

Review

On the Use of Quantum Chemistry for the Determination of Propagation, Copolymerization, and Secondary Reaction Kinetics in Free Radical Polymerization

Evangelos Mavrouidakis ^{1,2}, Danilo Cuccato ^{3,*} and Davide Moscatelli ¹

¹ Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Milano 20131, Italy; E-Mails: evangelos.mavrouidakis@polimi.it (E.M.); davide.moscatelli@polimi.it (D.M.)

² Environmental Research Laboratory, National Center for Scientific Research “Demokritos”, Agia Paraskevi Attikis 15310, Greece

³ Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, Eidgenössische Technische Hochschule Zurich, Zurich 8093, Switzerland

* Author to whom correspondence should be addressed; E-Mail: danilo.cuccato@chem.ethz.ch; Tel.: +41-446-326-183; Fax: +41-446-321-082.

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Abstract: Throughout the last 25 years, computational chemistry based on quantum mechanics has been applied to the investigation of reaction kinetics in free radical polymerization (FRP) with growing interest. Nowadays, quantum chemistry (QC) can be considered a powerful and cost-effective tool for the kinetic characterization of many individual reactions in FRP, especially those that cannot yet be fully analyzed through experiments. The recent focus on copolymers and systems where secondary reactions play a major role has emphasized this feature due to the increased complexity of these kinetic schemes. QC calculations are well-suited to support and guide the experimental investigation of FRP kinetics as well as to deepen the understanding of polymerization mechanisms. This paper is intended to provide an overview of the most relevant QC results obtained so far from the investigation of FRP. A comparison between computational results and experimental data is given, whenever possible, to emphasize the performances of the two approaches in the prediction of kinetic data. This work provides a comprehensive database of reaction rate parameters of FRP to assist in the development of advanced models of polymerization and experimental studies on the topic.

Keywords: free radical polymerization; quantum chemistry; reaction kinetics; copolymerization; secondary reactions; pulsed-laser polymerization

1. Introduction

One of the most common and versatile polymerization processes for the production of macromolecular materials is the free radical polymerization (FRP). High molecular weight polymers can be easily produced even under mild polymerization conditions using only monomer and a radical initiator. Since the 1980s, half of the production of synthetic polymers has been carried out through FRP processes [1]. Nowadays, still 45% of the manufactured plastic materials and 40% of synthetic rubber are obtained by FRP processes [2]. Such processes can exploit the large variety of vinyl compounds available on the market.

On the other hand, the complexity of the kinetic scheme of FRP and the large number of reactions involved often make it difficult to achieve a nice regulation of molecular weight distribution and polymer morphology. Basically, FRP is a network of reaction steps that involve a large number of different species, including very reactive radicals, which may vary in nature within the same system. An indefinite number of reaction pathways is therefore possible. The knowledge of the corresponding kinetics is very valuable for the prediction of certain final polymer features, from the chain microstructure to the macroscopic properties [3].

The accurate determination of these kinetic parameters is as essential for the synthesis of polymer materials with specific properties as it is complicated. The need for an experimental procedure that provided an accurate estimation of the individual rate coefficients of the reactions that govern the FRP encouraged the development of the pulsed laser polymerization (PLP) technique [4]. Since its invention in the late 1980s, PLP-based techniques have substantially improved the quality of the experimental measurements of rate parameters in FRP, particularly for propagation reactions. These techniques have also been widely used for the study of the homopolymerization and copolymerization of various monomers [5–18].

Nowadays, PLP coupled with size exclusion chromatography (SEC) is the method recommended by the International Union of Pure and Applied Chemistry (IUPAC) for the measurements of propagation rate coefficients [19–22]. The propagation rate coefficients for various important monomers evaluated by PLP are listed in Table 1. It should be noted that the propagation kinetics of water-soluble monomers can be largely affected by their concentration in aqueous medium. Therefore, the monomer concentration of such systems is also indicated in Table 1. Additionally, PLP coupled with other analytical methods allows the investigation of a relatively large number of reactions in FRP. In this regard, it is important to note the impact of the use of PLP coupled with electron paramagnetic resonance (EPR) on the understanding and kinetic characterization of termination and transfer reaction steps, particularly those involving mid-chain radicals (MCR) [12,14–17].

Table 1. Propagation rate coefficients, k , and Arrhenius parameters (activation energy, E_a , and pre-exponential factor, A) of the free radical polymerization of various monomers estimated through pulsed laser polymerization (PLP) experiments.

Monomer	Year	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s)	k (50 °C, L/mol/s)	Temperature range	Reference
MA	2013	17.3	7.15	2.25×10^4	−28 to 60 °C	[18]
BA	2008	18.1	7.36	2.71×10^4	10 to 70 °C	[7]
EHA	2010	15.8	6.96	2.54×10^4	10 to 82 °C	[23]
HEA	2012	16.8	7.24	3.33×10^4	20 to 60 °C	[24]
MMA	1997	22.4	6.43	6.42×10^2	−1 to 90 °C	[21]
EMA	2000	23.4	6.61	6.69×10^2	6 to 90 °C	[22]
BMA	2000	22.9	6.58	7.53×10^2	−20 to 90 °C	[22]
DMA	2000	21.0	6.40	1.01×10^3	9 to 90 °C	[22]
HEMA	1998	21.9	6.95	2.56×10^3	−4 to 70 °C	[25]
iBMA	1997	22.5	6.50	7.26×10^2	10 to 90 °C	[26]
iDMA	1997	20.8	6.34	9.47×10^2	10 to 90 °C	[26]
EHMA	1997	20.4	6.27	9.35×10^2	10 to 90 °C	[26]
EEMA	2010	24.1	6.73	6.80×10^2	4 to 61 °C	[27]
PEGEEMA	2010	24.4	6.97	1.06×10^3	4 to 61 °C	[27]
CHMA	2003	23.0	6.80	1.20×10^3	10 to 91 °C	[28]
GMA	2003	22.9	6.79	1.22×10^3	20 to 90 °C	[28]
BzMA	2003	22.9	6.83	1.34×10^3	6 to 90 °C	[28]
iBoMA	2003	23.1	6.79	1.13×10^3	0 to 90 °C	[28]
AA (10% w/w, H ₂ O)	2003	15.4	7.82	2.14×10^5	2 to 20 °C	[29]
NVP (40% w/w, H ₂ O)	2014	18.4	6.97	9.87×10^3	−5 to 80 °C	[30,31]
NVF (40% w/w, H ₂ O)	2010	20.2	6.79	3.34×10^3	5 to 60 °C	[32]
AAM	2005	13.4	7.20	1.08×10^5	6 to 50 °C	[33]
TRIS	2000	19.9	6.16	8.74×10^2	15 to 50 °C	[34]
NVC	2003	25.3	8.00	8.10×10^3	0 to 50 °C	[35]
VneoD	1997	22.2	7.31	5.25×10^3	−21 to 21 °C	[36]
VAc	1995	20.7	7.17	6.64×10^3	10 to 60 °C	[37]
1,3-butadiene	1989	35.7	7.90	1.34×10^2	30 to 60 °C	[38]
MAN	1995	29.7	6.43	4.23×10^1	10 to 60 °C	[39]
MAA	1997	17.7	5.78	8.27×10^2	20 to 60 °C	[40]
AN	2010	15.4	6.25	5.75×10^3	2 to 76 °C	[41]
St	1995	32.5	7.63	2.37×10^2	−12 to 93 °C	[42]

Table 1. Cont.

Monomer	Year	E_a (kJ/mol)	$\lg(A)$ (A, L/mol/s)	k (50 °C, L/mol/s)	Temperature range	Reference
4-MeO-St	1999	34.9	7.80	1.43×10^2	20 to 40 °C	[43]
4-Me-St	1999	32.4	7.45	1.62×10^2	20 to 40 °C	[43]
4-F-St	1999	32.0	7.54	2.32×10^2	20 to 40 °C	[43]
4-Cl-St	1999	32.1	7.65	2.88×10^2	20 to 40 °C	[43]
4-Br-St	1999	33.9	7.98	3.14×10^2	20 to 40 °C	[43]
Chloroprene	1993	26.6	7.29	9.73×10^2	10 to 55 °C	[44]

St, styrene; MA, methyl acrylate; BA, butyl acrylate; MMA, methyl methacrylate; EMA, ethyl methacrylate; BMA, butyl methacrylate; DMA, dodecyl methacrylate; EHA, ethylhexyl acrylate; HEA, hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; AA, acrylic acid; iBMA, isobutyl methacrylate; iDMA, isodecyl methacrylate; EHMA, 2-ethylhexyl methacrylate; AAm, acrylamide; TRIS, 3-(tris(trimethylsilyloxy)silyl) propyl methacrylate; NVC, *N*-vinylcarbazole; VneoD, Vinyl neo-Decanoate; VAc, vinyl acetate; MAN, methacrylonitrile; MAA, methacrylic acid; AN, acrylonitrile; EEMA, 2-ethoxyethyl methacrylate; PEGEEMA, poly(ethylene glycol) ethyl ether methacrylate; CHMA, cyclohexyl methacrylate; GMA, glycidyl methacrylate; BzMA, benzyl methacrylate; iBoMA, isobornyl methacrylate; PMOS, *p*-methoxystyrene; PMeS, *p*-methylstyrene; PFS, *p*-fluorostyrene; PCIS, *p*-chlorostyrene; PBrS, *p*-bromostyrene.

Nevertheless, many important kinetic steps are not yet accessible by experiments, or at least an accurate and sufficiently reliable determination of the corresponding rate coefficients is not yet achievable. For instance, the kinetic characterization of secondary reactions such as backbiting, MCR propagation, β -scission, and intermolecular chain transfers is often not a trivial task, especially concerning some novel and attractive acrylate polymer systems involving fully or partially ionized species. Even the simple propagation step turns out to be a difficult one to deal with if it is inserted in the context of copolymerization; indeed, no direct access to cross-propagation reaction kinetics can be obtained experimentally.

2. Quantum Chemistry

The development of computational chemistry and specifically of the advanced methods based on quantum mechanics (QM) has provided a powerful alternative approach to the investigation of reaction kinetics in FRP as reported in literature by Coote and Lin [45]. Computational methods can be applied to the study of individual reactions without the limitations of an experimental investigation, such as restricted ranges of temperature operability and toxicity of the materials. Moreover, with the use of QC one can focus on individual reaction pathways, which are not directly accessible by experiments. In this way, the complex kinetic scheme of FRP can be investigated with a high level of detail; the relevance of very specific reactions and their contribution in the polymerization mechanism can be understood and quantified.

Nowadays, a plethora of commercial and academic software packages can be adopted to perform QC calculations. Most common commercial ones include amsterdam density functional program package (ADF) [46], general atomic and molecular electronic structure system (GAMESS) [47], Gaussian [48],

Jaguar [49], MOLCAS [50], MOLPRO [51], Q-CHEM [52], Spartan [53], and Turbomole [54], while software packages such as advanced concepts in electronic structure (ACES) [55], BigDFT [56,57], CP2K [58], and FreeON [59] are free licensed. All of the reported software packages include the Hartree–Fock (HF) method [60] as well as the density functional theory (DFT) [61], which are the most widely adopted ones in the computational modeling of FRP kinetics.

QM approaches have reached a good level of reliability through a series of studies where the reported methods were applied to the kinetics investigation of several FRP systems and the obtained results were then compared to experimental data, whenever they were available. It is worth mentioning that a better description of reactive systems can be achieved by applying a higher level of theory calculations. Unfortunately, computer power is not yet sufficient to treat system with a very large number of electrons as it happens for polymers. Accordingly, the use of composite methods that can be implemented to treat different portion of the molecule at different levels of theory is proposed [45]. In many cases, the provided accuracy was found to be satisfactory compared to experimental uncertainties, although it is worth noting that more convincing results have been obtained so far for the reactivity ratios rather than for the absolute kinetic coefficients.

QM approaches are adopted to accurately determine molecular geometries (bond lengths, bond angles, and torsional angles). Starting from these data, frequencies of molecular species, energetic reaction profiles, vibrational transition state structures, and reaction frequency factors can be obtained explicitly and directly [62–66]. The rate constant of reactions involved in a FRP system can be expressed through the Arrhenius equation. Two parameters are then required to determine the kinetic constant: the frequency factor, A , and the activation energy, E_a . These parameters are evaluated through the classic transition state theory (TST) as:

$$k(T) = A e^{\left(\frac{-E_a}{k_b T}\right)} = \frac{k_b T}{h} \frac{Q^\ddagger}{Q^R} e^{\left(\frac{-E_a}{k_b T}\right)} \quad (1)$$

where k_b and h are the Boltzmann and Plank constants, respectively; in addition, T is the temperature, E_a is the activation energy of the process calculated from the difference between the electronic energy of the transition state (TS) and the energy of the reactants (including zero-point energy), and Q represents the product of the partition functions (q^{trans} , q^{vib} , q^{rot} and q^{el}) for the transition state (‡) and reactants (R). In particular, q^{el} is the electronic partition function while q^{trans} , q^{vib} and q^{rot} are the translational, vibrational, and rotational partition functions, respectively, calculated according to the following equations:

$$q^{\text{trans}} = \frac{(2\pi m k_b T)^{\frac{3}{2}}}{h^3} V \quad (2)$$

$$q^{\text{vib}} = \prod_{i=1}^{N_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_b T}\right)} \quad (3)$$

$$q^{\text{rot}} = \frac{8\pi^2(2\pi k_b T)^{\frac{3}{2}} \sqrt{I_x I_y I_z}}{\sigma h^3} \quad (4)$$

where V is the volume, m the particle mass, ν_i the vibrational frequency, $I_x I_y I_z$ the product of the three rotational constants, and σ the rotational symmetry number [67–69].

In general, geometries can be predicted with a high accuracy. The estimation of the activation energy suffers from uncertainty that is commonly assumed to be within 4 kJ/mol, while the larger inaccuracy

is found in the determination of the pre-exponential factor [45,70]. That is the reason why QC better estimates reactivity ratios, for which systematic errors are substantially decreased.

The computational results of the most relevant kinetic investigations on FRP that have been performed so far using QM methods are discussed hereinafter. Computational approaches were first applied to the kinetic characterization of propagation reactions of small radicals, and then progressively moved towards the investigation of larger molecules [71,72]. The development of cost-effective methods, such as those based on the DFT, in combination with the increasing power of the calculators has made possible of scale-up, which was required to investigate chain-length dependency of rate coefficients and lately the reactivity of MCRs. Therefore, the study of ultimate and penultimate unit effects in copolymer propagation as well as of a large variety of chain-transfer reaction was made feasible. The body of the review is structured by dedicating the sections to specific classes of reactions (*i.e.*, initiation and propagation, propagation in copolymerization, and secondary reactions), according to how they have been chronologically approached by QC investigations, trying to critically evaluate reported results, assisting for a future development.

3. From Initiation to Propagation

Several *ab initio* studies were dedicated to the investigation of Arrhenius parameters for the reactions of radical addition to the double bond in the late 1980s and the beginning of 1990s. The addition of a methyl radical to various moieties was first studied [73–75]. Later, the addition of larger radicals to alkenes was investigated, clarifying whether an enthalpy or a polar effect governs the radical reactivity [76]. These preliminary studies proved that the obtained results greatly depend on the selected computational method.

In the mid-1990s, great efforts were made to clarify which computational methods were best suited to the estimation of the Arrhenius parameters of radical addition to alkenes [65,77,78]. Different levels of theory were applied on various propagation reactions and a suitable approach for the prediction of energy barrier was proposed. In these studies, it was proposed that the penultimate unit could significantly affect the estimated values of the frequency factor for radical addition reactions. Some preliminary QC studies examined the presence of the penultimate unit effect on the computational predictions in the radical polymerization field [79–81].

All of the studies reported previously paved the way for the elaboration of the milestone study by Fischer and Radom, who studied the factors that control the addition of various carbon-centered radicals to alkenes [62]. In this study, they found that the predictions of the rate coefficients are more sensitive to the choice of the theoretical procedure than to the choice of the basis set. It was also demonstrated that there is a direct correlation between the applied level of theory used and the accuracy of the obtained results. In particular, as the level of theory increases, the deviation of computational results from experimental values decreases.

As anticipated, the development of the computational methods and the increase of the computing power enabled the study of addition reactions for larger radicals [68,82,83]. Therefore, the computational studies were moved from the radical initiation-like reactions discussed above to the true propagation reactions in FRP. The first computational studies of propagation reactions of FRP have been performed for homopolymer system of small molecules. In particular, propagation reaction of alkenes that are

characterized by very simple molecular structures such as ethene [84,85], vinyl chloride [86,87], and acrylonitrile [86–88] were studied. Gradually, the interest was turned to the study of homopolymer systems of more complex monomers such as styrene and various acrylates [66,89] and to that of monomers with larger substituent [88,90] such as α -substituted acrylates [91].

From the study of the aforementioned monomers with large substituent groups arose the need for the structural study of the reactants and the products of the propagation reactions. The presence of large or structurally complex substituent groups increases the number of the rotational degrees of freedom of the moieties, a factor that can significantly affect the reactivity of the radicals. Several studies have been focused to highlight the correlation between the geometries of the radicals and their reactivity [92–94].

In addition, the presence of chain length effect and intramolecular interactions were investigated through QC simulations for simple homopolymer systems [91,93,95]. The investigation of these issues needs to be addressed in order to estimate with accuracy the propagation reaction rates. Computational results obtained for the propagation reaction rate coefficients for the homopolymerization of various monomers are presented in Table 2.

Table 2. Propagation rate coefficients, k , and Arrhenius parameters (activation energy, E_a , and pre-exponential factor, A) of the free radical polymerization of various monomers estimated through quantum chemistry (QC) simulations.

Monomer	Method	Year	E_a (kJ/mol)	$\lg(A)(A,$ L/mol/s)	k (50 °C, L/mol/s)	Reference
St	B3LYP/6-31G(d,p)	2011	34.7	8.42	6.43×10^2	[96]
	BP86/cc-PVTZ (corrected with CCSD)	2009	41.5	6.57	7.22×10^{-1}	[97]
	B3LYP/6-311+G(d,p)// B3LYP/6-31G(d,p)	2009	34.6	8.25	4.51×10^2	[98]
MA	B3LYP/6-31G(d,p)	2011	27.4	8.55	1.31×10^4	[96]
	G3(MP2)-RAD// B3LYP/6-31G(d)	2010	21.8	7.50	9.43×10^3	[99]
	BP86/cc-PVTZ (corrected with CCSD)	2009	23.8	6.14	1.95×10^2	[97]
	MPWB1K/6-311+G(3df,2p)// B3LYP//6-31+G(d)	2009	24.3	6.52	3.89×10^2	[91]
	MPWB1K/6-31G(d,p)// B3LYP//6-31G(d)	2008	21.5	7.78	2.01×10^4	[89]
BA	B3LYP/6-31G(d,p)	2011	26.1	8.36	1.38×10^4	[96]
EA	B3LYP/6-31G(d,p)	2011	27.0	8.44	$1.18 \times 10^{10^4}$	[96]
HEA	B3LYP/6-31G(d,p)	2012	22.5	7.66	1.05×10^4	[24]
MMA	MPWB1K/6-31G(d,p)// B3LYP//6-31G(d,p)	2015	11.1	4.38	3.84×10^2	[100]
	B3LYP/6-31G(d,p)	2011	33.1	8.01	4.54×10^2	[96]
	BP86/cc-PVTZ (corrected with CCSD)	2009	26.0	6.06	7.16×10	[97]

Table 2. Cont.

Monomer	Method	Year	E_a (kJ/mol)	$\lg(A)(A,$ L/mol/s)	k (50 °C, L/mol/s)	Reference
MMA	B3LYP/6-311+G(d,p)// B3LYP/6-31G(d,p)	2009	26.0	7.10	7.86×10^2	[98]
	MPWB1K/6-31G(d,p)// B3LYP//6-31G(d)	2008	22.7	6.19	3.30×10^2	[89]
BMA	B3LYP/6-311+G(d,p)// B3LYP/6-31G(d,p)	2009	26.5	7.57	1.92×10^3	[98]
GMA	B3LYP/6-311+G(d,p)// B3LYP/6-31G(d,p)	2009	27.5	7.45	1.01×10^3	[98]
HEMA	B3LYP/6-311+G(d,p)// B3LYP/6-31G(d,p)	2009	26.8	7.10	5.83×10^2	[98]
	B3LYP/6-311+G(d,p)	2010	29.7	7.33	3.36×10^2	[101]
VAc	G3(MP2)-RAD// B3LYP/6-31G(d)	2010	17.6	6.10	1.79×10^3	[99]
	BP86/cc-PVTZ (corrected with CCSD)	2009	23.9	6.61	5.56×10^2	[97]
VDF	MPWB1K/6-31G(d,p)// B3LYP/6-31G(d,p)	2014	20.5	6.62	2.02×10^3	[102]
HFP	MPWB1K/6-31G(d,p)// B3LYP/6-31G(d,p)	2014	12.6	3.85	6.49×10	[102]
TFE	MPWB1K/6-31G(d,p)// B3LYP/6-31G(d,p)	2014	10.6	6.14	2.67×10^4	[102]
BCA	MPWB1K/6-31G(d,p)// B3LYP//6-31G(d,p)	2015	17.5	3.95	1.32×10	[100]
AA	BP86/cc-PVTZ (corrected with CCSD)	2009	24.2	6.29	2.38×10^2	[97]
	B3LYP/6-31+G(d)	2004	23.3	7.57	6.34×10^3	[103]
MAA	BP86/cc-PVTZ (corrected with CCSD)	2009	29.0	6.17	3.02×10	[97]
NVP	BP86/cc-PVTZ (corrected with CCSD)	2009	33.2	6.74	2.35×10	[97]
AN	B3LYP/6-31G(d,p)	2011	31.4	8.74	4.59×10^3	[96]
	G3(MP2)-RAD// B3LYP/6-31G(d)	2006	22.4	6.40	5.99×10^2	[86]
EHMA	MPWB1K/6-311+G(3df,2p)// B3LYP/6-31+G(d)	2012	24.4	5.26	2.06×10	[93]
	MPWB1K/6-31G(d,p)// B3LYP/6-31G(d,p)	2012	23.5	7.95	1.41×10^4	[104]
VC	B3LYP/6-31G(d,p)	2011	23.7	9.03	1.57×10^5	[105]
	BMK/6-311+G(3df,2p)// B3LYP/6-31G(d)	2007	32.7	3.90	4.09×10^{-2}	[106]
	G3(MP2)-RAD// B3LYP/6-31G(d)	2006	17.2	6.59	6.43×10^3	[86]

St, styrene; MA, methyl acrylate; BA, Butyl acrylate; EA, ethyl acrylate; MMA, methyl methacrylate; EMA, ethyl methacrylate; BMA, butyl methacrylate; HEA, hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; VAc, vinyl acetate; VDF, vinylidene fluoride; HFP, hexafluoropropylene; TFE, tetrafluoroethylene; BCA, butyl cyanoacrylate; AA, acrylic acid; AN, acrylonitrile; GMA, glycidyl methacrylate; EHMA, ethyl a-hydroxy methacrylate; VC, vinyl chloride; NVP, *N*-vinylpyrrolidone.

A comparison between computational and experimental results for the estimation of propagation kinetics is provided in Figure 1. For each homopolymer system, the relative distance between experimental and computational predictions of activation energy, pre-exponential factor, and rate constant are reported. It should be noted that only the systems for which both computational and experimental data were available are reported in Figure 1.

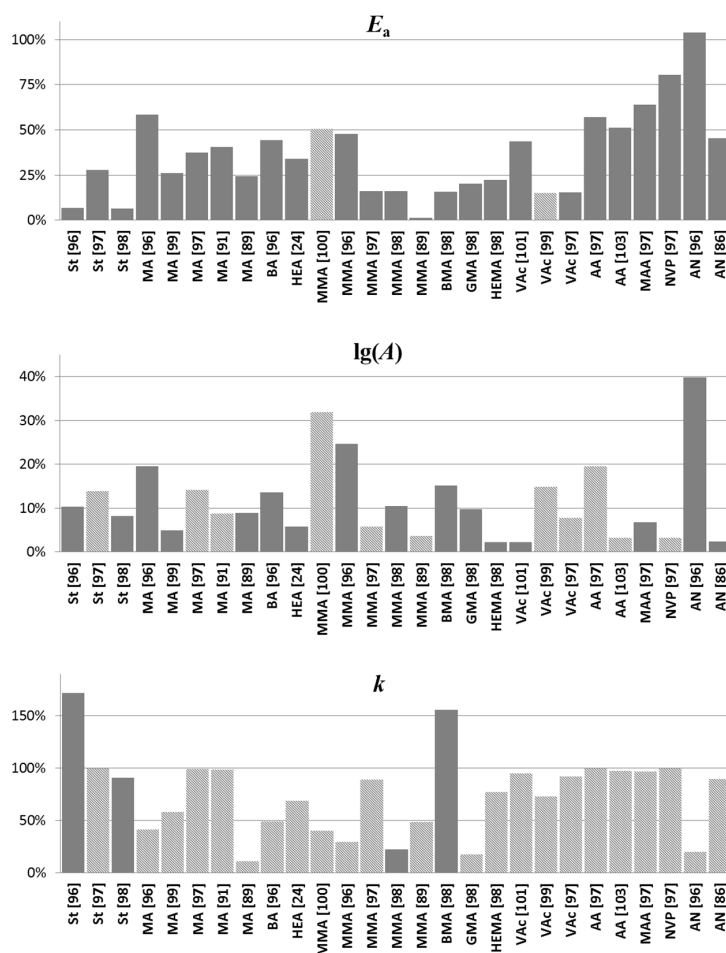


Figure 1. Mean unsigned error between experimental and computational results (*cf.* data in Tables 1 and 2 respectively) of activation energy, E_a , pre-exponential factor, $\lg(A)$, and rate constant at 50 °C, k , for the propagation reactions of various FRP systems. For each column, the number between square brackets indicates the literature source of the computational value adopted, with reference to the data in Table 2. The QC data either overestimate (filled columns) or underestimate (striped columns) the corresponding experimental parameters.

4. Copolymerization

The development of computational approaches suited to accurately investigate the addition reactions of large radicals and the chain length effect directed interest to copolymer systems. Reactions that could be in principle considered as copolymerization were first studied in the early 2000s [68]. However, the first complete computational study of a copolymer system was reported only a couple of years later. Namely, the copolymerization of ethylene with vinyl acetate was studied extensively and the kinetics of all the propagation reactions involved in its FRP process were characterized [107].

Since then, many copolymer systems of common acrylates and methacrylates, styrene, and functional acrylates as well as of other common monomers were studied applying both the terminal model (TM) [108] and the penultimate unit effect (PUE) [109,110] model [101,107,111–115], which are detailed in Figure 2. A list of relevant computational results for the copolymer systems studied by the application of QM methods is presented in Table 3. Whenever available, experimental results for the same systems are listed as well.

The study of copolymerization systems via QC leads to a better estimation of kinetic parameters compared with the study of homo-propagation reactions. As anticipated in the Quantum Chemistry Section, reactivity ratios are less affected by systematic errors and uncertainties are mutually eliminated allowing a good evaluation of kinetic parameters of primary importance in the polymer science, as is the case of the parameters reported in Table 3. Due to the huge number of possible copolymer systems of interest and the effort that has to be devoted for the experimental determination of kinetics in copolymer systems, QC represents a powerful tool for the study of copolymer reaction engineering.

$$\begin{aligned}
 & \text{Terminal model} \\
 & RM_i^* + M_j \xrightarrow{k_{p,ij}} RM_iM_j^* \quad i, j = 1 \text{ or } 2 \\
 & \left. \begin{aligned} r_i &= \frac{k_{p,ii}}{k_{p,ij}} \\ F_i^{inst} &= \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_j f_j^2} \\ k_{p,cop} &= \frac{r_i f_i^2 + 2f_i f_j + r_j f_j^2}{\left(\frac{r_i f_i}{k_{p,ii}}\right) + \left(\frac{r_j f_j}{k_{p,jj}}\right)} \end{aligned} \right\} i \neq j \text{ and } i, j = 1 \text{ or } 2 \\
 & \text{Penultimate unit model} \\
 & RM_iM_j^* + M_k \xrightarrow{k_{p,ijk}} RM_iM_jM_k^* \quad i, j, k = 1 \text{ or } 2 \\
 & \left. \begin{aligned} r_i &= \frac{k_{p,iii}}{k_{p,ijj}} \quad s_i = \frac{k_{p,jii}}{k_{p,iii}} \quad r_i' = \frac{k_{p,jii}}{k_{p,ijj}} \\ \bar{r}_i &= r_i' \left(\frac{f_i r_i + f_j}{f_i r_i' + f_j} \right) \quad \bar{k}_{p,ii} = k_{p,iii} \left(\frac{f_i r_i + f_j}{f_i r_i' + f_j} \right) \\ F_i^{inst} &= \frac{\bar{r}_i f_i^2 + f_i f_j}{\bar{r}_i f_i^2 + 2f_i f_j + \bar{r}_j f_j^2} \quad k_{p,cop} = \frac{\bar{r}_i f_i^2 + 2f_i f_j + \bar{r}_j f_j^2}{\left(\frac{\bar{r}_i f_i}{k_{p,ii}}\right) + \left(\frac{\bar{r}_j f_j}{k_{p,jj}}\right)} \end{aligned} \right\} i \neq j \text{ and } i, j = 1 \text{ or } 2 \\
 & \text{Implicit penultimate unit model: } \bar{r}_i = r_i = \frac{k_{p,ii}}{k_{p,ij}} \quad i \neq j \text{ and } i, j = 1 \text{ or } 2
 \end{aligned}$$

Figure 2. Definition of reactivity ratios and fundamental equations of the terminal and the penultimate unit models of copolymerization for a binary system. RM_i^* , radical with terminal monomer unit of type i ; M_j , monomer of type j ; k , propagation rate coefficient; r , monomer reactivity ratio; F , instantaneous copolymer composition; f , composition of the monomer phase; $RM_iM_j^*$, radical with terminal monomer unit of type j and penultimate unit of type i ; s , radical reactivity ratio.

Table 3. Parameter values of the reactivity ratios of various copolymer systems estimated by QC and comparison with experimental data.

Copolymer System	Computational						Experimental				
	Method	Copolymerization Model	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference	
ST/MMA	B3LYP/6-31G(d,p)	TM, IPUE	40	2011	$r_1 = 0.53; r_2 = 0.68;$ $s_1 = 0.23; s_2 = 0.99$	[96]	40	1985	$r_1 = 0.52; r_2 = 0.46;$ $s_1 = 0.30; s_2 = 0.53$	[110]	
		TM	100	2009	$k_{p,cop} = 5.05 \times 10^3$	[98]	20	1997	$r_1 = 0.39; r_2 = 0.51$	[116]	
ST/HEMA	B3LYP/6-31G(d,p)	TM	100	2012	$r_1 = 0.20; r_2 = 0.51$	[114]	50	2009	$r_1 = 0.27; r_2 = 0.49;$ $s_1 = 0.38; s_2 = 1.34$	[98]	
	M06-2X/6-31G(d,p)	TM	25	2014	$r_1 = 0.05; r_2 = 0.65$	[117]					
	B3LYP/6-31G(d,p)	TM	100	2009	$k_{p,cop} = 12.37 \times 10^3$	[98]					70
ST/GMA	B3LYP/6-31G(d,p)	TM	100	2012	$r_1 = 0.34; r_2 = 0.56$	[114]	50–160	2008	$r_1 = 0.31; r_2 = 0.51;$ $s_1 = 0.28; s_2 = 1.05;$	[118]	
		TM	100	2009	$k_{p,cop} = 7.37 \times 10^3$	[98]	70	2008	$k_{p,cop} = 1.64 \times 10^3$	[118]	
ST/BMA	B3LYP/6-31G(d,p)	TM	100	2012	$r_1 = 0.46; r_2 = 0.60$	[114]	50–150	2006	$r_1 = 0.61; r_2 = 0.42;$ $s_1 = 0.44; s_2 = 0.62$	[119]	
		TM	100	2009	$k_{p,cop} = 5.39 \times 10^3$	[98]	70–140	2006	$k_{p,cop} = 1.23 \times 10^3$	[119]	
ST/HEA	B3LYP/6-31G(d,p)	TM	50	2011	$r_1 = 0.31; r_2 = 0.14$	[120]	60	1998	$r_1 = 0.46; r_2 = 0.20$	[121]	
		EPUE	50	2012	$r_{11} = 0.72; r_{21} = 0.57;$ $r_{12} = 0.38; r_{22} = 0.62;$ $s_1 = 0.72; s_2 = 3.01$	[24]	50	2012	$r_1 = 0.44; r_2 = 0.18;$ $s_1 = 3.00; r_1 = 0.91$	[24]	
ST/MA	B3LYP/6-31G(d,p)	TM	25	2011	$r_1 = 0.22; r_2 = 0.11$	[82]	25	1991	$r_1 = 0.73; r_2 = 0.19$	[122]	
MMA/MA	MPWB1K/6-31G(d,p)	TM, IPUE	23	2008	$r_1 = 2.99; r_2 = 0.38;$ $s_1 = 1.71; r_1 = 0.39$	[115]	50	1971	$r_1 = 2.23; r_2 = 0.36$	[123]	
		EPUE	23	2008	$r_{11} = 2.81; r_{21} = 3.17;$ $r_{12} = 0.38; r_{22} = 0.37;$ $s_1 = 1.71; s_2 = 0.39$	[115]					
	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 0.83; r_2 = 0.49$	[113]					
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.97; r_2 = 0.41$	[113]					
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.06; r_2 = 0.37$	[113]					

Table 3. Cont.

Copolymer System	Computational						Experimental			
	Method	Copolymerization Model	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference
BA/BMA	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 0.44; r_2 = 0.84$	[113]	-	-	-	-
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.40; r_2 = 0.94$	[113]	-	-	-	-
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.36; r_2 = 1.06$	[113]	-	-	-	-
MA/BA	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 1.09; r_2 = 0.89$	[113]	-	-	-	-
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.04; r_2 = 0.97$	[113]	-	-	-	-
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.04; r_2 = 0.97$	[113]	-	-	-	-
MMA/BMA	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 0.99; r_2 = 1.01$	[113]	20	1988	$r_1 = 0.44; r_2 = 0.26$	[124]
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.02; r_2 = 0.99$	[113]				
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.02; r_2 = 0.99$	[113]				
MA/MEA	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 0.55; r_2 = 0.38$	[113]	-	-	-	-
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.52; r_2 = 0.42$	[113]	-	-	-	-
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.53; r_2 = 0.42$	[113]	-	-	-	-
MMA/MEA	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 1.85; r_2 = 0.40$	[113]	-	-	-	-
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 2.10; r_2 = 0.37$	[113]	-	-	-	-
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 1.96; r_2 = 0.43$	[113]	-	-	-	-
MA/VAc	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 6.76; r_2 = 0.10$	[113]	60	1994	$r_1 = 7.28; r_2 = 0.04$	[125]
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 6.77; r_2 = 0.10$	[113]				
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 6.62; r_2 = 0.10$	[113]				

Table 3. Cont.

Copolymer System	Computational						Experimental			
	Method	Copolymerization Model	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference	T (°C)	Year	Reactivity Ratios/Propagation Rate Coefficients (L/mol/s)	Reference
MMA/VAc	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 9.76; r_2 = 0.22$	[113]	40	1993	$r_1 = 27.8; r_2 = 0.014;$ $s_1 = 0.4; s_2 = 0.4$	[126]
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 11.9; r_2 = 0.16$	[113]				
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 13.14; r_2 = 0.16$	[113]				
	B3LYP/6-311G(d,p)	TM/IPUE	50	2010	$r_1 = 27.9; r_2 = 0.001$ $s_1 = 0.544; s_2 = 0.173$	[101]				
	B3LYP/6-311G(d,p)	TM/IPUE	40	2010	$r_1 = 31.0; r_2 = 0.001$ $s_1 = 0.538; s_2 = 0.176$	[101]				
Et/VAc	B3LYP/6-31G(d)	TM	25	2006	$r_1 = 0.36; r_2 = 1.86$	[113]	60	1971	$r_1 = 0.16; r_2 = 1.12$	[127]
	B3P86/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.31; r_2 = 1.85$	[113]				
	B971/6-311G(2d,2p)	TM	25	2006	$r_1 = 0.29; r_2 = 2.19$	[113]				
	B3LYP/6-31G(d)	TM	60	2002	$r_1 = 0.23; r_2 = 0.83$ $r_1 = 0.36; r_2 = 0.70$	[107]				
BCA/MMA	MPWB1K/6-31G(d,p)	TM	50	2015	$r_1 = 0.272; r_2 = 0.057$	[100]	50	2015	$r_1 = 0.236; r_2 = 0.057$	[100]
VDF/HFP	MPWB1K/6-31G(d,p)	TM	60	2014	$r_1 = 0.06; r_2 = 5 \times 10^{-5}$	[102]	120	2005	$r_1 = 2.9; r_2 = 0.12$	[128]
VDF/TFE	MPWB1K/6-31G(d,p)	TM	60	2014	$r_1 = 0.04; r_2 = 1.40$	[102]	80	1984	$r_1 = 3.73; r_2 = 0.23$	[129]
HFP/TFE	MPWB1K/6-31G(d,p)	TM	60	2014	$r_1 = 6.4 \times 10^{-5}; r_2 = 18.4$	[102]	100	1989	$r_1 \cong 0; r_2 = 10$	[130]

St, styrene; MMA, methyl methacrylate; HEMA, 2-hydroxyethyl methacrylate; GMA, glycidyl methacrylate; BMA, butyl methacrylate; HEA, hydroxyethyl acrylate; MA, methyl acrylate; BA, Butyl acrylate; MEA, methyl ethacrylate; Et, Ethylene; VAc, vinyl acetate; BCA, butyl cyanoacrylate; VDF, vinylidene fluoride; HFP, hexafluoropropylene; TFE, tetrafluoroethylene.

Another challenge relevant to propagation reaction kinetics in FRP on which attention has been focused lately is the solvent effect. Functional monomers and polymers are likely to interact with a polar solvent or reaction medium due to intermolecular forces, which can vary from polarization and dipole interactions to stronger hydrogen bonding. The standard polymerization behavior of the monomers and the radical species can be influenced by these interactions.

From the computational point of view, the solvent effect can be modeled considering explicit solvent molecules and characterizing the specific interactions, or using continuum models [71]. The former approach is clearly more effective, while it is often coupled with a prohibitive computational cost. Few works are reported in the literature in the attempt of investigating the influence of water on the propagation of acrylamide [131], acrylic acid, and methacrylic acid [132], as well as the solvent effect on the tacticity of a propagating MMA chain [133]. One of the major issues of this approach is represented by the restricted number of solvent molecules that can be treated, not to mention that the choice of their displacement around the reaction site that is often unavoidably arbitrary.

Continuum models for treating the solvent effect consider the solvent molecules as implicitly embedded in cavities surrounded by a dielectric continuum. Typical models belonging to this category are COSMO (conductor-like screening model) and PCM (polarizable continuum model), particularly suitable for treating large systems [134,135]. Continuum models are considered adequate for radical thermochemistry, and have been used in the determination of the solvent effect and its relevance for various FRP systems [86,89,99,103]. Encouraging results have been obtained using the quantum mechanics/molecular mechanics (QM/MM) method [132] and the Car–Parrinello molecular dynamics (CPMD) method [136]. Such methods can pave the way to overcome the difficulties in studying a range of solvent-sensitive systems.

5. Secondary Reactions

The continuously increasing potential of the QM approaches allowed the extension of the computational studies toward reactions that are lying beyond the fundamental scheme of FRP, the so-called side or secondary reactions. The investigation of secondary reaction kinetics is motivated by two main reasons: on the one hand, the overall process kinetics can be significantly affected by such reactions even under mild reaction conditions; on the other hand, secondary reactions are often responsible for deviations from the desired polymer properties and for the formation of defects in the polymer microstructure.

During the last years many studies were performed with the purpose of investigating the secondary reactions, which are most relevant in FRP processes. Intermolecular hydrogen abstractions like chain transfer to monomer and chain transfer to polymer were studied in various systems [106,137–141]. Intramolecular hydrogen abstractions were investigated as well, focusing on the backbiting reactions that occur when a chain-end radical (CER) abstracts a hydrogen from its own backbone, forming a mid-chain radical (MCR) [70,106,141–144]. Specific attention was paid to the 1:5 backbiting due to its energetically favorable transition state configuration involving a six-atom ring [145]. Chain transfer to small molecules in the reaction mixture like solvent [146,147] or chain transfer agent (CTA) [148,149] were studied in addition to the abstractions of hydrogen atoms from polymer or monomer [150].

Computational approaches based on QM were also applied to the determination of MCR reactivity. In particular, the rate coefficients of propagation reaction of MCRs were estimated for various systems [70,104,142,144]. Furthermore, both the two symmetric breaks of the carbon-carbon bonds that can occur when a MCR undergoes a β -scission reaction were studied [70,106,143,144,151,152]. Finally, reactions relevant in high temperature processes like thermal self-initiation were approached by quantum chemical investigations [151,153,154].

In recent years, the quantum tunneling (QT) phenomenon has often been taken into account for the kinetics characterization of reactions where a hydrogen abstraction occurs [155]. According to this phenomenon, a sufficiently small moving particle (*i.e.*, hydrogen radical) can overcome an energy barrier even if its energy is lower than the one required, as it happens in the case of reactions of hydrogen abstraction. QC simulations allow estimating a QT factor, which leads to higher kinetic coefficients of hydrogen abstraction when applied. The quantum tunneling effect is introduced multiplying each rate coefficient evaluated from Equation (1) by the tunneling factor, Q_{tun} , as shown in Equation (5). This parameter is defined as the ratio between quantum and classical fluxes across the energy barrier, as shown in Equation (6), where $P(E)$ is the transmission probability and E_1 the activation energy of the forward reaction.

$$k(T)_{\text{tun}} = k(T) Q_{\text{tun}} \quad (5)$$

$$Q_{\text{tun}} = \frac{\int_0^{\infty} P(E) e^{\left(\frac{-E}{k_b T}\right)} dE}{\int_{E_1}^{\infty} e^{\left(\frac{-E}{k_b T}\right)} dE} \quad (6)$$

The transmission probability can be calculated using the solution of the translational Schrödinger equation as reported in literature [155,156].

The estimated value of the QT factor and, consequently, its effect on the absolute rate coefficient value can be significant within the typical range of temperature of FRP reactions. A selection of the most relevant computationally estimated rate coefficients of secondary reactions in common FRP systems is reported in Table 4, while a schematic representation of some relevant secondary reactions is provided in Figure 3.

The aim of deepening the understanding of FRP mechanisms causes a continuous need for the characterization of reaction kinetics. This process pushes the interest towards increasingly complex and fascinating secondary reactions, such as those involving new types of radicals or originating very specific side-products and defects (e.g., side-backbiting producing short-branch radicals and their following propagation) [70,104]. Their kinetic characterization is still out of the reach of the experimental investigation, so this is the field where QC studies find the widest room for application.

Although in many cases these interesting reactions are part of FRP mechanisms that are not yet clearly well defined, one should not forget the role that QC can take in the improvement of the understanding of such mechanisms by guiding the identification of the most relevant reaction pathways. Especially in the area of secondary reactions, QC can help to clarify how a newly-proposed reaction or pathway can be relevant, thus orienting the investigation of FRP kinetics from the very basis.

Table 4. Rate coefficients, k , and Arrhenius parameters (activation energy, E_a , and pre-exponential factor, A) of secondary reactions of relevant free radical polymerization systems estimated by QC and comparison with the existing data obtained through PLP experiments. The reported rate coefficients are evaluated at the indicated temperatures (T).

Polymer/ Monomer	Computational							Experimental						
	Method	T ($^{\circ}\text{C}$)	Year	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reaction	QT	Reference	T ($^{\circ}\text{C}$)	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reference
PEA	UHF/6-31G(d)	160	2001	132.8	11.40	3.00×10^{-7}	Short-chain branching	–	[63]	–	–	–	–	–
PMA	UB3LYP/ 6-31G(d)// MPWB1K/ 6-31G(d,p)	100	2012	57.3	12.17	1.41×10^4	Backbiting	No	[145]	–	–	–	–	–
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	100	2013	50.7	10.66	4.12×10^3	Backbiting	Yes	[70]	–	–	–	–	–
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	100	2013	115.6	14.01	2.09×10^{-5}	β -Scission	–	[70]	–	–	–	–	–
	B3LYP/ 6-31G(d,p)	25	2014	57.3	11.36	6.60×10^2	Backbiting	Yes	[143]	–	–	–	–	–
	B3LYP/ 6-31G(d)	25	2014	100.0	13.02	3.84×10^{-5}	β -Scission	–	[143]	–	–	–	–	–
MA	M06-2X/ 6-31G(d,p)	25	2013	56.0	5.11	1.70×10^{-5}	Chain transfer to monomer	Yes	[140]	–	–	–	–	–

Table 4. Cont.

Polymer/ Monomer	Method	Computational								Experimental				
		T ($^{\circ}\text{C}$)	Year	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reaction	QT	Reference	T ($^{\circ}\text{C}$)	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reference
PBA	UB3LYP/ 6-31G(d)// MPWB1K/ 6-31G(d,p)	100	2012	73.2	13.65	2.57×10^3	Backbiting	No	[145]	50	33.3	7.97	3.83×10^2	[12,17]
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	25	2013	55.0	11.46	1.64×10^3	Backbiting	Yes	[144]					
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	25	2013	116.9	12.46	9.22×10^{-9}	β -Scission	–	[144]	–	–	–	–	–
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	25	2014	47.1	2.72	1.09×10^{-4}	Chain transfer to polymer	Yes	[150]	–	–	–	–	–
BA	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	25	2014	57.4	5.24	4.03×10^{-4}	Chain transfer to monomer	Yes	[150]	50	32.6	5.46	1.55	[157]
	M06-2X/ 6-31G(d,p)	25	2013	31.0	5.17	5.00×10^{-1}	Chain transfer to monomer	Yes	[140]					

Table 4. Cont.

Polymer/ Monomer	Computational							Experimental						
	Method	T ($^{\circ}\text{C}$)	Year	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reaction	QT	Reference	T ($^{\circ}\text{C}$)	E_a (kJ/mol)	$\lg(A)$ (A , L/mol/s or 1/s)	k (L/mol/s or 1/s)	Reference
EA	M06-2X/ 6-31G(d,p)	25	2013	41.0	5.10	9.90×10^{-3}	Chain transfer to monomer	Yes	[140]	–	–	–	–	–
PVC	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	57	2012	74.9	14.13	1.90×10^2	Backbiting	Yes	[104]	–	–	–	–	–
	B3LYP/ 6-31G(d,p)// MPWB1K/ 6-31G(d,p)	57	2012	98.1	12.81	1.96×10^{-3}	β -Scission	–	[104]	–	–	–	–	–
	B3LYP/ 6-31+G(d)// BMK/6-311+ G(3fd,2p)	57	2007	72.8	11.43	8.09×10^{-1}	Backbiting	No	[106]	–	–	–	–	–

PEA, poly ethyl acrylate; PMA, poly methyl acrylate; MA, methyl acrylate; PBA, poly butyl acrylate; BA, butyl acrylate; EA, ethyl acrylate; PVC, polyvinyl chloride.

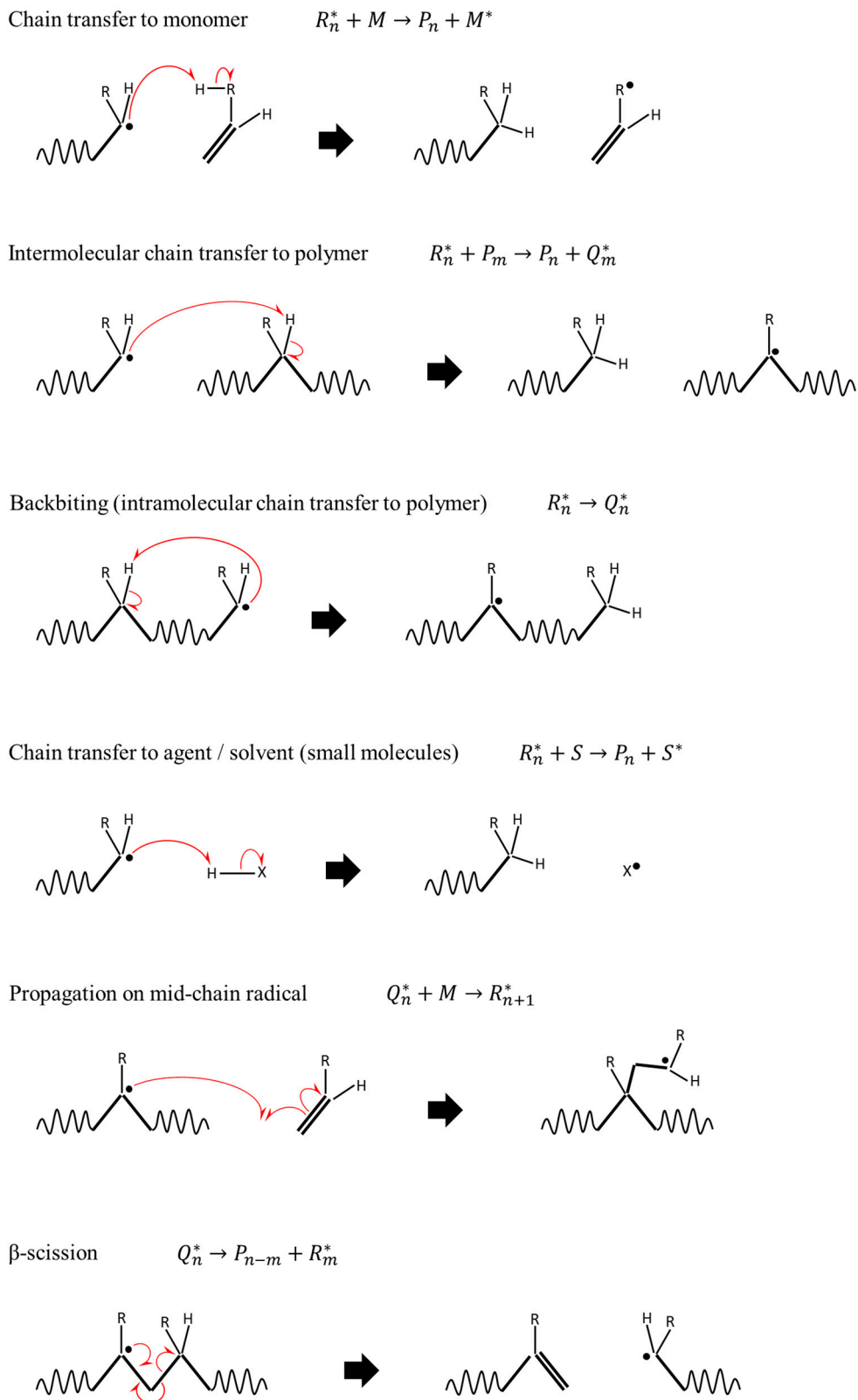


Figure 3. Schematic representation of relevant secondary reactions. R , terminal radical; M , monomer; P , dead polymer; Q , mid-chain radical.

6. Conclusions

Computational approaches show great potential for the investigation of many reaction steps of FRP. Nowadays, the computational power of computers allows studying the reactivity of large molecules at high levels of theory. Simultaneously, the continuous development of new methods that can be applied for studying polymer systems at a high level of theory and the control of their reliability through comparison with experimental studies increased the accuracy of the predicted rate coefficients that can be achieved through these approaches.

The use of such a powerful computational tool that is proven to be able to provide accurate predictions for the propagation reactions at FRP can help to overcome some of the experimental issues. In particular, computational approaches can be used for the investigation of the less accessible reactions in FRP. Furthermore, the potential of the approaches is motivation for the investigation of more challenging systems characterized by a high complexity, such as copolymer systems.

In the present review, it was attempted to collect all the computational studies for propagation and secondary reactions during free radical copolymerization. Additionally, experimental values for the same reactions are presented along with the experimental ones. The aim of this work is to provide the reader with a concise, comprehensive, and updated list of the computational studies that dealt with the propagation and the secondary reactions at free radical polymerization.

Conflicts of Interest

The authors declare no conflict of interest.

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