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Propagation Kinetics of Para-Substituted Styrenes: A Test of the Applicability of the Hammett Relationship to Free-Radical Polymerization

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ABSTRACT: In this work, pulsed laser polymerization measurements of the homopropagation rate coefficients (k_p) for a series of para-substituted styrene monomers (4-X-styrene: X = OCH_3, CH_3, F, Cl, Br) at 20, 30, and 40 °C are reported. On the basis of nonlinear least-squares fits of the Arrhenius model to these data, the following point estimates for the activation energy (kJ mol^{-1}) and frequency factor (× 10^7 L mol^{-1} s^{-1}) for each of the above five monomers were obtained: 34.9 and 6.35, 32.4 and 2.84, 32.0 and 3.50, 32.1 and 4.48, 33.9 and 9.57, respectively. The k_p data were also used to test the applicability of the Hammett relationship. It was found that neither the Hammett relationship nor the extended Hammett relationship could quantitatively describe the substituent effects on the rate coefficients, though both could provide a reasonable qualitative description of the trends in the data.

Introduction

Understanding substituent effects on the reactivity of the propagation step in free-radical polymerization is important in designing schemes for predicting reactivity ratios (and therefore copolymer composition and microstructure) in free-radical copolymerization. The Hammett relationship,[1] of widespread importance in organic chemistry,[2] is an empirical scheme for predicting the reactivity of a benzene derivative in a given reaction from the group contribution of its substituents. In the Hammett scheme, the rate or equilibrium constant for the reaction of a substituted benzene derivative (k_X) is related to that for the corresponding unsubstituted benzene derivative (k_H) by the following equation:

$$\log(k_X/k_H) = \rho\sigma_{px} \tag{1}$$

In this expression, the Hammett constant (σ_{px}) is characteristic of the substituent (X), while the reaction constant ρ is characteristic of the reaction. The subscript p in the Hammett constant refers to the fact that the substituent is in the para position; there are also σ_{mx} values for meta substitution. The reference reaction for which the substituent constants are measured is the acid dissociation equilibrium of benzoic acid and its para- or meta-substituted derivatives, for which the reaction constant ρ is set to unity in eq 1. Although this relationship is empirical, it is generally held[3] that the Hammett constant for a substituent is a measure of the relative effect of that substituent on the electron density at the reaction site, while the reaction constant is a measure of both the effectiveness with which the side chain can transmit the electrical effect of the substituent to the reaction site and the relative susceptibility of the reaction to changes in the electron density at the site. It has been established[3] that the Hammett equation is likely to describe the para- and meta-substituent effects in a particular reaction series provided that (1) within the reaction series the substituent effect on entropy either is constant or varies linearly with its enthalpic effect, (2) within the reaction series there is no change in the reaction mechanism, and (3) the reaction site is “insulated” from the benzene ring (by, for instance, one or more methylene groups) so that direct mesomeric interactions between the reaction site and the substituent are not possible.

When assumption 3 is violated, additional terms must be introduced into the Hammett equation in order to account for the additional effect on electron density at the reaction site by those substituents for which direct mesomeric interaction with the reaction site is possible.[3a] One such extended Hammett relationship is that of Yamomoto et al.,[4] which is as follows:

$$\log(k_X/k_H) = \rho\sigma_{px} + \gamma E_{Rx} \tag{2}$$

In this expression, γ is an additional reaction constant representing the susceptibility of the side chain to undergo resonance interactions with the substituents, E_{Rx} is an additional substituent constant representing the ability of the substituent to undergo resonance interactions with the side chain, and ρ and σ_{px} are as defined for the simple Hammett equation. The reference reaction for which the resonance substituent constants (i.e., E_{Rx} values) are measured is the hydrogen abstraction of nuclear substituted cumenes, for which it is assumed that $\rho = 0.7$ and $\gamma = 1$.

Given the above understanding of the physical basis of the Hammett (and extended Hammett) relationships, it is possible to use these structure−reactivity equations in mechanistic studies. By examining the applicability of the Hammett equation to a particular reaction series, the validity of its implicit assumptions (i.e., (1)−(3) above) for that particular reaction series can be tested. Furthermore, when either of these Hammett equations is applicable, the magnitude of the reaction constant ρ provides information on the relative sensitivity of a reaction to changes in the electron density at the reaction site, while the sign of ρ indicates whether a reaction is favored by electron-withdrawing or by electron-donating substituents. Finally, in reactions where direct resonance interactions between the substituents and reaction site are possible (and thus assumption 3

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is invalid), examining whether the simple Hammett relationship can nevertheless be applied provides information on the importance of resonance effects in the reaction. Thus, it can be seen that the Hammett relationship may provide a useful tool for studying the relationship between structure and reactivity in free-radical polymerization.

A number of previous studies have examined the applicability of the Hammett relationship for describing the effect of para or meta substituents on propagation and transfer steps in free-radical polymerization. These studies found that such substituent effects on the reactivity of substituted styrenes (propagation)[5−7] or cumenes (transfer)[8] with a given macroradical could be described by the extended, but not the simple, Hammett relationship. In contrast, it was found that the effect of para or meta substituents on the reactivity of substituted styryl macroradicals (propagation or transfer) with a given substrate[6,8] could be described by the simple Hammett equation. However, the above studies may be subject to considerable uncertainty since the relative reactivities were not measured directly, but instead extracted from monomer reactivity ratios or transfer constants—parameters that are not only subject to considerable experimental error, but the measurement of which is dependent upon model-based assumptions. Furthermore, in the studies of radical reactivity, values of the homopropagation rate coefficients (k_p) were required, and the above studies both employed the same set of k_p values,[9] which were measured using the now superseded[10] technique of rotating sector. More recent work,[11] in which the relative rates of addition of a series of para-substituted benzyl radicals to various given alkenes were measured directly, found that the radical reactivities could not be described by the simple Hammett relationship.

The failure of the Hammett relationship to describe the relative reactivities of para-substituted monomers in reactions with a given radical, and the likely failure of the Hammett relationship to describe the relative reactivities of para-substituted radicals in reactions with a given monomer, is not surprising given that, in all of the systems studied, the benzene ring is directly attached to (or conjugated with) the reaction center. Thus, for these reactions, assumption 3 is not valid, and it would thus be predicted that the extended, rather than the simple, Hammett equation would provide the best description of the data. Given this, it is perhaps surprising that studies have found that the simple Hammett equation can describe the effect of para or meta substituents on the k_p values[9] or, more recently, “apparent k_p” values[12] (in atom transfer polymerization) of substituted styrene monomers. Its ability to describe these data, despite the invalidity of assumption 3, would seem to indicate that direct mesomeric interactions between the substituent and the reaction center, though important in the cross-propagations of free-radical polymerization, are not important in the homopropagation reactions. A possible explanation for this may be that the mesomeric interactions between the substituent and reaction center are important only in the charge-transfer configurations[13,14] of the transition structure, which would in turn be predicted to be more important in the cross-propagations (when the radical and monomer bear different substituents and thus have more widely differing electronegativities) than in the homopropagations.

Nevertheless, it is still difficult to explain the apparent ability of the simple Hammett relationship to describe k_p values. For, when comparing these values, the simultaneous effect of substituents on both the radical and the monomer are studied. In the studies of the individual effects of either the monomer or radical substituents, values obtained for the reaction coefficient ρ were strongly dependent on the nature of the fixed species. For instance, Yamamoto et al.[8] found that values of ρ varied from 1.0 to 0.2 (depending on the radical substituent) for extended Hammett descriptions of substituent effects on para-substituted cumenes in transfer reactions with given para-substituted styryl radicals, while values of ρ varied from 0.68 to -0.65 (depending on the cumene substituent) for simple Hammett descriptions of substituent effects on para-substituted styryl radicals in transfer reactions with a given para-substituted cumene. Now, if the reaction constant is strongly dependent on the nature of the fixed species, in studies where both substituents are simultaneously altered, the reaction constant would not be expected to be constant. This inconstancy of the reaction “constant” would render invalid the simple/extended Hammett relationships unless the relative reaction constants are themselves linearly correlated with the Hammett parameters of the para substituents. While the reaction constants reported by Yamamoto et al.[8] are approximately correlated with the Hammett constant of the para substituent attached to the fixed species, there is nevertheless significant deviation from a linear correlation for a number of the substituents studied. Thus, the ability of the simple Hammett relationship to describe k_p values is surprising and again indicates that there may be additional interactions in the cross-propagation reactions that are not present in the homopropagations.

Given the above discussion, it appears that the ability of the simple Hammett relationship to describe the k_p values of para-substituted styrene monomers indicates that additional resonance interactions (perhaps present in the charge-transfer configurations of the transition structure) affect the cross-propagation but not the homopropagation reactions of free-radical polymerization. However, it is necessary to confirm the above results. To date, it has not been possible to test formally the goodness-of-fit or lack-of-fit of the Hammett relationship to any of the data as no results for replicate samples have been reported in any of the above studies. Furthermore, as noted above, the previous measurements[9] of the k_p values for the para-substituted styrene monomers were performed using the now superseded[10] technique of rotating sector. To illustrate the possible degree of uncertainty in this earlier data set (that of Imoto et al.[9]), the k_p for styrene (STY) and 4-Cl-styrene (PCS) can be compared with those measured in more recent rotating sector studies by Fukuda et al.[15,16] In the work of Imoto et al.,[9] the k_p of PCS at 30 °C (150 L mol^{-1} s^{-1}) was found to be 40% higher than the corresponding k_p of STY (106 L mol^{-1} s^{-1}). In the work of Fukuda et al.,[15,16] the k_p of PCS and STY at 40 °C were found to be identical (120 L mol^{-1} s^{-1}), a trend that is inconsistent not only with the earlier work of Imoto et al.[9] but also with the predictions of the Hammett scheme. This inconsistency demonstrates the need for a further study of these monomers, which we have undertaken herein.

We have thus remeasured the k_p values of the para-substituted styrene compounds (4-X-styrene: X = OCH_3,

CH_3, F, Cl, Br) using the IUPAC recommended[17] technique of pulsed laser polymerization (PLP).[18] To allow formal statistical testing of the goodness-of-fit or lack-of-fit of the Hammett relationship, several replicate measurements of the k_p values have been included. To further improve the accuracy of this study, we have utilized a set of critically evaluated Hammett constants, recently published by an IUPAC working party.[19] In addition, we have examined the effect of temperature on the k_p values of the para-substituted styrenes, with a view to determining the relative importance of entropic and enthalpic substituent effects in these reactions. In what follows, we present the results of this study and discuss their possible physical meaning.

Experimental Section

Experimental Design. Pulsed laser polymerization (PLP) experiments[18] were conducted so as to measure the k_p values for styrene (STY) and five para-substituted monomers: *p*-methoxystyrene (PMOS), *p*-methylstyrene (PMeS), *p*-fluorostyrene (PFS), *p*-chlorostyrene (PCS), and *p*-bromostyrene (PBrS). For each monomer, the k_p was measured at three temperatures: 20, 30, and 40 °C. At least five separate samples were included per monomer, per temperature. Within these replicate determinations, experimental conditions such as the laser pulsing rate, laser power, and initiator concentration were varied, as per IUPAC recommendations.[20] A full listing of these polymerization conditions, together with the k_p values obtained, is provided in Tables S1−6 of the Supporting Information.

All of the para-substituted styrene monomers (including styrene itself) have a small but finite extinction coefficient at the wavelength of the laser beam (355 nm). While, for most of the monomers studied, this absorbance was not a problem, for PMOS and PBrS the absorbance was strong enough to interfere with the PLP experiment. In an attempt to rectify this problem, some preliminary experiments were conducted on PMOS and PBrS using a visible-light photoinitiation system successfully applied to PLP by this group.[21] While, in this previous work, this visible-light initiation system was successful for measuring the k_p of methyl methacrylate, similar experiments were not successful with either PMOS or PBrS as two of the components in this initiation system did not appear to be soluble in these monomers. Given this problem, the PLP experiments were conducted at 355 nm, as for the other monomers, but an inert solvent was used in order to reduce the absorbance of the PMOS and PBrS monomers. Toluene was selected as the inert solvent as it had previously been used as an inert solvent in a PLP study of the homopolymerization of PMOS;[22] however, the possibility that toluene exerts a solvent effect on the k_p of either of these two monomers cannot be ruled out—especially given that toluene is known to exert a small solvent effect on the homopolymerization of PCS.[23] This problem will be discussed in more detail in a subsequent section.

Materials. Styrene (STY), 4-methylstyrene (PMeS), 4-fluorostyrene (PFS), 4-chlorostyrene (PCS), and 4-bromostyrene (PBrS) (Aldrich) were passed through a column of activated basic alumina, Brockmann 1 (Aldrich), while additional PCS (kindly donated by BASF) and 4-methoxystyrene (PMOS) (Aldrich) were distilled under vacuum. All monomers were refrigerated until required. The photoinitiators, 2,2′-azobis(isobutyronitrile) (AIBN) and benzoin, were recrystallized from ethanol. Toluene (Biolab Scientific) was refluxed over sodium until dry and then distilled. The SEC eluent, HPLC grade tetrahydrofuran (THF) (BDH, Hipersolv), was triply filtered through a 0.02 μm pore size filter and then stored in the dark until required.

Polymerizations. Propagation rate coefficients were measured using the technique of pulsed laser polymerization (PLP). Details of this technique may be found in the original paper of Olaj et al.[18] or in recent reviews.[24,25] Purified monomer, photoinitiator, and toluene (for the PMOS and PBRS samples) were weighed into Pyrex sample tubes (10 mm diameter by 60 mm height), which were then sparged by bubbling with nitrogen for 5 min and sealed with rubber septa. The reaction mixtures were equilibrated at the reaction temperature prior to laser exposure. The polymerizations were initiated by a pulsed Nd:YAG laser (Continuum Surelite I-20) with a harmonic generator (a Surelite SLD-1 and SLT in series), which was used to produce the 355 nm UV laser radiation, and a wavelength separator (Surelite SSP-2), which was used to isolate the 355 nm beam. The laser beam was directed at a constant pulsing rate through the sensitized monomer solution. The laser pulsing rate was controlled internally, as follows. The frequency of the flash lamp discharge, measured at 19.96 ± 0.04 Hz using a photodiode in conjunction with an oscilloscope, was controlled by a software oscillator, and the Q-switch (and thus the laser) was pulsed at various fractions of this rate, as set by a software divider function. During the polymerizations, the sample was held in a thermostated copper cell, the design and calibration of which have been described previously.[26] Polymerization activity was terminated by removing the sample from the laser and precipitating the polymer into methanol. Conversion was restricted to 2%, so as to satisfy the assumption of constant monomer concentration that is inherent in the PLP technique. The polymer was then isolated, further purified of residual monomer via a redissolution−reprecipitation technique, and then dried to constant mass in vacuo at 40 °C.

Size Exclusion Chromatography 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 3.0 μm bead-size guard column (50 by 7.5 mm) followed by four PL fixed pore size columns (a 10^6, 10^5, 10^4, and 10^3), an in-line filter (0.02 μm), and a Viscotek model 250 detector set. The detector set consisted of a differential viscometer (DV) and differential refractive index detector (DRI) connected in parallel. The data were collected using PL data capture units at a rate of 2 points/s using PL Caliber version 6.0 GPC/SEC software.[27] The eluent was THF at a flow rate 1 mL/min. Polymer analyte solutions were prepared with (accurately known) concentrations in the range 2−3 mg/mL, while sample injection volumes in the range 50−100 μL were used, depending upon the injection loop that was installed at the time. Lower concentrations were used for the narrow standards, depending upon their molecular weights.

SEC Analysis. The molecular weights of all samples were measured against a polystyrene (PSTY) calibration curve. This was compiled using a set of polystyrene (PSTY) (PL 1.25 × 10^3 to 9.80 × 10^5) narrow polydispersity index standards. The calibration and analysis were performed using PL Caliber version 6.0 GPC/SEC software.[27] The k_p values were obtained from the low-molecular-weight-side inflection point of the primary peak in the (linear scale) molecular weight distributions. For polymers other than PSTY, these k_p values were then adjusted to their correct values using the following formula.[28]

$$\log(k_{p,2}) = \left(\frac{1}{1+\alpha_2}\right)\log\left(\frac{K_1}{K_2}\right) + \left(\frac{\alpha_2-\alpha_1}{1+\alpha_2}\right)\log\left(\frac{1}{N}\right) + \left(\frac{1+\alpha_1}{1+\alpha_2}\right)\log(k_{p,1}) \quad (3)$$

In this equation N is given by the expression $N = [M]t_f M_{mon}$ where M_{mon} is the molecular weight of the monomer, t_f is the 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. Values of the MHS constants for STY in THF were taken from Benoit et al.,[29] while those for the para-substituted styrene polymers were measured from the PLP samples using SEC-DV and are reported elsewhere.[30]

Table 1. Density−Temperature Relationships Used in Estimating the Monomer Concentrations for the Polymerization

compound	density	T (°C)	references
styrene	0.9237 − 8.915E−04 × T^{a}	0−150	32
4-Me-styrene	0.9378 − 8.525E−04 × T	0−35	32, 40, 41
4-Cl-styrene	1.1105 − 1.147E−03 × T	20−40	9, 32, 41, 42
4-F-styrene	1.0286 − 4.561E−04 × T	4−30	9, 40, 41, 43
4-MeO-styrene	1.0110 − 7.336E−04 × T	4−30	9, 40, 43
4-Br-styrene	1.4015 − 2.291E−04 × T	4−30	9, 40, 43
toluene	0.8878 − 9.365E−04 × T	10−70	31

[a] Read as 0.9237 − 8.915 × $10^{-4}T$.

Densities. To obtain k_p from the inflection point, molecular weight values for the monomer concentrations were required, and these were obtained using the density−temperature relationships listed in Table 1. As there was insufficient material available for performing accurate density measurements via the density bottle available to us, these density−temperature relationships were obtained by fitting linear models to the available literature data. The relationship for toluene was calculated from densities reported in the DIPPR database.[31] For STY, an extensive data set from Coulter et al.[32] was used, while for the other monomers data from at least three different sources (and representing at least three different temperatures) were used. Although the temperature range covered in this study (20−40 °C) slightly exceeds that covered by some of the density−temperature relationships in Table 1, it was thought that these temperature ranges were close enough to avoid significant error.

Statistical Analysis Procedures. The Arrhenius parameters and their corresponding 95% joint confidence intervals were estimated by fitting the Arrhenius model to the k_p data via nonlinear least-squares analysis,[33] performed using the Contour program.[34] All model-fitting techniques must make assumptions as to the error structure in the data, and in applying a given technique to a particular set of data, that data set must meet the assumptions inherent in the procedure. In nonlinear least-squares analysis, it is assumed that the errors in the independent variable are negligible and that the errors in the dependent variable are independently random and normally distributed about the true model. For a discussion of the applicability of these assumptions to PLP-derived k_p data, the reader is referred to one of our earlier publications.[35] In addition to these basic assumptions, it is necessary to make additional assumptions about the size of the error at each individual data point, and several variants of the nonlinear least-squares technique are possible, depending upon the particular assumptions that are made. In the present work, two different variants of nonlinear least-squares analysis were employed: (1) a commonly used procedure, in which the uncertainties in the MHS parameters are ignored; (2) a procedure in which we attempted to take these uncertainties into account. In what follows, these alternative procedures are described.

First, only the relative sizes of the errors (needed to weight the residuals) at different data points were assumed to be accurately known, and these were measured as the standard deviation of the replicate samples at the individual data points. The magnitude of the error at the different data points was then estimated from the residuals as part of the model-fitting procedure, and the 95% joint confidence intervals for the parameters were thus calculated as the following:[33]

$$\mathrm{SS}(\theta_i) \leq \mathrm{SS}(\theta_0)\left(1 + \frac{p}{n-p}F_{z,p,(n-p)}\right) \tag{4}$$

where SS(θ_i) is the sum-of-squares of residuals for a given parameter set θ_i, θ_0 the set of parameters that minimizes SS(θ_i), p the number of parameters, n the number of data points, and z the level of significance. The so-called 95% joint confidence intervals obtained from this method are a measure of the precision but not necessarily the accuracy of the data. In particular, the uncertainties in the MHS parameters are ignored, and thus any error (arising either from their imprecision or from systematic calibration errors) in these parameters appears as a hidden systematic error in the k_p data.

Second, to take the uncertainty in the MHS parameters into account, a constant relative error of ±10% was assumed to be present in the k_p data, and the 95% joint confidence intervals were thus calculated as the following:[36]

$$\mathrm{SS}(\theta_i) \leq \mathrm{SS}(\theta_0) + \sigma^2\chi_{z,p}^{\;2} \tag{5}$$

where σ^2 is the (known) error variance in the data. A value of ±10% was assumed for the error as this was likely to represent an upper bound to the uncertainty in the k_p data, as arising from both the imprecision in the PLP technique and the uncertainty in the MHS constants of the polymers. This upper-bound error was estimated as follows. Sets of MHS constants for each of the homopolymers were taken from opposite extremes of their previously reported[30] 95% joint confidence intervals. The k_p data for each monomer were then recalculated using their corresponding sets of extreme MHS values. The 95% confidence intervals for the mean k_p of each monomer at each temperature were then calculated for the three different sets of k_p data (i.e., the k_p data calculated from the point estimates and from the two sets of extreme MHS constants). The formula used for calculating the confidence intervals is as follows:[37]

$$\bar{x} \pm \frac{s}{\sqrt{n}}t_{z,(n-1)} \tag{6}$$

where $\bar{x}$ is the sample mean, s the sample standard deviation, n the number of samples, and z the level of significance. Finally, the overall 95% confidence interval for the mean k_p for each monomer at each temperature was estimated as the maximum interval covered by the three overlapping 95% confidence intervals. These confidence intervals are tabulated with the mean k_p in Table 2 (see below). On the basis of these overall confidence intervals, a relative error of ±10% was estimated to represent an upper bound to the uncertainty in the data, as arising from both the imprecision in the PLP procedure and the uncertainty in the molecular weight analysis.

Results and Discussion

Propagation Rate Coefficients. Pulsed laser polymerization experiments were conducted at 20, 30, and 40 °C for styrene and the five para-substituted styrene monomers (4-X-styrene: X = F, Me, Br, Cl, MeO). An Arrhenius plot of the k_p data obtained for each monomer is given in Figure 1. A full listing of these k_p values, together with their corresponding experimental conditions, is provided in Tables S1−6 of the Supporting Information. Also included in Tables S2−6 are the range of k_p values possible for each data point given the previously reported[30] uncertainties in their corresponding MHS constants. The average k_p values obtained for each monomer at each temperature are listed in Table 2, together with two 95% confidence intervals for this mean: one based upon the precision of the k_p data alone and a larger one in which the uncertainty in the MHS constants has been taken into account (see above for details). The Hammett parameters[19] for each para substituent are also included in Table 2.

To compare the k_p values obtained in the present work with those of previous work, Table 3 lists the average k_p values from this work together with their corresponding previously measured values. This previously measured k_p data consists of the 30 °C rotating sector data of Imoto et al.,[9] the 40 °C values for the k_p of STY[15] and PCS[16] from rotating sector studies by Fukuda et

Table 2. Average k_p Values[a] at Each Temperature for the 4-X-Styrenes

		40 °C			30 °C			20 °C		
X	σ_{px}[b]	k_p[c]	CI$_1$[d]	CI$_2$[e]	k_p[c]	CI$_1$[d]	CI$_2$[e]	k_p[c]	CI$_1$[d]	CI$_2$[e]
MeO	−0.29	94	93−95	89−97	60	59−62	55−65	38	37−38	34−40
Me	−0.16	112	111−113	108−116	75	73−78	71−80	48	47−49	46−50
H	0	160	158−161		110	109−112		70	70−70	
F	0.05	159	157−162	154−167	104	101−108	99−111	69	68−70	67−71
Cl	0.22	197	196−199	194−201	133	131−135	131−135	85	83−86	83−86
Br	0.23	212	209−214	201−217	138	135−140	127−144	88	87−89	82−92

[a] The complete sets of propagation rate data and experimental conditions for each monomer at each temperature are provided in the Supporting Information. [b] Taken from ref 19. [c] The average values [L mol^{-1} s^{-1}] of the k_p data obtained using the point estimate MHS constants reported in ref 30. [d] A measure of precision: 95% confidence intervals for k_p [L mol^{-1} s^{-1}] based on the data obtained using the point estimate MHS constants reported in ref 30. [e] A measure of accuracy: maximum intervals spanned by the different 95% confidence intervals for k_p [L mol^{-1} s^{-1}] based on the different data sets obtained using MHS parameters taken from opposite extremes of their upper-bound 95% joint confidence intervals (as reported in ref 30).

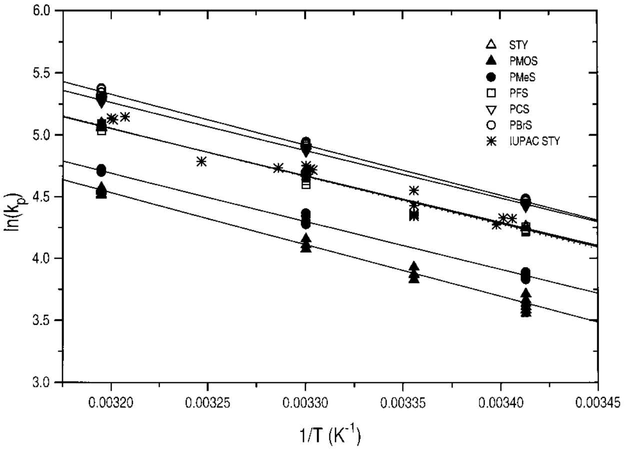

Figure 1. Arrhenius plots of the k_p values for styrene and each of the para-substituted styrene monomers (4-X-styrene; X = F, Cl, Br, Me, and MeO). Also included is the propagation rate data for styrene (over the same temperature range as the present data, 20−40 °C), as used in calculating the IUPAC benchmark Arrhenius parameters for styrene.[20] The solid lines are the corresponding Arrhenius plots based on the best-fit Arrhenius parameters for each monomer, while the dotted line is the Arrhenius plot for the IUPAC benchmark values for STY.

Table 3. Comparison of Average k_p [L mol^{-1} s^{-1}] Values at Each Temperature for the 4-X-Styrenes with Previously Reported Data

	40 °C k_p		30 °C k_p		20 °C k_p	
X	this work	previous	this work	previous	this work	previous
MeO	94	85[22]	60	71,[9] 64[22]	38	47[22]
Me	112		75	84[9]	48	
H	160	120,[15] 160[20]	110	106,[9] 106[20]	70	68[20]
F	159		104	112[9]	69	
Cl	197	120[16]	133	150[9]	85	
Br	212		138	186[9]	88	

al., k_p values for PMOS at each temperature calculated from the Arrhenius parameters of PMOS in toluene (at similar concentrations to the present work) as reported in a PLP study by Piton et al.,[22] and k_p values for STY at each temperature calculated from the IUPAC benchmark[20] Arrhenius parameters. Examining these data, it is clear that there is reasonable agreement between the average STY k_p values of this work and their corresponding IUPAC benchmark values. This is further reinforced when the raw k_p data (over the same temperature range as the present values) used in compiling these IUPAC benchmark values are compared with the raw k_p data from the present work. An Arrhenius plot of the IUPAC k_p data is included in Figure 1, and examining this plot, it is clear that the k_p data for STY from the present work falls well within the scatter of the collected IUPAC data. The close agreement between the present STY values and their corresponding IUPAC benchmark values provides confidence in the accuracy of the present work.

Although the STY data from the present work are in close agreement with the IUPAC benchmark values, there are some discrepancies between the present data and that of the other previous studies. The differences between the present PMOS values and those from a PLP study by Piton et al.[22] may be attributable to an error in the molecular weight analysis of the previous work. For, in this previous work, the SEC analysis was performed using THF as the eluent; however, the MHS constants for PMOS homopolymers in toluene were mistakenly used in the SEC calibration. It is possible that some of the discrepancies between the PMOS and PBrS values of the present work and those of Imoto et al.[9] may be attributable to a solvent effect. This is because the present k_p values for PMOS and PBrS were measured for solutions in toluene while the previous k_p values were determined for bulk solutions. However, there are nevertheless discrepancies between the present work and the previous rotating sector studies of Fukuda et al.[15,16] and Imoto et al.[9] for the monomers that were studied in bulk solutions in both cases. These discrepancies may be attributable to the problems associated with the rotating sector technique,[10] and it is perhaps noteworthy that the discrepancies between the present values and those of Imoto et al.[9] increase with the increasing intrinsic viscosity of the polymer chains (as based on the MHS constants for these homopolymers in THF[30]).

Arrhenius Parameters. Using the above k_p values, the Arrhenius parameters for each of the monomers were calculated. As explained in the Statistical Analysis Procedures section, two different analyses were performed. In the first, a commonly used procedure, the magnitude of the error in the k_p data (and thus the Arrhenius parameters) was estimated from the residuals as part of the model-fitting procedure. The point estimates obtained for the Arrhenius parameters are given in Table 4, and the so-called 95% joint confidence intervals for these parameters, as obtained from eq 4, are shown in Figure 2. As noted above, these joint confidence intervals are a measure of the precision of the k_p data but take no account of possible systematic errors—such as those arising from the uncertainty in the MHS parameters required for the molecular weight analysis. In the second model-fitting method, adopted in order to address this problem, it was assumed that

Table 4. Point Estimates[a] of the Arrhenius Parameters for Each Monomer

monomer	E_{act} [kJ mol^{-1}]	$A \times 10^{-7}$ [L mol^{-1} s^{-1}]
4-MeO-styrene[b]	34.9	6.35
4-Me-styrene	32.4	2.84
styrene	31.5	2.88
4-F-styrene	32.0	3.50
4-Cl-styrene	32.1	4.48
4-Br-styrene	33.9	9.57

[a] These point estimates were obtained from the first model-fitting procedure (in which the residuals were weighted individually by the standard deviation of the error at each data point).[b] In calculating the Arrhenius parameters of PMOS, four measurements of the k_p at 25 °C (reported previously in ref 44) were also included.

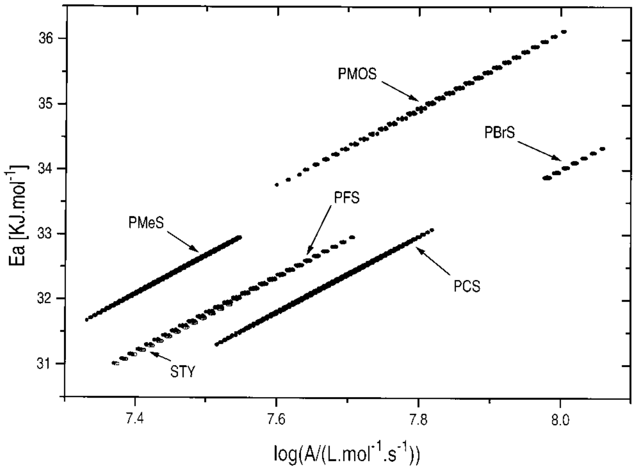

Figure 2. The so-called 95% joint-confidence intervals for the Arrhenius parameters of styrene and each of the para-substituted styrene monomers (4-X-styrene; X = F, Cl, Br, Me, and MeO) that are obtained when the uncertainty in the propagation rate data, as arising from the uncertainty in the MHS parameters of the polymer, is not taken into account (see text).

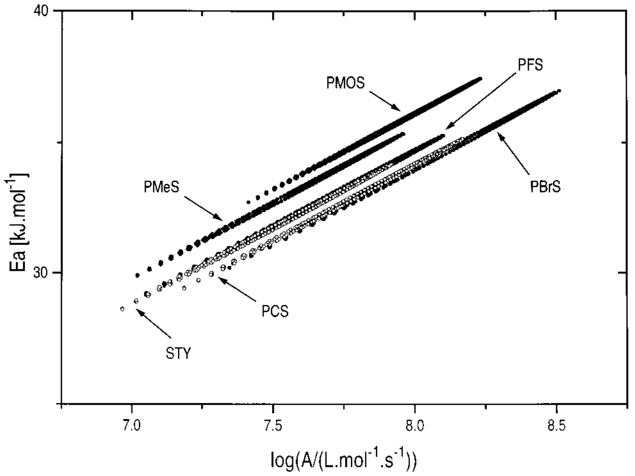

Figure 3. Upper-bound 95% joint-confidence intervals for the Arrhenius parameters of styrene and each of the para-substituted styrene monomers (4-X-styrene; X = F, Cl, Br, Me, and MeO), for which the uncertainty in the MHS parameters has been taken into account (see text).

the k_p data were subject to a (known) constant relative error of ±10%. The resulting 95% joint confidence intervals, obtained via eq 5, are shown in Figure 3. As explained above, a value of ±10% was selected as this was likely to represent an upper bound to the possible error in the data (as is evident in the upper-bound 95% confidence intervals for the average k_p values at each temperature, reported in Table 2), and thus the resulting 95% joint confidence intervals are also likely to represent upper bounds to their uncertainty.

Looking first at the "precision-only" 95% joint confidence intervals in Figure 2, it would seem that (1) the activation energies of PMeS, STY, PFS, and PCS are not significantly different from each other, (2) the activation energies of the PMOS and PBrS monomers are similar and significantly higher than those of the other monomers, and (3) the frequency factors increase in the order PMeS < STY/PFS < PCS < PBrS (with PMOS being difficult to place, given its large uncertainty). These trends are surprising given that it would have been expected that the principal effect of the para substituent should have been on the activation energy of propagation (rather than the frequency factor) of these sterically similar monomers, and on the basis of the Hammett parameters of the substituents, these activation energies should have increased in the order PBrS/PCS < PFS/STY < PMeS < PMOS. Given that the only two monomers with significantly different activation energies were the only two monomers not studied in bulk, these results would seem to indicate that a solvent effect might be responsible for the high activation energies observed in these two systems. Nevertheless, it is difficult to explain the observed trends in the Arrhenius parameters of the other monomers. For instance, although the frequency factors of these sterically similar monomers might be predicted to be weakly dependent on the molar mass of the monomers,[38] the observed trend in the frequency factors is not actually correlated with this quantity.

However, examining the "upper-bound" 95% joint confidence intervals in Figure 3, it is clear that, once the uncertainty in the MHS constants is taken into account, a number of these anomalous trends disappear. In particular, the 95% joint confidence intervals for PCS and PBrS overlap significantly, and thus the anomalously high activation energy of PBrS is not significant once the uncertainty in the molecular weight analysis is taken into account. Indeed, when the uncertainty in the molecular weight analysis is taken into account, the upper-bound 95% joint confidence intervals are large and the individual parameter uncertainties are highly correlated with each other, and it is thus difficult to establish any definite trends in the individual Arrhenius parameters. Nevertheless, it is clear that the upper-bound 95% joint confidence intervals fall into four distinct groups (PMOS, PMeS, STY/PFS, and PBrS/PCS) which, having once assumed the same value for one of the Arrhenius parameters, predict significantly different values for the other Arrhenius parameter. For instance, if we assume that all of these sterically similar monomers have the same frequency factor, these upper-bound 95% confidence intervals predict that the activation energies for these four monomer groups are significantly different from each other and increase in the order predicted by the Hammett relationship (i.e., PBrS/PCS < PFS/STY < PMeS < PMOS). However, it is also possible (within a 95% level of confidence) to assume that these monomers have the same activation energy and thus have frequency factors that decrease in the order PBrS/PCS > PFS/STY > PMeS > PMOS. Thus, while it is clear that the k_p values of these para-substituted styrene monomers are significantly affected by the nature of the para substituent, it is impossible, on the basis of these data, to determine with confidence whether this is attributable to an enthalpic and/or an entropic effect.

The failure of the present work to discriminate between substituent effects on the activation energy and frequency factor of the propagation reaction can in part be attributed to the narrow temperature range over which these effects were studied. However, given that the Arrhenius model is not strictly valid over wide temperature ranges,[3] the extent to which this situation could be improved is likely to be somewhat limited. Furthermore, on comparing Figures 2 and 3, it is clear that a significant component of the uncertainty in the Arrhenius parameters arises in the uncertainties in the MHS parameters, rather than in the limited temperature range. Thus, it would seem that, as was previously observed for the methacrylate series,[39] the uncertainty in the molecular weight analysis of PLP samples remains a considerable barrier to identifying small differences in the individual parameters for various monomers. However, as was previously noted for the methacrylate series,[39] it is possible to identify a number of significantly different clusters, each consisting of monomers that display similar behavior to one another. In the present work, these clusters consisted of (1) PBrS/PCS, (2) PFS/STY, (3) PMeS, and (4) PMOS. Given that the main difference between the monomers in these different clusters lies in the electronic (rather than the steric) properties of their substituents, it is likely that electronic substituent effects are dominant in this series.

Testing of the Hammett Relationship. To test the Hammett relationship, the quantity $\log(k_X/k_H)$ was calculated for each of the individual k_p values of the para-substituted styrenes, using the corresponding IUPAC benchmark value[20] for k_p of STY at the same temperature as the reference. The results were then plotted as a function of their Hammett parameters[19] (see Figure 4). Also included in Figure 4 is the corresponding rotating sector data of Imoto et al.[9] and some recent "apparent k_p" data from atom-transfer polymerization.[12] Under the Hammett relationship, this plot in Figure 4 should be linear and pass through the origin. Looking at the plotted data in Figure 4, it is clear that this is not the case for our data. While there is a rough qualitative ordering of the k_p values according to their Hammett parameters, the relationship is not predictive. This lack-of-fit of the Hammett relationship was confirmed via a formal lack-of-fit test. The Hammett relationship was first fitted to the collected 40 °C data via unweighted nonlinear regression. The resulting best-fit reaction constant ρ was 0.66, and the Hammett plot based on this reaction constant is included in Figure 4, where it can be seen that this best-fit plot does not pass through any of the 40 °C data points. Using the best-fit model predictions, a formal lack-of-fit test was then performed for the collected 40 °C data, and an F test statistic (having 4 and 35 as its first and second degrees of freedom, respectively) of 304 was obtained. This value is clearly significant even at the 1% level (for $F_{4,35,1\%}$ is 3.93), and the lack-of-fit of the simple Hammett relationship is thus statistically significant.

Since the simple Hammett relationship could not adequately describe the data, the extended Hammett relationship was fitted to the 40 °C data via unweighted nonlinear regression. Values of E_R for the substituents were taken from the original paper of Yamamoto et al.[4] Since no value for the fluorine substituent was reported in this paper, the PFS data were excluded from the analysis. The best-fit parameters obtained were 0.68 for ρ and -0.42 for γ, and the predictions of the extended Hammett relationship based on these parameters are included in Figure 4. It should be noted that, although these predictions have been plotted as a line graph (for the sake of clarity), this line does not necessarily represent the model predictions at the intervening values of σ_{px} since the E_{Rx} values at these intervening points are not known. Looking at Figure 4, it is clear that the extended Hammett relationship provides a better fit to the data; however, the improved fit to the data is not surprising given that the model has an additional adjustable parameter. Furthermore, upon closer inspection of Figure 4, it can be seen that the predictions of the extended Hammett model do not pass through any of the 40 °C data for PMeS. Since these data represented about a quarter of the data to which the model was fitted, it would seem that the fit of the extended Hammett equation is not adequate. This was confirmed via a formal lack-of-fit test, for which an F test statistic (having 2 and 30 as its first and second degrees of freedom, respectively) of 120 was obtained. This value is clearly significant even at the 1% level (for $F_{2,30,1\%}$ is 5.39), and thus, although providing a slightly better fit to the data, the lack-of-fit of the extended Hammett relationship is nevertheless statistically significant.

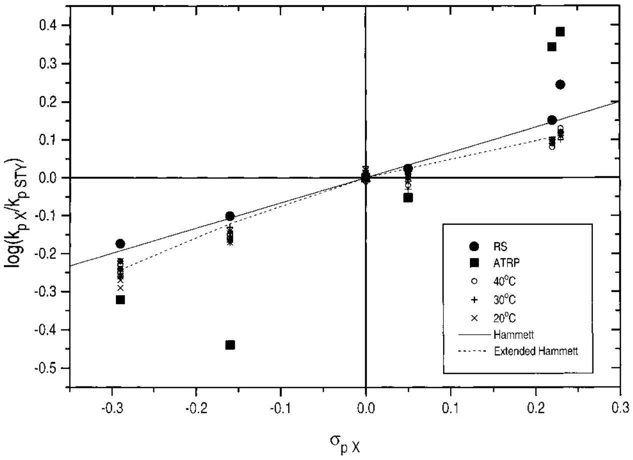

Figure 4. Hammett plots of the k_p values for styrene and each of the para-substituted styrene monomers (4-X-styrene; X = F, Cl, Br, Me, and MeO). The data at each temperature are plotted separately. Also included is the corresponding rotating sector (RS) data of Imoto et al.[9] and some recent "apparent k_p" data from atom-transfer polymerization (ATRP).[12] The solid line is the best-fit "predictions" of the simple Hammett equation to the 40 °C data, while the dashed line is the corresponding best-fit "predictions" of the extended Hammett equation. It should be noted that, although these predictions have been plotted as a line graphs, in the case of the extended Hammett equation this line does not necessarily represent the model predictions at the intervening values of σ_{px} since the E_{Rx} values at these intervening points are not known.

The present results thus indicate that, contrary to earlier results, neither the simple nor the extended Hammett relationships can describe quantitatively the trends in the k_p values. This result is not surprising and, as noted in the Introduction, can be explained via the inconstancy of the reaction "constant" when substituents on both the radical and monomer are simultaneously varied. However, the present results indicate that the simple Hammett relationship can provide a rough qualitative guide to the trends in the k_p data of the different monomers. From this, it appears likely that, although not strictly valid, the implicit assumptions of the simple Hammett relationship (as outlined in the Introduction) hold *approximately* for the homopropagation reactions and hence (1) the frequency factors for these monomers are approximately independent of the para substituents, (2) the reaction constants for the individual effects of the monomer or radical substituents are approximately correlated with the Hammett parameter of the para substituent attached to the fixed species, and (3) the direct mesomeric interactions between the para substituents and the reaction sites are only of minor importance in the homopropagation reactions.

Conclusions

In summary, contrary to earlier results,[9] the simple Hammett equation cannot quantitatively describe the substituent effects on the k_p values of a series of para-substituted styrene monomers (4-X-styrene: X = OCH_3, CH_3, F, Cl, Br), though it can provide a reasonable qualitative account of the trends in the data. While the extended Hammett relationship should have been more appropriate for this reaction series, given the fact that each para substituent is directly conjugated with the reaction site, the lack-of-fit of this relationship was also statistically significant. It seems likely that the failure of these Hammett equations was owing to the nonsystematic variation of the reaction constant as substituents on both reacting species were simultaneously altered. However, on the basis of the qualitative success of even the simple Hammett equation, it was concluded that these reaction constants were likely to be roughly correlated with the Hammett parameters of the para substituent. The qualitative success of the simple Hammett equation also indicated that deviations arising from possible differences among the frequency factors of these monomers, and from possible direct mesomeric interactions between the para substituents and the reaction site, were relatively minor.

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Supporting Information Available: Tables listing complete sets of propagation rate coefficients, and corresponding experimental conditions, for each monomer studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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