Optimisation and coupling of high performance photocyclic initiating systems for efficient holographic materials

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For fabrication of diffractive optical elements or for holographic data storage, photopolymer materials have turned out to be serious candidates, taking into account their performances such as high spatial resolution, dry processing capability, ease of use, high versatility. From the chemical point of view, several organic materials are able to exhibit refractive index changes resulting from polymerization, crosslinking or depolymerization, such as mixtures of monomers with several reactive functions and oligomers, associated to additives, fillers and to a photoinitiating system (PIS).

The most versatile process is the free radical photopolymerization which offers the most important choice of materials and potential PIS. The development of applications in holography is directly governed by the photosensitivity of the photopolymer and the diffraction efficiency which could be obtained. Therefore, there is a need for highly efficient photoinitiating systems capable to initiate the photopolymerization reaction at relatively low dose.

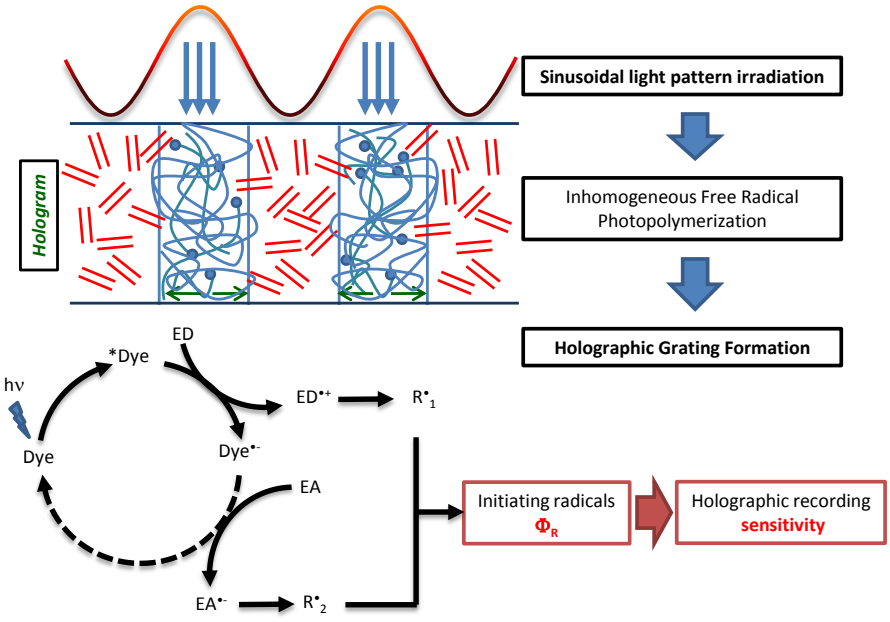

Figure 1. Photocyclic initiating system (PCIS) and holographic grating recording, EA: electron acceptor, ED: electron donor, R_i: initiating radicals, M: monomer.

In this work, the efficiencies of two and three component PIS as holographic recording materials are analyzed in term of photopolymerization kinetics and diffraction yield. The selected systems are based on visible dyes, electron donor (ED) and electron acceptor (EA) (Figure 1) as the third component. In order to investigate the influence of the photophysical properties of dye on the holographic recording material performance time resolved and steady state spectroscopic studies of the PIS are presented (i.e. nanosecond. laser flash photolysis). This detailed photochemical studies of the PIS outline the possible existence of photocyclic initiating systems (PCIS) where the dye is regenerated during the chemical process (see Figure 1). Simultaneously, these visible curable systems are associated to fluorinated acrylate monomers for the recording of transmission gratings. The irradiation of holographic resin formulation by a sinusoidal light intensity pattern leads to inhomogeneous photopolymerization in the medium and to microstructuration of the polymer (see Figure 2). A sinusoidal modulation of the refractive index is thus obtained in the photopolymerizable matrix.[1,2] It was demonstrated that the efficiency of light conversion into chemical energy directly impact the obtained refractive index modulation [3] and the final properties of the holographic grating. The fact that no chemical post-treatment was needed for this recording medium, allowed the continuous follow up of the process during exposure with an inactinic reading light beam (HeNe laser at 633 nm scheme 2). The diffraction efficiency at 633 nm (η) was defined by the ratio of the intensity of the first diffraction order to the diffracted plus transmitted light intensities in order to rule out Fresnel losses in the determination of the grating diffraction efficiency.

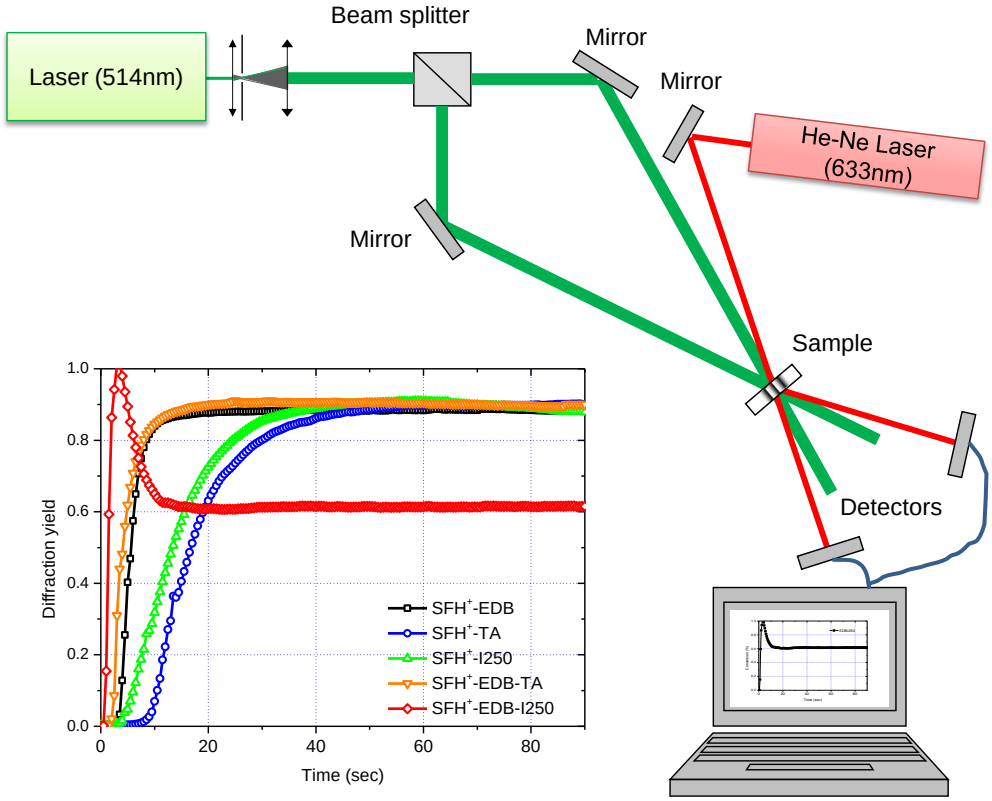

Figure 2. Holographic recording setup with time-resolved measurement of grating diffraction yield.

In order to get more insight into the hologram formation, gratings' recording curves (see Figure 2) were compared to those of monomer to polymer conversion obtained by real time Fourier transform infrared spectroscopy (RTFTIR). This work outlines the importance of the

coupling of the PIS (i.e. the photochemical reactions) and the holographic resin. It is demonstrated by RT-FTIR that the photocyclic behavior have a great positive impact on the photopolymerization efficiency. Moreover the application of the two PCIS in holographic recording outlines the importance of the photochemistry on final holographic material properties: here a sensitive material with high diffraction yield is described. Indeed, this work outlines the importance of the coupling between the photochemistry underlying the radical photogeneration and the holographic resin.

References:

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