Determination of Free-Radical Propagation Rate Coefficients for Cycloalkyl and Functional Methacrylates by Pulsed-Laser Polymerization

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ABSTRACT: Free-radical propagation rate coefficients (k_p) for three cycloalkyl methacrylates and two functional methacrylates were measured at temperatures between 30 and 110 °C. The data were obtained by analyzing molecular weight distributions of polymer produced by pulsed-laser polymerization − the PLP/MWD technique. Arrhenius parameters were compared with recent results reported for linear and branched alkyl methacrylates, including methyl methacrylate (MMA) and *n*-dodecyl methacrylate (DMA). The highest k_p value, for 2-hydroxypropyl methacrylate, is more than twice the MMA value, and is 50% higher than the DMA value at 50 °C. The monomer with the lowest k_p value, isobornyl methacrylate, has a coefficient of similar magnitude to DMA. Values for the other three monomers − glycidyl, cyclohexyl, and benzyl methacrylates − are intermediate between these two levels.

Introduction

The coatings industry is undergoing a period of rapid change, largely driven by legislative pressures to reduce environmental emissions and by customer demands to improve quality and reduce costs. In response to these challenges, many solventborne acrylic coating formulations now employ monomers with reactive functionalities, such as carboxyl, hydroxyalkyl, amino, and/or epoxy groups. Thus, it is possible to produce high conversion, low viscosity polymer solutions that further react in a second thermoset process to form a tough, cross-linked coating.[1,2]

Methacrylates containing cyclic groups also can provide beneficial properties for specific applications: benzyl methacrylate increases polymer hydrophobicity, whereas cycloalkyl methacrylates with bridged structures, such as isobornyl methacrylate, increase polymer glass transition temperature without a concomitant increase in solution viscosity. Matsumoto and coworkers[3,4] have used electron spin resonance (ESR) spectroscopy to study the polymerization of various cycloalkyl methacrylates, the majority with bridged structures. They found that polymerization proceeds at an enhanced rate compared with typical alkyl methacrylates, a behavior attributed to reduced rates of termination.

In light of these trends, it is useful to compare the free-radical polymerization behavior of methacrylate monomers containing cyclic and functional groups with that observed for more traditional alkyl methacrylates. The PLP/MWD technique, which combines pulsed-laser polymerization (PLP) with analysis of the ensuing polymer molecular weight distribution (MWD), has emerged as a powerful technique to study free-radical polymerization kinetics. The method provides a direct and robust measure of propagation rate coefficients (k_p),[5−7] and can also be used to infer information about low-conversion termination rate coefficients (k_t).[8,9]

This work reports k_p values for cyclohexyl (CHMA), benzyl (BzMA), isobornyl (iBoMA), glycidyl (GMA), and 2-hydroxypropyl (HPMA) methacrylates, as measured by the PLP/MWD technique between 30 and 110 °C. In support of this effort, Mark-Houwink-Sakurada (MHS) calibration constants necessary for MWD analysis by size exclusion chromatography (SEC) are measured. The resulting Arrhenius fits to these k_p data are compared with those reported for linear and branched alkyl methacrylates measured with the same experimental techniques.[10]

Experimental Section

The experimental pulsed-laser setup has been described previously.[10,11] A pulsed Nd:YAG laser (Quanta-Ray, GCR-190−100) with a harmonic generator emits light of wavelength 355 nm at pulse energies up to 70 mJ/pulse and a half-height pulse width of 6 ns. Experiments were performed with laser repetition rates controlled by a digital delay generator (Stanford DG-535) between 10 and 100 Hz, benzoin photoinitiator (Aldrich) at concentrations between 1 and 10 mmol·L^{-1} in bulk monomer, and pulse energies between 8 and 65 mJ. (In this work, the energy reported is the exit energy of the laser; the incident power that reaches the sample is not routinely measured, but is ∼20% less.) All monomers were examined in the temperature range of 30 to 110 °C, with a few data points obtained at lower temperatures (10 to 30 °C).

CHMA, iBoMA, GMA, HPMA (all from Aldrich) and BzMA (Rohm Tech) were used as received. After addition of the photoinitiator, the 3 mL bulk monomer samples were heated to the desired temperature and pulsed for sufficient time to convert a small fraction of the monomer to polymer. Conversions were not quantitatively determined; to qualitatively check for the presence of polymer, a drop of the reaction mixture was

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Table 1. Density and Mark-Houwink-Sakurada Calibration Constants for Methacrylates[a]

methacrylate	MW_{mon} (g·mol^{-1})	ρ_0 (g·cm^{-3})	$10^4 b$ (g·cm^{-3}·°C^{-1})	$10^5 K$ (dL·g^{-1})	a
cyclohexyl	168	0.98320	9.09	6.64	0.683
benzyl	162	1.05621	9.03	10.8	0.635
isobornyl	221	0.99798	7.96	13.5	0.560
glycidyl	142	1.09428	10.41	27.8	0.537
2-hydroxypropyl	144	1.04786	9.19	102	0.460

[a] MHS constants measured in tetrahydrofuran at 30 °C; ρ (g·cm^{-3}) = $\rho_0 - bT$/°C; $[\eta]$ (dL·g^{-1}) = KM^a.

added to methanol in order to precipitate the polymer. Heptane was used to check for polymer formation in HPMA.

Monomer densities were determined experimentally at 25, 50, and 80 °C with an Anton Paar DMA60/DMA412 density meter, using water and air for calibration. To estimate densities as a function of polymerization temperature, the measured values were fit by a linear relation:

$$\rho\ (\mathrm{g{\cdot}cm^{-3}}) = \rho_0 - bT/^\circ\mathrm{C} \tag{1}$$

Coefficients for the different monomers are given in Table 1. Measured densities are in good agreement with room-temperature values supplied by the manufacturers.

SEC analyses were performed at 30 °C 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). The PLP-generated samples were diluted in tetrahydrofuran (THF) to polymer concentrations in the range of 1 to 3 mg·mL^{-1} for SEC injection. (The magnitude of the SEC detector signal, proportional to polymer concentration, was also used as an indicator to ensure that monomer conversion induced by the laser pulses was kept low, in the range 0.5−3%.) Molecular weight distributions were calculated using universal calibration, based against a primary polystyrene (pS) calibration established with narrow-MW standards. The required MHS calibration parameters were measured using a previously described triple-detector SEC instrument,[11,12] and are summarized in Table 1. Calibration parameters for pS ($K = 11.4 \cdot 10^{-5}$ dL·g^{-1} and $a = 0.716$) were measured with the same instrumentation.[10−12]

Values of k_p are calculated from the characteristic molecular weight (M_0) of polymer chains with length controlled by the number of propagation steps that occur in the time between two laser pulses (t_0):

$$k_p = M_0/(1000\rho t_0) \tag{2}$$

It has been shown that the best measure of M_0 is the point of inflection on the low molar mass side of the peak of the polymer MWD,[5−7] determined in this work by searching for a maximum on the derivative of the experimental MWD.[13] Consistent with our most recent work,[10] the SEC weight-log form of the MWD is used to estimate k_p values; a recent theoretical study concludes that this method provides the most robust measure of M_0, because it is less sensitive to instrument broadening.[14]

Results

More than 30 data points were collected for CHMA, iBoMA, GMA, and HPMA; BzMA was not studied as extensively (14 experiments). Complete details of the individual experimental results are available as Supporting Information. Typical polymer MWDs for CHMA, iBoMA, GMA, and HPMA are shown in Figures 1−4; the curves for BzMA (not shown) are very similar to those for CHMA. All of these distributions are for samples pulsed at 90 °C and a range of pulse repetition rates. Although the shapes of the MWDs vary with repetition rate and monomer type (discussed in more detail later), they all show the multimodal structure characteristic of pulsed-laser MW control.[5,13] Well-defined primary and secondary inflection points were found in all cases, which is illustrated by Figure 5, a plot of the derivative curves from samples for all five monomers pulsed at 90 °C and 20 Hz. Vertical lines have been drawn to indicate the position of M_0 for iBoMA and HPMA; M_0 values obtained from derivative plots such as these are used to calculate k_p according to eq 2. As expected, the inflection points (and thus k_p values) were invariant with laser power (8−65 mJ/pulse) and photoinitiator concentration (1−10 mmol/L), an important consistency check for the PLP/MWD technique.[6,7]

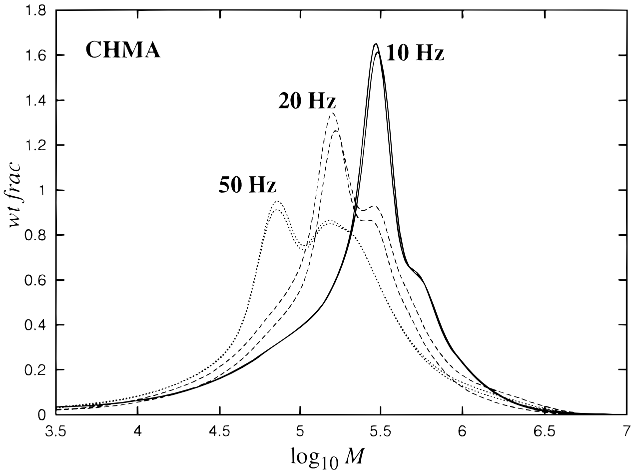

Figure 1. Polymer molecular weight distributions for cyclohexyl methacrylate bulk monomer samples pulsed at 90 °C with benzoin photoinitiator: (—) 10 Hz, 35 mJ/pulse, [**I**] = 3 mmol·L^{-1}; (---) 20 Hz, 40 mJ/pulse, [**I**] = 5 mmol·L^{-1}; (···) 50 Hz, 60 mJ/pulse, [**I**] = 5 mmol·L^{-1}.

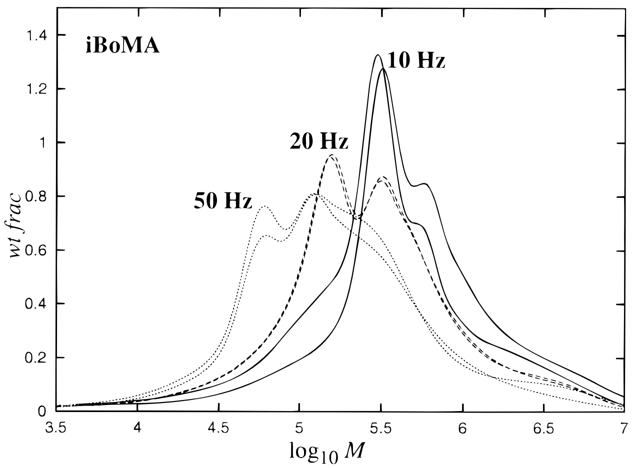

Figure 2. Polymer molecular weight distributions for isobornyl methacrylate bulk monomer samples pulsed at 90 °C with benzoin photoinitiator at 5 mmol·L^{-1}: (—) 10 Hz, 65 mJ/pulse; (---) 20 Hz, 40 mJ/pulse; (···) 50 Hz, 60 mJ/pulse.

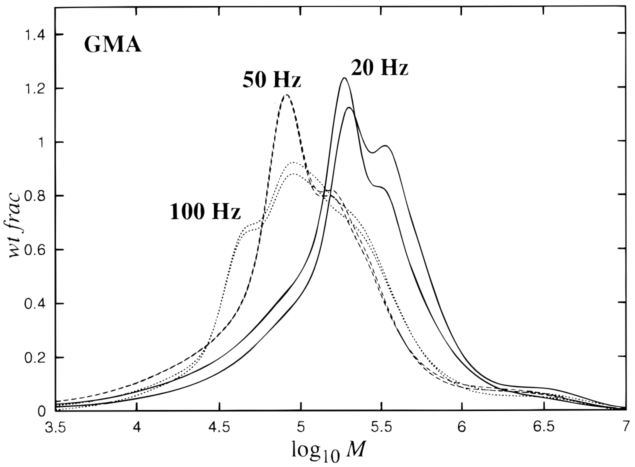

Figure 3. Polymer molecular weight distributions for glycidyl methacrylate bulk monomer samples pulsed at 90 °C with benzoin photoinitiator: (—) 20 Hz, 42 mJ/pulse, [**I**] = 1 mmol·L^{-1}; (---) 50 Hz, 31 mJ/pulse, [**I**] = 2 mmol·L^{-1}; (···) 100 Hz, 60 mJ/pulse, [**I**] = 1 mmol·L^{-1}.

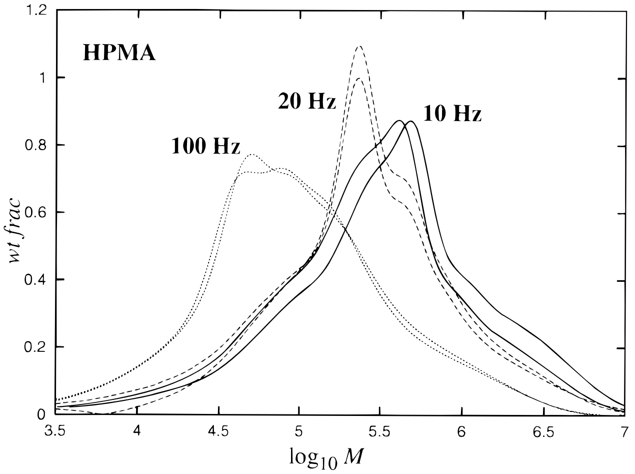

Figure 4. Polymer molecular weight distributions for 2-hydroxypropyl methacrylate bulk monomer samples pulsed at 90 °C with benzoin photoinitiator at 5 mmol·L^{-1}: (—) 10 Hz, 40 mJ/pulse; (---) 20 Hz, 35 mJ/pulse; (···) 100 Hz, 50 mJ/pulse.

Unfortunately, the observation of well-defined primary and secondary inflection points from the MWD does not guarantee an accurate measure of k_p, which is also highly dependent on the accuracy of the MHS calibration curve used for SEC analysis.[11] As in our previous work with linear and branched alkyl methacrylates[10,11] and acrylates,[12] a triple-detector SEC instrument has been employed to measure MHS calibration constants. For these previous monomer systems, the measured k_p values were in good agreement (within 10−20%) with values calculated using other published MHS constants. This validation of our calibration technique provides confidence in the accuracy of k_p determinations for the functional and cycloalkyl monomers examined in this work, for which no literature SEC calibration constants could be found.

Validation of SEC calibration and k_p estimates were also checked by running pulsed-laser experiments over a range of pulse repetition rates. Varying the laser pulse repetition rate between 10 and 100 Hz shifts the position of M_0 by an order of magnitude (see Figures 1−4). Obtaining consistent k_p estimates over such a wide range of MW values provides evidence supporting the accuracy of the SEC calibrations. Figures 6−9 show complete experimental results for CHMA, iBoMA, GMA, and HPMA, respectively, with the k_p data plotted according to the Arrhenius relationship and sorted by pulse repetition rate. No significant trends with repetition rate are found for CHMA (Figure 6), BzMA, or HPMA (Figure 9) within the range of repetition rates examined experimentally. For the other two monomers, however, small differences may exist. iBoMA k_p estimates (Figure 7) from experiments run at high repetition rate (50 Hz) are slightly lower than those at lower repetition rates (10 and 20 Hz); for GMA (Figure 8), the k_p estimates from the high repetition rate experiments are slightly higher. Although perhaps systematic for these two monomers, the variation over this wide range of repetition rate is still <20%. This uncertainty is most likely introduced by SEC calibration issues; because the same trend is not consistently observed among all monomers, it cannot be caused by an artifact of the pulsing technique. Although significant, 20% error is much smaller than the order of magnitude scatter that

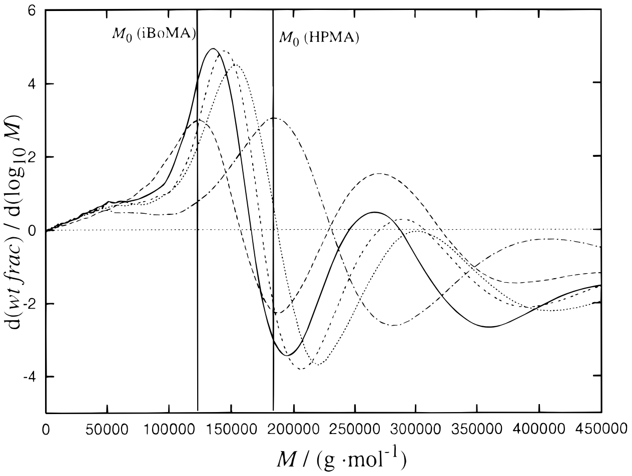

Figure 5. Derivative plots from MWDs obtained by PLP at 90 °C and 20 Hz for: (—) CHMA; (---) iBoMA; (···) GMA; (−·−) HPMA; and (-- --) BzMA. Position of primary inflection points (M_0) indicated for iBoMA and HPMA, with values for other monomers intermediate between these two. Corresponding MWDs shown in Figures 1−4, with the exception of benzyl methacrylate, which was produced by PLP experiments with 40 mJ/pulse, [**I**] = 5 mmol·L^{-1}.

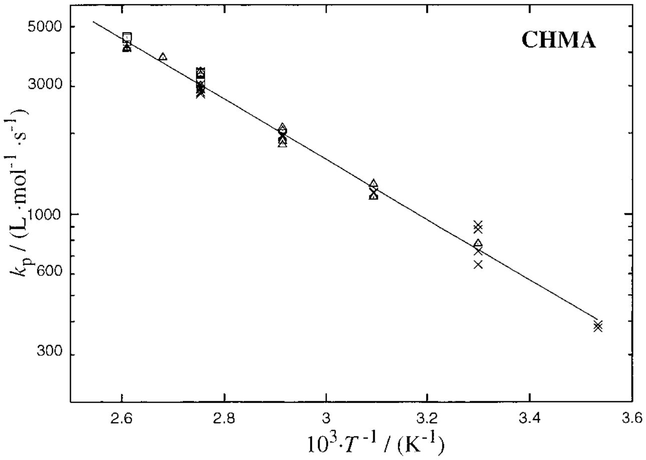

Figure 6. Arrhenius plots of the propagation rate coefficient (k_p) for cyclohexyl methacrylate. Points indicate experimental data collected at laser repetition rates of: (×) 10 Hz; (△) 20 Hz; (□) 50 Hz; and (+) 100 Hz. Curve is best fit of eq 3 to data; with coefficients summarized in Table 2.

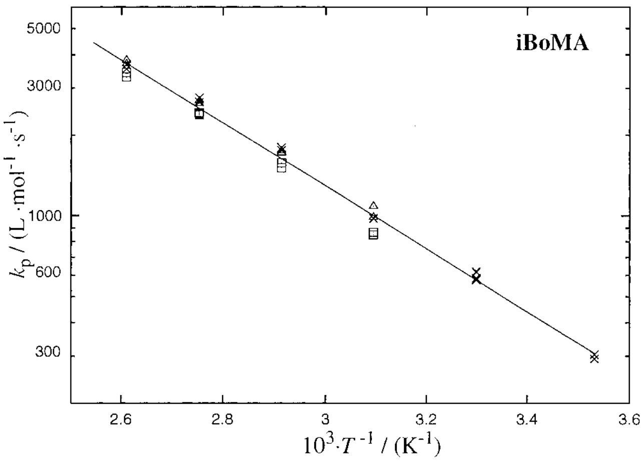

Figure 7. Arrhenius plots of the propagation rate coefficient (k_p) for isobornyl methacrylate. Points indicate experimental data collected at laser repetition rates of: (×) 10 Hz; (△) 20 Hz; and (□) 50 Hz. Curve is best fit of eq 3 to data; coefficients summarized in Table 2.

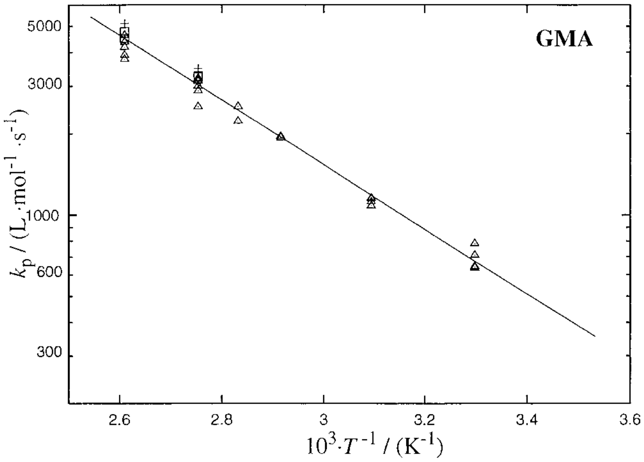

Figure 8. Arrhenius plots of the propagation rate coefficient (k_p) for glycidyl methacrylate. Points indicate experimental data collected at laser repetition rates of: (△) 20 Hz; (□) 50 Hz; and (+) 100 Hz. Curve is best fit of eq 3 to data; coefficients summarized in Table 2.

commonly existed in k_p estimates prior to the introduction of the PLP/MWD technique.[6,7]

The variations of k_p with temperature for all monomers are well-fit by the Arrhenius equation:

$$\ln[(k_p/(\text{L·mol}^{-1}\text{·s}^{-1}))] = \ln A - E/R(T^{-1}/\text{K}^{-1}) \quad (3)$$

Results from linear least-squares fitting, including standard error estimates, are summarized in Table 2. The lines plotted in Figures 6−9 are generated using these tabulated Arrhenius parameters. The number of data points and k_p values at 50 °C calculated from the Arrhenius fit are also tabulated, with results for methyl (MMA),[7] *n*-butyl (BMA),[10] and *n*-dodecyl (DMA)[10] methacrylates included for comparison purposes. In addition, joint confidence intervals (JCIs) for the Arrhenius parameters have been calculated assuming a constant relative uncertainty in k_p estimates using a nonlinear least-squares fitting routine available in the literature.[15] The Arrhenius parameter estimates obtained were identical to the linear fit, as is expected for this error structure.[7] Confidence intervals calculated at the 95% level are plotted in Figure 10.

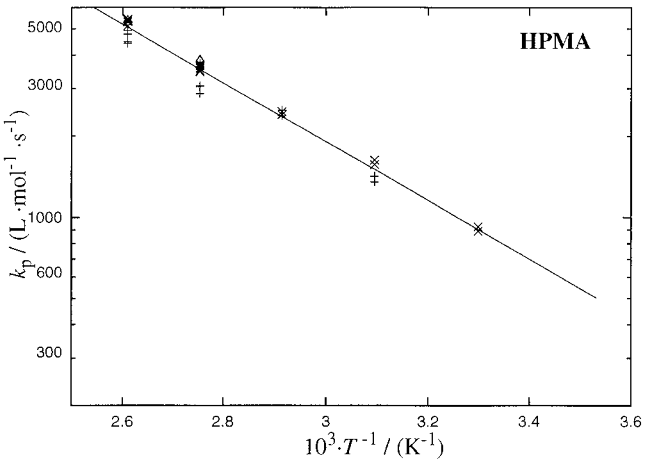

Figure 9. Arrhenius plots of the propagation rate coefficient (k_p) for 2-hydroxypropyl methacrylate. Points indicate experimental data collected at laser repetition rates of: (×) 10 Hz; (△) 20 Hz; and (+) 100 Hz. Curve is best fit of eq 3 to data; coefficients summarized in Table 2.

Table 2. Propagation Rate Coefficients for Methacrylates[a]

methacrylate	N_{pts}	ln A (L·mol^{-1}·s^{-1})	E/R	k_p at 50 °C (L·mol^{-1}·s^{-1})
cyclohexyl	44	15.14 ± 0.12	2587 ± 42	1257
benzyl	14	15.10 ± 0.13	2581 ± 44	1224
isobornyl	34	15.27 ± 0.14	2702 ± 47	1002
glycidyl	32	15.61 ± 0.19	2759 ± 69	1118
2-hydroxypropyl	37	15.07 ± 0.18	2505 ± 64	1504
methyl	69	14.80 ± 0.10	2689 ± 31	649
n-butyl	42	14.79 ± 0.14	2621 ± 49	794
n-dodecyl	48	14.67 ± 0.12	2503 ± 39	1011

[a] Arrhenius parameters include standard error; MMA data and fit from ref 7; BMA and DMA data and fit from ref 10.

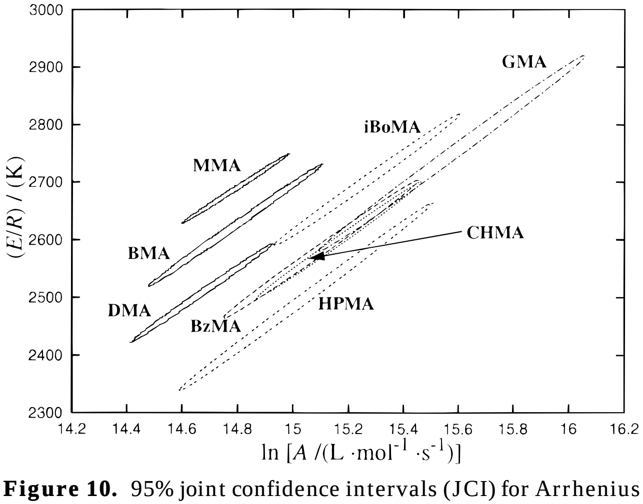

Figure 10. 95% joint confidence intervals (JCI) for Arrhenius parameters ln A and E/R (see eq 3), from nonlinear least-squares fitting of k_p data, calculated assuming constant but unknown relative error in k_p values. JCIs for CHMA (···) and BzMA (---) superimpose one another. JCIs for methyl methacrylate from ref 7, and for *n*-butyl and *n*-dodecyl methacrylates from ref 10.

There are several general statements that can be made from the k_p results and Arrhenius parameters summarized in Table 2 and Figure 10. First of all, k_p values for these five cycloalkyl and functional methacrylates are, for the most part, higher than those measured for linear and branched alkyl methacrylates. (Within a series of seven linear and branched alkyl methacrylates examined by the PLP/MWD technique, MMA had the lowest k_p value and DMA the highest.[10]) The highest k_p value is for HPMA; it is more than twice the MMA value and is 50% higher than the DMA value at 50 °C. The lowest k_p value from the new results, for iBoMA, is of similar magnitude to that for DMA. The other three monomers are between these extremes, with CHMA and BzMA exhibiting virtually identical propagation kinetics. These variations among the methacrylates, although small compared with the differences between acrylates and methacrylates,[12] are significant.

The Arrhenius fits and JCIs (Figure 10) provide some indication as to the source of the k_p variations. Activation energies are very similar for all methacrylates (20−23 kJ/mol). In our previous work, we suggest that small variations within this range may be responsible for the differences observed between MMA and DMA propagation behavior; the larger DMA k_p values were attributed to a slightly lower activation energy.[10] Another recent PLP/MWD study concludes, on the other hand, that the observed increase of k_p with ester size is due to an increase in frequency factor rather than a decrease in activation energy.[16] No systematic variation can be seen in E/R values determined for the cycloalkyl and functional methacrylates examined in this work. Instead, the results in Table 2 and Figure 10 suggest that the higher k_p values result from larger frequency factors. An explanation of these differences is beyond the scope of this paper. However, it is hoped that these and other PLP/MWD results will lead to new fundamental insights into how radical and monomer structure control reactivity.

There are very little data available for comparison purposes with these current results. Matsumoto et al.[4] studied the propagation behavior of several cycloalkyl methacrylates using ESR spectroscopic techniques, including CHMA and iBoMA. The magnitude of the reported k_p values are lower than the current PLP/MWD results by a factor of 3. This large difference may arise from ESR calibration problems. (ESR signals have to be calibrated with stable radical standards to measure the absolute radical concentrations necessary to estimate k_p.) It is hoped that future PLP and ESR work can resolve these differences. However, it is comforting to note that the relative difference between iBoMA and CHMA k_p values measured by ESR is very similar to the PLP results, with k_p of iBoMA 10−20% lower than that of CHMA.

Other recent PLP/MWD studies provide a comparison for some of the k_p data reported in this paper. A recent GMA study by Buback and Kurz[17] includes an independent determination of MHS parameters; the k_p values measured are in good agreement with this study. Zammit et al.[18] employ multi-detector SEC for direct analysis of PLP-generated MWDs for several different methacrylates. Results for ethyl and *n*-butyl methacrylates are in good agreement with our previous work.[10,11] BzMA k_p values are also collected in the temperature range 6−48 °C. The activation energy obtained is slightly higher than that of this work (22.7 versus 21.5 kJ/mol), as are the k_p values (1428 versus 1224 L/mol·s at 50 °C). This 17% difference is most likely a reflection of the accuracy that may be expected from SEC analysis of PLP/MWD results for new monomer systems.

Although propagation kinetics control the position of the MWD peaks (with k_p values estimated from the peak inflection points), the overall shape of the MWDs at a fixed laser repetition rate is strongly influenced by the termination kinetics in the system.[12,14,19] Different methodologies have been proposed to quantitatively estimate k_t from PLP-generated MWDs.[8,9] These procedures, however, require a careful measure of conversion per pulse, and require that the entire sample cell be illuminated. These conditions (not needed for k_p measurement) are not met with our experimental setup. Nonetheless, an examination of the MWDs shown in Figures 1−4 provides qualitative information about relative k_t values among these methacrylates. These polymer samples were produced under very similar experimental conditions of laser pulse energy and photoinitiator concentrations. Thus, the radical concentrations generated per pulse also can be expected to fall in a narrow range, facilitating this qualitative comparison.

Before proceeding, it is useful to review how the shape of the MWDs is affected by pulse repetition rate, which also has a large influence on the fraction of radicals terminated between pulses. This fraction, defined as β, is given by eq 4 (assuming chainlength-independent termination):[5]

$$\beta = [\Delta R\cdot]/[R\cdot]_{max} = k_t[R\cdot]_{max}t_0/(1 + k_t[R\cdot]_{max}t_0) \quad (4)$$

where $[\Delta R\cdot]$ is the increase in radical concentration created by each laser pulse, and $[R\cdot]_{max}$ is the radical concentration reached immediately after each pulse (the sum of surviving and newly generated radicals). Equation 4 indicates that β decreases (a greater fraction of the radicals survive the subsequent pulse) as laser repetition rate increases (t_0 decreases). As the mass fraction of polymer formed from the longer-lived radicals increases, the relative height of the primary peak decreases and that of the secondary peak increases. These trends with repetition rate are evident in the MWDs shown as Figures 1−4: the primary peaks of the MWDs produced by pulsing at high repetition rates (50 and 100 Hz) are smaller relative to those produced by pulsing at low repetition rates (10 and 20 Hz).

A decrease in k_t has the same effect on polymer MWDs as a decrease in t_0 (see eq 4): β decreases, the magnitude of the primary peak decreases, and the magnitude of the secondary overtone peak increases. Thus, it is interesting to compare the distributions of the various methacrylates pulsed at nearly identical conditions at a repetition rate of 20 Hz. Most striking is the difference between iBoMA and the other methacrylates. The iBoMA MWDs produced at 20 Hz (Figure 2) have smaller primary peaks relative to the secondary peaks than the MWDs of the other methacrylates, a strong indication that a smaller fraction of iBoMA radicals are terminated between subsequent pulses. From this result it can be concluded that, in accordance to the findings of Matsumoto et al.,[4] the bridged cycloalkyl group in iBoMA decreases k_t relative to other methacrylate monomers.

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Supporting Information Available: Tables 3−7, containing detailed results and experimental conditions for individual PLP experiments, are available as supporting material (11 pages). Ordering and Internet access information is given on any current masthead page.

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