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TRANSIENT ABSORPTION SPECTROSCOPY OF EXCITATION DYNAMICS AND RADICAL FORMATION IN DIFFERENT PHOTOINITIATORS

Marius Navickas[1], Edvinas Skliutas[1], Mangirdas Malinauskas[1], Mikas Vengris[1]

[1]Vilnius University, Laser Research Center, Sauletekio av. 10, LT-10223, Vilnius, Lithuania
marius.navickas@ff.vu.lt

Photopolymerization has attracted a great scientific and technological interest due to a large number of applications spanning from optoelectronics to medical areas [1, 2]. This process is promoted by photoinitiators which in a very short time scale produce free radicals that trigger the cross-linking reactions [3, 4]. Thus, the photopolymerization initiation becomes a significant process governing the chemical and physical nature of the final product. A large variety of different photoinitiators have been studied by various spectroscopic techniques, however, the excitation mechanisms are not fully understood. In this work, we present a comparative transient absorption (TA) spectroscopy study of photoinitiation behaviour in commercial BAPO, Irgacure 369, Irgacure 651 and TPO photoinitiators dissolved in isopropanol.

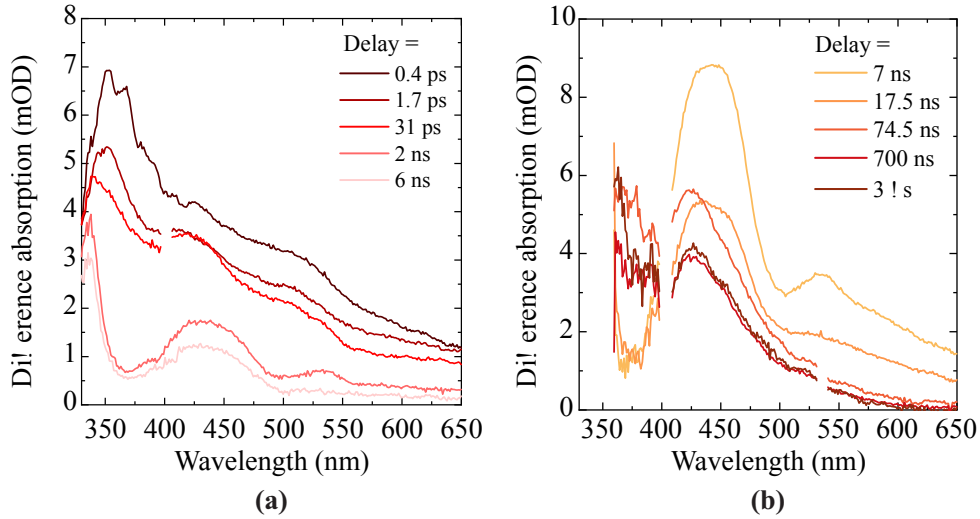

Fig. 1. Transient absorption spectra of BAPO photoinitiator obtained during the (a) pump-probe and (b) laser flash photolysis experiments.

Fig. 1 (a) represents the TA spectra of BAPO photoinitiator recorded during the ultrafast pump-probe experiments. This technique revealed that after one-photon excitation BAPO immediately cleaves into benzoyl, containing methyl groups, and phosphinoyl radicals. In addition, it was observed, that benzoyl radical features a significantly faster relaxation time than phosphinoyl radical. Further, we performed laser flash photolysis experiments to get a deeper knowledge of the radical relaxation timescale and formation mechanisms. The TA spectra observed by means of laser flash photolysis (Fig. 1 (b)) suggest that the latter radical relaxes in several tens of nanoseconds. These results are in a good agreement with the previously discussed photoinitiation mechanism and provide a deeper insight into the primary photoreactions of BAPO.

The TA spectra of Irgacure 369, Irgacure 651 and TPO feature only two broad induced absorption (IA) bands. In case of Irgacure 369, these IA bands span around ca. 350 nm and 470 nm. The presence of transient species was confirmed by the kinetic traces. We found that the IA band of Irgacure 369 grows up in 10 ps and after 100 ps starts to decay, meanwhile the second IA band relaxes after 100 ps. In addition, the laser flash photolysis of argon-saturated Irgacure 369 solution exhibits an increase of initial Irgacure 369 relaxation time, revealing the triplet character of the radical formation.

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