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Determination of Free-Radical Propagation Rate Coefficients for Alkyl Methacrylates by Pulsed-Laser Polymerization

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ABSTRACT: Values of free-radical propagation rate coefficients (k_p) for two new methacrylate monomers—2-ethylhexyl and isodecyl methacrylates—have been measured in the temperature range 10−90 °C by analyzing molecular weight distributions of polymer produced by pulsed-laser polymerization (the PLP/MWD technique). In addition, new PLP/MWD results for *n*-butyl and *n*-dodecyl methacrylates are reported, and previously published data for ethyl and isobutyl methacrylates are reanalyzed. The temperature dependence of k_p for these six monomers is compared to that recently reported for methyl methacrylate. A consistent increase of k_p with size of the ester group is observed, with values for *n*-dodecyl methacrylate 50−60% higher than those for methyl methacrylate. Although this increase is statistically significant, it is less certain whether it is attributable to a decrease in the activation energy or an increase in the frequency factor. The experimental results favor the former explanation.

Introduction

The lack of reliable kinetic rate coefficients often impedes attempts to obtain a better fundamental understanding of, and to build generalized models for, free-radical polymerization reaction systems. The problem is so well-recognized that an IUPAC working party has been formed to address the issue.[1,2] First efforts have concentrated on obtaining better values for propagation rate coefficients (k_p), with significant progress in the last few years largely due to the introduction of the PLP/MWD technique.[3] This method combines pulsed-laser polymerization (PLP) with analysis of the ensuing polymer molecular weight distribution (MWD) to provide a more direct and robust measure of k_p than previously available. Advantages of the technique are well-documented in the literature,[4,5] and consistent sets of styrene[6] and methyl methacrylate (MMA)[7] k_p values obtained by several research laboratories over a range of experimental conditions have been compiled by the IUPAC working party.

Evidence showing large differences in k_p values between monomer families continues to emerge, with PLP/MWD data published for styrene (see ref 6 and references therein), methacrylates,[5,7−10] vinyl acetate,[5] and acrylates.[11,12] Consistent, but much smaller, differences within a monomer family have also been observed. It was found that the activation energies for ethyl (EMA), *n*-butyl (BMA), and isobutyl (iBMA) methacrylates are very similar to the MMA value but that k_p values increase slightly as the monomer MW increases within the homologous series.[8]

One factor that limits the accuracy of k_p values measured by the PLP/MWD technique is its reliance upon determination of a characteristic chain length DP_0 from the polymer MWD. DP_0 is related to the number of propagation events which a radical undergoes in the time between two laser pulses (t_0):

$$DP_0 = k_p[M]t_0 \qquad (1)$$

where [M] is the monomer concentration. DP_0 is determined from the polymer MWD, which is generally measured by size exclusion chromatography (SEC) and calculated using the principle of universal calibration.[13] Thus, the accuracy of k_p determinations is directly dependent upon the accuracy of Mark−Houwink−Sakurada (MHS) calibration constants used for SEC analysis.[5] Recently we have employed a triple-detector SEC instrument to measure MHS calibration constants and have found reasonable agreement with published values.[5,12] Slight differences in MHS constants, however, shifted the k_p values for EMA, BMA, and iBMA reported in ref 8 by 10−20%;[5] the same study reports first results for *n*-dodecyl methacrylate (DMA). It is important to remember that this 10−20% uncertainty introduced by SEC calibration issues, while significant, is much smaller than the order of magnitude scatter that existed prior to the introduction of the PLP/MWD technique.[1,2]

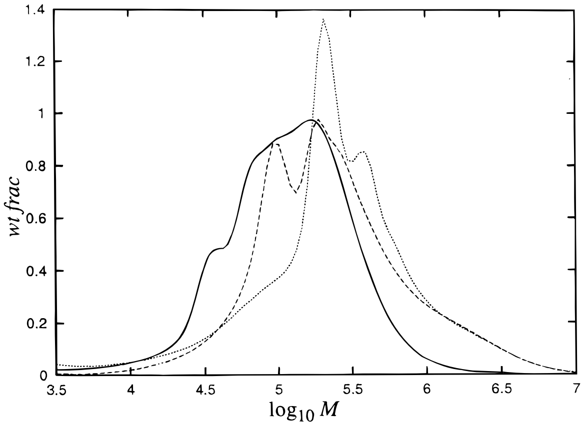

Figure 1. Polymer molecular weight distributions for 2-ethylhexyl methacrylate bulk monomer samples pulsed at 10 Hz and 10 mJ/pulse, with a benzoin concentration of 1 mmol·L^{-1}. Temperature of polymerization: (—) 10 °C; (- - -) 50 °C; (···) 90 °C.

Other MWD analysis issues of lesser significance have also been addressed. A consensus has emerged that the best estimate of DP_0 is the point of inflection on the low molar mass side of the peak of the MWD,[3,6,7] usually determined by searching for a maximum on a differential plot of the MWD (see Figures 1 and 2). A minor uncertainty that remains is the form of the MWD

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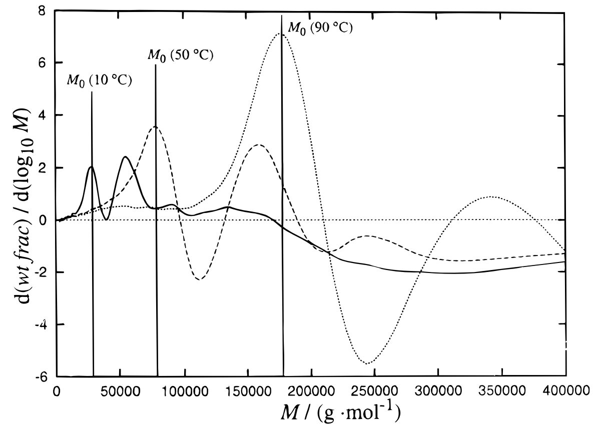

Figure 2. Derivative plots from poly(2-ethylhexyl methacrylate) molecular weight distributions shown in Figure 1: (—) 10 °C; (- - -) 50 °C; (···) 90 °C. $DP_0 = M_0/MW_{mon}$, with M_0 as indicated and monomer molecular weight from Table 1.

to use for analysis.[7,14] SEC provides a mass molecular weight distribution on a logarithmic scale; it is possible to transform the same data to either a mass or a number chain-length distribution plotted on a linear scale. It has been found that experimental measures of DP_0 from these different distributions are very similar, with the values from the weight−log distribution slightly (5−10%) higher.[4] In our previous PLP work with the methacrylates, the number chain-length distribution was used to estimate k_p values.[5,8] Other researchers typically measure DP_0 from the SEC weight-log distribution (see refs 6 and 7 and references therein), as we have also done for more difficult monomers, such as the acrylates, for which the number chain-length distribution does not provide a clearly defined inflection point.[12] A recent theoretical study concludes that the SEC weight−log distribution provides the most robust measure of DP_0, since it is less sensitive to instrument broadening.[14] Thus in this paper, our last on the low temperature (10−90 °C) bulk propagation kinetics of methacrylates with alkyl ester groups, we have reanalyzed previous EMA, BMA, iBMA, and DMA data,[5,8] now estimating k_p values from SEC weight−log MWDs.

In addition, we add 2-ethylhexyl (EHMA) and isodecyl (iDMA) k_p results to the methacrylate data set and provide additional data for BMA and DMA. Including the recent compilation of data for MMA,[7] propagation kinetics for seven methacrylates with branched and linear alkyl ester groups are compared to provide new insights about how reactivity varies with structure within the monomer family.

Experimental Section

The experimental pulsed-laser setup has been described previously.[4,5] 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 25 Hz, benzoin photoinitiator (Aldrich) at concentrations between 0.2 and 20 mmol·L^{-1} in bulk monomer, and pulse energies between 10 and 70 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 approximately 20% less.) All monomers were examined in the temperature range 10−90 °C.

Results for the following methacrylates are reported: ethyl (EMA), *n*-butyl (BMA), isobutyl (iBMA), *n*-dodecyl (DMA), isodecyl (iDMA), and 2-ethylhexyl (EHMA). All monomers were obtained from Aldrich, and used as received. After addition of the photoinitiator, the 4 mL bulk monomer samples were heated to the desired temperature and pulsed for sufficient time to convert 0.5−2.5% of the 4 mL monomer sample to polymer. For EMA, BMA, and iBMA, conversions were measured gravimetrically. Because of the low vapor pressure of the other monomers, conversions were not quantitatively determined. To qualitatively check for the presence of polymer in these cases, a drop of the reaction mixture was added to methanol in order to precipitate the polymer. Conversions were also estimated to be low on the basis of the size of the SEC detector signals.

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*
ethyl	114	0.935 38	11.12	9.70	0.714
n-butyl	142	0.914 54	9.64	14.8	0.664
isobutyl	142	0.905 94	9.71	9.70	0.705
2-ethylhexyl	198	0.900 72	8.35	6.30	0.707
isodecyl	227	0.896 51	7.91	5.39	0.710
n-dodecyl	254	0.887 94	7.57	5.18	0.720

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

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. In order to estimate densities as a function of polymerization temperature, the measured values were fit by a linear relation

$$\rho\ (\mathrm{g{\cdot}cm^{-3}}) = \rho_0 - bT/°\mathrm{C} \tag{2}$$

Coefficients for the different monomers are given in Table 1. Calculated values for EMA, BMA, iBMA, and DMA are very close (within 1%) to those used in previous work.[5]

SEC analyses were performed on an instrument consisting of a Waters pump (Model 590), a Waters autosampler (WISP 712), two SHODEX columns (KF80M), and a Waters differential refractometer (Model 410) at 30 °C. The PLP-generated samples (5−25 mg·mL^{-1} polymer in monomer) were diluted in tetrahydrofuran (THF) to polymer concentrations of 1−3 mg·mL^{-1} for SEC injection. Molecular weight distributions were calculated using universal calibration, based against a primary polystyrene (pS) calibration established with narrow-MW standards. MHS calibration parameters were measured using a triple-detector SEC instrument, as described previously.[5,12] Values for the various methacrylates are summarized in Table 1; the constants for EMA, BMA, iBMA, and DMA are as previously published.[5] Calibration parameters for pS ($K = 11.4 \times 10^{-5}$ dL·g^{-1} and $a = 0.716$) are also as used previously.[5,12]

Results and Discussion

All monomers were studied over the temperature range 10−90 °C. Because of the large quantity of data, results for individual experiments are not tabulated here, but are available as Supporting Information. BMA and DMA have been studied over a wide range of experimental conditions; 42 and 48 data points were collected, respectively, with laser repetition rates varied between 10 and 25 Hz, initiator concentrations between 0.2 and 20 mmol·L^{-1}, and laser energies between 10 and 70 mJ per pulse. No systematic changes in k_p were found within these ranges, indicating that the PLP/MWD experiments are yielding reliable estimates.[6,7] The experimental sets for the other methacrylates are smaller and do not cover such a wide range of conditions. However, their polymerization behavior and MWDs are very similar to those observed for BMA and DMA.

Table 2. Propagation Rate Coefficients for Methacrylates[a]

methacrylate	N_{pts}	ln *A* ($L \cdot mol^{-1} \cdot s^{-1}$)	E/R	k_p at 50 °C ($L \cdot mol^{-1} \cdot s^{-1}$)
methyl	69	14.80 ± 0.10	2689 ± 31	649
ethyl	30	15.00 ± 0.14	2720 ± 45	723
n-butyl	42	14.79 ± 0.14	2621 ± 49	794
isobutyl	9	14.97 ± 0.12	2704 ± 40	740
2-ethylhexyl	10	14.44 ± 0.09	2453 ± 29	944
isodecyl	10	14.60 ± 0.09	2500 ± 29	959
n-dodecyl	48	14.67 ± 0.12	2503 ± 39	1011

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

Well-defined MWD structures were obtained for all monomers, with primary and secondary inflection points clearly visible, another important consistency check for data validation.[3,4] Figure 1 illustrates typical MWD results from a set of EHMA experiments run at varying temperature levels, 10 Hz, a benzoin concentration of 1 $mmol \cdot L^{-1}$, and an energy level of 10 mJ/pulse. Figure 2 shows the corresponding derivative plots used to determine DP_0, calculated as described previously.[4] As expected, secondary inflection points are located at twice the molecular weight of the primary inflection point; in many cases, tertiary inflection points (at three times the primary value) are also observed. As temperature increases to 90 °C, the primary peak of the MWD becomes more pronounced; at the lower temperatures, this "peak" appears as a low MW shoulder on the distribution. Correspondingly, the magnitude of the primary inflection point and its size relative to the secondary inflection point increase (see Figure 2), suggesting that the fraction of radicals terminated between subsequent pulses increases with reaction temperature.[12] If the radical concentration generated per pulse remains constant within this experimental set (a reasonable assumption since it was run at constant initiator concentration and laser power), this result suggests that the termination rate coefficient is increasing with temperature.

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

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

Results from linear least-squares fitting, including standard error estimates, are summarized in Table 2. The coefficients for MMA are taken from the recent IUPAC compilation paper.[7] The number of data points and k_p values at 50 °C calculated from the Arrhenius fit are also tabulated. The values for EMA, BMA, iBMA, and DMA are slightly higher (7–8%) than previously published.[5] This difference is attributable to the fact that the previous values were estimated from the number chain-length distribution, while these updated estimates are based upon the SEC weight–log distribution. In addition, it is noted that the BMA and DMA results show excellent agreement with those from the PLP/MWD studies of Buback and co-workers.[9,10]

Figure 3 shows the Arrhenius fit to the experimental data for MMA, BMA, and DMA. Although some overlap occurs among the individual points from the three data sets, the increase in k_p with size of the methacrylate ester group can be seen clearly, as previously documented.[5,8,9] An important question to address is whether the increase is statistically significant. Joint confidence intervals for the Arrhenius parameters have been calculated using a nonlinear least-squares fitting routine available in the literature,[15] assuming a constant relative uncertainty in k_p estimates. 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 4. The regions for the three monomers do not overlap, indicating that the differences are statistically significant.

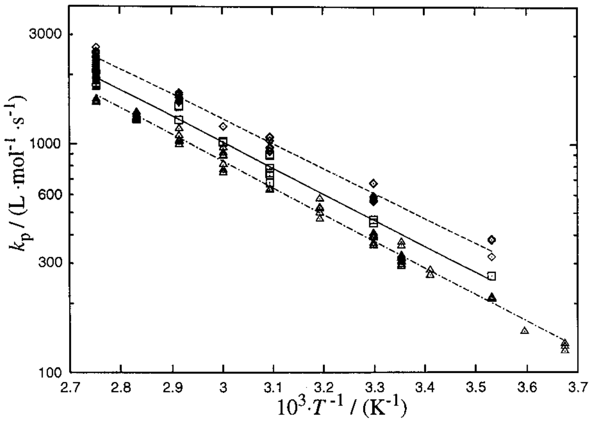

Figure 3. Arrhenius plots of the propagation rate coefficient (k_p) for methyl methacrylate[7] (△, —•—), butyl methacrylate (□, —), and dodecyl methacrylate (◇, - - -). Points indicate experimental data, and curves are the best fit of eq 3 to the data, with coefficients summarized in Table 2.

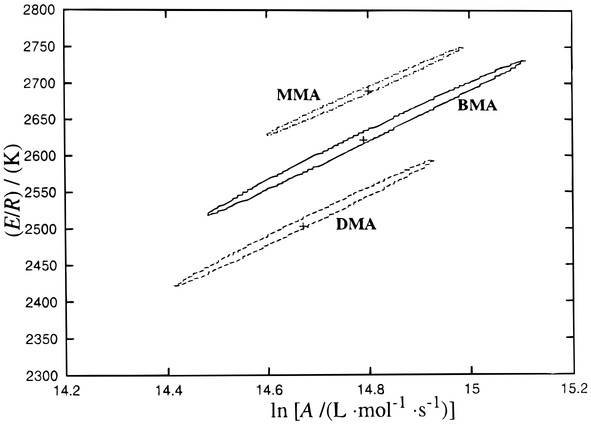

Figure 4. 95% joint confidence intervals for Arrhenius parameters ln *A* and *E*/*R* (see eq 3), from nonlinear least-squares fitting of k_p data for methyl methacrylate[7] (—•—), butyl methacrylate (—), and dodecyl methacrylate (- - -). Confidence intervals were calculated assuming constant but unknown relative error in k_p values.

The results for the other four methacrylates agree well with this general trend; Figure 5 plots the data and Arrhenius fits for these monomers, with the MMA, BMA, and DMA lines from Figure 3 shown for reference. The EMA and iBMA curves and data are virtually identical and lie between the MMA and BMA lines. Similarly, the EHMA and iDMA curves and data almost superimpose each other; the Arrhenius fits for these monomers lie slightly below that of DMA. Statistically, the EMA and iBMA data sets cannot be differentiated, nor can the EHMA and iDMA sets. However, their position relative to MMA, BMA, and DMA strongly supports the conclusion that the increase of k_p with size of the ester group observed for this series is real.

The next question to be addressed is whether the increase in k_p can be attributed to an increase in the frequency factor (*A*), or to a decrease in the activation energy (*E*). No systematic variation in ln(*A*) is observed;

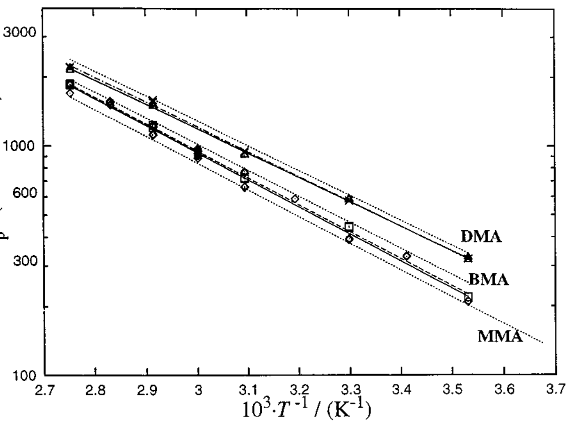

Figure 5. Arrhenius plots of the propagation rate coefficients (k_p) for ethyl methacrylate (◇, —), isobutyl methacrylate (□, - - -), 2-ethylhexyl methacrylate (△, —), and isodecyl methacrylate (×, —•—). Points indicate experimental data, and curves are the best fit of eq 3 to the data, with coefficients summarized in Table 2. Curves (···) for methyl, butyl, and dodecyl methacrylates were taken from Figure 3.

values vary between 14.44 and 15.00, and show no trend with size of the methacrylate ester group (see Table 2). E/R values, on the other hand, are between 2620 and 2720 (E between 21.8 and 22.6 kJ/mol) for MMA, EMA, BMA, and iBMA, but are only between 2450 and 2500 (E between 20.4 and 20.8 kJ/mol) for the heavier three methacrylates. The joint-confidence intervals of Figure 4 also suggest that, within experimental uncertainty, the preexponential factors for MMA, BMA, and DMA cannot be statistically differentiated but that the activation energy for DMA is significantly lower than that for MMA. There are dangers in overanalyzing the results, however, since a small error in SEC calibration parameters can lead to a systematic error in the magnitude of k_p and Arrhenius parameter estimates for a particular monomer.[5] More data, or data with greater precision and accuracy, are needed to answer this important question.

It is well documented in the literature that an understanding of how steric, polar, and electronic factors influence radical−monomer reaction rates is far from complete (see ref 16 for a good overview). For the systems studied in this paper, electronic and polar effects can be excluded, since the increase in ester size should not affect the polarity or electronic state of the reactants. It has recently been suggested, based on ab initio molecular orbital calculations and transition state theory, that the activation energy should be constant and the frequency factor should increase (due to an increase in the moment of inertia) with increasing molecular weight in a homologous monomer series.[17,18] Although the data in this paper conclusively show that k_p does increase with the size of the ester group, they suggest that the change is attributable to a decrease in activation energy rather than an increase in the frequency factor. It is hoped that these and other recently published experimental results[9,10] will advance the understanding of structure and reactivity in these systems and will spur further development in the a priori prediction of absolute and/or relative values of free-radical polymerization rate coefficients.

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Supporting Information Available: Tables 3−8, containing detailed results and experimental conditions for individual PLP experiments (11 pages). Ordering information is given on any current masthead page.

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