



## Review

## Fast photopolymerization of acrylate coatings: Achievements and problems

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## ABSTRACT

Coatings chemists often prepare (meth)acrylate coatings which meet their needs. However, analysis of kinetics of photopolymerization (UV-cure) is usually based on a classical scheme of the chain free radical polymerizations. That set of reactions with respective rate constants is valid only up till few percent of conversion of double bonds. Multiple studies of photopolymerization are focused not on reactions at large degree of polymerization but on selection of new photoinitiators. In the present paper we focused on fundamentals of photopolymerization rather than on multitude of applications, different formulations, sources of light, etc., and we try to avoid repetition of widely discussed in the literature issues. A special attention is devoted to cage effect during photodissociation of initiators. An increase of cage effect value with a degree of polymerization increase affects overall efficiency of photoinitiator at large conversions. IUPAC terms and notions are suggested.

## 1. Introduction

Photopolymerization is a modern way of coatings cure. It is a very impressive process: a viscous liquid in seconds or in a fraction of a second transforms into a solid polymer. Photopolymerization occurs under initiation by UV-, visible- and in rare cases by IR-light. The most common is UV-cure. In this paper we will deal with the free radical polymerization (FRP) of acrylates and methacrylates. UV-light has enough energy to break a chemical bond of so called Type I photoinitiator (PI) [1–3]. We will discuss mainly Type I PIs below. There are different vinyl compounds which can be used in coatings and which polymerize by FRP. However, “the biggest part of UV formulations is based on acrylates and methacrylates” [4]. There are many reasons for using (meth)acrylates, and the main of them is relatively high rate of polymerization, diversity of chemical structures capped by (meth)acrylates which lead to a variety of physical (mechanical) and chemical properties of the cured coatings. Urethane (meth)acrylates are probably the most widely used oligomers. Methacrylates are considered as less hazardous than acrylates. However, methacrylates usually polymerize slower than acrylates under similar conditions.

UV-curable formulations are solventless in most cases: almost all components of a formulation participate in polymerization or in copolymerization. A standard formulation may consist of:

- Oligomer(s) – the main component(s) essentially determining properties of the cured coating, ~70 wt.%
- Reactive diluents(s) (low MW monomer(s)) **M** which are added to reduce viscosity of oligomer, ~25 wt.%

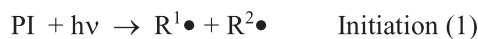
- PI or a blend of PIs, ~5 wt.%
- Additive(s) in low concentrations – flow control additives (surfactants), light stabilizers, chain transfer agent, colorants, stabilizers of the liquid coatings, etc.

Oligomers (or prepolymers or macromonomers) are relatively high MW compounds which are viscous. It is inconvenient to deal with very viscous compounds, and reactive diluents, which are low MW compounds (**M**) with a viscosity  $\eta \sim 1 \div 5$  cP. **M** is added to a formulation to get flowable (pourable) formulation and to dissolve other components. Properties of the cured coating provided by oligomer are altered by reactive diluents. Thus, chemist looks for a tradeoff. Oligomers with relatively low  $\eta$  are obviously valuable.

It is well-known that (photo)polymerization leads to a volume contraction of an individual monomer **M** or of a formulation. That becomes often a problem for a chemist working with a formulation. Oligomers are “almost polymers” in a sense: consumption of a low number of double bonds converts oligomer into polymer. Photopolymerization of individual low MW **M** in most cases leads to shattering or results in a hard polymer. (We will imply below that **M** means low MW monomer or an acrylate group of oligomer. The difference will be understood from the context.)

There are many books, collections of papers like this book, proceedings of conferences and multiple review articles devoted to photopolymerization, cf. e.g. 1–3, 5–7. We briefly consider basics of photopolymerization in this paper below and we will skip many applications. We attempt not to repeat extensively discussed in the literature topics.

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**Scheme 1.** A list of the main elementary reactions proceeding during photopolymerization.

A deeper understanding of photopolymerization helps coatings chemists in their everyday work. Nicholas Turro (1938–2012) and Charles Hoyle (1948–2009) studied fundamentals of photopolymerization and brought their knowledge to practitioners. This paper is an attempt to continue such work.

## 2. The main reactions during photopolymerization

As a brief reminder, photopolymerization of **M** occurs by the following main reactions of **Scheme 1**:

Here and below **M** stands for a vinyl monomer, a species with a dot like  $\text{R}^1\text{M}\bullet$  stands for a free radical – reactive species with unpaired electron. Reaction (5) can be also disproportionation, i.e., an exchange of H-atom between radicals.

Kinetic treatment of photopolymerization is usually starts with Eq. (6) for chain free radical reaction with bimolecular chain termination in a quasi-stationary regime:

$$v_t (M/s) = \sqrt{w_{in} \cdot \frac{k_p}{2k_t}} \cdot [M], \quad (6)$$

where  $v_t$  is a time-dependent rate of polymerization (disappearance of acrylate groups),  $k_p$  ( $2k_t$ ) is a rate constant ( $M^{-1} \cdot s^{-1}$ ) of chain propagation (bimolecular chain termination),  $[M]$ , is a concentration of a monomer, here a concentration of acrylate groups.  $w_{in}$  ( $M/s$ ) is the rate of chain initiation. A number of assumptions made upon derivation of Eq. (6) can be found in the literature [6a,6b].

There are other less known but useful kinetic equations for post-polymerization or dark polymerization [8]:

$$[M]_t/v_t - [M]_o/v_o = (2k_t/k_p) \cdot t \quad (7)$$

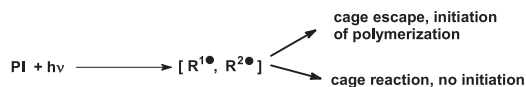
$$[M]_t = \frac{[M]_o}{(1 + 2k_t \cdot [M]_o \cdot t)^{2k_t/k_p}} \quad (8)$$

Formal kinetics leads to Eqs. (7), (8) for polymerization after termination of initiation. Here a subscript “o” stands for the initial moment when postpolymerization is observed (light turned off);  $[M]_o$  is the quasi-stationary concentration of  $\text{M}_n\bullet$  reached during polymerization.

Eq. (9) presents characteristic times on onset of this quasi-stationary concentration [9]:

$$\tau_{\text{onset}} = 1.5/(2k_t \cdot w_{in}) \quad (9)$$

Formal kinetics Eqs. (6)–(9) (applicable for individual **M** in diluted solutions, cf. below) do not account for a chain transfer to monomer (to solvent, to polymer), reaction with traces of dioxygen and impurities. These phenomena play role in FRP.



**Scheme 2.** Elementary reactions occurring during photoinitiation.

## 3. Cage effect during photolysis of photoinitiators

The first step (reaction 1) of photopolymerization is the formation of a pair of reactive free radicals (RP):

The quantum yield of RP generation in a solvent is denoted as  $\Phi_{\text{obs}}$ . 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.,  $\Phi_{\text{obs}} = 1.0$  for the yield of radical pairs (RPs) and the yield of individual free radicals is twice higher. In reality, common PIs (Irgacures, Darocur) have  $\Phi_{\text{obs}} = 0.2\text{--}0.6$  measured in non-viscous solvents [3,5]. It is well understood why many commercial efficient PIs have a benzoyl fragment [3,5]:

Photogenerated radicals exist for a certain time in a solvent cage [ $\text{R}^1\bullet$ ,  $\text{R}^2\bullet$ ] as a dynamic RP, see **Scheme 2**. RP participates in two competitive processes: recombination or disproportionation (within the cage) and dissociation (exit of radicals into 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:

$$f = 1 - \varphi_{\infty}, \quad (10)$$

where  $f$  is the cage escape value used in polymer chemistry, and  $\varphi_{\infty}$  is the cage effect value. We will introduce a value of  $\Phi$ , which is a quantum yield of photodissociation in the cage. *Evidently, the higher is the product  $\Phi \times f = \Phi_{\text{obs}}$  the more efficient the PI.* Fig. 1 is a pictorial presentation of cage phenomenon upon photolysis of PI in inert solvent (**Scheme 3**):

Practitioners usually successfully select a PI or a blend of PIs which allow them to cure formulations by FRP. There are many reports in the technical literature on “very efficient” PI. These PIs are used in specific formulations, and it is unknown how efficient “a very efficient” PI would perform in another coating. However, there are several universal requirements for an “efficient” PI. An obvious demand is the absorption of UV/vis light by PI from the light source. Another requirement is that photoexcited PI generates much of highly reactive towards double bonds free radicals. In this paper we stress the importance of high  $\Phi$  of the photodecomposition of PI and of low  $\varphi_{\infty}$ . Decrease of concentration of vinyl groups during photopolymerization leads to the fact that reaction (2) is not the dominant reaction of radicals  $\text{R}^1\bullet$  and  $\text{R}^2\bullet$  of the PI. These highly reactive radicals participate in self- and cross-termination [10b].

There are many other demands for an industrial PI such as low migration, low toxicity, lack of hazardous byproducts of the reactions of PIs, lack of odor, etc. Still, one would expect that PI plays a modest role – creation of reactive free radicals for initiation of polymerization. However, in practice it was noted that different PIs can lead to different properties of the cured coatings, say good or poor adhesion to a substrate. Reasons for such differences are poorly understood.

It was mentioned above, that in the case of an “ideal” PI all radicals formed from the PI exit the solvent cage.  $\text{R}^1\bullet$  and  $\text{R}^2\bullet$  of the “ideal” PI should have high reactivity towards vinyl compounds, and under high concentration of the latter, all  $\text{R}^1\bullet$  and  $\text{R}^2\bullet$  start polymerization [11]. At the later stages of polymerization PI is expected to be less efficient, cf. this Section below.

Cage effect has been studied for almost 85 years, and a number of publications have appeared during the last 30 years on the cage effect dynamics, i.e., temporal performance of RP:  $\varphi = \varphi(t)$  [11–14]. Cage effect dynamics is successfully described with so-called *generalized*

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