Copolymerization Propagation Kinetics of Styrene and Methyl Methacrylate—Revisited. 1. Pulsed Laser Polymerization Study

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ABSTRACT: A comprehensive set of propagation rate coefficients for styrene−methyl methacrylate bulk copolymerization has been obtained from pulsed laser polymerization experiments performed over a range of temperatures (18−57 °C). The copolymer molecular weight distributions were analyzed using size exclusion chromatography with on-line low-angle laser-light scattering (LALLS) and differential viscometry (DV) detectors. The molecular weight data obtained using these absolute detection methods were compared with data obtained by assuming the copolymer hydrodynamic volumes (HDVs) can be described by a weighted average of the homopolymer HDVs. The analyses via these three different approaches yielded virtually identical molecular weight data, validating previous work on this copolymerization system. The precision of the data obtained from LALLS and DV was worse than that obtained from the HDV-weighted approach. However, the errors in the molecular weight data from DV and LALLS analyses are believed to be a more correct representation of the true errors in the molecular weight measurement. A strategy for reducing the effect of the molecular weight errors in the $\bar{k}_p$ measurements, via the selection of slow laser flashing rates, is presented.

Introduction

The copolymerization of styrene (STY) with methyl methacrylate (MMA) has been extensively studied as the "fruit-fly" of free radical copolymerization. In 1985 Fukuda et al.[1] measured the kinetics of this system using the rotating sector technique. Their results clearly demonstrated that, although the copolymer composition was well described by the terminal model, this model failed to describe simultaneously the average propagation rate coefficient in copolymerization ($\bar{k}_p$) for this system. This work was subsequently confirmed by two independent studies[2,3] using the more accurate pulsed laser polymerization (PLP) technique.[4] Prior to this work, the terminal model was accepted as the basis of copolymerization kinetics, owing to its ability to describe the composition of most systems tested. The demonstration by Fukuda et al.[1] and subsequent workers that the terminal model failed to describe the propagation rate of this and other systems for which the terminal model composition equation was known to hold led to a search for a new basis of copolymerization kinetics. The first such model was published by Fukuda et al.,[5] who formulated a restricted penultimate unit model based on the premise that the radical stabilization energies were dependent on the penultimate unit. The derivation ignored entropic factors and assumed the validity of the Evans−Polanyi rule. Three important consequences of this model can be stated:

1. The magnitude of the penultimate unit effect (PUE) is independent of the substrate (monomer, terminator, or chain transfer agent). Fukuda et al.[5] showed that if this condition was satisfied, the penultimate unit effect would manifest itself only in the kinetics of a copolymerization and not in the composition or sequence distribution. This type of penultimate unit effect is known as an implicit PUE (IMPUE) in order to distinguish it from an explicit PUE (EPUE), which would also influence the composition and sequence distribution of a copolymer.

2. The magnitude of the IMPUE is dictated by the alternating tendency in copolymerization. That is, the model predicts that the product of the monomer reactivity ratios is equal to the product of the radical reactivity ratios: $r_1r_2 = s_1s_2$.

3. The effect is predicted to be a general case in copolymerization and applies in all cases except when $r_1r_2 = 1$.

Two alternative models have since emerged to explain the experimental data. Firstly, Maxwell et al.[6] showed that a "bootstrap" model could also simultaneously describe the bulk STY−MMA $\bar{k}_p$ and composition data. This bootstrap model[7] attributes deviations from terminal model behavior to nonideal monomer partitioning adjacent to the radical end. Secondly, Heuts et al.[8] have suggested that a PUE is operating but that the origin of the effect lies mainly in entropic rather than enthalpic factors.

While the previous kinetic studies[1−3] of the copolymerization kinetics of STY−MMA have clearly shown the failure of the terminal model, the data have so far proved deficient, in both quality and quantity, for careful model discrimination studies. The quality of the data has been jeopardized by the techniques used to measure $\bar{k}_p$. The study by Fukuda et al.[1] used the technique of rotating sector, in which values of $\bar{k}_p$ and the average termination rate coefficient, $\langle k_t \rangle$, are determined by combining separate measurements of $\bar{k}_p/\langle k_t \rangle$ and $\bar{k}_p^2/\langle k_t \rangle$, respectively obtained from a series of non-steady and steady state experiments. The validity of this procedure depends on the constancy of $\bar{k}_p$ and $\langle k_t \rangle$ throughout this set of experiments. Unfortunately, the extreme sensitivity of $\langle k_t \rangle$ to variables such as the chain length of polymer produced and the viscosity of the reaction medium renders it difficult, if not impossible, to maintain a constant $\langle k_t \rangle$ between the non-steady and steady state experiments. For this reason the technique is no longer recommended by IUPAC for the low conversion

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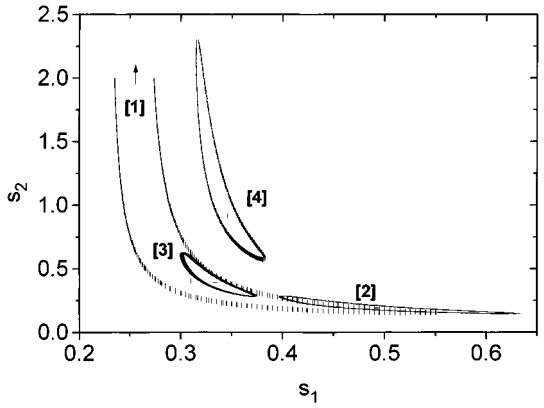

Figure 1. 95% joint confidence intervals for the radical reactivity ratios of STY−MMA, as obtained from the $\bar{k}_p$ data of [1] (40 °C) Fukuda et al.,[1] [2] (25 °C) Davis et al.,[3] and [3] (25 °C) and [4] (40 °C) Olaj et al.[2] All data sets were reanalyzed using the technique of weighted nonlinear least squares, and the residuals were weighted according to the size of the $\bar{k}_p$ values. In the analysis, the monomer reactivity ratios were fixed at the values of Fukuda et al.[1] ($r_1 = 0.523$ and $r_2 = 0.460$), and the homopropagation rate constants were fixed at the values determined in their respective studies.

measurement of $\bar{k}_p$, and instead the technique of PLP is favored.[9] In this technique, as developed by Olaj et al.,[10] $\bar{k}_p$ is determined from the molecular weight distribution of the polymer produced in a single non-steady state experiment. While this procedure is potentially very accurate, in practice its accuracy is limited by the accuracy of the molecular weight analysis. While the other two kinetic studies of STY−MMA[2,3] did use the IUPAC-recommended method of PLP, they used only conventional SEC to measure the molecular weight of the copolymers produced. In the absence of narrow standards or Mark−Houwink constants for the various compositions of STY−MMA copolymers, it was assumed that the calibration curve for a STY−MMA copolymer was simply a weighted average of the respective homopolymer calibration curves. Such an assumption is yet to be verified and has thus been criticized.[11] Hence, all of the previous studies of STY−MMA are not accurate enough for sensitive model discrimination. This is evident in the widely varying values of the fitted model parameters (s_1 and s_2) measured in the different studies of STY−MMA, as seen in Figure 1. The uncertainty in the values of these parameters renders it impossible to attach physical significance to them and, hence, them to test model predictions such as $r_1 r_2 = s_1 s_2$.

A second deficiency in the previous studies of STY−MMA is that they have not extensively examined the effect of temperature on the kinetic parameters. In the absence of such a temperature study, it is difficult to discriminate between the two implicit penultimate unit models because these two models are mathematically equivalent and differ only in their account of the origin of the IMPUE (and hence in the expected values of the fitted model parameters). A careful temperature study would provide a possible means of discriminating between these two models, as it would enable measurement of the average activation energy and frequency factor as a function of monomer feed ratio. Hence it may be possible to determine whether or not the origin of the IMPUE is entropic, enthalpic, or both. A study of temperature effects would also allow discrimination between the penultimate models and solvent effects models, as the temperature dependence of the fitted model parameters in the latter would be expected to be much stronger.

The intention of the work presented here was to obtain the most accurate and extensive kinetic data to date for the copolymerization of STY with MMA, and hence evaluate the different models for copolymerization kinetics. The accuracy of this study was to be maximized by using PLP in conjunction with two of the most accurate methods of molecular weight analyses currently available: SEC with on-line low-angle laser light scattering (LALLS) and differential viscometer (DV) detectors, in addition to a standard concentration detector (in this work a differential refractive index (DRI) detector). The advantage of these molecular weight sensitive detectors is that they avoid the need to use an equation relating intrinsic viscosity (IV) to molecular weight (MWT) (such as the Mark−Houwink−Sakurada equation[12,13]) to convert hydrodynamic volume into molecular weight. This is especially important for copolymers for which there are no calibration constants available. By using a large experimental design—incorporating 200 polymerizations and covering five temperatures and a range of monomer feed ratios—we hoped to obtain the best estimates possible for the fitted model parameters and, by studying the effects of temperature on the propagation rate coefficients, we believed that it would be possible to discriminate between the models described above. This work is split into two parts. In this paper, the pulsed laser polymerization study of STY−MMA will be described and the results presented and discussed. In the following paper, the alternative models for copolymerization kinetics will be fitted to the $\bar{k}_p$ data in an attempt to evaluate them.

Experimental Section

Materials. STY and MMA were passed through a column of activated alumina (Aldrich) and refrigerated until required. The photoinitiator 2,2′-azobis(isobutyronitrile) (AIBN) was purchased from BDH and used as received. The eluent for the SEC, HPLC Grade THF (BDH, Hiper Solv), was filtered through a 0.02 μm pore size filter (Whatman Anodisc 47, inorganic membrane) three times (so as to minimize baseline noise, especially in the LALLS detector) and then stored in the dark until required.

Polymerizations. Purified monomer and initiator were charged to Pyrex sample tubes (10 mm diameter by 60 mm height), deareated by bubbling with argon for 5 min, and sealed with rubber septa. The reaction mixtures were shaken vigorously before immersion in a constant temperature bath, in which they were heated to the reaction temperature. The samples were then placed in a thermostated copper sample cell and allowed further time to reach thermal equilibrium, before being exposed to pulsed UV laser light. This was produced using an experimental rig similar to the design of Davis et al.[14] It consisted of a Spectra Physics Quanta-Ray DCR-11 pulsed Nd:YAG laser with a HG-2 harmonic generator, which was used to generate 355 nm UV laser radiation that 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), for which the error in pulse times was ±0.0005%. The laser pulse energy, as measured using a scientific digital power meter (model 36-5002), was 38 mJ/pulse at a pulse half height of 8 ns. After the pulsed laser treatment, the polymerization activity was terminated by adding the reaction mixture to petroleum spirit, thereby precipitating the polymer from its monomer. Polymerizations were taken to conversions of less than 2%, so as to satisfy the low-conversion assumption inherent in the PLP technique and also to avoid composition drift in the copolymers.

Careful temperature control is one of the keys to a successful PLP experiment, and this was achieved by placing the feedback loop of the temperature controller (a K-type thermocouple) as close as possible to the Pyrex sample tube. The

sharp PLP characteristics obtained for the polymers produced (see for example Figure 3), verify the success of this setup. It is also necessary to know the exact temperature at which the $\bar{k}_p$ data were measured, and it is likely that some of the variation among previous PLP studies of the same system may be caused by systematic errors in the reported experiment temperature. To avoid such error in this work, the equilibrium temperature within the sample cell was measured as a function of the setpoint temperature on the temperature controller using a second thermocouple that was calibrated using iced and boiling (triply distilled) water and also boiling chloroform.

Size Exclusion Chromatography (SEC) Equipment. SEC analyses were performed on a modular system comprising a GBC Instruments LC1120 HPLC pump operating at room temperature; a SCL-10A Shimadzu autoinjector with a 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 μm mixed B, 2 × 5 μm mixed C and a 5 μm mixed D) and an in-line filter (0.2 mm). Three detectors were connected in a series configuration: a PL refractive index detector (DRI), PL low-angle-laser-light-scattering (LALLS) detector, and a Viscotek Model 250 differential viscometer (DV). The data were collected using PL data capture units (DCU) and analyzed using PL Caliber version 6.0 GPC/SEC software.[15] The eluent was THF at a flow rate of 1 mL·min^{-1}. The sample injection size was 200 μL in all cases. Data were collected at 2 points/s. A flow rate marker (dioctyl phthalate) was used in all runs.

Calibrations. In a previous publication from this group,[16] it was shown that the accuracy of SEC-DV and SEC-LALLS analysis was sensitive to the estimated interdetector delay (IDD). Specifically, it was shown that errors could occur if the IDD is treated as a constant since, as shown by Suddaby et al.,[17] the IDD is in fact molecular weight dependent. Now, the commercial SEC software used in this work[15] utilizes a single IDD. However, we have attempted to minimize the errors associated with this by carefully optimizing the IDD at a specific molecular weight (10^5) and then selecting PLP conditions so as to target this (peak) molecular weight for all samples. In this way the IDD could be considered to be roughly constant for the analysis. The accuracy of this calibration procedure (and indeed the calibration implemented for the analyses herein) has been verified in a separate publication from this group.[18] In this work, PLP homopolymers of styrene and methyl methacrylate—produced respectively at similar conditions to the high-styrene and high-methyl methacrylate copolymers of this current work—were analyzed using the two direct molecular weight techniques and using their respective DRI calibration curves. Good agreement between the $\bar{k}_p$ values measured by the three different techniques was obtained, and hence the calibration procedure was judged to be adequate for the measurement of $\bar{k}_p$.

Analysis. Each PLP polymer was analyzed by three different molecular weight analysis methods: the two molecular weight sensitive techniques (LALLS and DV) and also by conventional GPC. In the latter case, the copolymers were measured against the PMMA and PSTY calibration curves, and the result was averaged (on a mass basis) according to the composition of the copolymer samples. The composition was calculated using the reactivity ratios published by O'Driscoll et al.[19] For a description of the basic principles of the direct molecular weight analysis techniques, the reader is referred to a previous publication by this group.[16]

Numerical Analysis of the Molecular Weight Distributions. As shown by Olaj et al.,[10] the propagation rate coefficient ($\bar{k}_p$) of a free-radical polymerization can be determined from the molecular weight distribution of the polymer produced in a low-conversion PLP experiment. The molecular weight distribution of the polymer produced has a characteristic peak, corresponding to that polymer that grows between two successive pulses of the laser. The molecular weight that best corresponds to this polymer that grows between consecutive laser flashes is, according to IUPAC recommendations,[20] the low molecular weight side point of inflection of the first PLP peak in the molecular weight distribution. In order to determine this quantity, the molecular weight distributions were numerically transformed to number distributions on a linear scale and then differentiated, following the procedure outlined by Hutchinson et al.[21] The inflection point molecular weight, identified as the first maxima in the differentiated number distribution, was converted to a kinetic chain length by dividing by the average molecular weight of the repeat unit in the copolymer. To determine this quantity, an estimate of the copolymer composition was required, and reactivity ratios published by O'Driscoll et al.[19] were used for this purpose. The error introduced through using these reactivity ratios (which were measured at 60 °C) for all of the copolymers was small because the molecular weights of the repeat units for STY (104 144) and MMA (100 114) are very similar. The kinetic chain length at the inflection point of the molecular weight distribution (ν_p) is related to the propagation rate coefficient by the following expression:[10]

$$\bar{k}_p = \frac{\nu_p}{[M]t_f}$$

In this equation, [M] is the average monomer concentration and t_f is the dark time between consecutive laser flashes. In order to estimate the average monomer concentrations, the densities of the pure monomers at each temperature were required. These values were taken from Stickler et al.[22] and Coulter et al.[23] for MMA and STY, respectively. These densities were used to estimate the monomer concentrations for each of the pure monomers, which were then averaged according to the molar fractions of the comonomers in the feed. This provided an estimate of the initial monomer concentration which, as the conversions were very low (<2%), provided a good approximation to the instantaneous monomer concentration [M] throughout the PLP experiment. Once [M] was calculated and ν_p obtained, the propagation rate coefficient was calculated using the equation above.

Experimental Design. As explained above, it was decided to design the PLP conditions so that all of the samples had similar molecular weights, in this way, avoiding the need to use the Suddaby−Sanayei method[17] for the SEC-LALLS and SEC-DV techniques. A target (peak) molecular weight of 10^5 was selected for the samples, since in this range the sensitivities of the concentration detector and the two molecular weight sensitive detectors were not too dissimilar. In order to produce samples with approximately this molecular weight, the following laser pulsing rates were used. For high STY copolymers, laser pulsing rates of 1−2 Hz over the temperature range of 17.9−57.2 °C were used, while for high MMA copolymers, rates of 5−10 Hz were used over the same temperature range. This is only a general guide to the conditions used, and many of the samples were replicated at different pulsing rates, in accordance with IUPAC criteria. The laser pulsing rates used to produce each of the 200 samples are included in Tables 1−5.

It should be noted that the pulsing rates required to obtain molecular weights in the desired range for the systems showing a slow $\bar{k}_p$ (that is, the high-STY copolymerizations at the lower temperatures) were quite slow (1 Hz). At slow pulsing rates, the growing polymer chains can be susceptible to termination during the dark time. However, we found that this undesirable occurrence could be avoided by using low initiator concentrations (around 2.5 mmol/L) for all of the samples. In this way, PLP-type distributions were produced for all of the samples. The compliance of our PLP distributions with IUPAC criteria will be demonstrated in a subsequent section of this paper.

Results

The propagation rate coefficients ($\bar{k}_p$) for STY−MMA copolymerization were measured at five temperatures, over a temperature range of 17.9−57.2 °C. The data obtained at each of these temperatures is shown in Tables 1−5. For each PLP sample there are three estimates of $\bar{k}_p$, corresponding to the three methods of

Table 1. Styrene (1)/Methyl Methacrylate (2) At 17.9 °C

		$\bar{k}_p$ (L·mol^{-1}·s^{-1})		
f_1	dark time (s)	DRI	LALLS	DV
0.000	0.2	245.0	256.9	253.0
0.000	0.5	237.4	265.3	247.8
0.072	0.5	125.9	145.1	124.0
0.051	0.5	142.0	150.5	141.0
0.054	0.5	138.4	147.5	131.7
0.071	0.5	128.8	142.2	121.0
0.064	0.5	129.2	138.2	127.8
0.100	0.5	116.9	116.2	109.0
0.106	0.5	113.1	126.1	107.1
0.194	1.0	89.2	96.8	80.4
0.199	1.0	88.0	90.7	81.3
0.181	1.0	89.8	97.7	79.8
0.256	1.0	88.1	73.5	71.8
0.186	1.0	90.4	81.1	73.0
0.261	1.0	81.1	74.1	69.7
0.258	1.0	82.1	86.7	77.0
0.361	1.0	67.6	63.6	55.6
0.349	1.0	73.6	67.1	64.4
0.360	1.0	72.3	65.9	60.8
0.345	1.0	74.6	60.1	53.7
0.347	1.0	70.7	61.0	58.7
0.499	1.0	65.4	60.4	54.3
0.494	1.0	64.3	61.5	54.2
0.634	1.0	62.3	55.5	70.7
0.635	1.0	64.0		
0.627	1.0	61.4	51.8	54.2
0.618	1.0	61.3	57.2	55.3
0.642	1.0	57.9	58.2	48.2
0.798	1.0	59.8	56.2	51.3
0.785	1.0	58.3	50.2	47.0
0.796	1.0	57.8	60.8	49.1
0.796	1.0	57.5	57.7	52.2
0.781	1.0	58.1	58.0	50.3
0.956	1.0	56.7	68.8	54.5
0.933	1.0	58.3	58.4	51.1
0.950	1.0	58.1	60.9	52.5
0.949	1.0	58.7	66.3	54.6
0.960	1.0	59.9	72.2	56.8
1.000	1.0	62.8	55.7	57.0
1.000	1.5	61.1	64.8	57.6

molecular weight analysis used. As an example, the 37.6 °C data are plotted in Figure 2.

Because of the large number of samples included in this study, the molecular weight data that was used to produce these $\bar{k}_p$ values has not been reproduced in full. However, the peak and inflection point molecular weights, together with the molecular weight averages M_n, M_w, and M_z, for a set of representative samples from the 37.6 °C study, are given in Table 6.

PLP Consistency Checks. An IUPAC working party have recommended that a series of consistency checks accompany any PLP study.[20,24] These consistency checks may be loosely grouped into two categories: (1) those that test the applicability of the system under study to PLP (this would include criteria such as invariance of $\bar{k}_p$ to the flashing frequency, initiator concentration and type, laser power, and the absence of significant dark time initiation); (2) those that ensure that the PLP conditions are optimized so as to give clearly defined PLP features (this would include the condition that the molecular weight distribution exhibits overtones at multiples of the primary peak). Since the copolymerization of STY−MMA has previously been studied by PLP,[3] and the individual monomers the subject of IUPAC benchmark papers,[20,24] a thorough investigation of condition 1 was not necessary. Nevertheless, throughout this work laser power (in the range 32−38 mJ/pulse), initiator concentration (1.5−7.5 mmol/L), and laser flashing rate (see Tables 1−5) were allowed

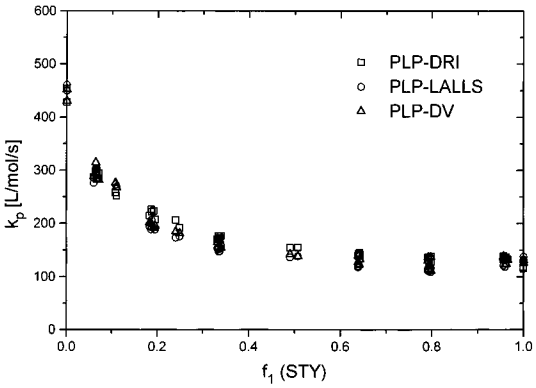

Figure 2. Plot of $\bar{k}_p$ versus f_1 for STY−MMA at 37.6 °C.

Table 2. Styrene (1)/Methyl Methacrylate (2) At 27.7 °C

		$\bar{k}_p$ (L·mol^{-1}·s^{-1})		
f_1	dark time (s)	DRI	LALLS	DV
0.000	0.25	311.5	308.1	294.3
0.000	0.50	308.6	295.7	280.6
0.069	0.50	191.0	180.5	170.7
0.066	0.50	193.8	179.3	166.9
0.056	0.50	206.0	184.7	181.1
0.056	0.50	199.8	172.5	179.8
0.078	0.50	182.7	151.0	152.4
0.123	0.50	159.4	132.5	136.9
0.110	0.50	168.5	138.5	145.4
0.178	0.50	142.1	125.7	115.0
0.191	0.50	141.4	113.3	98.3
0.188	0.50	140.2	122.0	126.2
0.184	0.50	144.2	124.6	119.4
0.203	0.50	138.6	118.7	113.7
0.259	0.50	129.7	110.0	124.5
0.267	0.50	124.6	108.1	122.3
0.344	0.50	111.1	92.7	121.7
0.334	0.50	121.4	102.3	113.0
0.309	0.50	120.8	104.9	111.6
0.342	0.50	122.0	105.6	104.5
0.332	0.50	120.7	109.6	113.4
0.482	0.50	110.0	89.0	98.2
0.481	0.50	114.9	95.0	96.6
0.635	0.50	99.1	81.7	87.1
0.614	0.50	98.2	90.0	93.0
0.644	0.50	95.0	86.2	90.8
0.634	0.50	97.8	82.7	86.3
0.634	0.50	95.9	89.1	82.6
0.787	0.50	88.9	81.4	86.9
0.766	0.50	94.8	75.7	82.8
0.964	0.50	105.3	84.6	92.0
0.788	0.50	89.8	77.3	85.1
0.790	0.50	94.1	78.6	83.5
0.732	0.50	86.8	73.3	86.8
0.952	0.50	86.8	79.4	89.5
0.947	0.50	86.7	75.4	89.4
0.968	0.50	91.9	80.8	84.2
0.941	0.50	89.6	81.2	78.7
1.000	0.50	96.6	88.9	89.8
1.000	1.00	89.4	87.0	83.4

to vary without causing significant differences between replicate samples.

In order to demonstrate that the PLP samples produced in this work satisfied condition 2, molecular weight distributions of a typical high-STY and high-MMA sample from this study are given in Figure 3. By inspection, it is clear that there are higher order overtones of the primary PLP peak present in the molecular weight distributions. For the high-STY sample the low molecular weight side inflection points of the overtones occur at 1.89 and 3.05 times the primary inflection point molecular weight, while for the high-MMA sample the inflection points of the overtones appear at 1.94 and 3.10 times the primary inflection

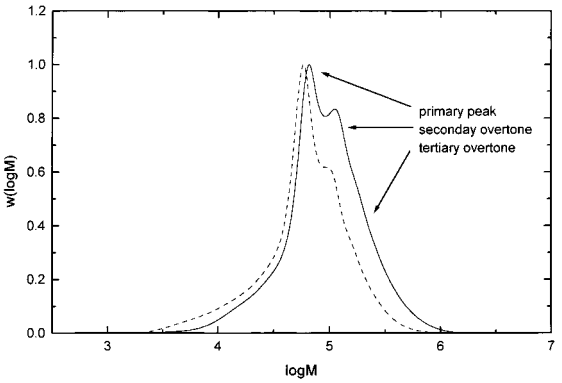

Figure 3. Molecular weight distributions of a typical high molecular weight MMA copolymer (- - -) and a typical high molecular weight STY copolymer (—). The high molecular weight MMA copolymer ($f_1 = 0.110$) was produced at 37.6 °C, with a laser pulsing rate of 4 Hz, while the high molecular weight STY copolymer ($f_1 = 0.792$) was produced at 37.6 °C, with a laser pulsing rate of 2 Hz. In the high molecular weight MMA distribution $\nu_2 = 1.94\nu1$ and $\nu3 = 3.10\nu1$ and in the high molecular weight STY distribution $\nu2 = 1.89\nu1$ and $\nu3 = 3.05\nu1$.

Table 3. Styrene (1)/Methyl Methacrylate (2) At 37.6 °C

		$\bar{k}_p$ (L·mol^{-1}·s^{-1})		
f_1	dark time (s)	DRI	LALLS	DV
0.000	0.25	454.2	461.2	452.1
0.000	0.5	428.1	449.4	430.4
0.060	0.25	287.3	276.1	289.4
0.071	0.25	294.4	285.8	281.5
0.066	0.25	295.0	303.6	282.5
0.064	0.5	297.0	302.7	314.8
0.065	0.5	291.7	295.8	300.4
0.108	0.25	257.9	273.3	276.4
0.110	0.25	252.0	268.8	267.7
0.188	0.25	222.3	207.0	194.4
0.186	0.25	226.6	188.9	200.3
0.192	0.25	223.6	197.0	192.2
0.195	0.5	207.8	188.7	195.7
0.183	0.5	214.8	194.2	201.8
0.240	0.25	206.7	173.2	184.9
0.249	0.25	191.7	175.7	181.6
0.340	0.25	176.9	158.0	154.0
0.335	0.25	176.8	147.4	169.8
0.334	0.25	177.1	151.6	157.0
0.337	0.5	173.5	148.0	169.0
0.332	0.5	170.5	153.4	164.8
0.490	0.5	154.9	136.3	142.2
0.507	0.5	155.3	138.6	138.2
0.641	0.5	145.0	131.1	123.3
0.639	0.5	142.6	125.7	122.4
0.642	0.5	142.6	132.3	133.2
0.638	1	139.9	120.4	139.5
0.638	1	139.7	117.9	127.6
0.791	0.5	136.5	112.0	130.2
0.798	0.5	138.3	116.3	137.2
0.792	0.5	136.1	115.4	136.8
0.798	1	127.9	108.8	111.0
0.794	1	125.1	110.2	119.5
0.956	0.5	138.7	133.1	135.8
0.962	0.5	136.3	132.8	123.7
0.959	0.5	136.0	118.5	134.4
0.956	0.5	132.2	121.3	138.6
0.965	0.5	133.0	132.6	131.8
1.000	0.5	118.0	132.0	131.4
1.000	1	115.5	137.7	126.3

point molecular weight. In both cases these overtones occur at approximately integer multiples of the primary PLP peak, and hence for both representative samples the molecular weight distributions satisfy the IUPAC criteria.

Assessment of the Homopropagation Data. The $\bar{k}_p$ of STY−MMA copolymerizations has previously been measured at two temperatures: 25 °C[2,3] and 40 °C.[1,2] Since neither of these temperatures correspond exactly to any of the temperatures studied in this work, the copolymerization data presented here could not be compared with that of previous studies. Instead, we included a small number of pure MMA and pure STY samples in our experimental design, in order to measure the homopropagation rate coefficients of the two comonomers. The values we obtained could then be compared with values from a previous study by this group,[18] and also with their respective IUPAC-recommended benchmark values.[20,24] Table 7 contains the average values for the homopropagation rate coefficients of this work (the LALLS, DV, and DRI estimates are presented separately), together with the average of the corresponding values reported by Zammit et al.[18] and the corresponding IUPAC benchmark value (as calculated from the IUPAC-recommended[20,24] Arrhenius parameters). The agreement between these different estimates of the homopropagation rate coefficients is very good and is well within the spread of the data accepted by IUPAC for the calculation of their benchmark values.[25] Hence we may conclude that the homopropagation rate coefficients reported here are accurate, which in turn suggests that the copolymerization data are reliable.

It might further be noted from Table 7 that the LALLS, DV, and DRI estimates of the homopropagation rate coefficients at a given temperature are very close to each other. Now, for STY and MMA homopolymers,

Table 4. Styrene (1)/Methyl Methacrylate (2) At 47.4 °C

		$\bar{k}_p$ (L·mol^{-1}·s^{-1})		
f_1	dark time (s)	DRI	LALLS	DV
0.000	0.2			
0.000	0.4			
0.061	0.2	413.0	421.0	405.5
0.061	0.2	426.7	411.2	387.6
0.061	0.2	423.9	428.7	396.2
0.062	0.4	409.6	415.5	459.5
0.064	0.4	424.1	438.1	432.9
0.098	0.2	386.9	384.8	381.8
0.111	0.4	372.2	341.2	387.5
0.183	0.2	329.6	310.4	319.9
0.186	0.2	328.8	307.8	325.2
0.192	0.2	328.6	309.0	316.2
0.189	0.4	318.8	311.8	331.1
0.196	0.4	315.1	298.0	310.0
0.246	0.3	295.8	286.2	286.4
0.242	0.6	288.2	267.9	283.9
0.328	0.3	268.2	243.1	247.3
0.335	0.3	256.3	250.9	255.7
0.340	0.3	261.9	230.2	252.5
0.334	0.6	255.8	237.3	249.2
0.341	0.6	258.4	232.7	242.4
0.490	0.4	233.6	219.2	218.7
0.489	0.8	226.1	195.8	224.8
0.631	0.5	206.3	195.9	202.5
0.628	0.5	214.7	185.2	196.9
0.626	0.5	210.9	186.1	189.3
0.642	1	209.5	199.1	184.6
0.637	1	204.8	195.8	206.7
0.798	0.5	198.4	194.3	204.8
0.789	0.5	198.0	184.1	210.7
0.793	0.5	199.1	193.6	176.9
0.777	1	204.0	188.9	191.0
0.786	1	200.4	184.0	188.9
0.960	0.5	199.0	217.7	204.4
0.950	0.5	196.4	223.1	186.0
0.935	0.5	203.2	207.9	179.8
0.953	1	185.4	193.8	207.6
0.954	1	183.0	197.0	209.4
1.000	0.5	221.7	206.3	223.4
1.000	1	204.6	214.9	220.4

Table 5. Styrene (1)/Methyl Methacrylate (2) At 57.2 °C

		$\bar{k}_p$ (L·mol^{-1}·s^{-1})		
f_1	dark time (s)	DRI	LALLS	DV
0.000	0.10	768.3	723.5	789.5
0.000	0.25	742.9	746.9	766.5
0.063	0.10	578.6	560.3	555.3
0.071	0.10	563.5	596.5	565.6
0.066	0.10	576.8	580.6	583.9
0.068	0.25	547.0	562.1	589.5
0.064	0.25	543.7	567.0	574.0
0.103	0.10	519.9	536.1	524.7
0.100	0.25	503.9	534.2	517.5
0.190	0.10	433.2	465.9	437.9
0.186	0.10	454.4	466.6	434.2
0.187	0.10	432.5	475.1	439.6
0.188	0.25	444.5	449.4	442.9
0.186	0.25	435.2	463.3	440.6
0.244	0.10	419.7	431.5	397.2
0.247	0.25	405.4	423.6	387.6
0.377	0.10	347.6	355.7	346.0
0.338	0.10	361.0	343.1	341.1
0.334	0.10	345.6	364.2	351.5
0.334	0.25	349.0	377.7	320.5
0.339	0.25	345.6	361.2	325.6
0.491	0.10	305.7	322.1	292.2
0.488	0.25	304.8	336.3	308.0
0.640	0.10	287.4	303.5	267.4
0.642	0.10	289.6	274.2	272.6
0.641	0.25	277.2	295.9	278.3
0.641	0.25	279.6	276.4	268.4
0.643	0.50	269.4	293.1	255.0
0.798	0.25	254.1	304.4	259.2
0.799	0.25	262.6	276.4	273.4
0.794	0.25	289.1	286.4	264.9
0.791	0.50	271.4	276.8	272.4
0.798	0.50	267.2	287.2	252.3
0.935	0.25	279.9	309.6	257.6
0.965	0.25	280.0	293.3	258.1
0.954	0.25	285.9	290.7	264.6
0.964	0.50	264.2	295.0	262.5
0.960	0.50	268.9	288.5	249.3
1.000	0.25	277.3		278.6
1.000	0.50	272.6		287.9

the conventional SEC analysis (that is, DRI) provides a direct measure of molecular weight, since these polymers are simply analyzed against their respective calibration curves. Hence the homopropagation DRI data may be considered to be very accurate, and the agreement between this data and the corresponding LALLS and DV data provides a further verification of the accuracy of the LALLS and DV calibrations used in this work.

Discussion

Comparison of the Molecular Weight Analysis Methods. When the $\bar{k}_p$ data in Tables 1−5 and Figure 2 are examined, it is evident that (1) the LALLS and DV data are more scattered than the DRI data, but (2) the data obtained from the three molecular weight analysis methods are not systematically different from each other. In what follows, we will explore these two observations and then discuss (3) their implications for the accurate measurement of $\bar{k}_p$ for copolymerization systems.

(1) Precision. As noted above, it is evident that the data from the direct molecular weight analysis techniques is more scattered than that from the DRI analysis. This is because these techniques use additional parameters in their analysis and are thus susceptible to additional sources of experimental error. Specifically, the LALLS and DV techniques require an accurate value for the amount of polymer injected, and also the exact integrals of the detector responses corresponding to this polymer. Hence errors in the injection volume, sample concentration, and peak integrals (arising from, for instance, a noisy baseline), will all affect the measured molecular weights. In contrast, conventional SEC analysis is not subject to these

Table 6. Selected Molecular Weight Data (37.6 °C)

f_1	t_f	inflection pt	M_n	M_w	M_z	M_p
SEC-DV Molecular Weight Analysis						
0	0.25	103 923	38 973	173 706	410 474	122 063
0	0.50	197 853	65 973	254 137	457 329	231 041
0.07	0.25	64 706	34 734	112 773	215 136	82 082
0.07	0.25	64 952	34 638	126 754	274 287	82 776
0.07	0.50	144 729	42 829	192 638	360 170	171 526
0.06	0.50	138 112	40 510	176 042	328 309	163 860
0.19	0.25	44 558	31 799	94 268	200 401	58 685
0.19	0.25	45 925	33 915	91 552	167 404	59 198
0.19	0.25	44 066	32 847	92 047	180 984	56 681
0.25	0.25	41 535	27 705	73 389	140 836	53 889
0.64	0.50	55 391	29 059	77 353	122 296	68 505
0.64	0.50	54 959	31 147	85 511	161 116	68 133
0.96	0.50	54 940	47 740	110 116	209 663	68 508
0.96	0.50	61 543	41 904	104 774	199 232	76 615
SEC-LALLS Molecular Weight Analysis						
0	0.25	106 000	51 979	181 811	389 362	135 980
0	0.50	206 600	50 344	243 082	498 744	210 228
0.07	0.25	65 710	33 591	114 154	221 836	81 525
0.07	0.25	69 800	40 259	129 041	261 979	87 889
0.07	0.50	139 200	42 137	186 729	344 827	167 846
0.06	0.50	136 000	41 686	174 010	321 995	162 699
0.19	0.25	47 450	32 807	92 449	184 729	58 898
0.19	0.25	43 300	30 886	89 846	171 427	56 254
0.19	0.25	45 160	34 309	91 876	176 764	57 775
0.25	0.25	40 186	20 408	60 535	119 866	43 268
0.64	0.50	58 883	23 577	63 906	101 840	56 090
0.64	0.50	56 480	24 354	70 862	137 383	56 109
0.96	0.50	58 963	52 806	112 149	199 570	72 579
0.96	0.50	53 865	60 681	142 872	262 757	105 730
Weighted DRI Molecular Weight Analysis						
0	0.25	104 400	50 633	163 057	359 520	119 790
0	0.50	196 800	88 444	271 798	506 056	234 932
0.07	0.25	67 673	41 337	114 674	218 369	82 932
0.07	0.25	67 811	43 574	123 684	255 230	84 440
0.07	0.50	136 545	55 161	179 138	320 016	162 369
0.06	0.50	134 139	54 065	166 554	291 500	158 161
0.19	0.25	50 963	39 043	101 772	205 759	64 783
0.19	0.25	51 953	41 513	101 842	186 815	65 902
0.19	0.25	51 265	42 201	100 578	184 758	64 756
0.25	0.25	43 846	32 593	78 068	139 524	58 643
0.64	0.50	65 124	39 138	90 220	140 217	79 685
0.64	0.50	64 054	40 337	96 948	179 791	78 362
0.96	0.50	60 539	57 821	114 500	205 555	73 953
0.96	0.50	58 700	46 416	95 792	167 462	72 227

Table 7. Comparison of Homopolymerization Rate Coefficients with Literature Data

(a) Styrene

	this work				
temp (°C)	DRI	LALLS	DV	Zammit et al.[18]	IUPAC[20]
17.9	62	60	57	60	62
27.7	93	88	87		96
37.6	117	135	129	136	145
47.4	213	211	222	193	214
57.2	275		283	290	307

(b) Methyl Methacrylate

	this work				
temp (°C)	DRI	LALLS	DV	Zammit et al.[18]	IUPAC[24]
17.9	241	261	250	228	258
27.7	310	302	287		349
37.6	441	455	441	459	464
47.4				576	605
57.2	756	735	778		776

sources of random experimental error, and the small scatter that is observed in the DRI data is caused instead by experimental error in the PLP technique itself (such as in sample preparation or temperature control), rather than in the molecular weight analysis of the PLP samples.

Although conventional SEC techniques are more precise than the direct methods, this does not necessarily mean that they will be more accurate. Even when narrow standards are available for the polymer being analyzed (which will thus allow the polymer to be analyzed against its own calibration curve), there are hidden sources of error in the conventional SEC technique. For, the narrow standards must themselves be characterized using direct molecular weight analysis techniques, and are thus subject to similar sources of error as the on-line LALLS and DV data. However, unlike the random error in the LALLS and DV techniques, this error is hidden as a possible systematic error in the calibration curve and does not affect the precision of the data. It should be noted that errors in the narrow standards will also affect the accuracy of the DV technique, as this method relies on a universal calibration curve.

However, when narrow standards are not available for the polymer being analyzed, conventional SEC relies upon a second calibration assumption. Typically, this is the Mark−Houwink−Sakurada (MHS) equation,[12,13] but in the present work it was the assumption that STY−MMA calibration curves could be approximated as a weighted average of the homopolymer calibration curves. This second calibration assumption is a potential source of systematic error in the data. The accuracy of the weighted average approximation will be discussed in the next section, but here the more frequently used MHS equation is examined. The MHS constants of a given polymer are typically subject to uncertainty. When these constants are used as point estimates in conventional SEC analysis this uncertainty is ignored, and it manifests itself as a hidden source of systematic error in the data. Any systematic errors in molecular weight analysis will undermine attempts at identifying structure−reactivity trends. This serious issue was recently noted by Hutchinson et al.[26] when attempting to identify small changes in kinetic parameters among a series of methacrylates. In this present work a similar problem would limit conclusions on the affect of temperature on the copolymerization reaction. In order to address this problem, we recommend that studies that use MHS constants report their uncertainty and take this uncertainty into account using sensitivity analysis when reporting the error in their final data.

In summary, although the direct molecular weight analysis methods are less precise than conventional SEC, this lack of precision does to some extent provide a more realistic measure of the errors inherent in all SEC methods.

(2) Accuracy. Although the LALLS and DV data are more scattered than the DRI data, the data sets obtained via the different molecular weight analysis techniques do not appear to be systematically different from each other. This conclusion is reinforced when the LALLS and weighted DRI estimates of the various molecular weight averages and artifacts are plotted against their corresponding DV estimates. Figure 4 depicts such a plot for the molecular weight data contained in Table 6. In this plot, the numbers are closely scattered about a line through the origin with a slope of one, and hence there appears to be good agreement between the molecular weights estimated by the different techniques. This agreement further verifies the accuracy of the molecular weight analysis, and hence the $\bar{k}_p$ data obtained. It also supports the assumptions previously made[2,3] about SEC analysis of STY−MMA copolymers—that the calibration curve of a STY−MMA copolymer (in THF) may be approximated as a weighted average of its respective homopolymer calibration curves. This conclusion supports that of a recent study by Kent et al.[27] who found that in a good solvent (such as THF) the hydrodynamic radius of a random STY−MMA copolymer is comparable to that predicted by the average values of the homopolymers.

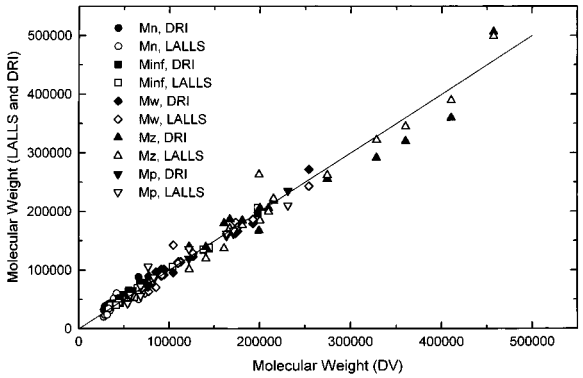

Figure 4. Comparison of the different molecular weight analysis methods: LALLS, DV, and DRI. Different molecular weight averages (M_n, M_w, and M_z) as well as the peak (M_p) and inflection point (M_{inf}) molecular weights, as measured by LALLS or DRI, are plotted against their corresponding DV estimate. Also plotted is the line LALLS = DV (or DRI = DV), around which the points are scattered.

Now, in general, treating the solution properties of a random copolymer as a weighted average of the homopolymer properties is not strictly valid, since the long and short range interactions of the heterodiads do affect the hydrodynamic volume (HDV). Indeed, a recent study by Hutchinson et al.[28] showed that the weighted average approximation was deficient for copolymers of MMA and *n*-butyl acrylate. This demonstrates that, although the weighted average approximation is valid for STY−MMA copolymers (in THF), it will not necessarily be valid for other copolymers. Therefore we recommend that the weighted average approximation be independently verified (using, for instance, direct measures of molecular weight) before it is used for the analysis of other copolymers.

(3) Implications. From the above, it appears that both the direct methods of molecular weight analysis and the conventional SEC analysis have problems. The direct methods require very careful calibration (especially with respect to the IDD) and are subject to several sources of random experimental error which, although they may provide a more honest indication of the true error in $\bar{k}_p$ data, render precise estimates of $\bar{k}_p$ very difficult. The conventional SEC analysis is, on the other hand, potentially very precise but this may merely be because of an underestimation of the true error in the data. Furthermore, when narrow standards are not available for the polymer being analyzed a secondary calibration assumption is required, and this is a potential source of systematic error in data—even when the MHS constants for the copolymers are directly measured.

Given these problems, other alternatives were explored. These include (1) the use of a "corrected"

calibration procedure accounting for the heterodiad interaction as suggested by Goldwasser and Rudin;[29] the preparation of calibration curves for all unknown polymers (2) by synthesizing narrow standards or (3) via fractionation of a broad standard; and (4) the use of an alternative technique for the measurement of molecular weight, namely matrix-assisted-laser-desorption-ionization mass spectrometry (MALDI). Unfortunately, all of these alternatives have problems. In order to implement option 1, additional parameters (such as the copolymer sequence distribution and the interaction parameter for the heterodiads) are required, and the measurements of these are subject to significant error. At present, option 2 is unsuitable for copolymers because narrow standards currently have to be synthesized using anionic polymerization—a mechanism that is not suitable for the preparation of random copolymers. However, developments in atom transfer polymerization may hold some promise in this respect. Option 3 is tedious to implement but does offer an alternative to on-line direct molecular weight analysis (although some form of direct molecular weight analysis is still necessary to characterize the fractions). Finally, option 4 is not at present a viable option for copolymers because the problem of selecting of an appropriate matrix for copolymers is yet to be addressed. Hence, at present, it appears that the preparation of individual calibration curves for different copolymer compositions via the fractionation of broad copolymer samples is the only viable alternative to on-line direct molecular weight analysis. However, given the need to characterize these fractions using a molecular weight sensitive technique, it seems unlikely that this approach would offer significant improvements to the accuracy of copolymer molecular weight analysis.

Further Problems in the Application of PLP to Copolymers. The IUPAC papers[9,20,24] have dealt extensively with errors in homopolymer PLP analyses. However, in the analysis of copolymers, further problems arise. Now, although the main source of error in a PLP experiment is the molecular weight analysis, the measured $\bar{k}_p$ values also depend upon the laser flashing rate, the molecular weight per repeat unit and the monomer concentration. Hence the uncertainties in these quantities will also affect the accuracy of the measured $\bar{k}_p$ values. Provided the pulsing of the laser is controlled by a pulse generator, the error in the laser flashing rate is usually negligible (±0.0005% for this work). Errors in the monomer concentrations may be significant, although these can be minimized through careful measurements of the monomer densities over the temperature range studied. In the analysis of homopolymers, the molecular weight of the repeat unit will be accurately known. However, this quantity is potentially an important source of error in the analysis of copolymers since the quantity is an average that will depend upon the copolymer composition. Since measurements of copolymer composition (or, alternatively, estimates of reactivity ratios) are often subject to a considerable error, the resulting uncertainty in the molecular weight per repeat unit is another source of error in measured $\bar{k}_p$ values. For the copolymerization system studied in this work, this error was not significant, because the molecular weights of the two different repeat units were very similar (100.114 for MMA compared to 104.144 for STY). However, this is not always the case, and hence we recommend that attention be given to this possible source of error in future PLP studies of copolymerizations.

Influence of the Dark Time on the Precision of PLP Studies. Although the error in the laser flashing rate is itself negligible, the magnitude of the flashing rate will exert a considerable influence on the error in the final $\bar{k}_p$ data. The reason for this is quite simple. As noted earlier, the calculation of $\bar{k}_p$ from the inflection point molecular weight (ΔM_{IP}) is performed using the following formula:

$$\bar{k}_p = \frac{M_{IP}}{[M]t_f \mathrm{MWT}}$$

Assuming that the predominant source of error is the molecular weight analysis, the error in $\bar{k}_p$ ($\Delta\bar{k}_p$) may be expressed as the following function of the error in the inflection point molecular weight (ΔM_{IP}):

$$\Delta\bar{k}_p = \frac{\Delta M_{IP}}{[\mathrm{M}]t_f \mathrm{MWT}}$$

Hence we see that the error in $\bar{k}_p$ is the error in the molecular weight, as scaled by the dark time (t_f), monomer concentration [M], and repeat unit molecular weight (MWT). It might further be argued that the error in $\bar{k}_p$ is in fact inversely proportional to the product of [M], t_f, and MWT, since, within reasonable limits (such as those imposed by the SEC columns and calibration curves), the molecular weight analysis may be considered to be subject to a constant absolute error. This is because the random error in the molecular weight analysis is dependent not upon the time at which the peak elutes but upon quantities such as the amount of polymer injected, detector sensitivities, and baseline noise—all of which might reasonably be expected to be consistent for all the samples analyzed in a given study. Finally, for this work, the monomer concentration (in the range 8.5−9.5 g/mL) and repeat unit molecular weight (100.114−104.144) were reasonably constant for all samples. Hence, for the data in this work, the error in $\bar{k}_p$ might be approximated by the following formula:

$$\Delta\bar{k}_p = \frac{\Delta \mathrm{M}_{IP}}{[\mathrm{M}]t_f \mathrm{MWT}} \approx \frac{\text{constant}}{[\mathrm{M}]t_f \mathrm{MWT}} \approx \frac{\text{constant}}{t_f}$$

This result has two important implications. Firstly, it provides a strategy by which errors in $\bar{k}_p$ may be minimized. Provided the PLP characteristics of the polymers produced are not compromised, the errors in PLP may be reduced through the choice of slow flashing rates. Secondly, it provides a strategy for weighting residuals when fitting kinetic models to PLP-determined $\bar{k}_p$ data. That is, it may be assumed that the error in $\bar{k}_p$ roughly scales inversely with the product of the dark time, monomer concentration, and the repeat unit molecular weight and, if the latter two quantities may be considered to be roughly constant, it will scale inversely with the length of the dark time.

Conclusions

In this work, PLP was used in conjunction with absolute methods of molecular weight analysis (that is, SEC with on-line LALLS and DV) in order to obtain the most accurate measurements of $\bar{k}_p$ for STY−MMA copolymerizations to date. The purpose of this study was to obtain accurate kinetic data for this system in order to discriminate between the alternative models

for copolymerization kinetics. The results of this kinetic analysis will be presented in a second paper. However, examination of the kinetic data alone has highlighted some of the sources of error in the PLP technique, and based on this work some recommendations for improving the accuracy of PLP data may be made. Firstly, we recommend that direct molecular weight analysis techniques be used for the analysis of copolymers (and indeed any polymers for which narrow molecular weight standards are not available), at least in the first instance, to justify the calibration assumptions needed for conventional SEC. Furthermore, when direct molecular weight analysis is not used, the uncertainty in SEC calibration curves should be taken into account (via sensitivity analysis) when estimating the error in the measured $\bar{k}_p$ data. Secondly, we recommend that careful consideration be given to estimation of the average molecular weight per repeat unit of the polymers, as this can also affect the accuracy of the measured $\bar{k}_p$ values. Finally, we recommend the use of slow laser flashing rates, since the error in the measured $\bar{k}_p$ values is roughly proportional to the flashing rate and can thus be exaggerated by fast laser repetition rates.

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