

Molecular dynamics study of the photonastic phenomenon: photochemical reaction in a polymer environment

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Photonastic materials perform light-induced movements, transforming light energy into mechanical energy, akin to the motions observed in plants and flowers. This study focuses on bio-inspired polymeric photoactuators with applications in microfluidics, biomedics, soft robotics, and motors. A polymer thin film containing photoactive molecules, particularly photochromes, can exhibit significant shape changes upon light excitation. By employing computational chemistry and particularly molecular dynamics (MD) simulations, we investigate the molecular processes governing the macroscopic behavior of these systems, which in our case consists of a derivative of azobenzene (AZ) embedded in a polybutadiene (PB) matrix.¹ Two types of chemical bonds between AZ and PB are tested, pure van der Waals interactions and a covalent bond. Our aim is to propose a strategy to investigate the coupling between the photochemical reaction and the intramolecular relaxation of the polymer. In a previous study, we assumed that these processes occurred at different time scales, the photo-induced reaction being considered instantaneous compared to the polymer relaxation.² However, subsequent results indicate that the characteristic time for the intramolecular relaxation of the polymer is roughly the same as the photo-induced reaction time (~ 100 fs to 1 ps). To improve the description of the system, we consider both phenomena simultaneously in the following way. A purely classical molecular mechanics model of AZ photoswitches in both their ground and first excited states (S_0 and S_1) is calculated. The photoreaction is modelled by switching between these two potential energy surfaces (PES). During MD simulations, we mimic electronic excitations and decay by switching between the S_0 and S_1 force fields along the photoreaction coordinate, while allowing the polymer chains to rearrange concomitantly. The local pressure tensor maps of the whole system are analyzed as a function of time after the switch to the S_1 PES. This molecular-scale exploration contributes to a comprehensive understanding of photonastic phenomena and the mechanical response of polymer-photochrome systems.

Keywords: photonastic materials, molecular dynamics, photochemical reaction, intramolecular relaxation.

¹ O. Villegas, M. Serrano Martínez, L. Le Bras, A. Ottochain, N. Pineau, A. Périer and C. Lemarchand, submitted

² L. Le Bras, C. Lemarchand, S. Aloïse, C. Adamo, N. Pineau and A. Périer, *J. Chem. Theory Comput.* 2020, 16, 11, 7017–7032