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Determination of Free-Radical Chain-Transfer Rate Coefficients by Pulsed-Laser Polymerization

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ABSTRACT: Analysis of the molecular weight distributions (MWDs) of polymer produced by pulsed-laser techniques—extensively used as a robust tool for the determination of free-radical propagation rate coefficients (k_p)—is shown to be an effective method for measuring chain-transfer rate coefficients (k_{tr}). In contrast to the determination of k_p, experimental conditions to study chain transfer must be chosen to minimize the effect of radical–radical termination on the MWD. Employing the slope of the semilog number distribution rather than number-average MW provides a robust, reproducible method for the estimation of k_{tr}/k_p. Methodology for the new technique is developed through an extensive study of chain transfer to *n*-dodecyl mercaptan (DDM) in methyl methacrylate (MMA), for which k_{tr}/k_p is shown to be independent of temperature in the range of 20–80 °C. Results for chain transfer to DDM in styrene, ethyl methacrylate (EMA), and *n*-butyl methacrylate (BMA) are also presented; the value of k_{tr}/k_p does not vary with methacrylate type but is 20 times higher for styrene than for the methacrylates.

Introduction

The use of pulsed-laser techniques as a probe to examine free-radical polymerization systems has grown rapidly in the past decade. In particular, pulsed-laser polymerization (PLP) combined with gel permeation chromatography (GPC) analysis has proven to be a direct and robust method for estimating free-radical propagation rate coefficients (k_p) from molecular weight distributions (MWDs). Since the pioneering work of Olaj and co-workers,[1,2] the technique has been used to measure k_p values for a number of monomers and even comonomer systems.[3,4] Our previous efforts have resulted in the determinations of k_p values over a wide temperature range for methyl methacrylate (MMA), styrene, and chloroprene;[5] vinyl acetate;[6] and ethyl methacrylate (EMA), butyl methacrylate (BMA) and isobutyl methacrylate.[7]

While precise measurement of free-radical propagation rate coefficients is essential for understanding and modeling overall reaction rates, it does not provide sufficient information about the molecular weight of the polymer produced. MW is controlled by the relative rate of chain growth (propagation) to chain-stopping events such as radical–radical termination and radical transfer to monomer, solvent, or added chain-transfer agents. The competitive nature of these events is evident by looking at a simple scheme for homopolymerization:

Initiation: $I \xrightarrow{k_d} 2I^{\bullet}$

$$I^{\bullet} + M \xrightarrow{\text{fast}} P_1$$

Propagation: $P_n + M \xrightarrow{k_p} P_{n+1}$

Chain Transfer:

to Monomer: $P_{\mathrm{n}} + M \xrightarrow{k_{tr}^{mon}} D_n + P_1$

to Agent: $P_n + A \xrightarrow{k_{tr}^{A}} D_n + I^{\bullet}$

Termination: $P_n + P_m \xrightarrow{P_m} D_n + D_m$

where *I* is the initiator, *A* is an additional chain-transfer agent, *M* is the monomer, P_n is a growing polymer chain of length *n*, and D_n is a dead polymer chain of length *n*. In this scheme, no attempt has been made to differentiate the nature of primary radical species denoted by $I^{\bullet}$, and the termination reaction has been written as a disproportionation mechanism showing no chain-length dependence.

In early work, Olaj employed the PLP/GPC technique in order to estimate low-conversion termination rate coefficients (k_t).[8] However, the calculations were dependent on careful measure of the overall reaction rate and the assumption that chain-transfer reactions were negligible. These requirements are in contrast to the use of PLP for determination of k_p, where the strength of the technique is that it requires no rate measurements and no assumptions about other polymerization mechanisms. Thus, the power and simplicity of the PLP/GPC technique for k_p determination is lost when extended to k_t. Other laser techniques combined with on-line spectroscopy provide a more appropriate means of probing the diffusion-controlled kinetics of the termination reaction; these techniques have been developed by Buback and co-workers.[9,10]

For many industrially-important systems, it is the chain-transfer reactions which control the polymer MW. In some cases the chain-transfer agent (CTA) is added purposely in order to lower the polymer MW; for other systems a powerful CTA may be present in the system as an unwanted impurity. In either case, a good

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estimate of the transfer rate coefficient (k_{tr}) is needed. It is often difficult to separate out the effects of transfer to CTA from other chain-stopping events. Historically, this separation is achieved by performing experiments over a range of CTA concentrations ([A]), and plotting the resultant number-average chain length ($\mathrm{DP_n} = \mathrm{M_n}/\mathrm{MW_{mon}}$) according to:

$$1/\mathrm{DP_n} = 1/\mathrm{DP_0} + (k_{\mathrm{tr}}^{\mathrm{A}}/k_{\mathrm{p}})[\mathrm{A}]/[\mathrm{M}] \qquad (1)$$

where $\mathrm{DP_0}$ represents the polymer number-average chain length in the absence of added CTA. (See ref 11 for an overview of the classical methods for examining chain transfer.) This type of analysis, which requires accurate determination of $\mathrm{M_n}$, was first suggested by Mayo and is quite sensitive to baseline errors on the low-MW side of the distribution. As a result, some workers have used $\mathrm{M_w}$ and the assumption that $\mathrm{M_w/M_n} = 2$ to analyze chain-transfer mechanisms with eq 1.[12] More recently, it has been suggested by Gilbert and co-workers[13-15] that a more robust measure of chain transfer is obtained by examining the slope of the appropriately transformed MWD.

In this work, the analysis technique suggested by Gilbert and co-workers is combined with the speed and robustness of PLP. The strengths and limitations of applying PLP techniques for the estimation of k_{tr} are examined both theoretically and experimentally. Through an extensive set of experiments examining the transfer ability of *n*-dodecyl mercaptan (DDM) in MMA, confidence is gained in the technique, and criteria are defined for use of PLP for chain-transfer studies. Results are also presented for chain transfer to DDM in styrene, EMA, and BMA monomer systems.

Theoretical Considerations

The competitive nature of propagation, transfer, and termination events is reflected in the balance on radicals with chain length n, based upon the kinetic scheme given previously:

$$\frac{\mathrm{d}P_{\mathrm{n}}}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}]P_{n-1} - (k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0)P_n \qquad (2)$$

where the total growing polymer chain concentration is defined as $\mu_0 \equiv \sum_{n=1}^{\infty} P_n$. Making the quasi-steady state assumption (QSSA) on radical concentration leads to a recursive relationship for P_n:

$$P_n = \left(\frac{1}{1 + \dfrac{k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0}{k_{\mathrm{p}}[\mathrm{M}]}}\right) P_{n-1} \qquad (3)$$

Through repeated substitutions P_n can be related to P_1, the concentration of monomeric radicals:

$$P_n = \left(\frac{1}{1 + \dfrac{k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0}{k_{\mathrm{p}}[\mathrm{M}]}}\right)^{n-1} P_1 \qquad (4)$$

To complete the derivation, a balance for P_1 is written:

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = R_{\mathrm{init}} + (k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}])\mu_0 - (k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0)P_1 \qquad (5)$$

where R_{init} represents the generation rate of new radicals through initiation. An algebraic relation results by again invoking QSSA; substitution into eq 4 leads to:

$$P_n = \left(\frac{R_{\mathrm{init}} + k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}]\mu_0 + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}]\mu_0}{k_{\mathrm{p}}[\mathrm{M}]}\right) \times \left(\frac{1}{1 + \dfrac{k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0}{k_{\mathrm{p}}[\mathrm{M}]}}\right)^{n} \qquad (6)$$

This expression is well approximated by an exponential relationship between P_n and n, providing that the probabilities of transfer and termination events are small compared to propagation (valid for the production of long-chain polymer):

$$P_n \sim \exp\left(-\frac{k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0}{k_{\mathrm{p}}[\mathrm{M}]} n\right) \qquad (7)$$

The instantaneous distribution of dead polymer chains (D_n) follows the same relationship for systems for which termination by combination is not important. A semilog plot of $f(n)$—the number fraction of polymer molecules of length n ($\equiv D_n/\sum_{n=1}^{\infty} D_n$)—vs n yields a slope of:

$$\frac{\mathrm{d}\ln(f(n))}{\mathrm{d}n} = -\frac{k_{\mathrm{tr}}^{\mathrm{mon}}[\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{A}] + k_{\mathrm{t}}\mu_0}{k_{\mathrm{p}}[\mathrm{M}]} \qquad (8)$$

An estimate for $k_{\mathrm{tr}}/k_{\mathrm{p}}$ is obtained by examining how the slope of the semilog number distribution varies with CTA level:

$$\frac{\mathrm{d}\ln(f(n))}{\mathrm{d}n} = a - \left(\frac{k_{\mathrm{tr}}^{\mathrm{A}}}{k_{\mathrm{p}}}\right)[\mathrm{A}]/[\mathrm{M}] \qquad (9)$$

where a includes the contribution of all other chain-stopping events.

The forms of eqs 9 and 1 are similar. Both are based upon eq 7 and, with no errors in the analysis, both will give the same estimate for $k_{\mathrm{tr}}/k_{\mathrm{p}}$. However, using the slope of the MWD—the method outlined by Gilbert and co-workers[13-15]—provides a more robust estimate for transfer in the system, since it less dependent on the tails of the distribution. For whichever method of analysis is used, however, the best estimate for $k_{\mathrm{tr}}/k_{\mathrm{p}}$ is obtained when the contributions of the other chain-stopping mechanisms are small compared to that from the chain-transfer mechanism under study; in other words, the intercept value of eq 9 (or the $1/\mathrm{DP_0}$ value of eq 1) should be close to zero.

The derivation behind eqs 8 and 9 has been presented in detail in order to emphasize the underlying assumptions:

(1) The concentrations of all radical species are at quasi-steady state, so that the recursive relationship between P_n and P_1 (eq 4) is valid.

(2) Equations 7 and 8 describe the *instantaneous* MWD of the polymerizing system. For the cumulative MWD to equal the instantaneous distribution, it is necessary to run experiments so that any variation in [M], [A], and μ_0 (radical concentration) does not have a large effect on the analysis.

(3) Equation 8 applies when termination is by disproportionation, with no chain-length dependence. In this work, experimental conditions are chosen so that chain transfer to agent dominates the MWD. Thus, the

results reported are not affected by the exact mechanism of radical–radical termination. Cases in which the chain-length dependence and termination by combination are important are discussed in detail by Clay and Gilbert.[14]

It is necessary to determine under what conditions it is possible to combine PLP—inherently a non-steady-state process—with the analysis technique developed assuming a steady state.

The PLP technique involves the exposure of a monomer/photoinitiator system to laser flashes, which generate a burst of new initiator radicals in a controlled and periodic fashion. Between flashes, which occur every t_0 seconds, radical concentration in the system decreases due to radical–radical termination:

$$\frac{d\mu_0}{dt} = -k_t\mu_0^2; \qquad kt_0 < t < (k+1)t_0 \tag{10}$$

Integration of this equation leads to an explicit expression for the variation of the total radical concentration with time:

$$\mu_0(t) = \frac{\mu_0^{\max}}{1 + k_t\mu_0^{\max}(t - kt_0)}; \qquad kt_0 < t < (k+1)t_0 \tag{11}$$

where $\mu_0^{\max}$ is the radical concentration immediately following the kth laser pulse.

To determine k_p using PLP, it is necessary that a fraction of the growing polymer radicals survive without undergoing a termination or transfer event, until the next pulse of radicals are generated t_0 seconds later. Those radicals will have propagated to a chain length P_0, given by the simple equation:

$$P_0 = k_p[M]t_0 \tag{12}$$

When the next flash arrives, these surviving radicals are exposed to a high concentration of newly generated radicals, which leads to a greatly increased probability for their termination. Thus, the formation of dead polymer molecules with length close to P_0 is favored. With a measure of P_0 from the GPC analysis, k_p can be directly calculated from eq 12.

When determining k_p, conditions are chosen to minimize the number of transfer events between laser pulses and to ensure that the radical concentration decreases significantly between pulses. Under these conditions, the laser pulse is the major source of monomeric radicals (P_1), and dead polymer is formed predominantly by radical–radical termination. Thus, it is not possible to use the QSSA for eqs 2 and 5, and the recursive relationship between P_n and P_1 (eq 4) is not valid. The conditions required for the study of chain transfer are much different; it is necessary to design the experiments so that the majority of radicals undergo a chain-transfer event before the next pulse arrives. Radical concentration in the PLP system still varies with time according to eq 11, but now most of the dead polymer chains are formed by transfer rather than termination events, and a large fraction of monomeric radicals are also formed through transfer events. Under these conditions, eq 4 can be shown to provide a reasonable approximation of the system.

The two situations are contrasted by the simulation results shown in Figures 1 and 2. The simulations represent PLP of bulk MMA at 40 °C with and without the addition of DDM as a chain-transfer agent. Other simulation parameters are summarized on the figures.

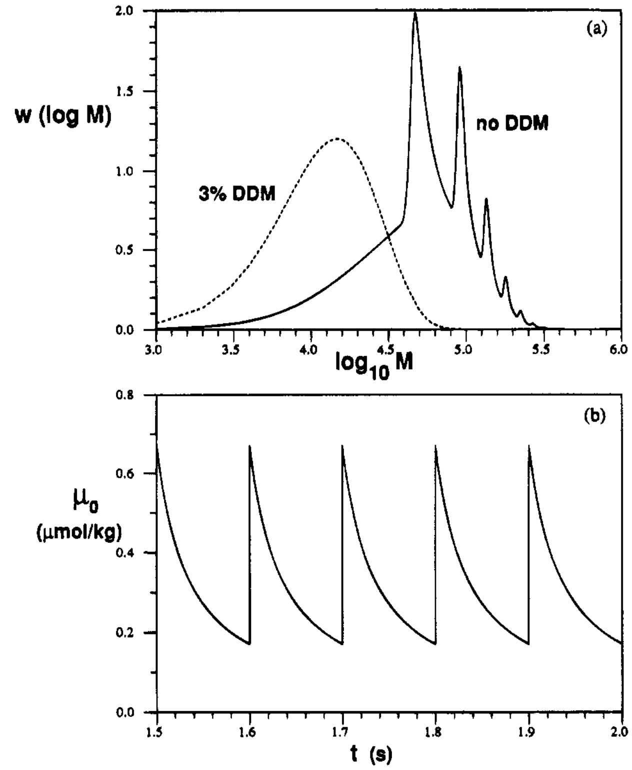

Figure 1. Simulation of PMMA produced at 40 °C by PLP at 10 Hz (t_0 = 0.1 s), with and without the addition of 3 wt % DDM: (a) GPC mass MWD; (b) total raddical concentration vs time. Simulation parameters: 0.5 μmol/kg radicals generated per pulse; total time = 2 s (20 pulses); k_p = 478 L/mol·s; $k_t = 4.8 \times 10^7$ L/mol·s; $k_{tr}^{A}/k_p = 0.7$; ϱ_{mon} = 0.9194 g/mL.

The model used to generate the figures includes full differential chain balances based upon the kinetic mechanisms given in the introduction; a full description of the model development and implementation was presented previously.[6] To simplify this example, chain transfer to monomer (which is negligible for MMA under these conditions) is set to zero.

The resultant MWDs for the two simulations are shown in Figure 1a. Multiple narrow peaks are observed on the MWD simulated for pure MMA. It is the lowest MW peak from which the estimate of P_0 used to calculate k_p is obtained (see eq 12). Secondary peaks are created by polymer chains which survive multiple laser pulses.[1] When DDM is added to the system as a CTA, the MWD shape and position changes radically; the entire distribution shifts to a lower MW range, and the sharp peaks disappear. It is important to note that, despite the very different appearances of the MWDs, both were generated by PLP with the same time-varying radical profile shown in Figure 1b. Roughly 75% of the radicals are consumed between subsequent pulses, with a sudden burst of termination occurring every t_0 seconds as the next population of monomeric radicals is generated by the laser.

Even though *total* radical concentrations (Figure 1b) are the same for the two cases, the *distributions* of radical chain lengths are very different. Parts a and b of Figure 2 show snapshots of radical distributions (concentration vs chain length) at 0.01, 0.04, 0.07, and 0.10 s following a laser pulse; the distribution at 0.10 s is that seen at the instant the next laser pulse arrives. In the absence of chain-transfer events (Figure 2a), the distributions remain narrow, shifting to longer chain lengths with increasing time. (The secondary peaks observed in Figure 2a at longer chain lengths are radicals which have survived from the previous laser

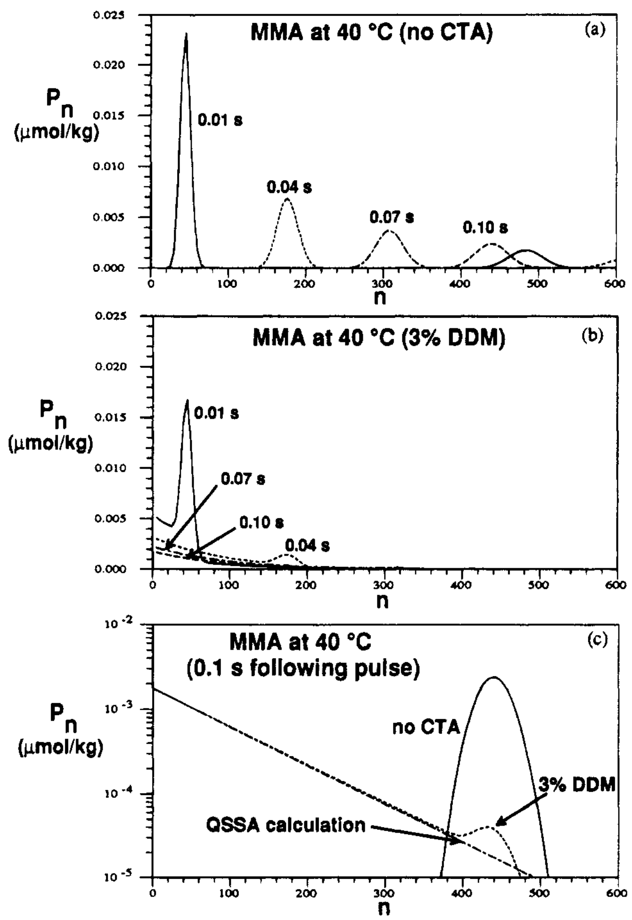

Figure 2. Radical chain-length distributions for simulations of Figure 1. Snapshots of distributions taken at 0.01, 0.04, 0.07, and 0.10 s following a laser pulse: (a) no added CTA; (b) with 3% DDM. (c) Snapshot at 0.10 s following a pulse compared with that calculated according to eq 4.

pulse; this secondary radical wave causes the secondary MWD peak observed in Figure 1a.) The position of the radical wave front is directly related to time, since the only generation of monomeric radicals (P_1) is from the laser pulse. As outlined by Olaj *et al.*,[1] this time–chain length relation is the whole premise for the estimation of k_p by eq 12. For this case (no chain transfer), it is obvious that the concentration of P_n is not related to P_1 according to eq 4. The addition of significant rates of chain transfer changes the nature of the system; the radical chain-length distributions (Figure 2b) now have two components. The periodic generation of P_1 at each laser pulse still occurs, but the radical wave dissipates rapidly following the pulse due to chain transfer. These chain-transfer events continuously generate new P_1 species, which populate the radical distribution behind the moving pulse wave front.

Figure 2c provides a closer look at the radical chain-length distributions for the two cases just before the arrival of the next pulse, at $t_0 + 0.1$ s. On the semilog scale, the radical wave created by the laser pulse is evident as the peak observed at chain length 440. Without added CTA, this peak contains the entire population of radicals in the system. For the system with added CTA, however, the peak is small compared to the rest of the distribution. Also shown on Figure 2c is the distribution calculated according to eq 4, which assumes a steady-state relationship between chains; the values of μ_0 and P_1 are taken from the simulation. Equation 4 provides a good representation of the radical distribution for the case where chain transfer dominates the system. This agreement illustrates that the use of eqs 8 and 9 for the calculation of k_{tr}/k_p from pulsed-laser-generated polymer is valid, as long as chain transfer is the MW-controlling mechanism.

Two conditions must be met in order to measure transfer rates by PLP. First, chain-transfer events must dominate termination events:

$$k_t\mu_0 \ll k_{tr}^{A}[A] + k_{tr}^{mon}[M] \qquad (13)$$

where μ_0 varies with time according to eq 11. Transfer is favored if (a) the time between pulses is increased, allowing the radical concentration to decline to lower values, (b) the radical concentration generated per pulse (and thus μ_0^{max}) is lowered, and (c) the rate of chain-transfer events is increased. The second condition for transfer dominance is that the transfer rate must exceed the laser pulse rate. After each laser pulse, the total radical concentration in the system increases to the value of μ_0^{max}. At that time, if there is a significant fraction of radicals remaining from the previous pulse that have not undergone a chain-transfer event, the characteristic k_p peak will be generated at the chain length given by eq 12. For a system in which chain transfer dominates, however, most radicals will have undergone at least one chain-transfer event in t_0 seconds, and no k_p peak will be seen. Mathematically, this second condition is expressed by:

$$\frac{1}{t_0} < k_{tr}^{A}[A] + k_{tr}^{mon}[M] \qquad (14)$$

Again, this condition is favored by increasing $k_{tr}^{A}[A]$ or increasing t_0.

Equation 14 provides a more easily observable criterion than eq 13; the condition is met if the MWD for the monomer/CTA system is below the termination-dominated k_p peak for the same system without CTA. Note that the establishment of eq 14 as a criterion for analyzing PLP results for chain transfer means that it is not possible to estimate k_p and k_{tr} values from a single experiment. To ensure that the criterion of eq 13 is satisfied, it is necessary to perform experiments to ensure that the results are not affected by the level of termination in the system. Both conditions must be met to verify the validity of analyzing PLP-generated MWDs according to eq 8.

This discussion highlights the limitations of PLP as a tool for measurement of k_{tr} values. For example, there would be no advantage for using PLP to study transfer to methacrylate monomers, since very long pulse times are necessary to satisfy eq 14 in the absence of added CTA. However, PLP offers advantages for studying chain transfer in systems for which the mechanism can easily be made to be the dominant event. The laser-generated radical population quickly destroys small amounts of inhibitors and other impurities that may be present in the system. Reproducible results are obtained without careful monomer purification, and total polymerization times are low (1–10 min). Although the radical concentration is high immediately following a pulse, it is much lower toward the end of the interval between pulses. Thus, the effect of termination on the chain-transfer-dominated MWD is minimized in the high-MW range that is used for the measurement of d ln($f(n)$)/dn. It is of utmost importance, however, to verify that experimental conditions are chosen to create a transfer-dominated system.

Experimental Section

The experimental setup has been described previously.[5] A Quanta-Ray pulsed DCR11 Nd:YAG laser with a harmonic generator is used to generate light of wavelength 355 nm at a pulse energy of 70 mJ/pulse and a half-height pulse width of 6 ns. All experiments are run with a pulse repetition rate of 10 Hz ($t_0 = 0.1$ s) for a total time sufficient to allow 0.5–1.5% conversion of the 4-mL monomer sample to polymer; conversions were measured gravimetrically. The benzoin photoinitiator, styrene, and methacrylate monomers were obtained from Aldrich Chemical Co. and used as received. Calculations indicate that initiator consumption is small for the pulse times used in this work; any consumption that does occur only serves to make the reaction system more transfer-dominated.

The samples were diluted with tetrahydrofuran to polymer concentrations of 0.1–0.3% and analyzed by GPC at 30 °C using tetrahydrofuran as the eluant on a system consisting of a Waters pump (Model 590), Waters autosampler (WISP 712), two Shodex columns (KF80M), and a Waters differential refractometer (Model 410). PS and PMMA calibrations were direct, based upon narrow-distribution standards. PEMA and PBMA analyses were based upon universal calibration using narrow-distribution polystyrene standards (MW ranging from 500 to 8.5 × 10^6) and known Mark–Houwink coefficients,[16] as described previously.[7]

DDM chain-transfer agent was added to samples at room temperature with a syringe on a volume basis. The molar ratio of DDM to monomer is calculated according to:

$$[\mathrm{DDM}]/[\mathrm{M}] = v_{\mathrm{frac}}\left(\frac{\varrho_{\mathrm{ddm}}/\mathrm{MW}_{\mathrm{ddm}}}{\varrho_{\mathrm{mon}}/\mathrm{MW}_{\mathrm{mon}}}\right) \qquad (15)$$

with v_{frac} indicating the volume ratio of DDM to monomer in the system, $\varrho_{\mathrm{ddm}} = 0.846$ g/mL, $\mathrm{MW}_{\mathrm{ddm}} = 202.4$, and ϱ_{mon} is the monomer density at room temperature.

To analyze the experimental data, it is necessary to transform the GPC data from a mass MWD on a logarithmic scale to a number distribution on a linear scale. As described previously,[5] this is a two-step process. The relationship between a linear and log scale distribution is given by:

$$w(\log M) = \ln(10) M w(M) \qquad (16)$$

where $w(\log M)$ is the weight differential of chain molecular weight M on a logarithmic plot, and $w(M)$ is the weight differential of chain molecular weight M on a linear plot. The final transformation to a number differential curve is performed according to the relationship:

$$f(M) \sim w(M)/M \qquad (17)$$

$w(\log M)$ and $w(M)$ are normalized so that the area under the MWD is unity; $f(M)$ is not normalized. The slope described by eq 8 is obtained from the semilog plot of $f(M)$ vs M, with the final value for d $\ln(f(n))$/dn calculated according to:

$$\frac{\mathrm{d}\ln(f(n))}{\mathrm{d}n} = (\text{exptl slope}) \ln(10)\mathrm{MW}_{\mathrm{mon}} \qquad (18)$$

Results

MMA/DDM. As an example of the experimental procedure and analysis, consider the data shown in Figure 3. This set of samples was pulsed at 80 °C at a benzoin concentration of 0.04 mmol/L, with varying amounts of DDM in the MMA monomer. Pairs of samples were run at each condition, with excellent reproducibility. Figure 3a shows the GPC distributions, plotting $w(\log M)$ vs $\log(M)$. The same data are shown in Figure 3b, transformed to a semilog plot of $f(M)$ vs M. The PMMA produced in the absence of DDM shows the characteristic GPC trace (Figure 3a) for a PLP-generated polymer—a sharp primary peak and a higher-MW secondary shoulder. Although greatly decreased during the transformation, the primary peak (at $M \sim 1.5 \times 10^{-5}$) can also be seen on the number distribution (Figure 3b). The inflection point of this primary peak is the characteristic chain length used for the determination of k_p from eq 12. (See refs 1–7 for a complete description of this procedure.)

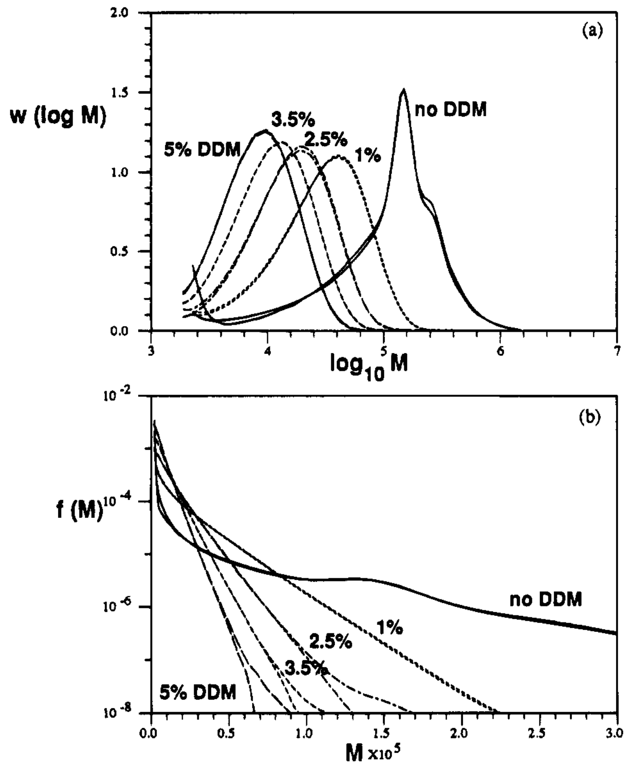

Figure 3. PMMA produced at 80 °C by PLP at 10 Hz, with varying amounts of DDM chain-transfer agent: (a) GPC mass MWD; (b) number MWD on semilog scale. ([Benzoin] = 0.04 mmol/L; duplicate samples at each experimental condition.)

Figure 3a illustrates how the MWD shifts to lower MW values and the shape of the distributions change as the concentration of DDM in the MMA is increased. The addition of even 1 vol % DDM has changed the system from a termination-controlled MWD to a transfer-dominated system. Note that the MWDs for the DDM-containing samples shown in Figure 3a are almost entirely contained to the left of the no-DDM k_p peak. This is in accordance with the criterion of eq 14—the majority of the growing polymer chains undergo a chain-transfer event before being exposed to the next burst of laser-generated radicals. The MWDs are asymmetric, with the distribution skewed to the low-MW side. This is due to the periodic nature of the radical concentration expressed by eq 11—the concentration of polymer radicals is high immediately following a pulse, leading to higher rates of termination and the formation of short chains. The concentration of radicals is much lower when the radicals have reached greater length, at which point the dominant chain-stopping mechanism is chain transfer.

The effect of the periodic radical concentration is also seen in the semilog number distributions shown in Figure 3b. Some of the distributions deviate from linear behavior at low-MW values ($M < 1 \times 10^4$), due to termination effects (and changing radical concentrations) at short chain lengths. However, all of the PMMA samples produced in the presence of DDM have a distinct linear region on the semilog scale, with the magnitude of the slope increasing with increasing DDM levels. (The deviations from linearity at the tail end of each curve are due to baseline noise.) The values of d $\ln(f(n))$/dn are calculated according to eq 18 from the slopes of these linear regions.

An important question to address when using PLP to study chain transfer is whether system conditions

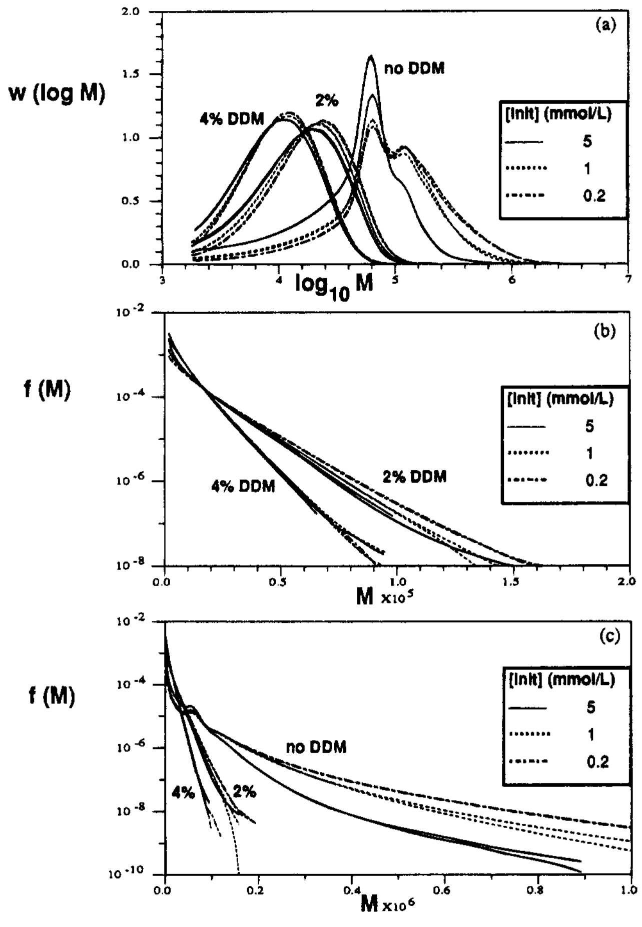

Figure 4. PMMA produced by PLP at 40 °C and 10 Hz, with varying amounts of DDM and benzoin photoinitiator: (a) GPC mass MWD; (b) number MWD on a semilog scale (2 and 4% DDM); (c) number MWD on an expanded scale, including experiments without DDM. Duplicate samples at each experimental condition.

have been chosen such that the termination contribution to the MWD slope is minimized (eq 13). There are different means for controlling the level of termination in PLP experiments; the one used in this work was the initiator concentration ([I]). Figure 4 plots the MWDs obtained at three [I] levels (5, 1, and 0.2 mmol/L) for MMA pulsed at 40 °C with three different levels of DDM (0, 2, and 4 vol %). Once again, duplicate experiments are shown at each condition. It can be immediately seen from the GPC traces (Figure 4a) that [I] has the most effect on the MMA samples pulsed in the absence of DDM. It can also be seen that, at a constant DDM level, increasing [I] shifts the MWD to lower values. Both of these effects can be readily understood in terms of the "termination vs transfer" competition discussed previously. Increasing [I] has the least effect for the 4% DDM system, since transfer to DDM dominates the MWD (in eq 7 $k_{tr}^{A}[A] \gg k_t\mu_0$). At 2% DDM, the effect of [I] is more noticeable, and in the absence of DDM, [I] affects not only the intensity of the primary PLP peak but also the high-MW tail.

Note that the biggest effect of [I] is seen on the low-MW side of the Figure 4a distributions for the polymer produced in the presence of DDM. At the high-MW side, the distributions are more similar. This can be understood by considering the periodic radical concentration generated by the laser. Immediately following a laser pulse, radical–radical termination of the very short chains makes a large contribution to the total number of polymer chains being formed; thus, the low-MW side of the distribution is most affected by [I]. As the remaining live chains grow in length, the radical concentration in the system is much reduced. These chains have a high probability of being terminated through transfer with DDM; the high-MW side of the distribution is less affected by [I]. This fact is very important, since it is from the slope of this high-MW side that k_{tr}/k_p is estimated. Figure 4b is a plot of the distributions (with 2 and 4% DDM) transformed to a semilog number scale. No initiator effect can be discerned from the slopes for the polymer pulsed with 4% DDM, but a slight effect can be seen with the polymer pulsed with 2% DDM, with the magnitude of the slope increasing with increasing [I]. It is obvious from theory that better estimates for k_{tr}/k_p will be obtained if radical concentrations (and thus [I]) are kept low; experimentally it was found that there is no meaningful difference in the measured slopes of the semilog number distributions as long as [I] is sufficiently low (<1 mmol/L for this system).

It is interesting to examine the effect of [I] on the MMA samples pulsed without DDM. The focus of this work was not the determination of k_p. However, with each set of experiments, two control samples were run without added chain-transfer agent. A wide range of benzoin photoinitiator concentrations (0.04–5.0 mmol/L) and temperatures (20–80 °C) was covered. Consistent with previously reported results,[6] the inflection points and k_p estimates were independent of [I] and are in good agreement with our previously reported Arrhenius fit.[5] Although [I] does not have an effect on the peak position of the samples produced without DDM, Figure 4a illustrates that it does have a large effect on the relative size of the peaks and on the shape of the distributions. As [I] is lowered, a greater fraction of the radicals produced survive the subsequent pulse.

The variation in [I] does affect the slope of the semilog number distributions for the pure MMA samples, as shown in Figure 4c. Although linear regions are observed, the value of d ln($f(n)$)/dn is dependent on [I] and even at the lowest initiator concentrations is much higher ((1–4) × 10^{-4}) than reported values for k_{tr}^{mon}/k_p.[12,17] It has been suggested that k_p and k_{tr} values can be obtained from a single PLP experiment.[15] It is our opinion that the two measurements are diametrically opposed, since k_p determination must be performed at experimental conditions in which termination is the dominant chain-stopping mechanism, while for accurate determination of k_{tr}, termination must be minimized in the system. The presence of a PLP "k_p peak" precludes the use of the distribution for estimating k_{tr}, in accordance to the criterion of eq 14.

Experiments studying chain transfer to DDM in MMA were run over a wide range of initiator concentrations (0.04–1.0 mmol/L), temperatures (20–80 °C), and DDM levels (1–5 vol %). The complete set of experimental slopes (measured from plots such as Figures 3b and 4b) are plotted in Figure 5 vs [DDM]/[MMA], according to eq 9. Each data point reflects two experiments run at identical conditions on the same day; data pairs which showed significant differences among themselves were not included. The data are sorted according to temperature; no observable trends could be seen with [I], for [I] < 1 mmol/L. The slopes from Figure 5 yield the estimates of k_{tr}^{DDM}/k_p for the system; the best fit value (with standard deviation) for each temperature is marked on the figure.

It is possible to use the values from Figure 5 to construct an Arrhenius plot of the data. This is shown in Figure 6, where the error bars indicate the standard

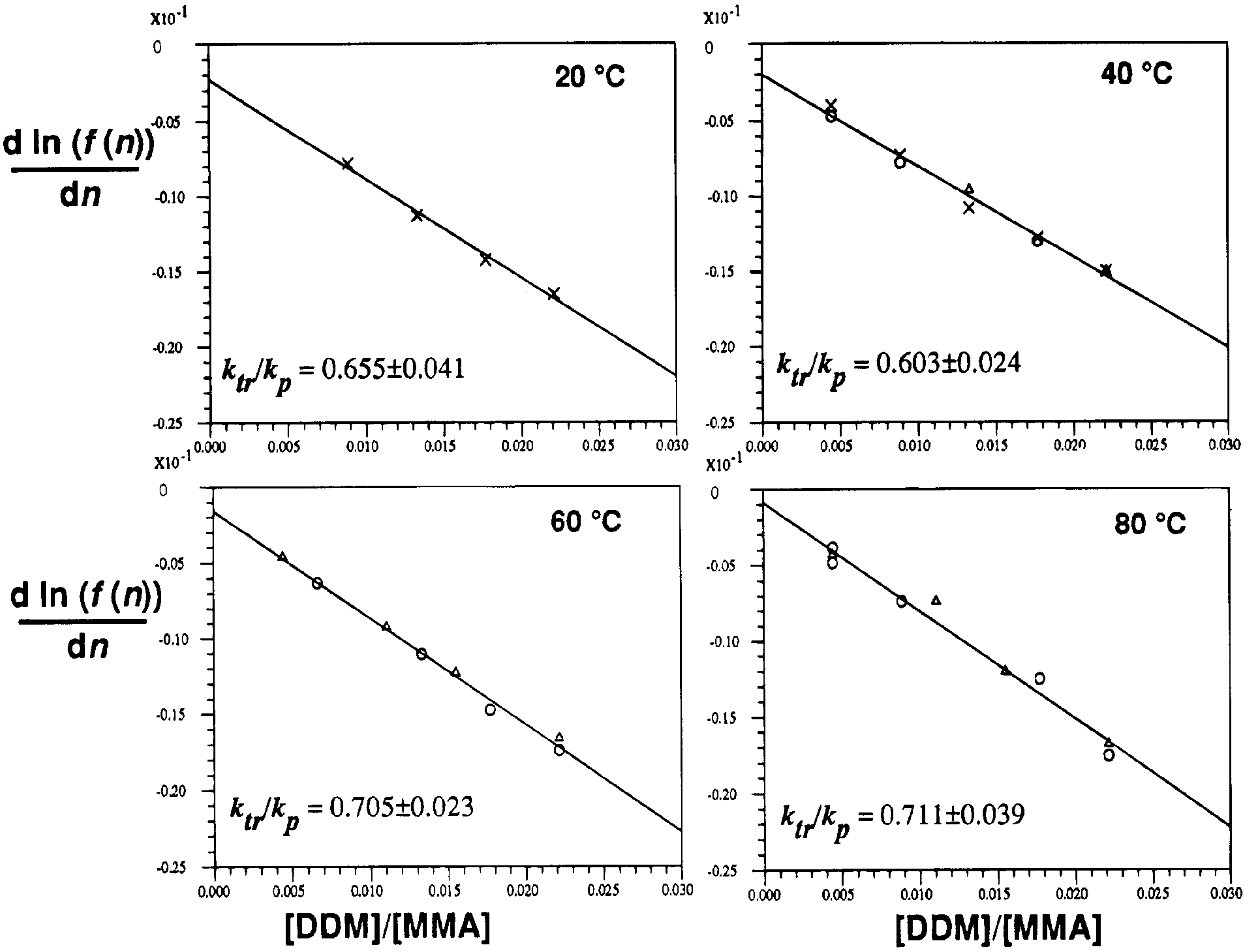

Figure 5. Slopes from semilog number distributions vs [DDM]/[MMA] for PMMA produced by PLP at 10 Hz and various photoinitiator concentrations: 1.0 (○), 0.2 (×), and 0.04 (△) mmol/L. Lines indicate the best fit, with slope (k_{tr}/k_p) and standard deviation as marked.

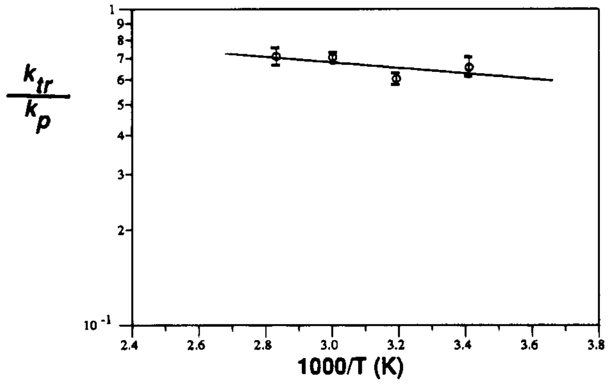

Figure 6. Arrhenius plot for k_{tr}/k_p for DDM in MMA. The line is best fit to data (○), as described in the text. (Error bars indicate the standard deviation around each data point.)

deviation around the estimate at the individual temperatures. The Arrhenius fit leads to:

$$\ln\left(\frac{k_{tr}^{A}}{k_p}\right) = (0.222 \pm 0.513) - (202 \pm 164)/T \quad (19)$$

This estimated activation energy for the chain-transfer ratio is so close to zero that it cannot be said to be significant. This is further illustrated by Figure 7, a plot of the entire data at all temperatures against [DDM]/[MMA]. From the complete data set, a temperature-independent value of 0.68 ± 0.02 is estimated for k_{tr}/k_p. Also plotted on Figure 7 are results obtained from two thermally-initiated polymerizations, performed at low initiator concentration and 80 °C, with 2 and 4 vol % DDM. The slopes obtained from the semilog number distributions of these samples are in excellent agreement with the PLP results.

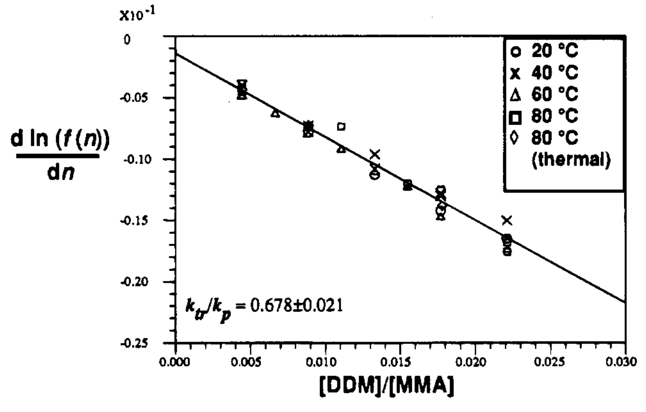

Figure 7. Temperature-independent fit of semilog number distributions vs [DDM]/[MMA] for PMMA produced by PLP at 10 Hz. The line indicates the best fit to all data, with slope (k_{tr}/k_p) and standard deviation as marked.

This estimate for k_{tr}/k_p of the MMA/DDM system can only be indirectly compared to other literature data. In a compilation by Bamford *et al.*,[18] the chain-transfer value for *n*-butyl mercaptan to MMA at 60 °C is given as 0.67. The same reference states that chain transfer

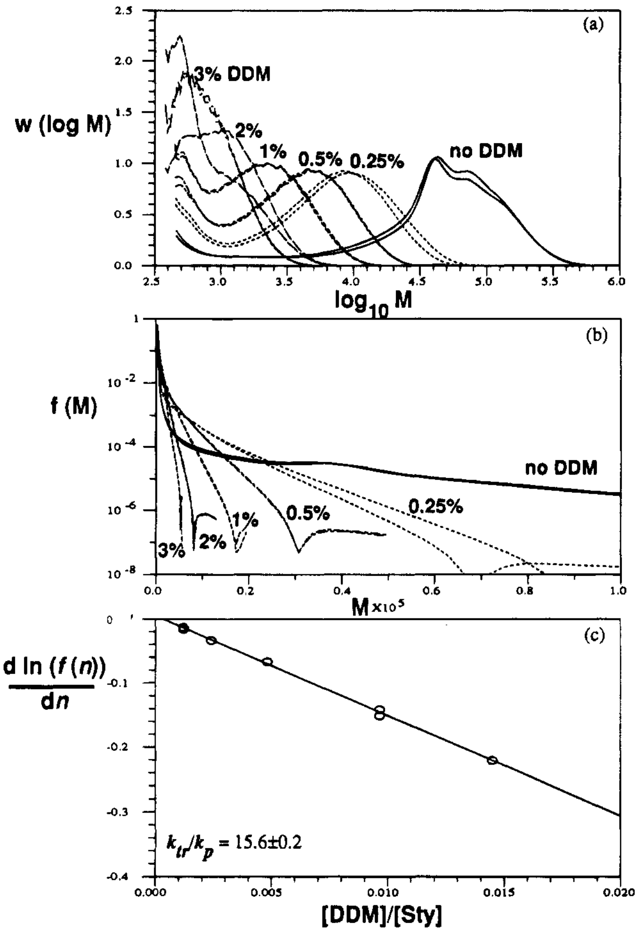

Figure 8. Determination of chain transfer for DDM in styrene at 60 °C with PLP: (a) GPC mass MWD; (b) number MWD on a semilog scale; (c) slope of semilog number distributions vs [DDM]/[Sty], with slope (k_{tr}/k_p) and standard deviation as marked. Duplicate samples at each experimental condition.

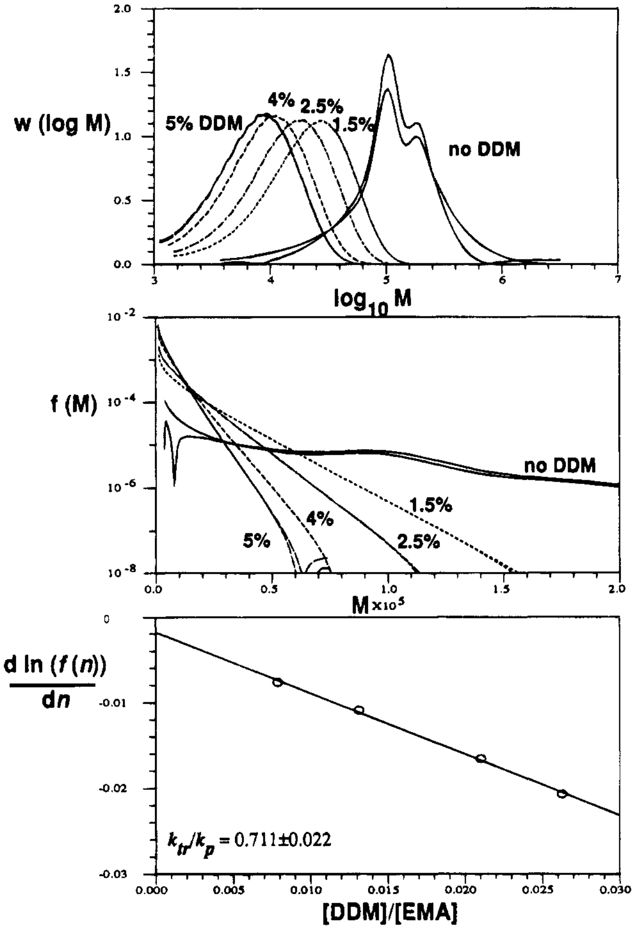

Figure 9. Determination of chain transfer for DDM in ethyl methacrylate at 60 °C with PLP: (a) GPC mass MWD; (b) number MWD on a semilog scale; (c) slope of semilog number distributions vs [DDM]/[EMA], with slope (k_{tr}/k_p) and standard deviation as marked. Duplicate samples at each experimental condition.

to *n*-mercaptans appears to be independent of their molecular weight; *n*-dodecyl and *n*-butyl mercaptans both have the same chain-transfer coefficient to styrene. These limited data suggest that our value of 0.68 for DDM in MMA seems quite reasonable. The negligible temperature dependence observed for k_{tr}/k_p is in reasonable agreement with the results of Gregg *et al.*,[19] who measure that the activation energy of the transfer reaction for styrene to mercaptans is close to, or even less than, that of the propagation reaction.

Styrene/DDM. Bamford *et al.*[18] report that styrene undergoes chain transfer to mercaptans more readily than MMA; Gregg *et al.*[19] measure a value of 14–19 for k_{tr}/k_p in the styrene/DDM system at 60 °C. Based upon our extensive work with the MMA/DDM system and this literature estimate for k_{tr}/k_p, it was decided to run the styrene/DDM experiments covering the range of 0.25–3 vol % DDM, with benzoin photoinitiator at 0.2 mmol/L. The results from this single set of experiments are shown as Figure 8, with Figure 8a containing the GPC traces and Figure 8b the corresponding number distributions (semilog scale). Although the MWs of the polymer produced at high DDM levels are low, the number distributions show a very nice linear region and are well within the calibration range of the instrument. The transfer coefficient is obtained, as before, by plotting the slopes of the semilog number distributions against [DDM]/[Sty] (Figure 8c). A value of 15.6 ± 0.2 is obtained for k_{tr}/k_p, in good agreement with the value measured by Gregg *et al.*[19]

This set of experiments illustrates the power and convenience of using pulsed-laser techniques to study chain transfer. Each of the samples was pulsed for 5 min, sufficient to obtain the desired 1% conversion of monomer to polymer. This can be compared to the work of Gregg, where the samples were held at 60 °C for 10–20 h in order to obtain 1% conversion. The results captured in Figure 8 were produced and analyzed in a day.

EMA/DDM and BMA/DDM. Previously, we compared the relative propagation activity of MMA with EMA and BMA, as measured by PLP.[7] A definite increase in k_p is observed when progressing from MMA to EMA to BMA throughout the complete 10–90 °C range of experimentation. It was decided to examine the trends for chain transfer to DDM for the same series. Experimental conditions were selected based upon the MMA results: 60 °C, [I] = 0.2 mmol/L and varying the volume ratio of DDM to EMA and BMA monomers between 0 and 5%. Results are presented as Figures 9 and 10. The MWDs are very similar to those presented in Figure 3 for MMA, with distinct linear regions observed in the semilog number distribution plots.

At 60 °C, k_p is 790 (L/mol·s) for MMA, 950 for EMA, and 1080 for BMA.[7] The experimental results of Figures 9 and 10 indicate that the absolute values for k_{tr} to DDM increase by the same factor. The k_{tr}/k_p ratios obtained (0.71 ± 0.02 for EMA and 0.65 ± 0.02 for BMA) are not significantly different from the 0.68 ± 0.02 value

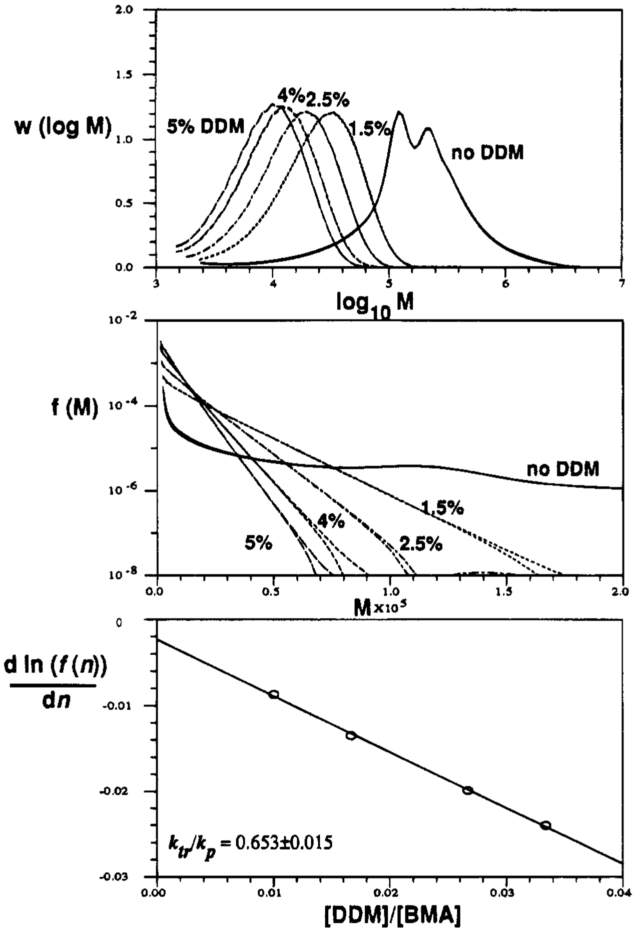

Figure 10. Determination of chain transfer for DDM in butyl methacrylate at 60 °C with PLP: (a) GPC mass MWD; (b) number MWD on a semilog scale; (c) slope of semilog number distributions vs [DDM]/[BMA], with slope (k_{tr}/k_p) and standard deviation as marked. Duplicate samples at each experimental condition.

estimated for MMA. This result is very significant if proven to be generally true, since it means a single set of experiments can be done to characterize the chain-transfer ability of an agent with an entire monomer family. More work in this area is planned, including the study of DDM with other methacrylates and the study of other chain-transfer agents.

Conclusions

This work demonstrates that the PLP technique is an effective tool for measuring chain-transfer as well as propagation rate coefficients. The method of analysis suggested by Gilbert and co-workers[13-15]—taking the high-MW slope of the semilog number distribution—provides a robust measure of chain transfer. When coupled with the PLP advantages of fast, robust, and reproducible operation, it is now possible to measure transfer rate coefficients for added agents quickly and reliably. Two generalized criteria are proposed to ensure that valid estimates for k_{tr}/k_p are obtained from PLP-generated MWDs. First, experimental conditions must be found so that the MWD for the monomer/CTA system is below that of the termination-dominated k_p peak for the same system without CTA. Second, it must be shown that the measured slope from the semilog number distribution is independent of termination rate; this criterion was tested in this work by varying the concentration of the photoinitiator.

Extensive experimentation with the DDM/MMA system was performed to determine the conditions necessary for reliable estimation of k_{tr}/k_p. A value of 0.68 was obtained, which was indepenent of temperature (20 < T (°C) < 80). Chain transfer to DDM in other monomer systems was also measured at 60 °C. The k_{tr}/k_p value determined for DDM/styrene showed good agreement with literature, while the k_{tr}/k_p ratio of DDM with methacrylates proved to be independent of the ester length (MMA, EMA, and BMA). The generality of this last result will be further explored.

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