

Toward a Better Understanding of the Mechanism of a Dual Bicyclic Photoinitiating System for Synthesis of Organic – Inorganic Hybrid Materials

J. Christmann, S. Shi, X. Allonas, A. Ibrahim, C. Ley, C. Croutxé-Barghorn

University of Haute-Alsace, Laboratory of Macromolecular Photochemistry and Engineering,
F-68093 Mulhouse, France

E-mail: julien.christmann1@uha.fr, xavier.allonas@uha.fr

Among the materials formed under light, organic/inorganic hybrid materials present interesting properties due to the elegant combination of the properties of organic polymers and inorganic materials through the *in-situ* formation of interpenetrated network or generation of chemical bonds between organic and inorganic components. However, the one-pot synthesis of organic – inorganic hybrid materials under light requires specific photoinitiating systems which are able to release several different initiating species after light absorption. Therefore, the development of photoinitiating systems able to release simultaneously radicals and protons in a single process is then particularly attractive. In this paper, the reaction mechanism of a photocyclic three-component initiating system based on isopropylthioxanthone (ITX) as photoinitiator, an iodonium salt (IOD^+) and a thiol (RSH) as co-initiators was studied.^[1,2]

Time-resolved transient absorption experiments by laser flash photolysis reveal that a photocyclic mechanism actually occurs, with photoexcited ITX first reacting with the iodonium salt or the thiol to produce initiating radicals (Fig. 1). Secondary dark reactions involving the ITX-derived photoproduct ensure regeneration of the photosensitizer, while supplementary radicals and protons are produced. Detection of the proton production at the microsecond scale was performed by use of a proton probe, allowing the determination of the proton quantum yield for each of the two considered photochemical pathways. Mechanistic investigations are finally confirmed by photosol-gel and radical photopolymerization experiments.^[3]

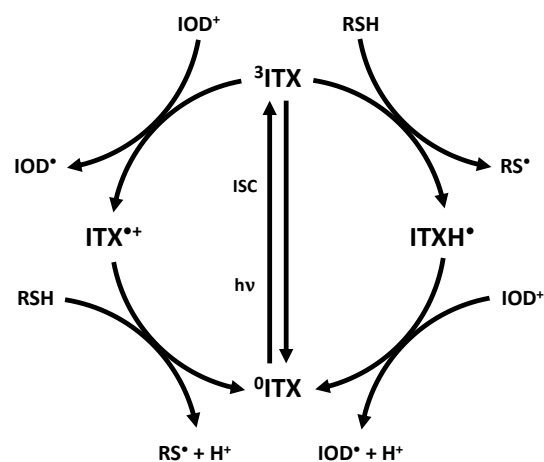


Figure 1. Mechanism of the photocyclic initiation of organic-inorganic hybrid materials synthesis.

References:

- [1] S. Shi, X. Allonas, C. Croutxé-Barghorn, A. Chemtob, *New J. Chem.*, **2015**, 39, 5686.
- [2] S. Shi, F. Karasu, C. Rocco, X. Allonas, C. Croutxé-Barghorn, *J. Photopolym. Sci. Technol.*, **2015**, 28, 31.
- [3] J. Christmann, S. Shi, A. Ibrahim, C. Ley, C. Croutxé-Barghorn, M. Bessières, X. Allonas, *J. Phys. Chem. B*, DOI: 10.1021/acs.jpcc.6b11829.