SP−PLP−EPR Study of Chain-Length-Dependent Termination in Free-Radical Polymerization of *n*-Dodecyl Methacrylate, Cyclohexyl Methacrylate, and Benzyl Methacrylate: Evidence of "Composite" Behavior[†]

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The chain-length dependence of the termination rate coefficient in *n*-dodecyl methacrylate (DMA), cyclohexyl methacrylate (CHMA), and benzyl methacrylate (BzMA) bulk free-radical homopolymerizations at ambient pressure and at temperatures from −20 to 0 °C is deduced using the recently developed technique of SP−PLP−EPR: pulsed-laser polymerization (PLP) in which time-resolved EPR measurement of radical concentration, c_R, is made following each single pulse (SP) of an excimer laser. The decay of c_R results from termination of radicals of almost identical size. Their chain length, i, increases linearly with time, t, after applying a SP. The rate coefficient, $k_t^{i,i}$, for termination of two radicals of size i is determined by fitting the experimental c_R vs t data. This process demonstrates that (at least) two power-law exponents are necessary to describe $k_t^{i,i}$ over the extended chain-length range of $i = 1$ to 1000. This is consistent with the so-called "composite model" , which uses power-law exponents α_S and α_L to describe termination of radicals either shorter or longer, respectively, than a crossover chain length, i_c. The fourth parameter obtained from fitting the SP−PLP−EPR data with this model is $k_t^{1,1}$, the termination rate coefficient for two radicals of degree of polymerization 1. Previous DMA experiments are reanalyzed while new experimental results are reported and analyzed for CHMA and BzMA. The parameter values for CHMA and BzMA termination at 0 °C are almost identical—$k_t^{1,1} \approx 3 \times 10^7$ L mol^{-1} s^{-1}, $\alpha_S \approx 0.50$, $i_c \approx 90$, and $\alpha_L \approx 0.21$—and they are close to those for DMA at 0 °C: $k_t^{1,1} \approx 1 \times 10^7$ L mol^{-1} s^{-1}, $\alpha_S \approx 0.64$, $i_c \approx 50$, and $\alpha_L \approx 0.18$. The results fully support the composite model in that the chain-length dependence is more pronounced for shorter than for longer radicals, i.e., $\alpha_S > \alpha_L$. Moreover, the power-law exponent that characterizes termination of long-chain radicals is close to the theoretical value of $\alpha_L = 0.16$. In fact all parameter values—including the small differences between DMA and CHMA/BzMA—are more-or-less in accord with expectations based on polymer dynamics. Furthermore, our results suggest that termination of methacrylate radicals with large cyclic or long *n*-alkyl substituents may be affected by steric shielding of the radical functionality.

Introduction

To the outsider, the kinetics of free-radical polymerization (FRP) appear to be a simple matter. This impression is deceptive in that the nonaficionado is unaware of the many complicating factors that are operative. Primary among these is that the termination reaction is diffusion-controlled.[1] The first evidence of this emerged long ago in the form of the so-called Trommsdorff−Norrish[2,3] or "gel" effect: in many FRPs there is an acceleration in rate as the reaction proceeds, and it is agreed that this is caused by the termination rate coefficient, k_t, decreasing as a consequence of the viscosity increasing as polymer forms. Because of this one should always anticipate that k_t will change during the course of a FRP, even if in some systems it does not.[1]

In addition to its conversion dependence there is another complicating consequence of termination being diffusion-controlled: because long chains are more ponderous in their motions than are short chains, it should always be expected that termination will be chain-length dependent in rate.[1] While this was clearly grasped at least as long ago as the early 1960s,[4,5] the experimental study of this phenomenon has proven to be far more difficult. The reason for this is simple: because polymerizing radicals are by definition reactive, in conventional FRP systems it is not possible to create a monodisperse radical population, and thus it is not possible to directly measure, e.g., $k_t^{i,i}$, the rate coefficient for termination between radicals of degree of polymerization i. Rather, the measured k_t in such systems is an ensemble average,[1] denoted $\langle k_t \rangle$, over all $k_t^{i,j}$, the rate coefficient for termination between radicals of degree of polymerization i and j, respectively. Of course it is the entire matrix of $k_t^{i,j}$ values that one would ultimately like to know, because this is what fully describes the chain-length dependence of termination.

In response to the above situation, considerable effort has been expended on the complicated matter of relating $\langle k_t \rangle$ values to the underlying $k_t^{i,i}$ and $k_t^{i,j}$, so that these microscopic termination rate coefficients may be inferred from experimental data, a topic that has recently been reviewed in two different contexts.[6,7] The best data from such studies come from measurements of time-averaged $\langle k_t \rangle$ in periodic pulsed-laser

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polymerization (PLP) carried out at low conversion.[8,9] However, almost from the advent[10,11] of PLP it has been evident that it might be exploited in a more profound way for the study of the chain-length dependence of termination: because the interaction of a laser pulse with a photoinitiator creates a population of identical radicals essentially instantaneously on the time scale of polymerization, time-resolved (cf. time-averaged) measurements of the subsequent kinetics must reveal the variation of k_t as these radicals grow.[12] In other words, the Holy Grail of $k_t^{i,i}$ can be obtained directly.

What has held back the exploitation of the so-called single-pulse PLP (SP−PLP) technique for the measurement of $k_t^{i,i}$ is that the experiments are a genuine physical chemistry challenge. One impediment is that the standard way of following polymerization kinetics is to measure the concentration of monomer, c_M, as a function of time, t, and it is the second derivative of such data that yields $k_t^{i,i}$.[13,14] Thus, one has a noise difficulty. Recognizing this,[13] de Kock et al. developed an alternative method in which the molecular weight distribution (MWD) from a SP−PLP experiment is intensively analyzed, these workers having astutely realized that $k_t^{i,i}$ could be unraveled from such MWD data.[15] Remarkably, Olaj et al. independently published a variant of this approach at much the same time.[16] While promising results were obtained by one group for several acrylates[15] and by the other for methyl methacrylate and styrene,[16] a recent review has concluded that all MWD-based methods for determining k_t are problematic in several general ways.[7] One of these is that assumptions must be made about the nature and extent of chain-stopping reactions in a system. For example, if any sort of transfer is occurring to a significant extent, then the SP−PLP−MWD method for determining $k_t^{i,i}$ is invalidated. A greater problem is that this method can only be used for so-called "zero-conversion" conditions, because if any polymer is already present, then the MWD from the SP−PLP experiment alone cannot be determined.

Given that the capacity to measure the conversion dependence of k_t is highly valued, it is clear that there is strong motivation to develop an alternative to the SP−PLP−MWD method, even if this method is an ingenious piece of science. How else, then, may the above problem of noise in the second derivative of $c_M(t)$ be overcome and $k_t^{i,i}$ determined from *concentration−time* data of a SP−PLP experiment? It has always been evident that the way to improve this situation is instead to measure radical concentration, c_R, directly. This was recently achieved for the first time by coupling SP−PLP apparatus with an EPR spectrometer capable of c_R measurement on a microsecond time scale.[17,18] This enabled determination of $k_t^{i,i}$ as essentially the first derivative of the data (reducing the noise problem), and, of course, the conversion dependence could also be obtained (because $c_R(t)$ can still be measured when polymer is present). The results of these initial experiments were so promising that the so-called SP−PLP−EPR method for studying termination has already been recommended by an IUPAC task-group reviewing methods for measuring k_t.[7]

SP−PLP−EPR is not the only new method for measuring $k_t^{i,i}$ to emerge in recent times: mention should also be made of two living free-radical polymerization methods, one involving steady-state[19] and the other SP−PLP[20] systems, that have been successfully used. However, both these methods are compromised for the study of long chains in that the (unavoidably) changing conversion also affects the value of $k_t^{i,i}$ by the time i becomes large.[7] On the other hand, the above-mentioned methods involving chain-length-averaged $\langle k_t \rangle$[8,9] have yielded information about medium-size and long-chain $k_t^{i,i}$ only.[7] One aspect of the SP−PLP−EPR method that therefore stands out is that it allows determination over a narrow conversion range of the chain-length dependence of $k_t^{i,i}$ over a wide span of i up to about $i = 1000$, as was demonstrated in our initial study using *n*-dodecyl methacrylate (DMA).[17] The present paper extends these investigations to benzyl methacrylate (BzMA) and cyclohexyl methacrylate (CHMA). In contrast to the previous study, the more refined method of analysis of SP−PLP−EPR traces that was recently suggested by Smith and Russell[21] will be used. It will be seen that the SP−PLP−EPR method is exceptionally powerful in that it yields $k_t^{i,i}$ for a wide range of chain lengths, and further, it does so as a function of conversion.

Experimental Section

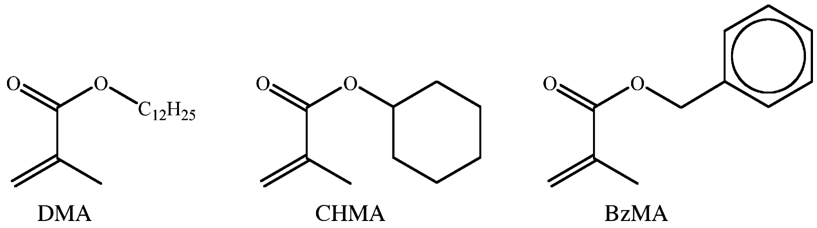
EPR spectra were recorded on a Bruker Elexsys E 500 series CW-EPR spectrometer on sample solutions contained in a quartz tube of 5 mm outer diameter and 4 mm inner diameter. The tube was fitted into a cavity equipped with a grid. The sample was irradiated through the grid with a COMPex 102 excimer laser (Lambda Physik) operated on the XeF line at 351 nm. The laser energy per pulse was around 50 mJ. The cylindrical axis of the sample tube was perpendicular to the direction of the laser beam. The EPR spectrometer and the excimer laser were triggered by a pulse generator (Scientific Instruments 9314). The decay in radical concentration after firing a laser pulse was measured at fixed magnetic field strength via the intensity of the central line of the EPR spectrum, as has also been done in previous studies.[17,22,23] That this intensity is proportional to the double integral of the EPR spectrum, which is an accurate measure of radical concentration, was checked before each experiment. Absolute radical concentrations were obtained through calibration with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 99%, Aldrich Chemie) dissolved in the monomer under conditions as close as possible to those of the actual SP−PLP−EPR experiment.

To improve signal-to-noise quality, up to 20 individual $c_R(t)$ traces from a series of SP−PLP−EPR experiments were coadded. Each series was measured within a short time interval over which overall monomer conversion increased by no more than 2%. Between applying successive such series of laser pulses, the EPR tube was inserted into the sample chamber of an IFS 88 FT-NIR spectrometer (Bruker) in order to measure (overall) monomer concentration via the absorbance at around 6160 cm^{-1} of the first C−H stretching overtone (at the C=C double bond).[24]

The photoinitiator α-methyl-4(methylmercapto)-α-morpholinopropiophenone (MMMP, 98%, Aldrich Chemie) was used as received at initial concentrations of about 1×10^{-2} mol L^{-1}. In a glovebox, under an argon atmosphere, MMMP was added to the monomer, and then an EPR sample tube was filled with the solution. *n*-Dodecyl methacrylate (DMA, Scheme 1) (>95%, stabilized with hydroquinone monomethyl ether, Fluka Chemie) was treated with an inhibitor remover (Aldrich Chemie) and then distilled under reduced pressure. Cyclohexyl methacrylate (CHMA, Scheme 1) (97%, stabilized with hydroquinone monomethyl ether, Fluka Chemie), and benzyl methacrylate (BzMA, Scheme 1) (96%, stabilized with hydroquinone monomethyl ether, Aldrich Chemie) were distilled under reduced pressure in the presence of K_2CO_3. BzMA was additionally treated with an inhibitor remover (Aldrich Chemie). Prior to the experiments, each monomer was subjected to several freeze−pump−thaw cycles in order to remove dissolved oxygen. Note that all experiments were bulk polymerizations at ambient pressure.

Data acquisition and analysis were carried out in three steps: (1) The software Xepr v1.0 (Bruker), which also controls the

SCHEME 1: Chemical Structures of the Three Monomers of This Work: *n*-Dodecyl Methacrylate (DMA), Cyclohexyl Methacrylate (CHMA), and Benzyl Methacrylate (BzMA)



spectrometer settings, was used for primary data acquisition. (2) The integration of the spectra and the calculation of absolute radical concentrations were then carried out using Matlab. (3) $c_R(t)$ traces were fitted using the software packages Matlab and Origin in order to obtain $k_t^{i,i}$ parameter values.

Theoretical Background and Data Fitting

Diffusion coefficients are often found to show a power-law variation with chain length. Therefore, it is not just for pragmatic reasons that

$$k_t^{i,i} = k_t^{1,1}\, i^{-\alpha} \tag{1}$$

is commonly used to describe homotermination rate coefficients. Here $k_t^{1,1}$ is the rate coefficient for termination between radicals of degree of polymerization 1, while the exponent α quantifies the strength of the chain-length dependence of termination. The key feature of SP−PLP is that a uniform crop of primary radicals is created by irradiation at $t = 0$ and that these all grow with frequency $k_p c_M$, where k_p is the propagation rate coefficient and c_M the monomer concentration. Thus, to good approximation one can say that $i = k_p c_M t$ gives the (evolving) length of all radicals in the system. Substituting this into eq 1, one may now integrate the rate law $dc_R/dt = -2k_t^{i,i} c_R^2$, obtaining

$$\frac{c_{R,0}}{c_R} - 1 = \frac{2c_{R,0}k_t^{1,1}(k_p c_M)^{-\alpha}}{(1-\alpha)} t^{1-\alpha} \tag{2}$$

This equation (or a rearrangement thereof) has been presented by various workers over the years.[12,16,17,25] New to the SP−PLP−EPR presentation was the suggestion of plotting the measured $c_R(t)$ data as $\log((c_{R,0}/c_R) - 1)$ vs $\log t$, so that the important parameter α could be obtained easily from the slope (=1 − α) of a straight-line fit.[17] When this elegant idea of a log−log plot was put into practice for the first time, it was observed that the DMA data were much better represented by two straight lines,[17] as is evident from inspection of Figures 1 and 2 (which will be discussed in more detail further below). It was found that the early-time linear fit had a slope of 0.5 (suggesting $\alpha = 0.5$), that the long-time linear fit had a slope of 0.8 (suggesting $\alpha = 0.2$), and that the two linear fits intersected at a time corresponding to $i = 100$.[17] These findings were uncannily consistent with independent theoretical work of the year before, work that had arrived at the conclusion that, rather than eq 1, a superior description of methyl methacrylate (MMA) and styrene termination at low conversion is provided by the following 4-parameter model:[26]

$$\begin{aligned} k_t^{i,i} &= k_t^{1,1}\, i^{-\alpha_S}, \quad i \le i_c \\ &= k_t^{1,1}\, (i_c)^{-\alpha_S+\alpha_L}\, i^{-\alpha_L}, \quad i > i_c \end{aligned} \tag{3}$$

This basis of this "composite" [26] model is that the rate-determining step for termination is different for short and long chains: for long chains it is chain-end encounter upon coil overlap, with theory predicting[27] and experiment verifying[8,9,28] $\alpha_L \approx 0.16$ for styrene and MMA, but short chains are too small to display coillike behavior, and so for their termination a different α value is to be expected.[26] It was proposed that $\alpha_S \approx 0.5$ and $i_c \approx 100$,[26] values that turned out to be in remarkable agreement with those from the double-linear interpretation of DMA SP−PLP−EPR data.[17]

Notwithstanding the above success, it is of concern that eq 2 and the double-linear interpretation of SP−PLP−EPR traces are based on several assumptions.[21] A rigorous exploration of

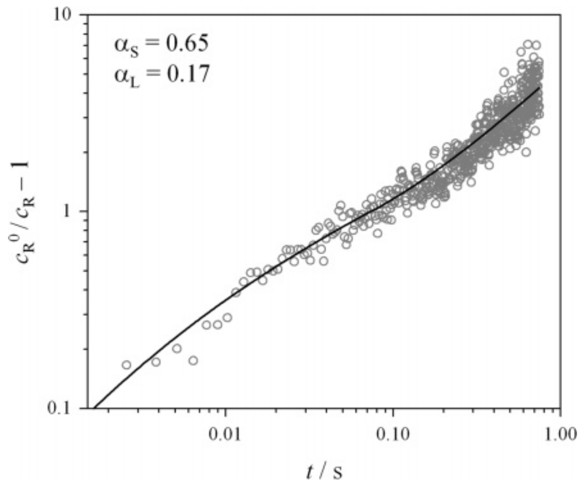


Figure 1. A log−log plot of $(c_{R,0}/c_R - 1)$ vs time for SP−PLP−EPR data of DMA at 0 °C and 12.9% conversion with $c_{MMMP} = 6.3 \times 10^{-3}$ mol L^{-1}. Key: points, experiment; line, eq 4 with $k_t^{1,1} = 1.5 \times 10^7$ L mol^{-1} s^{-1}, $\alpha_S = 0.65$, $\alpha_L = 0.17$, and $i_c = 50$.

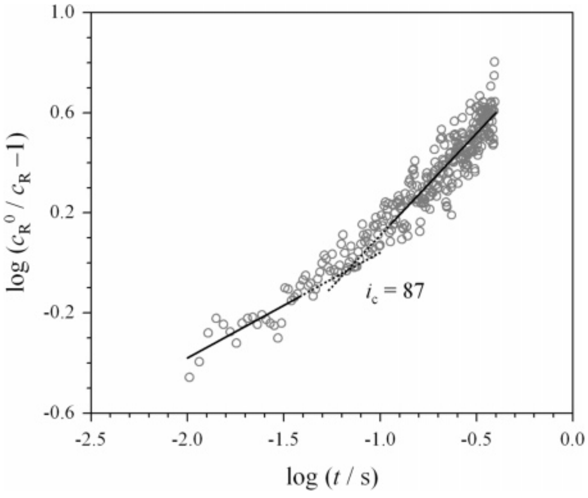


Figure 2. A log−log plot of $(c_{R,0}/c_R - 1)$ vs time for SP−PLP−EPR data of CHMA at 0 °C and 12.7% conversion with $c_{MMMP} = 9.7 \times 10^{-3}$ mol L^{-1}. Key: points, experiment; full lines, linear fits to data such that $15 < i < 50$ and $150 < i < 500$; dotted lines, extrapolations of linear fits, providing an argument for choosing $i_c \approx 90$ (see text).

the underlying kinetics was therefore carried out.[21] Among other things, it was found that when eq 3 is applied to the situation of SP−PLP, the following equation giving $c_R(t)$ is obtained:[21]

$$\frac{c_{R,0}}{c_R} - 1 = \frac{2c_{R,0}k_t^{1,1}[(k_p c_M t + 1)^{1-\alpha_S} - 1]}{k_p c_M(1 - \alpha_S)},\ t \le t_c \quad (4a)$$

$$\frac{c_{R,0}}{c_R} - 1 = \frac{2c_{R,0}k_t^{1,1}[(i_c)^{1-\alpha_S} - 1]}{k_p c_M(1 - \alpha_S)} - \frac{2c_{R,0}k_t^{1,1}(i_c)^{1-\alpha_S}}{k_p c_M(1 - \alpha_L)} + \frac{2c_{R,0}k_t^{0}(k_p c_M t + 1)^{1-\alpha_L}}{k_p c_M(1 - \alpha_L)},\ t > t_c \quad (4b)$$

Here $t_c = (i_c - 1)/(k_p c_M)$ is the time at which the crossover from short-chain to long-chain termination behavior occurs, and $k_t^0 = k_t^{1,1}(i_c)^{-\alpha_S+\alpha_L}$ is the apparent value of $k_t^{1,1}$ if only long-chain termination is considered (see eq 3). Although eq 4 is surprisingly complicated compared with eq 2, consideration of limiting behavior sheds light on why this is so: (1) The long-time limit of eq 4a is eq 2.[21] The reason for this inaccuracy in eq 2 is that it assumes $i = k_p c_M t$, which results in an infinite value of $k_t^{i,i}$ at $t = 0$ (see eq 1). Thus, eq 2 overestimates the rate of termination at early times, and hence it overestimates the value of $c_{R,0}/c_R$.[21] More physically realistic is to use, as does eq 4, $i = k_p c_M t + 1$. This results in downward curvature in a log−log plot of $(c_{R,0}/c_R) - 1$ vs t at early times,[21] as is evident in Figure 1. (2) The long-time limit of eq 4b is also eq 2 (except in that $k_t^{1,1}$ is replaced by k_t^0), however this limiting behavior is not reached until times well beyond t_c.[21] Thus, even though there is a sharp transition in $k_t^{i,i}$ at $i = i_c$ (see eq 3), no such sharp transition is observed in the behavior of $\log((c_{R,0}/c_R) - 1)$ vs $\log t$. Rather, as is visible in Figure 1, there is a smooth transition that commences at $t = t_c$.[21]

The above findings call in question the accuracy of double-linear fitting of data. Therefore, we carried out a reanalysis of all our DMA data,[17] this time fitting it with eq 4 in order to determine all 4 parameters of eq 3. Figure 1 shows a typical result. The findings can be understood in terms of the two effects outlined above, and therefore they—and the remainder of this section—will be framed in those terms. (1) Using eq 4 we find $\alpha_S = 0.65$ whereas previously,[17] after use of the double-linear approach, it was reported that $\alpha_S = 0.49$ for this particular data set. The reason for this difference is that the downward curvature of eq 4 at early times means that a straight-line fit of the same data will have a higher slope than the long-time (limiting) slope, and hence α will be underestimated. (2) Using eq 4 we find $i_c = 50$ and $\alpha_L = 0.17$, whereas previously[17] we stated that $i_c \approx 100$ and $\alpha_L = 0.14$ from this experiment. The overestimation of i_c by the double-linear method arises as follows. Equation 4 shows that after t_c there is a transition from slope $1 - \alpha_S$ to a limiting slope of $1 - \alpha_L$ some time later. So fitting all the data with two straight lines must result in lines that intersect in the transition region, which of course is after the true value of i_c. There is also the potential to overestimate α_L with the double-linear method, because $\alpha_L < \alpha_S$ means that eq 4 shows upward curvature in the period after t_c, as the slope increases from $1 - \alpha_S$ to $1 - \alpha_L$. Thus, a linear fit that includes this region will have slope less than $1 - \alpha_L$, and so α_L will be overestimated. Although this was not observed with the data of Figure 1 (because of the much lower value of i_c), it will be seen that we did observe this in fitting other data sets. This illustrates that there can be a tradeoff in fitting to obtain both i_c and α_L; e.g., in the case of Figure 1, the double-linear approach gave α_L accurately (see the values stated above) but i_c was too high.

The quantitative effects of using the more formally correct eq 4 for data analysis are exactly as anticipated in ref 21. In that these effects are not large, and sometimes they are nonexistent (e.g., the α_L values quoted above), the simpler and more elegant double-linear approach can be said to be validated.[21] Nevertheless, the more exact approach should be preferred if all else is equal. In this respect, it must be mentioned that eq 4 is a challenge to employ: not only is it highly complicated, but its proper use requires some expertise in statistics, whereas obviously the double-linear approach is more straightforward. While we found the fitting of eq 4 to be a statistically robust procedure for obtaining values of $k_t^{1,1}$ and α_S, the problem with this method of data analysis is, as has already been implied, that it is relatively insensitive to variation of i_c and α_L. For example, while one can be confident that $\alpha_L \le 0.25$ and that i_c is somewhere in the range of 40−100 for the data of Figure 1, it is hard to be more precise than this, because there is only marginal change in the statistical quality of the fit for variations within these ranges. The reason for this is all too evident from Figures 1 and 2: the value of c_R is small at long times, and thus a high degree of scatter in $c_{R,0}/c_R$ is unavoidable, scatter which makes it difficult to distinguish between the small variations in eq 4 output that result from the indicated ranges of α_L and i_c values. The development of better EPR equipment will ameliorate this situation in the future, as will the employment of more sophisticated statistical techniques in the fitting of data.

Given the above, the double-linear approach, based on eq 2, was also employed in this work, for it has the advantages of being simpler and clearer, particularly in relation to estimation of i_c and α_L. This is illustrated in Figure 2, which shows a double-linear fit to a CHMA data set. From the considerations of this section, the following guidelines emerge for employment of the double-linear approach: (1) What eq 2 does not describe is the region of downward curvature at very early times. Thus, if one is using eq 2, as in the double-linear approach, one should leave out of the fit the data from very early times: paradoxically, the omission of data will result in a more accurate estimate of α_S being obtained. Hence, in Figure 2 we have fitted data only for $t \ge 0.01$ s, whereas in Figure 1 we fitted down to much shorter times. (2) Similarly, fitting should not include the region of upward curvature in the time period shortly after t_c, because this period is not described by eq 2. Thus, a more accurate estimate of α_L is obtained by omitting this intermediate time period from fitting. The implementation of this guideline is clear in Figure 2, whereas in Figure 1, by contrast, we fitted data over the entire time period. Finally, if the double-linear approach is used according to the just-given guidelines, then it affords a reasonable estimate of t_c, and hence i_c, from extrapolation of the two linear fits and determination of their point of intersection. Again, this practice is clearly illustrated in Figure 2. The resulting estimate of i_c could then be used as a fixed value in subsequent fitting of the same data with eq 4, thus helping to overcome the problem of such fitting being relatively insensitive to i_c. Whenever we used eq 2 in this work to obtain estimates of parameter values, we always checked that those parameters gave an accurate representation of data when used in eq 4.

Last, we note that the IUPAC-recommended values of $k_p = 256$ L mol^{-1} s^{-1} for DMA at 0 °C,[29,30] 250 L mol^{-1} s^{-1} for CHMA at 0 °C,[31] 280 L mol^{-1} s^{-1} for BzMA at 0 °C,[31] 191 L mol^{-1} s^{-1} for BzMA at −10 °C,[31] and 126 L mol^{-1} s^{-1} for BzMA at −20 °C[31] were used in data analysis. Initial monomer concentrations of $c_{M,0} = 3.37$ mol L^{-1} for DMA at 0 °C,[30] 5.84 mol L^{-1} for CHMA at 0 °C,[32] 5.99 mol L^{-1} for BzMA at 0

TABLE 1: Parameter Values from the Fitting of Eq 4 to Selected SP−PLP−EPR Experiments

monomer	temp [°C]	conversion [%]	i_c	α_S	α_L	$k_t^{1,1}$ [L mol^{-1} s^{-1}]
DMA	0	3	50	0.72	0.16	1.60×10^7
		4	50	0.74	0.05	1.07×10^7
		9	50	0.66	0.06	1.11×10^7
		11	50	0.64	0.19	8.14×10^6
		13	50	0.65	0.17	1.49×10^7
		16	50	0.63	0.21	1.21×10^7
		19	50	0.62	0.03	7.32×10^6
		25	50	0.54	0.20	8.44×10^6
CHMA	0	4	90	0.51	0.18	1.43×10^7
		7	90	0.49	0.02	1.29×10^7
		11	90	0.40	0.13	5.41×10^7
		20	90	0.47	0.19	3.93×10^7
BzMA	0	2	90	0.49	0.16	6.16×10^6
		12	90	0.54	0.05	2.65×10^7
	−10	3	90	0.41	0.15	1.24×10^7
	−20	3	90	0.56	0.14	2.18×10^7
		9	90	0.51	0.15	2.40×10^7

°C,[32] 6.04 mol L^{-1} for BzMA at −10 °C,[32] and 6.09 mol L^{-1} for BzMA at −20 °C[32] were calculated from the indicated density measurements. The value of c_M used in data fitting was the value of $c_{M,0}$ adjusted according to the measured conversion (see the Experimental Section).

Results and Discussion

In previous work we analyzed our DMA SP−PLP−EPR traces using the double-linear approach.[17] Now that it is known that this procedure is not strictly correct,[21] we undertook to reanalyze these traces using eq 4. Figure 1 shows a typical result, while Table 1 lists parameter values from reanalysis of a selection of experiments spanning all conditions. As with our previous analysis,[17] no major conversion dependence was evident in any parameter value over the investigated range of conversion (0−30%), and therefore we recommend the following conversion-averaged values for DMA at 0 °C as being the best estimates from this work: $k_t^{1,1} = 1.1 \times 10^7$ L mol^{-1} s^{-1}, $\alpha_S = 0.64$, $\alpha_L = 0.13$ and $i_c = 50$. These may be compared with the previously reported and less accurate averages of $\alpha_S = 0.48$, $\alpha_L = 0.18$, and $i_c = 100$.[17] It has already been explained above why using eq 4 to analyze data results in the given alteration of parameter values.

A result that stands out from Figure 1 is the exceptional quality of the fit to the data that is provided by eq 4 over almost 3 orders of magnitude of variation of time. Fits of similar quality were obtained for all data sets examined in this work. Of course it might be argued that a model with four parameters is destined to give an excellent fit to data. In this respect it is highly significant that the best-fit parameter values are all physically realistic.[26] Thus, the results of this work provide a ringing endorsement of the composite termination model,[26] as also has other recent work,[19,20,33] although it would have to be argued that SP−PLP−EPR experiments provide the sternest examination in that they alone probe the free-radical concentration directly. Certainly the experimental data in Figure 1 are not linear through to long times, and thus it provides a clear demonstration that a single value of α does not describe $k_t^{i,i}$ over all i—this is the sense in which composite behavior is verified. However the question remains as to whether the variation of $k_t^{i,i}$ might be more complicated still than eq 3, e.g. the suggestions of a continuous decrease with i of α from 0.5 to 0.1[34] or of having α_S, α_L, and $\alpha \approx 1$ at intermediate chain lengths.[15,19] In that the fundamental concept of the composite model is simply that α is larger for short chains than for long chains, it admits of possibilities such as these.[26] However, it is evident from Figure 1 that SP−PLP−EPR data are not yet precise enough to distinguish between such suggestions. Rather, all that can be concluded is that at least a two-α model is necessary to describe termination. That said, the suggestion of a high α for intermediate chain lengths would manifest itself as a flattening out of our log−log plots (due to $1 - \alpha$ approaching zero). This was not observed in any of our results (e.g., see Figures 1 and 2). So the apparent observation of $\alpha \approx 1$ around $i \approx 30$ for styrene[19] and acrylates[15] is either an artifact of the methods used in those studies or else is behavior peculiar to these monomers and not shown by DMA, CHMA, or BzMA.

Turning now to the parameter values found for DMA, the first thing to say is that, as already explained, the value of α_L cannot be determined with high precision, and so our findings—average $\alpha_L = 0.13$ by one fitting method and 0.18 by the other—are fully consistent with the anticipation from theory[27] that $\alpha_L = 0.16$. Indeed, the majority of the α_L values in Table 1 are in the range 0.16−0.21, and the average is only dragged down to 0.13 by the large scatter in several values. Thus, the accepted picture of the rate of long-chain termination being determined by segmental motions of overlapping coils is confirmed yet again.[8,9,28] The values of i_c and α_S are also in line with the depiction of termination put forward in ref 26. Interestingly, measurements of center-of-mass diffusion coefficients, D, of poly(MMA) and poly(butyl methacrylate) oligomers at 25 and 40 °C found $D \sim i^{-0.66}$ at low conversion,[35] which suggests $\alpha_S = 0.66$ if the rate of termination is determined by translational diffusion and the capture radius is independent of i. This value is remarkably similar to the (average) value found here using eq 4; viz., $\alpha_S = 0.64$. Also interesting is that, in recent butyl acrylate experiments, Buback et al.[20] measured $\alpha \approx 1$ for $i \leq 10$ and speculated that this may reflect the scaling of surface area with chain length, with the shielding of radical functionality playing an important role in termination. If this is so then it could equally explain the present finding of $\alpha_S > 0.5$. Finally, the fact that the value $k_t^{1,1} = 1.1 \times 10^7$ L mol^{-1} s^{-1} is low is qualitatively consistent with the low temperature (0 °C), the large size of the monomer and its high viscosity (remembering that the Stokes−Einstein equation decrees that D is inversely proportional to both viscosity and size). Nevertheless, given that $k_t^{1,1}$ for MMA is (almost certainly) 5×10^8 L mol^{-1} s^{-1} or greater (see discussion in ref 26), it seems highly unlikely that a value of $k_t^{1,1}$ as low as has been found here for DMA can be explained on the basis of low D alone. For example, ref 35 found that D for butyl methacrylate is half the corresponding MMA value, so there is no reason to think that D for DMA is a factor of 50 lower than for MMA. Therefore, it seems plausible that steric hindrance must be contributing to $k_t^{1,1}$ being so low, i.e., on some occasions the long dodecyl groups physically block what would otherwise be successful termination encounters.[36] The relative importance of each of translational diffusion and steric effects in determining the value of $k_t^{1,1}$ remains to be established; data such as viscosities and diffusion coefficients would help to shed more light on this interesting matter.

Next we consider our CHMA data, which are new to this work. Results of a typical SP−PLP−EPR experiment are presented in Figure 2. In fitting of such data with eq 4 it was found to be difficult to decide on an optimum value of i_c. By contrast, no such problem was encountered with DMA data. Therefore, with the CHMA data, we used the double-linear approach, applied with the guidelines presented above, to estimate the value of i_c. This is shown in Figure 2, for which particular data set it was found that $i_c = 87$. Over a variety of

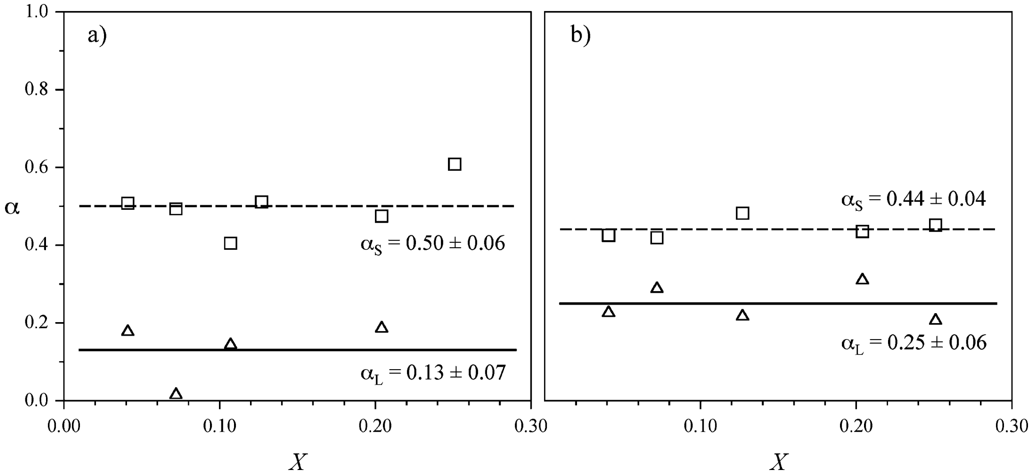


Figure 3. Conversion (X) dependence of α_S (squares) and α_L (triangles) from SP−PLP−EPR of CHMA at 0 °C with $c_{\mathrm{MMMP}} = 9.7 \times 10^{-3}$ mol L^{-1}, 16.5 × 10^{-3} mol L^{-1} and 20.8 × 10^{-3} mol L^{-1}: (a) from fitting of eq 4 with $i_c = 90$; (b) from double-linear fitting with $i_c = 100$. Lines: conversion-averaged values of α_S (dashed) and α_L (full).

TABLE 2: Best Estimates of Parameter Values from This Work

monomer	temp [°C]	conversion range [%]	i_c	α_S	α_L	$k_t^{1,1}$ [L mol^{-1} s^{-1}]
DMA	0	0−30	50	0.64	0.18	1.1 × 10^7
CHMA	0	0−25	90	0.50	0.22	3.7 × 10^7
BzMA	0	0−17	90	0.51	0.21	2.4 × 10^7
BzMA	−10	0−14	90	0.45	0.16	1.3 × 10^7
BzMA	−20	0−12	90	0.55	0.18	2.3 × 10^7

data sets the average value of $i_c \approx 90$ emerged. It was therefore decided to use this as a fixed value in fitting of eq 4. Selections of results are given in Table 1 and Figure 3a. Exactly as with DMA, no major conversion dependence is evident in any CHMA parameter value over the investigated range of conversion (0−25%), and therefore in Table 2 we recommend the following conversion-averaged values as being the best estimates for 0 °C from this work: $k_t^{1,1} = 3.7 \times 10^7$ L mol^{-1} s^{-1}, $\alpha_S = 0.50$, and $i_c = 90$.

Not yet given is a recommended value for α_L. While the fitting of eq 4 was found to be statistically robust for obtaining estimates of α_S and $k_t^{1,1}$ (which are determined by early-time data points), the same cannot be said about α_L. Quite often the fitting of eq 4 returned $\alpha_L = 0$, values which we omitted from Figure 3a. However, in such cases we found that the fitting residual was extremely insensitive to the value of α_L, reflecting that significant changes in α_L resulted only in small movements of eq 4 output relative to the scatter in the data at $t > 0.1$ s (see Figure 2). To overcome this problem and be able to obtain estimates of α_L, we therefore elected to apply the double-linear approach to our data, i.e., using the slope of a linear fit to determine α via eq 2. Rather than trying to choose chain-length regimes of closest-to-linear behavior, we attempted to eliminate such subjectivity by fitting all points with $15 < i < 100$ to obtain α_S, and all points with $100 < i < 1000$ to obtain α_L. However this is not to say that we recommend $i_c = 100$, because we recognize that the double-linear approach is not exact.

Results from double-linear fitting of the experiments of Figure 3a are presented in Figure 3b. It is evident that the α_S values from linear fitting (Figure 3b) are very close to but slightly lower than those from fitting of eq 4 (Figure 3a). This effect is as expected (see above), and its small magnitude gives confidence in the value of α_S from fitting of eq 4. Also as expected is that linear fitting gives a higher value of α_L than fitting of eq 4. What is important, however, is that the linear fitting always gives an estimate of α_L that is sensible, as opposed to the estimate of $\alpha_L = 0$ that one sometimes obtains with eq 4. Where this problem occurs regularly, we therefore recommend the use of linear fitting and eq 2 to obtain α_L. However it needs to be recognized that this method slightly overestimates the value of α_L. For example, fitting of several CHMA experiments was found to yield α_L on average 0.06 higher by the linear method than by eq 4 in cases where the latter gave a sensible result. For the sake of consistency, all the α_L values of Table 2 are from use of eq 2 (even DMA). However, for the reason just given these values should be regarded as an upper bound, with the real value most likely being of order 0.05 lower.

We come now to our BzMA experiments, also new to this work. These were carried out at temperatures of 0, −10 and −20 °C. The SP−PLP−EPR traces were always akin to those of Figures 1 and 2, so there is no need to present any explicitly. As with CHMA we found it difficult to estimate i_c using eq 4, so we used the approach of Figure 2. At all three temperatures it was found that $i_c = 90$. This was then used as a fixed value in fitting of eq 4. Selected results from this process are given in Table 1 and Figure 4, while Table 2 reports average values of α_S and $k_t^{1,1}$ at each temperature over the ranges of conversion investigated (again, no definite conversion dependence was in any case evident).

As with CHMA data, it was found that eq 4 was unreliable for α_L determination, and therefore the double-linear approach was called into action. The α_S estimates are presented in Figure 5, and it is evident that in this case they are essentially the same as from using eq 4 (see Figure 4). This consistency check gives confidence in the values of α_L, which are presented for BzMA at 0 °C in Figure 6. As is evident, the ease of use of the double-linear approach facilitates the analysis of a large number of experiments. Also presented in Figure 6 are the α_L values from all CHMA experiments, as opposed to the limited number of Figure 3. The equivalents of Figure 6 for the other systems of this work have been presented elsewhere;[17,37] Table 2 records the average value for each case.

Having presented all our results, it is appropriate to consider the values we have obtained. The first thing to say is that the considerations raised above in discussing the parameter values of DMA apply equally to CHMA and BzMA, so what needs to be discussed now are the variations—or lack thereof—of parameter values from system to system.

In considering the results of Table 2, the first striking finding is how similar are the values of α_L for all monomers. This is also illustrated by Figure 6, which shows values for CHMA

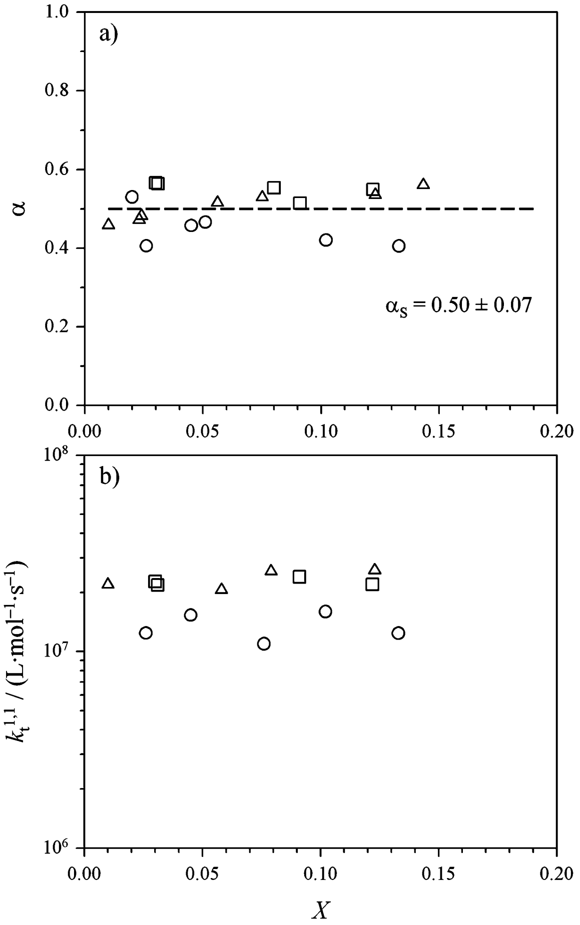


Figure 4. Parameter values from fitting of eq 4 with $i_c = 90$ to SP−PLP−EPR results for BzMA with $c_{\mathrm{MMMP}} = 22.9 \times 10^{-3}$ mol L^{-1}: conversion (X) dependence of (a) α_S and (b) $k_t^{1,1}$. Polymerizations were carried out at 0 (triangles), −10 (circles), and −20 °C (squares). The dashed line shows the average of all α_S values.

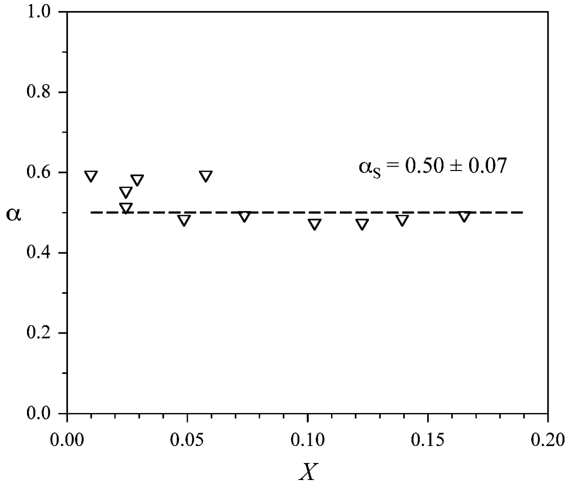


Figure 5. Conversion (X) dependence of α_S from double-linear fitting with $i_c = 100$ of SP−PLP−EPR results for BzMA at 0 °C with $c_{\mathrm{MMMP}} = 22.9 \times 10^{-3}$ mol L^{-1}. The dashed line is that of Figure 4a.

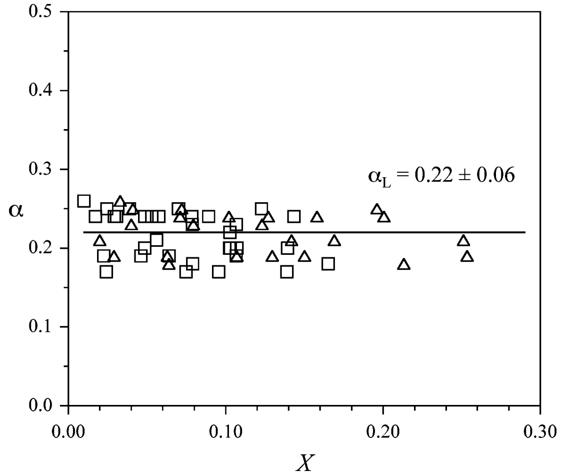


Figure 6. Conversion (X) dependence of α_L from double-linear fitting with $i_c = 100$ of SP−PLP−EPR results for BzMA (squares) at 0 °C and CHMA (triangles) at 0 °C. For each monomer three initial MMMP concentrations were used: 9.7×10^{-3}, 16.5×10^{-3}, and 20.8×10^{-3} mol L^{-1} for CHMA and 13.8×10^{-3}, 17.4×10^{-3}, and 22.9×10^{-3} mol L^{-1}for BzMA. The full line shows the mean of all α_L values.

and BzMA at the same temperature. Not only this, but α_L is always very close to 0.16, especially when one considers that the values in Table 2 and in Figure 6 are almost certainly a slight overestimate, as already discussed. In fact all this is fully consistent with theory,[27] which says that for end-chain radicals, $\alpha_L = 0.16$ for all polymers in a good solvent. In a styrene investigation, it was found that α_L decreased from 0.17−0.20 at 20 °C to 0.08−0.11 at 70 °C.[38] This was ascribed to a decrease of solvent quality with increasing temperature. The BzMA results of this work display no such effect, which is presumably because at the low temperatures that were investigated, the monomer is always a good solvent for the polymer, and hence α_L stayed constant at the good-quality value.

Next we consider our $k_t^{1,1}$ values. It is evident from Table 2 that DMA has a lower $k_t^{1,1}$ than BzMA and CHMA, which is consistent with DMA being more massive and having a higher viscosity. It appears that CHMA has a higher value of $k_t^{1,1}$ than BzMA, which implies that the diffusion of CHMA is faster. In the absence of any viscosity measurements for both these monomers, one might regard styrene and MMA as being in this respect a similar pair, in that both have similar molecular mass, and one has a pendant phenyl group (Sty/BzMA) but the other does not (MMA/CHMA). Therefore, it is interesting that styrene has a higher viscosity than MMA, e.g., measurements of 0.609[39] and 0.445 cP,[40] respectively, at 40 °C. This of course leads to the expectation of the monomer with a pendant phenyl group having the lower $k_t^{1,1}$, exactly as we have found. Also consistent with this is that BzMA (1.26 cP) has been measured as having a larger viscosity than the slightly more massive 2-ethylhexyl methacrylate (1.03 cP).[41] The correlation of $k_t^{1,1}$ with monomer viscosity should, however, not be over-interpreted, as—according to the above discussion for DMA—it is quite likely that steric shielding of the radical functionality is contributing to the BzMA and CHMA values of $k_t^{1,1}$ being as low as they are in magnitude.

The conclusion above about the relative values of $k_t^{1,1}$ for BzMA and CHMA is justified on the basis that all three BzMA values are less than the value for CHMA. However, unfortunately the three $k_t^{1,1}$ values for BzMA of themselves show no regular variation with temperature (see Table 2). On the basis of diffusion coefficient measurements on monomer-like molecules (e.g., toluene measurements[42]) and measurement of the temperature variation of the viscosities of some alkyl methacrylates,[41] one would expect the activation energy of $k_t^{1,1}$ to be close to 10 kJ mol^{-1}. This leads to $k_t^{1,1}(0\ ^\circ\mathrm{C})/k_t^{1,1}(-20\ ^\circ\mathrm{C}) \approx 1.4$. Our data are not inconsistent with such a variation; indeed, in the sense that our $k_t^{1,1}$ values for BzMA definitely do not show a strong variation with temperature, they can be said to demonstrate that the activation energy for $k_t^{1,1}$ is small, exactly as expected. Nevertheless it is something of a disappointment that $k_t^{1,1}$ cannot be determined with higher precision: clearly only one significant figure is justified. This is a problem that assails all methods of $k_t^{i,i}$ measurement, not just the present one. It seems to be related to the fact that a small variation in α results in a large compensation in $k_t^{1,1}$. This can be seen clearly in the BzMA values of Table 2: where α_S is smallest (−10 °C), $k_t^{1,1}$ is also smallest. Thus, the weaker decline in $k_t^{i,i}$ with i is compensated for by a lower value of $k_t^{i,i}$ at $i = 1$, so that the overall rate of termination over the course of the experiment is much the same as with higher α_S and $k_t^{1,1}$ values. In other words, exactly as with the determination of activation energy (E_a) and preexponential factor (A) from measurements of a rate coefficient as a function of temperature, the values of α_S and $k_t^{1,1}$ are correlated, and a small amount of scatter (see BzMA values in Table 2) in α_S (like E_a) translates into a much larger scatter in $k_t^{1,1}$ (like A). Given that $k_t^{1,1}$ values have the freedom to span orders of magnitude, this is perhaps not surprising. What this emphasizes is the difficulty of precisely measuring both absolute values of $k_t^{i,i}$ and its variation with i.

The next finding that stands out in Table 2 is that α_S seems to be higher for DMA than for CHMA and BzMA. It has already been mentioned that the value $\alpha_S = 0.64$ for DMA is consistent with measurements of translational diffusion coefficients for poly(alkyl methacrylate) oligomers. An earlier study by the same research group found $D \sim i^{-0.51}$ for polystyrene oligomers at low conversion.[43] This is remarkably consistent with the α_S values of this work for CHMA and BzMA, which of course are similar to styrene in having a cyclic pendant group.

The last values of Table 2 to consider are the i_c values. As with α_S, it is evident that BzMA and CHMA show the same behavior, while DMA is slightly different. Of course we cannot guarantee this, because—as has been made clear—it was difficult to say with certainty the value of i_c. Nevertheless in fitting the data it was reasonably clear that $i_c = 90$ gave an inferior fit to DMA data compared with $i_c = 50$, and vice versa for BzMA and CHMA. So it does seem that the polymers with cyclic pendant groups once again have different behavior to the system with alkyl pendant groups. It seems plausible to ascribe this behavior to alkyl groups having a greater tendency to become entangled with another chain than do spherical groups, which would explain that i_c is smaller for DMA and that α_S is larger. Of course these trends have been observed in this work right down to dilute solution conditions, in which chains ordinarily are not entangled with each other. However, here it is essential to remember that the act of termination always involves chains overlapping with each other, so it is reasonable to talk of an entanglement effect on termination even at very low conversions. One might also wonder whether there is an effect due to self-entanglements, i.e., pendant groups influencing diffusion through entanglement with another part of the chain to which they belong. In some ways this is equivalent to the issue of stiffness, i.e., that i_c is higher for BzMA and CHMA because the spherical pendant groups render the chain stiffer, and similarly for α_S. In this discussion, one sees once again the need for closer overlap between those studying termination and those who understand the intricacies of polymer dynamics.[1] In fact it is a big advance that SP−PLP−EPR yields termination data of a sufficiently “mechanistic” nature that genuine connections with the field of polymer dynamics can for the first time be made.

Finally, a comment should be made on the lack of any strong conversion dependence in all the parameters of this work. To some extent this must be a consequence of the relatively small ranges of conversion investigated. Indeed, a priority is to extend the use of SP−PLP−EPR to higher conversions, because an outstanding feature of the SP−PLP method is its capacity to measure the conversion dependence of k_t.[7] Even so, 0−30% conversion, as investigated for DMA, is a large enough range for there to be major decreases in polymer center-of-mass diffusion coefficients, and so one might have expected to see a marked change in termination behavior, as opposed to the weak changes evident in the parameter values of Table 1. This finding is consistent with other measurements of the conversion variation of k_t for DMA, e.g., of an essentially constant value of k_t for 0−60% conversion,[36] a finding that was related to the steric effects already discussed in this paper and to shielding effects.[36] Also playing a role is probably that the pendant dodecyl groups act as internal solvent, i.e., even though there is a significant change in polymer amount, this has no large effect on segmental (and other) diffusion behavior due to the pendant groups acting like solvent. Clearly these various considerations also hold for CHMA and BzMA, consistent with our results for those monomers too.

Conclusion

In recent times a paradigm shift has occurred in our understanding of termination in FRP:[44] where previously it was debated “Is termination chain-length dependent?”, now an affirmative answer is accepted and it is deliberated “What is the chain-length dependence?” This advance has largely been because of the advent of techniques[7] like SP−PLP−EPR, as has been powerfully demonstrated in this paper. In fact progress has been sufficiently rapid that one might suggest that we now understand the chain-length dependence of termination better than we do its conversion dependence. For example, the ideas behind the composite termination model are clear and are based on polymer physics,[26] whereas the origin of the Trommsdorff-Norrish (gel) effect remains unclear,[45] and it is not certain why some systems do not show any decrease in k_t across a wide conversion range, even though (bulk) viscosity changes by many orders of magnitude.[1,36] This situation is highly surprising given that the conversion dependence of k_t was recognized long ago and that such variations are considerably easier to measure than are variations of $k_t^{i,i}$ with chain length.[7] It is hoped that SP−PLP−EPR, with its ability to probe the conversion dependence of $k_t^{i,i}$, will improve this situation. It is also a matter of priority to extend the use of SP−PLP−EPR to acrylate systems in order to investigate more carefully the current indications[15,20] that chain-length-dependent termination is significantly different for that family of monomers compared with methacrylates. As this discussion emphasizes, and to end as this paper started, there are many complexities about FRP kinetics still to be unraveled, including also the task of measuring $k_t^{i,j}$ values, not just $k_t^{i,i}$. Not only is solving these puzzles technologically important, but it is also scientifically stimulating, as should be evident from this paper.

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