Cage Effect Dynamics under Photolysis of Photoinitiators

Igor V. Khudyakov [a] **and Nicholas J. Turro** [b,*]

[a] Bomar Specialties, Torrington, CT 06790, USA
[b] Chemistry Department, Columbia University, New York, NY 10027, USA

Abstract
The efficiency of photoinitiators depends upon the quantum yield of photogeneration of reactive free radicals and the cage effect value. Only radicals that escape the cage can initiate free radical polymerization. The modern concept of the cage effect is presented. Dependencies of the cage effect upon increasing of solvent viscosity in the course of polymerization are discussed. Cage effect dynamics or kinetics of geminate recombination is of special interest. Results of a kinetic study on the cage effect using ns laser flash photolysis are described.
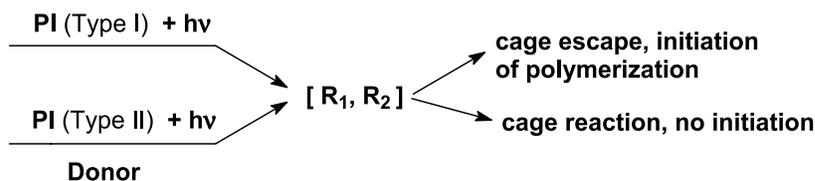© Koninklijke Brill NV, Leiden, 2010

1. Introduction

The first step of photopolymerization is the formation of a pair of reactive free radicals (RP). These radicals are produced during photodissociation of a photoinitiator (Type I PI) or by hydrogen abstraction (electron transfer) by a triplet state of PI from a hydrogen (electron) donor (Type II PI) (Scheme 1).

The quantum yield of RP generation is denoted as Φ. An ideal PI upon absorption of one einstein of photons by photoreactive band(s) in its absorption spectrum produces two moles of reactive free radicals, i.e., $\Phi = 1.0$ for the yield of radical pairs and $\Phi = 2.0$ for the yield of individual free radicals. In reality, common Type I PIs (Irgacure, Darocur) have $\Phi = 0.2$–0.6 measured in non-viscous solvents [1, 2]. Photogenerated radicals exist for a certain time in a solvent cage [R_1, R_2] as a dynamic RP, see Scheme 1. Originally, the cage effect of the liquid phase pointed to the fact that in the liquid, contrary to the gas phase, reactive fragments do not separate promptly but undergo a series of collisions or contacts. Nowadays cage effect means a certain probability of chemical reaction of the pair-wise generated reactive species in the condensed phase between reagents in a pair. That proba-

---

* To whom correspondence should be addressed. Fax: (1-212) 932-1289; e-mail: njt3@columbia.edu

PI (Type I) **+ hν**

PI (Type II) **+ hν**

Donor

[R₁, R₂]

cage escape, initiation
of polymerization

cage reaction, no initiation

Scheme 1. Photogeneration of reactive free radicals in the liquid state.

bility is a cage effect value, and it is denoted in this work as φ_∞; $0 \leqslant \varphi_\infty \leqslant 1.0$. For an introduction into the cage effect, see Refs [3, 4]. An RP participates in two competitive processes: recombination (within the cage) and dissociation (exit of radicals in the solvent bulk). We undermine here for brevity under 'recombination' also disproportionation or any other cage reaction of radicals leading to inactive products.

The latter process is important: radicals which escaped cage can encounter reactive monomers (oligomers) and initiate polymerization. Cage recombination (the 'cage' effect) is a side reaction of photoinitiation decreasing the efficiency of PI. Obviously, a sum of probabilities of recombination and dissociation equals 1.0, or:

$$f = 1 - \varphi_\infty, \tag{1}$$

where f is the cage escape value and φ_∞ is the cage effect value. Evidently, the higher is the product $\Phi \cdot f$, the more efficient the PI. Strictly speaking, experimental values of Φ presented above for commercial Type I PIs are in fact $\Phi \times f$. However, the triplet RPs in non-viscous liquids have a f of approx. 1 (φ_∞ approx. 0).

The cage effect has been studied for 75 years, and a number of publications have appeared during the last 30 years on the cage effect dynamics, i.e., temporal performance of RP: $\varphi = \varphi(t)$ [5–8]. In the present work we analyze a kinetic law which describes cage effect dynamics (or kinetics of geminate recombination) and solvent viscosity effect on φ_∞.

2. Exponential Model

There is a common simple but not justified approach to consider cage recombination and cage dissociation (Scheme 1) as the first-order reactions with rate constants k_R (s⁻¹) and k_D (s⁻¹), respectively [9]. That approach is the exponential model of the cage effect. The exponential model leads to a simple expression for φ_∞:

$$\varphi_\infty = k_R / k_{obs}, \tag{2}$$

where $k_{obs} = k_R + k_D$.

The usual assumption is that k_R does not depend upon solvent viscosity (η) and k_D is inversely η-dependent. Then one can obtain the simple equation:

$$C(t) = C_0 \times e^{-k_{obs} \times t} + C_\infty, \tag{3}$$
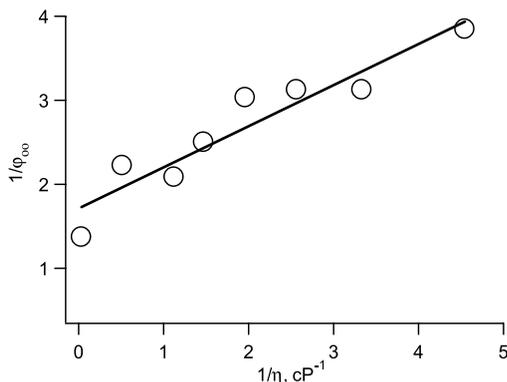
Figure 1. Experimental dependence of $1/\varphi_\infty$ *vs* $1/\eta$ for an RP described in Ref. [5]. Here and below in Figs 2 and 3 a straight line is the linear fit to the experimental data.

where C_0 is the initial concentration of a radical of a RP which is monitored and C_∞ is the concentration of radicals that have escaped the cage or:

$$\varphi(t) = \varphi_\infty \times (1 - e^{-k_{obs} \times t}). \tag{4}$$

Further, equation (5) should be valid for the exponential model:

$$1/\varphi_\infty = 1 + A/\eta, \tag{5}$$

where $A > 0$ is a constant [9]. Thus, the experimental data are expected to be a linear dependence of $1/\varphi_\infty$ *vs* $1/\eta$ with an intercept of 1.0. Such linear plots have been observed, *cf.*, for review Refs [10, 11]. However, one can find examples in the literature of curved dependences and/or linear dependences with an intercept different from 1.0. We present below three plots based on recent direct measurements of φ_∞ by laser flash photolysis [5–8].

One can see in Figs 1–3 that an intercept is noticeably larger than 1.0 is in violation of equation (5) of the exponential model.

Whether disappearance of RP follows the exponential law with k_{obs} or not can be verified in time-resolved experiments. We have observed in a viscous media a large conversion of RP with $\varphi_\infty = 0.9$ ($f = 0.1$) [12] which allowed rather accurate simulation of cage effect dynamics, *cf.*, Fig. 4.

At first glance the kinetics are satisfactorily described by the exponential model, *cf.* Fig. 4. However, in the logarithmic coordinates a significant deviation from linearity and a decrease of a slope the time increase are observed. It seems that only initial part of the curve $t \leqslant 1$ μs fits into the exponential model. We conclude based on the data of Figs 1–4 that the exponential model is a merely a rough approximation.
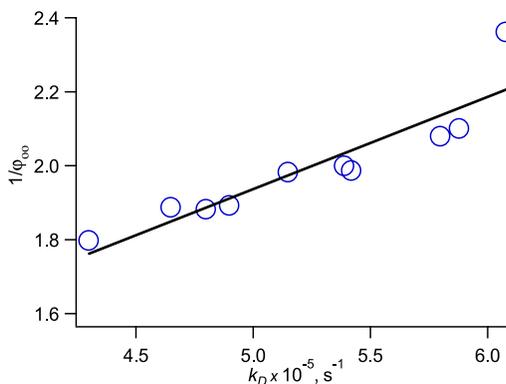
We will use the following function $R(t)$ which describes the experimental data:

$$R(t) = \frac{C(t) - C_\infty}{C_0 - C_\infty}, \tag{6}$$

cf. Fig. 5. Evidently, $R(t)$ changes from 1.0 to 0 with time.
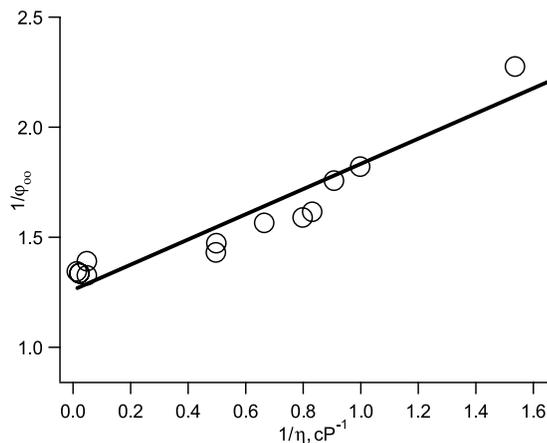
Figure 2. Experimental dependence of $1/\varphi_\infty$ *vs* $1/\eta$ for an RP described in Ref. [6].


Figure 3. Experimental dependence of $1/\varphi_\infty$ *vs* k_D for an RP described in Ref. [7].

3. Contact Model

The contact model assumes that reactive species (R_1, R_2 in our case) undergo a series of contacts/separations prior their final separation. It follows from the principles of random walking in 3D space, that the probability of these contacts and the probability of recombination decreases in time as the nominal probability of a reaction $h(t) \sim t^{-3/2}$ at very large time [13]. Thus, $R(t) \sim t^{-1/2}$ at $t \rightarrow \infty$ [7, 13]. It is possible to explain the experimentally observed spin and magnetic field effects in free radical reactions assuming only the separation of radicals and their return to a distance ρ equal to a sum of van der Waals radii of radicals (a contact) [4].

A simple expression for $R(t)$ based on the contact model was suggested in Ref. [14]:

$$R(t) = e^{t/t_o} \times erfc\sqrt{t/t_o}, \tag{7}$$
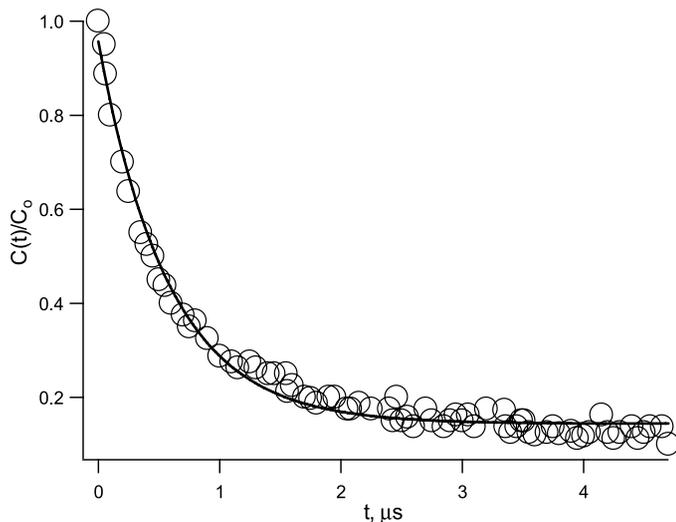
Figure 4. Kinetics of RP decay. The RP is described in Ref. [12]. A solid line is the exponential fit to the experimental data. Plateau of the curve corresponds to R_1 and R_2 in the solvent bulk. Their decay in the solvent bulk occurs at much larger time scale.
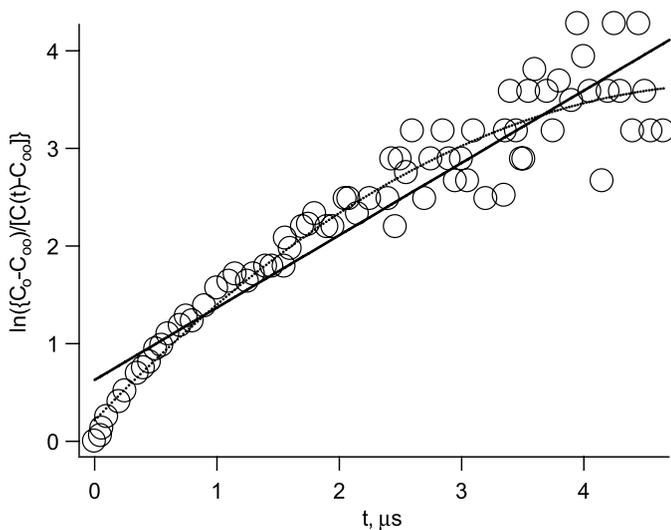
Figure 5. Kinetics of RP decay, *cf.*, Fig. 4. The straight line is the exponential model fit to experimental data. The curved line is a polynomial with a better fit.

$R(t)$ of equation (7) has the expected asymptote of approx. $t^{-1/2}$ at $t \gg t_o$:

$$R(t) = \sqrt{t_o/(\pi t)}. \tag{8}$$

Time t_o is proportional to the characteristic time of an encounter between two radicals ρ^2/D_{12}, where ρ is a reaction radius (*cf.*, above) and D_{12} is a mutual diffusion coefficient.

It can be seen from Fig. 6 that equation (7) poorly fits the experimental data.

4. Generalized Model

It was noticed that the initial part of the kinetic curve can be successfully described by the exponential model, whereas the 'tail' can be described by the contact model, *cf.*, Fig. 7.

Usually the truth is between the two extremes. We expect that a generalized model should embrace both exponential and contact models in order to adequately
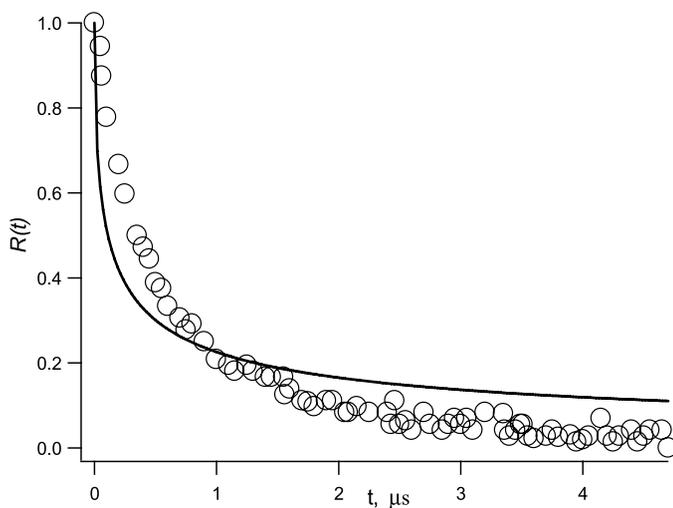
Figure 6. Fit of experimental data to the $R(t)$ function, *cf.*, equation (7).
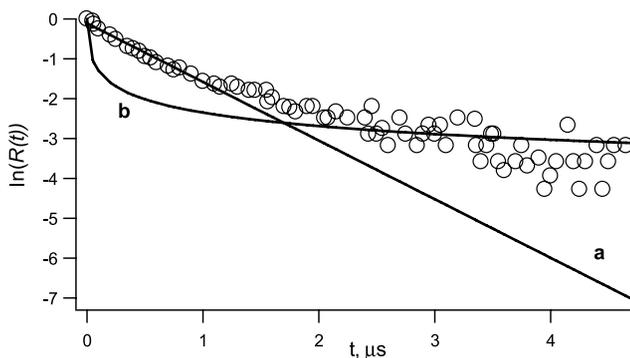
Figure 7. Fit of experimental data presented as $\ln(R(t))$ by exponential (a) and by contact (b) models. The 'best' $t_o = 0.029$ μs (equation (7)).

describe cage effect dynamics. An analytical solution of the problem was obtained by Khudyakov *et al.* [15]. Figure 8 presents a quite satisfactory fitting of the generalized model to the experimental data.

5. Cage Effect in Media of Different Viscosity

We present an effect of η on the kinetics of decay of photogenerated radicals, *cf.*, Scheme 2. In non-viscous solvents triplet RPs dissociate, and $\varphi_\infty \approx 0$. As above, strictly speaking, experimental values of Φ presented above for commercial Type I PIs are in fact $\Phi \times f$. However, the triplet RPs in non-viscous liquids have f approx. 1 (φ_∞ approx. 0).

Radicals in the solvent bulk participate in reactions with monomers, with (traces) of dioxygen, in bimolecular self-termination, etc. Increase of η should lead to an increase of φ_∞, *cf.*, Scheme 2. The exponential model predicts faster decay of RP than that experimentally observed (Scheme 2) [12, 15]. It is expected that PIs become less efficient with time starting from the beginning of photopolymerization: the media becomes more viscous, less radicals enter the solvent bulk, concentration of vinyl groups is reduced, and absorption of light becomes lower due to PI consumption.

6. Cage Effect in the Very Viscous Media

Figures 1–3 demonstrate that, contrary to the expectation of the exponential model, $\varphi_\infty < 1$ at $\eta \to \infty$. This observation makes questionable the suggestion of indepen-
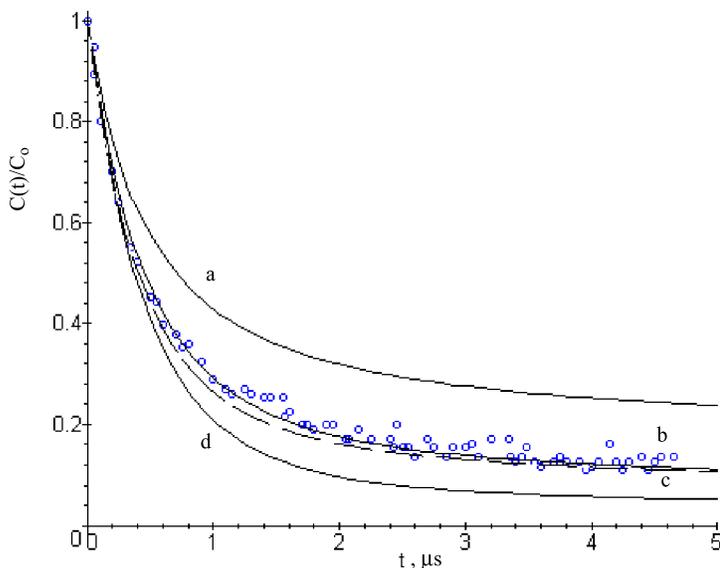
Figure 8. Fit of experimental data into the generalized model with different fitting parameters. For details, see Ref. [15].
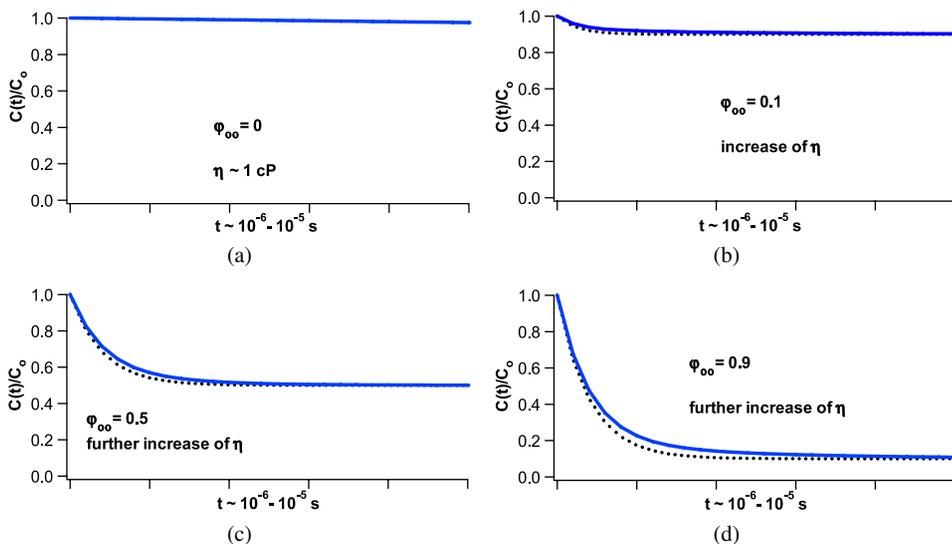
Scheme 2. A presentation of characteristic experimental kinetic traces (solid lines) for a decay of RP of PI in a media of increasing η (a–d). Dashed curves are comparative predictions of the exponential model, *cf.*, Section 2.
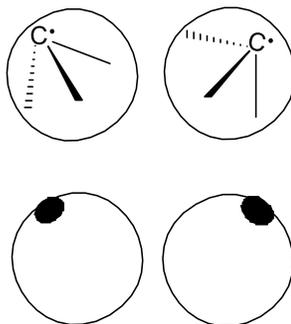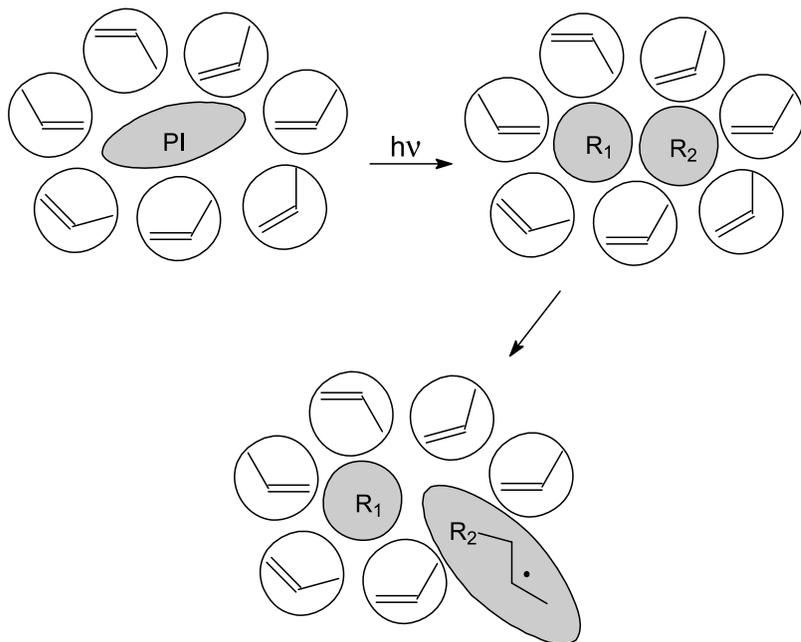

Scheme 3. Pictorial presentation of a possible mutual orientation of C-centered radicals in RP immediately after its photogeneration. The black spot represents a reactive site on a radical surface.

dence of k_R upon η. We have to assume that both recombination and separation are proportional to η^{-1}, leading to $\varphi_\infty < 1$. A possible explanation is that RP at the first moment is generated in a mutual orientation that is unfavorable for recombination (Scheme 3) [10].

Both dissociation of RP and reaching of a favorable mutual orientation for recombination are retarded by η. A favorable contact is reached by the rotational and translational diffusion.

7. Cage Effect in a Solvent–Monomer

There is an interesting situation when reactive species, low MW monomers, are a solvent or a co-solvent surrounding RP. They constitute a cage 'wall', *cf.* Ref.

Scheme 4. Pictorial presentation of possible reactions of a Type I PI in a solution of a vinyl monomer.

[11]. Many authors believe that radicals are necessarily generated within the first coordination sphere what is usually called 'the primary cage', *cf.*, Scheme 4. It is plausible but it has not been proven so far to the best of our knowledge. Bond elongation during its cleavage in Type I PI can lead to a formation of radicals separated by a solvent molecule.

Radicals are capable of initiating polymerization while in a solvent cage (as RP). In such a case φ_∞ will be lower than φ_∞ for the same RP photogenerated in an inert solvent of a similar η. An analytical solution of this case with a Noyes function $h(t)$ [13] was suggested in Ref. [11].

Evidently, scavenging of radicals by a 'wall' can be observed at the initial stage of photopolymerization of a monomer when its concentration is high.

8. Conclusions

Practitioners usually successfully select a PI or a blend of PIs which allow them to cure formulations by free-radical polymerization. There are many reports in the technical literature on 'very efficient' PI(s). These PI(s) are used in specific formulations, and it is unknown how 'efficient' these PI(s) will be in another coating. However, there are several universal requirements for an 'efficient' PI [1, 2]. An obvious demand is the absorption of UV-Vis from the light source used. Another demand is that PI generates highly reactive towards double bonds free radicals of PI. In this report we stressed the importance of the demand of high Φ of the photodecomposition of PI and of low φ_∞. We suggest that a modest increase of φ_∞

(decrease of f) with the progress of photopolymerization is a very important for an overall high efficiency of PI.

The ideal PI has $\Phi \times f = 1.0$, and all radicals formed from the PI exit the solvent cage. In the case of high reactivity of R_1 and R_2 towards vinyl compounds and a high concentration of the latter, all R_1 and R_2 will start polymerization. At the later stages of polymerization PI becomes less efficient, *cf.*, Section 5 above. There are cases when η of a liquid containing macromolecules measured by viscometer is very high (high 'macroviscosity') but a viscous drug imposed on low-MW molecules (radicals) is modest like in a non-viscous liquid (low 'microviscosity') [16]. This report focuses on the cage effect and its dynamics. Cage effect dynamics are successfully described with a generalized model which combines exponential and contact models of cage effect dynamics. Further development of the theory considers the S–T evolution of RP [4], anisotropy of reactivity of radicals (Scheme 3) [10] and a decrease of D_{12} in RP relative to D_{12} in a solvent bulk [7].

It happens that the present report addresses a recent mentioning that 'it is paramount to elucidate which reactions occur immediately after the birth of the primary radicals before the reaction with monomer units' [17].

Acknowledgement

References

1. J.-P. Fouassier, *Photoinitiation, Photopolymerization, Photocuring: Fundamentals and Applications*. Hanser, Munich (1995).
2. I. V. Khudyakov and N. J. Turro, in: *Carbon-Centered Free Radicals and Radical Cations*, M. D. E. Forbes (Ed.), Chapter 12. Wiley, New York, NY (2010).
3. N. J. Turro, V. Ramamurthy and J. C. Scaiano, in: *Principles of Molecular Photochemistry*, Chapter 7.37. University Science Books, Sausalito, CA (2009).
4. J. R. Woodward, *Prog. React. Kinet.* **27**, 165 (2002).
5. A. B. Oelkers, L. F. Scatena and D. R. Tyler, *J. Phys. Chem. A* **111**, 5353 (2007).
6. A. A. Braden, E. E. Parrack and D. R. Tyler, *Photochem. Photobiol. Sci.* **1**, 418 (2002).
7. I. Khudyakov, P. Levin and V. Kuzmin, *Photochem. Photobiol. Sci.* **7**, 1540 (2008).
8. J. L. Male, B. E. Lindofors, K. J. Covert and D. R. Tyler, *J. Am. Chem. Soc.* **120**, 13176 (1998).
9. A. M. North, *The Collision Theory of Chemical Reactions in Liquids*. Methuen, London (1964).
10. I. V. Khudyakov and B. I. Yakobson, *Russ. J. Gen. Chem.* **54**, 3 (1984).
11. T. Koenig and H. Fischer, in: *Free Radicals*, J. K. Kochi (Ed.), Vol. 1, p. 157. Wiley, New York, NY (1973).
12. P. P. Levin, I. V. Khudyakov and V. A. Kuzmin, *J. Phys. Chem.* **93**, 208 (1989).
13. R. M. Noyes, *Progress React. Kinet.* **1**, 129 (1961).
14. A. I. Burshtein, *Adv. Chem. Phys.* **129**, 105 (2004).
15. I. Khudyakov, A. Zharikov and A. Burshtein, *J. Chem. Phys.* **132**, 014104 (2010).
16. V. A. Kuzmin, P. P. Levin and I. V. Khudyakov, *Bull. Acad. Sci. Chem. Ser.*, 437 (1987).
17. C. Barner-Kowollik, *Angew. Chem. Int. Edn* **48**, 9222 (2009).