

Photoinitiators

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Photoinitiators is a popular topic of technical and scientific review articles on photopolymerization (“UV-cure”). The reason is that light-induced elementary reactions of photoinitiators (PIs) are very well understood and studied in great detail. However, these studies were performed in individual solvents. As we detail in these memos, UV-cure of solvent-less formulations is a rapid transformation of a (viscous) liquid into solid polymer. After 1-5% of conversion of a vinyl monomer (or macromonomer or oligomer) a formulation becomes, simply speaking, a complete mess. Rate constants, quantum yields of photo-reactions, concepts of chain reactions become inapplicable to solvent-less and, in addition, complex systems during their polymerization. That is why the knowledge of reactivity of a PI in solvents has only limited application to real systems.

Formulator selects PI or a blend of PIs and their concentrations based on his previous experience, expectations, and extrapolation of properties of PIs in solvent onto his specific formulation. We refer every chemist working with PIs to an excellent compilation of properties and performance of PIs written by Dr. Dietliker of Ciba Additives (Basel, Switzerland): **Dietliker, K. *A Compilation of Photoinitiators Commercially Available for UV Today*; SITA: Edinburgh, 2002.**

In this paper we will briefly remind the reader the basics of PIs reactivity during UV-cure.

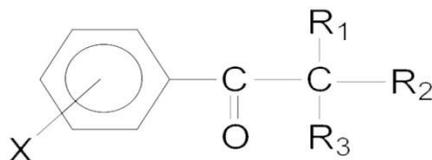
Two Types of PIs

In this report we will deal with PIs for *free radical polymerization* of vinyl monomersacrylates, methacrylates, allyl oxides, vinyl oxides, styrene, and other enes. In order to run free radical polymerization one needs to produce free radicals. In UV-cure, free radicals are produced via photolysis of PI. PIs of Type I are compounds that undergo photodissociation under UV/Vis-irradiation:

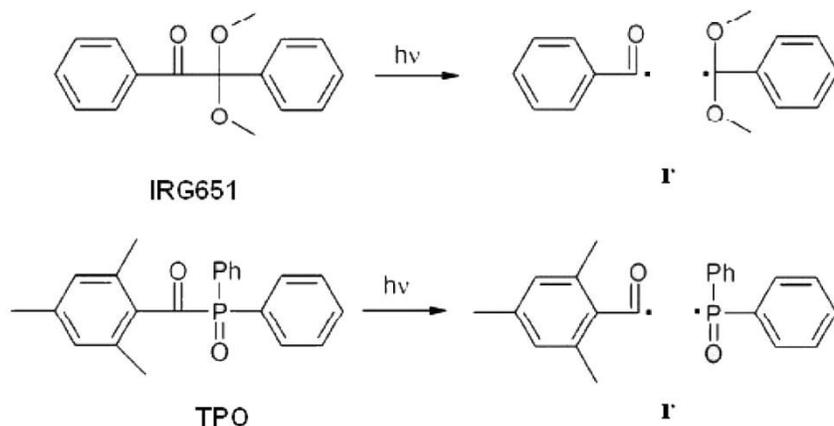


We will designate radicals of PI as r or as r_1 and r_2 . The obvious requirement for PI is that it should absorb UV light emitted by the available light source, and produce r with a high yield throughout the cure. There are many other demands for industrial PIs: low migration, low toxicity, lack of hazardous byproducts of reactions of PIs, lack of odor, etc.

A large family of PIs, manufactured by Ciba Additives under the trade names Irgacure® and Darocur®, has a benzoyl fragment in their molecules:

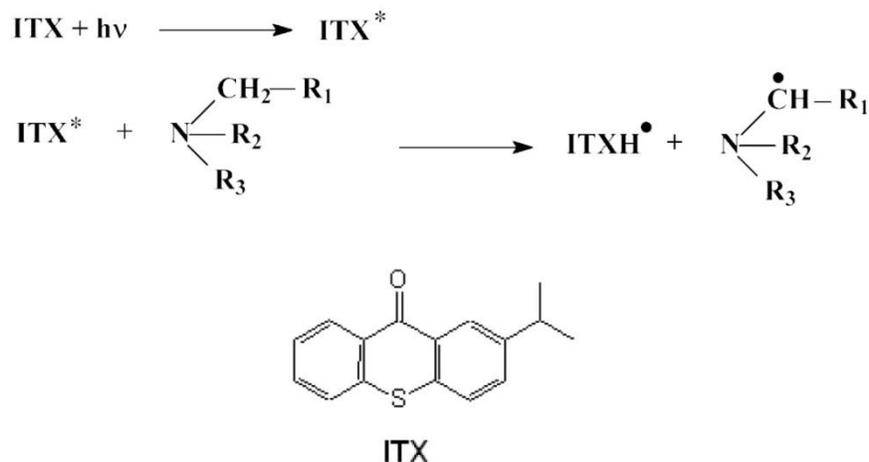


These molecules usually rapidly dissociate into free radicals in the so-called triplet state and undergo α -cleavage, i.e. a bond breaks to the right of C=O group. Two examples, photo-dissociation of Irgacure 651 and of Lucirin TPO of BASF (a.k.a. Irgacure TPO of Ciba additives) are presented below:¹



¹ This is Norrish I type process in ketones.

PIs of Type II are benzophenone, 2-isopropyl thioxanthene-9-one (**ITX**), and other compounds, capable in the excited state to abstract hydrogen or electron from a donor, which is usually amine, and produce radicals:²



Only the reactive radical of aminoalkyl initiates polymerization.³ Radicals of benzophenone or **ITX** can even play a negative role reacting with macroradicals R_n^\bullet and decelerating cure. (Speaking about **ITX**, it is worthwhile to recall that few years ago **ITX** was found leaching from inks of children's milk bottles and **ITX** had been promptly prohibited in the European food packaging market after that.

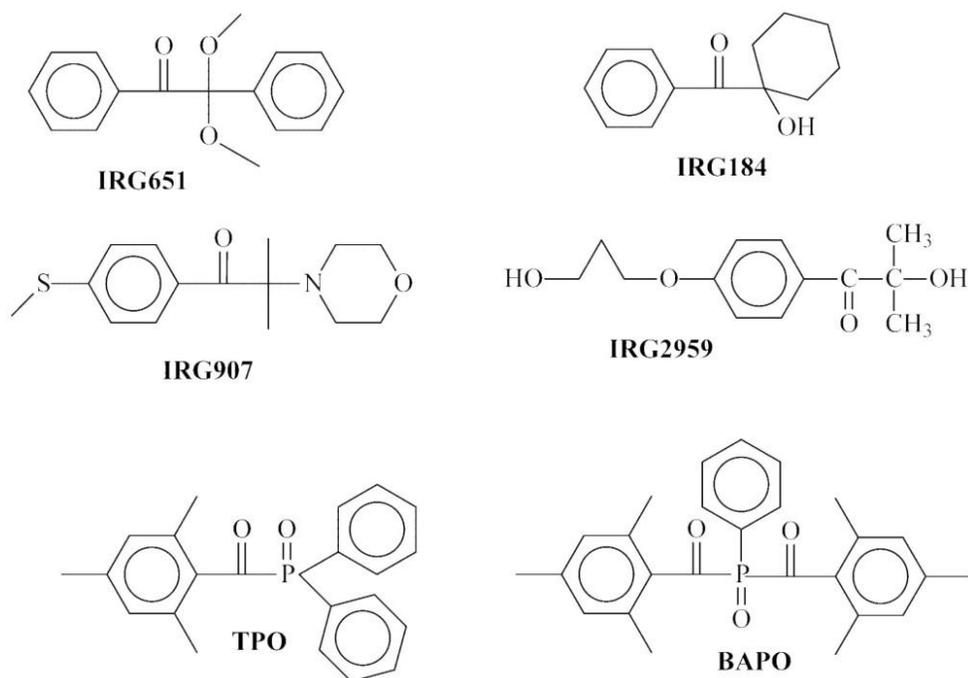
Efficiency of PI

Scheme 1 presents chemical structures and our designations of several common Type I PIs. An important parameter of Type I PI is its quantum yield of photodissociation ϕ_{diss} . The latter is the probability of radical pair formation under absorption of a light quantum. Say, 1.0 billion photons were absorbed, and 0.45 billion of radical pairs (r_1 , r_2) were formed. That means that $\phi_{\text{diss}} = 0.45$. Energy of 0.55 billion of absorbed light quanta will be released as heat. The higher ϕ_{diss} (up till 1.0) the more efficient is PI. ϕ_{diss} for different common were measured in non-viscous solvents, and typical values of ϕ_{diss} for PIs used in industry are 0.3 to 0.6.⁴

² Unfortunately, Type II PIs are often confused with the Norrish process II. The latter is intramolecular hydrogen abstraction.

³ Another common mistake is to say that Type II PI "abstracts protons" (H^+). Add acid to your formulation. Acid releases protons, which will NOT be a reducing agent for a Type II PI.

⁴ It is wrong to call PIs photocatalysts. Catalyst accelerates a chemical reaction, but it is not consumed in the reaction. PIs are reagents; they are consumed during UV-cure.



Scheme 1. Chemical structures of widely used PIs and their suggested abbreviations. **IRG** with a number stands for Ciba's designation of a PI: *Irgacure 2959*, etc. **DAR** stands for Ciba's *Darocur 1173*, for **TPO** – see above, **BAPO** stands for *bis-acyl phosphine oxide* or *Irgacure 819* of Ciba.

Now we have an interesting situation. Two highly reactive radicals (r_1 , r_2) are produced in the proximity. It is an excellent opportunity for them to react with each other with the formation of the original PI or another molecule! Fortunately, a pair (r_1 , r_2) is formed in a so-called triplet state. Triplet pairs can't recombine and they have to separate into r_1 and r_2 , and to do what they are "designated to do", i.e., attack vinyl (acrylate) compounds and initiate polymerization.

Efficiency of thermoinitiators (peroxides, azo compounds) in polymer chemistry is often designated as ϕ , where ϕ is *probability to escape each other*. Thermoinitiators form a singlet radical pair, and there is no prohibition for self-termination:



That is way most of thermoinitiators have $\phi \ll 1.0$.

Photoinitiators in non-viscous media have $\phi \approx 1.0$. In general, efficiency of PI is $\phi_{\text{diss.}} \cdot \phi$. Obviously, the ideal efficiency of a Type I PI is 1.0, which means that every absorbed light quantum of the UV-light leads to a pair of reactive radicals (r_1 , r_2) that escape recombination with each other. In this report we will mainly focus on Type I PIs. Similar considerations can be applied to Type II PI.

The increase of media viscosity in the process of UV-cure leads to an increase of radical pair (r_1, r_2) lifetime. Increase of viscosity slows down molecular diffusivity, and allows a conversion of triplet pair into the reactive singlet pair. Experimental measurements demonstrate that f decreases with an increase of solvent viscosity. One can expect that PI becomes less and less efficient in the course of UV-cure.

Absorption Spectra of Formulations and of PI

Absorption of light by PI leads to photodissociation of PI with one or another efficiency. Absorption spectra of many PIs are known, and Ciba has available on the Internet technical data sheets with absorption spectra of their PI taken in solvents under several concentrations, cf. an example below:

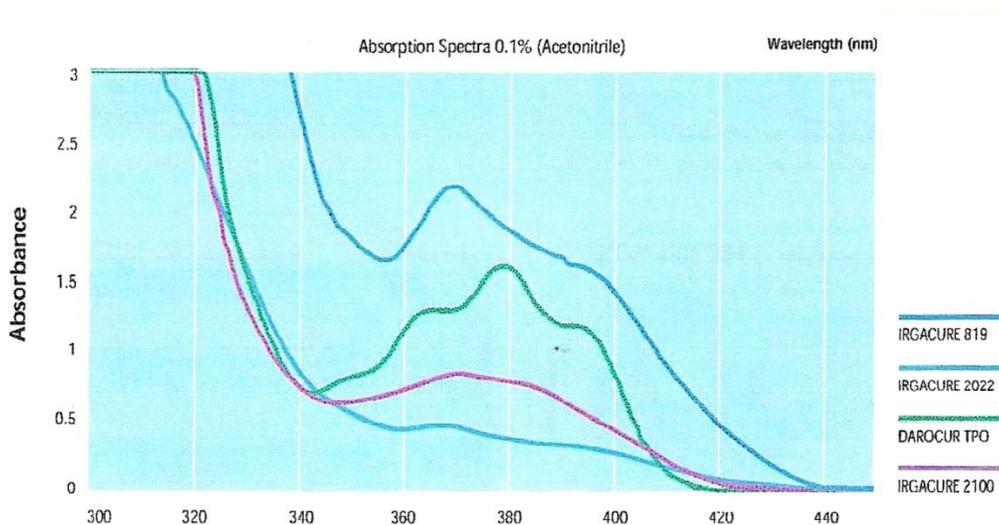


Figure 1. Spectra of four Ciba-Additives PIs (0.1 wt.%) in acetonitrile.

It is always easy to recognize TPO as a PI in UV/Vis spectrum of unknown formulation by its characteristic spectrum with two shoulders, cf. the Figure 1. “Light intensity” of a light beam exponentially decreases with: distance (thickness of a coating layer), molar absorptivity (extinction coefficient) of a PI at a selected wavelength, and with a concentration of PI. It is possible to calculate, or at least to estimate, how much light was absorbed by a coating layer, knowing the emission spectrum of a bulb and its “light intensity,” thickness of a coating, concentration of PI. In the real life coatings chemists ignore molar concentrations and extinction coefficients and select PI or a blend of PIs in a concentration 0.5-5 wt.% in a formulation.

The first law of photochemistry says that only *absorbed* light can initiate any photoreactions. Thus, a UV chemist needs to look for a good overlap of the emission spectrum of a bulb and the absorption spectrum of PI. The task becomes more complicated when the formulation has other additives (pigments, dyes, colorants) absorbing UV/Vis-light of a bulb. A formulation can have some color without any special additives (often yellow or brown due to oxidation.) Under such circumstances one needs to take UV/Vis spectrum of a formulation, notice valleys in the spectrum and select PIs, which absorb in the area of valley(s):

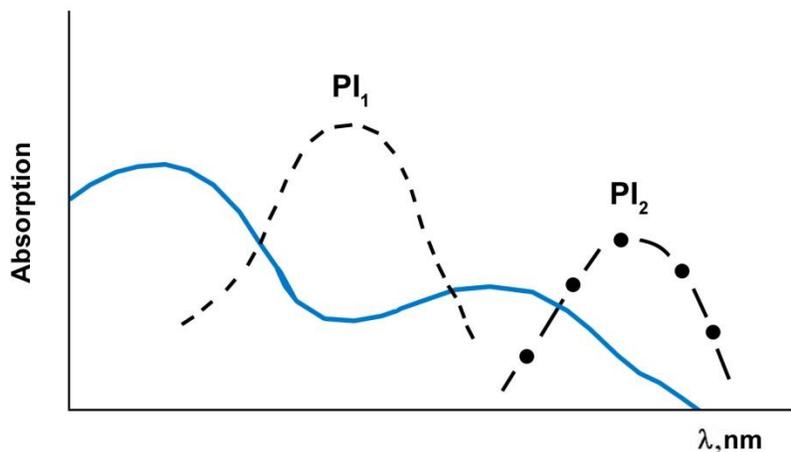
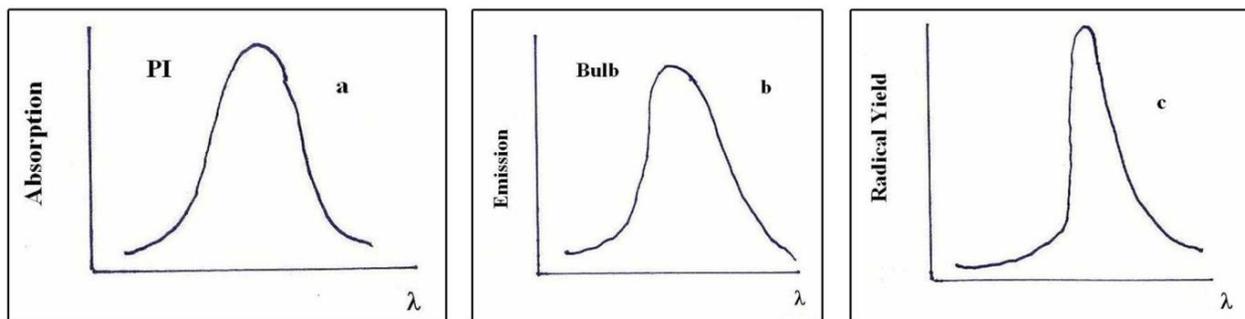


Figure 2. A possible absorption spectrum of formulation and of PIs.

For example, a solid line in the Figure 2 above demonstrates absorption spectrum of a formulation which should be UV-cured. One can select PI₁ which has an absorption band in a valley of absorption spectrum and/or PI₂.⁵

Evidently, a bulb should emit in spectral area where PI absorbs. However, here is something interesting. Let us assume that the formulator has flexibility in selection of an emission spectrum of a bulb (lamp). It is *not necessary* to select a bulb with emission, which mimics absorption spectrum of PI (Figure 3):



⁵ Light can be absorbed by a band of absorption spectrum, but that does not guarantee that a chemical reaction will take place. All absorbed energy can be released as luminescence or as heat. In the cases under discussion, light absorbed by PIs in their different bands in UV/Vis area of the light spectrum does lead to chemical reactions.

Figure 3. Emission spectrum of a light source that mimics absorption band of PI.

In the case presented in the Figure 3, most of the light will be absorbed in the maximum of absorption and the most radicals will be produced basically by an irradiation in a narrow band. If we want to have an equal yield under absorption at all wavelength of a band, we will need to select another light source, cf.

the Figure 4 on the next page. The point we want to make is that there is no need to search for the best possible overlay of emission and absorption spectra of a bulb and of PI band, respectively. Modern intensive light sources with different emission spectra, efficient bleaching under light PIs of phosphine oxide family (TPO, BAPO, some others) allow to make miracles and to cure even thin black coatings. Figure 5 demonstrates that there is a window to cure heavily pigmented coatings. It is often possible to get efficient cure by UV-light of formulations which contain UV-absorbers (!), antioxidant, pigments. The PIs with red-shifted spectra and PIs absorbing light in the absorption minima of the formulation make it possible. 5. Initiation by visible light. Sensitization TPO and BAPO absorb visible light (λ 400-430 nm), cf Figures above. These remarkable PIs produce very reactive P-centered radicals. Moreover, they bleach under UV/Vis irradiation allowing deep cure. Any dentist nowadays can cure UV dental fillings using a Type II PI, namely camophorquinone and amine. There is a chance that dentist uses an approved Type I PI TPO. Cure of dental filling is initiated by visible light and occurs at depths of 5-6 mm from the top.

It is possible to use dyes, which absorb visible light as Type II PIs. Evidently, the formulation will be colored. The color may or may not disappear during cure. If color has practically gone due to bleaching of a dye under light, it may return under storage due to oxidation of the reduced dye by air dioxygen.

Sensitizer (Sens) is a molecule, which absorbs light, becomes electronically excited, and transfers its excitation to other molecules like PI, cf. Scheme 2.

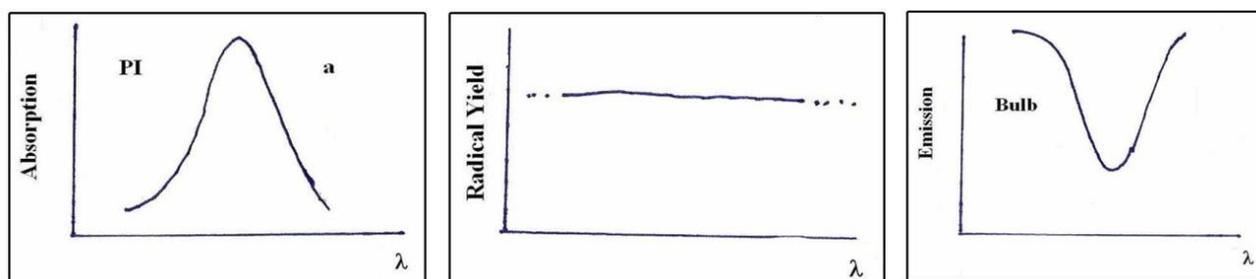


Figure 4. Emission spectrum of a light source which has a mirror shape to the absorption band of PI.

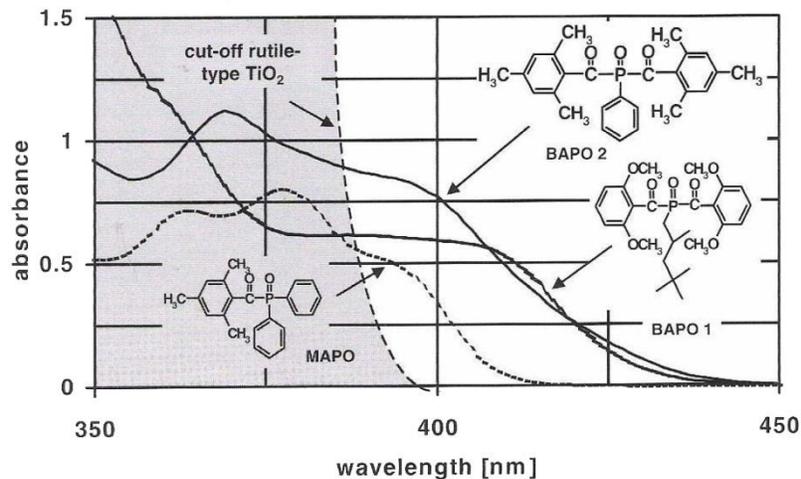
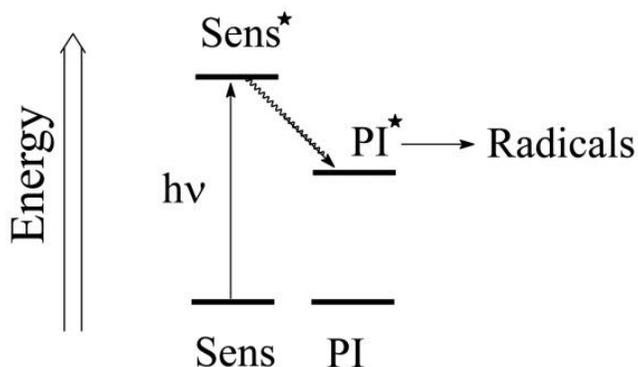


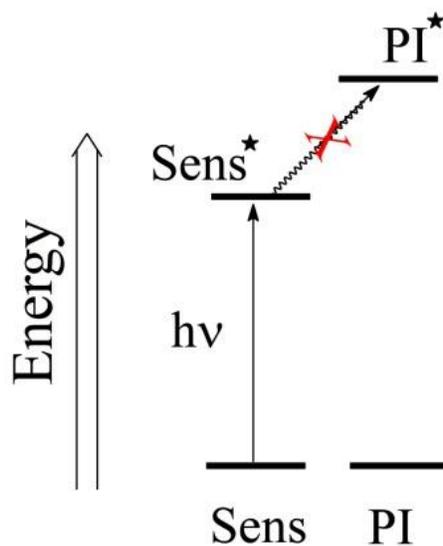
Figure 5. Absorption spectra of a formulation with a pigment rutile. The formulation can be easily cured with three PIs taken in the same weight concentration: two BAPOs⁶ and TPO.



Scheme 2. Exothermic energy transfer.

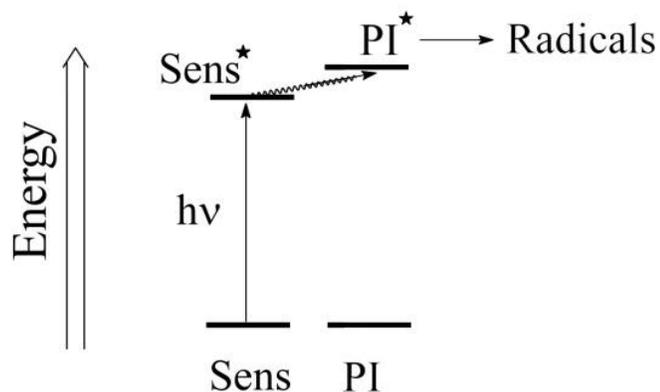
Electronically excited PI dissociates or abstracts hydrogen/electron. Use of Sens may be a convenient resolution of a situation when one can't excite PI directly but found a valley with low absorbance (high transmittance) in the spectrum of a formulation where Sens absorbs. However, it is necessary to keep in mind that energy is spontaneously transferred downhill (exothermic process). One cannot expect an efficient endothermic energy transfer, just like one does not expect a ball rolling by itself uphill.

⁶ The second BAPO with a branched alkyl chain is manufactured by Ciba as a solution in Darocur 1173 under the name Irgacure 1700. That individual BAPO with a branched alkyl chain is considered hazardous.



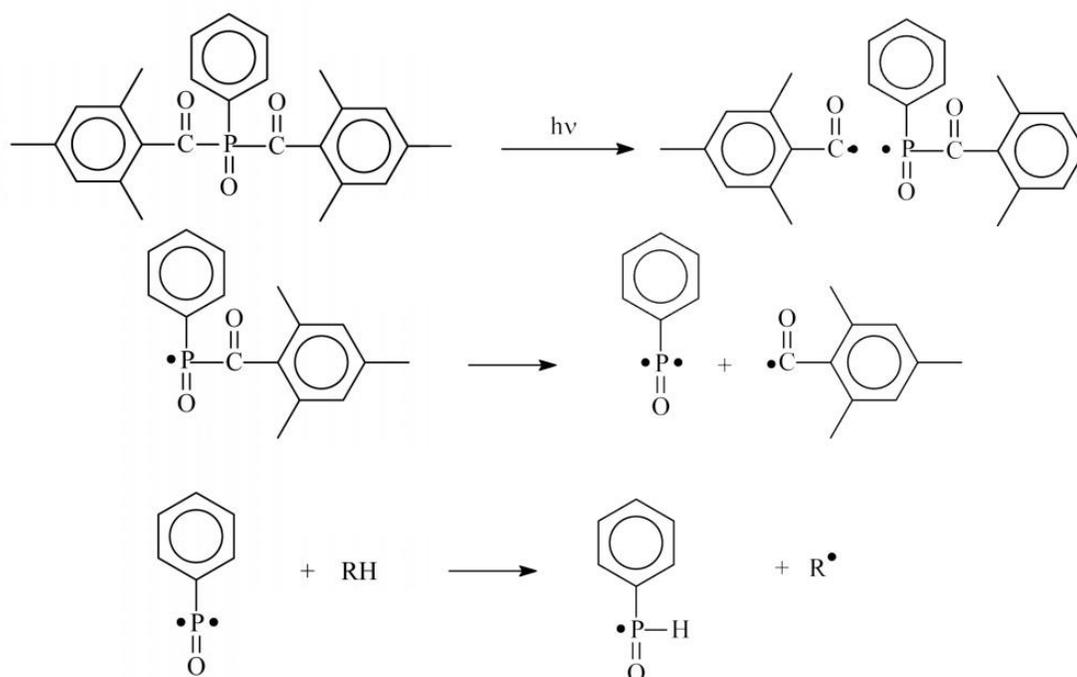
Scheme 3. Endothermic energy transfer does not occur.

We can assume that in the Scheme 3 above PI absorbs UV-light and has high-energy excited states, whereas Sens is colored or is a dye and it absorbs visible light and has lower energy excited states. We have found that ITX transfers excitation to BAPO and to TPO. Energy levels of ITX (~260 kJ/mol) are very close to those of BAPO (TPO), Scheme 4:



Scheme 4. Slightly endothermic energy transfer can occur with acceptable efficiency in the presence of high concentration of PI.

In the conclusion of this section, we will say a few more good words about BAPO. P-centered r of BAPO is believed to dissociate during its lifetime, if r is not promptly intercepted by an acrylate:



Scheme 5. Photolysis and the probable dark reactions accompanying photolysis of BAPO.

A trivalent P-compound phosphene abstracts hydrogen from a C-H of surrounding molecules bond with a formation of two radicals. Thus, BAPO can produce up to four radicals upon absorption of one photon. One absorbed *einsteins* (one mole of quanta) can produce up to four moles of reactive radicals. That makes BAPO a very efficient PI.

Conclusions

In the “old good days” of 1930-1960 chemists studied polymerization of vinyl monomers (styrene, acrylates, etc.) in inert solvents like benzene. Polymerization occurred as a chain reaction initiated by thermo-initiators (benzoyl peroxide BPO, azo-*bis*-isobutyronitrile AIBN, others.) The role of the thermo-initiator was rather modest: to produce reactive free radicals with one or another rate of initiation w , s⁻¹. There was practically no difference in polymerization when different initiators r with the same w . Those chemists would be probably surprised that we put too much faith into PIs in UV-cure. The main difference is that we run photopolymerization in solventless media which dramatically changes during polymerization.

All properties, and in particular efficiency of a PI ϕ changes and most probably ϕ decreases. With an increase of conversion media becomes more and more viscous, a pair (r_1, r_2) separates ($\phi \ll 1$) and initiates polymerization with low efficiency.

Several other problems are related to photochemistry of PI (light absorption, possible sensitization and its dependence upon media). Fortunately, dioxygen does not affect very rapid dissociation of Type I PIs.

Here are some guidelines in a selection of PI:

- Take a UV-Vis absorption spectrum of your formulation without PI. Look at the known absorption spectra of PI, and select one or more PIs;
- A typical concentration of common PI is 0.5-5.0 wt.%;
- The best PIs and their concentration can be selected in the course of design of experiments (DOE);
- Be sure that your solid PI has dissolved in a viscous formulation. Liquid PIs with phosphine oxides are very convenient like Darocur 4265 (TPO in Darocur 1173) or Irgacure 1700, cf. footnote 8. Solid PI may be pre-dissolved in a non-viscous diluent;
- Be concerned about other properties of PI like migration. Bomar[®] LS[®] oligomers with grafted PI allow alleviate migration and leachability, and one need not worry on solubility.



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