

# PHOTORESPONSIVE COUMARIN-FUNCTIONALIZED PDMS NETWORKS FOR CONTROLLING SURFACE TOPOGRAPHY WITH LIGHT

*Michaël Alexandre, Rachid Jellali, Christine Jérôme*

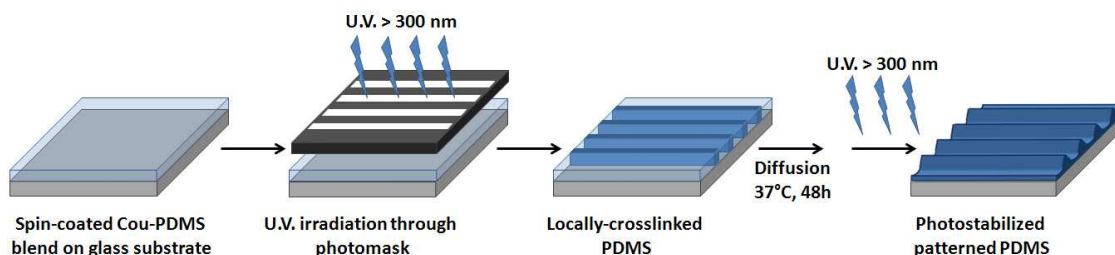
Center for Education and Research on Macromolecules (CERM), Chemistry Institute, University of Liege, Building B6a, Sart Tilman, B-4000 Liège, Belgium

**Abstract** – Over the last years, photoresponsive polymeric systems have attracted lot of interest as functional materials and played essential roles in various applications such as microelectronics, medical, optoelectronic devices, printing, inks, and coatings. These systems are important because light-induced processes are economical, easy, rapid, non destructive and can be localized as well as remotely activated. Besides, the material properties can be controlled by tuning light parameters (wavelength, power, and time of irradiation). Therefore, polymers bearing photoresponsive functionalities have been used to prepare various types of polymer networks.

While a large amount of research has been devoted to the preparation of polymer networks based on the photo-initiated radical polymerization of (meth)acrylate- or vinyl-bearing polymers, another method, involving covalent bond formation by photodimerization at a given wavelength can be advantageously used to promote the formation of “smart” networks since those dimers can be photocleaved when exposed to another wavelength range, opening the way to the preparation of photo-controlled reversible networks. Such control can be achieved when using photosensitive groups such as cinnamate, anthracene, thymine and coumarin derivatives.

Coumarin derivatives are of high interest as they possess some valuable properties such as excellent fluorescent properties with high photoluminescence quantum efficiency, excellent photostability and extended spectrum range for the dimerization/cleavage reactions. Indeed, coumarin derivatives can undergo a [2 + 2] photodimerization upon irradiation with wavelengths longer than 300 nm giving access to a cyclobutane-type dimer. The dimer can be cleaved when irradiated at wavelengths shorter than 290 nm.

In this study, polydimethylsiloxane copolymers bearing coumarin groups along the chain as well as  $\alpha$ ,  $\omega$  di-coumarin polydimethylsiloxane have been synthesized and their blends have been evaluated for their ability to form reversible patterned films by interdiffusion. The synthesis of photoresponsive coumarin-functionalized PDMS (Cou-PDMS) was achieved by amidation of a coumarin acid chloride derivative with various commercially available amine-functionalized PDMS. Photocrosslinking and photocleavage kinetics of Cou-PDMS blends cast into films have been monitored using UV-vis spectroscopy and fluorescence spectroscopy. Under exposure of  $\lambda > 300$  nm UV light, PDMS-Cou blends can form crosslinked networks via [2+2] photocycloaddition of coumarin moieties. On the other hand, the formed polymer networks containing coumarin dimer moieties could be degraded via photo-cleavage of cyclobutane dimers upon illumination by light source at 254 nm. The linear PDMS interdiffusion in a locally-crosslinked network using various photomasks and its ability to deeply modify the topography of the resulting coating was then studied. Using fluorescence microscopy, we have demonstrated that interdiffusion was dependent on the molecular weight of diffusing oligomer and on the network structure. Surface topography controlled modification was investigated by scanning electron microscopy and profilometry. This developed methodology can easily leads to the formation of complex surface patterning using easy method (photomasking and interdiffusion) and can be used in several applications, such as smart intra-ocular lens (IOLs), reversible photopatternable systems or photoswitched controlled release devices.



Methodology to produce patterned PDMS surfaces by photopatterning and polymer interdiffusion