Determination of Free-Radical Propagation Rate Coefficients of Butyl, 2-Ethylhexyl, and Dodecyl Acrylates by Pulsed-Laser Polymerization

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ABSTRACT: Analysis of the molecular weight distributions (MWDs) of polymer produced by pulsed-laser polymerization (PLP) is an effective method for the determination of free-radical propagation rate coefficients (k_p). The PLP technique has been successfully applied to many slowly propagating monomers, but k_p determination by PLP for faster propagating systems such as the acrylates is more difficult. Experimental conditions for the polymerization must be selected so that laser pulses are the dominant chain-starting and chain-stopping events. Interference from excessive chain-transfer reactions, or from termination reactions which are either too fast or too slow, results in MWDs which are not suitable for k_p determination. Guidelines for design of successful experiments are outlined using an extensive *n*-butyl acrylate data set, from which k_p has been determined over the temperature range 5−30 °C; limited data for *n*-dodecyl acrylate and 2-ethylhexyl acrylate are also presented.

Introduction

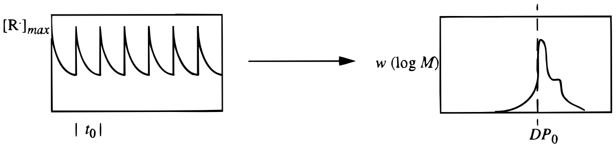
Analysis of the molecular weight distribution (MWD) produced during pulsed-laser polymerization (PLP) can be used to estimate the free radical propagation rate coefficient (k_p) of the system.[1] The PLP/MWD technique, introduced by Olaj and co-workers,[2,3] involves the exposure of a monomer solution with photoinitiator to repeated laser pulses. At each pulse a population of new radicals is formed and begins propagating. Between pulses, propagation of live radicals continues, while the overall concentration of radicals decreases due to radical−radical termination. Repeating pulses create a periodic radical concentration profile, as shown schematically in Figure 1a. At the end of the time period between two pulses, t_0, those radicals which were formed by the previous pulse and have escaped termination (and chain-transfer) have propagated to a chain length DP_0 given by:

$$\mathrm{DP}_0 = k_p[\mathrm{M}]t_0 \tag{1}$$

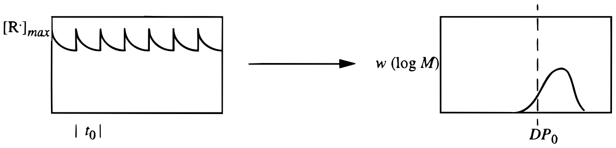
where [M] is the monomer concentration. Termination of these radicals is enhanced after the arrival of the next pulse due to the increase in radical concentration which occurs as the next generation of radicals is created. As a result, formation of polymer chains with degree of polymerization close to DP_0 is favored.

PLP/MWD has been used successfully to evaluate k_p for styrene,[1] monomers in the methacrylate family,[4−6] and vinyl acetate.[6,7] The IUPAC working party on free-radical kinetics considers this method to be the benchmark technique for the determination of k_p.[1] Despite these successes, quantifying k_p in fast monomer systems such as the acrylates has proven difficult,[8] except at low temperatures.[9,10] The PLP/MWD method requires that the laser pulse is the dominant chain-starting and chain-stopping process. When this condition is met, t_0 represents the characteristic time scale of the experiment and eq 1 can be used to analyze the results. In this work we consider situations in which this condition is not always observed and describe experimental techniques to return to the robust operating regime for the determination of k_p. These methods are used in the study of *n*-butyl acrylate (BA); new k_p results for this monomer, as well as *n*-dodecyl acrylate (DA) and 2-ethylhexyl acrylate (EHA), are presented.

(a) Intermediate termination:



(b) Low termination (small β):



(c) High termination (large β):

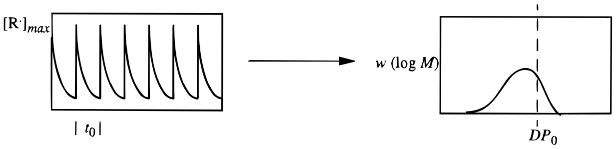


Figure 1. Schematic illustration describing effect of termination level on PLP-generated MWD (β defined in text; $M_0 = \mathrm{MW}_{\mathrm{mon}}\mathrm{DP}_0$).

Figure 1a shows schematically the radical concentration profile and the corresponding MWD which are characteristic of a well-behaved PLP experiment. The MWD has a primary peak which occurs near DP_0 and the shoulder of a peak near twice DP_0. This secondary peak corresponds to chains which grow for two pulse intervals. Olaj *et al.*[2] have demonstrated that the low molecular weight inflection point of the primary peak in either the number or weight distribution is the best measure of DP_0. This point may be determined by locating the maxima of the derivative of the MWD. Although derivative plots are always used to determine DP_0 in this work, the original MWD can also be used to interpret qualitatively the success of a PLP experiment.

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Where such qualitative observations are being made in this work, the terms primary and secondary peaks will refer to peaks of the MWD (and not its derivatives). Primary and secondary inflection points refer to the low molecular weight inflection points of these peaks which are the corresponding maxima in the derivative MWD plots. The presence of a primary peak with inflection point at DP_0 and a secondary inflection at approximately twice DP_0 is of key significance in the analysis and ensures that the MWD is suitable for determination of k_p.[2,4] Other criteria, such as invariance of k_p estimate with initiator concentration, laser power, pulse repetition rate, and [M], should also be used to further verify that consistent results are obtained.[1]

In order to assure that the MWD exhibits these features, experimental conditions must be chosen so that the peaks are not lost due to excessive chain-transfer or due to termination which is either too fast or too slow for the laser pulse rate. In order to establish the appropriate level of termination, consider the fraction of radicals, β, which are terminated prior to the next pulse. (This definition of β follows the convention of Olaj *et al.*,[2] but is different from that in our prior work[7] in which β was used to represent the fraction of radicals which survive until the subsequent pulse.) Assuming radical–radical termination without chain-length dependence, β is given by:

$$\beta = \frac{[\Delta R^\bullet]}{[R^\bullet]_{max}} = \frac{k_t[R^\bullet]_{max}t_0}{1 + k_t[R^\bullet]_{max}t_0} \qquad (2)$$

where k_t is the termination rate coefficient, $[\Delta R^\bullet]$ is the increase in radical concentration after a pulse, and $[R^\bullet]_{max}$ is the maximum radical concentration during the experiment, which is related to $[\Delta R^\bullet]$ by:

$$[R^\bullet]_{max} = [\Delta R^\bullet]\left[\frac{1}{2} + \left(\frac{1}{4} + \frac{1}{k_t[\Delta R^\bullet]t_0}\right)^{1/2}\right] \qquad (3)$$

It can be seen from eq 2 that the high termination limit is approached when $t_0 \gg 1/k_t[\Delta R^\bullet]_{max}$, and the low termination limit is approached for $t_0 < 1/k_t[\Delta R^\bullet]_{max}$, as previously discussed by Sarnecki and Schweer.[11] (Note that one section of the text in ref 11 mistakenly reverses these definitions, altough the two cases are correctly contrasted through simulation.) β can be controlled by changing t_0 or by varying experimental conditions which influence either k_t or $[\Delta R^\bullet]$; modifying $[\Delta R^\bullet]$ experimentally is most easily accomplished by changing initiator concentration or laser pulse energy.[7,11] Figures 1b and 1c schematically illustrate the limiting cases in which either too little (small β) or too much (large β) termination occurs.

Low-Termination Limit. At low levels of termination (Figure 1b), most radicals survive the subsequent pulse and β approaches zero; the laser pulse results in only a small perturbation of a large background radical concentration, and it is no longer the dominant chain-stopping event. The effect of this limiting case on the MWD is also shown on Figure 1b; in the limit of low termination, the MWD is shifted to higher values and is without primary or secondary peaks, resembling that of a chemically-initiated polymerization.

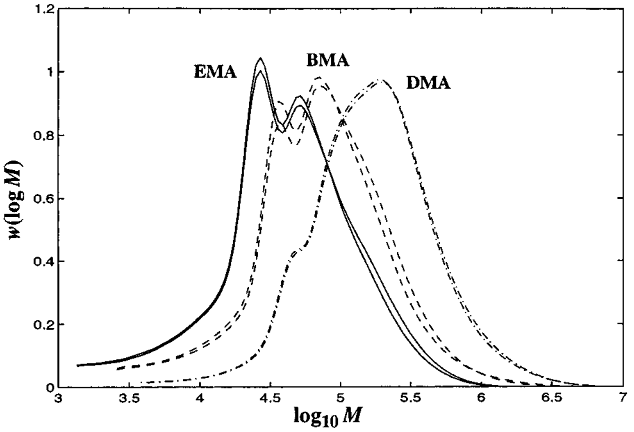

Figure 2. MWDs of PLP-generated polymer from ethyl (EMA), *n*-butyl (BMA), and *n*-dodecyl (DMA) methacrylates produced at equivalent conditions: laser repetition rate = 10 Hz, T = 10 °C, 1 mmol/L benzoin photoinitiator, laser power =70 mJ/pulse. Duplicate experiments shown for each monomer.

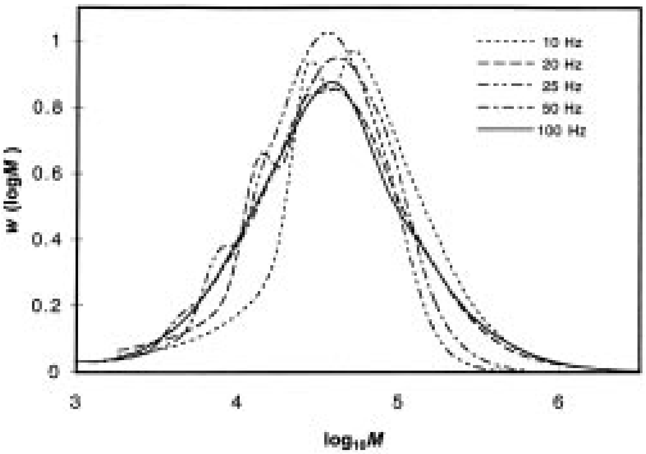

Figure 3. MWDs of PLP-generated pMMA, with laser repetition rate varied between 10 and 100 Hz. T = 10 °C, 1 mmol/L benzoin photoinitiator.

Figure 2 illustrates the influence of k_t on the shape of the MWD as the level of termination changes. Shown are the MWDs of PLP-generated polymer from identical experiments on ethyl (EMA), *n*-butyl (BMA), and *n*-dodecyl (DMA) methacrylate.[5,6] Within this homologous series of monomers, k_p is known to increase weakly as methacrylate group size increases (k_p for DMA is approximately 50% higher than k_p for EMA).[6] This increase is visible in a trend of the MWDs to shift to higher values as larger monomers are considered. It should be pointed out that this effect is somewhat exaggerated in the presentation of Figure 2, as the polymer molecular weight and not DP is shown on the abscissa. Much more significant than the increase in k_p is the order of magnitude decrease in k_t with increasing methacrylate size.[12–14] The lower termination level (lower β) causes the shape of the MWD to change, with the secondary peak increasing in size relative to the primary peak. Although the DMA experiment still yields good estimates for k_p, it is clear that the low termination limit (Figure 1b) is being approached.

The approach to the low termination limit is also illustrated in Figure 3, which shows polymer MWDs for methyl methacrylate (MMA) produced by PLP at 10 °C at varying repetition rates. As the pulse frequency increases from 10 to 100 Hz (t_0 decreases from 0.1 to 0.01 s), an order of magnitude decrease in the position of DP_0 and the primary peak of the MWD is expected (see eq 1). Indeed, the expected shift is observed as the repetition rate is increased from 10 to 50 Hz. It is also seen that as the laser repetition rate increases, the relative magnitude of the primary peak decreases with respect to the secondary peak. With a further increase to 100 Hz, no secondary peak or inflection point is observed, and the primary inflection point is no longer at the expected DP_0; instead a unimodal distribution at higher MW is seen. This behavior results from the decrease in β caused by decreasing t_0 (see eq 2); at the higher repetition rate the system is at the low termination limit (Figure 1b) and the MWDs which are obtained do not permit a reliable estimate of k_p.

High Termination Limit. The opposite limiting case of very high termination results in a value of β which approaches unity. Simulations suggest that, at the high termination limit, a k_p-controlled primary peak will still be observable on the MWD and that this peak is a better estimate of DP_0 than the inflection point.[11] Experiments indicate that operation at the high termination limit, however, is not desirable, as demonstrated by the results of Hutchinson *et al.*[7] for VAc, a high k_t system. Figure 7 of that work illustrates that the entire MWD moves almost an order of magnitude to lower MW values as the initiator concentration ([I]) is increased by 2 orders of magnitude; the position of the MWD peaks (and corresponding inflection points) shift to values more than 5 times lower than DP_0. (Increased [I] results in an increase in $[\Delta R^\bullet]$ and causes β to increase in value toward the high termination limit of unity.) These experiments, as well as results presented later in the current work, illustrate that no reliable k_p information can be obtained at the high termination limit. This concept is illustrated schematically by Figure 1c; if a large majority of radicals is terminated before they reach chain length DP_0, the resultant MWD will be shifted to lower values and cannot be used to determine k_p. Instead, experimental parameters must be modified to bring the system back to the robust "intermediate β" operating regime, in which both primary and secondary inflection points are observed.

Chain-Transfer Limit. To this point, the discussion has focused on the role that termination (through the variation of β) has on PLP-generated MWDs. Other potential interferences in resolving DP_0 during PLP are chain-transfer reactions. Transfer events provide a continuous supply of monomeric radicals and thus can start chain growth at any time during the interval between pulses. In addition, transfer serves as an additional chain-stopping mechanism. Both of these effects decrease the number of chains that reach length DP_0 and increase the number of shorter chains. As the level of transfer increases in the system, the characteristic multimodal shape of the distribution disappears and the secondary inflection point disappears from the derivative plot. In a study evaluating the use of PLP/MWD to measure transfer coefficients,[15] it was noted that, for systems where chain transfer is dominant, the laser pulse is neither the primary source of monomeric radicals nor is the primary stopping event for the growing chains. Under these conditions, a smooth unimodal distribution with an inflection point at values less than the proper DP_0 appears. Since the activation energy of transfer is nearly equal to that of propagation, this transfer-dominated peak shows little variation with temperature.[15]

The characteristic chain length for transfer, DP_{tr}, is the average chain length that a radical propagates before undergoing a transfer event, defined by:

$$DP_{tr} = \frac{k_p[M]}{k_{tr,M}[M] + k_{tr,A}[A]} \tag{4}$$

where $k_{tr,M}$ and $k_{tr,A}$ are the rate coefficients for transfer to monomer and to transfer agent (or diluent), respectively. The ratio of DP_{tr} to the characteristic chain length for propagation, DP_0, is a measure of the relative importance of chain-transfer to pulse-derived chain growth events in the system, and can be calculated by substituting the expressions for DP_0 and DP_{tr} from eq 1 and eq 4:

$$\frac{DP_{tr}}{DP_0} = \frac{1}{t_0(k_{tr,M}[M] + k_{tr,A}[A])} \tag{5}$$

Values of $DP_{tr}/DP_0 \gg 1$ indicate that termination is the dominant chain-stopping event and that characteristic PLP features may be seen. When DP_{tr}/DP_0 approaches unity, transfer dominates and a broad, featureless MWD is expected.

To demonstrate the effect of transfer on the k_p determination, PLP/MWD experiments with MMA and varying amounts of a chain-transfer agent were performed. *n*-Dodecyl mercaptan (DDM) was selected as the transfer agent because its chain-transfer kinetics to MMA have been previously studied.[15] Figure 4a shows the MWDs of pMMA obtained by PLP at DDM concentrations of up to 1.0 vol % at a temperature of 40 °C and laser repetition rate of 10 Hz; Figure 4b shows the corresponding derivative plots. A gradual loss of the secondary peak and a broadening of the primary peak is seen as [DDM] increases; at the highest level of chain-transfer, the entire MWD has shifted to lower values. The increasing influence of transfer reactions is also apparent in the derivative plots, where the clearly identifiable primary and secondary inflection points which are observed in the absence of chain-transfer agent become less intense as [DDM] increases. At the highest value of [DDM], the primary inflection point has shifted to a lower value and the secondary inflection disappears altogether; this indicates that the experiment no longer provides a reliable k_p estimate.

It is interesting to note that the loss of k_p information (clear primary and secondary inflection points) occurs when DDM levels reach about 0.5 vol %. Using the known kinetic rate constants for this system,[15] this corresponds to a DP_{tr}/DP_0 ratio of about 2. This value might be considered as a rough estimate of the level of transfer at which the PLP technique no longer yields reliable k_p data. For fast-propagating systems which have larger values of DP_0, it is possible to approach this limit solely through chain-transfer to monomer. This is illustrated by the VAc data of Hutchinson *et al.*,[7] where no meaningful inflection points could be found for bulk VAc pulsed at 10 Hz at temperatures of 30 °C and greater. Using the kinetic coefficients at 30 °C given in that work, $DP_0 = 4300$ and $DP_{tr} = 5000$ are calculated. Experimentally, the DP_{tr}/DP_0 ratio can be increased, reducing the effect of transfer, by decreasing t_0 or by decreasing [M] in a diluent which has significantly reduced chain-transfer ability relative to monomer. Both of these strategies have been used successfully with VAc.[6,7]

The arguments presented in this introduction describe how the nature of the PLP-generated MWDs change outside the robust operating regime as conditions approach the "high-termination", "low-termination", or "chain-transfer-dominated" limiting cases. The bound-

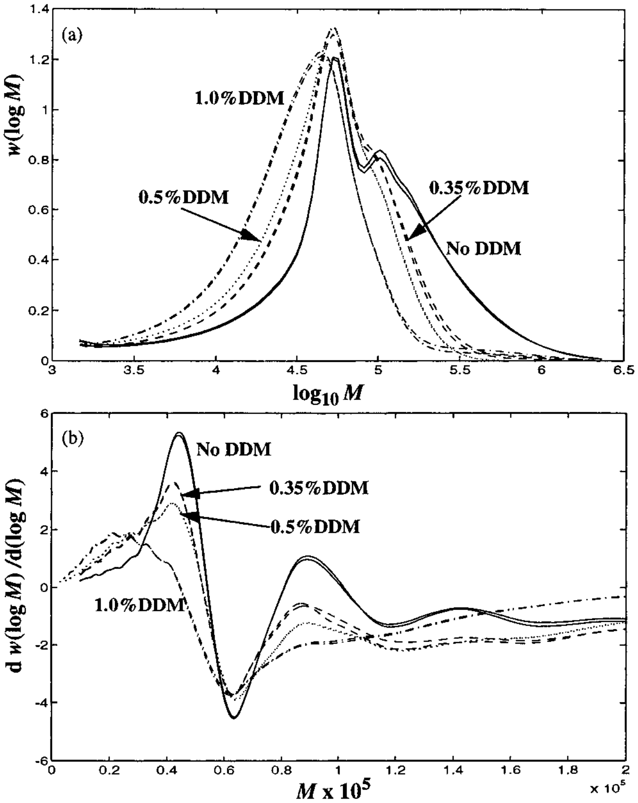

Figure 4. MWDs of PLP-generated pMMA, with variable levels of DDM (vol %) chain-transfer agent: (a) MWDs from SEC; (b) derivative curves. $T = 40$ °C, 10 Hz, 1 mmol/L benzoin photoinitiator, 30 mJ/pulse. Duplicate curves at each condition.

ing arguments do not replace the need for detailed simulation of the PLP-generated MWD (for a discussion of such detailed simulations see refs 7 and 11 and the references contained therein), but illustrate how experimental conditions, through variation of [I], pulse energy, t_0, and [M], can be judiciously changed in order to remain within the robust operating regime where the laser pulses are the dominant chain-starting and chain-stopping processes and the resulting MWDs have primary and secondary inflection points suitable for k_p determination. If chain-transfer reactions become excessive (small DP_{tr}/DP_0) or if the extent of termination is either too great (β large) or too small (β small), this condition is violated. The resulting MWDs lack the characteristic secondary inflection points and cannot be used reliably to determine k_p. These concepts have been previously used (but not as clearly stated) to obtain reliable k_p information for VAc, a monomer that has high termination, significant chain-transfer to monomer, and high k_p values.[6,7] In this work, they are applied to acrylate systems, which have proven to be an even greater challenge.

Experimental Section

The experimental pulsed-laser setup has been described previously.[6] The Quanta-Ray pulsed Nd:YAG GCR-190-100 laser with digital delay generator (Stanford DG-535) allows repetition rates to be adjusted up to a maximum of 100 Hz. A harmonic generator provides light of wavelength 355 nm which has a half-height pulse width of 6 ns. At 100 Hz the maximum pulse energy is 75 mJ. (In this work, the energy reported is the exit energy of the laser; the incident power that reaches the sample is ~20% less.)

The *n*-butyl acrylate (BA; Kodak) samples containing either benzoin (Aldrich) or 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba-Geigy) as photoinitiator were pulsed for sufficient time to convert 0.5–2.5% of the 4 mL monomer sample to polymer; conversion was measured gravimetrically. Care was taken to assure that the temperature during pulsing did not rise more than 3–4 °C; in most polymerizations the temperature increased by less than 2 °C. (For BA, a 4 °C temperature rise increases k_p less than 5%, well within the experimental scatter observed.) The photoinitiators were used as received. BA was distilled under vacuum prior to polymerization, and then stored at 5 °C. The acrylate experiments were run with a laser pulse repetition rate of 100 Hz, pulse energies of 2–75 mJ, and photoinitiator concentrations ([I]) of 0.2–20 mmol/L. For the experiments in which low molecular weight pMMA ($M_w = 6210$) was added prior to polymerization, 1.8 g of the polymer was dissolved in 30 mL of BA by shaking the mixture overnight. The benzoin was dissolved in 10 mL of BA on the day of the experiment, and the two solutions were mixed and shaken to give a final benzoin concentration of 0.25 mmol/L. Polymerizations of *n*-dodecyl acrylate (DA; Aldrich) and 2-ethylhexyl acrylate (EHA; Aldrich) were performed in the same way except that they were used as received, without removal of inhibitor. The transfer studies with methyl methacrylate (MMA; Aldrich) and *n*-dodecyl mercaptan (DDM; Aldrich) were also carried out using the reagents as received, with a 10 Hz laser pulse repetition rate, 1 mmol/L benzoin, and pulse energies between 30 and 40 mJ.

Table 1. Mark–Houwink Parameters at 30 °C in THF

polymer	K (dL/g)	a	ref
pS	11.4×10^{-5}	0.716	TD-SEC (6)
pBA	12.2×10^{-5}	0.700	TD-SEC (this work)
	7.4×10^{-5}	0.75	Penzel, Goetz (17)
	8.57×10^{-5}	0.865	Davis *et al.* (8)
pEHA	8.2×10^{-5}	0.695	TD-SEC (this work)
	11.1×10^{-5}	0.68	Penzel, Goetz (17)
pDA	29.2×10^{-5}	0.585	TD-SEC (this work)
	27.3×10^{-5}	0.58	Penzel, Goetz (17)

SEC analyses were performed on an instrument consisting of a Waters pump (Model 590), a Waters autosampler (WISP 712), two SHODEX columns (KF80M), and a Waters differential refractometer (Model 410) at 30 °C. The PLP-generated samples (5–25 mg/mL polymer in monomer) were diluted in THF to polymer concentrations of 1–3 mg/mL for SEC injection. Except for pMMA, which was calibrated directly using narrow-MW pMMA standards, the analyses were based upon universal calibration referenced against a primary polystyrene (pS) calibration established with narrow-MW standards. Details were reported previously on the transformation of the MWD as pS into the MWD of the polymer of interest.[6] The Mark–Houwink (M-H) parameters necessary for this procedure were determined by the use of a triple detector instrument (TD-SEC) consisting of a refractive index detector, a multiangle light scattering detector, and a viscometer. Details on this multidetector system are found in the literature.[6,16] As described previously, numerous checks were employed to validate the TD-SEC results, and the M-H parameters determined for styrene, vinyl acetate, and a variety of methacrylates were in good agreement with previously published values.[6] The Mark–Houwink constants obtained for pBA, pEHA, pDA, and pS are included in Table 1, along with other values found in the literature.

Figure 5 demonstrates the influence of these different M-H parameters for pBA on the MWD of a single polymer sample. The MWDs obtained using the M-H parameters from TD-SEC and those published by Penzel and Goetz[17] show very good agreement, whereas the MWD calculated with M-H parameters reported by Davis *et al.*[8] is shifted so that the molecular weights are roughly half the values obtained using the other two sets. For pEHA and pDA, the agreement of the MWDs from calibration with M-H parameters from TD-SEC and those reported by Penzel and Goetz[17] is as good as presented for pBA. This good agreement, combined with the previous excellent results for the TD-SEC system,[6] leads to the conclusion that the parameters published by Davis *et al.*[8] are in error and should not be used.

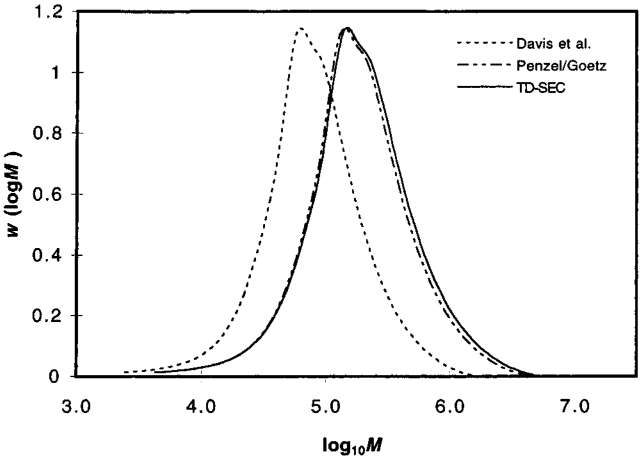

Figure 5. Effect of SEC calibration on PLP-generated MWDs of pBA. M-H parameters taken from 3 different sources (see Table 1 for references).

Inflection points are obtained by fitting the experimental MWD with cubic smoothing splines followed by differentiation of the splines. The SEC data (mass MWD on a logarithmic or *w*(log *M*) scale) are converted to mass (*w*(*M*)) and number distributions (*f*(*M*)) on a linear scale, with inflection points calculated from all three distributions.[4] For the lower temperatures of 5 and 10 °C, the position of the inflection point in all three derivatives did not differ significantly; as reported earlier,[4] the consistency of the inflection point location can be used as an additional check of data validity. However, inflection points are not easily discernible from *f*(*M*) and *w*(*M*) derivative plots for the higher temperature acrylate MWDs, which are broader with less pronounced inflection points (see discussion below). Thus, the inflection points obtained from the acrylate *w*(log *M*) distribution are used to calculate k_p values from a rearranged form of eq 1:

$$k_p = \frac{M_0}{1000 \rho t_0} \tag{6}$$

where M_0 is the polymer MW at the inflection point, k_p has units of L mol^{-1} s^{-1}, and monomer density ρ has units of g/cm^3. Monomer densities as a function of temperature were taken from DIPPR[18] and are tabulated with the detailed experimental results.

Quantitative estimates of the radical concentration generated by a laser pulse, [ΔR•], can be made based on measured values of [I] and laser pulse energy using the following expression:[19]

$$[\Delta R^{\bullet}] = 2\Phi n_A \frac{1}{V} = 2\Phi \frac{E_p}{E_\lambda}(1 - 10^{-A})\frac{1}{V} \tag{7}$$

where Φ is the quantum yield, which represents the fraction of radicals which begin to propagate, n_A is the number of photons absorbed by the sample, V is the sample volume, E_p is the pulse energy incident on the sample, E_λ is the energy of 1 mol of photons, and A is the absorbance of the sample. For this system, Φ is not known and E_p must be approximated with the laser exit energy; thus, an alternative quantity, [ΔR•]′, is defined as a relative measure of radical concentration:

$$[\Delta R^{\bullet}]' = \frac{[\Delta R^{\bullet}]}{2\Phi} = n_A \frac{1}{V} = \frac{E_p}{E_\lambda}(1 - 10^{-A})\frac{1}{V} \tag{7a}$$

In eq 7a, E_p, pulse exit energy, is measured using a laser power meter (Coherent Labmaster Ultima, Model 30V sensor) for known laser pulse repetition rate, E_λ is determined for the laser wavelength of 355 nm, and the sample volume is 4 mL. The absorbance of the sample at 355 nm was calculated according to Lambert−Beer's law, $A = \epsilon[\mathrm{I}]d$, with known initiator concentration and cell path length (d = 4 cm), and molar extinction coefficients, $\epsilon = 33 \times 10^3$ cm^2/mol and 200×10^3 cm^2/mol, for benzoin and DMPA, respectively. It must be emphasized that [ΔR•]′ is not an absolute estimate of radical concentration, but simply provides a relative measure of effective radical concentration for a given laser setup; even the values of [ΔR•]′ for different initiators should not be compared since the quantum efficiencies may be different. This relative measure, however, is a valuable tool for analyzing the relative levels of termination between experiments with different pulse energies and [I].

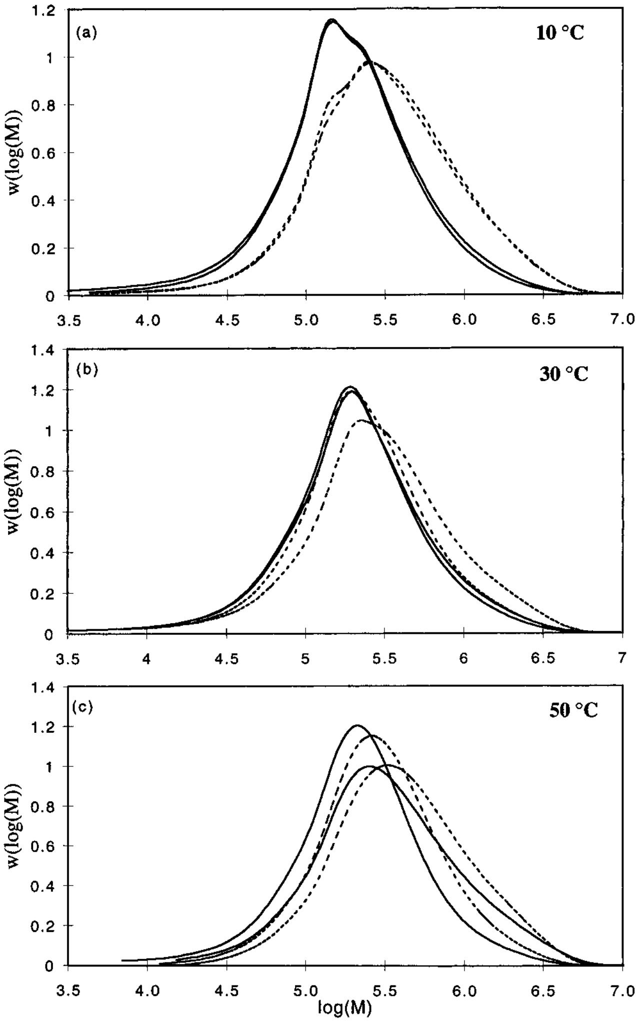

Figure 6. MWDs of PLP-generated pBA pulsed at 100 Hz with 5 mmol/L benzoin photoinitiator at (a) 10 °C, (b) 30 °C, (c) 50 °C. (—) 8 mJ/pulse, (- - -) 2 mJ/pulse.

Results

Figures 6 and 7 show the results of two sets of BA experiments which had the same 5 mmol/L initiator concentration, 10−50 °C temperature range, and 100 Hz pulse rate, but were performed at different laser power levels. Figure 6a shows that the peaks of the MWDs of polymer obtained at 10 °C are sharper and are shifted to lower molecular weights when the experiments are run at higher laser power. As the temperature is increased to 30 °C (Figure 6b), this difference becomes less pronounced, and at 50 °C (Figure 6c) the peaks obtained at different power levels are almost at the same molecular weights and equally broad. The derivative plots in Figure 7 show pronounced primary and secondary inflection points, indicated by the maxima M_0 and $2M_0$, respectively, at 10 °C for both power levels; note that, despite the difference in MWD peak positions (Figure 6a), consistent inflection points are found. At

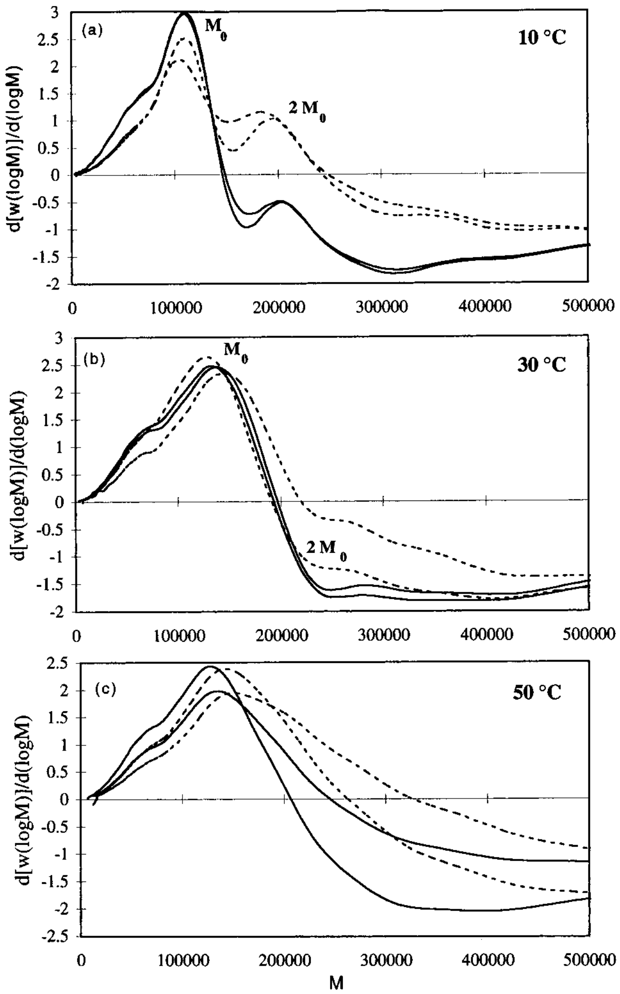

Figure 7. Derivative plots for PLP-generated pBA MWDs of Figure 6: (a) 10 °C, (b) 30 °C, (c) 50 °C. (—) 8 mJ/pulse, (- - -) 2 mJ/pulse.

30 °C secondary inflection points are still observable but are much smaller, and at 50 °C secondary inflection points cannot be seen. Furthermore, it can be seen that the primary inflection points for the 50 °C experiments occur at the same molecular weight as those measured at 30 °C. When both primary and secondary inflection points are observed, as at 10 and 30 °C, the experiments are included in the k_p data set; when there is no evidence of secondary inflection points (as at 50 °C), the results are not considered valid. The primary inflection points for the 10 and 30 °C experiments of Figures 6 and 7 correspond to k_p values of 12 000 L mol^{-1} s^{-1} and 15 500 L mol^{-1} s^{-1}, respectively.

Table 2 contains a summary of all successful BA experiments, reporting k_p values as a function of temperature, laser energy, and initiator concentrations; all data are for a pulse repetition rate of 100 Hz. Also included in the table are calculated values of $[\Delta R^\bullet]'$, a relative measure of radical concentration generated per pulse calculated by eq 7a; the experiments cover a wide $[\Delta R^\bullet]'$ range, with no observable effect on k_p. Experiments were also performed at temperatures greater than 30 °C over a wide range of $[\Delta R^\bullet]'$. However, like the 50 °C data of Figures 6 and 7, these experiments did not meet the selection criteria and are thus not included in Table 2. Further discussion of these results, both successful and unsuccessful, is reserved for the following section.

Table 2. Details of Successful Butyl Acrylate k_p Determinations from 100 Hz PLP Experiments[a]

T (°C)	E_p (mJ)	[I] (mmol/L)	$[\Delta R^\bullet]'$ (μmol/L)	M_0 (g/mol)	k_p (L mol^{-1} s^{-1})
5	57	0.5	6.0	108 780	11 878
($\rho = 0.9158$ g/cm^3)	57	0.5	6.0	108151	11 809
	72	0.5	7.5	104 557	11 417
	71	0.5	7.4	104 018	11 358
	70	1	14	96 842	10 575
	70	1	14	95 140	10 389
10 ($\rho = 0.9106$)	17	1	3.3	119 795	13 156
	17	1	3.3	115 474	12 681
	8	5	4.9	109 092	11 980
	8	5	4.9	110 439	12 128
	2	5	1.2	114 304	12 553
	2	5	1.2	108 464	11 911
	63	0.5	6.6	113 009	12 410
	63	0.5	6.6	118 323	12 994
	68	0.5	7.1	109 770	12 055
	68	0.5	7.1	110 669	12 153
	66	1	13	116 791	12 826
	66	1	13	110 849	12 173
	69	0.25[b]	3.7	124 367	13 658
	68	0.25[b]	3.7	113 819	12 499
15 ($\rho = 0.9054$)	63	0.5	6.6	124 548	13 756
	62	0.5	6.5	125 631	13 876
	55	0.5	5.8	124 728	13 776
	55	0.5	5.8	127 980	14 135
	67	0.5	7.0	122 743	13 557
	66	0.5	6.9	122 743	13 557
	66	1	13	115 800	12 790
	64	1	12	114 089	12 601
20 ($\rho = 0.9002$)	10	10	7.1	125 116	13 899
	9	10	6.4	124 033	13 778
	9	5	5.1	128 457	14 270
	8	5	4.6	129 270	14 360
	60	0.5	6.3	134 399	14 930
	60	0.5	6.3	134 671	14 960
	32	0.5	3.3	133 856	14 870
	64	0.25[b]	3.6	127 618	14 177
	63	0.25[b]	3.5	126 805	15 443
25 ($\rho = 0.8949$)	60	0.5	6.3	145 179	16 223
	60	0.5	6.3	139 378	15 575
	51	0.5	5.3	144 000	16 091
	50	0.5	5.2	149 897	16 750
30 ($\rho = 0.8896$)	8	5	4.8	137 412	15 447
	8	5	4.9	132 163	14 856
	2	5	1.2	150 843	16 956
	2	5	1.2	131 168	14 745
	6	5	3.7	138 771	15 599
	6	5	3.7	139 587	15 691
	62	0.5	6.5	141 190	15 871
	60	0.5	6.2	163 713	18 403
	60	0.5[c]	27	145 632	16 371
	59	0.5[c]	26	160 347	18 025
	56	1[c]	35	141 462	15 902
	55	1[c]	34	139 831	15 718
	63	0.25[b]	17	139 016	16 360
	64	1	40	148 345	16 676
	63	1	40	138 925	15 617

[a] All experiments with benzoin photoinitiator, unless otherwise marked. [b] With added PMMA. [c] DMPA photoinitiator.

Table 2 demonstrates that the k_p values are not only independent of the calculated radical concentration, but also of initiator type and added pMMA. These latter experiments were performed in an attempt to reduce the effective termination rate coefficient of the system by adding 5 wt % of pMMA prior to polymerization. A low MW pMMA was used to minimize overlap with the pBA MWD. Figure 8a presents the MWDs (on an expanded *y*-scale) obtained from these experiments conducted at 10–40 °C; the small insert shows the whole distribution for a polymerization at 10 °C. Although the peaks resulting from the pBA in the system are very small relative to the pMMA peak, the two polymers are clearly separated in the SEC columns. As seen in Figure 8b, the derivative plots show pronounced primary and secondary inflection points for the 10–30 °C

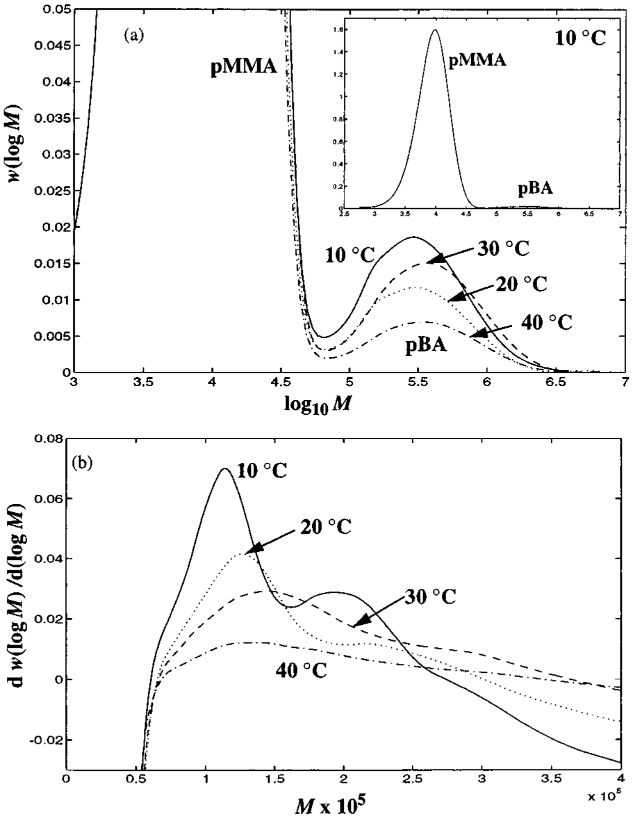

Figure 8. MWDs of PLP-generated pBA pulsed in the presence of 5% low-MW pMMA at 100 Hz with 0.25 mmol/L benzoin: (a) pBA MWDs on expanded scale (insert shows entire distribution for 10 °C experiment); (b) derivative curves.

experiments. However, the derivative plots for the higher temperature experiments again fail to show secondary inflection points and, thus, are not included in Table 2.

The Arrhenius diagram for the 57 k_p data points is presented in Figure 9. The variation of k_p with temperature is well fit by the following relation in the range 5 °C ≤ T ≤ 30 °C:

$$\ln[k_p\ (\mathrm{L\ mol^{-1}\ s^{-1}})] = (13.51 \pm 0.23) - (1157 \pm 68)\frac{\mathrm{K}}{T} \quad (8)$$

Very recently, Lyons and co-workers[10] have reported the successful application of the PLP-MWD to BA in the temperature range of −67 to −5 °C; experimental attempts at higher temperatures were deemed unsuccessful. Figure 10 plots both sets of experimental data. Although obtained in two very different temperature ranges, the data show reasonable consistency. An Arrhenius fit of the combined data sets yields:

$$\ln[k_p\ (\mathrm{L\ mol^{-1}\ s^{-1}})] = (16.71 \pm 0.09) - (2092 \pm 25)\frac{\mathrm{K}}{T} \quad (9)$$

This equation corresponds to an activation energy of 17.4 kJ/mol and a pre-exponential factor of 1.8 × 10^7 L $\mathrm{mol^{-1}\ s^{-1}}$. This activation energy is much closer to the value of 17.3 kJ/mol determined by Lyons *et al.*[10] from the low temperature data than the 9.6 kJ/mol value of eq 8, most likely due to the narrow temperature range over which k_p was determined in this work. It is further noted that recent PLP-MWD results of Buback *et al.*[20] are in good agreement with Figure 10.

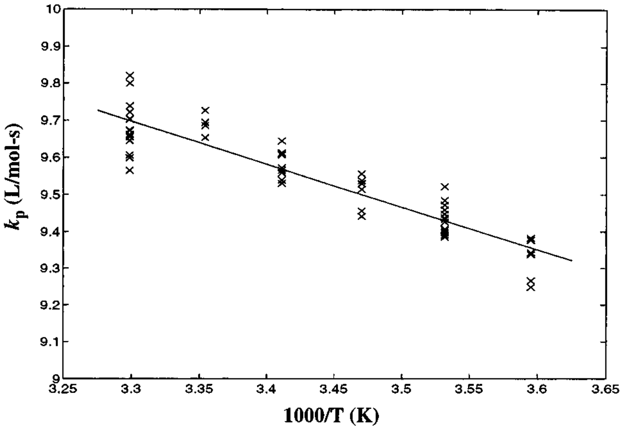

Figure 9. Arrhenius plot of all successful k_p determinations for BA (5 ≤ T (°C) ≤ 30). Best-fit line to the data is described by eq 8 in text.

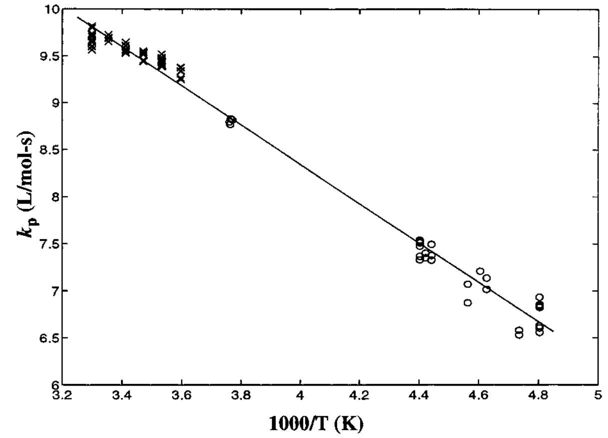

Figure 10. Arrhenius plot of all successful k_p determinations for BA from this work (×, 5 ≤ T (°C) ≤ 30) and from Lyons *et al.*[10] (○, −67 ≤ T (°C) ≤ −5). Best-fit line to the data is described by eq 9 in text.

Discussion

In this work, k_p of BA has been successfully determined for temperatures up to 30 °C, over a wide range of relative radical concentrations (see Table 2). At temperatures higher than 30 °C, however, variations of the estimated radical concentration over nearly 2 orders of magnitude did not produce MWDs from which k_p could be determined. To understand why PLP experiments fail at these higher temperatures, the experimental conditions and the resulting MWDs have been examined according to the concepts outlined in the introduction. To guide this discussion, rate coefficients for the termination and chain-transfer to monomer reactions must also be estimated. Literature values for these coefficients are sparse, show large scatter, and are usually reported as a ratio with k_p.[21] Using eq 8 for k_p, however, allows the reasonable estimation of the other important parameters.

Before discussing the effects of chain-transfer and termination, a few other possible interferences are considered. First, we have previously argued that SEC resolution may become a problem when the inflection points occur at relatively high molecular weights (>200 000).[7] Since that conjecture, however, we have used the same SEC instrument to distinctly resolve sharp inflection points at even higher molecular weights during a k_p study of dodecyl methacrylate.[6] Thus, poor SEC resolution is not a valid explanation.

Second, it has been shown that the choice of the photoinitiator may influence the MWDs such that the evaluation of k_p values becomes impossible.[22] Problems occur if the lifetime of the initiator triplet state is long compared to the addition rate of monomer units to the newly-formed radical; the noninstantaneous radical production leads to significant broadening of the MWDs.[22] Benzoin has a triplet lifetime of 10 ns[23] and has proven to be an effective initiator for PLP studies of many different systems.[1−8] However, since BA has a much faster addition rate than these other monomers, it was decided to use DMPA, which has a shorter triplet lifetime of 0.1 ns.[24] Of the DMPA experiments performed at 30, 35, and 40 °C, only the 30 °C data showed primary and secondary inflection points on the derivative plot; these data are included in Table 2 and are in good agreement with the k_p values measured with benzoin. As with benzoin, no secondary inflection points were observed in the MWDs produced at higher temperatures. Thus, it must be concluded that choice of photoinitiator (benzoin or DMPA) has no effect on these BA results.

Finally, it has also been argued that intramolecular chain-transfer (backbiting) reactions may occur with BA; at higher temperatures this competing reaction may become important enough to create a branched structure that affects SEC separation.[10] Alternately, it may be argued that backbiting reactions lead to a tertiary radical structure of differing reactivity than a secondary BA radical.[25] To examine this possibility, ^{13}C NMR analysis was performed on pBA generated by PLP at 50 °C; this technique can detect backbiting levels of greater 0.5% by examining for quaternary carbons.[25,26] No evidence of quaternary carbons was seen, strongly indicating that the lack of k_p information from the higher temperature experiments is not related to polymer branching reactions.

With these various arguments considered and rejected, we now turn to an examination of the effects of chain transfer and termination level on BA PLP experimental results.

Chain-Transfer. A few bounding experiments have been performed in order to establish the level of chain-transfer to monomer for BA, since no estimates could be found in the literature. A value of $(1.3 \pm 0.5) \times 10^{-4}$ was estimated for $k_{tr,M}/k_p$ using a PLP method described elsewhere;[15] no temperature dependence could be seen in the range of 40−80 °C within this scatter. This result is in reasonable agreement with an estimate of 8.2×10^{-5} from chemically-initiated polymerization experiments performed at 80 °C and is also comparable to a value of 9.3×10^{-5} measured for methyl acrylate at 50 °C using the same PLP technique.[27] In the analysis that follows, a temperature-independent value of 1×10^6 is assigned to M_{tr} ($=\mathrm{MW}_{mon}\mathrm{DP}_{tr}$), corresponding to $k_{tr,M}/k_p = 1.3 \times 10^{-4}$.

Termination. The conversion dependence of the coupled parameter k_p/k_t has been obtained for BA by Buback and co-workers[28,29] using the specialized pulsed-laser techniques developed in that lab. This prior work shows that the ratio of k_p/k_t changes only slightly in the 5−80% conversion range where k_t is controlled by reaction-diffusion[28,30] and that this ratio is independent of temperature. The value of k_t is not as well established, however, at the very low conversions (<2%) at which PLP experiments are performed to determine k_p.

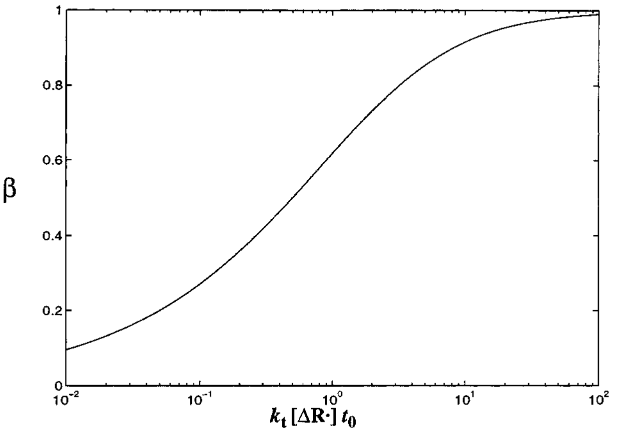

Figure 11. Fraction of radicals terminated between two successive laser pulses (β) as a function of $k_t[\Delta R^\bullet]t_0$, as calculated from eqs 2 and 3.

If it is assumed that the measured ratio for k_p/k_t of 2.5×10^{-4} (50 °C data from Figure 3 of ref 29) can be extrapolated back to zero conversion, an absolute value of $k_t = 6 \times 10^7$ L mol^{-1} s^{-1} is estimated at 30 °C (with k_p calculated from eq 8). If, however, termination is controlled by translational diffusion at low conversion, the absolute value may be significantly higher. We choose 3×10^8 L mol^{-1} s^{-1} as a reasonable bounding estimate. (Note that the value of k_p/k_t reported in ref 29 has been halved for this work. This is because eq 2 implies a termination rate expression of $k_t[R^\bullet]^2$, whereas ref 29 uses the convention that termination rate is $2k_t[R^\bullet]^2$.)

In order to design experiments from which k_p values may be successfully evaluated, it is necessary to maintain an intermediate value of β. Figure 11 contains a graphical representation of eqs 2 and 3, plotting β vs the product of $k_t[\Delta R^\bullet]t_0$. It is important to note that it is the product of the three variables that controls the level of termination in the system, and that adjustments to the experimental conditions ($[\Delta R^\bullet]$ or t_0) may be needed in order to find the right operating window for a particular monomer. Changing repetition rate from 10 to 100 Hz (t_0 from 0.1 to 0.01 s) necessitates a 10-fold increase in $[\Delta R^\bullet]$ in order to maintain β constant. Similarly, if an (arbitrarily-chosen) value of ~0.6 is desired for β at 100 Hz for the BA system, then $[\Delta R^\bullet]$ must be in the range of 1.7×10^{-6} mol/L if $k_t = 6 \times 10^7$ L mol^{-1} s^{-1}, and must be a factor of 5 lower if $k_t = 3 \times 10^8$.

It is instructive to re-examine the BA results using the above discussion as a guide. Figure 12 shows MWDs from many of the successful 10 and 30 °C experiments summarized in Table 2, as well as many unsuccessful 50 °C experiments. Conditions for the individual curves are not marked, but follow the expected trend that as $[\Delta R^\bullet]'$ decreases in value (see Table 2), the distributions move to higher MW values. Also included on the three plots are the expected position of the inflection points (M_0 calculated using k_p values from eq 8) and the estimated transfer limit of $M_{tr} = 1 \times 10^6$.

Table 2 indicates that radical concentrations were shifted over an order of magnitude by varying experimental conditions. The results of these shifts are seen clearly in Figure 12: at 10 °C the position of the distribution peak shifts from 1.5×10^5 to 4.0×10^5, while the observed inflection point remains invariant at $(1.1−1.2) \times 10^5$. The same is true of the 30 °C data—despite the wide range in peak position, all of

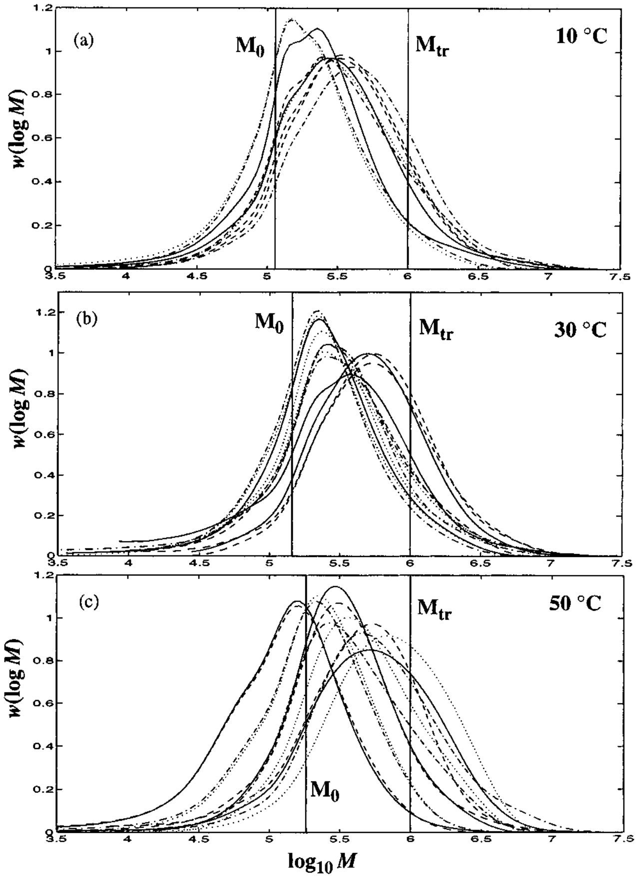

Figure 12. MWDs of PLP-generated pBA pulsed at 100 Hz at (a) 10 °C, (b) 30 °C, (c) 50 °C. Vertical lines indicate expected value of M_0 and estimated value of M_{tr}.

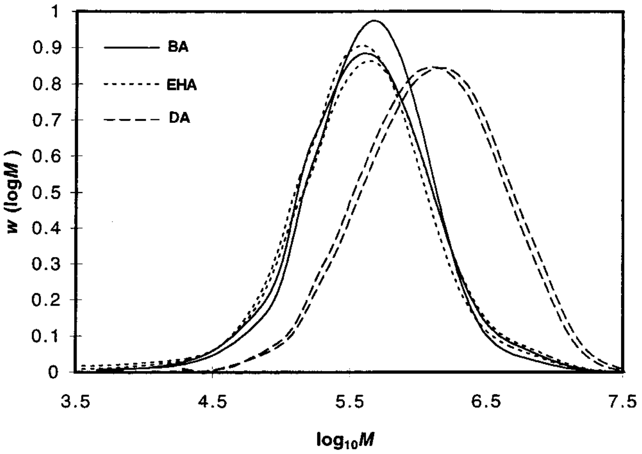

Figure 13. PLP-generated MWDs for pBA, pEHA, and pDA pulsed at identical conditions: 10 °C, 100 Hz, 0.5 mmol/L benzoin photoinitiator, 60 mJ/pulse. Duplicate experiments shown for each monomer.

these curves yielded consistent k_p estimates, and all had observable secondary inflection points on the derivative plots. However, the resolution of the inflection points from the 30 °C derivative plots is more difficult than at 10 °C (see Figure 7). Unfortunately, this loss of resolution continues with increasing temperature. Despite the success at 10 and 30 °C, no k_p estimates could be obtained at 50 °C, even though experiments were conducted over a wide range of radical concentrations. Indeed, Figure 12c shows that the expected position of the 50 °C inflection point (2×10^5) is encompassed by the experimental MWDs, whose peak positions cover the range of $(1.6-8.0) \times 10^5$. It was not possible to extend the temperature range for k_p evaluation either by reducing effective k_t (adding 5% of pMMA to the solution to increase viscosity) or by varying radical concentrations over a wide range. These data—both unsuccessful and successful—provide a strong argument against using the MWD peak position as an estimate of M_0, as suggested by Sarnecki and Schweer.[11]

We can offer no definitive explanation as to why the attempts to determine k_p for BA at temperatures greater than 30 °C were not successful. An examination of Table 3, however, provides some insights. Rate coefficients for MMA,[5-7] VAc,[6,7] and BA are used to calculate DP_0 values and DP_{tr} estimates. It is obvious that chain transfer does not interfere with determination of k_p for MMA. However, the lower MMA k_t value does make k_p determination at 100 Hz more difficult, as the low termination limit is approached (see Figure 3). Examination of VAc at 10 Hz was difficult because of both high termination and high levels of chain transfer;[7] operation at 100 Hz made it possible to simultaneously move away from both of these limits.[6] The termination behavior of BA is probably intermediate between MMA and VAc, and experimental conditions were varied to cover a wide range of relative termination levels (see Figure 12). While yielding k_p values at 30 °C and lower, this approach was not successful at higher temperatures. Thus, we conclude that part of the difficulty with BA arises due to chain transfer; with increasing temperature the value of DP_0 approaches the DP_{tr} limit. (If $k_{tr,M}/k_p$ increases slightly with increasing temperature, as is commonly observed,[21] DP_{tr} will decrease, exacerbating the problem.) The MMA/DDM data of Figure 4 indicate that resolution of the inflection points becomes difficult when $DP_{tr}/DP_0 \sim 2$. Although the estimated ratio for BA is higher than this (5.5 at 50 °C), significant chain-transfer combined with a higher termination rate is hypothesized to be the source of the experimental difficulties. In addition, simulations have shown that termination by combination, thought to be more significant for BA than VAc, can further obscure the detection of secondary inflection points.[11]

Other Acrylates. It is instructive to compare BA PLP-MWD results with those obtained for 2-ethylhexyl acrylate (EHA) and *n*-dodecyl acrylate (DA). These heavier acrylates are known to have significantly lower k_t values than BA;[9] Figure 2 illustrates how the corresponding decrease in k_t in the methacrylate family significantly changes the shape of the PLP-generated MWD. Figure 13, however, indicates that MWDs produced by PLP of EHA and DA are similar in shape to the BA curves, despite the order-of-magnitude decrease in k_t. This result is consistent with the conclu-

Table 3. A Comparison of MMA, VAc, and BA Kinetic Coefficients and Characteristic Chain Lengths

	k_p (L mol^{-1} s^{-1})	k_{tr}/k_p	k_t (L mol^{-1} s^{-1})	DP_{tr}	DP_0 (10 Hz)	DP_0 (100 Hz)	DP_{tr}/DP_0 (100 Hz)
MMA (30 °C)	400	8×10^{-6}	3×10^7	125000	370	37	3380
VAc (30 °C)	4 000	2.0×10^{-4}	20×10^7	5000	4300	430	11.6
BA (10 °C)	12 500	1.3×10^{-4}	$(6-30) \times 10^7$	7700	8900	890	8.6
BA (30 °C)	16 300	1.3×10^{-4}	$(6-30) \times 10^7$	7700	11300	1130	6.8
BA (50 °C)	20 700	1.3×10^{-4}	$(6-30) \times 10^7$	7700	14000	1400	5.5

Table 4. Details of Successful 2-Ethylhexyl (EHA) and *n*-Dodecyl (DA) Acrylate k_p Determinations from 100 Hz PLP Experiments with Benzoin Photoinitiator

	T (°C)	ρ (g/cm^3)	E_p (mJ)	[I] (mmol/L)	$[\Delta R^\bullet]'$ (μmol/L)	M_0 (g/mol)	k_p (L mol^{-1} s^{-1})
EHA	5	0.8972	63	0.5	28	109 845	12 243
			63	0.5	28	103 709	11 559
	10	0.8932	59	0.5	26	119 561	13 338
			58	0.5	26	116 750	13 025
	15	0.8892	34	1	21	146 077	16 429
			33	1	21	135 935	15 288
	20	0.8851	57	0.5	25	144 860	16 366
			56	0.5	25	144 937	16 375
			31	1	20	150 802	17 038
			31	1	19	150 802	17 038
	25	0.8811	31	1	19	158 253	17 962
			31	1	19	159 437	18 096
DA	10	0.878	31	1	19	165 138	18 808
			31	1	19	158 297	18 029
			55	0.5	25	150 554	17 147
			54	0.5	24	146 401	16 674
	20	0.870	51	0.5	23	162 227	18 647
			49	0.5	22	164 281	18 883
	30	0.862	21	1	13	187 568	21 760
			23	1	14	193 656	22 466

sion that these experiments are performed near the chain-transfer limit for the acrylates.

Table 4 contains a summary of successful k_p determinations for EHA and DA. As with BA, experiments were unsuccessful at temperatures above 30 °C. Activation energies are not reported because of the narrow temperature range, the scatter in the data, and the limited number of values; the DA results are consistent with previous work by Kurz.[9] A comparison of these k_p values with the BA results indicate that k_p increases with increasing acrylate size; preliminary methyl acrylate results are consistent with this trend.[9,31] A similar increase in k_p with length of the ester group has also been reported for the methacrylates.[6]

Conclusions

For the successful determination of k_p using the PLP-MWD technique, it is necessary that successive laser pulses provide the dominant chain-starting and chain-stopping mechanisms. Experimental results clearly illustrate transitions from the robust operating region (where both primary and secondary inflection points are observable on the MWD derivative plot) to high-termination, low-termination, and chain-transfer-dominated regions where the determination of k_p is not possible. These insights are used to guide an extensive PLP/MWD study of BA, and the successful evaluation of k_p up to 30 °C. The results were obtained over a wide range of radical concentrations and are consistent with a recent low temperature study of the same monomer.[10] However, it was not possible to determine k_p at higher temperatures despite the variation of radical concentrations over nearly 2 orders of magnitude. This failure is attributed to approaching the chain-transfer limit, suggesting that it should be possible to measure k_p at higher temperatures by pulsing with even higher laser repetition rates in order to increase the ratio of DP_{tr}/DP_0. Solution experiments may also extend the k_p temperature range,[7] provided that a solvent whose chain-transfer activity is significantly less than that of BA monomer can be identified.

Limited k_p data are also reported for DA and EHA. These and other emerging PLP/MWD results for the acrylates[9,10,20,31] provide a consistent picture of chain-growth behavior. Like the methacrylates,[6] k_p increases in magnitude with increasing ester size. Acrylate k_p values are 20−30 times higher than those of the corresponding methacrylates, however, and have a significantly smaller temperature dependence.

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