Effect of the Ester Side-Chain on the Propagation Kinetics of Alkyl Methacrylates—An Entropic or Enthalpic Effect?

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ABSTRACT: The technique of pulsed-laser polymerization (PLP) was used to measure homopropagation rate coefficients for styrene (STY), methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (BMA), and benzyl methacrylate (BzMA). Special attention was given to the molecular weight analysis of PLP distributions by size exclusion chromatography (SEC) with online low-angle laser-light scattering (LALLS), differential viscometry (DV), and differential refractive index (DRI) detectors connected in series. The PLP distributions were analyzed using two different approaches: first, by transformations to the universal calibration curve via Mark−Houwink−Sakurada (MHS) constants and, second, by direct analysis of the molecular weight distributions using absolute detection methods. The accuracy and precision of the two approaches is discussed with reference to the measured Arrhenius parameters. The variation in the propagation rate coefficients with ester side chain size is attributed primarily to the preexponential factor. This is consistent with theoretical predictions but in opposition to a recent PLP study of this series. An explanation for this apparent contradiction is suggested.

Introduction

A number of pulsed laser polymerization (PLP) studies have examined the variation of the Arrhenius parameters of *n*-alkyl methacrylates with the size of the ester chain. The early work was done by Davis et al.[1] on ethyl, *n*-butyl, and dodecyl methacrylates (EMA, BMA and DMA). They showed that the difference in activation energies for the lower methacrylates was small, although DMA yielded a low activation energy of around 16 kJ/mol. Clearly there were problems with the accuracy of this early work: in particular, the authors had problems in the selection of Mark−Houwink−Sakurada (MHS) constants. Pascal et al.[2] reported the Arrhenius parameters for *tert*-butyl methacrylate, with an activation energy of 28 kJ/mol which in retrospect seems rather high. However, this work[2] preceded the consistency tests that are now realized to be essential for reliable PLP data, and so it could well be the case that the Arrhenius parameters are not valid. Since then, Hutchinson et al.[3−5] have published three papers on the methacrylate series. Despite a large experimental design and a recalculation of MHS values, their conclusions remain essentially identical to the earlier work of Davis et al.[1] It appears that k_p increases with ester chain length, but attempts to determine whether this variation in k_p arises in the activation energy or pre-exponential factor have been inconclusive—although in the most recent work of Hutchinson et al.,[5] the data appeared to show that the side-chain primarily influenced the activation energy. This runs counter to accepted wisdom,[6] so Hutchinson et al.[5] placed a caveat on their work that systematic errors in SEC could not be ruled out.

It was established sometime ago that the limitation to accurate and precise k_p measurements from PLP was the size-exclusion-chromatography (SEC) calibration.[7] Therefore it seems sensible to concentrate on the accuracy and precision of the SEC analyses if reliable structure−reactivity correlations are to be established. When narrow standards are available for the polymer being analyzed, as in the cases of polystyrene (PSTY) and poly(methyl methacrylate) (PMMA), the errors in the SEC analysis are generally small—as seen in the consistency of k_p estimates for STY and MMA from a number of different groups.[8,9] The problem arises when narrow standards are not available, and the universal calibration procedure must be adopted. There is no doubt that the universal calibration procedure yields an effective SEC calibration; however, problems arise in converting the hydrodynamic volume of the polymer (as measured from the universal calibration curve) to molecular weight. To date, two different approaches have been adopted. The first is to use a calibration relationship, such as the MHS equation, to relate intrinsic viscosity to molecular weight. The problem with this approach is that there are often significant errors in the MHS constants (as seen in the wide discrepancy between MHS constants for the same polymer), and these errors propagate as a hidden systematic error in the molecular weights (and thus k_p values) measured by this technique. All previous PLP studies have adopted this approach, and hence, as noted above, systematic error in these studies cannot be ruled out.

The second approach is to use, in addition to the concentration sensitive detector used in conventional SEC, a molecular weight sensitive detector such as a differential viscometer (DV) or a low-angle laser-light-scattering detector (LALLS). Combination of the response from the two detectors yields, in the case of SEC−DV, the intrinsic viscosity of the polymer (which may then be converted to molecular weight using the universal calibration curve), and yields, in the case of

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SEC−LALLS, the molecular weight directly (without recourse to the universal calibration curve). However, these direct molecular weight analysis methods are not without problems. First, in performing direct molecular weight analysis, it is necessary to know the injected amount of polymer and the exact values for peak integrals, and these additional sources of experimental error reduce the precision of the analysis—although, as argued previously,[10] this reduced precision may in fact provide a more honest estimate of the true errors in SEC. Second, the calibration of these detectors is difficult, and small calibration errors (resulting from, for instance, a poorly tuned inter-detector delay) may lead to large systematic errors in the measured molecular weights (and thus k_p values).[11] However, unlike conventional SEC, there are a number of strategies by which the systematic calibration error of direct molecular weight analysis may be detected and eliminated. These are as follows: (1) simultaneously using two independently calibrated direct molecular weight methods (such as SEC−LALLS with SEC−DV) and comparing the results from each; (2) benchmarking the calibration using polymers for which narrow standards are available (such as PSTY and PMMA) by comparing the results obtained from the direct molecular weight analysis methods with those from conventional SEC. A further advantage of benchmarking the calibration with PMMA and PSTY, is that the k_p results obtained for these monomers may be compared with their respective IUPAC benchmark values.

In this work, we will apply direct molecular weight analysis, in conjunction with strategies (1−2) above, to a PLP study of the alkyl methacrylates, in order to reexamine the structure−reactivity relationship for this series. As part of this work, we will examine the method of measuring MHS constants from SEC−DV data and investigate the effect of errors in the MHS constants on the measured k_p values and Arrhenius parameters. The monomers selected for this study are STY and MMA (to benchmark the calibration), EMA and BMA (the subject of all previous alkyl methacrylate studies), and a new monomer—benzyl methacrylate (BzMA).

Experimental Section

Materials. Styrene (STY), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA), ethyl methacrylate (EMA) and benzyl methacrylate (BzMA) (Aldrich) were passed through a column of activated basic alumina, Brockmann 1 (Aldrich), and refrigerated until required. The photoinitiator 2,2′-azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The SEC eluent tetrahydrofuran (THF) was purchased from BDH (HiperSolv) and filtered three times through a 0.02 mm filter (Whatman Anodisc 47) before use.

Polymerizations. Purified monomer and initiator were charged to reaction cells (10 mm diameter × 60 mm height), which were then deareated by bubbling with Argon for 5 min and sealed with rubber septa. The reaction mixtures were equilibrated at the reaction temperature prior to laser exposure. All reactions were performed in bulk with conversion of monomer to polymer kept to below 10%. Polymerization activity was terminated by precipitation of the polymer into methanol. The polymer was dried to constant mass in vacuo at 40 °C.

The experimental rig employed in these experiments was similar to the design of Davis et al.[12] A Spectra Physics Quanta-Ray DCR-11 pulsed Nd:YAG laser with a HG-2 harmonic generator was used to generate 355 nm UV laser radiation. Laser pulse energy was measured at 38 mJ at a half-height of 8 ns and was pulsed at a constant frequency through the sensitized monomer solution. The laser was externally triggered from a microprocessor-controlled pulse generator (BWD Instruments, Model 101) with the error in pulse times being ±0.0005%. Isothermal reaction conditions were maintained using a recirculated water system and a feedback thermocouple which was attached to the side of the reaction cell.

Size Exclusion Chromatography (SEC). Equipment. SEC analyses were performed on a modular system comprising the following: GBC Instruments LC1120 HPLC pump operating at room temperature, a SCL-10A Shimadzu autoinjector with 99 position sample rack and variable injection loop facility, a column set, which consisted of a PL 5.0 μm bead-size guard column (50 × 7.5 mm) followed by mixed bead Polymer Laboratories (PL) columns (300 × 7.5 mm, 10 mm mixed B, 2 × 5 mm mixed C and a 5 mm mixed D), an in-line filter (0.2 mm), and the following three detectors in series, LALLS (PL), DRI, and DV (Viscotek Model 250). The data were collected using PL data capture units (DCUs) and analyzed using PL Caliber version 6.0 GPC/SEC software.[13] The eluent was THF at a flow rate of 1 $\mathrm{mL \cdot min^{-1}}$. Sample injection size was 200 mL in all cases with data being collected at 2 points/s. A flow rate marker (diethyl phthalate) was included with all runs. The polymer analyte solutions in THF were diluted to approximately 4 $\mathrm{mg \cdot mL^{-1}}$ prior to SEC analyses.

Calibrations. The differential refractive index detector was calibrated with a PSTY narrow polydispersity index (PDI) set consisting of 10 individual standards purchased from PL (1.25×10^3 to 2.95×10^6 MWT) and a further five PSTY standards purchased from Tosoh (1.8×10^4 to 2.89×10^6 MWT). A PMMA set purchased from PL (1.14×10^3 to 1.577×10^6 MWT) was used to generate a PMMA calibration curve. The supplier determined peak maxima molecular weight (M_p) was used in the generation of the calibration curves. The universal calibration curve used in the conventional SEC analysis was constructed from the PMMA and PSTY calibration curves using the MHS constants for these polymers, taken from Rudin and Hoegy[14] and Benoit et al.,[15] respectively.

The LALLS and DV used throughout these experiments have been described in detail in a previous publication,[16] as has a detailed discussion of their calibration. In this previous work, it was shown that the accuracy of these multidetector SEC techniques was sensitive to the estimated inter-detector delay (IDD), and errors could arise if the molecular weight dependence of this quantity[17] was ignored. Now, for the analysis of the PLP samples in this work we opted for commercially available SEC software[13] that utilizes a constant IDD. However, we attempted to minimise possible errors associated with this by carefully optimizing the IDD at a specific molecular weight, 10^5 g/mol, using a methodical calibration approach similar to that reported by Mourey and Balke[18] and selecting PLP conditions so as to target this (peak) molecular weight for all samples. The validity of this calibration method for measurement of k_p will be tested via the comparison of the k_p values for STY and MMA as obtained by the direct and conventional molecular weight analysis methods.

Our previous work[16] indicated that quantities derived from MWT−IV relationships (such as MHS constants) were particularly sensitive to the IDD. Hence, in the measurement of the MHS constants for PBzMA from the SEC−DV analysis of broad PBzMA polymers, we used our own SEC−DV software, based on the calibration method suggested by Suddaby et al.[17] In this method the two detectors (in this case the DRI and DV detectors) are calibrated individually without recourse to a single IDD. For a full description of this technique, the reader is referred to our previous publication[16] and the original work of Suddaby et al.[17]

Analysis. The PLP samples were analyzed by three different molecular weight analysis methods: the two molecular weight sensitive techniques (LALLS and DV) and also by conventional SEC. The direct molecular weight analysis methods have been described in a previous publication.[16] The conventional SEC analysis was performed as follows. The polymers PMMA and PSTY were analyzed against their respective DRI calibration curves (fitted with third-order polynomials). The conventional SEC analysis of PBMA and PEMA was performed twice: once for each of the sets of MHS constants used in previous PLP studies of alkyl methacrylates. These two sets were those of Samay et al.,[19] as used in the study by Davis et al.[1] and in the earlier work of Hutchinson et al.,[3] and the values recently measured and used by Hutchinson et al.[4,5] Since MHS constants for PBzMA were not available, these were measured as part of this study from the SEC−DV analysis of a set of six broad polymer samples (the results of this analysis are described in a subsequent section).

In performing the conventional SEC analysis of a polymer sample for different sets of MHS constants, advantage was taken of an equation derived by Lyons et al.[20] that relates the k_p values obtained in a PLP experiment to the MHS parameters used in the molecular weight analysis.

$$\log(k_{p,2}) = \left(\frac{1}{1+\alpha_2}\right)\log\left(\frac{K_1}{K_2}\right) + \left(\frac{\alpha_2-\alpha_1}{1+\alpha_2}\right)\log\left(\frac{1}{N}\right) + \left(\frac{1+\alpha_1}{1+\alpha_2}\right)\log(k_{p,1})$$

In this equation N is given by the expression $N = [\mathrm{M}]t_f M_{\mathrm{mon}}$, where M_{mon} is the molecular weight of the monomer, t_f is time between laser flashes, and $[M]$ is the monomer concentration. This equation enables k_p to be recalculated for different MHS values, without repeating the entire molecular weight analysis.

Having obtained the molecular weight, the number molecular weight distribution was determined for each polymer via previously published transformations,[21] and the low molecular weight inflection point was determined by taking the maxima of the derivative of the distribution.

Monomer Densities. Monomer densities for MMA,[22] STY,[23] EMA,[3] and BMA[3] were obtained from the literature. The density of the monomer BzMA was determined at various temperatures (over the range of 0−50 °C) using a glass density bottle. The monomer density was found to obey the expression

$$\text{density} = 1.258 - 6.573 \times 10^{-4}T - 3.521 \times 10^{-7}\mathrm{T}^2\ \mathrm{g{\cdot}cm^{-3}}$$

where T is temperature in K.

Statistical Analysis Procedures. Fitting of the MHS model to the molecular weight vs intrinsic viscosity data sets was performed using nonlinear least-squares analysis, implemented using programs written in the Matlab software. These programs yield both the parameter estimates and their 95% joint confidence intervals (JCIs). In fitting the Arrhenius model to the k_p data, advantage was taken of the Contour[24] program; however, this program was unable to cope with the larger data sets, and so for these larger sets our Matlab programs were used.

Nonlinear least-squares analysis, its assumptions and limitations have been discussed in detail in a previous publication.[25] For this present work, the validity of the assumptions inherent in this type of statistical method are somewhat questionable. In the case of the fitting of the MHS equation to the molecular weight and intrinsic viscosity data, it is unlikely that that the errors in each data point are independently random and normally distributed about the true model. This problem will be discussed in detail in a subsequent section and will be dealt with by suggesting possible upper and lower bounds to the 95% JCIs of the MHS parameters of PBzMA—rather than the (invalid) 95% JCIs yielded from the model-fitting software.

In fitting the Arrhenius model to the k_p vs temperature data, the assumption of negligible error in the independent variable (temperature) is not necessarily valid. However, errors in the temperature are difficult to quantify and are likely to be systematic (rather than independently random)—hence the adoption of an error-in variables method did not offer a viable solution to this problem. Instead, we attempted to eliminate systematic errors by measuring the temperature inside our PLP sample cells (for a given set temperature on our water bath) using a thermocouple that was carefully calibrated from primary standards (such as, for instance, the temperature of boiling water at sea level). The temperature control and measurement for our PLP equipment has been detailed in a previous publication.[10] For the remainder of this work, we will ignore the errors in the temperature but suggest that careful attention (such that described in our previous publication) is given to elimination of errors in the measurement of temperature for PLP experiments.

Results and Discussion

A. Measurement of the MHS Constants of PBzMA. 1. Theory: Applicability of Model Fitting Procedures. Traditionally, the MHS constants of a polymer have been measured by fitting the MHS equation

$$\log(\mathrm{IV}) = \log(K) + \alpha{*}\log(\mathrm{MWT})$$

to molecular weight (MWT) vs intrinsic viscosity (IV) data, as obtained from a capillary viscometric analysis of a set of narrow molecular weight distribution (MWD) samples. A major disadvantage of this technique is the need to obtain a set of polymer samples with narrow MWDs. The development of on-line DV detectors has enabled MWT−IV data to be obtained from the SEC−DV analysis of a *single* broad polymer sample, thereby providing a much easier method of measuring MHS constants. Now, although this approach has been widely adopted for the estimation of MHS constants, and claims have been made as to the superior accuracy of the parameters obtained,[4] as yet there has been no investigation of the applicability of common model fitting procedures to such data. (In particular, there are as yet no accepted methods for combining the data obtained from *multiple* broad samples and estimating the parameter uncertainties.) In applying a given model fitting procedure to a set of data, that data set must meet the assumptions inherent in the procedure. In what follows it will be shown that the MWT−IV data obtained from SEC−DV fails to meet the assumptions of common model fitting procedures, such as nonlinear least squares analysis.

In the technique of SEC−DV, two on-line detectors are used: a concentration-sensitive detector (in this case a DRI detector) and the differential viscosity detector (DV), which measures the inlet and differential pressures across a Wheatstone bridge. The normalized response of the DRI detector, combined with a universal calibration curve, yields the hydrodynamic volume distribution for the polymer, as in conventional SEC. The responses from the DV and DRI detectors (appropriately shifted to account for the interdetector delay) are combined to yield the IV distribution of the polymer. The exact formula for calculating IV from matched slices of a DRI response and a DV response depends upon the make of the viscometer, but a typical example of the calculation is shown in the following formulas. (The conversion factors have been omitted for the sake of clarity).

$$\mathrm{IV\_i} = \frac{\eta_{\mathrm{sp\_i}}}{\mathrm{conc\_i}} = \left(\frac{4 \times \mathrm{DP\_i}}{\mathrm{IP} - 2 \times \mathrm{DP\_i}}\right) \Big/ \left(\frac{\mathrm{inj\_conc} \times \mathrm{inj\_vol} \times \mathrm{DRI\_i}}{\mathrm{flow\_rate} \times \mathrm{sampling\_rate} \times \mathrm{sum(DRI\_i)}}\right)$$

where the following are *data-point-independent* quantities

DP_i = response of DV detector (differential pressure)

DRI_i = response of DRI detector

and the following are *sample-independent* quantities

inj_conc = concentration of polymer analyte solution injected

inj_vol = volume of polymer analyte solution injected

flow_rate = flow rate of the eluent

sampling_rate = sampling rate of the detectors

sum(DRI_i) = sum of slice responses of DRI detector (same units as DRI_i)

IP = inlet pressure of DV detector (same units as DP_i)

Finally, the hydrodynamic volume distribution of the polymer is divided by the IV distribution to yield the molecular weight distribution.

Given this procedure, it can be seen that the MWT–IV data obtained from SEC–DV is such as to invalidate the assumptions inherent in nonlinear least-squares analysis. This model fitting procedure makes three main assumptions. First, it assumes that the errors in the independent variable (arbitrarily selected to be the MWT for this case) are negligible. This is violated in SEC–DV since the MWT data is derived from the IV data, and thus any error present in this data will be present to some degree in the MWT data. Second, the procedure assumes that the errors in the data points are independent. This is violated because many of the important sources of experimental error in the calculation of IV (namely, the injection volume, injected concentration, the flow rate, the inlet pressure, and the integral of the DRI peak) are not independent for every data point but only for every separate polymer sample analyzed. Third, the procedure assumes that the error in the data points is normally distributed about the "true" model. This is also violated since, if we assume that the measurement errors of all the quantities in the above formulas are normally distributed, we see that, once all of these Gaussian distributions are combined in the calculation of IV and MWT, the resultant error distributions in the MWT and IV are complicated functions of Gaussian distributions but are not themselves Gaussian. Hence, the MWT–IV data obtained from SEC–DV fails to meet the three main assumptions inherent in nonlinear least-squares analysis, and thus the results obtained from using such a procedure will be invalid.

However, given the complicated nature of the error distributions that are expected for such data (in particular the complicated dependence of the MWT errors on the IV errors, and the IV errors on the sample-independent quantities), it would be difficult to design an appropriate model fitting procedure. For these reasons, we have used nonlinear least-squares analysis for the estimation of the MHS constants of PBzMA but have modified the calculation of the 95% JCIs to take into account one of the most important issues raised above: the absence of independent errors in individual data points. In calculating the 95% JCIs for the parameter estimates, it is necessary to specify the number of *independent* points used in calculating the sum-of-squares of errors. In the case that the sample-independent errors dominate the data-point-independent errors, the number of points will be approximated by the number of polymer samples analyzed, while in the reverse case the number of independent points will be given by the total number of data points. It is likely that the true 95% confidence interval will lie somewhere between these two extremes, and a third (intermediate) estimate of the parameter uncertainty is obtained via the following procedure. Assuming that there is a common MWT range covered by all the samples, this range is partitioned into a number of equal slices, the number of slices being given by the number of polymer samples. The IV of each polymer sample at each slice is included in the least squares analysis, and the standard deviation of the collected IV data at each slice is used as an estimate of the error (for the purposes of weighting the residuals). For this work, all three cases described above will be considered in estimating the uncertainty in the MHS constants of PBzMA.

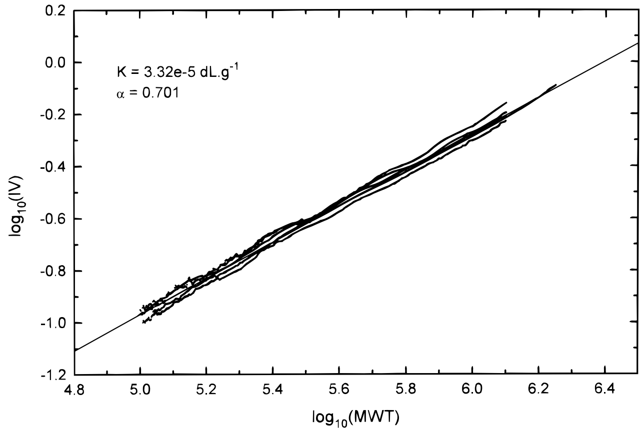

Figure 1. Mark–Houwink–Sakurada plot for six poly(benzyl methacrylate) samples.

Table 1. MHS Constants for PBzMA, As Obtained from the Six Individual Samples, the Combined Data Set, the Sliced Data Set and the Extremes of the 95% Joint Confidence Intervals for the Latter Two Parameter Estimates

source	log(*K*)	α
sample x654	−4.472	0.699
sample x654	−4.628	0.725
sample x654	−4.347	0.679
sample x654	−4.488	0.699
sample x654	−4.368	0.684
sample x654	−4.594	0.726
combined data set	−4.479	0.701
sliced data set	−4.502	0.706
combined JCI (6 indept. pts.)	−5.000	0.795
combined JCI (6 indept. pts.)	−4.000	0.615
sliced JCI	−4.360	0.681
sliced JCI	−4.620	0.720

2. Results. Six PBzMA samples with relatively broad molecular weight distributions were analyzed using the technique of SEC–DV, yielding the molecular weight (MWT) vs intrinsic viscosity (IV) distributions of each polymer. A double-log plot of the data is given in Figure 1. Using nonlinear least-squares methods, the MHS equation was fitted to the data of each individual polymer sample, as well as the combined data and the "sliced" data set (as described above). The point estimates of the MHS parameters are given in Table 1. In performing the conventional SEC analysis of PBzMA PLP samples, the parameters estimated from the combined data were used as the optimum parameters, and the others were used for sensitivity analysis. The 95% JCIs were calculated from the combined data set (using the limiting cases described above) and also from the

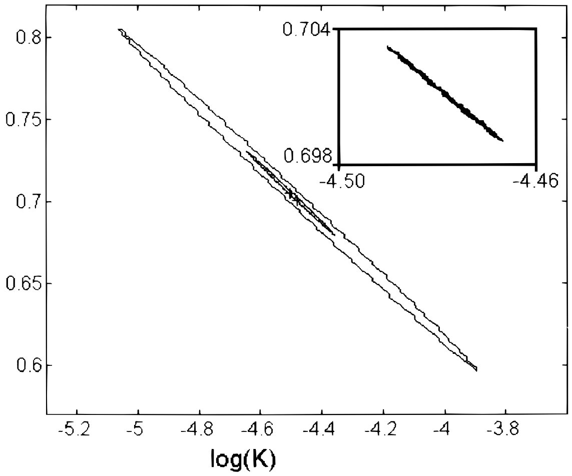

Figure 2. Upper and lower bounds to the 95% JCI for the MHS constants of BzMA. The largest JCI was based on the assumption the sample-independent errors dominate the data-point-independent errors, while the smallest JCI (inset) was based on the reverse assumption. The intermediate JCI was formed from the "sliced" data set (see text for explanation).

"sliced" data set. These three 95% JCIs are plotted in Figure 2. Points taken from the extremes of the two largest 95% JCIs are also included in Table 1 for the purposes of sensitivity analysis in a subsequent section.

Examining the 95% JCIs plotted in Figure 2, we see that the assumption of the sample-independent errors dominating the data-point-independent errors leads to a very large 95% JCI, while the reverse assumption leads to an extremely small 95% JCI. It is therefore useful to make some judgement as to which of these two extremes is more likely to represent the true 95% JCI. Now, sample-independent errors would be expected to cause the MWT−IV data of each polymer sample to be systematically different from each other, while data-point-independent errors would be expected to lead to scatter in the log(MWT) vs log(IV) plots. Examining the MWT−IV data plotted in Figure 1, we see that there are six systematically different log(MWT) vs log(IV) lines, each line corresponding to an individual polymer sample. However, the systematic difference between the samples is not much larger than the extent of scatter in the plots from the individual samples. Hence, we may conclude that the sample-independent errors are more important than the data-point-independent errors but that both are operating on the data. In other words, the true 95% JCI lies somewhere between the two extremes, though probably closer to the larger one. It is, perhaps, best approximated by the intermediate 95% JCI obtained from the "sliced" data set.

3. Recommendations. In summary, *common model fitting procedures are not applicable to the estimation of MHS constants from the MWT−IV data obtained from SEC−DV analysis of broad polymer samples.* This remains a source of uncertainty in the MHS constants obtained via this technique and renders invalid the 95% JCIs obtained from such model fitting software. Although a full solution to this problem is not readily apparent, the problem can to some extent be addressed via the procedure described above, and we recommend that in future measurements of MHS constants such a procedure be implemented. Finally, it is evident, both from a consideration of the errors in SEC−DV and from the examination of the PBzMA data obtained in this work, that the sample-independent errors in such MWT−IV data are, at the very least, as important as the data-point-independent errors. Therefore, the analysis of a *single* broad polymer sample by SEC−DV may be considered to provide only a point estimate of the MHS parameters, from which no information regarding their uncertainty can be obtained. Thus we recommend that when SEC−DV is used to estimate MHS constants, *multiple* polymer samples be considered.

B. Propagation Rate Coefficients. 1. Results. The propagation rate coefficients (k_p) of the five monomers were measured at a number of temperatures over the range 6.1−57.2°C, using the technique of PLP−SEC. Each PLP sample was subjected to three different types of molecular weight analysis—the two direct measures (SEC−LALLS and SEC−DV) and conventional SEC-analysis—thus giving multiple estimates of k_p. The k_p data obtained via each of these techniques are summarized in Table 2. In this table, only the average (of six replicates) k_p values are reported; however, the full data (including the laser flashing rates used and the inflection point molecular weight data from which k_p was calculated) are available as supporting information.

2. Benchmarking the Data. As mentioned in the introduction to this paper, the possibility of systematic error in the calibration of the SEC equipment can be detected (and therefore eliminated) by the strategy of (1) simultaneously using two independently calibrated direct molecular weight methods (such as SEC−LALLS with SEC−DV) and comparing the results from each, (2) benchmarking the calibration using polymers for which narrow standards are available (such as STY and MMA) by comparing the results obtained from the direct molecular weight analysis methods with those from conventional SEC, (3) comparing the STY and MMA results with those collected in the IUPAC benchmark papers for these two monomers. In what follows, we apply tests 1−3 to the k_p obtained in this work in order to verify its accuracy.

Examining the average k_p values reported in Table 2, we see that in all cases the SEC−LALLS and SEC−DV estimates of k_p for a given monomer at a given temperature are very similar (on average the difference is less than 1%), and in the case of STY and MMA, these direct measures of k_p show close agreement with those estimated from their respective calibration curves. This close agreement between two independently calibrated direct molecular weight analysis techniques and two calibration curves compiled from narrow standards provides strong evidence for the accuracy of the SEC calibrations used in this work. Furthermore, the STY and MMA k_p values fit well within the scatter of data accepted by IUPAC for their benchmark values.[8,9] This is illustrated in Figure 3, in which the MMA and STY data of this work, together with the IUAPC data, is plotted as an Arrhenius-type plot. Hence it appears to be unlikely that the data presented in this work are subject to systematic error arising from the SEC calibrations.

3. PLP Consistency Checks. A further test of the accuracy of the k_p data concerns the consistency checks that have been recommended by an IUPAC working party to verify the accuracy of data generated from PLP experiments.[8] The following consistency checks are recommended: (1) k_p must be invariant to laser flashing frequency, initiator concentration and type, and laser

Table 2. Average k_p Values for the Five Monomers at Each Temperature, As Obtained via SEC−DV, SEC−LALLS, and Conventional SEC (DRI)[a]

temp (°C)	k_p DRI [1] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p DRI [2] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p DRI [3] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p LALLS [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p DV [$L \cdot mol^{-1} \cdot s^{-1}$]
			Styrene		
17.9	59			60	60
37.6	136			136	135
47.4	193			194	192
57.2	288			292	289
			Methyl Methacrylate		
6.1	160			160	161
17.9	228			226	228
37.6	455			453	468
47.4	573			577	578
			Ethyl Methacrylate		
6.1	153	147		155	154
17.9	224	216		224	224
27.7	318	306		323	318
37.6	428	414		431	437
47.4	558	540		568	568
			Butyl Methacrylate		
6.1	190	190		188	188
17.9	272	270		269	269
27.7	368	370		367	367
37.6	513	512		509	508
47.4	680	668		681	678
			Benzyl Methacrylate		
6.1	391	397	384	396	392
17.9	554	560	546	557	559
27.7	779	802	754	786	780
37.6	1050	1064	1033	1067	1074
47.4	1374	1425	1320	1390	1392

[a] The DRI estimates were obtained as follows: MMA and STY were analyzed against their respective calibration curves; EMA and BMA were analyzed using the MHS constants of [1] Hutchinson et al.[4] and [2] Samay et al.;[19] BzMA was analsysed using MHS constants taken from both [1] the point estimates and [2] and [3] the extremes of the largest 95% JCI for the combined analysis of the broad samples in this work

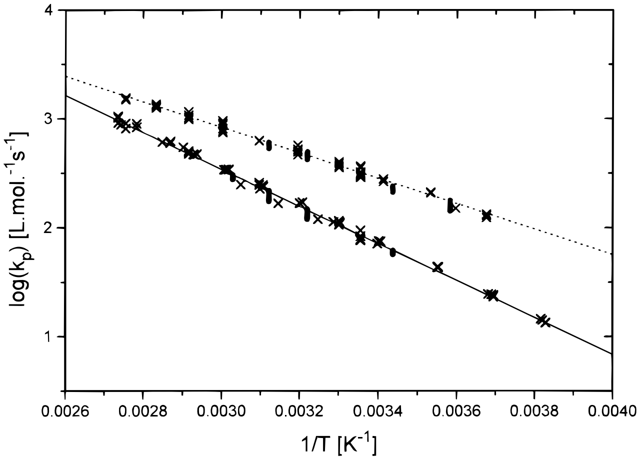

Figure 3. Arrhenius plot of the IUPAC collected data (×) for MMA and STY, with the MMA and STY k_p data of this work (●) included. (The dotted line is the Arrhenius fit to the MMA data and the solid line is the corresponding fit to the STY data).

power, and (2) the molecular weight distribution should exhibit overtones of the primary peak, with the peak maxima of these overtones occurring at integer multiples of the primary peak maxima molecular weight. The PLP data presented in this work comply with both of these criteria. With regard to the first criterion, a preliminary study confirmed the invariance of k_p (for each monomer) to initiator type (AIBN and benzoin), concentration (1.5×10^{-3} to 7.6×10^{-3} $mol \cdot L^{-1}$), and laser power (20 to 40 mJ). Throughout this work laser flashing frequency (in the range 1−10 Hz) was allowed to vary between replicate samples without causing a significant difference in the k_p values obtained (see the supplementary information for details). The molecular weight distributions of all the samples met the second criterion, and a typical one is shown in Figure 4 for the monomer STY. For this typical sample, the secondary and tertiary overtones are 1.99 and 3.17 times the primary peak molecular weight, respectively.

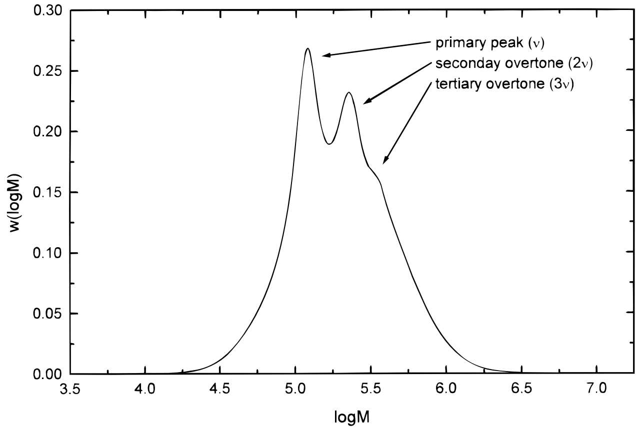

Figure 4. Typical PLP derived poly(styrene) MWD showing primary peak and corresponding overtones.

Effect of the MHS Constants on the k_p Data. Examining the k_p data in Table 2, it can be seen that the different sets of MHS constants used in the conventional SEC analysis of EMA and BMA do not lead to large differences in the k_p values obtained for these monomers. For BzMA, the k_p values obtained using the

MHS constants taken from the extremes of the largest 95% JCI differ by less than 4% from those obtained using optimum parameters. Thus it appears that uncertainties in the MHS constants of a polymer do not lead to large errors in k_p values obtained via PLP with conventional SEC. However, this encouraging result needs to be qualified, as follows.

First, it should be observed that the full uncertainty in the EMA and BMA MHS constants has not been taken into account—we have merely compared the *point estimates* from two separate studies. Nevertheless, since the previous studies of *n*-alkyl methacrylates have used MHS constants from one or other of these two studies, it does not appear that systematic calibration errors arising from the MHS constants are responsible for the anomalous structure–reactivity trends observed in the recent work of Hutchinson et al.[5] This will be examined more carefully in the next section, when the k_p data is used to estimate the Arrhenius parameters of the monomers.

Second, k_p was estimated from polymers with inflection point molecular weights of around 10^5 g/mol. At this molecular weight, the MHS constants did not lead to large differences in k_p. However, had k_p been measured from samples with molecular weights higher or lower than this, the different MHS constants would have led to significant differences in k_p. Hence, in order to minimize the error associated with conventional SEC analysis, the MHS constants should only be used within the molecular weight range at which they were measured.

Finally, the small variation in k_p that was observed when the different MHS constants were used did exceed the variation in the LALLS and DV numbers—and this was particularly evident in the BzMA data, for which the full uncertainty in the MHS constants could be taken into account. Hence, as noted previously,[10] if the full uncertainty in MHS constants was to be into account when estimating the uncertainty in k_p numbers obtained from conventional SEC, it would be seen that the errors in the resulting data would exceed that observed in the direct methods of molecular weight analysis. We therefore recommend that all future PLP studies using conventional SEC take into account the uncertainties in any MHS constants used when estimating the uncertainty in k_p measurements.

C. Arrhenius Parameters. The Arrhenius model was fitted to the k_p data of all five monomers. For each monomer, the LALLS, DV, and various conventional SEC data sets were treated separately, and in addition, the Arrhenius parameters from the combined LALLS and DV data sets were obtained. For BMA and EMA two conventional SEC k_p data sets were used (corresponding to the two sets of MHS constants), while for BzMA several conventional SEC data sets were used (corresponding to each of the sets of MHS constants listed in Table 1). The point estimates obtained from the combined LALLS and DV data sets are given in Table 3. In performing the nonlinear least-squares analysis, the data was individually weighted by the standard deviation of the error (as measured from the six replicates at each temperature). The 95% JCIs for the Arrhenius parameters of EMA, BMA and BzMA, as obtained from the individual and combined k_p data sets, are shown in Figures 5–7, respectively. Also plotted in Figures 5 and 6 are the 95% JCIs obtained from the previous studies[1,3,5] of EMA and BMA, respectively. In recalculating the 95% JCIs for these previous studies, it was assumed (as in the recent study by Hutchinson et al.[5]) that the data were subject to a constant relative error.

Table 3. Point Estimates for the Arrhenius Parameters for the Monomers, As Obtained from the Combined LALLS and DV k_p Data Sets

monomer	E_a [kJ/mol]	A [$\times 10^{-6}$L/(mol/s)]
STY	32.0	32.7
MMA	24.1	4.94
EMA	23.9	4.45
BMA	23.6	4.78
BzMA	23.2	8.50

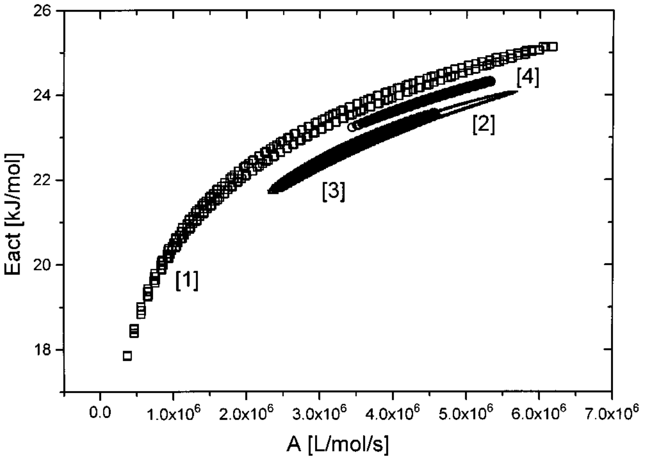

Figure 5. 95% JCIs for the Arrhenius parameters of EMA from: (1) the data of Davis et al.[1]; (2) the original data of Hutchinson et al.[3]; (3) the recent data of Hutchinson et al.[5]; (4) this work (individual data sets plotted separately but are indistinguishable on the scale of the graph).

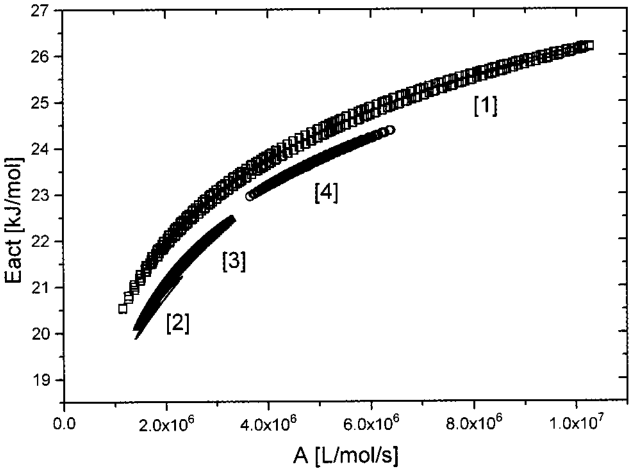

Figure 6. 95% JCIs for the Arrhenius parameters of BMA from (1) the data of Davis et al.,[1] (2) the original data of Hutchinson et al.,[3] (3) the recent data of Hutchinson et al.,[5] (4) this work (individual data sets plotted separately but are indistinguishable on the scale of the graph).

Examining Figures 5–7, it is apparent that the 95% JCIs calculated from the k_p data obtained from the different SEC methods are virtually indistinguishable. Even for BzMA, for which a range of different MHS values were used, the effect of the SEC calibration on the Arrhenius parameters is only small; however, when the uncertainty in the MHS constants is taken into account, the resulting uncertainty in the parameters obtained from conventional SEC is greater than that in the parameters obtained via the direct methods of

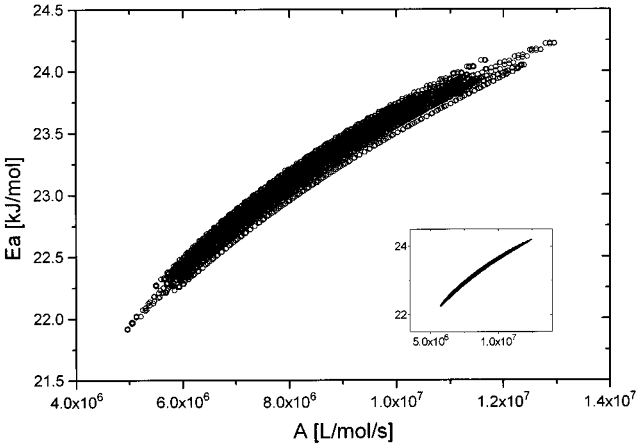

Figure 7. 95% JCIs for the Arrhenius parameters of BzMA from this work, showing the 95% JCIs obtained from each of the conventional SEC methods and (inset) from each of the direct SEC methods.

molecular weight analysis. This is not surprising, given the small effect of the MHS constants on the k_p data. However, an important consequence of this result is that the uncertainty in the SEC calibrations are unable to account for the differences between the Arrhenius parameters estimated in the previous studies of BMA and EMA, as seen in Figures 5 and 6. Hence these differences must be attributed to other sources of experimental error, such as the temperature measurements.

Given the difficulty in making judgements about the relative accuracy of this work and the previous studies of the alkyl methacrylates, it was decided to estimate overall Arrhenius parameters for EMA and BMA by combining the data of this work with that of the previous studies.[1,3,5] An estimate of the MMA Arrhenius parameters was obtained by combining the data of this work with the IUPAC collected data.[9] In performing the nonlinear least-squares analysis, the residuals were weighted in proportion to the size of k_p only, with no distinction made between the different data sets. The overall 95% JCIs obtained are given in Figure 8. Also included in this figure are the 95% JCI for the combined LALLS and DV BzMA data, and two 95% JCIs for the Arrhenius parameters of DMA: one obtained from the k_p data recently published by Hutchinson et al.[5] and the other obtained from the same data but reanalyzed with the MHS parameters of Mahabadi and O'Driscoll,[26] which were used by Davis et al.[1] in the original study of DMA. The DMA data of Davis et al.[1] was not included in the reanalysis because the individual k_p data points, from which the published average values were calculated, were no longer available. However, the point estimates obtained by Davis et al.[1] for the Arrhenius parameters of DMA are consistent with the trend recently reported by Hutchinson et al.[5]

Examining Figure 8, we see that the Arrhenius parameters of MMA, EMA, and BMA are virtually indistinguishable. Although the 95% JCIs from the overall analysis do not overlap, they are very close and would overlap if the (collected) 95% JCIs from the separate studies were used as a measure of the true uncertainty in the Arrhenius parameters. However, it is evident that the Arrhenius parameters of BzMA and DMA are significantly different from those of MMA, EMA, and BMA. In the case of BzMA, we see that the increase in k_p arises solely in the increased frequency factor, while in the case of DMA we see that the frequency factor is slightly lower, but a much lower activation energy leads to a higher k_p.

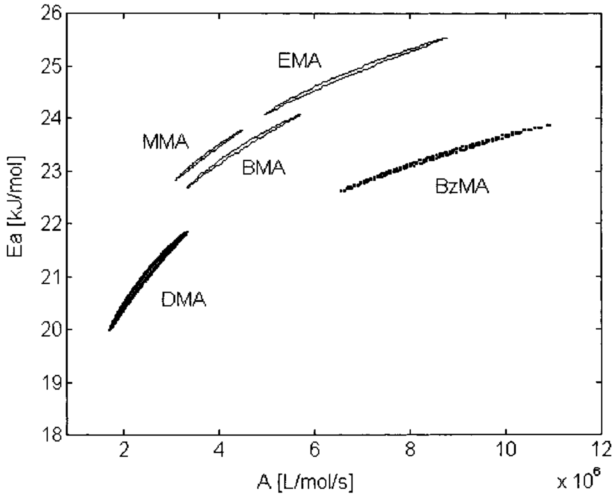

Figure 8. Overall 95% JCIs for Arrhenius parameters of the methacrylate series. The EMA and BMA JCIs were obtained from the combined data of all previous work,[1,3,5] the MMA JCI was obtained from the combined IUPAC data[9] and the data of this work, the BzMA JCI was obtained from the combined LALLS and DV data of this work, and the two DMA JCIs were obtained from the recent data of Hutchinson et al.[5] and a reanalysis of the same data but with the MHS constants[26] used by Davis et al.[1] in the original work.

Prima facie, these results are inconsistent with each other and, in the case of the DMA data, are also inconsistent with theoretical predictions. For, assuming the ester chain of the alkyl methacrylates is extended, the frequency factor would be expected to increase with increasing chain length, owing to the increasing monomer mass.[27] Given the distance of the ester chain from the radical center (and the lack of any conjugation with the radical center), the activation energy would not be expected to be much affected by the ester chain. The results of BzMA fit with this trend, but the DMA results do not. However, this apparently anomalous result is easily explained when it is noted that the ester chain of DMA will not necessarily be fully extended in either the radical or the monomer. If this long alkyl chain was instead coiled, it is possible that part of the alkyl chain (on the terminal unit of the radical) could lie quite near to the radical center. In this case, the activation energy could be affected via some through-space interaction between the alkyl chain and the unpaired electron, and the frequency factor could be decreased via some form of steric hindrance. This could thus account for the observed decrease in both the activation energy and frequency factor of DMA. In contrast, the ester chain of the BzMA, containing only one CH_2 unit followed by a (rigid) phenyl ring, could not interfere with the radical center, and neither could the shorter *n*-alkyl chains of MMA, EMA, and BMA. Hence, the absence of any significant activation energy differences in these monomers may also be explained.

Therefore we conclude that provided the ester chain is either short or relatively rigid, the ester chain will exert a negligible effect on the activation energy of the propagation reaction and only a small mass effect on the frequency factor. However, if the chain is not rigid and is long enough to lie near the radical center, such trends will break down, and on the basis of the DMA results of Hutchinson et al.[5] and Davis et al.,[1] it appears that both the activation energy and frequency factors will decrease. A PLP study of some intermediate *n*-alkyl methacrylate ester, such as octyl methacrylate, may be used to test this idea by identifying the chain length at which the activation energy is altered.

Conclusions

The most important conclusion that emerges from this PLP work is that provided the MHS constants have been accurately determined, the imprecision in their measurement is unlikely to lead to systematic errors in measured rate coefficients. Therefore small differences among kinetic parameters in a homologous series (such as the methacrylates) can be identified with confidence. However, if the imprecision in the MHS constants is ignored in the kinetic analyses, it could lead to false confidence in the precision of the kinetic rate coefficients (and hence the Arrhenius parameters). In the specific case of the methacrylate series we conclude that the differences in activation energy for DMA, and frequency factor for BzMA, from the lower methacrylates are significant, and we suggest tentative reasons for this behavior.

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Supporting Information Available: Tables containing the raw data used in the analyses described in this paper (5 pages). Ordering information is given on any current masthead page.

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