Copolymerization Propagation Kinetics of Para-Substituted Styrenes: A Critical Test of the Implicit Penultimate Model

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ABSTRACT: In this work, composition data and propagation rate coefficients for the copolymerizations of *p*-chlorostyrene with styrene and with *p*-methoxystyrene at 40 °C were obtained. It was found that the terminal model provided an adequate simultaneous description of the copolymer composition and propagation kinetics in the *p*-chlorostyrene with *p*-methoxystyrene system, though not in the *p*-chlorostyrene with styrene system. For both of these systems it could be shown that, even given the uncertainties in the estimated monomer and radical reactivity ratios, it was clear that the monomer (r_1r_2) and radical (s_1s_2) reactivity ratio products were significantly different to each other (i.e. $r_1r_2 \neq s_1s_2$)—a result which is inconsistent with the radical stabilization model. The implications of this result for the implicit and explicit penultimate models are discussed.

Introduction

The terminal model[1−3] is still widely used for describing the composition and microstructure of the copolymers produced by free-radical copolymerization. This is despite the fact that it has been clearly demonstrated that this model is incapable of simultaneously describing the overall propagation rate for the majority of these systems.[4] The terminal model composition, triad/pentad fraction, and propagation rate equations all follow from the same basic assumption—namely that the terminal unit of a polymer radical is the only unit affecting the rate of the propagation step. It would therefore seem that, on the basis of the frequent failure of the terminal model propagation rate equation, this assumption, and thus the terminal model triad/pentad fraction and composition equations that depend on it, is not likely to be valid for the majority of copolymerization systems. To justify the continued use of the terminal model composition and triad/pentad fraction equations in such systems, the implicit penultimate model has been proposed.[5] In this model, it is assumed that both the terminal and penultimate units of a polymer radical affect its reactivity; however, the magnitude of this penultimate unit effect is assumed to be independent of the nature of the reacting monomer. In other words, the penultimate unit is assumed to affect the reactivity but not the selectivity of the polymer radical. From this assumption, it can be shown that while there is a penultimate unit effect in the propagation rate equation, the composition and triad/pentad fraction equations follow the terminal model, and thus the continued use of these equations is justified.

In kinetic terms, this implicit penultimate unit model may be described as follows. The equations for composition (eq 1) and $\langle k_p \rangle$ (eq 2) under a *terminal model*, are as follows:[1−3]

$$\frac{F_1}{F_2} = \frac{f_1}{f_2}\frac{r_1f_1 + f_2}{r_2f_2 + f_1} \tag{1}$$

$$\langle k_p \rangle = \frac{r_1{f_1}^2 + 2f_1f_2 + r_2{f_2}^2}{[r_1f_1/k_{11}] + [r_2f_2/k_{22}]} \tag{2}$$

where f_1 and f_2 are the molar fractions of the monomers in the feed, F_1 and F_2 are the molar fractions of the monomers in the copolymer, and k_{11} and k_{22} are the homopropagation rate coefficients. In these equations, there are four characteristic constants: two homopropagation rate coefficients (k_{ii}) and two reactivity ratios (r_i). The latter are defined as follows:

$$r_i = \frac{k_{ii}}{k_{ij}} \quad \text{(where } i \neq j \text{ and } i, j = 1 \text{ or } 2\text{)} \tag{3}$$

The unrestricted or *explicit penultimate model*[6] (in which it is simply assumed that both the terminal and penultimate units affect the rate of the propagation reaction) may be obtained using the following extensions to the k_{ii} (eq 4) and r_i (eq 5) terms in the terminal model equations:

$$\bar{k}_{ii} = k_{iii}\left(\frac{r_if_i + f_j}{r_if_i + f_j/s_i}\right) \tag{4}$$

$$\bar{r}_i = r_i'\left(\frac{f_ir_i + f_j}{f_ir_i' + f_j}\right) \tag{5}$$

In place of the four characteristic constants of the terminal model, there are eight characteristic constants in the explicit penultimate model: the two homopropagation rate coefficients (k_{iii}), four monomer reactivity ratios (r_i and r_i') and two radical reactivity ratios (s_i). The monomer and radical reactivity ratios are defined as follows:

$$r_i = \frac{k_{iii}}{k_{iij}} \tag{6}$$

$$r_i' = \frac{k_{jii}}{k_{jij}} \tag{7}$$

$$s_i = \frac{k_{jii}}{k_{iii}} \tag{8}$$

Finally, the *implicit penultimate model*[5] is obtained by assuming that the equality $r_i = r_i'$ holds, and thus that

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these penultimate model monomer reactivity ratios are equivalent to their corresponding terminal model ratios. Under this assumption, the penultimate unit effect appears only in the s_i parameters and, since these s_i parameters appear only in the $\langle k_p \rangle$ equation, this implicit penultimate unit effect appears only in the $\langle k_p \rangle$ equation, and not the composition or triad/pentad fraction equations.

From the above equations, it is apparent that, under the implicit penultimate model, the continued use of the terminal model composition and triad/pentad fraction equations in systems where the terminal model propagation rate equation fails can be justified. However, under the explicit penultimate model, the continued use of the terminal model composition and triad/pentad fraction equations in these systems cannot be justified. Thus, to determine whether the terminal model provides a physically meaningful description of the composition and sequence distribution data of common copolymerization systems, it is necessary to establish whether penultimate unit effects are implicit or explicit.

Discrimination between the explicit and implicit penultimate models has not as yet been possible for the majority of copolymerization systems. This is because both of these models contain characteristic constants (i.e. the monomer and radical reactivity ratios) which are not independently measured but are instead treated as adjustable parameters in the model fitting procedure. In consequence of this, both penultimate models can easily be fitted to existing data. Furthermore, unlike the terminal model, the propagation rate equations of the penultimate models contain additional adjustable parameters (i.e. the radical reactivity ratios) that do not appear in the composition or triad/pentad fraction equations. It is therefore not possible to predict the propagation rate data for these penultimate models using parameters measured independently from composition data and homopropagation rate data. Thus, unlike the terminal model, these alternative penultimate models cannot be critically tested by comparing corresponding predicted and measured values of the propagation rate coefficients.

In principle, a critical test of the implicit and explicit penultimate models could be made using simultaneous measures of composition and triad/pentad data. This is because the same set of adjustable parameters appear in the both the composition and triad/pentad equations of each model and thus, in principle, one data set could be predicted from parameters measured using the other data set. In practice, however, such critical testing of these models is not usually possible since additional information—namely, the peak assignments and coisotacticity factor— is required in order to convert the peak fractions from the measured NMR spectra into the triad/pentad fractions predicted by the copolymerization models. In the majority of systems considered thus far, the coisotacticity factor cannot be independently measured and must instead be estimated by fitting the measured data to the predictions of a particular model (usually the terminal model), thereby invalidating any model discrimination based upon this fitted data. For instance, recent studies[7,8] have noted that the sequence distribution for copolymers of styrene with methyl methacrylate can be adequately predicted by the terminal model using reactivity ratios measured from composition data. This would appear to provide strong evidence for the validity of the terminal model composition and triad/pentad fraction equations for this system. However, in these studies, the “measured” triad/pentad fraction data was calculated from the measured peak fractions of the NMR spectra using the coisotacticity parameter ($\sigma = 0.44$) that was reported by Aerdts et al.[9] In this original work, Aerdts et al.[9] measured the coisotacticity parameter by fitting (via a nonlinear least squares technique) the “measured” triad/pentad fractions (i.e., those converted from the peak fractions via the peak assignments and the σ value) to the predictions of the terminal model (as made using the reactivity ratios estimated from the composition data). Hence, the sequence distribution data that was measured in the subsequent studies[7,8] using this coisotacticity parameter was implicitly fitted to the terminal model via this coisotacticity parameter, and was thus not suitable for critically testing the terminal model. However, it is perhaps significant that, in one of the few cases where triad fraction data could be obtained independently of a fitted coisotacticity factor (and thus critical testing of the alternative models was possible), it was found that the explicit penultimate model provided the best simultaneous description of the composition and microstructure of styrene−acrylonitrile copolymers.[10]

A more promising strategy for discriminating between the implicit and explicit penultimate models is to examine which (if either) of these two models provides an accurate account of the chemistry of the propagation reaction. To date, three different possible origins for the penultimate unit effect have been suggested.

(1) Radical stabilization model:[11] The penultimate unit affects the stability of the propagating radical which, provided the Evans−Polanyi rule[12,13] holds, results in an implicit penultimate unit effect in the barrier.

(2) Polar model:[14,15] The penultimate unit stabilizes the charge-transfer configuration of the transition state, resulting in an explicit penultimate unit effect in the barrier.

(3) Entropic model:[16] The penultimate unit exerts a steric effect on the frequency factor of the propagation reaction, which can result in either an implicit or explicit penultimate unit effect in the frequency factor, depending upon the degree of steric difference between the comonomers.

Thus, it can be seen that establishing the relative importance of these different possible causes of penultimate unit effects can enable us to determine whether an implicit or explicit penultimate model should be applied to a given copolymerization system.

To discriminate between models 1−3, it is necessary to measure the monomer and radical reactivity ratios in various types of copolymerization systems. Some direct experimental[14,17,18] and theoretical[15,19] measures of these reactivity ratios in small radical addition reactions have supported the polar model (2). However, to date, these studies have only involved a limited range of monomers (including highly polar monomers such as acrylonitrile and acrolein), and no such studies have been performed for common copolymerizations such as those involving styrene with acrylate or methacrylate monomers. Indeed the size of these monomers renders high level theoretical studies of these monomers, at least at present, computationally prohibitive. Unfortunately, experimental studies of copolymerization systems, which measure these reactivity ratios indirectly, have not been successful in obtaining accurate and precise values of reactivity ratios. This was highlighted in a recent pulsed laser polymerization study of a typical copolymerization: styrene with methyl methacrylate.[20,21] Despite obtaining the most extensive set of $\langle k_p \rangle$ data for any copolymerization to date, the uncertainty in the radical reactivity ratios was still too large to attach any physical significance to their point estimates. Nevertheless, it did appear that there was a temperature effect on the radical reactivity ratios—an effect that was consistent with either of the enthalpic models, 1 and 2 but not the entropic model, 3— but, within a 95% confidence limit, it was impossible to determine the extent of this temperature dependence.

It is clear from this previous work that for sensitive model discrimination it is necessary to study copolymerizations in which merely establishing the presence or absence of penultimate unit effects is sufficient for model discrimination. One such type of copolymerization system is that involving sterically similar but electronically different para-substituted styrene monomers. Under the radical stabilization model (model 1), many of these monomer pairs would be expected to display penultimate unit effects. This is because a prediction of this model is that, provided that there are no penultimate unit effects in the frequency factors, the product of the radical reactivity ratios equals that of the monomer reactivity ratios (i.e. $r_1r_2 = s_1s_2$), and, for many of these monomer pairs, the product of the monomer reactivity ratios is not equal to unity ($r_1r_2 \neq 1$). Thus, under the radical stabilization model, the product of the radical reactivity ratios would not be expected to equal unity for such monomer pairs ($s_1s_2 \neq 1$, and thus s_1 and/or $s_2 \neq 1$). Since a penultimate unit effect results if either of the s_i values are not equal to unity, the radical stabilization model would thus predict a penultimate unit effect in such systems. Hence, provided the monomer reactivity ratio product is not equal to unity, testing for penultimate unit effects in copolymerizations of certain pairs of para-substituted styrene monomers provides a critical test of the radical stabilization model.

To date, the only pulsed-laser polymerization[22] study of a para-substituted styrene copolymerization was of the system *p*-methoxystyrene with styrene (PMOS−STY).[23] No penultimate unit effect was found for this system which, since the monomer reactivity ratio product was equal to unity, was consistent with the radical stabilization model. In this work, we examine two para-substituted styrene copolymerizations for which it was hoped that the monomer reactivity ratio product would not be equal to unity. These two systems are *p*-chlorostyrene with styrene (PCS−STY) and *p*-chlorostyrene with *p*-methoxystyrene (PCS−PMOS). Previous measures of the monomer reactivity ratios for these monomer pairs place the monomer reactivity ratio products in the range 0.29−0.87[24] and at 0.336[25] for PCS−STY and PCS−PMOS, respectively. To confirm that these two copolymerization systems have monomer reactivity ratio products that are not equal to unity, we will first check these using composition data to measure the monomer reactivity ratios. We will then use these monomer reactivity ratios to obtain the terminal model prediction for the propagation rate coefficients. Finally we will test this terminal model prediction by using pulsed laser polymerization[22] to measure the propagation rate coefficients for each copolymerization system, thereby determining if penultimate unit effects are present and thus providing a critical test of the radical stabilization model.

Experimental Section

Experimental Design. For each copolymerization system, samples were prepared at a representative range of monomer feed ratios. The reaction conditions (such as laser flashing rate, laser power, and initiator type and concentration) were varied among replicate samples according to IUPAC recommendations.[26] Pulsed laser polymerization (PLP) experiments for both copolymerization systems were conducted at 40 °C. The conversion was restricted to less than 2% in all cases, so as to validate the use of the (simpler) low conversion kinetic equations. Although all of the monomers had a small but finite extinction coefficient at the wavelength of the laser radiation (355 nm), for the system PCS−STY, this absorption was very low and this system was thus studied in bulk. However, for the system PCS−PMOS, the absorption did present a problem and so, as was done previously for the system PMOS−STY,[23] polymerizations were conducted in an inert solvent so as to reduce the absorption. The solvent selected, toluene, was chosen as it has a dielectric constant similar to that of styrene[27] and had previously been used as an inert solvent in polymerizations involving styrene and para-substituted styrene monomers.[23,28] Nevertheless, to test whether toluene was inert in this system, we measured the homopolymerization propagation rate coefficient of the PCS monomer in toluene and compared this to the bulk value. The results of this test are detailed in a subsequent section. A full listing of monomer feed ratios, solvent concentrations and other reaction conditions are tabulated with the corresponding $\langle k_p \rangle$ data in Tables 3−5. The composition data was obtained using a selection of the PLP samples.

Materials. Styrene (STY) and *p*-chlorostyrene (PCS) (Aldrich) were passed through a column of activated basic alumina, Brockmann 1 (Aldrich), additional PCS (kindly donated by BASF) was distilled under vacuum, and *p*-methoxystyrene (PMOS) (Aldrich) was used as received. All monomers were refrigerated until required. The photoinitiators used, 2,2′-azobisisobutyronitrile (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. Purified monomer, photoinitiator and toluene (for the PCS−PMOS system) were weighed into Pyrex sample tubes (10 mm diameter by 60 mm height), which were then dearated 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 has been described previously.[21] Polymerization activity was terminated by removing the sample from the laser, and precipitating the polymer into methanol. 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, and 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 (10^6, 10^5, 10^4, and 10^3 Å), 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, and the raw data files were processed (converted into ascii data) using PL Caliber version 6.0 GPC/SEC software.[29] The eluent was THF at a flow rate of 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. The calibration of these injection loops has been described previously.[30] Lower concentrations were used for the narrow standards, depending upon their molecular weights.

SEC Analysis. The molecular weights of all samples were measured directly using the technique of differential viscometry (SEC−DV), as described previously.[31] The universal calibration curve for the DRI detector was compiled using sets of polystyrene (PSTY) (PL 1.25×10^3 to 9.80×10^5) and poly(methyl methacrylate) (PMMA) (PL 2.90×10^3 to 6.60×10^5) narrow polydispersity index standards. In constructing the universal calibration curve, Mark−Houwink−Sakurada (MHS) constants for PSTY and PMMA in THF were taken from Benoit et al.[32] and Rudin and Hoegy,[33] respectively. A universal calibration curve for the DV detector was compiled from these standards using the method of Suddaby et al.,[34] and the SEC−DV analysis was performed using our own software,[35] based on this method. Details of this calibration method are provided in a previous publication.[31] Before analyzing the PLP samples of this work, the calibration was fully checked using a number of PSTY broad polydispersity index samples. The peak molecular weights obtained from our SEC−DV calibration for these PSTY polymers agreed closely with those obtained via a conventional SEC analysis of the polymers against their own (i.e. PSTY) primary calibration curve, thereby demonstrating the reliability of the SEC−DV calibration. The results of this calibration test are published elsewhere.[30]

In addition to the SEC−DV analysis, the copolymer samples were also analyzed by conventional SEC. To do this it was assumed that the calibration curve for a copolymer of a given composition was a weighted average of the calibration curves for its respective homopolymers. The calibration curves for homopolymers of PCS and PMOS were constructed using previously reported[30] MHS constants for these polymers in THF. By comparison of the results of this analysis with the SEC−DV data, the validity of this calibration assumption for these two copolymerizations could be tested. The conventional SEC analysis was performed using the PL Caliber software.[29]

Determination of the Propagation Rate Coefficients. The propagation rate coefficients were measured using the technique of pulsed laser polymerization (PLP). Details of this technique may be found in the original paper by Olaj et al.[22] or in recent reviews.[36,37] In the present work, the propagation rate coefficients were obtained from the low-molecular weight-side inflection point of the primary peak in the (linear scale) molecular weight distributions. The repeat-unit molecular weights of the various copolymers were estimated using the reactivity ratios measured from the composition data (see below). The monomer concentrations were estimated using densities for STY, PCS, PMOS, and toluene that were calculated from previously reported density−temperature relationships.[38]

Composition Analysis. The composition of the PCS−STY and PCS−PMOS copolymers was determined via elemental analysis for chlorine. The analyses were performed by the Microanalytical Unit of the Research School Chemistry at the Australian National University. Samples were combusted in "oxygen flasks", and then the ash was titrated with standardized mercuric nitrate so as to determine the chloride concentration. The error in the % Cl results was quoted at ±0.3%.

Table 1. Composition Data for PCS−STY at 40 °C

f_{PCS} (in monomer mixture)	% Cl (in copolymer)	F_{PCS} (in copolymer)
0.080	4.21	0.129
0.091	5.20	0.161
0.173	8.54	0.274
0.192	8.30	0.265
0.198	9.36	0.303
0.206	8.53	0.273
0.214	8.74	0.281
0.231	9.49	0.307
0.250	9.88	0.321
0.337	14.15	0.482
0.345	13.42	0.453
0.373	14.41	0.492
0.403	14.72	0.505
0.483	16.29	0.569
0.488	15.69	0.544
0.494	16.08	0.560
0.506	16.63	0.583
0.508	16.28	0.568
0.519	16.60	0.581
0.519	16.46	0.576
0.589	18.87	0.679
0.667	19.54	0.709
0.674	20.22	0.739
0.779	22.34	0.838
0.804	21.88	0.816
0.886	24.06	0.922
0.894	23.72	0.906
0.894	23.40	0.890

Statistical Analysis Procedures. Reactivity ratios were measured by fitting the terminal model composition equation to the composition data, using the technique of nonlinear least-squares analysis. This procedure was implemented using the *Contour* program.[39] The assumptions inherent in this technique and their applicability to the measurement of monomer and radical reactivity ratios from copolymerization data have been discussed previously.[40] In particular, the importance of weighting the residuals correctly was highlighted. For the present work, it was decided to weight the residuals according to the size of the dependent variable (composition), thereby assuming that the data were subject to a constant relative error. This assumption was based on the quoted ±0.3% error in the % Cl analyses, from which the copolymer composition was calculated. The *Contour* program[39] was also used to fit the implicit penultimate model to the propagation rate data. Since there were insufficient replicates for estimating the size of the error at different data points, the residuals were simply weighted according to the size of the dependent variable—thereby assuming, as in the previous IUPAC benchmark papers,[26,41] that the relative error in the propagation rate data was constant. A simplified version of the implicit penultimate model, in which the constraint of $r_1r_2 = s_1s_2$ was imposed, was also fitted to the data. For this model-fitting we used our own nonlinear regression programs[42] in conjunction with *Matlab* software.

Results and Discussion

Composition Data. Values of the copolymer composition as a function of the comonomer feed ratio for PCS−STY and PCS−PMOS are listed in Tables 1 and 2, respectively. The terminal model fit to these data yielded values for the monomer reactivity ratios of $r_{PCS} = 1.10$ and $r_{STY} = 0.545$ (for PCS−STY), and $r_{PCS} = 1.04$ and $r_{PMOS} = 0.410$ for (PCS−PMOS). The 95% joint confidence intervals for these monomer reactivity ratios are plotted in Figure 1, and the terminal model fits to each set of composition data, together with the measured data points, are plotted in Figure 2. The monomer reactivity ratio products, as calculated from the point estimates of the monomer reactivity ratios for these two systems are $r_{PCS}r_{STY} = 0.60$ and $r_{PCS}r_{PMOS} = 0.43$, and

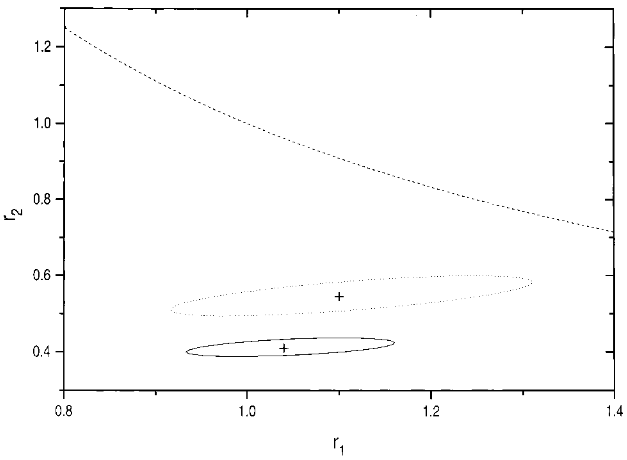

Figure 1. 95% joint confidence intervals for the monomer reactivity ratios of PCS[1]−STY[2] (···) and PCS[1]−PMOS-[2] (—). The point estimates are $r_{PCS} = 1.10$ and $r_{STY} = 0.545$ for PCS−STY and $r_{PCS} = 1.04$ and $r_{PMOS} = 0.410$ for PCS−PMOS. Also plotted is the curve $r_1r_2 = 1$ (- - -).

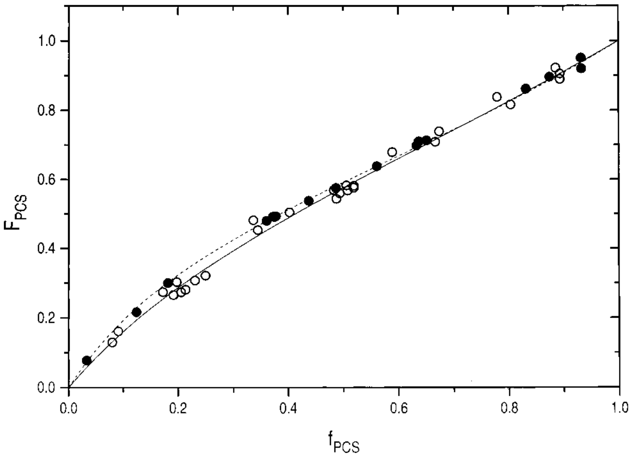

Figure 2. Composition data for PCS−STY (○) and PCS−PMOS (●), together with the corresponding terminal model fits for PCS−STY (—) and PCS−PMOS (- -).

Table 2. Composition Data for PCS−PMOS at 40 °C

f_{PCS} (in monomer mixture)	% Cl (in copolymer)	F_{PCS} (in copolymer)
0.033	1.97	0.077
0.125	5.50	0.216
0.182	7.65	0.300
0.361	12.23	0.480
0.375	12.52	0.491
0.378	12.58	0.493
0.438	13.72	0.538
0.487	14.66	0.575
0.561	16.27	0.638
0.633	17.80	0.698
0.637	18.11	0.710
0.651	18.19	0.713
0.832	21.97	0.862
0.875	22.85	0.896
0.933	23.47	0.920
0.932	24.26	0.951

thus the r_1r_2 product is not equal to unity for either monomer pair. Furthermore, even when the uncertainty (at a 95% level of confidence) in the monomer reactivity ratios is taken into account, this product still cannot equal unity. This is demonstrated in Figure 1, in which the curve $r_1r_2 = 1$ clearly lies outside of the 95% joint confidence intervals for the reactivity ratios of both monomer pairs. Thus, as hoped, the r_1r_2 product does not equal unity for either monomer pair, and these two copolymerization systems are therefore suitable for critically testing the radical stabilization model.

Homopropagation Rate Coefficients for PCS in Toluene. Since the PMOS monomer had a significant extinction coefficient at the wavelength of the laser beam (355 nm), it was necessary to perform the PCS−PMOS copolymerizations in the presence of an added solvent. As explained above, toluene was selected as the solvent as it has a similar dielectric constant to styrene,[27] and has previously been used as an inert solvent for studies of the copolymerization PMOS with STY,[23] and for STY with methyl methacrylate.[28] To determine whether it was likely to be an inert solvent in the PCS−PMOS copolymerization, the homopolymerization rate coefficient of the PCS monomer in toluene (at monomer concentrations in the range 2.4−3.0 mol·L^{-1}) was measured. PLP experiments were conducted at 40 °C, and the resulting samples were analyzed via both SEC−DV and conventional SEC (using the previously reported MHS constants[30] for the PCS homopolymer in THF). The results are summarized in Table 3. On the basis of the conventional SEC results, an average value for the propagation rate coefficient for PCS in toluene at 40 °C of 175 L·mol^{-1} s^{-1} was obtained. This value is about 10% lower than the corresponding bulk value for PCS (197 L·mol^{-1} s^{-1}) which was measured at the same time as these experiments, but is reported elsewhere.[38] Thus, toluene is not an inert solvent for homopolymerization of PCS, and is therefore unlikely to be an inert solvent for the copolymerization of PCS with PMOS. Indeed the possibility that toluene also exerts an effect the homopropagation rate coefficient of PMOS cannot be ruled out—since PLP experiments on this monomer have not as yet been successful for bulk solutions. During the course of this work, some preliminary experiments were conducted on this monomer using a visible-light photoinitiation system successfully applied to PLP by this group.[43] While, in this previous work, this visible-light initiation system was successful for measuring the propagation rate coefficient of methyl methacrylate, similar experiments were not successful with PMOS as two of the components in this initiation system did not appear to be soluble in this monomer. Thus, even when this visible-light initiation system was used, an added solvent was required in order to dissolve the initiator; hence, the bulk copolymerization of PCS−PMOS could not be studied. Given this problem, we decided to proceed with the PCS−PMOS copolymerization in toluene—despite the small solvent effect observed— but endeavored to minimize any kinetic complications arising from this solvent effect by conducting the copolymerizations in a constant excess of toluene across the entire monomer feed range.

Propagation Rate Coefficients for the Copolymerizations of PCS with STY and PMOS. The propagation rate coefficients for the copolymerization of PCS with STY and PMOS at 40 °C were measured using pulsed laser polymerization in conjunction with conventional SEC analysis (using a weighted average approximation for the copolymer calibrations curves, as described above) and, where sufficient polymer was available for preparing solutions of accurately known concentration, also via SEC−DV analysis. These propagation rate coefficients, together with the experimental conditions used to obtain them, are listed in Tables 4 and 5 for the copolymerizations PCS−STY and PCS−

Table 3. Experimental Conditions and Propagation Rate Coefficients[a] for the Homopolymerization of PCS in Toluene at 40 °C

					SEC−DV		conventional SEC		
initiator	[I], mmol/L	[M], mol/L	energy, mJ/pulse	T_f, s	M_{ip}	k_p	M_{ip}[b]	k_p[c]	error[d]
	5.076	2.352	4.0	0.80	45 662	175	40 436	172	170−173
AIBN	6.175	2.952	7.5	0.50	36 945	180	32 849	178	176−180
AIBN	5.154	2.616	7.5	0.60	40 950	188	34 883	178	176−180
AIBN	5.627	2.949	7.5	0.50	35 284	172	31 636	172	170−174
AIBN	4.796	2.835	7.5	0.60	39 767	168	36 762	173	171−175

[a] k_p in L·mol^{-1}·s^{-1}. [b] These molecular weights are the uncorrected molecular weights as obtained using a PSTY calibration curve. [c] These propagation rate coefficients have been corrected to the PCS calibration using the point-estimate PCS MHS constants in ref 30. [d] This error represents the maximum variation possible in k_p when different MHS constants for PCS, taken from within their upper-bound 95% joint confidence interval (as reported in ref 30), are used for the conventional SEC analysis.

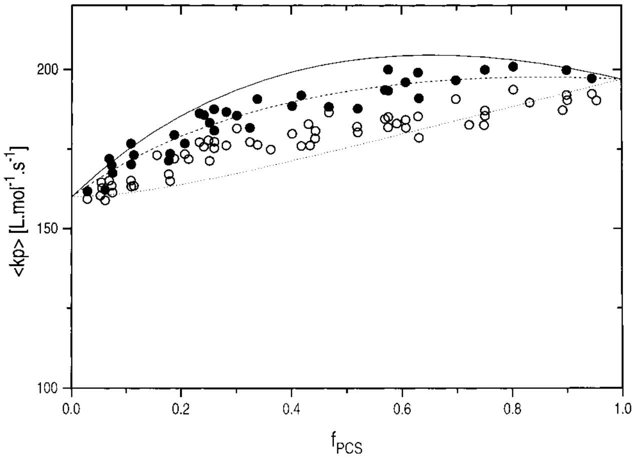

Figure 3. Plot of the propagation rate coefficients for PCS-[1]−STY[2] at 40 °C, together with the terminal model predictions (—) and the implicit penultimate model "predictions" using the best-fit radical reactivity ratios of $s_1 = 0.819$ and $s_2 = 1.07$ (- -) and using the best-fit single parameter $s = 0.820$ such that $s_1 = s$ and $s_2 = r_1r_2/s$ (···). The conventional SEC (○) and SEC−DV (●) data sets are plotted separately.

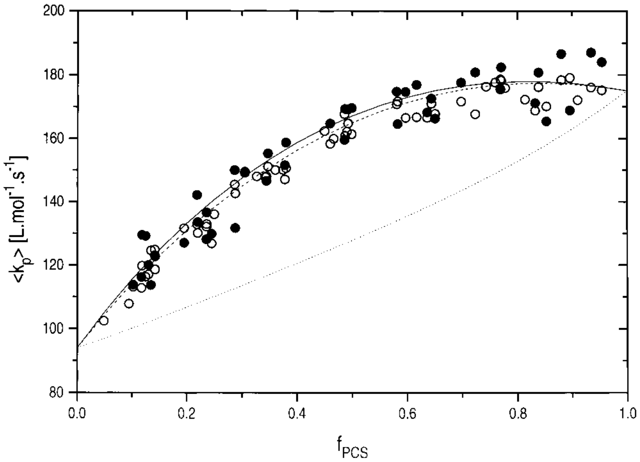

Figure 4. Plot of the propagation rate coefficients for PCS-[1]−PMOS[2] in toluene at 40 °C, together with the terminal model predictions (—) and the implicit penultimate model "predictions" using the best-fit radical reactivity ratios of $s_1 = 1.08$ and $s_2 = 0.899$ (- -) and using the best-fit single parameter $s = 0.609$ such that $s_1 = s$ and $s_2 = r_1r_2/s$ (···). The conventional SEC (○) and SEC−DV (●) data sets are plotted separately.

PMOS, respectively. Also included in Tables 4 and 5, are the corresponding terminal model predictions. These were made using the monomer reactivity ratios and homopropagation rate coefficients summarized in Table 6. The 40 °C homopropagation rate coefficients for bulk PCS and STY and for PMOS in toluene (at concentrations in the range of 2.0−2.8 mol·L^{-1}) are the averages of the homopropagation rate coefficients for these monomers that were measured at the same time as the present work but are reported separately.[38] For the PCS−PMOS system, the average homopropagation rate coefficient for PCS in toluene at 40 °C (at the same concentration as the copolymerizations) was used, and this was calculated from the conventional SEC data in Table 3. The propagation rate data for the two copolymerization systems are plotted together with the corresponding terminal model predictions in Figures 3 and 4, for PCS−STY and PCS−PMOS, respectively. In each case, the SEC−DV and conventional SEC data are plotted separately.

Looking first at Figure 4, we see that the SEC−DV data of the PCS−PMOS system is well described by the terminal model predictions. This qualitative observation was confirmed by performing a goodness-of-fit test. It was not possible to perform a strictly quantitative test as there were insufficient replicate samples with which to estimate the size of the error in the data. Instead, a rough estimate of the error in the SEC−DV data was obtained using the 5 replicate analyses of the homopropagation rate coefficient for PCS in toluene (see Table 3). Using these data, the error was estimated to be around 5%. Assuming this constant level of relative error in the data, the χ^2 test statistic (having 44 degrees of freedom) was 31.6—which indicated a level of confidence in the terminal model of 89% for this system. While higher order models cannot be ruled out for this system, the ability of the terminal model to accurately predict the propagation rate coefficients, without recourse to any additional adjustable parameters, is strong evidence for the validity of this model. Under the terminal model, there is no penultimate unit effect and thus the radical reactivity ratios (s_1 and s_2) are equal to unity, as is of course their product (i.e. $s_1s_2 = 1$). In contrast, the monomer reactivity ratio product for the PCS−PMOS system is not equal to unity (since $r_1r_2 = 0.43$); hence, we have the result $s_1s_2 \neq r_1r_2$—a result which is inconsistent with the radical stabilization model of Fukuda et al.[11]

Examining next the plotted data in Figure 3, we see that there is a small systematic difference between the SEC−DV data for the PCS−STY system and the corresponding terminal model predictions. Now, as explained above, the radical stabilization model would predict a penultimate unit effect for this system since the monomer reactivity ratio product ($r_1r_2 = 0.60$) of this system is not equal to unity. (For, if $r_1r_2 = s_1s_2$ and $r_1r_2 \neq 1$, then $s_1s_2 \neq 1$ and thus $s_1 \neq 1$ and/or $s_2 \neq 1$.) Thus it would seem that the results for the PCS−STY system support the radical stabilization model. Nevertheless, it is necessary to confirm that the values of the radical reactivity ratios (at least within their 95% confidence limits) are such as to validate the prediction $r_1r_2 = s_1s_2$.

Table 4. Experimental Conditions and Propagation Rate Coefficients[a] for the Copolymerization of PCS with STY at 40 °C

						SEC−DV		conv SEC		
f_{PCS} (MON)	[M], mol/L	initiator	[I], mmol/L	energy, mJ/pulse	T_f, s	M_{ip}	k_p	M_{ip}[b]	k_p[c]	terminal k_p
0.519	8.109	AIBN	4.79	3	0.73			127 343	182	203
0.250	8.336	benzoin	3.84	3	0.73			121 567	178	190
0.214	8.367	AIBN	3.81	3	0.73			116 979	172	187
0.062	8.496	AIBN	3.27	4	0.50	74 332	162	72 063	159	169
0.114	8.451	AIBN	4.05	4	0.50	80 887	173	75 003	163	176
0.178	8.397	AIBN	4.85	4	0.50	81 560	171	77 507	167	183
0.363	8.241	AIBN	10.28	4	0.50			82 798	175	197
0.444	8.172	AIBN	5.52	4	0.50			84 962	178	201
0.570	8.066	AIBN	8.79	4	0.50	98 617	194	88 492	185	204
0.723	7.936	AIBN	8.89	4	0.50			88 165	183	204
0.029	8.523	benzoin	3.67	4	0.25	36 557	162	35 806	159	165
0.055	8.502	AIBN	3.71	4	0.25			37 221	165	168
0.056	8.501	AIBN	3.59	4	0.25			36 830	163	169
0.073	8.486	AIBN	4.09	4	0.30	46 944	170	44 572	163	171
0.301	8.293	AIBN	2.75	4	0.25	45 391	186	42 566	182	194
0.955	7.740	AIBN	5.24	4	0.25			45 854	190	199
0.946	7.747	AIBN	4.20	4	0.30	62 890	197	55 777	192	199
0.893	7.792	benzoin	3.74	4	0.25			45 048	187	201
0.282	8.309	AIBN	6.92	4	0.25	45 497	187	41 233	176	192
0.260	8.328	AIBN	3.81	4	0.25	45 505	188	40 942	175	191
0.260	8.327	AIBN	5.87	4	0.30	52 645	181	49 759	177	191
0.591	8.048	benzoin	4.38	4	0.25			43 634	183	204
0.607	8.034	AIBN	5.43	4	0.25	50 150	196	43 944	184	204
0.576	8.061	AIBN	5.01	4	0.25	50 966	200	44 100	185	204
0.608	8.034	AIBN	6.24	4	0.30			52 118	182	204
0.434	8.181	AIBN	4.52	4	0.25			41 672	176	201
0.431	8.183	AIBN	5.19	4	0.30			52 001	183	201
0.444	8.172	AIBN	8.35	4	0.25			42 794	181	201
0.751	7.912	AIBN	2.94	4	0.25			44 442	186	204
0.750	7.914	AIBN	6.01	4	0.25			43 728	183	204
0.752	7.912	AIBN	4.51	4	0.25	51 995	200	44 845	187	204
0.069	8.489	AIBN	7.39	30	0.25	39 531	172	37 456	165	170
0.469	8.151	AIBN	6.57	30	0.25	47 318	188	44 231	187	202
0.234	8.350	AIBN	6.56	25	0.25	44 926	186	41 276	177	189
0.157	8.415	AIBN	7.66	25	0.25			39 913	173	181
0.207	8.372	AIBN	8.36	25	0.40	67 806	177	64 569	173	186
0.902	7.785	AIBN	12.25	7.5	0.25			45 817	190	201
0.900	7.786	AIBN	11.74	7.5	0.30	63 395	200	55 600	192	201
0.833	7.843	AIBN	18.38	7.5	0.30			54 794	190	202
0.803	7.869	AIBN	13.83	7.5	0.25	52 550	201	46 505	194	203
0.699	7.957	AIBN	8.54	7.5	0.25	50 846	197	45 647	191	204
0.632	8.014	AIBN	13.03	7.5	0.30	58 799	191	51 237	179	205
0.576	8.061	AIBN	8.85	7.5	0.40	78 852	193	69 637	182	204
0.521	8.107	AIBN	10.05	7.5	0.40	76 024	188	68 856	180	203
0.630	8.015	AIBN	18.73	7.5	0.30	61 270	199	53 185	185	205
0.419	8.194	AIBN	10.91	7.5	0.40	76 597	192	66 816	176	200
0.402	8.208	AIBN	19.13	7.5	0.30	56 320	189	51 046	180	199
0.338	8.262	AIBN	12.97	7.5	0.40	75 170	191	66 565	176	196
0.325	8.273	AIBN	12.49	7.5	0.40	71 435	182	66 816	177	195
0.241	8.344	AIBN	10.29	7.5	0.45	80 802	186	73 969	176	189
0.252	8.335	AIBN	12.63	7.5	0.40	71 028	183	64 113	171	190
0.181	8.395	AIBN	10.72	7.5	0.45	74 384	174	68 856	165	184
0.188	8.389	AIBN	11.41	7.5	0.40	68 507	179	63 873	172	184
0.109	8.455	AIBN	10.10	7.5	0.50	79 377	170	74 830	163	176
0.075	8.484	AIBN	11.60	7.5	0.45	69 472	168	66 067	161	171
0.053	8.503	AIBN	6.78	7.5	0.50			72 585	160	168
0.109	8.456	AIBN	7.00	7.5	0.45	74 179	177	68 083	165	176

[a] k_p in L·mol^{-1}·s^{-1} . [b] These molecular weights are the uncorrected molecular weights as obtained using a PSTY calibration curve. [c] These propagation rate coefficients have been corrected to a PCS−STY calibration assuming a weighted average approximation (see text).

To estimate the radical reactivity ratios, the implicit penultimate model was fitted to the SEC−DV data. This model was also fitted to the SEC−DV data of the PCS−PMOS system in order to confirm that, even when the radical reactivity ratios were treated as fit parameters, the result $r_1r_2 \neq s_1s_2$ was obtained for this system. In performing the analysis, the monomer reactivity ratios (as measured from the composition data) and the homopropagation rate coefficients (as measured in separate homopolymerization experiments) were treated as fixed parameters. It was found that the implicit penultimate model could be made to fit the propagation rate coefficients for both systems, and the approximate 95% joint confidence intervals obtained for the radical reactivity ratios are shown in Figure 5. Plots of the implicit penultimate model "predictions" using these best-fit parameters are included in Figures 3 and 4, for PCS−STY and PCS−PMOS, respectively. Examining the values obtained for the radical reactivity ratios, it is clear that, for *both* systems, these values are such as to invalidate the equality $r_1r_2 = s_1s_2$. This can be seen in Figure 5 in which plots of $r_1r_2 = s_1s_2$ (calculated using

Table 5. Experimental Conditions and Propagation Rate Coefficients[a] for the Copolymerization of PCS with PMOS at 40 °C

						SEC−DV		conv SEC		
f_{PCS} (MON)	initiator	[I], mmol/L	[M], mol/L	energy, mJ/pulse	T_f, s	M_{ip}	k_p	M_{ip}[b]	k_p[c]	terminal k_p
0.125	AIBN	1.836	4.479	2.5	0.75	58 766	129	46 568	116	120
0.375	AIBN	1.828	3.548	2.5	0.75			48 436	150	156
0.487	AIBN	2.087	4.421	4	0.75	76 916	169	65 169	161	166
0.651	AIBN	2.804	3.791	4	0.75	65 054	166	58 774	168	175
0.361	AIBN	1.971	3.996	4	0.75			54 517	150	155
0.378	AIBN	2.437	4.425	4	0.75	68 710	152	59 242	147	157
0.832	AIBN	3.885	3.760	4	0.75	66 714	171	59 242	169	178
0.637	AIBN	2.029	6.290	4	0.75	109 170	168	97 097	167	175
0.245	AIBN	3.889	3.015	4	0.85	45 306	130	39 105	127	140
0.287	AIBN	3.759	2.537	4	0.90	46 674	150	40 069	145	146
0.492	AIBN	3.431	2.266	4	0.85	44 666	169	38 686	165	167
0.723	AIBN	5.061	2.572	4	0.80	51 269	181	42 549	168	177
0.910	AIBN	3.848	1.900	4	0.75			30 400	172	177
0.743	AIBN	2.856	3.092	4	0.80			53 979	176	177
0.814	benzoin	6.001	2.435	4	0.80			41 560	172	178
0.618	AIBN	4.986	3.141	4	0.80	61 110	177	51 485	167	174
0.896	benzoin	4.283	2.306	15	0.70	37 733	169	35 888	179	177
0.778	AIBN	6.401	2.430	5	0.70			36 952	176	178
0.853	AIBN	5.324	2.253	3	0.70	36 071	165	33 208	170	178
0.135	AIBN	4.600	2.273	20	0.70	24 507	114	23 704	125	122
0.119	benzoin	4.296	2.376	3	1.00	41 670	129	33 941	120	119
0.142	AIBN	4.887	2.337	3	1.00	38 970	123	34 846	125	123
0.196	AIBN	4.906	2.060	7	1.10	39 097	127	35 777	132	132
0.490	AIBN	5.176	1.943	3	0.70			26 842	162	166
0.466	benzoin	3.734	1.892	3	0.70			25 732	160	165
0.450	AIBN	4.708	1.926	3	0.70			26 583	162	163
0.486	AIBN	4.180	1.983	7	0.60	26 013	160	24 258	168	166
0.306	AIBN	5.370	2.407	7	0.70	34 264	149	30 410	149	148
0.347	AIBN	4.318	1.697	7	0.70	25 172	155	21 695	151	153
0.343	AIBN	2.925	1.727	7	0.60			18 508	148	153
0.327	AIBN	3.197	1.762	7	0.60			18 897	148	151
0.250	AIBN	4.836	1.900	7	0.60			18 668	136	141
0.049	AIBN	4.282	1.720	3	1.00			20 941	102	105
0.095	AIBN	4.528	2.165	7	1.00			27 811	108	114
0.102	AIBN	4.086	2.071	7	0.90	28 694	114	25 151	113	116
0.597	AIBN	5.474	1.862	3	0.60	26 806	175	22 702	167	173
0.935	AIBN	8.805	3.098	7.5	0.80	64 236	187	54 590	176	177
0.954	AIBN	6.871	2.945	7.5	0.60	45 098	184	38 593	175	176
0.880	AIBN	5.122	2.925	7.5	0.60	45 314	187	38 883	178	178
0.839	AIBN	4.221	2.681	7.5	0.55	36 842	181	32 116	176	178
0.770	AIBN	4.634	2.931	7.5	0.55	40 576	182	35 457	178	178
0.769	AIBN	5.169	3.273	7.5	0.70	55 480	176	50 668	179	178
0.698	AIBN	5.216	2.765	7.5	0.60	40 584	178	35 014	172	177
0.644	AIBN	5.410	2.766	7.5	0.60	39 397	173	34 800	171	175
0.583	AIBN	4.689	2.559	7.5	0.65	37 586	165	34 931	172	172
0.581	AIBN	4.357	2.938	7.5	0.70	49 361	175	43 032	171	172
0.460	AIBN	5.083	3.050	7.5	0.65	44 716	165	38 203	158	164
0.760	AIBN	4.450	3.116	7.5	0.70			47 924	178	178
0.499	AIBN	5.624	2.805	7.5	0.65	42 374	170	35 856	161	167
0.380	AIBN	5.859	2.643	7.5	0.70	40 124	159	33 774	151	157
0.345	AIBN	4.063	3.362	7.5	0.60	40 361	147	36 125	148	153
0.288	AIBN	4.804	2.757	7.5	0.60	29 687	132	28 460	143	146
0.236	AIBN	4.658	3.009	7.5	1.10	57 689	128	52 585	132	139
0.220	AIBN	5.293	2.959	7.5	1.10	59 099	134	50 857	130	136
0.143	AIBN	4.842	3.182	7.5	1.00	52 911	123	45 061	119	123
0.131	AIBN	4.489	2.697	7.5	1.10	48 236	120	41 430	117	121
0.118	AIBN	4.828	3.279	7.5	1.10	56 735	116	48 461	113	119
0.236	AIBN	3.982	2.892	7.5	1.10	59 112	137	50 856	133	139
0.219	AIBN	4.241	3.140	7.5	1.00	60 678	142	50 104	133	136

[a] k_p in L·mol^{-1}·s^{-1}. [b] These molecular weights are the uncorrected molecular weights as obtained using a PSTY calibration curve. [c] These propagation rate coefficients have been corrected to a PCS−STY calibration assuming a weighted average approximation (see text).

the r_1 and r_2 values measured from the composition data) were included for both copolymerization systems. Despite the large level of uncertainty in the estimated values of the radical reactivity ratios, it is nevertheless clear that the radical reactivity ratio products were significantly different from their predicted values, based on the monomer reactivity ratio products.

The above result was confirmed by attempting to fit the implicit penultimate model to the propagation rate data under the constraint that $r_1r_2 = s_1s_2$. This was done by fitting for a single parameter s, such that $s_1 = s$ and $s_2 = r_1r_2/s$, where r_1r_2 was calculated from the r_1 and r_2 values measured from the composition data. It was found that it was impossible to adequately fit the data under this constraint, and this can be seen in Figures 3 and 4, in which the implicit penultimate model "predictions" made using the best-fit s parameters are included with the raw propagation rate data. Clearly,

Table 6. Summary of the Parameters Used in Obtaining the Terminal Model Predictions for PCS−STY and PCS−PMOS

copolymerization	temp, °C	r_1	r_2	k_{11}[a]	k_{22}[a]
PCS[1]−STY[2] (bulk)	40	1.10	0.545	197[b]	160[c]
PCS[1]−PMOS[2] (in toluene)	40	1.04	0.412	175[d]	94[e]

[a] k_p in L·mol^{-1}·s^{-1}. [b] The average bulk value at 40 °C from ref 38. [c] The average bulk value at 40 °C from ref 38. This value is the same as that predicted using the IUPAC[26] Arrhenius parameters for STY. [d] The average of the conventional SEC values in present work (see Table 3). [e] The average value for PMOS in toluene (monomer concentrations in the range 2.0−2.8 mol·L^{-1}) at 40 °C, taken from ref 38.

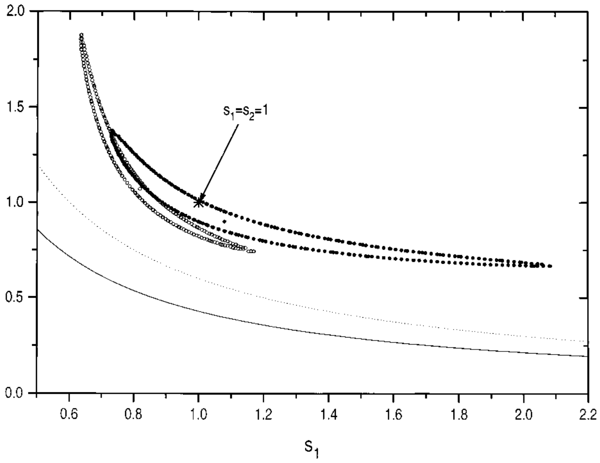

Figure 5. 95% joint confidence intervals for the monomer reactivity ratios of PCS[1]−STY[2] (○) and PCS[1]−PMOS[2] (●). The point estimates are $s_{PCS} = 0.819$ and $s_{STY} = 1.07$ for PCS−STY and $s_{PCS} = 1.08$ and $s_{PMOS} = 0.899$ for PCS−PMOS. Also plotted is the point $s_1 = s_2 = 1$ (∗) and the curve $r_1r_2 = s_1s_2 = 0.60$ for PCS−STY (- -) and the curve $r_1r_2 = s_1s_2 = 0.43$ for PCS−PMOS (—).

even these best-fit predictions cannot describe the data. Thus, even when the radical reactivity ratios are treated as fit parameters, it is clear that the equality $r_1r_2 = s_1s_2$ does not hold, a result that is inconsistent with the radical stabilization model of Fukuda et al.[11] This result, and its implications, will be discussed in more detail in the next section.

A further observation that may be made concerning the data in Figures 3 and 4 is that while the conventional SEC and SEC−DV data sets are not significantly different from each other for the PCS−PMOS system, in the PCS−STY system, a systematic difference is evident. Clearly, the weighted average approximation is not strictly valid for PCS−STY copolymers in THF. The inadequacy of the weighted average approximation has previously been demonstrated for copolymers of *n*-butyl acrylate with methyl methacrylate,[44] and the present results further highlight the danger of using conventional SEC to study copolymerizations without first checking the validity of inherent calibration assumptions.

Implications for Copolymerization Kinetics. In the present work, we have taken two pairs of sterically similar para-substituted styrene monomers and shown that the monomer and radical reactivity ratio products are significantly different to each other (i.e. $r_1r_2 \neq s_1s_2$)—a result which is inconsistent with the radical stabilization model of Fukuda et al.[11] Furthermore, these counterexamples have been obtained in systems of sterically similar monomers, and thus the failure of the radical stabilization model in these systems cannot be attributed to steric interactions that, as explained by Fukuda et al.,[11] fall outside of the scope of this model. Furthermore, for one of these systems (PCS−PMOS), the terminal model can provide an adequate description of the data and thus it would seem that the failure of the radical stabilization model cannot be attributed to other nonclassical effects (such as solvent effects) as these should have resulted in the failure of the terminal model. In other words, it would seem that the present results indicate a much more general failure of the radical stabilization model. In what follows, we investigate the likely cause of this failure and discuss its implications for copolymerization kinetics.

The prediction that the monomer reactivity ratio product (r_1r_2) is equal to the radical reactivity ratio product (s_1s_2) is derived in the original paper by Fukuda et al.[11] and follows from two principal assumptions: (1) the penultimate unit only affects the stability of the propagating radical, and there are thus no penultimate unit effects in the frequency factors; (2) the Evans−Polanyi rule[12,13] (which states that the barrier is proportional to the enthalpy) is valid for the propagation reactions.

In the present examples, the first assumption is likely to be valid as the monomer pairs are sterically similar. Furthermore, for one of these systems (PCS−PMOS) our results indicate that the terminal model can provide an adequate description of the copolymerization kinetics—thus it seems likely that there is no penultimate unit effect at all in this system. Thus it would seem that the present failure of the radical stabilization model is attributable to the invalidity of the Evans−Polanyi rule for these systems.

Recent high-level theoretical studies[45] of the transition structure in free-radical addition reactions indicate that the Evans−Polanyi rule will break down if the transition state is stabilized by polar interactions. Polar interactions are said to occur when either of the charge-transfer configurations of the transition state are sufficiently low in energy to contribute to the ground-state wave function, thereby stabilizing the transition structure (and thus lowering the reaction barrier) via partial charge-transfer.[46] Recent high level ab initio molecular orbital calculations[45] for the addition of substituted methyl radicals to substituted alkenes have confirmed the presence of polar interactions and the corresponding failure of the Evans−Polanyi rule, in these radical addition reactions when one of the coreactants is electrophilic and the other is nucleophilic. Furthermore, recent high-level ab initio molecular orbital calculations[15,19] for the addition of substituted propyl radicals to substituted alkenes indicate that polar interactions can also be responsible for γ-substituent effects (i.e. penultimate unit effects) in these reactions.

Thus it seems reasonable to suppose that polar interactions might be important in the cross-propagation reactions of free-radical copolymerizations. Indeed, the idea that the alternating tendency (i.e., the r_1r_2 product) in copolymerization is governed by polar interactions is not new. As early as 1946, Price[47] proposed that the alternating tendency was a result of polar interactions between permanent charges in the transition structure. Under the $Q-e$ scheme,[48] the alternating tendency is given by the product of the e parameters, which Alfrey and Price[49] proposed as a measure of the “charge” on the monomer or its corresponding radical in the transition state. This theory was later discounted by Mayo and Walling[50] and subsequent workers, when correlations between the reactivity ratios of a copolymerization and the dielectric constant of the reaction medium were not observed. However, there is certainly evidence for small solvent effects on the reactivity ratios for most copolymerization systems studied.[51] This solvent effect can, in some instances, be correlated with the polarity of the solvent,[52] and in cases where there is no direct correlation, it may be that other processes such as complexation or nonideal mixing are obscuring the small polar effect. Certainly the widespread presence of polar interactions in free-radical copolymerization cannot be ruled out—in particular given the direct evidence for these effects in small radical addition reactions.

In summary, the present results are inconsistent with the radical stabilization model, and it appears likely that the failure of this model for these systems is attributable to the presence of polar interactions in the cross-propagation steps of these reactions. These polar interactions undermine the validity of the Evans—Polanyi rule—one of the principal assumptions of the model. If this result is generally true, then it would appear that where penultimate unit effects in the reaction barrier do exist, they are likely to be explicit rather than implicit. While, in the present work, large penultimate unit effects were not observed, in theoretical[15,19] and experimental[20,21] studies of other systems it has been shown that penultimate unit effects in the barrier are likely to be significant. Furthermore, in the theoretical studies,[15,19] it was shown that the penultimate unit effects observed were likely to contain a significant polar component. Therefore it is reasonable to suppose that explicit penultimate unit effects in the barrier do exist in common copolymerizations such as STY-MMA. For this particular system, this conclusion is based on the observation that (1) the reactivity ratios vary with the dielectric constant of the solvent[52] (which indicates that polar interactions are likely to be important in this system and that the Evans—Polanyi rule is thus unlikely to hold[45]) and (2) the penultimate unit effect in this system is temperature dependent[20,21] (which indicates that there is likely to be a penultimate unit effect in the reaction barrier). Since, by point 1, the assumptions of the radical stabilization model would be unlikely to hold, the penultimate unit effect in the barrier is likely to be explicit rather than implicit. While the presence of implicit penultimate unit effects in the frequency factors of these reactions cannot be ruled out, nonetheless, if the penultimate unit effects in the barrier are explicit, it follows that the *overall* penultimate unit effects will also be explicit.

The present results, together with those of recent theoretical studies[15,19,45] and evidence for the solvent dependence of reactivity ratios,[52] suggest that the polar interactions are likely to be important in the transition structure of free-radical propagation reactions. Since these polar interactions undermine the Evans—Polanyi rule,[45] an essential assumption of the radical stabilization model, it appears likely that penultimate unit effects in the barrier, where they exist, are likely to be explicit rather than implicit. However, it should be acknowledged that, as yet, there is only limited experimental evidence for this idea. In the present work, both the copolymerization systems studied involved PCS as a comonomer which, as the homopolymerization results in this work show, may be subject to solvent effects. In this regard, these copolymerizations may be exceptional, and it would be unwise to overgeneralize these results. Similarly, while there is strong evidence from both experimental[14,18,53] and theoretical[15,19] small-radical studies for explicit polar penultimate unit effects, these studies have all involved highly polar monomers such as acrylonitrile and acrolein, which may be exceptional in their behavior. Finally, while most reactivity ratios are solvent sensitive,[51] this solvent dependence may also be attributable to other factors such as a bootstrap effect.[54] Nevertheless, while the evidence for explicit penultimate unit effects is limited, there appears to be no direct evidence as yet for implicit penultimate unit effects. Thus, based on existing evidence, we suggest that the explicit penultimate model should be adopted rather than the implicit penultimate model. It might be thought that this suggestion is counterintuitive, and that Occam's razor should instead lead us to adopt the mathematically simpler implicit penultimate model (it having six parameters rather than eight). However, if we examine the *assumptions* of these alternative models, it is clear that the explicit penultimate model is in fact the simpler. For, although both models assume that the terminal and penultimate units affect the rate of the propagation step, the implicit model makes the additional assumption that this effect is independent of the coreactant. By application of Occam's razor, it would thus make sense to adopt the explicit rather than the implicit penultimate model, until there is sufficient evidence for this additional assumption.

If the explicit penultimate model is applicable to common copolymerization systems, the terminal model composition equation will not be valid. Hence the previously measured terminal model monomer reactivity ratios for these systems, though providing rough estimates of the average reactivity ratios of the polymer radicals, will not necessarily reflect their proposed physical meaning and may thus lead to false predictions of the other quantities which depend on them (such as the microstructure of the copolymers or the radical concentrations in the copolymerization system). Unfortunately, the use of the more physically realistic explicit penultimate model may not offer a substantive solution to this problem since, under this model, the large number of parameters that are required to fully describe the propagation reaction, coupled with the limited experimental data that is obtainable, renders their accurate and precise measurement difficult if not impossible. For instance, it has recently been shown that, under the explicit penultimate model, multiple sets of monomer reactivity ratios can describe with reasonable accuracy the composition data from STY—MMA copolymerizations.[55] Thus it would appear that, even when the correct model is fitted, the kinetic parameters obtained from model fitting procedures may convey only limited physical meaning and thus the further development of alternative techniques for measuring these quantities (such as end-group studies or experimental/theoretical studies of small-radical addition reactions) is important.

Conclusions

In the present work, it was shown that, for the copolymerizations of PCS with STY and with PMOS, the monomer and radical reactivity ratio products are significantly different to each other (i.e. $r_1r_2 \neq s_1s_2$)—a result which was inconsistent with the radical stabilization model of Fukuda et al.[11] It was argued that the failure of the radical stabilization model is probably attributable to the presence of polar interactions in the cross-propagation steps of these reactions, which would serve to undermine the validity of the Evans−Polanyi rule—one of the principal assumptions of the model. Furthermore, it was shown that these polar interactions were likely to be common in free-radical copolymerization, given the direct evidence for these effects in small radical addition reactions and given the solvent dependence of most reactivity ratios. Finally it was shown how the presence of such polar interactions (which would render any penultimate unit effects in the barrier explicit rather than implicit), together with recent evidence for the existence of penultimate unit effects in the barrier, suggests that the explicit penultimate model may in general provide a more physically realistic description of copolymerization kinetics than the more widely used implicit penultimate model. Thus, on the basis of existing evidence, the terminal model should only be applied to those exceptional systems (such as the PCS−PMOS system in the present study) for which it can simultaneously describe *both* the propagation rate coefficients and composition/sequence distribution data.

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