Molecular dynamics simulations of photo-responsive polymer networks

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Molecular photoswitches which are able to efficiently switch between two or more (meta)stable isomers through reversible photochemical reactions are crucial for the development of smart materials[1]. Azobenzene-based molecular switches are promising candidates to achieve light-controlled functionality in polymers.

Azobenzene stars (see Fig. 1) have proven to be a potential building block of photo-responsive polymers[2]. However, an atomistic insight into these dynamic networks is missing so far. To obtain a molecular picture of these photo-responsive polymers, we have developed an efficient and accurate atomistic model describing both the structural and dynamic properties including the photo-isomerization of the azobenzene units. The interatomic potentials were developed based on density functional theory calculations and by applying the recently developed parametrization strategies (on-the-fly training and population swapping genetic algorithm technique[3,4]).

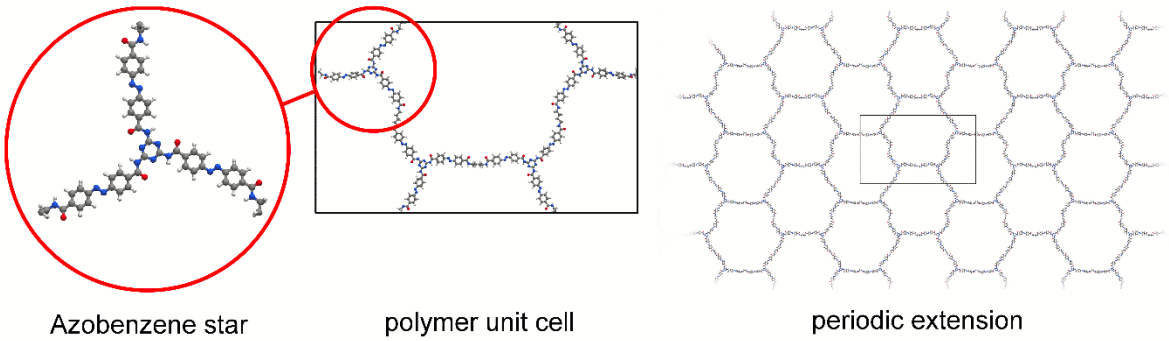

Figure 1. Construction of hexagonal unit cell for a 2D-polymer using azobenzene stars.

The 2D polymer network shown in Fig. 1 is being studied in aqueous solution by performing classical Molecular Dynamics (MD) simulations in the NpT ensemble to achieve the necessary configurational sampling for different degrees of photo-switching (i.e., for isomerization of X% of the azobenzene units, $X \in \{0, 25, 50, 75, 100\}$).
Our results show a contraction by 25% in the network plane, if all azobenzene units are photo-switched (see Fig. 2).

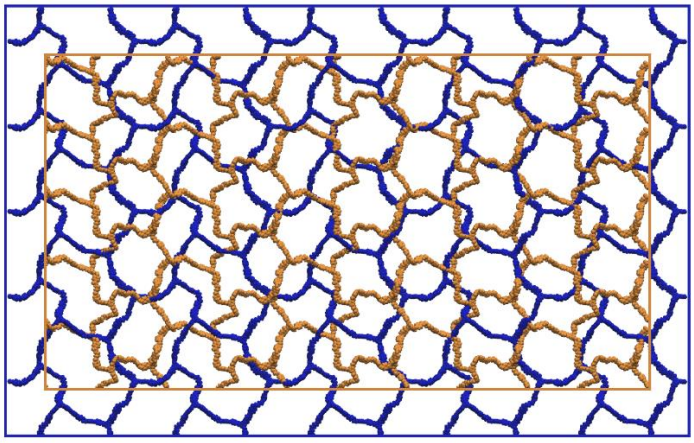

Figure 2. Polymer network plane before (blue) and after (orange) trans-to-cis-isomerization of all azobenzene units.

[1] M. Russew, S. Hecht, Advanced Materials, **22(31)** (2010) 3348-60.

[2] D. Pirone et al., Polymers, **11** (2019) 904.

[3] S. Amirjalayer, Adv. *Theory Simul*., **4** (2021) 2100017.

[4] E. Kolodzeiski, S. Amirjalayer, *J. Chem. Theory Comput*., **17** (2021) 7010.