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COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
Working Party on Modeling of Kinetics and Processes of Polymerization*

CRITICALLY-EVALUATED PROPAGATION RATE COEFFICIENTS IN FREE RADICAL POLYMERIZATIONS

I. STYRENE AND METHYL METHACRYLATE

(Technical Report)

Prepared for publication by
ROBERT G. GILBERT
Chemistry School, Sydney University, NSW 2006, Australia

*Membership of the Working Party for varying periods during which this report was prepared was as follows:

Chairman: R. G. Gilbert (Australia); *Members:* M. Buback (Germany); T. P. Davis (Australia); T. Fukuda (Japan); D. J. T. Hill (Australia); S. Beuermann (USA); R. Hutchinson (USA); A. Jenkins (UK); A. F. Johnson (UK); M. Kamachi (Japan); V. A. Kaminsky (Russia); D. V. Keight (UK); B. Klumperman (The Netherlands); M. B. Lachinov (Russia); E. L. Madruga (Spain); B. Manders (The Netherlands); G. Maschio (Italy); G. Moad (Australia); M. Nomura (Japan); K. F. O'Driscoll (Canada); O. F. Olaj (Austria); J. C. Padget (UK); F. Pla (France); G. T. Russell (New Zealand); J. Schweer (Germany); J. Shen (China); M. Stickler (Germany); D. G. Westmoreland (USA); B. Yamada (Japan).

Critically-evaluated propagation rate coefficients in free radical polymerizations—I. Styrene and methyl methacrylate (Technical Report)

Synopsis

Critically evaluated rate coefficients and confidence limits, with derived Arrhenius parameters and confidence ellipses, are reported for the propagation rate coefficients of styrene and methyl methacrylate at low conversion in bulk. Data were obtained by pulsed-laser polymerization in several laboratories, and obey the consistency criteria established for this technique. These results provide useful "benchmarks" for measurements of propagation rate coefficients by other workers and other techniques.

Introduction

Modelling and mechanisms of free-radical polymerizations are important for science and industry, but often completely different model assumptions and parameter values are reported for ostensibly the same systems. This Working Party aims to rectify this situation through international collaboration, by producing critically evaluated kinetic parameters, whose values are reliable and which can be used by the international polymer community. It has been established (refs. 1–6) that the method of choice for determining the propagation rate coefficient, k_p, is the analysis of the molecular weight distribution (MWD) of polymer produced in pulsed-laser-initiated polymerization (PLP), or "PLP-MWD", *provided* that the data are subject to consistency tests (ref. 6).

The technique involves the exposure of a system containing monomer and photoinitiator to laser pulses, each of which generates a burst of short radicals which then proceed to initiate polymerization. Some (but by no means all) chains photo-initiated by one laser pulse are terminated "instantly" by short radicals formed from the subsequent one. If one can identify υ_p, the degree of polymerization of the chains so terminated, the value of k_p can then be found from a knowledge of the monomer concentration [M], and t_f, the time between pulses:

$$\upsilon_p = k_p[M]t_f \qquad (1)$$

Modelling with a wide variety of possible kinetic schemes shows that υ_p corresponds closely to the point of inflection on the size-exclusion chromatography trace of the polymer formed in the process. The consistency tests include checking if the point of inflection is slightly below the maximum in this GPC trace, and if higher harmonics are observed above this (the latter corresponding to termination by radicals formed two or more pulses after the initiating one), with the first harmonic yielding a value of υ_p close to twice that of the first point of inflection. Other tests are that the value of k_p should be determined at various initiator concentrations and/or laser intensities, and various laser pulse rates; k_p should be independent of all of these.

The identification of the inflection point in PLP-MWD as lying very close to the "kinetic" chain length expressed in eq 1 is empirical (being verified by extensive modelling under a wide range of assumptions), and is not an exact result. Indeed, it is possible (ref. 7) to find conditions where υ_p is much closer to the maximum in the GPC trace than to the point of inflection. It is therefore emphasized that it is essential that one or more of the consistency tests be obeyed for data to be deemed reliable. Indeed, some earlier PLP-MWD data cannot be considered reliable, since the data were not subject to these consistency tests (being published before the importance of the tests was established). It is also noted that the Arrhenius parameters deduced from such data should always be reported with the associated confidence ellipse so that uncertainty may be quantified.

Results

PLP-MWD data for bulk polymerization at low conversion have been collected in a number of different laboratories. For styrene, these laboratories were located in Eindhoven (The Netherlands), Vienna (Austria), Toronto (Canada), Leverkusen and Göttingen (Germany), and Wilmington (USA). Temperatures ranged from –12 to 93°C, laser pulse frequencies from 0.1 to 10 Hz, and a variety of initiators, laser intensities, lasers and configurations were used (refs. 7–13). There was no systematic trend of k_p values with pulse frequency, etc., and hence these data are deemed to obey the consistency criteria. Figure 1 shows these data, which can be fitted by:

$$k_p = 10^{7.630}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\exp\left(\frac{-32.51\ \mathrm{kJ\,mol^{-1}}}{RT}\right) \qquad (2)$$

The 95% confidence ellipse from these Arrhenius parameters, obtained as in refs. 8 and 14, is shown in Fig. 2; the range of k_p values lying within this ellipse is shown as shading in Fig. 1.

These styrene data are in accord with k_p values obtained by some workers with very different techniques, viz., EPR (ref. 15) with particular means of calibration, etc., and emulsion polymerization (refs. 16, 17) the latter under special and unusual conditions. This is taken as confirmation of the overall correctness of the PLP-MWD method, and of the means used to obtain k_p values from these particular EPR and emulsion polymerization data.

Corresponding data for MMA (methyl methacrylate), as collected in ref. 18, have been collected from laboratories in Wilmington, Göttingen, Vienna, Toronto and Leverkusen (refs. 2, 7, 9, 12, 13, 19–21). The temperature range was –1 to 90°C, and the pulse frequency covered the range 0.5 — 25 Hz. Again, these data obey the various consistency criteria, and are fitted by:

$$k_p = 10^{6.423}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\exp\left(\frac{-22.34\ \mathrm{kJ\,mol^{-1}}}{RT}\right) \qquad (3)$$

The data and 95% confidence limits are collected in Figs. 3 and 4.

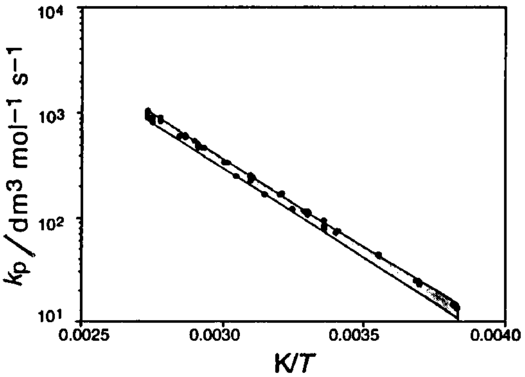

Figure 1. Arrhenius plot of rate coefficients for propagation of styrene. Points: measured by PLP-MWD; shaded area, 95% confidence limits, as given by the confidence ellipse of the Arrhenius parameters of Fig. 2. Data re-processed from ref. 6.

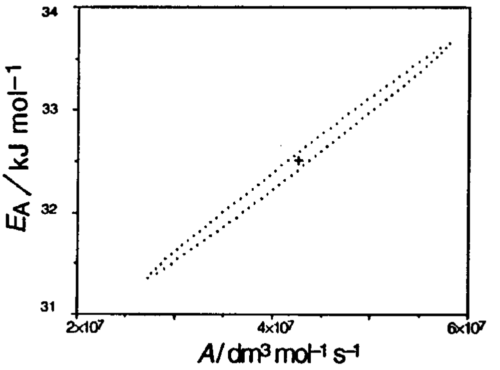

Figure 2. 95% confidence ellipse of Arrhenius parameters (activation energy E_A and frequency factor A) for styrene k_p from data of Fig. 1; the central point indicates the values of eq 2. Re-processed from ref. 6.

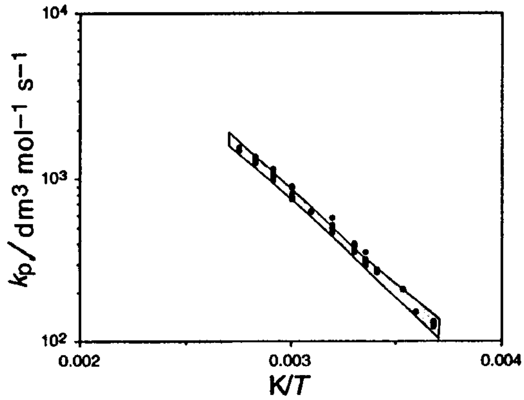

Figure 3. Arrhenius plot of rate coefficients for propagation of MMA. Points: measured by PLP-MWD; shaded area, 95% confidence limits, as given by the confidence ellipse of the Arrhenius parameters of Fig. 4. Data re-processed from ref. 18.

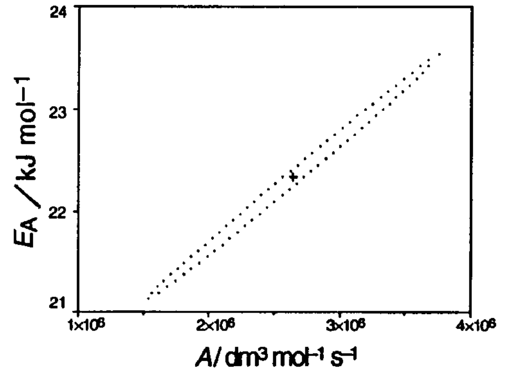

Figure 4. 95% confidence ellipse of Arrhenius parameters (activation energy $E_A$and frequency factor A) for MMA k_p from data of Fig. 3; the central point indicates the values of eq 3. Re-processed from ref. 18.

Conclusions

The rate coefficients for the propagation of styrene and MMA obtained by PLP-MWD are seen to obey the various consistency criteria, as well as in some cases being in accord with data from quite different techniques, and thus these data, and the Arrhenius parameters deduced therefrom, are deemed reliable. The critically-evaluated data and uncertainties given here are useful for (a) the checking of methods and equipment for measuring propagation rate coefficients; (b) modelling involving these monomers; and (c) are also of sufficiently high accuracy that they can be used for critical tests of the results of *a priori* calculations.

In the near future, corresponding critically-evaluated data for certain methacrylates and acrylates will be published by this Working Party.

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