Photo semiconductor nanoparticles as initiators for free radical polymerization up into the visible range

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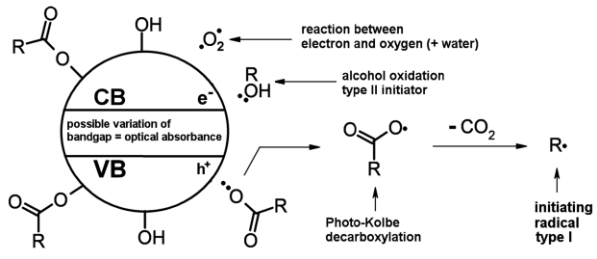
The development of photoinitiators is an important and challenging topic due to the many applications, as they are used both on an industrial scale and for consumer (3D printing). The advent of new light sources (LED, LCD) has further increased the demand for new photoinitiators. As the various photoinitiators are highly reactive chemicals, they must also be evaluated in terms of their risk to human health relative to their benefit. In particular, bulk free radical polymerization and interaction with photoinitiators and other compounds in resin blends is a difficult subject that is very complex, especially with regard to interaction with the atmosphere (oxygen). From a practical point of view, migration, which can be defined as any process leading to possible contamination by photoinitiators, such as diffusion or gas phase transport (e.g. into the interior of food packaging), is of crucial importance. We have tested and discovered different types of photoinitiators where the chromophore is based on an inorganic particle. These photosemiconductors are low-migration or migration-free initiators because their size prevents them from diffusing or evaporating. ESR studies indicate that the radicals formed behave differently from similar radicals released by organic chromophores (they are in a lower vibrational state). The prototype ZnO-based fragmentation PI works well in the UV-A region. Even a first study addressing the red shift of adsorption has been published in a communication. A number of challenges have been identified that can be addressed in a scientific study:

- Improve / redshift the absorbance of particle-based initiations systems to the visible range, ZnO/S seems to be promissing
  - Keeping the dispersion qualities similar to previously reported systems
- Understand the improvement of precipitation conditions for ZnO based systems with the DoE or **ML process**. (Crystallinity, size, aggregation, surface charge, dispersion quality aspects in different resins)
- Testing the understanding of the relationships between surface modification and quality in different resin blends (overlapping "storage" time relationships). (measuring of the hiding power of different dispersions, sedimentation stability)
- Testing the understanding of the relationships between surface modification and quality in different resin blends in terms of photo inducing the radical polymerization (overlapping oxygen diffusion/inhibition, …).



Scheme 1 : ZnO-light induced fragmentation of surface attached groups leading to radicals.

[1] **M. Schmitt**, Nanoscale, 7, 9532-9544 (2015).