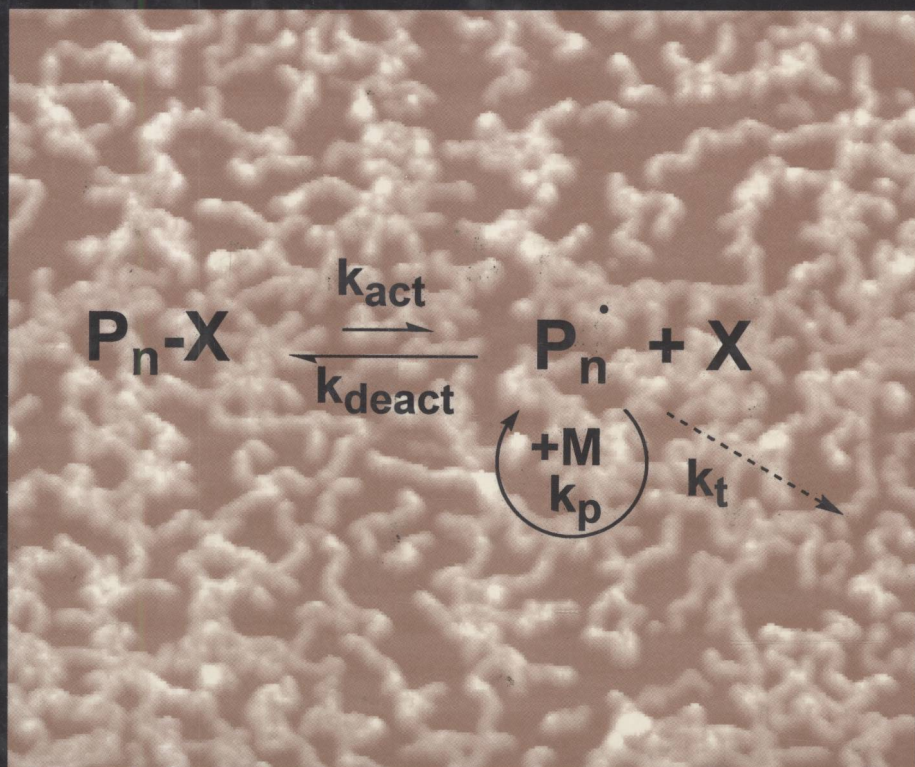


# HANDBOOK OF RADICAL POLYMERIZATION



Edited by Krzysztof Matyjaszewski  
and Thomas P. Davis

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# HANDBOOK OF RADICAL POLYMERIZATION

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# **HANDBOOK OF RADICAL POLYMERIZATION**

# INTRODUCTION

Free radical polymerization has been an important technological area for seventy years. As a synthetic process it has enabled the production of materials that have enriched the lives of millions of people on a daily basis. Free radical polymerization was driven by technological progress, and its commercialization often preceded scientific understanding. For example, polystyrene and poly(methyl methacrylate) were in commercial production before many of the facets of the chain polymerization process were understood.

The period 1940–1955 were particularly fruitful in laying down the basis of the subject; eminent scientists such as Mayo and Walling laid the framework that still appears in many textbooks. This success led some scientists at the time to conclude that the subject was largely understood. For example, in the preface to Volume 3 of the *High Polymers Series on the Mechanism of Polymer Reactions* in 1954, Melville stated “In many cases it is true to say that the kinetics and chemistry of the reactions involved have been as completely elucidated as any other reaction in chemistry, and there is not much to be written or discovered about such processes.”

From 1955 through to 1980 scientific progress was incremental, bearing out (to some limited extent) the comments made by Melville. The ability to measure rate constants accurately was limited by scientific methods and equipment. Measuring molecular weights by light scattering and osmometry was time-consuming and did not provide a visualization of the shape of the molecular weight distribution. Techniques such as rotating sector were laborious, and there were significant inconsistencies among propagation and termination rate data obtained from different groups. Indeed an IUPAC working group set up under the leadership of Dr. Geoff Eastmond had great difficulty in getting agreement among experimental rate data (via dilatometry) from different laboratories. This inability to obtain accurate and consistent kinetic data has been a major impediment to developing improved control over conventional free radical polymerization, and has led to the cynical (though amusing) labeling of the *Polymer Handbook* as the ‘book of random numbers.’ Despite these difficulties, some notable progress was made in understanding the importance of diffusion control in termination reactions and in elucidating the mechanisms of emulsion polymerization.

In the 1980s industrial and academic attention was focused on polymerization mechanisms that offered the prospect of greater control, such as cationic and anionic chain reactions. The scope of these reactions was expanded, and group transfer polymerization was invented and heralded as a major breakthrough. At that time, major investments in research and scale up were made by polymer producing companies in

an attempt to exploit the greater control offered by these improved ionic polymerizations. However, the limitations of ionic processes—intolerance to functionality and impurities—proved too difficult to overcome, and free radical polymerization proved stubborn to displace as an industrial process. The commercial driving force behind the search for control over the polymerization mechanism was the prospect of improved materials. The ability to make specific (bespoke) polymer architectures remained a powerful incentive to develop new polymerization methods. However, the lesson learned from the failure to exploit ionic mechanisms was that improved control could not come at the expense of flexibility. Consequently, free radical polymerization remained dominant because it was (relatively) easy to introduce on an industrial plant, it was compatible with water, and it could accommodate a wide variety of functional monomers.

From the mid-1980s step changes in the understanding and exploitation of free radical polymerization began to occur. The mechanism of copolymerization came under scrutiny and the general failure of the terminal model was demonstrated. Advanced laser techniques were invented to probe propagation and termination rate coefficients. This ability to accurately measure rate constants led to the establishment of IUPAC working parties to set benchmark kinetic values, and thus enhanced the ability to create computational models to predict and control free radical polymerization reactions. The cost of computation reduced substantially, and advanced modeling methods began to be applied to free radical polymerization, leading to increased understanding of the important factors governing free radical addition and transfer reactions.

Also in the 1980s the seeds were laid for an explosion in the exploitation of free radical polymerization to make specific polymer architectures by using control agents. Catalytic chain transfer (using cobalt complexes) was discovered in the USSR and subsequently developed and exploited to produce functional oligomers by a number of companies. The use of iniferters was pioneered in Japan and alkoxyamines were patented as control agents by CSIRO.

The major growth of living (or controlled) free radical polymerization occurred in the 1990s, commencing around 1994 with the exploitation of nitroxide-mediated polymerization, atom transfer radical polymerization, degenerative transfer with alkyl iodides, and addition-fragmentation transfer approaches allowing for the facile production of a multitude of polymer architectures from simple narrow polydispersity chains to more complex stars, combs, brushes, and dendritic structures. Moreover, synthesis of block and gradient copolymers enabled preparation of many nanophase separated materials.

This book aims to capture the explosion of progress made in free radical polymerization in the past 15 years. Conventional radical polymerization (RP) and living radical polymerization (LRP) mechanisms receive extensive coverage together with all the other important methods of controlling aspects of radical polymerization. To provide comprehensive coverage we have included chapters on fundamental aspects of radical reactivity and radical methods in organic synthesis, as these are highly relevant to the chemistry and physics underpinning recent developments in our understanding and exploitation of conventional and living free radical

polymerization methods. The book concludes with a short chapter on the areas of research and commercial development that we believe will lead to further progress in the near future.

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# 1 Theory of Radical Reactions

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## 1.1 INTRODUCTION

Free-radical polymerization proceeds via a chain mechanism, which basically consists of four different types of reactions involving free radicals:<sup>1</sup> (1) radical generation from nonradical species (initiation), (2) radical addition to a substituted alkene (propagation), (3) atom transfer and atom abstraction reactions (chain transfer and termination by disproportionation), and (4) radical-radical recombination reactions (termination by combination). It is clear that a good process and product

control (design) requires a thorough knowledge of the respective rates of these reactions, and, preferably, a knowledge about the physics governing these rates.

In this chapter, the role that theoretical chemistry has played and can play in further elucidating the physical chemistry of these important radical reactions will be discussed. We often wish to answer questions that cannot be addressed directly through experiments, such as “Why does this reaction follow pathway A instead of pathway B?” or “How will a particular substituent affect the rate of a reaction?” In many cases, the required information needs to be extracted from elaborate experiments that address the question in an indirect way, involving many assumptions and/or simplifications; in other cases, the required information is simply impossible to obtain by current state-of-the-art experimental techniques. In such instances, theoretical chemistry, and in particular computational quantum chemistry, can provide the chemist with the appropriate tools to address the problems directly. This is particularly true for radical reactions (where the reactive intermediates are very short-lived) and for obtaining information about the transition state of a reaction; the importance and difficulties in obtaining information regarding transition structures are evidenced by the award of the 1999 Nobel Prize for Chemistry to Zewail.<sup>2</sup> The advent of increasingly powerful computers and user-friendly computational quantum-chemistry software make computational chemistry more accessible to the nontheoretician, and it is the aim of this chapter to provide the reader with some insight into the theory and applications of theoretical chemistry in radical polymerization. This chapter is not intended to be a rigorous introduction to theoretical chemistry, but rather aims at simple qualitative explanations of fundamental theoretical concepts so as to make the theoretical literature more accessible to the nontheoretician. The reader interested in more rigorous introductions is referred to some excellent textbooks and reviews on the various topics: transition state theory,<sup>3–9</sup> statistical mechanics,<sup>10</sup> quantum chemistry,<sup>11–14</sup> and organic reactivity.<sup>15–20</sup>

First, the framework provided by the pioneers in free-radical polymerization will be discussed, as this framework has been a guide to the polymer scientist for the past decades and has provided us with a working understanding of free-radical polymerization.<sup>21</sup> This discussion will then be followed by an outline of chemical dynamics and quantum-chemical models, which can provide us with a physically more realistic picture of the physics underlying the reactions of concern. With the seemingly ever-increasing computation power, these methods will become increasingly accurate and applicable to the systems of interest to the polymer chemist. Unfortunately, this ready availability may also lead to incorrect uses of theoretical models. With this in mind, the chemical dynamics and quantum-chemical sections were written in such a way to enable the nontheoretician to initiate theoretical studies and interpret their results. Realizing that many quantitative aspects of this chapter may be replaced by more accurate computational data within a few years (months?) after publication of this book, the discussion will focus on general aspects of the different computational procedures and in which situations particular procedures are useful. Several different examples will be discussed where theory has provided us with information that is not directly experimentally accessible and where future opportunities lie for computational studies in free-radical polymerization.

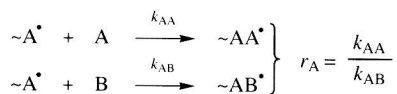
## 1.2 CLASSICAL THEORIES OF MONOMER AND RADICAL REACTIVITY

Although great progress has been made since the early 1980s in understanding radical reactivity, there seems to be a tendency among polymer chemists to think in models about radical and monomer reactivity which were laid down in the sixties and early 1970s.<sup>21</sup> Since these models have greatly influenced our thinking and the development of polymer science, they will be briefly discussed here.<sup>1,21</sup>

Traditionally, the reactivities of monomers and radicals have been studied by means of copolymerization data. In a series of monomer pairs {A, B} with fixed monomer A, the series of respective  $1/r_A$  values represents a series of relative reactivities of these monomers B toward a radical  $\sim A^\bullet$  (see Scheme 1.1).

These studies and early studies on small radicals have led to the current framework in which we tend to think about radical and monomer reactivities. The factors that govern the reactivity are generally summarized in the following four features: (1) polar effects, (2) steric effects, (3) (resonance) stabilization effects, and (4) thermodynamic effects.<sup>1,21</sup>

1. *Polar Effects.* From the numerous observations that nucleophilic radicals readily react with electrophilic monomers (and vice versa), it is concluded that polar effects can be very important in radical reactions. The importance of polar effects has been well established since the early 1980s through both experimental and theoretical studies.
2. *Steric Effects.* Perhaps the most convincing observations that steric effects play an important role in radical reactions is that the most common propagation reaction is a head-to-tail addition and that head-to-head additions hardly ever occur. Furthermore, several studies to date indicate that 1,2-disubstituted alkenes do not readily homopolymerize (although they might copolymerize quite readily), which could possibly be attributed to steric hindrance.
3. *Stabilization Effects.* These effects can arise if delocalization of the unpaired electron in the reactant and product radicals is possible. If the reactant radical has a highly delocalized electron, it will be relatively stable and have a relatively low reactivity. On the other hand, if the addition of a monomer will lead to a radical that has a highly delocalized electron, it is said that the monomer is relatively more reactive. In general, the order of reactivity of a range of monomers is the reverse of the order of reactivity of their respective derived radicals.



Scheme 1.1

4. *Thermodynamic Effects.* These effects can be ascribed to differences in the relative energies between reactants and products, lowering or increasing the reaction barrier. For many reactions, including propagation and transfer reactions, an approximate linear relationship exists between the activation energy,  $E_{\text{act}}$ , and reaction enthalpy,  $\Delta H_r$ , the so-called Bell–Evans–Polanyi relation:<sup>22,23</sup>

$$E_{\text{act}} = \rho \Delta H_r + C \quad (1)$$

where  $\rho$  and  $C$  are constants.

Attempts have been made to quantify the abovementioned concepts in several semi-empirical schemes. These schemes were developed in order to predict the reaction rate coefficients of propagation and transfer reactions, and particularly to predict monomer reactivity ratios. Here, the two most interesting among these models will be briefly described: the  $Q$ - $e$  scheme of Alfrey and Price<sup>21,24,25</sup> and the “patterns of reactivity” scheme of Bamford and co-workers.<sup>21,26–28</sup>

### 1.2.1 The $Q$ - $e$ Scheme

This scheme was one of the first to appear<sup>21,24,25</sup> and is probably still the most widely used for the semiquantitative prediction of monomer reactivity ratios. It is based on the assumptions that a given radical  $\sim A^\bullet$  has an intrinsic reactivity  $P_A$ , a monomer  $A$  has an intrinsic reactivity  $Q_A$ , and that the polar effects in the transition state can be accounted for by a factor  $e_A$ , which is a constant for a given monomer (it is assumed that  $e$  in the radical derived from a particular monomer is the same as  $e$  for that monomer). The reaction rate coefficients of the reactions shown in Scheme 1.1 may then be represented as in Eqs. (1.2a) and (1.2b), which result in the expression of Eq. (1.2c) for the resulting monomer reactivity ratio,  $r_A$ :

$$k_{AA} = P_A Q_A \exp(-e_A^2) \quad (1.2a)$$

$$k_{AB} = P_A Q_B \exp(-e_A e_B) \quad (1.2b)$$

$$r_A = \frac{k_{AA}}{k_{AB}} = \frac{Q_A}{Q_B} \exp\{-e_A(e_A - e_B)\} \quad (1.2c)$$

After defining styrene as a reference monomer, with standard  $Q = 1.00$  and  $e = -0.80$ ,<sup>29</sup> the  $Q$  and  $e$  values for other monomers can be obtained by measuring the monomer reactivity ratios. This leads to a “unique” set of  $Q$ - $e$  parameters for a wide range of monomers (there are major solvent effects on these parameters), which are relatively successful in predicting monomer reactivity ratios of any pair of comonomers. Although the scheme is fundamentally flawed in that reaction rate coefficients are not only composed of individual contributions from the two reactants but also contain a large contribution from specific interactions in the transition state of the reaction, the scheme is very successful in practical applications. The reason for this lies partially in the fact that the transition states for all propagation



reactions are rather similar, and that predictions involve the *ratios* of two rate coefficients.

### 1.2.2 Patterns of Reactivity

This approach, which is applicable to both propagation and transfer reactions, is based on Hammett-type relationships between the reaction rate coefficient and certain electronic substituents.<sup>21,26–28</sup> As in the case of the  $Q-e$  scheme, a general reactivity is assigned to the radical. In this case, however, it is apparently better defined and taken to be the rate coefficient,  $k_{tr,T}$ , of the  $H$  abstraction from toluene by the radical. The contribution by the substrate (i.e., a monomer or chain transfer agent) to the reaction rate in the absence of polar effects is given by a constant  $\beta$ . Polar effects are taken into account by using two different parameters  $\alpha$  and  $\sigma_p$  for the substrate and radical, respectively (as compared to the single  $e$  for monomer and radical in the  $Q-e$  scheme). The rate coefficient can now be expressed by

$$\log k = \log k_{tr,T} + \alpha\sigma_p + \beta \quad (1.3)$$

Although this scheme does improve on some of the assumptions made in the  $Q-e$  scheme, it still suffers from the fundamental shortcoming that a rate coefficient is not just composed of the separate individual contributions of the two reactants, but contains their interactions in the transition state. As in the case of the  $Q-e$  scheme, this scheme is rather successful in predicting monomer reactivity ratios, but since the former scheme is much simpler, it seems to be more popular with the general polymer community.

### 1.2.3 Beyond Classical Theories

It is clear that the “classical” theories have helped us greatly advance our understanding of free-radical polymerization and its development, however, these theories are now too limited to answer our current questions. Many studies in small-radical organic chemistry since the early 1980s have significantly improved our understanding of radical reactions, and together with the use of fundamental theory outlined later in this chapter, some general trends in barrier heights for radical additions have been clearly identified. The interested reader is referred to an excellent recent review article by Fischer and Radom on this topic.<sup>30</sup> After analysis of the available data on radical additions to alkenes to date, they identified the following trends in reactivity:

- Enthalpy effects as given by the Bell–Evans–Polanyi relationship [Eq. (1.1)]; these effects are always present, but may be obscured by the presence of other effects
- Polar effects, which can decrease the barrier beyond that indicated by the enthalpy effect