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## Advances in photoinitiation and kinetics of photopolymerization of acrylates

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### Abstract

*Cage effect dynamics  $\phi = \phi(t)$  under photoexcitation of the photoinitiator (PI) of polymerization benzophenone in a viscous media is discussed. The cage effect  $\phi$  increases with an increase in the media viscosity, and the efficiency of photoinitiators decreases. A new family of urethane acrylate oligomers, which have grafted photoinitiators (PIs), are described. Commercially available Type I PIs with hydroxylalkyl substituents were grafted to oligomers during oligomers syntheses. These oligomers have the name of UV-light sensitive ( $LS^m$ ) oligomers. Rates and efficiency of cure of  $LS^m$  oligomers are similar to those of corresponding oligomers with a dissolved same PI in the same concentration. Simple formulae describing kinetics of photopolymerization are presented. Application of*

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*a moderate magnetic field accelerates free radical polymerization initiated by PIs which dissociate via the triplet state.*

## Introduction

Free radical photopolymerization of acrylate coatings, acrylate oligomers, and individual solventless acrylates is of both commercial and scientific interest. Free radicals, which initiate polymerization, can be generated by different ways. The most common is UV-cure with UVA- ( $\lambda$  315-380 nm) and/or UVB-light ( $\lambda$  280-315 nm) in the presence of photoinitiators (PIs). In this paper we will consider the current status and advances in photoinitiation and photopolymerization (UV-cure) of acrylates.

### The cage effect $\phi$ during photoinitiation

First, we discuss some general aspects of photoinitiation. The primary event of photoinitiation of free-radical polymerization is the formation of a radical pair (RP)  $R_1^{\cdot}$ ,  $R_2^{\cdot}$  as a result of a bond cleavage (Type I<sup>1,2</sup> PI) or hydrogen atom or electron abstraction by a PI from a coinitiator (Type II<sup>1,2</sup> PI). RPs are important intermediates, and their reactivity toward radical-radical combination or disproportionation (cage effect  $\phi$ ) affects the efficiency of polymerization, with a high cage effect leading to a low efficiency of polymerization and a low cage effect leading to a high efficiency of photoinitiation.

Free radical photopolymerization is accompanied by a formation of magnetic transients with a non-zero spin angular momentum: free radicals, RPs, triplet states of photoinitiators. UV-cure often occurs in the presence of a stable molecules in a triplet state, namely, molecular oxygen. All these species play role in the course and efficiency of photopolymerization. Because of their participation, there can be occurrences of magnetic field and spin effect in free-radical photopolymerization, cf. below.

The outcome of a photochemical reaction depends on a spin-state dynamics of the initial RP, cf. Figure 1. Photolysis of the most of commercial PIs results in a *triplet* radical pair  $^3(\text{RP})$ . In non-viscous media free radicals of PI completely dissociate into free radicals  $^3(\text{RP}) \rightarrow \text{FR}$  (cage effect  $\phi \approx 0$ ), and free radicals initiate polymerization. There is a low probability that  $^3\text{RP}$  will undergoes intersystem crossing by HFC and/or by SOC mechanism<sup>3,4</sup> with formation of a singlet  $^1\text{RP}$ . That probability is higher in a viscous media.<sup>3,4</sup> Singlet  $^1\text{RP}$  recombines (or disproportionates) within a cage, and the cage effect becomes  $\phi > 0$ . The longer the lifetime of  $^3\text{RP}$ , the higher is the probability of intersystem crossing, the higher is  $\phi$ , and thus the lower is the efficiency of initiation.<sup>5</sup>

Figure 1 schematically presents Type I PIs, which undergo Norrish process I, and Type II PI. As an example of the latter we have selected benzophenone (BP) in the presence of a reducing agent or a coinitiator RH.

Figure 2 demonstrates dynamics of cage effect  $\phi = \phi(t)$  under ns laser flash photolysis of BP in the presence of 1.0 M of p-cresol (RH) in glycerol.<sup>6-8</sup> The time of formation of the RP was much shorter than a characteristic time of its geminate recombination. Thus, at the first moment after a laser flash it was possible to monitor kinetics of geminate recombination of RP, following a decay of absorption of benzophenone ketyl free radical.<sup>9</sup> Radicals, which escaped cage recombination, decay in

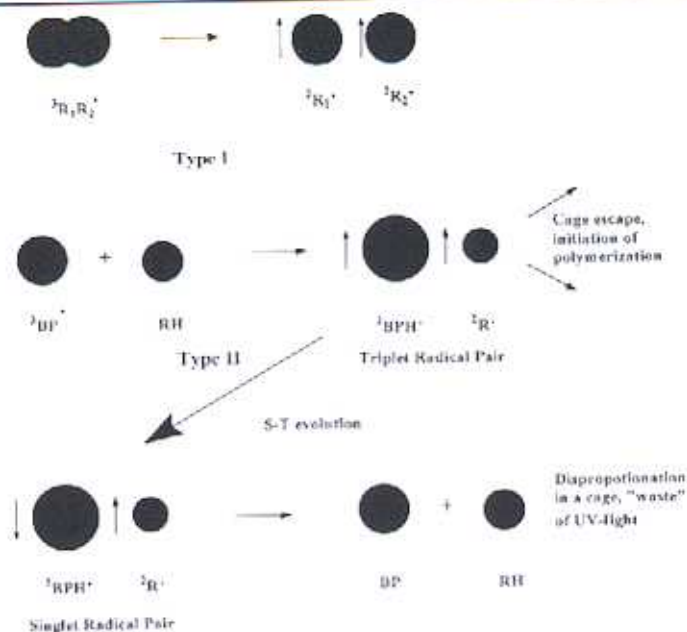


Figure 1. Pictorial presentation of photolysis of PIs of Types I and II.

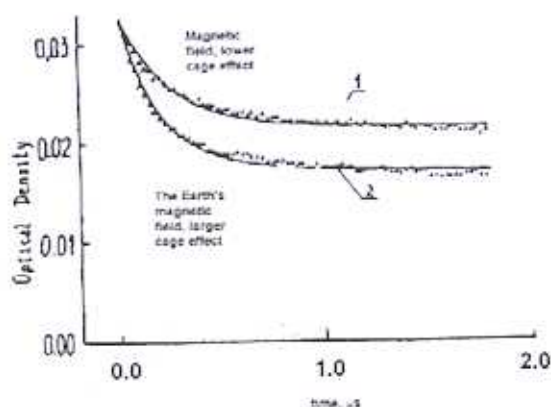


Figure 2. Kinetics of decay of ketyl radical of benzophenone in a viscous media following ns laser flash photolysis under a magnetic field of 0.34 T (1) and in the Earth's magnetic field (2) at 20 °C. Solid lines are theoretical simulation. Adopted after ref. 6,7.

a bimolecular radical-radical termination in a solvent bulk with much slower rates compared to a rate of a cage (or geminate) recombination.<sup>9</sup>

Experimental measurements demonstrate that cage effect  $\phi$  increases with an increase of solvent viscosity.<sup>6,7,14</sup> An increase of media viscosity, which usually takes

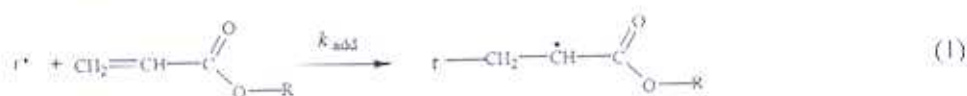
place upon polymerization, results in a decrease of rate of polymerization.<sup>14</sup> Thus, the assumption of a constant photoinitiator efficiency during polymerization<sup>15</sup> is unjustified.

Another important conclusion can be drawn from data of Figures 2:  $\phi$ , and thus efficiency of initiation, depends upon application of moderate magnetic field, cf. below.

Not only does the temperature/viscosity of media affect  $\phi$ . Another possible way of that  $\phi$  increases in a system with the same reagents was found in ref. 16. Photopolymerization of acrylamide initiated by PI Irgacure 2959 (cf. Figure 3 below) was studied in aqueous solution in the presence of poly(methacrylic acid) (PMA).<sup>16</sup> It was found, that PMA forms a cluster around the PI at pH < 6.9, and a cluster holds RP in proximity. As a result, the cage effect  $\phi$  increases, and the rate of photopolymerization decreases.<sup>16</sup>

### Addition of free radicals of PI to acrylates

Addition of free radicals of PI to acrylates leads to polymerization.



This process is well studied, cf. e.g.,<sup>17-20</sup>. Much data was obtained by ns laser flash photolysis and TR ESR. It was been believed for some time that  $\alpha$ -type benzoyl radical is highly reactive. However, direct kinetic measurements demonstrated that counter radicals, which are substituted alkyl radicals, formed under  $\alpha$ -cleavage many commercial PIs (Figure 3) have a higher reactivity than benzoyl radical. For example, rate constants an addition of benzoyl and substituted benzoyl radical to *n*-butyl acrylate in acetonitrile solution at room temperature are  $k_{\text{add}} \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , which is two orders of magnitude lower than  $k_{\text{add}}$  for many counter radicals.<sup>20</sup> To the best of our knowledge, the highest rate constant of addition of a free radical of PI to acrylate at room temperature is  $k_{\text{add}} = (3.3 \pm 0.1) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . It was obtained for an addition of phosphinoyl radical to vinyl acrylate in ethyl acetate at 23 °C.<sup>18</sup>

TR ESR technique allowed determining structure of primary adducts, and it is a valuable method of photoinitiation study. Direct photolysis of mono- and bis-phosphine oxides PIs (MAPO or Lucerin TPO and BAPO or Irgacure 819) leads to the known CIDEP pattern.<sup>17,18</sup> Phosphinoyl radical ( $r^{\bullet}$ ) is much more reactive in addition to double bonds than a counter radical, viz. substituted benzoyl. In the presence of acrylate polarization of  $r^{\bullet}$  is transferred into spin-adduct (eq. 1). The CIDEP pattern is conserved under fast addition, and spin adduct has the same polarization pattern as  $r^{\bullet}$ .<sup>17,18</sup>

Analysis of TR ESR spectra of spin-adducts of a number of additions of phosphinoyl radical to acrylates allowed identifying the main adduct of  $r^{\bullet}$ , which is a "tail" adduct like it is presented in eq. 1 and in Figure 4 below.<sup>18</sup>

### LS<sup>®</sup> oligomers

UV-cure of acrylates has drawbacks related to the use of PI, such as the leaching of residual PIs from cured coatings, and a smell of cured coatings. Our goal was to eliminate or at least alleviate drawbacks related to the use of Type I PIs.

The main part of UV-curable urethane acrylate coatings is urethane acrylate oligomer, which is formed by a reaction of polyol with isocyanate, i.e., by a reaction of  $-OH$  with  $-NCO$  groups. A number of available PIs have primary, secondary or tertiary aliphatic hydroxyl groups<sup>1,2</sup> (Figure 3), and they can react with isocyanate termini of oligomer.

We used the latter route for synthesis,<sup>21</sup> and we grafted PI on to urethane acrylate oligomers. Such oligomers, with grafted PI, were named UV-Light Sensitive (LS<sup>®</sup>) oligomers.<sup>22</sup>

We used benzoin as a PI. In our experience, benzoin is a very efficient photoinitiator despite a relatively long lived triplet state compared to some other PIs of the same family.<sup>1</sup> The photochemistry of benzoin and reactivity of corresponding free radicals are well documented, cf. e.g., ref. 1,23.

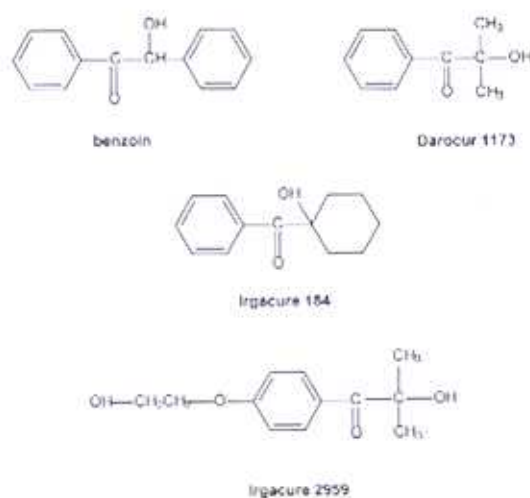


Figure 3. Chemical structures of commercially available hydroxyalkyl substituted PIs.

Figure 4 is a pictorial presentation of initiation of polymerization of difunctional acrylate oligomer by grafted and by dissolved Type I PI:

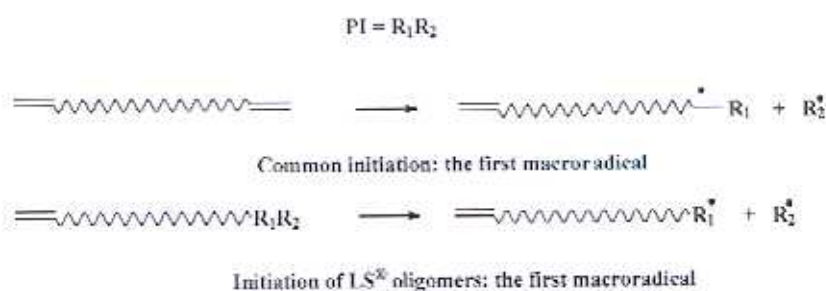


Figure 4. Pictorial presentation of initiation of polymerization of a common difunctional acrylate oligomer and of LS<sup>®</sup> oligomer. The same PI is either dissolved or grafted, cf. the text.

Evidently, LS<sup>®</sup> oligomers with 0.5 – 5.0 wt.% of grafted PI have slightly less concentration of acrylate groups than its conventional analogue. Grafting in a level of less than 5 wt.% produced minor effect on the properties of liquid and cured coatings.

Diols like Irgacure 2959 (Figure 3) can be used as chain extenders, and they can be grafted by two OH-groups. The primary hydroxyl group in Irgacure 2959 (Figure 3) is more reactive than the tertiary hydroxyl. Oligomers endcapped by Irgacure 2959 at the primary OH group were prepared.<sup>19</sup> Photolysis of such oligomeric PI results in formation of a substituted benzoyl free radical bound to a chain and free 2-hydroxy-2-propyl radicals. An increase of oligomer chain results in a slower tumbling of benzoyl fragment. The latter suggestion allows explaining an increase of intensity of an ESR signal of substituted benzoyl radical and an increase of relaxation time  $T_1$  of benzoyl radical measured in FT-TR ESR experiments with oligomeric PI.<sup>19</sup>

Our recent experiments demonstrate that a migration and leachability the residual PI profoundly decreases from cured coatings with LS<sup>®</sup> oligomers.<sup>24</sup> That should be expected for grafted compounds.

#### Efficiency of initiation by grafted vs. dissolved PI

Polymeric or oligomeric PIs are used in UV-curable formulations.<sup>1,25-29</sup> LS<sup>®</sup> oligomers (formulations with LS<sup>®</sup> oligomers) are different from formulations with polymeric PIs. Polymeric PI is a macromolecule with *many PI fragments* incorporated in its structure. Usually polymeric PI has dangling PI fragments. On the contrary, LS<sup>®</sup> oligomers have a backbone of acrylated urethane oligomer; few percent of such macromolecules have *one PI fragment*.

There are different observations on the efficiency of polymeric PI vs. very similar monomeric PI.<sup>1,25-29</sup> In many cases polymeric PI turn out to be rather efficient photoinitiators.<sup>27-29</sup> In some cases a poor efficiency of a polymeric PI is observed.<sup>1,26</sup> Relatively poor efficiency is usually ascribed to a low diffusion coefficient of oligomeric PI and of oligomeric free radical.<sup>1,26</sup>

The original PI and a grafted PI are two different PIs with the same chromophore. The PI and grafted PI can have slightly different absorption spectra and different photophysics, such as quantum yield of a triplet state population, rate constant or quantum yield of dissociation in a triplet state, and different cage effect ( $\phi$ ) values. It was demonstrated that substituents in PIs with a benzoyl fragment (Figure 3) significantly affect quantum yield of photodissociation in a non-viscous solvent.<sup>30</sup>

We speculate that formation of oligomeric free radical of PI instead of low MW radical in RP leads to a longer lifetime of RP due to lower diffusivity of oligomeric radical and thus to a higher  $\phi$  and to lower rate of polymerization of LS<sup>®</sup> oligomer. We consider photopolymerization of common formulations vs. formulations with LS<sup>®</sup> oligomers: all conditions being very similar with the only difference being that the PI was grafted and the PI was dissolved. On the other hand, photolysis of LS<sup>®</sup> oligomer leads to a formation of oligomeric free radical after photolysis, which may be considered as an advanced stage of polymerization. It is possible to suggest that LS<sup>®</sup> oligomers should cure faster. Experimental data on relative efficiency of grafted and dissolved PIs are presented in the next section.

### Rates of cure of LS<sup>®</sup> oligomers

Figures 5,6 present experimental data on comparative rates of cure of common and of LS<sup>®</sup> oligomers. It follows from data of Figures 3,4, that formulations with LS<sup>®</sup> oligomers cure with rates close to those of common oligomers. LS<sup>®</sup> oligomers with di-grafted PI like Irgacure 2959 (Figure 3) often (but not always) cure slower than their common counterparts.<sup>24</sup>

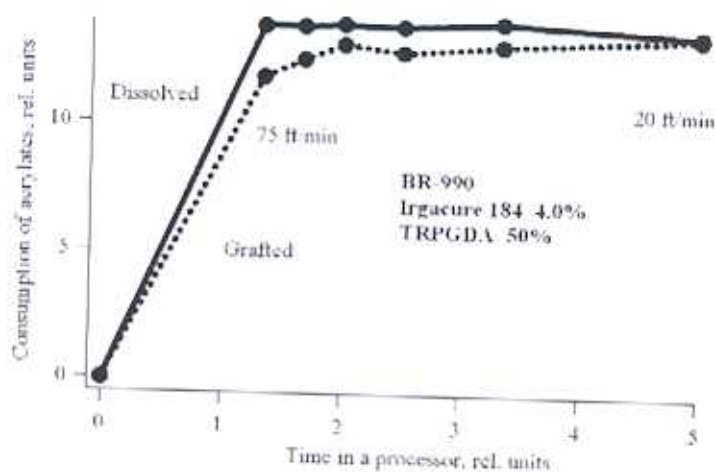


Figure 5. Relative efficiency of UV-cure of oligomer BR-990 of Bomar with a dissolved and with a grafted PI at ambient temperature. Oligomer was diluted twice by tripropylene glycol diacrylate (TRPGDA). The values in ft/min are the conveyor belt speed. Adopted from ref. 24

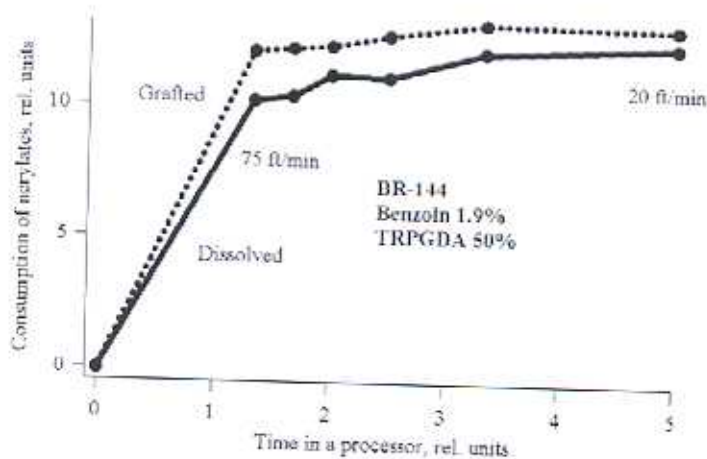


Figure 6. Relative efficiency of UV-cure oligomer BR-144 of Bomar with a dissolved and with a grafted PI at ambient temperature. Oligomer was diluted twice by TRPGDA. The values in ft/min are the conveyor belt speed. Adopted from ref. 24

We observed that LS<sup>®</sup> oligomers with benzoin cure faster than oligomers with dissolved benzoin in the most studied cases. Our data indicate that *neat* LS<sup>®</sup> oligomers of relatively low viscosity cure faster than their common analogues.<sup>31,32</sup>

### Kinetics of photopolymerization

Kinetics of free-radical polymerization of diluted solutions of vinyl monomers, and acrylate monomers in particular, follows well known kinetic laws, cf. e.g., ref. 1,33,34. However, it is impossible to apply formal kinetics to photopolymerization of acrylate coatings, mono- and multifunctional acrylate oligomers and even solventless individual acrylates. Dramatic changes in the reaction media and in the structure of a reagent-multifunctional acrylate during the polymerization process makes it impossible to use rate constants  $k_p$ ,  $2k_t$ , etc. A concept of "reaction" or "residual diffusion"<sup>35</sup> is a palliative approach allowing semiquantitative prediction of kinetics of cure.<sup>14,35</sup>

Thus, with most of the kinetic curves of cure obtained with one or another experimental method (cf. Figure 7 below) it is impossible to deconstruct the data to elementary rate constants. Computer simulation of kinetics of cure is a developing promising area.

Cure profiles are useful as a reaction *series* with one-two changing parameters for understanding of relative reactivity of similar formulations. Dependencies upon structure of oligomer and its MW, radiant excitation and radiant exposure ("light intensity",  $W/m^2$  and "dose",  $J/m^2$ , respectively), thickness of a coating layer, concentration of oxygen, concentration of PI, concentration of diluent, temperature, etc., help to understand kinetics and to make some predictions at empirical level.

It was demonstrated that a relation between the temperature of cure and  $T_g$  of a forming polymer has a profound effect on a degree of cure  $\xi_{max}$ .<sup>14</sup> A cure profile is usually a smooth curve, and we have found that eq. 2 successfully describes the polymerization:

$$\xi/\xi_{max} = 1 - A_1 \cdot \exp(-k_1 \cdot t) - A_2 \cdot \exp(-k_2 \cdot t), \quad (2)$$

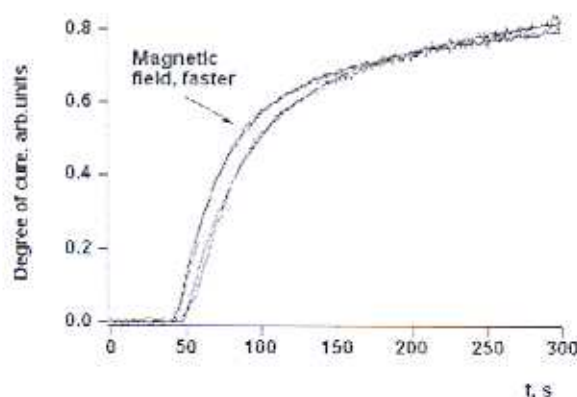


Figure 7. Magnetic field effect under photopolymerization of oligomer CN966 of Sartomer at ambient temperature. Adopted from ref. 34



where  $\Lambda_1$ ,  $A_2$ ,  $k_1$  and  $k_2$  are fitting parameters,  $\xi$  is a current, and  $\xi_{\max}$  is the maximum obtained conversion of acrylates.<sup>33,34</sup> For a cure of multifunctional acrylates below  $T_g$  usually  $\xi_{\max} < 1.0$ .<sup>14,35</sup>

Application of moderate magnetic field accelerates the polymerization initiated by PIs which react in a triplet state to form a triplet RP.<sup>5,14,16</sup> Figure 7 presents two experimental kinetic curves and their simulation with eq. 2. Induction period of ca. 50 s was excluded from simulation.<sup>34</sup>

Polymerization of monomers in diluted solutions almost promptly terminates after completion of initiation. However, postpolymerization of multifunctional acrylates and acrylate coatings plays important role in cure leading to significant additional conversion after cessation of irradiation.<sup>17</sup> This phenomenon finds application in the fast cure of coatings with two or more light pulses.<sup>14,37</sup> Kinetics of postpolymerization can be described by biexponential or monoexponential kinetic law like almost any smooth descending curve. More physical sense may have eq. 3 with two fitting parameters  $a$  and  $b$ :

$$[M]_t = \frac{[M]_0}{(1 + a \cdot t)^b} \quad (3)$$

where  $[M]_t$  and  $[M]_0$  are current and the initial concentration of acrylate,  $a$  in the formal kinetics of postpolymerization is  $2k_t/[R_n]_0$ ,  $s^{-1}$ ,  $b = k_p/2k_t$ ;  $[R_n]_0$  is initial concentration of macroradicals.<sup>37</sup> The word "initial" in postpolymerization stands for a concentration of species after cessation of initiation (turning off light). Our experiments demonstrate that eq. 3 successfully describes postpolymerization.<sup>37</sup>

## Conclusions

Initiation of free radical photopolymerization includes photogeneration of free radicals from a PI and their addition to vinyl group of a monomer. These processes are well understood and can be studied for any given system when necessary. TR ESR technique gives an insight on a detailed mechanism of photoinitiation and ns laser flash photolysis allows get rate constants of addition  $k_{add}$ .

On the contrary, kinetics of photopolymerization of solventless acrylates and coatings is poorly understood, and it is currently largely at a stage of empirical observations. Dependencies of the rate of photopolymerization upon one or another parameter give some insight into the process.

Oligomers with grafted photoinitiators (LS<sup>®</sup>) demonstrate in many cases superior properties to similar oligomers with dissolved photoinitiators. Rates of cure of LS<sup>®</sup> oligomers are close to those of relevant common oligomers. In a number of cases we observed significantly faster cure of LS<sup>®</sup> oligomers. Cured formulations with LS<sup>®</sup> oligomers have much less leachable free PIs and benzaldehyde. The latter makes LS<sup>®</sup> oligomers promising candidates for food packaging coatings.

LS<sup>®</sup> oligomers are slightly modified urethane acrylate oligomers which do not need an addition of PI. Chemists and manufacturers running standard UV-cure do not need to be concerned with a selection and addition of PI. Evidently, grafting of PI eliminates a concern on PI's compatibility.

Dynamics of the cage effect under photolysis of Type II PI benzophenone in the presence of *p*-cresol was discussed. An increase of viscosity, which usually goes along with polymerization, leads to an increase of cage effect  $\phi$  and to a decrease of rate of polymerization. Application of moderate magnetic field accelerates free radical polymerization initiated by PI reacting via a triplet state.

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