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Determination of the propagation rate coefficient for 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate by pulsed-laser polymerization

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Abstract

The free radical propagation rate coefficient of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate was measured by pulsed-laser polymerization over the temperature range 288–323 K. The activation energy and pre-exponential factor were determined, by fitting the propagation data to the Arrhenius equation, as 19.9 kJ/mol and 1.44×10^6 l mol^{-1} s^{-1}, respectively. This value for the activation energy is significantly less than that obtained for the lower alkyl methacrylates and is similar to that previously reported for dodecyl methacrylate. The Mark–Houwink–Kuhn–Sakurada (MHKS) values for poly(3-[tris(trimethylsilyloxy)silyl] propyl methacrylate) in tetrahydrofuran were also determined using size exclusion chromatography with on-line viscometry and refractive index detectors. The molecular weight–intrinsic viscosity distributions were measured for forty-four independent samples yielding MHKS constants of 1.67×10^{-5} dl/g and 0.74 for K and α respectively.

Keywords: Propagation coefficient; 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate; Pulsed-laser

1. Introduction

A number of papers have appeared on the determination of propagation rate coefficients (k_p) for methacrylate derivatives using pulsed-laser polymerization [1–7]. There remains some confusion as to whether trends in the activation energies (E_a) and pre-exponential factors (A) can be ascribed to monomer structure. Heuts et al. [8,9] predicted a dependence of the A factor on monomer mass on the basis of theoretical studies. Three independent research groups [1–7] have studied a range of methacrylates and there is a clear trend in the k_p values at a given temperature. Each individual study has also discerned some differences among the Arrhenius parameters within the methacrylate monomer family. However, it is not clear that any significant systematic structure–reactivity trend is evident in the Arrhenius parameters (when the results from the three groups are judged together).

In this work, we study the propagation kinetics of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS), which is an important monomer in contact lens materials synthesis. The high silicon content of the monomer is important in imparting high oxygen permeability to lenses and TRIS is often used as a component in terpolymer compositions. We became interested in TRIS as a component in block and graft copolymers, for synthesising high oxygen permeability materials. As contact lenses frequently require some hydrophilicity, TRIS is often copolymerized with monomers containing hydrophilic functionality such as hydroxyl or amino groups. This requirement tends to rule out anionic polymerization methods for block and graft polymer synthesis. Consequently, we began examining free radical techniques such as atom transfer radical polymerization (ATRP), catalytic chain transfer (CCT) and reversible addition–fragmentation transfer (RAFT) as possible routes to bespoke polymer structures. In order to fully understand and control these polymerization methods, we embarked on a kinetic study of TRIS free radical polymerization. This paper describes the results obtained from experiments using pulsed-laser polymerization to measure the propagation rate coefficient of TRIS.

2. Experimental

2.1. Polymerizations

The propagation rate coefficients were measured using

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the technique of pulsed laser polymerization (PLP). Details of this technique may be found in the original paper by Olaj et al. [10] or in recent reviews [11,12]. Purified monomer and photoinitiator were weighed into pyrex sample tubes (10 mm diameter by 60 mm height), which were then sparged 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 [13]. 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 60°C.

2.2. Size-exclusion-chromatography equipment

Size-exclusion-chromatography analyses were performed on a modular system comprising a GBC Instruments LC1120 HPLC pump operating at room temperature; a SCl-10A Shimadzu autoinjector with a 99 position sample rack and variable injection loop facility; a column set, which consisted of a PL 3.0 μm bead-size guard column (50×7.5 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.[1] The eluent was THF at a flow rate 1 ml/min. Polymer analyte solutions were prepared with (accurately known) concentrations in the range 2–3 mg/ml, while sample injection volumes in the range 50–100 μl were used, depending upon the injection loop that was installed at the time. The calibration of these injection loops has been described previously [14]. Lower concentrations were used for the narrow standards, depending upon their molecular weights.

2.3. Size-exclusion-chromatography analysis

In order to measure the MHKS constants of PTRIS, the molecular weights of all samples were measured directly using the technique of differential viscometry (SEC-DV), as described previously [15]. The universal calibration curve for the DRI detector was compiled using sets of polystyrene (PSTY) (PL 1.25×10^3–9.80×10^5) and polymethylmethacrylate (PMMA) (PL 2.90×10^3–6.60×10^5) narrow polydispersity index standards. In calculating the universal calibration curve, previously measured values of the MHKS constants for PSTY and PMMA were taken from Benoit et al. [16] and Rudin and Hoegy [17], respectively. A universal calibration curve for the DV detector was compiled from these standards using the method of Suddaby et al. [18], and the SEC-DV analysis was performed using our own software[2], based on this method. Details of this calibration method are provided in a previous publication [15]. Before analysing the PTRIS 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 [14].

Having obtained the intrinsic viscosity versus molecular weight distributions of the PTRIS samples, the MHKS constants were measured by fitting of the MHKS model to the pooled molecular weight versus intrinsic viscosity data via non-linear least squares analysis. Details of this method, and our modifications to it, have been outlined previously [14]. The method was implemented using our own programs[3] written in the *Matlab* software. In performing the regression, we made use of a built-in function minimizer (called 'fmins.m') that numerically minimized the sum-of-squares of residuals via a simplex search method. Multiple initial parameter estimates were used to ensure that global (rather than merely local) minima were located.

Having obtained the MHKS constants of PTRIS, the molecular weights of all samples were obtained via conventional SEC. The molecular weights were first measured against a polymethyl methacrylate (PMMA) calibration curve. This was compiled using a set of PMMA narrow

[1] PL Caliber GPC/SEC Viscometry and LALLS Software version 6.0 Polymer Laboratories Ltd., Essex Rd., Church Stretton, Shropshire, SY6 6AX, UK 1995.

[2] Program *Suddaby. m*, written by M.D. Zammit and M.L. Coote, to be used in conjuction with *Matlab* software; details available from Prof T.P. Davis, School of Chemical Engineering and Industrial Chemistry, UNSW, Sydney 2052, Australia.

[3] Programs *nl_regr.m* and *get_cont.m* written by L.P.M. Johnson and M.L. Coote to be used in conjunction with *Matlab* software; details available from Prof T.P. Davis, School of Chemical Engineering & Industrial Chemistry, UNSW, Sydney 2052, Australia.

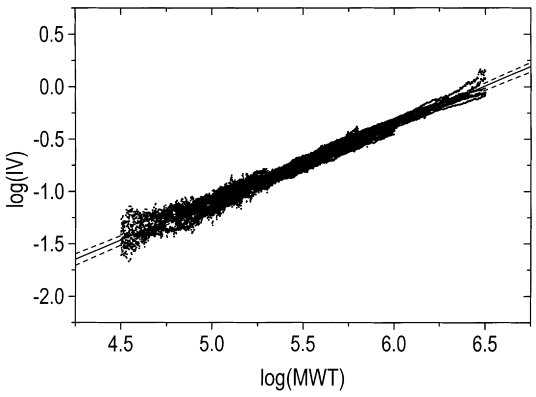

Fig. 1. Plots of the log(IV) versus log(MWT) data for the 44 TRIS samples. The solid line is the prediction of the MHS relationship using the point estimates of the MHS constants ($\log(K) = -4.7766, \alpha = 0.7362$), while the two dashed lines were obtained using two sets of MHS constants ($\log(K) = -5.000, \alpha = 0.775$ and $\log(K) = -4.550$ and $\alpha = 0.695$) taken from opposite extremes of the 95% joint confidence interval.

polydispersity index standards. The calibration and analysis was performed using PL Caliber version 6.0 GPC/SEC software (see footnote 1). 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. These k_p values were then adjusted to their correct values using the following formula [1].

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

In Eq. (1), N is given by the expression $N = [M]t_f M_{mon}$ where M_{mon} is the molecular weight of the monomer, t_f is time between laser flashes and $[M]$ is the monomer concentration. The TRIS concentrations were estimated using densities that were measured using the density bottle method. This equation enables k_p to be re-calculated for different MHKS values, without repeating the entire molecular weight analysis. Values of the MHKS constants for PMMA in THF were taken from Rudin and Hoegy [17], while those for the PTRIS samples were those obtained in the present study.

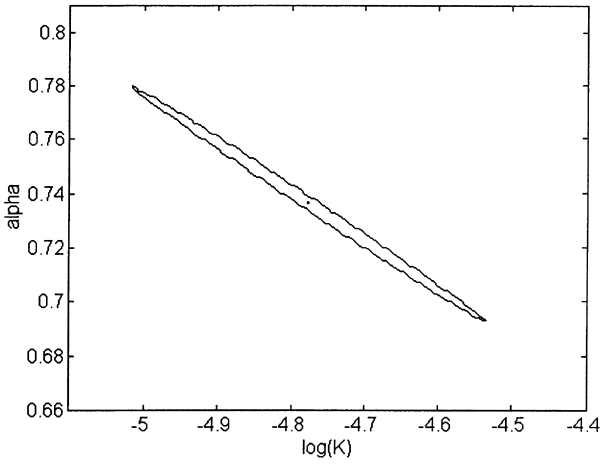

Fig. 2. The upper-bound to the 95% JCI for the MHS constants of TRIS. The JCI was calculated by assuming that the errors in the 44 different samples were independent, but the errors in the data points within an individual sample were not independent. Residuals were not weighted.

3. Results and discussion

3.1. Mark–Houwink–Kuhn–Sakurada parameters

The MHKS parameters of PTRIS in THF were measured using the technique of SEC with online viscometric detection. For a description of this technique, the reader is referred to our previous publications in this area [1]. The molecular weight (MWT) versus intrinsic viscosity (IV) distributions were measured for 44 different samples, and the linear portions of the resulting log(IV) versus log(MWT) data for each sample are plotted in Fig. 1. The MHS relationship was then fitted to the combined data using unweighted non-linear least squares analysis, thereby yielding point estimates for the MHKS constants of 1.67×10^{-5} dl/g and 0.74 for K and α, respectively. It is noteworthy that the value obtained for K is an order of magnitude lower than that of STY or MMA which is consistent with the high molecular weight of the repeat unit. A 95% joint confidence interval for these constants is plotted in Fig. 2. In calculating this joint confidence interval it was assumed that, while the errors in the 44 different samples were independent, the errors in the data points within each individual sample were not independent. As explained in our previous work [1,14], this assumption produces an approximate upper-bound to the 95% joint confidence interval. To confirm that this joint confidence interval gave a reasonable estimate of the uncertainty in the MHKS constants, we plotted the predictions of the MHKS equation for the point estimates, and also two sets of MHKS constants taken from opposite extremes of the 95% joint confidence interval, and compared these predictions with the raw log(MWT)–log(IV) data (see Fig. 1). Examining this data, it may be seen that the joint confidence interval provides a good description of the uncertainty in the MHKS constants, at least over the molecular weight range ($10^{4.5}$–$10^{6.5}$) for which the MHKS constants were measured.

3.2. Propagation rate coefficients

The molecular weight distributions of the polymers formed in the pulsed-laser polymerization process were multi-modal and ‘classical’ as shown in Fig. 3. A number of inflection points were observed and the secondary and tertiary peaks appeared at chain length multiples (2×, 3×, etc.) of the primary peak. The experimental protocol followed the guidelines suggested by an IUPAC working party [19] to ensure reliable data. The results are given in

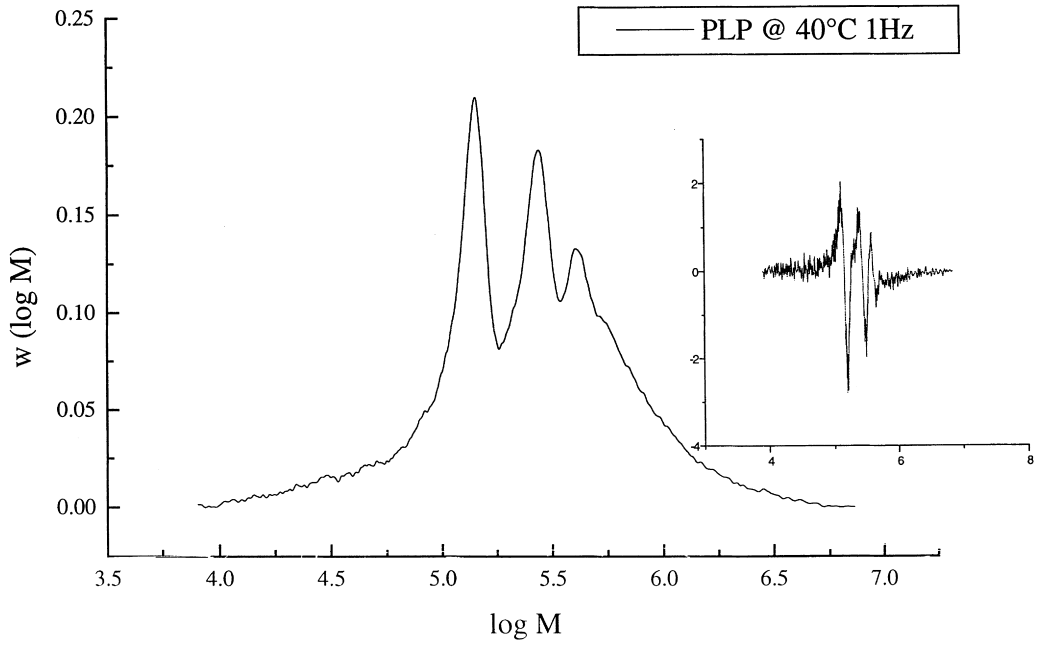

Fig. 3. Molecular weight distribution obtained from the pulsed-laser polymerization of TRIS at 40°C at 1 Hz. The inset shows the differential clearly showing the inflection points of the primary and secondary peaks.

Table 1. The Arrhenius plot is given in Fig. 4, which shows the k_p data derived from both a SEC calibration based on PMMA standards and the calibration transformed with the MHKS parameters we calculated for PTRIS. It is evident from this plot that the MHKS parameters have a significant influence on the intercept of the Arrhenius plots, however, the slope is virtually unchanged and consequently the value obtained for the activation energy, E_a, is virtually the same, regardless of the calibration (this is not a general result, it just happens to be the case for this particular polymer). The

Table 1
Data obtained from PLP experiments with TRIS

Temperature (°C)	[*M*] (mol/l)	[*I*] (mmol/l)	t_f (s)	M_{inf}, MMA	k_p, MMA (l mol^{-1} s^{-1})	k_p, TRIS (l mol^{-1} s^{-1})
15	2.20	1	0.5	67 608	145	353
15	2.20	1	0.5	67 608	145	353
15	2.20	1	1.0	134 896	145	347
15	2.20	5	0.5	67 608	145	353
15	2.20	5	1.0	131 826	142	339
15	2.20	5	1.0	134 896	145	347
25	2.18	1	0.1	19 498	211	528
25	2.18	1	0.2	35 481	192	474
25	2.18	1	0.5	87 096	189	456
25	2.18	1	1.0	169 824	184	438
25	2.18	5	0.1	17 783	193	483
25	2.18	5	0.2	36 308	197	485
25	2.18	5	0.5	87 096	189	456
25	2.18	5	0.5	87 096	189	456
25	2.18	5	1.0	169 824	184	438
40	2.15	1	1.0	257 040	283	667
40	2.15	1	1.0	263 027	290	682
40	2.15	1	0.5	141 254	311	743
40	2.15	1	0.5	141 254	311	743
40	2.15	5	1.0	239 883	264	623
40	2.15	5	1.0	239 883	264	623
40	2.15	5	0.5	128 825	284	679
40	2.15	5	0.5	128 825	284	679
50	2.13	1	1.0	338 844	377	881
50	2.13	1	1.0	323 594	360	843
50	2.13	1	0.5	165 959	369	878

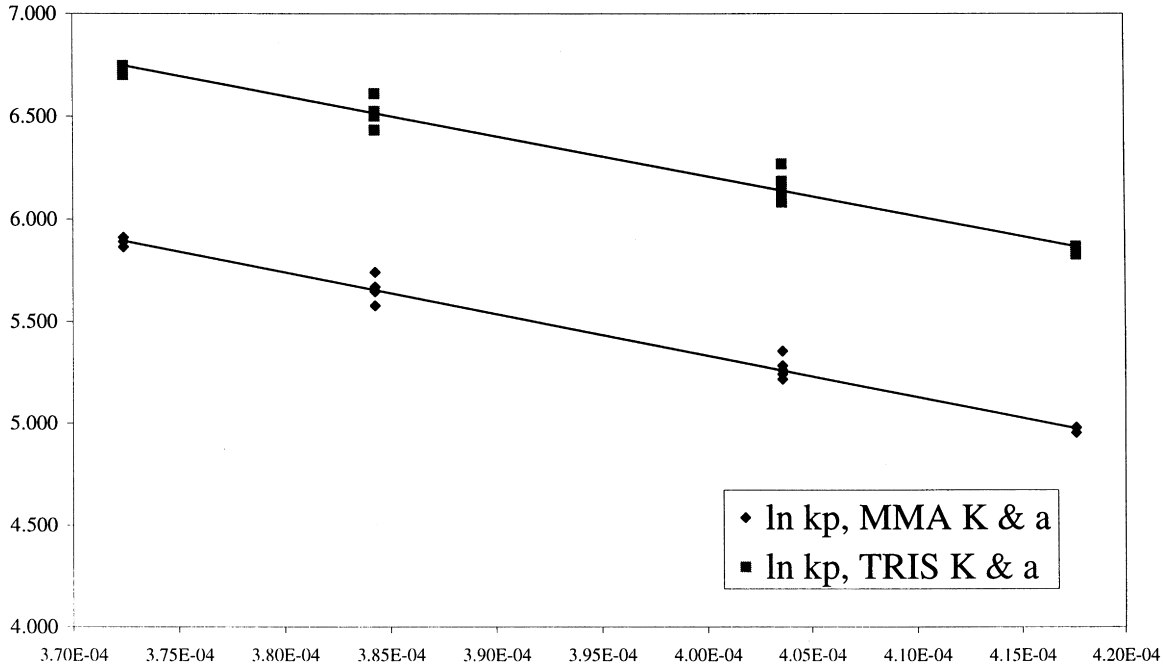

Fig. 4. Arrhenius plots for the propagation rate coefficients of TRIS, based on a PMMA SEC calibration and a calibration corrected for PTRIS using the MHKS parameters reported in the text.

point estimates of the Arrhenius parameters are shown in Table 2. It thus appears that the E_a value for TRIS propagation is similar to that obtained by Hutchinson et al. [3] for dodecyl methacrylate (DMA) i.e. the E_a value is 2–3 kJ mol^{-1} lower than the lower alkyl methacrylates. The 95% joint confidence intervals for the estimation of k_p for MMA, DMA and TRIS are shown in Fig. 5. It seems highly unlikely that the methacrylate ester chain can play any significant role in the electronic stabilisation of the radical or in moderating the reactivity of the monomer. In a previous work [1] we attributed the lower E_a value (by default) to a possible specific intramolecular interaction between the longer alkyl chain and the radical centre. If the alkyl chain is fully extended then it will remain distant

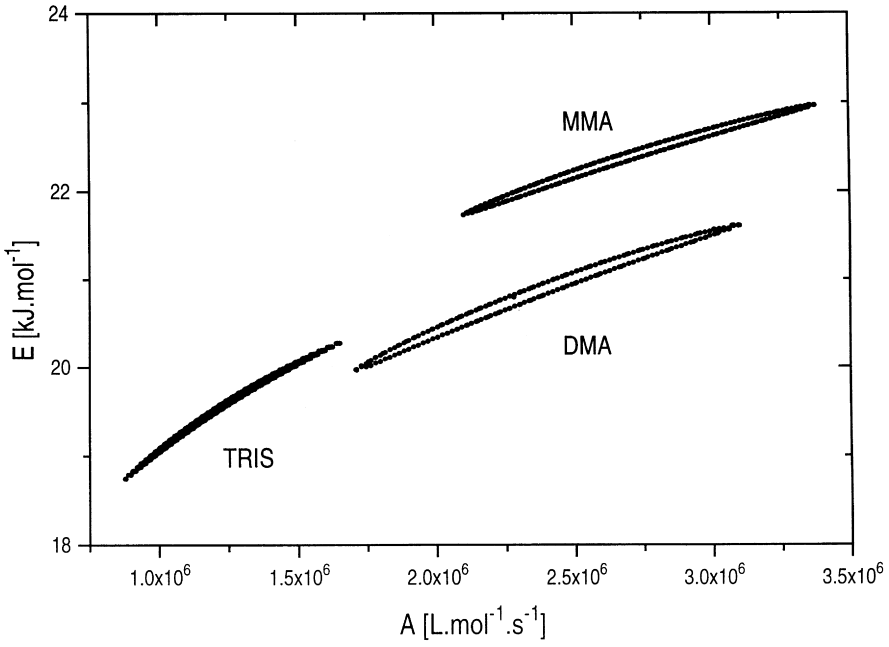

Fig. 5. 95% joint confidence contours for the Arrhenius parameters for DMA, TRIS and MMA. The data for DMA were obtained from Hutchinson et al. [3] and those for MMA were taken from an IUPAC working party [19].

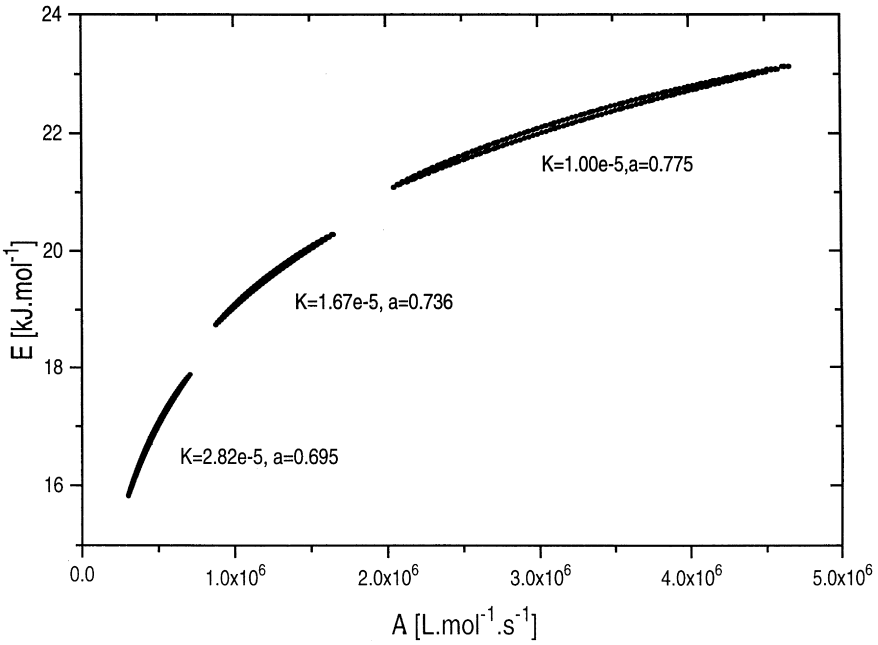

Fig. 6. 95% joint confidence contours for TRIS showing the influence of MHKS parameters on the accuracy and precision of the Arrhenius parameters.

from the radical centre and it will not influence the radical or transition state. However, more likely, the longer/bulkier sidechains adopt a coiled conformation and it becomes feasible that a through-space interaction can occur, with the potential for influencing both the radical stability and the transition state. The same explanation appears tenable here and emphasises the problems with attempting to identify trends in the Arrhenius parameters within a homologous series of monomers. The small changes in E_a and A that may be predicted theoretically are hostage to many small specific interactions—both intermolecular (solvent effects—which may also be present in the bulk monomers) and intramolecular which serve to confound structure–reactivity relationships. In addition the uncertainties introduced by the estimation and application of MHKS parameters dominate the experimental errors in PLP, as discussed previously [1,13], and thus it is vital that these are accounted for. To illustrate this we have plotted, in Fig. 6, three different 95% joint confidence contours for the activation parameters for TRIS based on MHKS parameters obtained from the 'best' point estimates and the two 'worst cases' based on the extremes of our MHKS confidence interval. Therefore, if a pessimistic interpretation of the data is applied it suggests that all the methacrylates have the same E_a and A values when experimental error is taken into account. A more optimistic scenario (to which we subscribe) is that the methacrylate k_p Arrhenius data may be falling into specific clusters with the longer/larger side-group methacrylates exhibiting significantly lower E_a values than the lower methacrylates.

Table 2
Arrhenius parameters for the propagation of TRIS

	With MMA K and α	With TRIS K and α
Eact (kJ/mol)	20.61	19.93
lnA	13.58	14.18
A (l mol^{-1} s^{-1})	7.89×10^5	1.44×10^6

Acknowledgements

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