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WORKING PARTY ON MODELLING OF POLYMERIZATION
KINETICS AND PROCESSES[†]: MICRO SUBGROUP[*]

# CONSISTENT VALUES OF RATE PARAMETERS IN
# FREE RADICAL POLYMERIZATION SYSTEMS

(Technical Report)

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

[*]Membership of the Micro Subgroup of the Working Party during the preparation of this report (1989–91) was as follows:

*Chairman*: R. G. Gilbert (Australia); *Members*: M. Buback (FRG); T. P. Davis (UK); L. H. Garcia-Rubio (USA); J. Guillot (France); A. Hamielec (Canada); D. Hill (Australia); M. Kamachi (Japan); B. Klumperman (Netherlands); H. K. Mahabadi (Canada); G. Moad (Australia); M. Nomura (Japan); K. O'Driscoll (Canada); O. F. Olaj (Austria); P. Pomery (Australia); J. Shen (Chinese Chemical Society, Beijing); M. Stickler (FRG); M. Tirrell (USA); M. A. Winnik (Canada); P. Zuren (Chinese Chemical Society, Beijing).

[†]Membership of the Working Party during 1989–91:

*Chairman*: K.-H. Reichert (FRG); *Members*: B. W. Brooks (UK); M. Buback (FRG); Dueflhard (FRG); A. G. Faraday (UK); R. G. Gilbert (Australia); J. Guillot (France); A. E. Hamielec (Canada); D. Hill (Australia); G. Maschio (Italy); G. Moad (Australia); H.-U. Moritz (FRG); D. H. Napper (Australia); M. Nomura (Japan); J. H. O'Donnell (Australia); K. F. O'Driscoll (Canada); O. F. Olaj (Austria); Z. Pan (Chinese Chemical Society, Beijing); W. H. Ray (USA); H. Regner (FRG); J. Shen (Chinese Chemical Society, Beijing); D. Solomon (Australia); M. Stickler (FRG); M. Tirrell (USA); J. Villermaux (France); M. A. Winnik (Canada); P. Wittmer (FRG).

# Consistent values of rate parameters in free radical polymerization systems (Technical Report)

## Abstract

To overcome the wide divergence in literature values of kinetic parameters for free radical polymerizations under ostensibly the same conditions, agreed values are given of some fundamental kinetic parameters for simple monomers: propagation rate coefficients and initiator efficiencies for styrene and MMA obtained independently using quite different methods and assumptions. These results and the methodologies employed provide useful "benchmark" tests for other workers and for new techniques. Literature discrepancies are ascribed to subtle mechanistic assumptions made in data interpretation, which are considered in detail. A series of recommendations to assist in overcoming these problems, and to highlight their origins, are presented, with emphasis placed on new techniques including those employing laser photolysis and EPR.

## INTRODUCTION

Examination of compilations of literature values of rate parameters often reveals a very wide range of reported values for any particular rate parameter. With such a wide range of values, it is often possible that conflicting mechanistic suppositions can be supported with 'evidence' from the literature. This Working Party was formed at the IUPAC polymer conference in Berlin in October 1986, with the objective of establishing firm and agreed values and methods for fundamental rate parameters in free radical polymerizations, and of critically examining important mechanisms. The aim is to establish benchmarks that can be used to establish mechanisms and to test the reliability of experimental techniques for determining kinetic parameters. The group has met thereafter in Santa Margharita (Italy), Toronto (Canada), Lyon (France), Montréal (Canada), and Sydney (Australia). The Working Party Subcommittee's deliberations have thus far resulted in two multiple-author papers (refs. 1, 2). In the first paper (ref. 1) the group pointed out some instances where values of rate parameters that are in agreement with each other have been obtained by different workers using completely independent techniques. In the second paper in this series (ref. 2), the problems of determining reliable, well characterized values of kinetic parameters in free-radical polymerizations are discussed. The origins of the fact that experimental determinations of rate coefficients of ostensibly identical systems often result in quite different values being reported can be ascribed to subtle mechanistic assumptions made in data interpretation, which are considered in detail. A series of recommendations to assist in overcoming these problems, and to highlight their origins, are presented, with emphasis placed on new techniques including those employing laser photolysis and EPR. Recent data are collected and critically examined in order to shed new light on the use of experiment to obtain requisite rate parameters. A guiding principle used in evaluating results is that rate parameters should be deduced from data in a manner that invokes minimum model-based assumptions. Since it is recognized that it is impossible to make any interpretation of data without calling upon some mechanistic assumptions, an immediate conclusion is it that it is essential that *such assumptions be clearly stated in reporting values of rate coefficients*. The information and opinions collected here should prove useful for experimental design and interpretation, and hence should be of real use to the polymer community as it seeks to understand the mechanism of free radical polymerizations. Specific topics discussed were the following.

## CONVERSION REGIMES

It is both usual and convenient to break the course of a polymerization into separate regimes. *It is therefore recommended that the usual division of the course of a polymerization into regimes of low, intermediate and high conversion be adopted as standard.* The low-conversion regime is defined as being the period of an *ab initio* polymerization (i.e., one in which there is no preformed polymer) prior to any acceleration in rate: in bulk polymerizations, that period during which classical polymerization kinetics are displayed to within a good approximation. The *high-conversion* regime is defined as beginning where propagation becomes diffusion controlled and/or initiator efficiency starts to drop dramatically. The signature of the high-conversion regime is thus a decelerating and low (relative to that of the intermediate-conversion regime) rate. Polymerizations being conducted at a temperature below the glass transition temperature ($T_g$) of the formed polymer usually have a high-conversion regime, whereas if the polymerization temperature exceeds the $T_g$ of the product polymer, there may be no high-conversion regime. The region of *intermediate conversion* is that between the low and high-conversion regimes. The mechanism that determines the rate of a reaction may change during this period of conversion.

## CHEMICAL AND PHYSICAL CONTROL OF KINETICS

A polymerization reaction occurring in a condensed phase can be (crudely) broken down into two sequential steps: (1) the encounter step, which entails the reactants diffusing towards each other (this is usually understood in terms of polymer physics); and (2) the actual reaction step, in which the reacting species overcome an activation barrier: a chemical step. Denoting $k_{diff}$ and $k_{chem}$ as the rate coefficients a polymerization reaction would have if the chemical and diffusion steps respectively of that reaction were effectively instantaneous, one can express the observed rate coefficient $k$ for that reaction as follows:

$$\frac{1}{k} = \frac{1}{k_{diff}} + \frac{1}{k_{chem}}$$

Usually $k_{diff} \gg k_{chem}$ or $k_{chem} \gg k_{diff}$; it is unusual for both the diffusion and chemical steps to be simultaneously rate-determining. However, transitions from one conversion regime to another are commonly characterized by a change in the rate determining step of at least one polymerization reaction. In the low and intermediate-conversion regimes $k_p \approx k_{p,chem}$, where $k_p$ is the rate coefficient for propagation, while in the high conversion regime it is frequently the case that $k_p \approx k_{p,diff}$.

## PROPAGATION RATE COEFFICIENTS

### Low conversion

A number of techniques appear to give consistent values of $k_p$ at low conversion (ref. 1). These techniques, which are recommended, are all 'transient' polymerization techniques and are as follows: the rotating-sector method, and in particular spatially intermittent polymerization (SIP) (ref. 3); pulsed-laser polymerization (PLP) (ref. 4) (this technique for measuring $k_p$ seems to be free of model-based assumptions, and so it is highly recommended); and time-resolved pulsed-laser polymerization (TR-PLP) (ref. 5). In aqueous phase polymerizations, the value of $k_p$ may be extremely sensitive to the pH of the system. *It is therefore recommended that pH conditions be given* in reporting measured $k_p$ values for water-soluble monomers.

The agreed $k_p$ values for different monomers at low conversion are given in ref. 1.

### Intermediate conversion

Two techniques which have been used to determine $k_p$ at intermediate conversions are TR-PLP and electron paramagnetic resonance (EPR) spectroscopy. Both have problems associated with their use: the determination of initiator efficiency with the former, and the calibration and the possibility of non-propagating free radicals with the latter. An area for future work is to understand more clearly the details of the polymerization process that EPR spectroscopy is revealing; until this issue has been better resolved, some suspicion must attend values of $k_p$ (and other rate parameters) determined using this technique. Despite this, EPR values of $k_p$ are probably accurate for systems of lower molecular weights and/or lower conversions. Trapping of radicals and/or high rates of formation of oligomers may very well be associated with a decrease in initiator efficiency at high conversion (ref. 6) which would be reflected in the molecular-weight distribution of the system. Apart from this, if two ostensibly similar polymerizing systems have quite different molecular-weight distributions, then this immediately signifies that the similarities between these systems are only superficial. It is therefore *recommended that wherever possible workers strive to characterize their experimental systems, particularly by determination of molecular-weight distributions.* Under special circumstances highly accurate intermediate-conversion values of $k_p$ can be obtained from emulsion polymerization rate data (ref. 1).

### Copolymerization systems

Just as the accuracy of the PLP and rotating sector techniques for measuring $k_p$ has been established in low-conversion homopolymerization systems, so too have these techniques been shown to be in accord in this respect for low-conversion copolymerization of methyl methacrylate and styrene (refs. 7, 8). The problem is interpreting these rates of propagation, which has usually been with the terminal or Mayo-Lewis model, invoking simple monomer reactivity ratios only. This model can explain much copolymer composition and sequence distribution data. However, the terminal model has been shown to be inadequate for describing the rate of low-conversion copolymerization of numerous monomer pairs for which this model adequately explains composition data (e.g., (refs. 7, 8). In all these cases the rate data have been explained by a penultimate-unit effect. While this does not prove that such effects are operative, it does highlight the following. (1) Even at low conversions it is at this stage necessary to invoke many more model-based assumptions in interpreting copolymerization data than in interpreting homopolymerization data. It is *therefore essential that the model employed for doing so be clearly stated in reporting interpretations of copolymerization kinetics;* (2) The sensitivity of copolymerization data to the values of model parameters should be given wherever possible, confidence limits being the usual way of expressing this sensitivity; and (3) It is important to consider if an experiment can distinguish between copolymerization models.

## TRANSFER RATE COEFFICIENTS

Chain-transfer constants have invariably been determined using Mayo plots. However, there are many difficulties with this method. These include eliminating effects from impurities (e.g., working at conversions as low as possible so as to minimize transfer to polymer) and the model-based assumptions involved in using the method. The most serious (see the section on termination) is that $k_t$ does not vary as other system variables (e.g., initiator concentration) are altered and the molecular weight of formed polymer changes. *New means of determining $k_{tr}$ are therefore needed*, to provide an independent check of values obtained using Mayo plots. Some steps in this direction have been taken (ref. 9).

## RATES OF INITIATION

The rate of initiation in a free radical polymerization is usually expressed in terms of a rate coefficient for initiator decomposition $k_d$ and an initiator efficiency $f$. Although only the value of the product $fk_d$ is important as far as polymerization is concerned, it is usual to determine both quantities. Several independent techniques are available for measuring $k_d$ and $f$ under dilute solution conditions (e.g., (ref. 1)), which yield values in acceptable agreement. Because of effects such as viscosity change as monomer is converted into polymer, $fk_d$ is a function of conversion and thus its variation with conversion needs to be determined. The various methods for determining high-conversion values of $f$ (or equivalently, rates of initiation) await application to the same system, *a project which should be carried out as a matter of priority*.

It is difficult to define the concept of initiator efficiency in a way that is satisfactory to all. Given this situation, in reporting values of $f$, (1) it is essential to define precisely what is meant by this quantity and to detail how it is measured, and (2) *it is desirable to investigate (e.g, by GPC) the extent of oligomer formation in the system being studied.*

## TERMINATION RATE COEFFICIENTS

Two basic concepts should be borne in mind in considering termination between free radicals. The first is that almost invariably experimental values of termination rate coefficients derive from the *macroscopic* relation:

$$\text{overall rate of loss of free radicals by termination} = 2{<}k_t{>}\,[\text{R}^\bullet]^2$$

(note that the factor of 2 is IUPAC-preferred) where [R$^\bullet$] is the *overall* concentration of free radicals. At a *microscopic* level, termination rate coefficients can only be defined for a specific reaction, i.e., molecular-level descriptions of termination rest on defining $k_t^{ij}$ as the rate coefficient for termination between free radicals of degrees of polymerization $i$ and $j$ respectively. Because [R$^\bullet$] is the concentration of free radicals of *all chain lengths*, termination rate coefficients ${<}k_t{>}$ obtained using this relation are some mean of $k_t^{ij}$ values. Even if two systems are such that all $k_t^{ij}$ values are the same, the values of ${<}k_t{>}$ observed in these systems will only be exactly identical if all chain-length concentrations are identical. Thus it is expected that values of ${<}k_t{>}$ will vary in otherwise identical systems as initiator concentration, for example, is varied. The second point is that if, as is always held to be the case, termination between an $i$- and a $j$-mer is diffusion controlled, then the diffusion coefficient may depend on the molecular weight of *dead* polymer chains in a polymerizing medium, and so $k_t^{ij}$ can depend on the kinetic history of a sample.

For these reasons it is clear that any factors which influence either microscopic radical concentrations or values of $k_t^{ij}$ may affect ${<}k_t{>}$. It is therefore likely that virtually any change to a polymerizing system will result in some change in ${<}k_t{>}$, although not all such changes will have a significant effect. This may explain the large variation to be found in literature values of ${<}k_t{>}$ for ostensibly similar systems. It also emphasizes the need to give *all* details of polymerization in reporting values of ${<}k_t{>}$. *Workers are especially encouraged to determine molecular-weight distributions in association with measurements of ${<}k_t{>}$.*

### Experimental methods

The best *kinetic* method for determining termination rate coefficients would seem to be after-effect experiments: using a means of initiation to build up a relatively high concentration of free radicals, then switching off the source of initiation and observing the free radical concentration as it declines due to the occurrence of termination. This observation may be effected through direct or indirect means. Other kinetic means of determining ${<}k_t{>}$ can loosely be classified as steady-state methods. Thirdly, there are means of inferring termination rate coefficients from the dynamics of non-polymerizing systems. Being indirect, these have been but little used. It follows that it is virtually impossible to compare directly values of ${<}k_t{>}$ obtained using different experimental methods, for what really needs to be compared are $k_t^{ij}$ values, although some progress here has been made (ref. 2).

## Mechanisms

Because values of $<k_t>$ are so system specific, development of means for accurately predicting this quantity is desirable. The basic problem is that theories predict the value of the microscopic quantity $k_t^{i,j}$, whereas experiments have almost exclusively measured the value of the macroscopic quantity $<k_t>$. Thus it has been difficult to evaluate properly the merit of any model for termination rate coefficients, and aided also by the large ranges to be found in literature values of $<k_t>$, many theories for predicting rates of termination have prospered. *The development of an accurate mechanistic description of intermediate-conversion termination is a matter of priority.*

## CONCLUSIONS

*(1) No interpretation of free-radical polymerization is completely 'model free', and this is a problem which is exacerbated in copolymerization. For this reason workers should always state clearly the models they have used in interpreting kinetic data.*

*(2) Workers should report experimental details as completely as is reasonably possible. On the one hand this includes providing experimental conditions; this should assist subsequent interpretation of data using alternative models. On the other hand this involves taking steps to characterize experimental systems (in particular, by determining the molecular-weight distribution of product polymer); this will aid in detecting unsuspected differences between systems for which rate parameters are being compared.*

The second Working Party paper (ref. 2) discusses the merits of many current methods for determining free-radical polymerization rate coefficients. Virtually all these methods have difficulties, although the indications are that a few of these methods are accurate. There is a clear need to develop more widely applicable means of accurately determining rate coefficients; many specific projects are suggested in the course of this paper.

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