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E.s.r. measurements of the propagation rate coefficient for styrene free radical polymerisation

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Electron spin resonance (e.s.r.) spectroscopy should be useful for the measurement of propagation rate coefficients (k_p) in free radical polymerisations, since the propagating radical concentration can be directly observed. However, in previous studies, k_p values have generally been inconsistent, and disagreed with data from other accepted experimental techniques, such as pulsed laser polymerisation. This study shows that for styrene, consistency can be obtained, but only when experimental conditions are selected such that polymer of sufficiently high molecular weight is formed; otherwise incorrect rate constants may be measured. The measured Arrhenius parameters were in good agreement with IUPAC accepted data. The values at 343 K for both thermally and photochemically initiated experiments were found to be consistent, suggesting that photoinitiated systems may polymerise in the ground state. Some previously inconsistent data could be explained in terms of selection of experimental conditions. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: electron spin resonance; styrene; propagation rate coefficient)

INTRODUCTION

Electron spin resonance (e.s.r.) spectroscopy is in principle an experimental tool with great potential to obtain detailed information on the structure, dynamics, and environment of free radical species formed in polymerisation reactions.[1-10]. The technique has been applied by several authors[5-21] to the determination of the propagation rate coefficient (k_p) in free radical polymerisations. However, there have been difficulties in the experimental methods, evident in the lack of agreement between apparent values of k_p measured by different e.s.r. kinetic data for the same system between groups[12-14], and between e.s.r. values and other experimental techniques, such as PLP[22-28].

An important advantage of e.s.r. spectroscopy over other (kinetic) experimental techniques is that it allows essentially *direct* observation of the free radical species present in the reaction. In order to correctly measure k_p, the concentration of the propagating radical species (and *only* the propagating species) in the locus of polymerisation must be measured. In cases where radical species other than the propagating radical are observed, it is possible that the k_p value measured may be incorrect. Furthermore, such species may be present in experiments using other techniques, and in such experiments, these species may not be readily detectable. This possibility allows the potential for incorrect measurement of k_p (and possibly other rate parameters, such as the transfer rate coefficient), due to unobserved side reactions.

Other experimental techniques used for the measurement of k_p may have difficulties for some systems; for example, PLP is usually only suitable for the measurement of k_p at low polymer fractions. For some of these systems, e.s.r. spectroscopy may be a valid alternative to the more conventional techniques, if it can be shown to be quantitative.

Although the measurement of k_p by e.s.r. spectroscopy is simple in principle, there exist many potential sources of error. Some of these sources of error are systematic in nature, and thus potentially lead to misinterpretation not only of the absolute values of rate coefficients, but also the qualitative understanding of the experimental system.

AIMS OF THE STUDY

The original purpose of this study was to measure k_p for the free radical polymerisation of styrene by e.s.r. spectroscopy, as a function of temperature. Initially, the aim was to obtain self-consistent data for this experimental system, and from that point, to compare the Arrhenius parameters (frequency factor and activation energy) with the IUPAC-accepted values. Any discrepancies between the systems were to be identified, and explained, if possible.

A further aim of this study was to identify the principal potential sources of error, particularly those of a systematic nature. The possible effects of these sources of error were analysed, with particular emphasis on the testing of these for the current experimental system. Methods were sought to reduce or eliminate these sources of error.

EXPERIMENTAL

The e.s.r. spectra were recorded on a JEOL JES RE-2X computer-controlled e.s.r. spectrometer, in the X-band

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region, using a TE_{011} cavity. The temperature was controlled to 0.2 K by gas flow through the cavity. Spectra typically were recorded as a single 8 min scan, with a time constant of 0.3 s, using 100 kHz field modulation (amplitude 0.1–0.5 mT), and microwave power of 1 mW. In a number of experiments, e.s.r. spectra of both the background and the propagating radicals were recorded at more than one modulation amplitude, to investigate the expected independence of the measured k_p values of the modulation amplitude. The especially high sensitivity of this device is particularly useful for the present purpose of detecting species of low concentration with a single scan.

Photoinitiation of the samples was performed by irradiation of the e.s.r. tube with a 500 W ultra-high-pressure mercury lamp (Ushio USH-500D), which was focused on the e.s.r. cavity, and a light-sensitive initiator (either *t*BPO (*tert*-butyl peroxide) or MAIB (methyl azobisisobutyrate)). The front of the cavity was free of any obstacles, such that the incident radiation intensity on the lower part of the e.s.r. tube was approximately constant. The sample depth was always adjusted such that the entirety on the sample was within this region.

Gas chromatography (GC) analysis was performed on a Shimadzu GC-8A gas chromatograph.

All chemicals used in this study were supplied by Wako Pure Chemical Industries, Ltd, Japan, with the exception of the 4-*tert*-butyl catechol, which was supplied by Nacalai Tesque, Japan. The styrene monomer was distilled under reduced pressure, and dried over anhydrous calcium hydride before use. The light-sensitive initiators (*t*BPO and MAIB) were used without further purification. The 'inert' diluents toluene and benzene were used without further purification. The poly(styrene) used was a GPC standard (*ca.* 10^5 g mol^{-1} M_n, $M_w/M_n = 1.03$).

The general experimental procedure (except where otherwise specified) consisted of the following steps: mix components (usually initiator, monomer, and other additives, where appropriate), add to e.s.r. tube, flush with argon, seal, place in e.s.r. cavity, record background spectra (often at more than one modulation amplitude), irradiate, record radical spectra (at the same modulation amplitudes as the background spectra). All spectra were recorded at low conversions in the solution free radical polymerisation of styrene, and the system was in an approximately steady state throughout the duration of the experiment. Small volumes of sample were removed from the e.s.r. tube at various times throughout the reaction for GC analysis of the rate of polymerisation.

Two principal values are required for the measurement of k_p: the rate of reaction and the *propagating* radical concentration. The rate of reaction is determined from the change in relative monomer concentration with time:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{R}^{\cdot}][\mathrm{M}] \qquad (1)$$

so,

$$-\ln\{[\mathrm{M}]_t/[\mathrm{M}]_0\} = k_p[\mathrm{R}^{\cdot}] \qquad (2)$$

where [M] is the monomer concentration, and $[R^{\cdot}]$ is the propagating radical concentration.

In this experimental setup, the relative monomer concentration was measured by gas chromatography, by comparison with an inert toluene internal standard. Since the concentration of toluene does not change during the reaction, the relative monomer concentration as a function of time is measured by comparing the styrene:toluene peak areas. The propagating radical concentration was measured by comparison of the double integrals of the propagating radical e.s.r. signal with that from an accurately-known TEMPOL (4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy) standard.

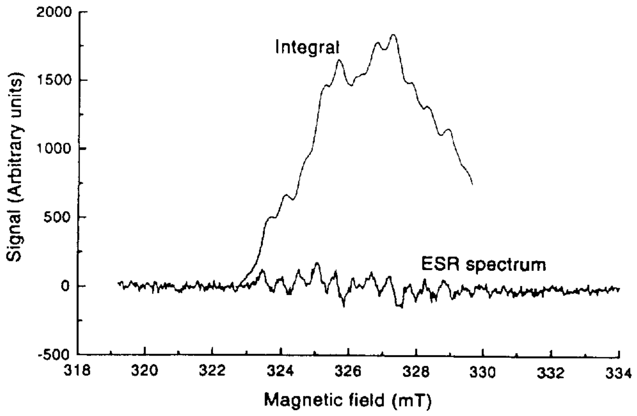

Figure 1 E.s.r. spectrum of the poly(styryl) propagating radical with an apparently flat background, with its first integral. Note the background on the integral is not flat, which could lead to an incorrect estimate of the radical concentration

The e.s.r. spectra of the propagating radicals were recorded at a sufficiently low microwave power to avoid saturation. Background spectra of samples containing the samples were recorded using the same instrumental and experimental parameters (with the exception of 343 K, where thermal polymerisation introduced errors in both the radical concentration and the rate of reaction). The resulting spectrum contained cavity and tube backgrounds, and also serves as a check for the presence of e.s.r.-active impurities in the sample. The background spectra were subtracted from the propagating radical spectra prior to integration. In some cases, the difference spectrum showed a relatively flat baseline, but in several cases, the subtraction was not perfect (probably due to small differences in the experimental conditions), and baseline compensation was required in the calculation of the radical concentrations (see *Figure 1*). Due to the difficulties with background compensation, the first integrals of the difference spectra were carefully examined, and only used if the absorption spectrum had the correct shape. Note that large errors may occur in the calculation of the propagating radical concentration as a result of incorrect baseline compensation. Once the baseline compensation yielded acceptable first integral spectra, the double integrals of the spectra were calculated. These double integrals were compared with those of a accurately-known standards (which also had their background spectra subtracted, and were examined as for the propagating radical spectra), to give an estimate of the propagating radical concentration.

TEMPOL standards were prepared at several concentrations near the typical propagating radical concentration (10^{-7}–10^{-6} M). A small quantity of TEMPOL was dissolved in toluene, and diluted by weight multiple times to the desired concentrations, with thorough mixing. The errors in the concentrations of the standards are expected to be less than 10%. Although it is desirable to use standards dissolved in exactly the same solvent as for the kinetic measurements, toluene was chosen as the solvent over styrene due to the thermal decay of the standard signal in styrene, which can introduce significant errors above room temperature. The e.s.r. spectra of these standards were recorded between 278 and 343 K.

Since detector response may vary with environment, toluene-based standards were diluted in known quantities of both styrene (to give a styrene:toluene ratio of approximately 4:1, which was typical for the kinetic measurements) and toluene. The e.s.r. spectra were compared at 278 K, and later, at 323 K (as close to preparation time as possible, due to apparent loss of signal by 20% in 50 min), to examine the detector responses for the actual system studied in the kinetic measurements and for the toluene system. The e.s.r. detector response was apparently 10% higher in the styrene/toluene mixture over this temperature range, thus the effects of changing solvent appear to be relatively small for the purposes of determination of radical concentration in this system. The measured radical concentrations were corrected (reduced) accordingly.

Background spectra of the e.s.r. tubes were recorded before addition of the standard solutions, under the full range of measurement conditions. The e.s.r. spectra of the standards were recorded under several different spectrometer and experimental conditions, and the background-corrected double integral spectra compared to check internal consistency.

COMMENTS ON IMPURITIES

Under some conditions, unexpected e.s.r.-active species were observed during the free radical polymerisation of styrene, of which none could be positively identified. However, since the rate of polymerisation and apparent radical concentrations may be affected by these species, it is important to avoid their formation. In each case, experimental conditions could be found such that these species were not formed.

E.s.r.-active species observed during the solution (in toluene) free radical polymerisation included the following: an apparent singlet with a slightly different g-value from the poly(styryl) propagating radical; and an apparent broad, anisotropic doublet (with an extremely large apparent hyperfine coupling constant), which appeared to be associated with the singlet. The latter two species were observed in the presence of radiation of wavelength less than 310 nm.

The sharp singlet and the apparently associated anisotropic doublet signal (see *Figure 2*) are apparently due either to the interaction of the UV radiation with the glass in the e.s.r. tube, or with an impurity on the glass of the e.s.r. tube. Although these signals are apparently associated, the relative amounts of each signal changed in each experiment. It was also noted that the relative intensity of the singlet decreased with time, as the relative intensity of the doublet signal increased. Possible assignments that were experimentally eliminated include: initiator-derived radicals, radicals derived by chain transfer to polymer, oxygen-derived radicals, and impurities in the monomer. However, these spectra were also observed when preparing standards under vacuum, which again throws doubt onto the assignment of these signals. Furthermore, the central singlet signal was significantly broadened in the presence of benzene, which suggests a relatively strong interaction between the e.s.r.-active centre and its environment. Such an interaction may also have an effect on the kinetics of the polymerisation process, which is obviously undesirable. Thus, all further experiments were performed with a 310 nm UV-cutoff filter, in order to eliminate the formation of these species.

RESULTS AND DISCUSSION

Initial analysis of experimental data (see *Figure 3*) suggested an activation energy for propagation (25 kJ mol^{-1}, corresponding frequency factor $10^{6.125}$ s^{-1}) that was not in accordance with the IUPAC-accepted value (32.51 kJ mol^{-1})[27]. Note that there is significant scatter in the data in *Figure 3*, and that the best fit is not necessarily linear. There were three main likely candidates for the difference in activation energies: (i) the e.s.r. experiment was measuring a different chemical process from the IUPAC-accepted data, (ii) there were systematic errors (relating to instrumental effects) occurring in the e.s.r. experiments, or (iii) the experimental conditions (governing the chemical processes) for the e.s.r. measurements were not appropriate for the determination of k_p.

The first of these explanations is feasible, but since the e.s.r. spectrum gives a relatively clear indication of the structure of the propagating radical species, this possibility would indicate that the IUPAC-accepted experiments were measuring chemical processes other than propagation. Since these data were measured by a variety of experimental techniques, this explanation is unlikely, although not impossible.

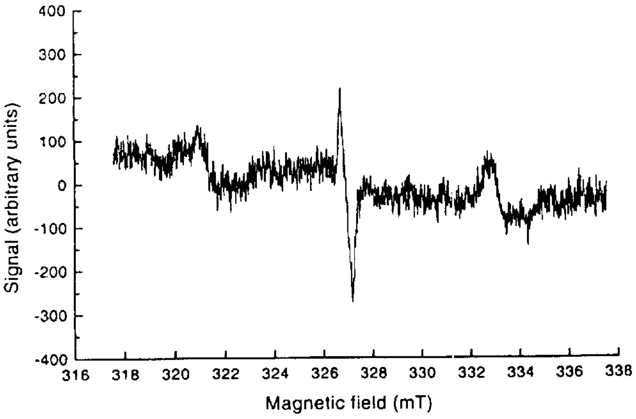

Figure 2 Apparent broad, anisotropic doublet signal and central singlet signal observed in the photoinitiated free radical polymerisation of distilled styrene in the presence of toluene. Experimental conditions: T = 343 K; modulation amplitude 0.2 mT, 2 mol% *t*BPO photoinitiated by ultra-high-pressure Hg lamp

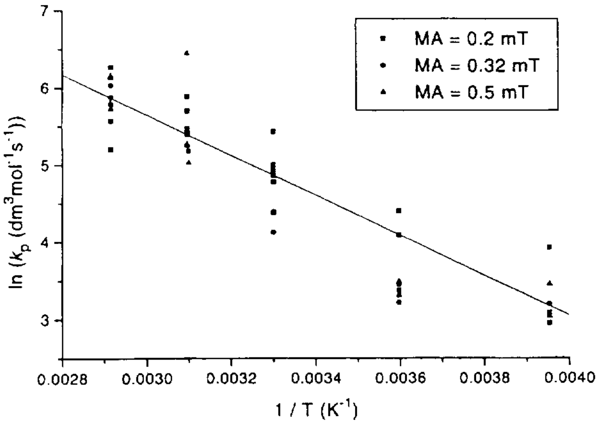

Figure 3 Arrhenius plot of initial analysis of experimental k_p data. All experiments at low conversion for the solution free radical polymerisation of styrene

The second explanation is possible, since the measured k_p value is dependent on the double integration of both the propagating radical signal and the standard signal. In the general case, the sensitivity of the e.s.r. instrument is dependent on several experimental parameters which may change with temperature. Such changes may lead to a temperature-dependent calibration, giving a temperature-dependent systematic error in the measurement of k_p.

The third explanation is also possible, and could certainly show a temperature dependence. It will now be shown that this was indeed the likely source of the discrepancies between the e.s.r. and IUPAC-accepted values, due to the likely dependence of k_p on propagating chain length for very short oligomeric radicals.

The possibility that there were systematic changes in the sensitivity of the e.s.r. instrument was carefully investigated. Due to the instability of the standard radicals in styrene solution, standard spectra were initially collected only at 243 K, and used without temperature correction for the determination of the propagating radical concentration at higher temperatures. The highest temperature used in these experiments was 343 K, and thus it was expected that a Boltzmann correction would cause a significant change in the calculated k_p values. However, such a correction would reduce the apparent activation energy, so this was obviously not the only source of error. Opposing the Boltzmann factor is the likely increase in relaxation times for the propagating radicals: the linewidth of the e.s.r. spectrum of the propagating radicals increased rapidly with temperature, which indicates faster relaxation times with increasing temperature. Such an effect would increase the apparent activation energy, in opposition to the Boltzmann factor. Finally, the environment inside the cavity can strongly affect the sensitivity of the e.s.r. instrument: there was an apparent difference in sensitivity between standards in toluene and those in styrene. This difference may also be temperature-dependent, which could change the apparent activation energy.

Consequently, the sensitivity was investigated as a function of temperature for a wide variety of standards in toluene solution (to avoid decay in the standard signal with time), from 278 to 343 K. Surprisingly, within experimental error, it was found that there was no apparent change in the sensitivity over this temperature range. It seems likely that this temperature independence was due to the approximate cancellation of the reduced sensitivity due to the Boltzmann factor, and the increased sensitivity due to the faster relaxation times. Thus, the only possible remaining temperature-dependent e.s.r. factor is the change in environment from toluene to styrene. As described in the experimental section, this possibility was tested by comparison of a standard diluted in toluene with the same standard in styrene. Obviously, such a test will not give an absolutely correct comparison, due to the decay of the signal in styrene. However, the comparison was made first at the lower temperature, before being made immediately afterward at the higher temperature, in an attempt to minimise the effects of the decay. It was found that, within experimental error, there was no clear indication that there was a temperature-dependent effect on the sensitivity when changing the solvent from toluene to styrene.

Thus, there appear to be no significant temperature-dependent effects on the e.s.r. sensitivity to account for the apparent discrepancy in the activation energies for propagation.

The experimental conditions for the measurement of k_p by e.s.r. were thus carefully investigated. There are two immediate criteria to be observed: the system must be in an approximate steady state (with correspondingly constant rate of polymerisation) throughout the duration of the experiment (requiring initiator decomposition rate to be sufficiently low and there must be relatively little change in conversion, such that the average termination rate is approximately constant), and the rate of initiation must be sufficiently high such as to give a detectable e.s.r. signal which is suitable for double integration. All experiments that were used for the purposes of measuring k_p met these criteria.

Due to the high initiation rates in this system, it was found that the apparent k_p value measured by e.s.r. spectroscopy at 253 K was usually much higher then the IUPAC-accepted value. This leads to a discrepancy in the apparent activation energy for propagation. A possible explanation for this observation is that under these conditions, the majority of the propagating radicals may be very short (oligomeric). Although the structure (geometry) of the propagating radicals may change slightly with chain length for very short species, such differences may not always be readily detectable in the e.s.r. spectrum. The hypothesis that the majority of the propagating radicals may be very short was supported by GPC measurements, which although unlikely to be quantitatively correct, indicated extremely little polymer of molecular weights greater than very short oligomers. This was further supported by the lack of detectable methanol-insoluble products. It has been pointed out previously[29] that this situation has probably arisen in earlier reports of k_p values obtained by e.s.r. spectroscopy. This effect will invalidate the apparent k_p values so obtained.

Therefore, it appeared to be likely that at 253 K, the propagating radical distribution was dominated by very short oligomers. For very short species, there is considerable evidence[30–34] to suggest that the propagation rate coefficient is chain-length-dependent, especially when there is a different initiator-derived end-group. Such a dependence is unlikely to be significant for radicals of degree of polymerisation greater than three, but for radicals shorter than this critical degree of polymerisation, the propagation rate coefficient is likely to be greater than the long-chain limit, *i.e.*, $k_{p,1} > k_{p,2} \geq k_{p,3} \geq k_{p,\mathrm{long}}(= k_p)$. Thus, under such conditions, the measured k_p value will be grater than the 'real' k_p: the long-chain limit.

Since the aim of the experiments was to measure $k_{p,\mathrm{long}}$, any experiments where the propagating radical distribution is dominated by oligomers is undesirable. Further experiments should be performed under experimental conditions where the average propagating chain length is long (degree of polymerisation greater than at least three). The main experimental factor which causes the propagating radical chain length to become dominated by very short oligomers is the very high rate of initiation (the product of the initiator concentration, the initiator efficiency, and the initiator decomposition rate coefficient (k_d)). The average propagating radical chain length can be increased by decreasing this initiation rate. Unfortunately, due to e.s.r. spectrometer sensitivity limitations, the radical concentration, and thus, the rate of initiation, needs to be kept as high as possible. Due to the conflict between these factors, it is difficult to find experimental conditions that simultaneously meet both criteria. Computer simulations of the propagating radical distribution were thus used to assist in the search for appropriate experimental conditions.

These computer simulations estimated the number of propagating radical chains as a function of degree of polymerisation. The number of propagating radical chains of degree of polymerisation less than five (five was used, rather than four, for safety) were compared with the total number of propagating radical chains. If this ratio was greater than approximately 0.1 (below which, based on assumed ratios of $k_{p,1}/k_{p,long}$ of approximately 10 (note that the computer simulations are not especially sensitive to this ratio), the average k_p should be approximately equal to $k_{p,long}$), then such an experiment was likely to give a measured k_p value which was greater than $k_{p,long}$.

The computer simulations estimate the number of propagating radical chains of each degree of polymerisation by iteratively solving the steady-state form of the coupled partial differential equations which describe the population balance (chain creation, growth, and death events) as a function of chain length[35–38]. The model assumes simple scaling laws for the calculation of the bimolecular termination reaction rates (which are far more important than transfer for the control of chain length in this system, due to the very high radical concentrations). Such simulations require a large number of input experimental parameters, and thus, the best estimates of experimental conditions are required for the most accurate output. The input parameters of most importance for such simulations for this system are the initiation rates (radical flux for photoinitiator, or, for thermal initiation, the initiator concentration, and the product of the initiator efficiency and k_d), propagation rate coefficient (as a function of chain length), monomer diffusion coefficient, and the scaling law coefficients. Note that the gradient of the distribution may depend on the type of the initiator, since the rate coefficients for the first two propagation steps will probably depend on the initiator type. Some of these parameters are only approximately known, and when combined with possible limitations of the model, limit the utility of the model to estimating the propagating chain length distribution only qualitatively. However, the predictions of the model were in qualitative agreement with the experimental observations of very low molecular weights, and thus, general trends could be observed from the simulations. Typical input parameters are shown in *Table 1*, and the output plotted in *Figure 4*.

The general findings of the simulations indicate that, for this photoinitiated styrene free radical polymerisation system: propagating radical chains tend to be very short, due to the extremely high radical flux; the average propagating radical chain length increases with increasing temperature, since the activation energy for propagation is much greater than for diffusion (the termination rate coefficients are strongly dependent on the diffusion coefficients of the radicals); and the average propagating radical chain length increases with decreasing initiation rates.

Table 1 Typical input parameters[39] for estimation of the propagating radical chain length distributions at 253 K. Note that most parameters change with temperature

Parameter	Value
k_p	8.28 dm^3 mol^{-1} s^{-1}
k_{tr}	2.7×10^{-5} dm^3 mol^{-1} s^{-1}
k_d	10^{-5} s^{-1}
σ (interaction diameter)	6.02 Å
D_{MON}	$10^{-5.3966}$ cm^2 s^{-1}
a (rms end–end distance)	0.74 nm
u_1	0.697
u_2	1.77
[I]	1.6×10^{-1} mol dm^{-3}
p	0.25
$k_{p,1}/k_p$	10
$k_{p,2}/k_p$	4

The parameters u_1 and u_2 are scaling law coefficients as a function of weight fraction polymer ($D(i, w_p) = D_{MON}/i^{(u_1 + u_2 \times w_p)}$, i is degree of polymerisation), and p is the probability of termination when two radicals meet, based on the requirement that the spins must be opposed

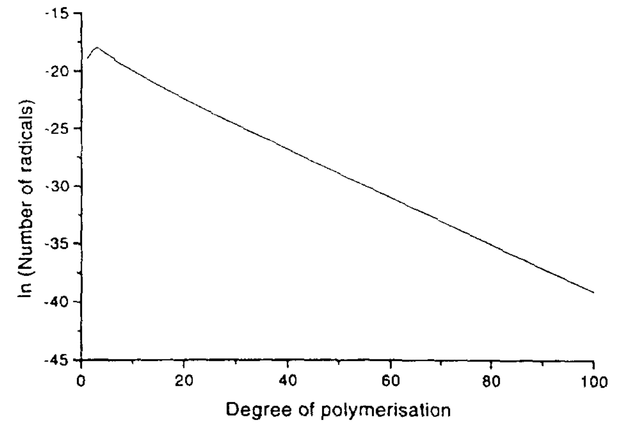

Figure 4 Typical computer simulation output for the propagating radical chain length distribution, plotted as the natural logarithm of the number of chains of degree of polymerisation. Input parameters are given in *Table 1*. Note that under these experimental conditions, the distribution is predicted to be dominated by oligomers

Uncertainties in rate parameters (especially radical flux for photoinitiated systems) mean that the output from the simulations is not truly quantitative (unless experimental measurements of the molecular weight distributions quantitatively support the predicted distributions). Hence it is generally best to use the simulations as a qualitative guide to ensure that the experimental molecular weights are biased towards radicals of degree of polymerisation much greater than oligomers. Further, where possible, the radical flux should be varied to ensure that the apparent k_p values are independent of this variable, which will strongly indicate that there is no measurable influence from very short propagating radicals. In the final data set discussed below, the apparent k_p values were independent of radical flux and initiator type, where these could be varied.

The computer simulations indicated that, at 253 K, due to the experimental limitation that a relatively high propagating radical concentration is required for the double integration of the spectrum, it was impossible to find experimental conditions to simultaneously meet the requirements that the majority of the propagating radicals were of a sufficiently high degree of polymerisation, and that the propagating radical concentration was sufficiently high for measurement. Thus, all experimental data recorded at 253 K were likely to indicate a measured k_p value higher than $k_{p,long}$. Consequently, all experimental data at 253 K were rejected from the data set. It is also clear that most data at 253 K in *Figure 3* were higher than would be expected by the Arrhenius best-fit.

Further simulations indicated that the propagating radical populations in many of the experiments at higher temperatures and irradiation intensities were also likely to be dominated by very short propagating radical chains. Since many of these experiments could potentially measure an incorrect value of k_p, the data set was examined carefully, using the simulation results as a guideline. Any experiment where either the irradiation intensity or the initiator concentration (or simply the initiator concentration, in the

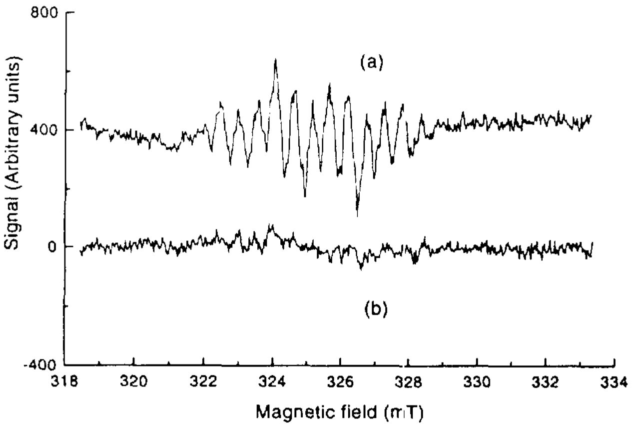

Figure 5 Comparison of two e.s.r. spectra of the propagating radicals in the solution free radical polymerisation of styrene, under very different radical flux conditions. Experimental conditions: (a) $T = 343$ K, [MAIB] = 0.9 M, MA = 0.2 mT; (b) $T = 278$ K, [tBPO] = 0.15 M, MA = 0.2 mT. Note that spectrum (b) is more desirable for the measurement of k_p, due to the much lower radical flux, although the signal:noise ratio is lower

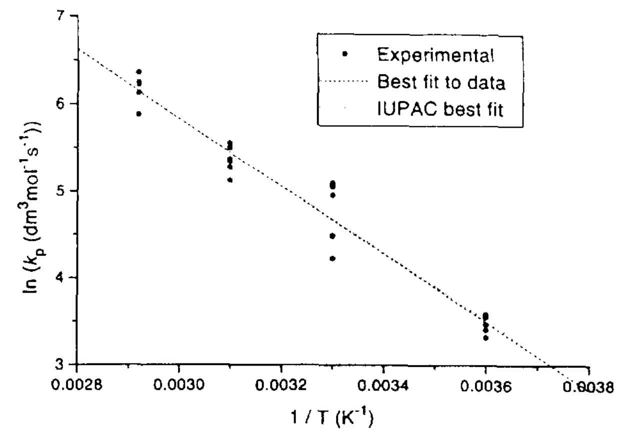

Figure 6 Arrhenius plot of the restricted k_p data set for the solution free radical polymerisation of styrene, including only experiments with lower radical flux

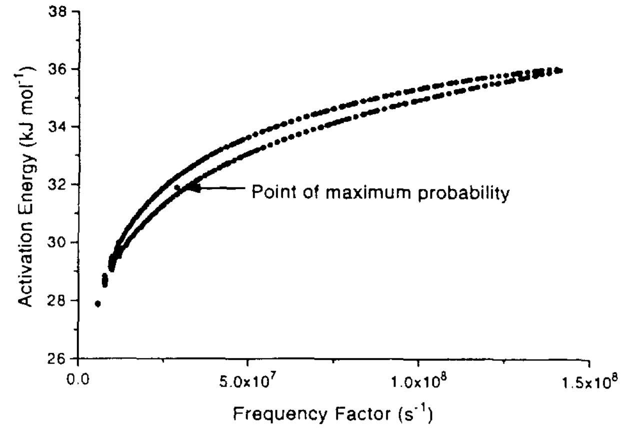

Figure 7 Plot of 95% joint confidence intervals for the restricted k_p data set, as shown in *Figure 6*

case of the thermally initiated experiments) was too high (such that the simulations indicated that the most propagating radicals were likely to be very short) was removed from the data set. All further experiments were restricted such that both k_d and the initiator concentration were kept very low (to allow a long steady state and the formation of longer propagating radicals). Experimental observations indicated that the average propagating radical chain lengths had indeed increased: the average molecular weights were much higher (although still low: several thousands to tens of thousands), and a significant fraction of methanol-insoluble products.

Although the signal:noise ratio for the e.s.r. spectra of the propagating radicals was far from optimal in such experiments, it was found that the signals could usually, when treated carefully, be used consistently for the determination of the propagating radical concentrations, *i.e.*, giving consistent k_p values that were independent of modulation amplitude). Therefore, it was considered desirable to ensure that the average propagating radical chain length was sufficiently long, rather than to increase the quality of the e.s.r. spectra. A comparison of two experimental spectra under very different experimental conditions illustrates this point in *Figure 5*.

The final data set includes only experiments that meet the following criteria: the initiator decomposition rate coefficient is sufficiently low to allow a steady state (observable both in the rate of reaction and estimates of the initiator decomposition rate) much longer than the duration of the experiment; appropriate background spectra were recorded; there exists a sufficiently high propagating radical concentration such that this could be accurately measured; no e.s.r.-active species other than the propagating radicals were detected; and the initiation rates were sufficiently low such that the majority of propagating radical chains were of a degree of polymerisation greater than five (as estimated by computer simulations) and the apparent k_p values were independent of these rates. Given equipment capable of accurately measuring final molecular weights, it is recommended that the final polymer molecular weight distributions be checked for e.s.r. measurements of k_p, to ensure that $k_{p,\mathrm{long}}$ is the quantity measured. It is recommended that the majority of the dead chains (*e.g.*, GPC distribution) should be of degree of polymerisation greater than 30, such that the influence of very short propagating radicals is negligible.

With such restrictions, a reasonable level of confidence can be attributed to the measured k_p values. The uncertainties varied for each estimate of the propagating radical concentration, depending on the quality of the background-corrected spectra. The uncertainties were dominated by the uncertainties in the determination of the propagating radical concentrations. The final uncertainties in the measured k_p values are expected to be less than 40% (assuming a maximum 25% error in double integration of both background and radical spectra, and 10% in rate measurements).

Analysis of an Arrhenius plot (*Figure 6*) and an analysis of the 95% joint confidence intervals[39] (*Figure 7*) of the remaining data set gives very different best-fit parameters from the original fit to the unrestricted data set. The agreement between the best-fit values for the activation and the frequency factor, and the IUPAC-accepted values is very good. The activation energy for the revised data set is 31.9 ± 3.1 kJ mol^{-1} (IUPAC: 32.51 kJ mol^{-1}), and the frequency factor is $10^{(7.66 \pm 1.01)}$ s^{-1} (IUPAC: $10^{7.630}$ s^{-1}). The agreement between activation energies is particularly important, since this now indicates that the different experimental techniques are measuring the same chemical processes. Although the agreement between frequency factors is also good, this is considered to be less important.

Errors in standard concentrations will affect the frequency factor, but not the activation energy, for the propagation process.

The differences between the initial and the final data sets illustrate the importance of careful selection of experimental conditions. The unrestricted data set contains experiments that measure additional information on reactions other than the long-chain propagation process. The apparent difference in activation energies is due to this measurement of additional reactions in some of the experiments, *i.e.*, some of the e.s.r. experiments were measuring different chemical processes from the IUPAC experiments. The restricted data set contains only experiments that are measuring the same chemical process as in the IUPAC experiments, thus the good agreement between the experimental systems.

The final data set also illustrated that the measured k_p values were independent of variations in experimental conditions. The experimental conditions that were varied included e.s.r. modulation amplitude, initiator type and concentration (note that the valid range of initiator concentrations was necessarily small), concentration of toluene, irradiation intensity, and mode of initiation (some experiments at 343 K were thermally initiated). Although tests of the independence of these experimental conditions were not exhaustive, there were no apparent correlations. The comparison between the thermally and photochemically initiated experiments at 343 K is important, due to the possibility that for the photoinitiated experiments (the majority), polymerisation may be occurring in an excited state. Although consistency was obtained, the comparison was not made at lower temperatures, and thus this possibility could not entirely be discounted. Nevertheless, the data are consistent with polymerisation occurring in the ground state of the propagating radical, even under photoinitiation conditions.

CONCLUSIONS

Given careful selection of experimental conditions, accurate values for the propagation rate coefficient can be measured by e.s.r. spectroscopy for styrene free radical polymerisation. Experiments using a relatively low radical flux, such that the propagating radical concentration was sufficiently high for quantitative e.s.r. detection, but the propagating radical chain length distribution was not dominated by very short oligomers, allowed long-chain k_p values to be measured, which were in good agreement with the IUPAC-accepted values. The good agreement between experimental techniques indicated that these techniques were measuring the same chemical processes, and that e.s.r. spectroscopy can be used quantitatively to measure k_p for free radical polymerisations.

Since other experimental techniques may be problematic for some monomers, it may be advantageous to use e.s.r. spectroscopy as an alternative experimental technique for the determination of k_p. However, due to experimental limitations, e.s.r. may be a difficult or impossible technique for acquiring accurate kinetic data for some systems. e.s.r. spectroscopy is most useful for systems in which the monomer is of low polarity, the propagating radical signal is relatively narrow (which minimises uncertainties due to baseline correction in the calculation of the propagating radical concentrations), and the average termination rate is relatively low (which gives a high propagating radical concentration). E.s.r. spectroscopy is currently the only model-independent experimental method for measuring k_p at high conversions, particularly in glassy polymers. E.s.r. spectroscopy is particularly useful for the identification of the propagating radical structure, and may also allow identification of possible impurities or side reactions, where radical species are involved.

However, extreme care must be taken when utilising e.s.r. spectroscopy for kinetic measurements. The main danger areas are: the only radical species present should be the propagating radicals, which should be positively identified (for example, use of very large modulation amplitudes may make positive identification of the radical species difficult); use of incorrect or inappropriate standards (the standard concentrations should be accurately known, prepared in an environment (solvent) as similar as possible to that in the experiments, and measured under the same experimental and instrumental parameters as in the kinetic experiments); the reaction should be in an (approximately) steady state for the duration of the experiment; the double integration step is highly prone to error, such that background correction should be carefully used, and checked by inspection of the first integral of the e.s.r. spectrum; and the rate of initiation should be kept sufficiently low such that the propagating radical distribution is dominated by chains of pentameric length or greater, which can be roughly checked by computer simulations of the distribution. Given that the above criteria are met, and an integrable propagating radical concentration exists, e.s.r. spectroscopy can be used quantitatively to measure k_p in free radical polymerisations.

Computer simulations of the propagating radical chain length distribution for this experimental system indicated that under high radical flux conditions (which are often necessary for achieving a sufficiently high radical concentration for e.s.r. observation), the distribution can become dominated by very short chains. This may be a common difficulty for other similar experimental systems, which may explain some of the past difficulties in obtaining consistent kinetic data from e.s.r. experiments. Note, however, that the quantitative behaviour changes with monomer: for example, under similar experimental conditions, the distribution for MMA is usually biased to slightly longer chains, due mainly to the higher k_p value, with a lower ratio of activation energies between propagation and monomer diffusion (which dominates the termination events, and consequently, the chain lengths in this system).

The likely dependence of k_p on chain length for very short oligomeric radicals can qualitatively explain some apparent inconsistencies in kinetic data. For example, an increase in the apparent k_p value with increasing irradiation intensity or initiator concentration is likely to be due to the propagating radicals becoming shorter with increasing radical flux. The average k_p value will consequently increase under such conditions, which is consistent with this observation. It should be noted that usually the average propagating radical chain length will decrease with temperature. If the propagating radical chains are sufficiently short, then the ratio $\langle k_{\mathrm{p,observed}}\rangle / k_{\mathrm{p,long}}$ will decrease with increasing temperature. This will result in an apparently low activation energy for propagation. Furthermore, if the initiation rates are varied widely in such systems, it may be impossible to measure self-consistent data.

To summarise, the following precautions are recommended when measuring k_p by e.s.r.

- Final MWDs should be checked where possible. If by GPC, appropriate columns and calibration are necessary.

- The e.s.r. spectra integration steps are a potential source of significant error. Care needs to be taken, and the first integrals should be checked.
- If possible, different initiators should be used under the same experimental conditions. It is especially useful to compare photochemically and thermally initiated systems at several temperatures. The apparent k_p values should be independent of initiator.
- Short-wavelength radiation should be avoided for photoinitiated experiments. Photoinitiators which absorb well into the visible region are preferable, such that high intensity UV radiation is unnecessary.
- The apparent k_p values should be independent of radical flux.
- At least one e.s.r. spectrum should be recorded at a sufficiently low modulation amplitude, such that the propagating radical can be positively identified. The propagating radical(s) should be the only e.s.r.-active species present.
- The radical flux should be kept as low as is practical, rather than attempting to maximise the e.s.r. signal.
- A steady state rate of reaction is necessary for the analysis used in this study. Some systems may not reach a true steady state, which makes analysis of the data more difficult and increases uncertainties.
- Self-consistent radical standards in appropriate solutions are very important. Standards used in this study were of similar concentration and environment to the propagating radicals. Note that standards were dissolved in toluene, since the radical concentrations decreased with time in styrene solutions.

From the experimental results and accompanying discussion, it can be concluded that e.s.r. spectroscopy can be used quantitatively to measure k_p in free radical polymerisations, given the many experimental limitations. It is likely that many previous studies have failed to meet the above criteria, thus giving unreliable or inconsistent results. The most likely source of error in many systems is introduced when attempts are made to increase the propagating radical concentration, which in turn may cause the apparent k_p value to be greater than the 'real' long-chain k_p value. It is recommended that most emphasis is placed on ensuring that the average propagating radical is 'long', rather than maximising the propagating radical concentration. If the simultaneous criteria of a sufficiently high propagating radical concentration for integration, and a sufficiently low initiation rate such that the average propagating radical is long, cannot be met, then the system is not useable (under the current experimental conditions) for the accurate measurement of k_p by e.s.r. spectroscopy. If possible, the final molecular weight distributions (*e.g.*, well-calibrated GPC using appropriate columns) should be checked to ensure that the majority of the distribution of dead chains are significantly longer than oligomeric. Finally, since photoinitiation may result in polymerisation occurring in an excited state, the Arrhenius parameters for k_p should be checked for consistency between both thermally and photochemically initiated experiments.

If these criteria can be simultaneously met, then it is likely that the system is useable for the reliable measurement of k_p by e.s.r. spectroscopy. In such cases, e.s.r. spectroscopy may be a useful alternative experimental technique for the measurement of k_p, especially for systems which may present difficulties for other experimental techniques.

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