1.0×10^8 L mol^{-1} s^{-1}) and upper (1.7×10^8 L mol^{-1} s^{-1}) bound estimates for the long-chain propagation frequency factor. To these data we fitted Eq. (4) and found that the

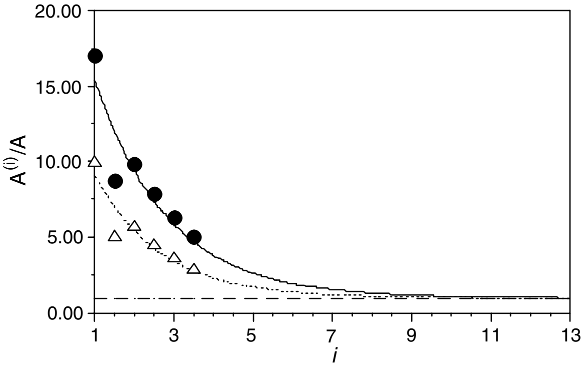


Fig. 7. Dependence of the frequency factor $A^{(i)}$ on the chain length i (expressed in number of CH_2–CH_2 units) for the addition of n-alkyl radicals to ethylene, a model for the first few steps in ethylene polymerization. Shown are the ratios of $A^{(i)}$ over the long-chain value A, as taken from Ref. [27]: (●) using $A = 1.0 \times 10^8$ L mol^{-1} s^{-1} and a fit (—) of Eq. (4) with $C_1 = 14.4$ and $i_{1/2} = 1.27$; (△) using $A = 1.7 \times 10^8$ L mol^{-1} s^{-1} and a fit (···) of Eq. (4) with $C_1 = 8.1$ and $i_{1/2} = 1.13$.

parameter sets of $\{C_1 = 8.1$ and $i_{1/2} = 1.13\}$ and $\{C_1 = 14.4$ and $i_{1/2} = 1.27\}$ for the upper and lower bounds, respectively, describe the data well. Furthermore, the data suggest that $A^{(i)}$ converges to its long-chain value after about 10 addition steps, a finding which has been confirmed recently in (theoretical) studies where the addition of longer alkyl radicals to ethylene was studied explicitly [30,81]. Clearly, these findings further support the physical feasibility of our model for chain-length-dependent propagation and the deduction that C_1 is of the *order* of 10 and $i_{1/2}$ of the *order* of 1.

So far we have only considered the frequency factors and naturally we should not forget the activation energy. We are not aware of any studies that have explicitly investigated the effect of chain length on activation energy, and hence we must enter speculative territory. Although it is conceivable that the chain length affects the activation energy (both through the value of E_0 and through its temperature correction via the partition functions), it is not likely that this effect will be very large. The effect on E_0 may arise from the fact that in the case of a dimeric addition there is a γ-substituent effect that does not exist in the case of a monomeric addition. As shown by high level ab initio molecular orbital calculations, different γ-substituents (i.e., penultimate units) can affect the activation energy by a few kJ mol^{-1} [44–46], but from these studies it is not clear how and to what extent γ-substituents would affect the activation energy in homopropagation. In any case, any possible electronic effect is expected to decrease with increasing chain length and is probably insignificant after the second addition step [82]. Furthermore, very limited results suggest that there could be a small increase in the activation energy in going from a monomeric addition to an *i*-meric addition due to different temperature corrections [28], but this effect is not likely to change any further upon increasing the chain length. Hence we conclude that the limited data available suggest that although it is conceivable that the activation energy is chain-length dependent, it is most likely that the effect is small and rapidly converges to its long-chain value, and in particular it does so much more rapidly than the frequency factor. This is in line with the limited experimental data that are available (Table 1), which suggest that the activation energies for long-chain propagation are very similar or only slightly higher than those for the addition of the analogue monomeric radicals (remember that the data for MMA and styrene provide the surest indication, as they are the systems for which long-chain $\langle k_p \rangle$ have been most accurately determined).

As an aside we note that the chain-length dependence of E_{act} for propagation is an area ripe for investigation, something that is becoming increasingly feasible as more powerful computers enable the quantum calculations for sufficiently large molecules to be carried out.

To summarize this section, it is probably safe to conclude that transition state theory predicts a chain-length dependence in the propagation rate coefficient which is largely controlled by a decreasing frequency factor ($A^{(1)} \gg A^{(2)} > A^{(3)} > \cdots A^{(9-10)} \approx A$) whose chain-length dependence can be well described by Eq. (4) with $C_1 \approx 10$ and $i_{1/2} \approx 1$. The reason we have gone into some detail in explaining this is in order to convey the important point that this finding is not radical-specific; rather, being based essentially on size effects, it is to be expected for the great majority of systems of interest. Results available to date suggest that the activation energy is not greatly affected by chain length and that the chain-length dependence of k_p^i appears to reflect the chain-length dependence of A.

6. Conclusion

From the summary and discussion of relevant studies on the addition of small radicals to monomer and of polymerization studies focusing on the first few addition steps, it is clear that at small chain lengths there exists a significant chain-length dependence of k_p. This chain-length dependence is characterized by an initial high value for the first addition step, which exponentially decays to its long-chain value within a relatively small number of addition steps (<∼10). These findings, backed up by transition state theory, which predicts that the chain-length dependence of k_p is largely caused by a decreasing frequency factor with increasing chain length, lend a physical credibility to a previously proposed functional form that describes the chain-length dependence of $k_p : k_p^i/k_p = C_1 \exp[-\ln 2 \times (i-1)/i_{1/2}] + 1$, where C_1 and $i_{1/2}$ are of the order of 10 and 1, respectively. Through kinetic simulations it was shown that the chain-length dependence of k_p, even though its *microscopic* effect is limited to relatively short chains, can have a significant effect on the observed *macroscopic* kinetics (i.e., on $\langle k_p \rangle$ and $\langle k_t \rangle$) when studying systems of relatively small average degree of polymerization (DP$_n$ of approximately 100 or less). Furthermore, the situation has been investigated in which the activation energy of the first addition step is significantly higher than that for (long-chain) propagation. It was found that in this event it is possible that the first addition step is significantly slower than the long-chain propagation reaction (the proposed model for chain-length-dependent propagation would obviously not be valid in this case for k_p^1), and that this can lead to an observed macroscopic propagation rate coefficient that is significantly smaller than the long-chain value for k_p, and correspondingly to a strong retardation of the polymerization rate. From all these results it is clear that when considering polymerization kinetics at low chain lengths, it is important to explicitly consider chain-length-dependent propagation and the nature of the initiating radical.

In the second paper of this series we will summarize and analyze the results obtained in polymerizing systems and investigate the possible existence and nature of a chain-length dependence of k_p at higher chain lengths, as recently proposed by Olaj and co-workers [18,26].

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