Analysis of Pulsed-Laser-Generated Molecular Weight Distributions for the Determination of Propagation Rate Coefficients

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ABSTRACT: The pulsed-laser polymerization technique is a direct and reliable method for estimating propagation rate coefficients, k_p, from molecular weight distributions (MWDs). This work illustrates that proper numerical treatment of the data not only yields an accurate measure of k_p but also provides checks on the validity of the analysis. The technique and amplified consistency checks are applied to obtain k_p estimates over a wide temperature range for methyl methacrylate, styrene, and chloroprene. Vinyl acetate provides an example for which the analysis indicates clearly that a true k_p value cannot be obtained from GPC analysis of the laser-generated MWD at the conditions studied.

Introduction

The rate of chain growth in a polymerizing system controls not only the rate of polymer conversion and observed initiator productivity but also the molecular weight distribution (MWD) of the polymer produced. Despite its significance, the propagation rate coefficient, k_p, has proven to be a difficult parameter to determine quantitatively. This problem is illustrated by the wide range of values reported in the *Polymer Handbook*[1] even for widely studied monomers such as styrene and methyl methacrylate (MMA). Values for other monomers, if available at all, have higher uncertainty, posing a major difficulty in understanding and modeling polymerization reactors.

An IUPAC working party on "Modeling of Free Radical Polymerization Kinetics and Processes", made up of leading academic experts in the area, has examined the wide divergence of reported values for kinetic coefficients.[2,3] The authors point out a number of important gaps in the verification of parameters and techniques. Stressed are the needs to deduce parameters from data with a minimum of model-based assumptions and to state clearly all assumptions made during data reduction. For example, conventional rotating sector techniques yield a ratio of k_p/k_t where k_t is the rate coefficient of bimolecular termination. This ratio can only be resolved into individual parameters by combining this information with other experiments which yield the ratio $k_p/k_t^{1/2}$. The procedure is tedious, involves multiple experiments, and is dependent on assumptions concerning termination and chain-transfer reactions.[2] In addition, it is necessary to repeat the set of experiments at multiple temperatures to obtain an activation energy for propagation.

A number of new experimental techniques have been discussed which make it possible to determine kinetic parameters more directly and accurately.[2,3] One such technique known as pulsed-laser polymerization (PLP), pioneered by Olaj and co-workers,[4,5] allows the direct measurement of k_p from a single experiment using a straightforward procedure and analysis. In brief, a monomer system with photoinitiator is exposed to periodic laser flashes which generate a periodic profile of polymer radicals. Between flashes, the radical concentration decreases due to radical–radical termination. At the end of the period between flashes, t_0, the radicals which have escaped termination up to this moment have propagated to a chain length P_0. This chain length is given by the simple equation[4]

$$P_0 = k_p[\mathrm{M}]t_0 \qquad (1)$$

where [M] is the monomer concentration. When the next flash arrives, these 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, it is possible to estimate directly a value for k_p using eq 1. Olaj *et al.*[4] analyzed theoretical MWD curves to show that the best measure of P_0 is the inflection point on the laser-generated MW peak. The theoretical distributions are also used to show that the same value for P_0 should be obtained from both molar and mass distributions. Finally, the presence of secondary peaks is predicted, resulting from chains that live for a period of $2t_0$.

The validity of the PLP technique has been experimentally established. Davis *et al.*[6] measured P_0 for PMMA and polystyrene (PS) as a function of laser pulse frequency and monomer concentration. The k_p values calculated were found to be independent of these parameters, providing experimental confirmation of eq 1. Olaj *et al.*[5] tabulated experimental inflection points for PMMA and PS that correspond to chains that have had a lifetime of one (t_0), two ($2t_0$), and even three ($3t_0$) periods. The k_p values reported by both groups for the two monomers coincide and show reasonable agreement with literature values.

After verifying the technique with the well-known MMA and styrene systems, Davis *et al.*[7] successfully used the technique to estimate k_p values for other methacrylates. They were unsuccessful, however, in estimating k_p values for the homopolymerization of methyl acrylate and butyl acrylate.[8] No distributions were shown, but the authors stated that they were broad as opposed to the characteristically sharp peaks obtained with other monomers. The variation of k_p as a function of monomer composition during copolymerization with styrene was also examined. A recent note by Pascal *et al.*[9] describes the use of PLP for the determination of k_p for *tert*-butyl methacrylate.

Despite the growing use of PLP to determine k_p values, there is little published on the analysis and interpretation

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of the experimental gel permeation chromatography (GPC) traces. Indeed, some of the references do not even include MWD data, reporting only calculated k_p values. The work by Davis *et al.*[8] indicates that there are some systems for which the technique is not successful. As determined by Olaj's theoretical analysis,[4] the GPC trace itself contains consistency checks as to the validity of the calculation. In this paper, a method of analyzing experimental MWDs to obtain inflection points and to check the appropriateness of the data is outlined. Results for MMA and styrene are presented over a much wider temperature range than by previous workers[5-7] and compared with other literature data. In addition, PLP is used to obtain a reasonable estimate for k_p of chloroprene, a monomer for which there are little data available. Finally, an example of a system (vinyl acetate) for which PLP does not yield a true k_p value is given, in agreement with results found by other workers[8] for acrylates.

Experimental Section

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 40 mJ/pulse and a half-height pulse width of 6 ns. The beam (diameter of 6.5 mm) is directed vertically into a glass sample holder containing the monomer and initiator solution. All experiments were run with a pulse repetition rate of 10 Hz (t_0 = 0.1 s). After the sample has equilibrated at the desired temperature (controlled by a circulating water bath within ±0.5 °C), the sample is exposed to the pulsed laser for a predetermined time (3–30 min) to allow for about 0.5–1.0% conversion of monomer to polymer.

Styrene, MMA, and vinyl acetate were used as received. Each experiment used 4.0 mL of monomer, containing 5×10^{-3} mol/L benzoin photoinitiator. The solutions were transferred to the sample cells under an argon purge to minimize exposure to oxygen. An induction period was observed—negligible conversion occurred during the first 1 or 2 min of pulsing—indicating that some inhibitor may have been present in the monomer. Although the presence of inhibitor affects the rate of polymerization, it has no effect on the determination of k_p according to eq 1.

Heavily inhibited chloroprene monomer was obtained internally at DuPont and stored at −50 °C. The as-received monomer contained approximately 1.5 wt % of inhibitor. The chloroprene for the pulsed-laser experiments was purified as needed by passing it through a packed alumina column that had been evacuated with a vacuum pump and then purged with argon before adding the chloroprene. This procedure was repeated with two fresh columns to remove as much of the inhibitor as possible. The purified chloroprene was transferred to the individual 1.0-mL sample cells under an argon purge to minimize exposure to oxygen.

The initial chloroprene pulsed-laser experiments with benzoin photoinitiator produced very little polymer. Therefore, the initiator was switched to nitrile systems; azobis(isobutyronitrile) (AIBN) was used in the range of 10–40 °C and 1,1′-azobis(cyclohexanecarbonitrile)(Vazo 88) in the range of 35–55 °C. Some thermal initiation did occur during the pulsed-laser experiments with chloroprene; however, as discussed in more detail below, this was not enough to obscure the laser-induced termination peak. Other pulsed-laser polymerization studies have also successfully used AIBN as a low-temperature photoinitiator.[7,8]

All GPC analyses were performed at 30 °C using tetrahydrofuran as 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). The PS and PMMA samples were analyzed based upon calibration curves obtained from narrow-distribution PS and PMMA standards. Polychloroprene and poly(vinyl acetate) analysis was based upon universal calibration using known Mark–Houwink constants.[10,11]

Data Analysis

The theory outlined by Olaj and co-workers[4] suggests that P_0 in eq 1 is given by the inflection point found from a molar chain-length distribution on a linear scale. GPC analysis, however, yields a mass molecular weight distribution on a logarithmic scale. Thus, it is necessary to perform the correct transformation during analysis of the data.

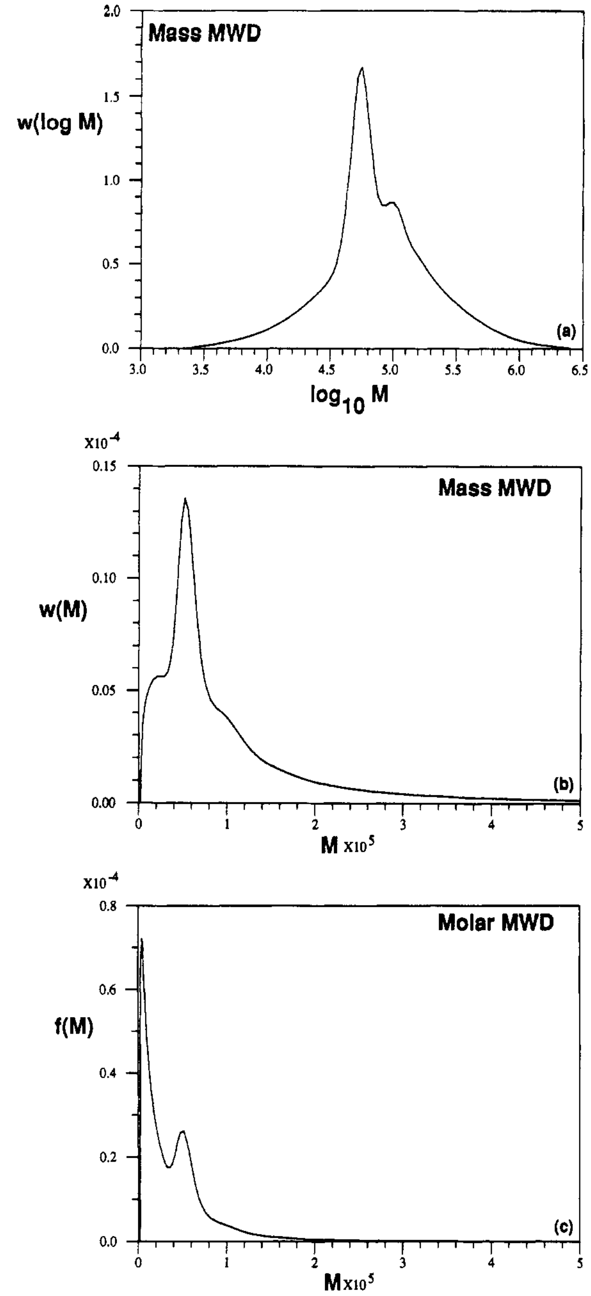

Figure 1. PMMA produced at 40 °C by pulsed-laser polymerization at 10 Hz: (a) GPC mass MWD, (b) mass MWD on a linear scale, (c) molar MWD on a linear scale. Experimental data are fit by cubic splines.

The relationship between a linear and log scale distribution is given by[12]

$$w(\log M) = \ln(10)\, M\, w(M) \qquad (2)$$

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

$$f(M) \sim w(M)/M \qquad (3)$$

$w(\log M)$ and $w(M)$ are normalized so that the area under the MWD is unity; $f(M)$ is unnormalized and is shown on an arbitrary scale.

The relationship between these distributions is illustrated in Figure 1 for a PMMA sample produced at 40 °C

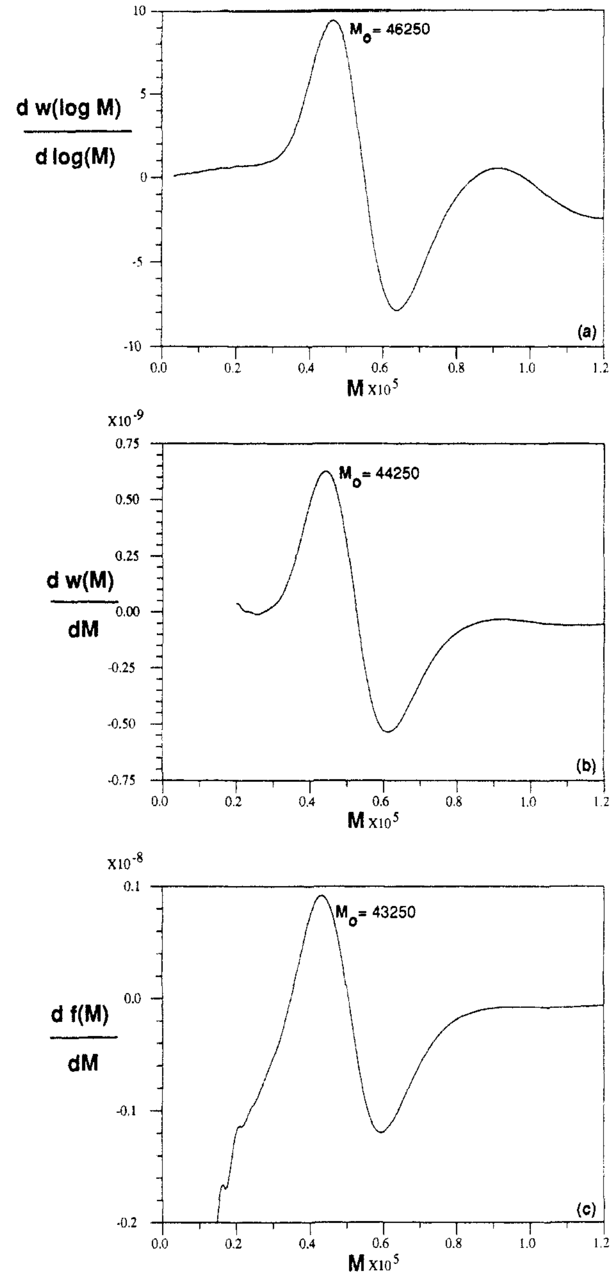

Figure 2. Derivatives (arbitrary units) calculated from Figure 1 molecular weight distributions (PMMA produced at 40 °C by pulsed-laser polymerization at 10 Hz).

at a laser pulse rate of 10 Hz. The $w(\log M)$ distribution from the GPC shows a sharp primary peak and a distinct higher MW secondary peak. As the curve is transformed according to eqs 2 and 3, the relative magnitude of the high-MW fractions decreases and the distributions change significantly in shape. Through the transformations, the primary peak at 6×10^4 remains but the secondary peak observed in the $w(\log M)$ plot is transformed to a shoulder in the $w(M)$ curve and is barely observed in the $f(M)$ distribution.

The inflection points from these MWDs are obtained by taking the derivative of the ordinate with respect to the abscissa. The derivatives are calculated numerically from the raw data using IMSL math library routines.[13] The original 100-point distribution is fit with cubic smoothing splines. Each plot in Figure 1 shows the MWD curve as fit by the cubic splines, as well as the actual points from the original data. It can be seen that the splines give an excellent fit to the data—the two curves cannot be distinguished. The spline functions are then analytically differentiated. Figure 2 shows the derivative plots from the three distributions of Figure 1. Even though the three distributions are significantly different, the shapes of the derivative plots are very similar. These plots are expanded on a linear scale in the molecular range of interest. Maxima and minima correspond to inflection points on the distribution up-slopes and down-slopes, respectively. Zeros on the plots correspond to peak maxima and minima on the Figure 1 distributions. The maxima of Figure 2, corresponding to up-slope inflection points, are the quantities of interest for the calculation of k_p.

It is interesting to compare the primary inflection points calculated from the $w(\log M)$ and the $w(M)$ distributions. By differentiating eq 2, the relationship between the two derivatives is

$$\frac{dw(M)}{dM} = \frac{1}{(\ln(10)M)^2}\left(\frac{dw(\log M)}{d\log(M)} - \ln(10)\, w(\log M)\right) \tag{4}$$

This equation indicates that the inflection point from the $w(M)$ distribution will always occur at a slightly lower value of M than that calculated from the $w(\log M)$ distribution. The M_0 values reported on Figure 2 support this conclusion. Although the differences are not great, the results from this work indicate that using the $w(\log M)$ distribution to estimate k_p gives values that are 3–7% higher than those estimated from the $w(M)$ distribution. Raw $w(\log M)$ data should not be used to determine k_p. Without making the correct transformation, a bias is introduced.

The results of Figure 2 clearly support the theoretical interpretation of Olaj and co-workers.[4] First, the inflection points obtained from the number and mass distributions are almost equal. Second, a secondary inflection point is observed at twice the chain length observed for the first inflection point. Because of the nature of the distributions, this secondary inflection point is most evident on the $w(\log M)$ distribution, is less apparent on the $w(M)$ distribution, and is nonexistent on the $f(M)$ distribution. In this work, the $w(M)$ distributions are shown to make the secondary inflection point more visible. M_0 values from both the $w(M)$ and $f(M)$ distributions are presented in tabular form. In accordance with the original theory, the inflection point from the molar distribution is used to calculate k_p, using a rearranged form of eq 1 for a pure monomer system:

$$k_p = M_0/1000\rho t_0 \tag{5}$$

where M_0 is the polymer MW at the inflection point, k_p has units of (L/mol·s), and monomer density ρ has units of (g/cm^3). Monomer densities are calculated as a function of temperature (T_c in °C) for MMA,[1] styrene,[14] and chloroprene[15] according to

$$\rho_{mma} = 0.9569 - 1.2129 \times 10^{-3}T_c + 1.6813 \times 10^{-6}T_c^{\,2} + 1.0164 \times 10^{-8}T_c^{\,3} \tag{6}$$

$$\rho_{sty} = 0.9240 - 9.18 \times 10^{-4}T_c \tag{7}$$

$$\rho_{chl} = 0.97849 - 1.1408 \times 10^{-3}T_c \tag{8}$$

A full discussion of the data analysis has been presented in this section to emphasize its importance. With proper analysis, a single experiment not only yields a k_p estimate but also checks the validity of the estimate. The criteria used in this work are that the M_0 values estimated from the molar and mass distributions show reasonable agreement and that a secondary inflection point be observed at roughly $2M_0$. Only if the analysis of the experimental MWD produced by PLP obeys these criteria can confidence be placed in the estimate of k_p.

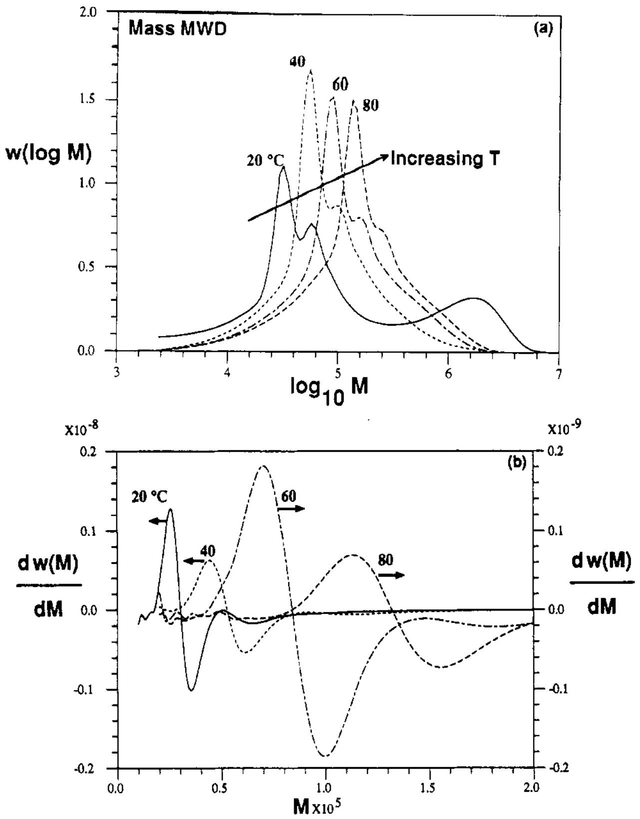

Figure 3. Analysis of PMMA produced by pulsed-laser polymerization at 10 Hz: (a) mass distributions at 20, 40, 60, and 80 °C; (b) corresponding derivative plots, from $w(M)$ distributions.

Table I. Pulsed-Laser Polymerization with MMA (t_0 = 0.1 s)

T (°C)	M_0 molar MWD	M_0 mass MWD	k_p (L/mol·s)
20	25 250	25 750	267
25	28 500	29 250	304
	29 750	30 250	318
40	43 250	44 250	470
60	69 000	70 250	769
70	87 500	88 750	989
80	111 750	113 000	1278
	112 750	114 000	1289
90	129 750	131 500	1504

Results

MMA. MMA was chosen as the first test system since it has been widely studied in the literature. Pulsed-laser experiments were performed in the range of 20–90 °C. Figure 3 shows GPC mass distributions and derivative plots (based on $w(M)$ distributions) for typical experiments. It can be clearly seen how the distributions and the inflection points shift to higher molecular weights as the polymerization temperature increases. The cause of the high molecular weight shoulder for the 20 °C experiment is not known but does not affect the lower molecular weight inflection point. A summary of the complete results is shown as Table I.

Repeated GPC analysis on the same sample gave the same value (±1000) for the inflection points. Repeated pulsing experiments at 25 and 80 °C also show the reproducibility of the technique (see Table I). M_0 from the number distributions are very close to the mass distribution values but are slightly lower in all cases. Since the theory is based on number distributions, these values are used to calculate k_p. Figure 4 shows an Arrhenius plot of the data, which is fit by linear regression according to (T in K)

$$\ln k_p = (14.685 \pm 0.105) - (2669 \pm 34)/T \qquad (9)$$

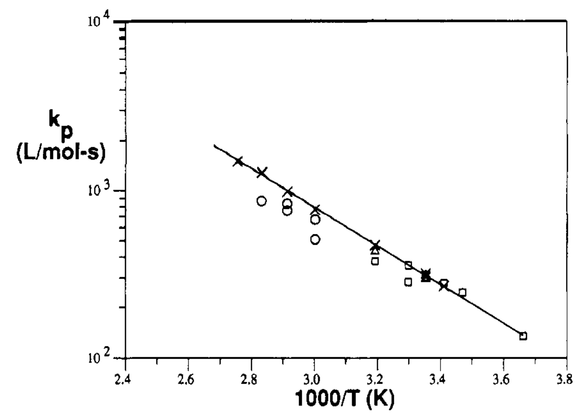

Figure 4. Arrhenius plot for the MMA propagation rate coefficient. (×) Values estimated from this work (pulsed-laser polymerization). Literature values from ESR (○), PLP (△), and rotating sector (□) techniques.

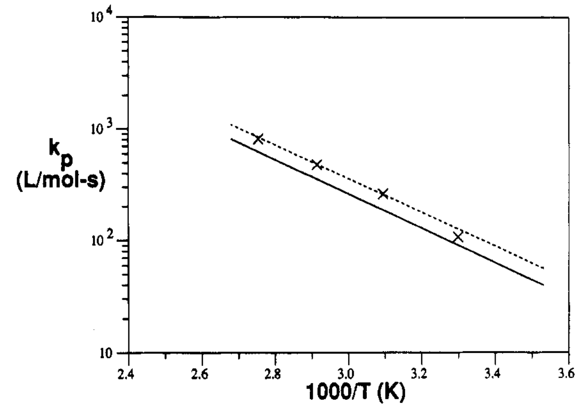

Figure 5. Arrhenius plot for the styrene propagation rate coefficient. (×) Values determined from pulsed-laser polymerization. Lines are from eqs 11 (solid) and 12 (dotted).

or

$$k_p\ (\text{L·mol}^{-1}\text{·s}^{-1}) = 2.39 \times 10^6 \exp\left(\frac{-5300\ \text{cal·mol}^{-1}}{RT}\right) \qquad (10)$$

Also shown in Figure 4 are other recent experimental data taken from the literature. These data were measured by a variety of techniques, including PLP,[5,6] electron spin resonance,[16–18] and rotating sector.[19–22] The data from this report cover a much wider temperature range than any of the reported sets and extend the data to higher, more industrially important, temperatures. The agreement with other recent data is excellent compared to the typical scatter reported in the literature.[1]

Styrene. Styrene is another widely studied system. The k_p–temperature relationships determined from spatially intermittent polymerizations[20] in the temperature range of 15–30 °C

$$k_p\ (L\text{·mol}^{-1}\text{·s}^{-1}) = 1.10 \times 10^7 \exp\left(\frac{-7050\ \text{cal·mol}^{-1}}{RT}\right) \qquad (11)$$

and from emulsion polymerization rate data[23] in the range 45–65 °C

$$k_p\ (\text{L·mol}^{-1}\text{·s}^{-1}) = 1.26 \times 10^7 \exp\left(\frac{-6930\ \text{cal·mol}^{-1}}{RT}\right) \qquad (12)$$

have been reported. These two data sets, plotted in Figure 5, show good agreement.

In this work, PLP has been used to examine the styrene system in the extended temperature range 30–90 °C. Table II is a summary of the observed inflection points from both number and mass distributions and the k_p values calculated from the number distribution. As for MMA,

Table II. Pulsed-Laser Polymerization with Styrene (t_0 = 0.1 s)

T (°C)	M_0 molar MWD	M_0 mass MWD	k_p (L/mol·s)
30	9 600	9 800	107
50	22 800	23 400	260
70	41 200	42 200	479
90	68 600	69 800	815

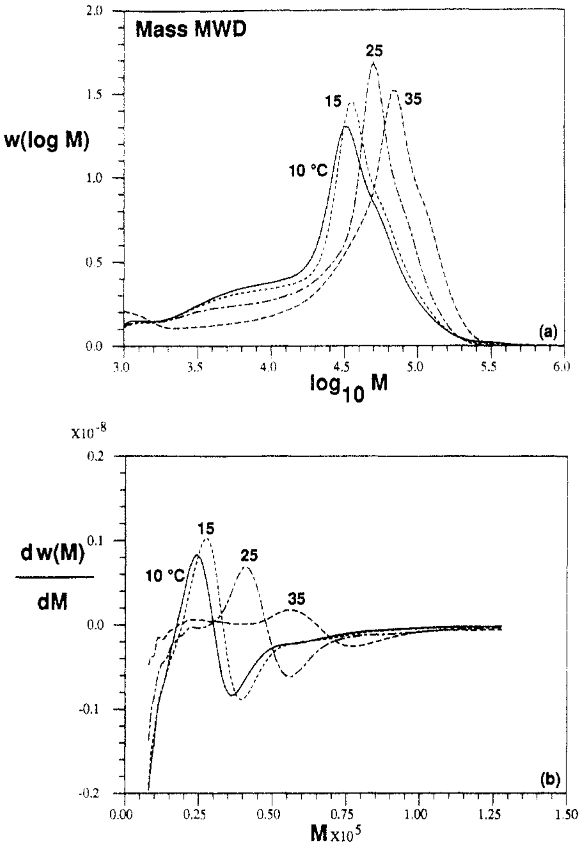

Figure 6. Analysis of polychloroprene produced by pulsed-laser polymerization at 10 Hz with AIBN: (a) mass distributions at 10, 15, 25, and 35 °C; (b) corresponding derivative plots, from $w(M)$ distributions.

the analysis checks indicate that the technique yields a true estimate of k_p. As shown by the data points on Figure 5, the PLP values from this work show excellent agreement with the Arrhenius relationships estimated by different techniques. No attempt was made to estimate an activation energy from the four points, although the data appear to be slightly better represented by eq 12.

Chloroprene. With confidence in the technique and data analysis, it is possible to examine a new monomer system, such as chloroprene. The only k_p estimate to be found in the literature is from the work by Hrabák and co-workers.[15] Their k_p value is derived from emulsion polymerization rate data employing the assumption that the average number radicals per particle is $^1/_2$, an assumption that is not valid for systems which exhibit significant radical desorption. PLP offers the possibility of obtaining an estimate for k_p with no model-based assumptions.

Figure 6 shows sample mass MWDs and derivatives obtained with AIBN as the photoinitiator. The distributions show the sharp primary peak and a secondary higher MW shoulder characteristic of pulsed-laser polymerization. Inflection points from both the mass and molar distributions have been calculated. As with styrene and MMA, the measured inflection points from the two distributions are very close. The inflection points and k_p values are reported in Table III.

Table III. Pulsed-Laser Polymerization with Chloroprene (t_0 = 0.1 s)

T (°C)	M_0 molar MWD	M_0 mass MWD	k_p (L/mol·s)
	AIBN		
10	21 400	21 400	221
	24 000	24 200	248
15	27 000	27 400	281
20	36 800	37 600	385
25	44 600	44 800	469
	40 400	40 800	425
30	45 800	46 200	485
35	55 800	56 000	595
40	62 800	63 000	673
	Vazo 88		
35	51 000	48 200	543
40	58 800	58 800	630
45	77 400	77 000	835
50	91 000	91 600	988
55	111 600	113 000	1219

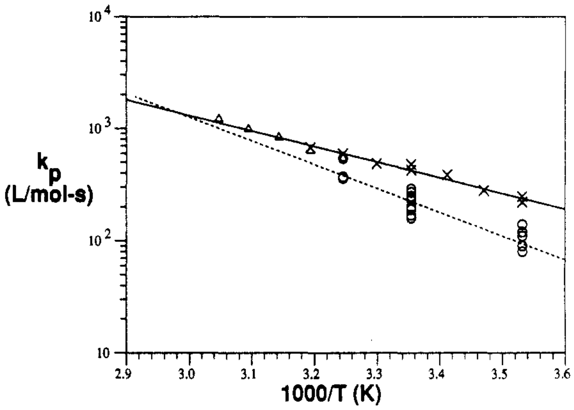

Figure 7. Arrhenius plot for the chloroprene propagation rate coefficient: (×, Δ, —) pulsed-laser polymerization data and fit; (○, - - -) data and fit from Hrabák *et al.*[15]

As mentioned in the Experimental Section, nitrile initiators were used for the chloroprene PLP experiments. However, the analysis of the experimental data provides several indications that the MWD of the polymer produced is dominated by laser-induced photoinitiation rather than by thermal initiation. The agreement between k_p values calculated from molar and mass distributions is similar to that obtained for MMA and styrene. As well, a faint secondary peak at twice M_0 can be seen from some derivative plots, as predicted by theory (see Figure 6). These observations strongly support the conclusion that thermal initiation is not a factor in the data analysis.

The k_p values from Table III have been used to create the Arrhenius plot of Figure 7. The individual k_p estimates are well fit by the Arrhenius relation:

$$\ln k_p = (16.786 \pm 0.435) - (3204 \pm 13)/T \qquad (13)$$

or

$$k_p\ (\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}) = 1.95 \times 10^7 \exp\left(\frac{-6365\ \mathrm{cal{\cdot}mol^{-1}}}{\mathrm{RT}}\right) \qquad (14)$$

Figure 7 also shows the k_p estimates of Hrabák and co-workers.[15] The points are taken from their tabulated data, and the line is their suggested fit:

$$k_p\ (\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}) = 2.9 \times 10^9 \exp\left(\frac{-9700\ \mathrm{cal{\cdot}mol^{-1}}}{RT}\right) \qquad (15)$$

Considering the scatter in the Hrabák *et al.* data and the modeling assumptions made during estimation of k_p, the agreement with the PLP data is not unreasonable but perhaps coincidental. The polymerization rate, R_p, in an

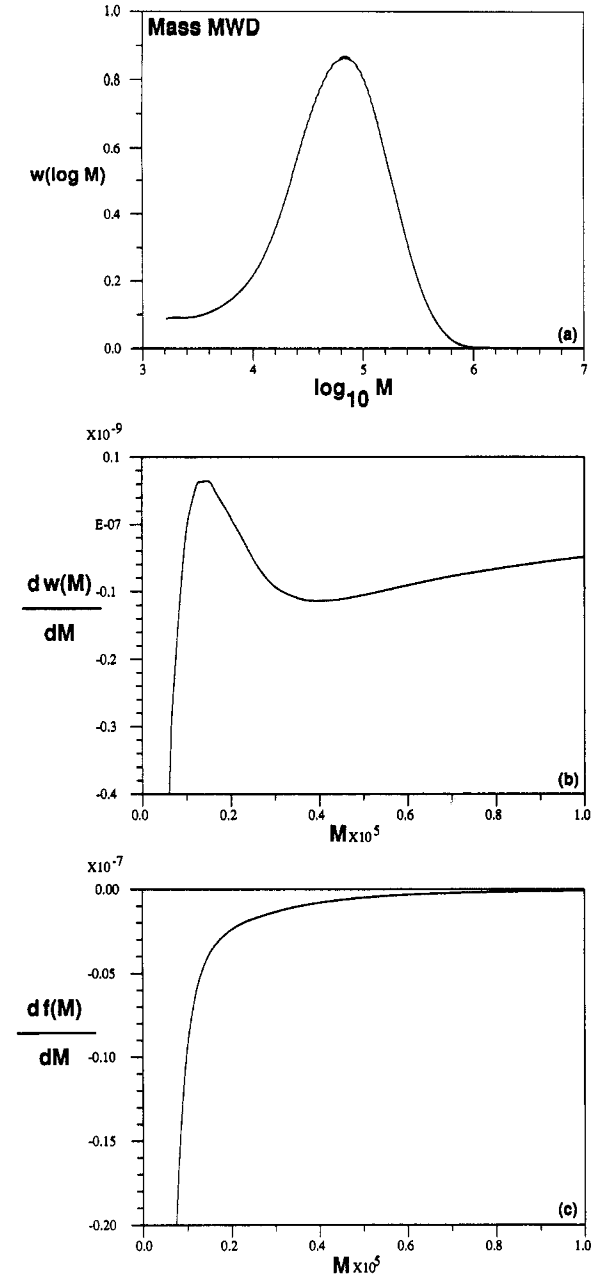

Figure 8. Analysis of poly(vinyl acetate) produced by pulsed-laser polymerization at 40 °C: (a) mass MWD; (b) derivative plot from $w(M)$ distribution; (c) derivative plot from $f(M)$ distribution.

emulsion system is given by:[15]

$$R_p = k_p\bar{n}N[\mathrm{M}] \qquad (16)$$

where $\bar{n}$ is the number of radicals per particle, and N is the molar concentration of particles in the emulsion. Hrabák *et al.* assumed that $\bar{n} = {}^1/_2$ and used measured values of R_p, N, and [M] to calculate values of k_p with eq 16. The assumption that $\bar{n} = {}^1/_2$ is valid if the radical entry rate into the particles is high, the desorption rate from the particles is low, and chain termination in the particles is high. Since it is unknown if these conditions were met during their experiments, it is believed that the results from the pulsed-laser technique, based upon a direct measurement without any modeling assumptions, are more accurate.

Vinyl Acetate. The importance of fully analyzing molecular weight distributions produced by PLP is illustrated by Figure 8a, a mass MWD of poly(vinyl acetate) produced at 40 °C at a pulse rate of 10 Hz. Parts b and c of Figure 8 show the corresponding derivative curves, as calculated from the mass and number distributions. In contrast to the other monomers discussed above, the maxima from the two distributions do not coincide. In fact, because of the smooth nature of the distribution, the derivative plot from the $f(M)$ distribution has no clear maximum. In addition, no secondary peak corresponding to polymer with lifetime $2t_0$ can be seen from the $w(M)$ distribution. The criteria for calculating k_p from this pulsed-laser-generated polymer sample are not met. Davis *et al.*[8] observe the same type of broad, featureless distributions for methyl acrylate and butyl acrylate. Work is underway to determine why PLP fails for these more difficult systems and whether a set of experimental conditions can be found to yield estimates for k_p.

Conclusions

With proper analysis, a single PLP experiment not only yields a direct estimate of k_p but also provides consistency checks as to the validity of the estimate. It is shown that styrene, MMA, and chloroprene all meet the self-contained consistency criteria. The data presented for styrene and MMA cover a wider temperature range than any other individual data sets in the literature, while the k_p estimates for chloroprene are thought to be the most complete and accurate to be published to date.

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References and Notes

(1) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.

(2) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 293.

(3) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 851.

(4) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(5) Olaj, O. F.; Schnöll-Bitai, I. *Eur. Polym. J.* **1989**, *25*, 635.

(6) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.

(7) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1990**, *23*, 2113.

(8) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Polym. Int.* **1991**, *24*, 65.

(9) Pascal, P.; Winnik, M. A.; Napper, D. H.; Gilbert, R. G. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 213.

(10) Coleman, M. M.; Fuller, R. E. *J. Macromol. Sci., Phys.* **1975**, *11*, 419.

(11) Atkinson, C. M. L.; Dietz, R. *Eur. Polym. J.* **1979**, *15*, 21.

(12) Peebles, L. H. *Molecular Weight Distributions in Polymers*; Interscience Publishers: New York, 1971.

(13) *IMSL Problem-Solving Software Systems Math/Library User's Manual, Version 1.0*; IMSL, Inc.: Houston, TX, 1987.

(14) Patrode, W.; Scheiber, W. J. *J. Am. Chem. Soc.* **1939**, *61*, 3449.

(15) Hrabák, F.; Bezděk, M.; Hynková, V.; Pelzauer, Z. *J. Polym. Sci.* **1967**, *C16*, 1345.

(16) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Polymer* **1990**, *31*, 154.

(17) Shen, J.; Tian, Y.; Wang, G.; Yang, M. *Makromol. Chem.* **1991**, *192*, 2669.

(18) Carswell, T. G.; Hill, D. J. T.; Londero, D. I.; O'Donnell, J. H.; Pomery, P. J.; Winzor, C. L. *Polymer* **1992**, *33*, 137.

(19) Yokawa, M.; Ogo, Y.; Imoto, T. *Makromol. Chem.* **1974**, *175*, 179.

(20) Mahabadi, H. K.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1977**, *A11*, 967.

(21) Fukuda, T.; Ma, Y.-D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.

(22) Sack-Kouloumbris, R.; Meyerhoff, G. *Makromol. Chem.* **1989**, *190*, 1133.

(23) Landsdowne, S. W.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *J. Chem. Soc., Faraday Trans.* **1980**, *76*, 1344.