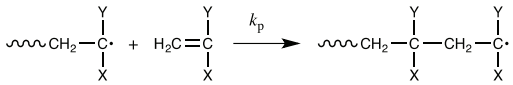
Modeling of Polymerization Kinetics and Processes—from Voting to Toting

by Gregory T. Russell

The reaction at the heart of radical polymerization is:



Termed propagation, it now occurs to the tune of a stupendous 100 million tons per annum. It is therefore no surprise that right from the moment the mechanism of radical polymerization was fir t elucidated, which was in the late 1930s, there has been strong interest in determining propagation rate coefficients k_p. After 50 years of mortal toil, the state of play in this regard was captured by Fig. 1, which presents bulk polymerization values of k_p for methyl methacrylate (Y = CH_3, X = CO–O–CH_3) from the 1989 edition of the Polymer Handbook [1], a compendium of polymer-related data.

For what is such a fundamental and important rate coefficient Fig. 1 paints a deplorable picture: there is near order-of-magnitude uncertainty in k_p ! An obvious question is whether there is something recalcitrant about the monomer methyl methacrylate, from which Perspex is made. The answer is that it has been referred to as the fruit fly of radical polymerization kinetics, for it is the most studied monomer in this regard. Therefore, one may wonder whether the problem of measuring k_p was ever taken seriously. The answer is that many upstanding groups had addressed it, and at least three Nobel Prize winners—Paul Flory, Ronald G.W. Norrish and Pierre-Gilles de Gennes—had dipped their toes into the turbulent waters of radical polymerization kinetics, so Figure 1 does not reflect that lightweights were at work!

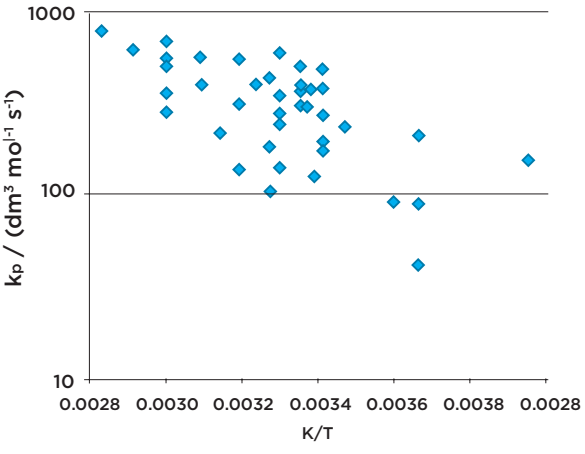


Fig. 1. Arrhenius plot of measured propagation rate coefficients, k_p, for bulk polymerization of methyl methacrylate, as of the late 1980s [1].

Of course, it is obvious from Figure 1 that there must be a fundamental problem, and in fact in the late 1970s an IUPAC Working Party under the leadership of Dr. Geoff Eastmond of the University of Liverpool was formed to investigate this [2]. Painstakingly, it was shown that the problem is not one of irreproducibility of raw data, for when laboratories in different parts of the world were given the task of determining the same raw data (*e.g.* monomer densities, for use in dilatometric studies), the results were far too close to explain the scatter. Thus, by the time the Eastmond Working Party wound up in 1987, there seemed to be cause for despair. And yet, just under a decade later, another IUPAC Working Party published Figure 2, a highly precise set of benchmark k_p values for methyl methacrylate [3], in which not one of the 1989 points remains. What had brought about this remarkable transformation?

With the benefit of hindsight, one may now discern that radical polymerization's equivalent of the 1927 Solvay Conference [4] took place in May 1987, namely the (1st) International Symposium on "Free Radical Polymerization: Kinetics and Mechanisms," held at the stunning Santa Margherita Ligure on the Italian Riviera. Pleasingly, IUPAC was right behind this conference.

The fir t significant event of 1987 conference was that Professor Bob Gilbert of the University of Sydney called a meeting of his newly minted IUPAC Working Party on "Modeling of Polymerization Kinetics and Processes", the successor to Geoff Eastmond's. A man of scientific gravitas, great charisma and irresistible drive, Bob was exactly the right person to be handed this chalice at this time. In view of the situation depicted in Figure 1, he would irreverently refer to the *Polymer Handbook* as "the book of random numbers." This was not intended as an offence, but merely to convey that the state of play was thoroughly inadequate. Indeed, Bob reports a Damascene moment at the 1987 meeting when it was proposed to decide the correct value of k_p for styrene through a vote: he knew things had to change—rate coefficient are determined by accurate measurement, not by plebiscite!

As fate would have it, the desired change was immediately facilitated by the reporting at the 1987 conference of a new method for measuring k_p, namely the "pulsed-laser polymerization – size exclusion

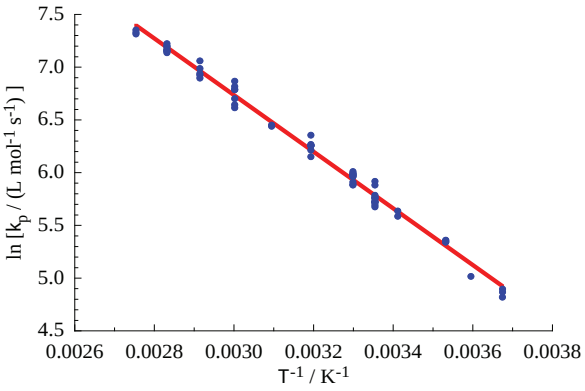


Fig. 2. IUPAC's replacement of Fig. 1: critically evaluated values of methyl methacrylate k_p, as determined by the IUPAC-recommended technique of PLP SEC [3].

chromatography" (PLP SEC) method of Professor Oskar Friedrich Olaj and colleagues at Wien Universität [5]. The cartoon of Fig. 3 depicts how this method works.

Imagine a population of creatures is born at t = 0. This is the result of the laser pulse in the left-hand box of Figure 3. Then imagine that these creatures grow at a constant but unknown rate, which it is desired to determine. This is what is happening in the second box of Fig. 3. At a known time later, action is taken to stop the growth of the creatures, while at the same time some new creatures are generated. This is the effect of the laser pulse in the third box of Figure 3, hence the "PLP" part of the experiment. The dead creatures are then taken away and their size measured—this is the "SEC" part of the experiment. Thus, one obtains the size grown in a known duration of time. The rate of growth—equivalent to k_p in radical polymerization—is thus trivially obtained. That is the beauty of the PLP SEC method.

How devoid of assumptions the PLP SEC method should be evident. A third thing that started to become crystal clear at the 1987 conference was that a phenomenon known as chain-length-dependent termination acts in such a way as to make termination rate coefficients k_t, sensitive even to the most seemingly minor variations in conditions. Given that constancy of k_t had hitherto been assumed in determining k_p values, the origin of the scatter in Figure 1 becomes clear, and the fundamental problem referred to above is revealed. The PLP SEC method was revolutionary in that it liberated k_p determinations from this yolk, for it involves no assumptions about k_t values.

This is the fertile ground that has given rise to nearly three decades of hugely successful endeavor by the Working Party (now Subcommittee) on "Modeling of Polymerization Kinetics and Processes." Of course, nothing is ever as simple as it sounds, and there is more to it than just toting the k_p values. Initially the Working Party focused on establishing "consistency criteria" to indicate if a PLP SEC experiment was generating reliable k_p values [7]. Later on, the Subcommittee played a key role in unraveling issues that beset the polymerization of acrylates (Y = H, X = CO–O–R), in which a reaction known in the vernacular as backbiting— more

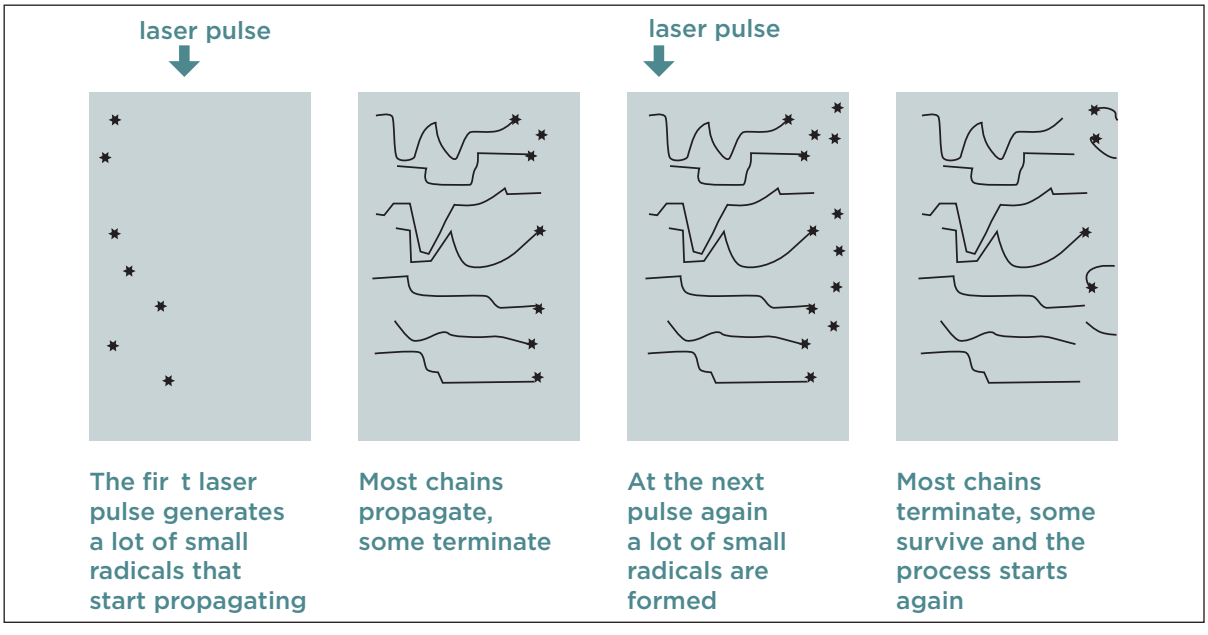


Fig. 3. Schematic representation of a PLP experiment for determination of k_p (reproduced from [6]).

formally, intramolecular chain transfer to polymer—acts to interrupt chain growth, thus compromising the simple correlation between polymer size and pulse time [8], as described above. There have been other complicating scientific issues—cottage industries always mushroom around a big, successful venture—but these have been the main ones.

Not to be underestimated is the power of IUPAC to bring people together to work in harmony. It is easy to say that anyone could have collated data to produce Figure 2. But the IUPAC imprimatur imparts Figure 2 with an authority and objectivity it would lack if any individual had produced it. This is because behind Figure 2 stands group agreement that every datum within has credibility. Essential to this process has been leadership. As already mentioned, initially this was provided by Bob Gilbert, a larger-than-life figu e who immediately grasped the transformative potency of PLP SEC when coupled with the IUPAC brand. Bob acted as a beacon to bring disparate workers into the IUPAC fold, and he brought his scientific acumen to bear on the "critical evaluation" and publication processes. Equally, he made sure there were capable leaders to follow: in turn, Michael Buback (Universität Göttingen), myself (though I say it myself), and now Robin Hutchinson (Queen's University) have led the Subcommittee—see Fig. 4.

The extent and impact of the Subcommittee's oeuvre may be gleaned from Table 1. First of all, this table shows the steady, accumulative nature of the work that has taken place—IUPAC has to wait until a critical mass of individual work has occurred before it can step in and decree a benchmark data set. Secondly it shows the variety of monomers that have been investigated by now—most (but not all) major classes of vinyl monomers are represented. But what really stands out is the impact of the work, emphasizing its value to the scientific community and the consensus it has generated. It may well be that no IUPAC scientific paper has ever been cited as heavily as the fir t paper of Table 1 [7].

There are several important things that Table 1 does not convey. One is the volume of data in each publication. For example, the most recent paper, that on vinyl acetate, contains 178 individual k_p measurements from 6 different laboratories [9]. These are serious numbers. Secondly, behind every line of Table 1 is a plot like that of Fig. 2, together with Arrhenius parameters and their uncertainties. Thirdly, these publications are more than just compilations of accurate numbers. What they have progressively revealed is that there are clear patterns in these data, something unimaginable from the 'pin-the-tail-on-the-donkey' nature of Fig. 1. Specifically, it has emerged that within a monomer family,

Fig. 4. Three Men in a Boat—(l. to r.) Greg Russell, Michael Buback and Robin Hutchinson contemplating rate coefficients under the high-temperature conditions of the Bosphorus in mid-summer (August 2013).

the activation energy, E_a, for propagation is constant whereas the pre-exponential factor increases with the size of the pendant group. Transition-state theory can explain this, while quantum chemistry can explain how E_a varies from family to family. These are tremendously useful scientific advances. Fourthly, radical polymerization has a chain-reaction mechanism, which means that its overall rate of reaction is a function of several elementary rate coefficients With the problem of k_p well and truly nailed, it has been possible to shift focus to some of these other rate coefficients most notably—but not restricted to—that for termination. The key here is that once k_p is accurately known, generally k_t may also be accurately determined. This has led to well-cited IUPAC outputs, with more in the pipeline. Mention should also be made of an important IUPAC paper on the mechanism of RAFT polymerization [10]. The point here is that while k_p has been the cornerstone of the Kinetics Subcommittee's work, other plants have been watered and have bloomed—my apologies, I cannot resist mixing good metaphors when the opportunity presents.

I should like to end with a thought-provoking observation. The annual budget of the IUPAC Polymer

Monomer(s)	Journal	Year	Citations
1. Styrene	*Macromol. Chem. Phys.*	1995	584
2. Methyl methacrylate	*Macromol. Chem. Phys.*	1997	455
3. *n*-Alkyl methacrylates	*Macromol. Chem. Phys.*	2000	201
4. Functional methacrylates	*Macromol. Chem. Phys.*	2003	84
5. *n*-Butyl acrylate	*Macromol. Chem. Phys.*	2004	256
6. Methacrylic acid	*Pure Appl. Chem.*	2007	52
7. Methyl acrylate	*Polym. Chem.*	2014	37
8. Vinyl acetate	*Macromol. Chem. Phys.*	2017	1

Table 1. Publications by the IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes on "Critically evaluated propagation rate coefficients in radical polymerization." Citation numbers are from Web of Science on 17 June 2017.

Division is USD 25k. Over the period of existence of the Subcommittee on Modeling of Polymerization Kinetics and Mechanisms, this translates into US$ 750k of funding. But the Subcommittee is only one of four in the Division. So, Table 1 has cost under US$ 200k to produce. Think now of 100 million tons of (commercial) product per annum, and the importance to this of the information in the publications of Table 1. The only possible conclusion is that this table is a billion dollar return on the cost of just 1 or 2 PhD students. And to think that people question whether IUPAC returns anything of value from its meager national subscriptions!

Lastly, I would like to thank all members of the IUPAC Subcommittee on Modeling of Polymerization Kinetics and Mechanisms who have given freely of their time to make this cooperative a success. You can read more about us on iupac.org/body/428 [11].

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11. IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes webpage, https://iupac.org/body/428

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