

Cage Effect Dynamics under Photolysis of Photoinitiators

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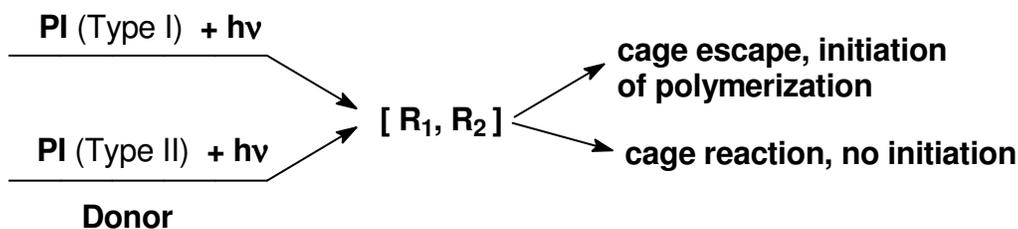
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Abstract

Efficiency of photoinitiators (PI) depends upon quantum yield of photogeneration of reactive free radicals and upon 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.

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 I. Photoinitiation of free-radical polymerization with PIs

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 (Irgacures, Darocure) 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 I.^{3,4} An RP participates in two competitive processes: recombination⁵ (within the cage) and dissociation (exit of radicals in the solvent bulk). 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:

$$f = 1 - \Phi_{\infty}, \quad (1)$$

where f is the cage escape value, and Φ_{∞} is the cage effect value. *Evidently, the higher is the product $\Phi_{\infty} f$ the more efficient the PI.*⁶

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:

$\Phi = \Phi(t)$.⁷ 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 I) as the first-order reactions with rate constants k_R, s^{-1} and k_D, s^{-1} , respectively.⁸ That approach is the *exponential model* of the cage effect. The exponential model leads to a simple expression for Φ_{∞} :

$$\Phi_{\infty} = k_R / k_{obs}, \quad (2)$$

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 equations:

$$C(t) = C_0 \times e^{-k_{obs} \times t} + C_{\infty}, \quad (3)$$

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

$$\Phi(t) = \Phi_{\infty} \times (1 - e^{-k_{obs} \times t}) \quad (4)$$

Further, eq. 5 should be valid for the exponential model:

$$1/\Phi_{\infty} = 1 + A/\eta, \quad (5)$$

where $A > 0$ is a constant.⁸ Thus, the experimental data are expected to be a linear dependence of $1/\Phi_{\infty}$ vs. $1/\eta$ with an intercept of 1.0. Such linear plots have been observed, cf. for review ref. 9,10. 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 plots based on recent direct measurements of Φ_{∞} by laser flash photolysis:⁷

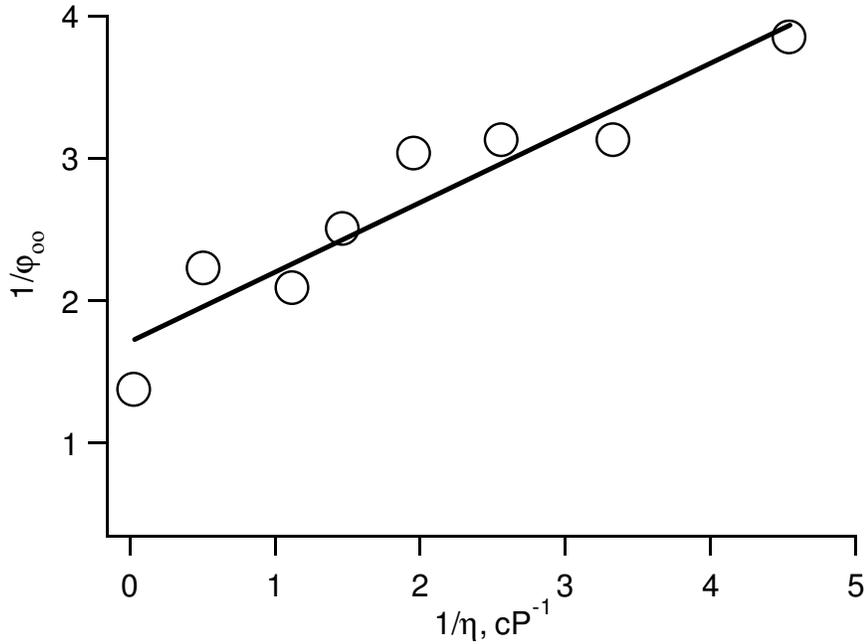


Figure 1. Experimental dependence of $1/\phi_{\infty}$ vs. $1/\eta$ for an RP described in ref. 7a. Here and below in Figures 2, 3 a straight line is the linear fit to the experimental data

One can see in Figures 1-3 that an intercept is noticeably larger than 1.0 in violation of eq. 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 $\phi_{\infty} = 0.9$ ($f = 0.1$)¹¹ which allowed rather accurate simulation of cage effect dynamics, cf. Figure 4. At the first glance kinetics are satisfactorily described by the exponential model, cf. Figure 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 $t \leq 1 \mu\text{s}$ fits into the exponential model, cf. Figure 5. We conclude based on the data of Figures 1-5 that the exponential model is a merely a rough approximation.

We will use the following function $R(t)$ which describes the experimental data:

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

cf. Figure 5. Evidently, $R(t)$ changes from 1.0 to 0 with time.

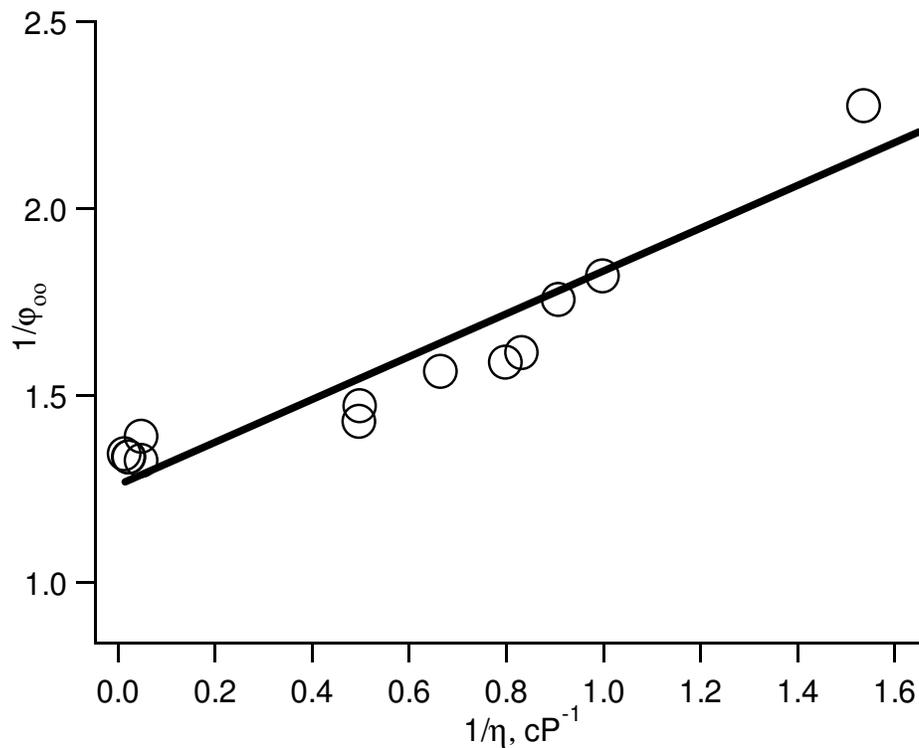


Figure 2. Experimental dependence of $1/\phi_{\infty}$ vs. $1/\eta$ for an RP described in ref. 7b

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.¹² Thus, $R(t) \sim t^{-1/2}$ at $t \rightarrow \infty$.^{7c, 12} 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

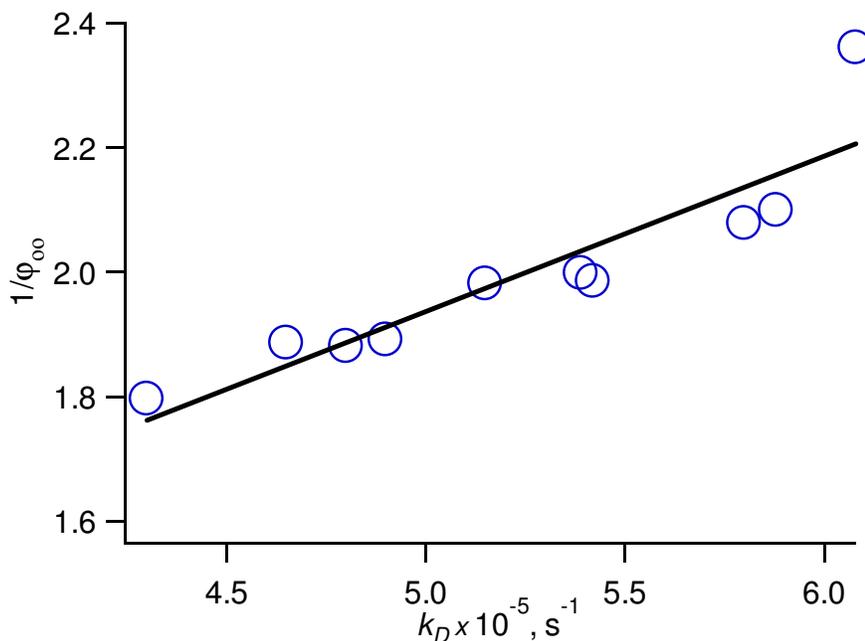


Figure 3. Experimental dependence of $1/\phi_{\infty}$ vs. k_D for an RP described in ref. 7c

A simple expression for $R(t)$ based on the contact model was suggested in ref. 13:

$$R(t) = e^{-t/t_0} \times \operatorname{erfc} \sqrt{t/t_0} \quad (7)$$

$R(t)$ of eq. 7 has the expected asymptote of $\sim t^{-1/2}$ at $t \gg t_0$:

$$R(t) = \sqrt{t_0/(\pi t)} \quad (7a)$$

Time t_0 is proportional to the characteristic time of an encounter between two radicals ρ^2/D_{12} , where ρ is a reaction radius (cf. above), D_{12} is a mutual diffusion coefficient.

It can be seen from Figure 6, that Eq. (7) poorly fits the experimental data.

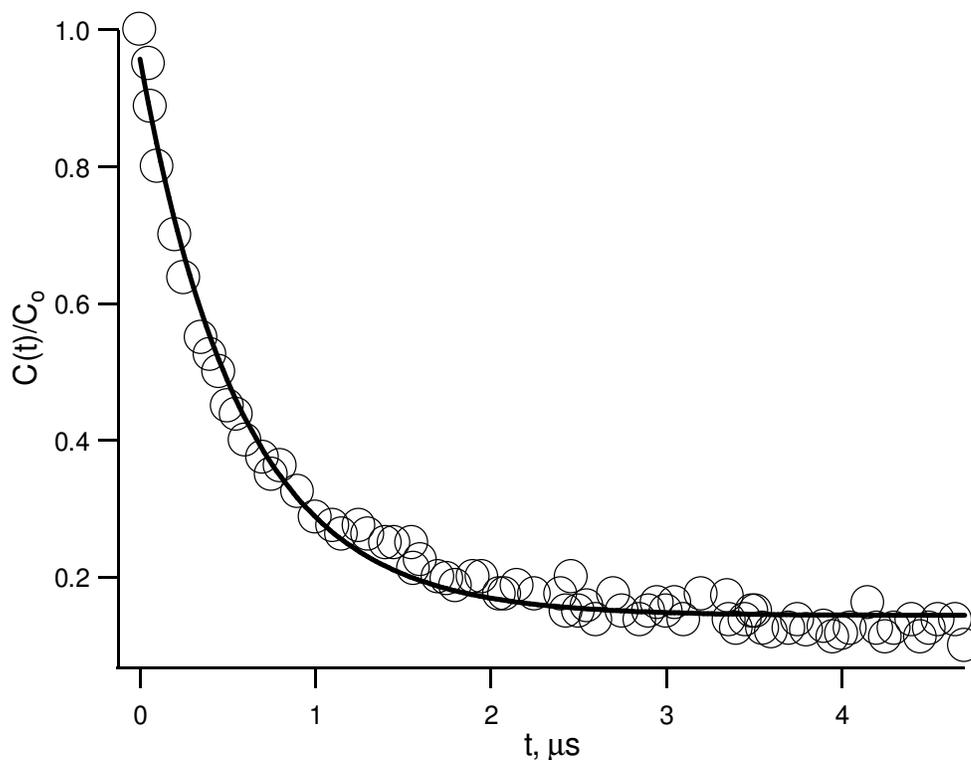


Figure 4. Kinetics of RP decay. The RP is described in ref. 11. A solid line is the exponential fit to the experimental data. Plateau of the curve corresponds to R_1 and R_2 in the solvent bulk. They decay in the solvent bulk at much larger time scale

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. Figure 7 below.

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 describe cage effect dynamics. An analytical solution of the problem was obtained by Zharikov and Burshtein.¹⁴ In fact, quite satisfactory fitting of the generalized model to the experimental data is presented in ref. 14.

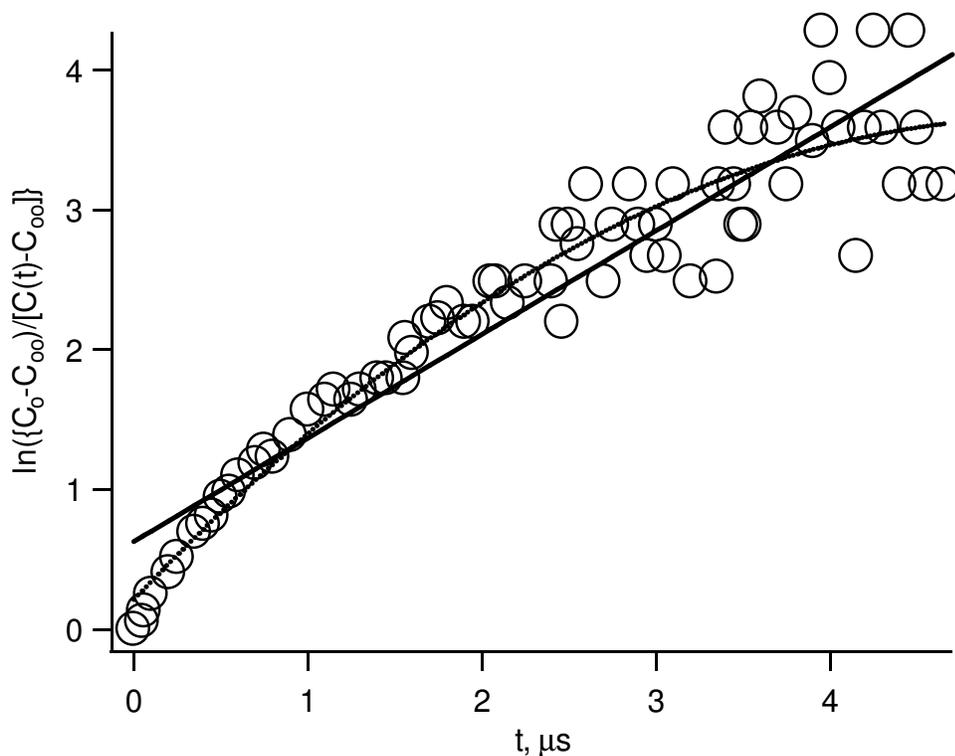


Figure 5. Kinetics of RP decay, cf. Figure 4. The straight line is the exponential model fit to experimental data. The curved line is a polynomial with a better fit

5. Cage Effect in Media of Different Viscosity

We present an effect of η on the kinetics of decay of photogenerated radicals, cf. Scheme II below. In non-viscous solvents triplet RPs dissociate, and $\Phi_{\infty} \approx 0$.⁶ 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 II. The exponential model predicts faster decay of RP than that experimentally observed, Scheme II.^{11,14}

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, $\Phi_{\infty} < 1$ at $\eta \rightarrow \infty$. This observation makes questionable the suggestion of independence of k_R upon η . We have to assume that *both* recombination and separation are proportional to η^{-1} leading to $\Phi_{\infty} < 1$.

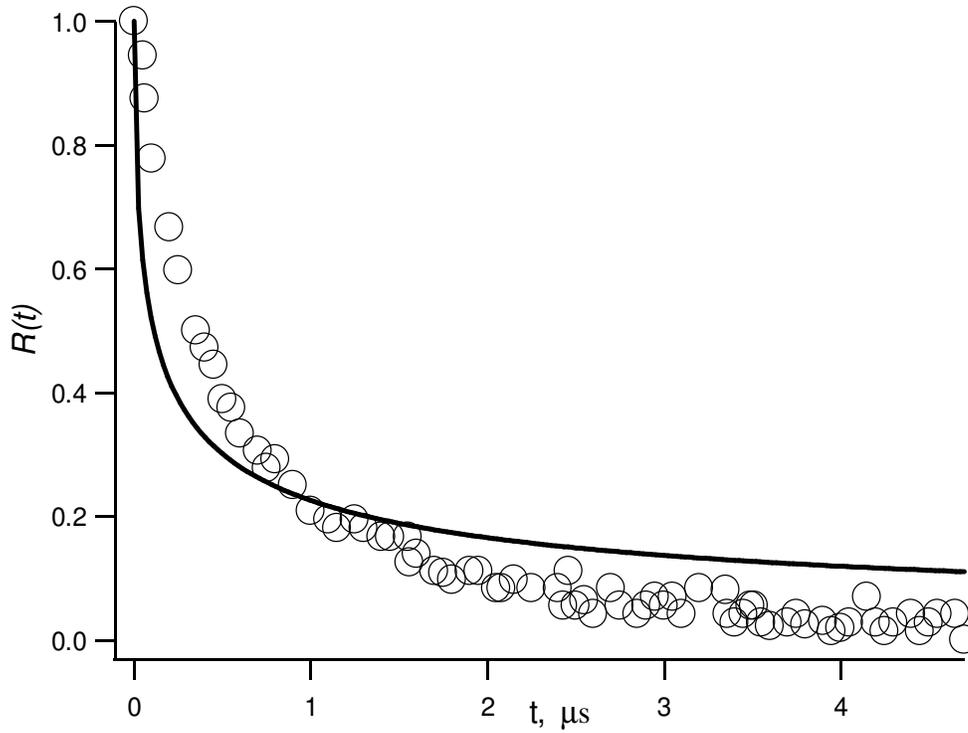


Figure 6. Fit of experimental data into $R(t)$ function, cf. eq. 7

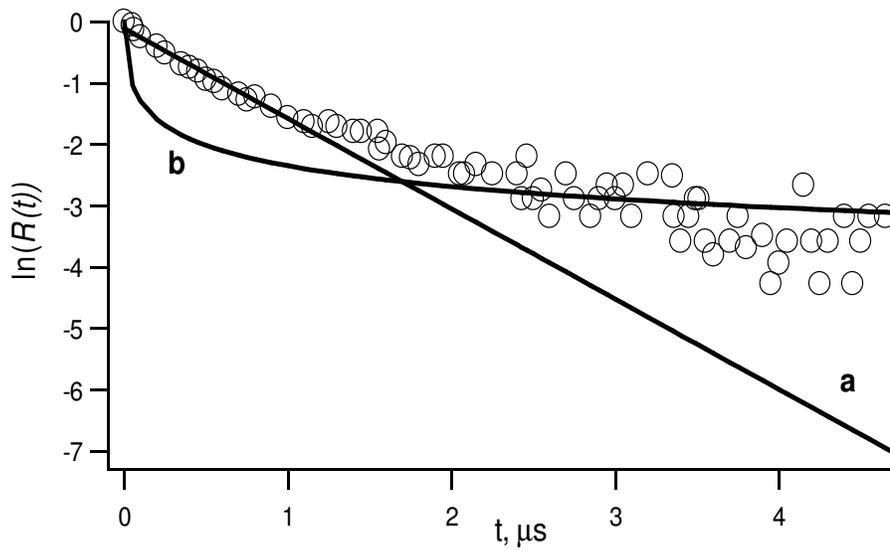
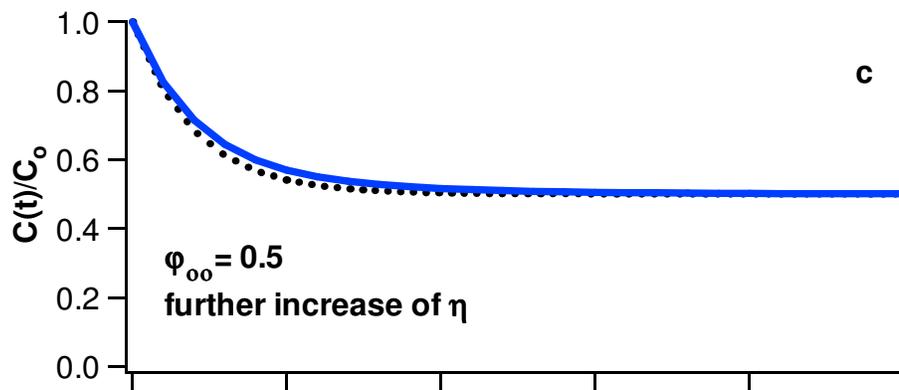
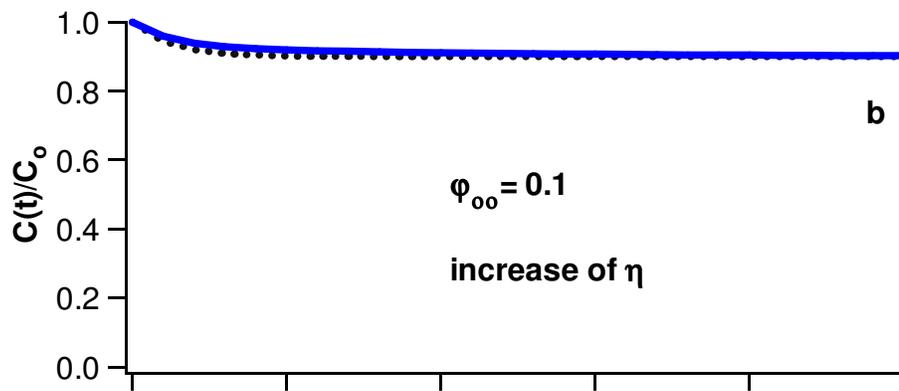
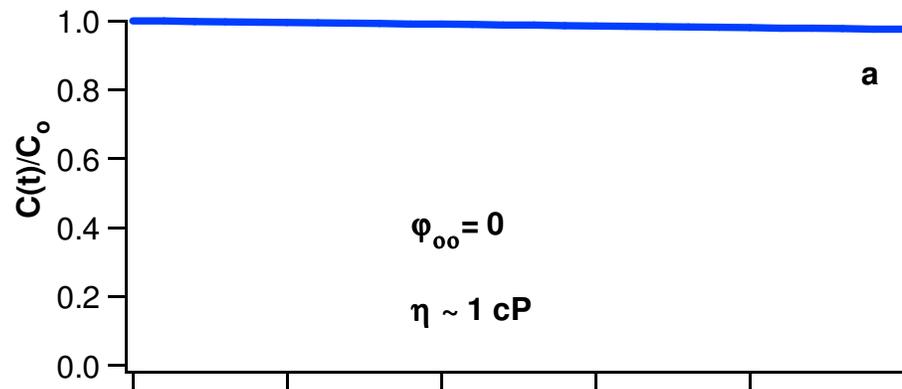
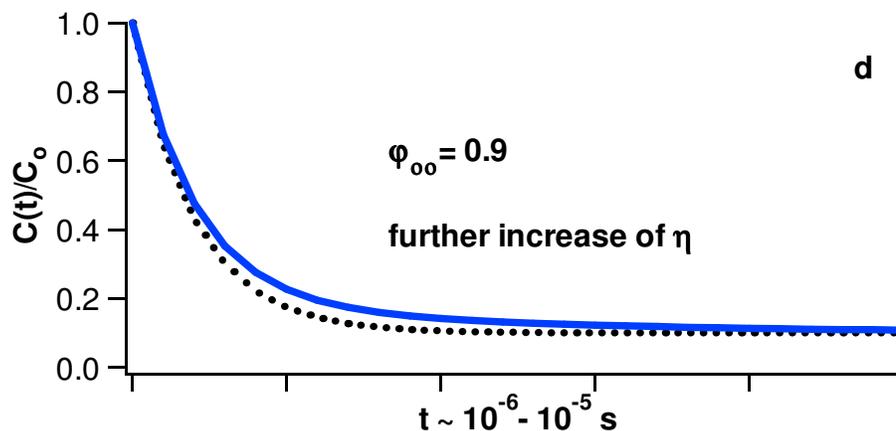


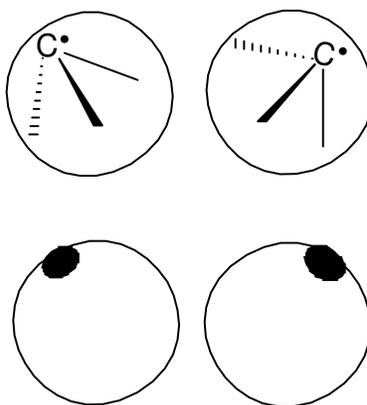
Figure 7. Fit of experimental data presented as $\ln(R(t))$ by exponential (a, eq. 3) and by contact (b, eq.7) models. The 'best' $t_0 = 0.029 \mu\text{s}$ (eq. 7)





Scheme II. A presentation of characteristic experimental kinetic traces (solid lines) for a decay of RP of PI in a media of increasing η (Figures from *a* to *d*). Dashed curves are comparative predictions of the exponential model, cf. Section 2 above

A possible explanation is that RP at the first moment is generated in a mutual orientation that is unfavorable for recombination:⁹

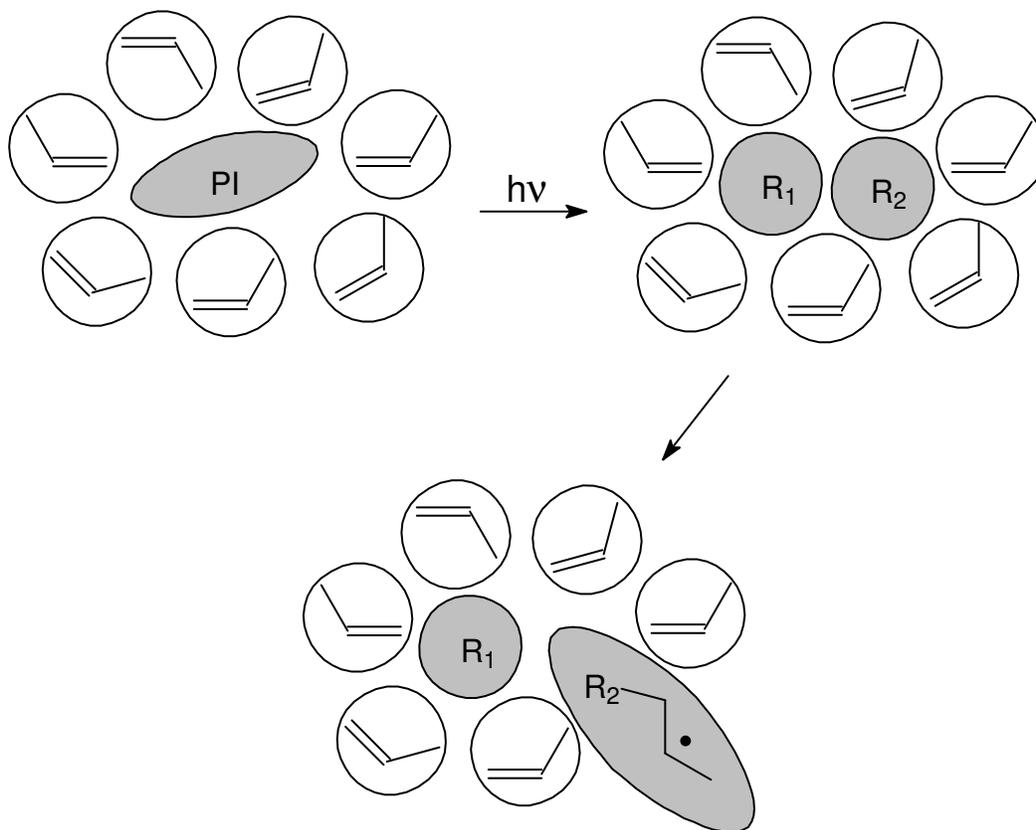


Scheme III. Pictorial presentation of a possible mutual orientation of C-centered radicals in RP immediately after its photogeneration. Black spot represents a reactive site on a radical surface

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 cosolvent surrounding RP. They constitute a cage “wall”, cf. ref 10,15.



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

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 . Evidently, scavenging of radicals by a “wall” should be expected 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} In this report we stressed the importance of the demand of high Φ of the photodecomposition of PI and of low ϕ_{∞} . An increase of ϕ_{∞} (decrease of f) with the progress of photopolymerization is important for an overall efficiency of PI.

The ideal PI has $\Phi_x f = 1.0$, 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.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 consider the S-T evolution of RP,⁴ anisotropy of reactivity of radicals (Scheme III)⁹ and a decrease of D_{12} in RP relative to D_{12} in a solvent bulk.^{7c}

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

9. Acknowledgment

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10. References

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3. 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 probability is a cage effect value, and it is denoted in this work as ϕ_{∞} ; $0 \leq \phi_{\infty} \leq 1.0$. For an introduction into the cage effect, see: Turro, N.J.; Ramamurthy V; Scaiano, J.C. *Principles of Molecular Photochemistry*, University Science Books, 2009, ch. 7.37.
4. Woodward, J. R. *Prog. React. Kinet.* **2002**, *27*, 165.
5. We undermine here for brevity under “recombination” also disproportionation or any other cage reaction of radicals leading to inactive products.
6. 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 $f \sim 1$ ($\phi_{\infty} \sim 0$).
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15. Many authors believe that radicals are necessarily generated within the first coordination sphere what is usually called “the primary cage”, cf. Scheme IV. 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.
16. 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”), cf. e.g.: Kuzmin, V.A.; Levin, P.P.; Khudyakov, I.V. *Bull. Acad Sci. Chem. Series* **1987**, 437.
17. Barner-Kowollik, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9222.