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# Thiol-Ene Photo-Click Hydrogels with Tunable Mechanical Properties Resulting from the Exposure of Different -Ene Moieties through a Green Chemistry

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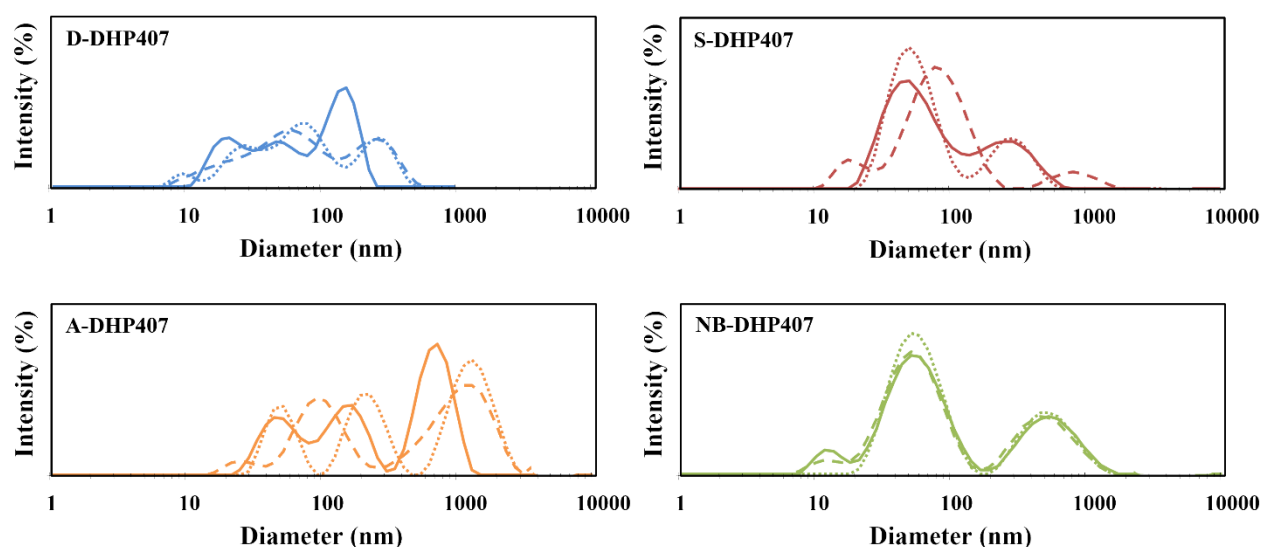
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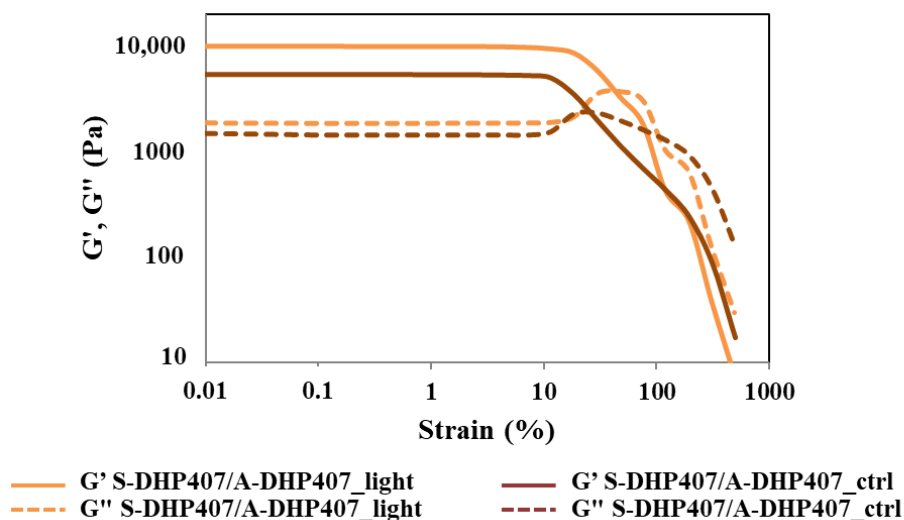
† These authors equally contributed to this work

## Evaluation of the thermo-responsiveness of functionalized poly(ether urethane)s at the nano-scale



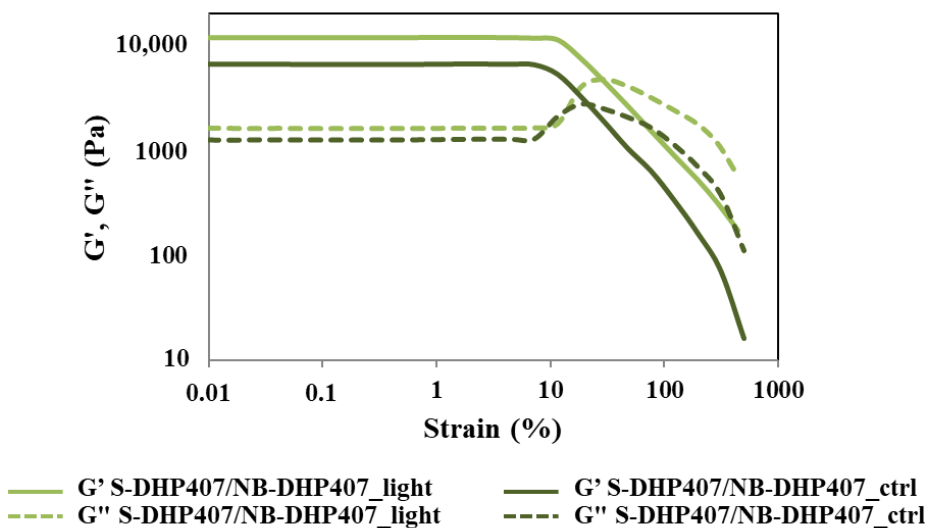
**Figure S1.** Intensity patterns of the polymeric structures contained in D-DHP407 (blue), S-DHP407 (red), A-DHP407 (orange) and NB-DHP407 (green) solutions (0.5% w/v polymeric concentration) as measured through DLS analysis at 25 °C. In each graph, continuous, dotted and dashed lines represent profiles acquired by analyzing three independent samples.

## Thiol-acrylate photo-click hydrogels



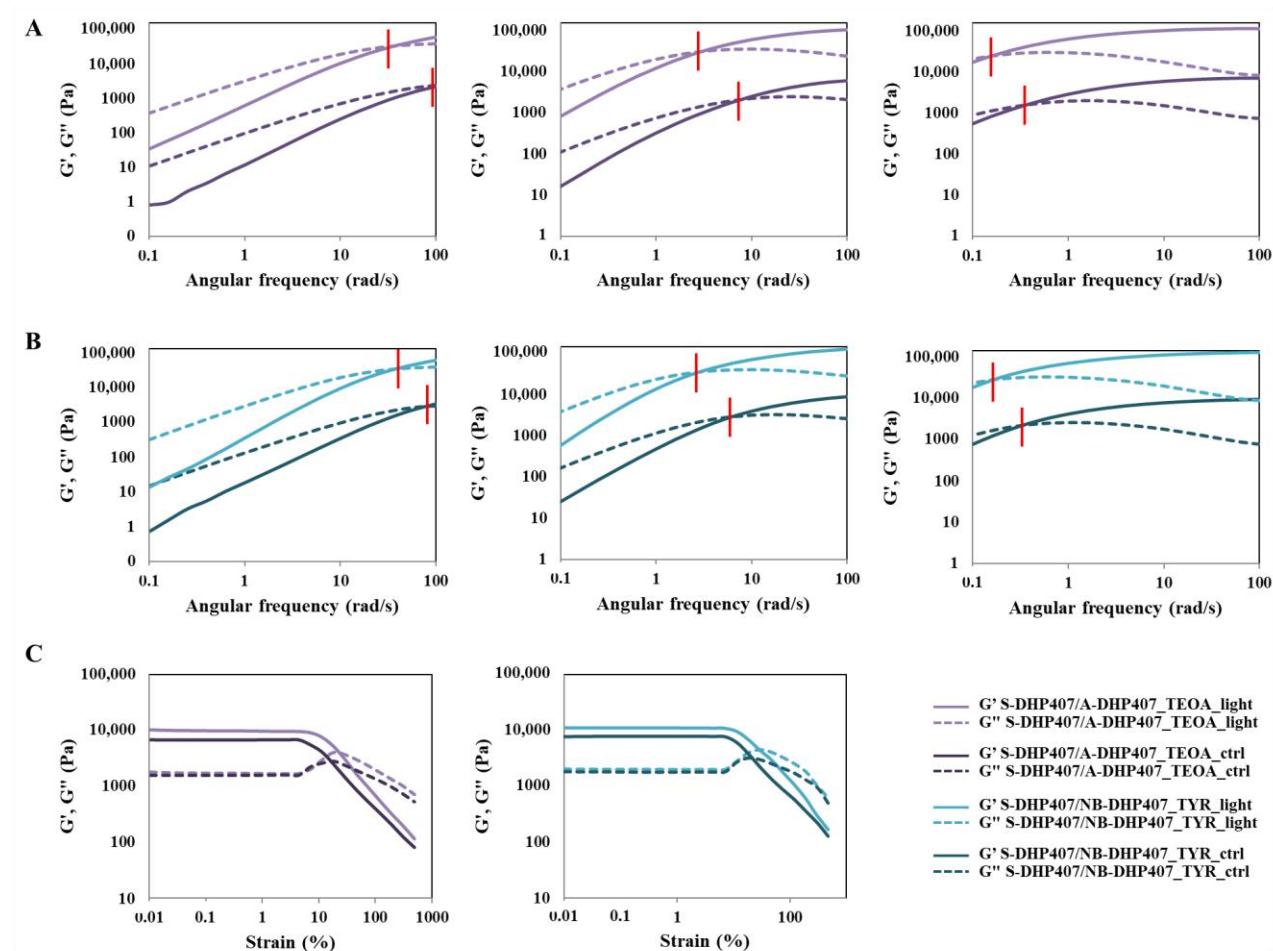
**Figure S2.** Strain sweep test at 37 °C performed on S-DHP407/A-DHP407 before (dark orange) and after (light orange) exposure to green light (525 nm, 80000 Lux, 10 min). Continuous and dashed lines represent the storage ( $G'$ ) and loss ( $G''$ ) moduli, respectively.

## Thiol-norbornene photo-click hydrogels



**Figure S3.** Strain sweep test performed at 37 °C on S-DHP407/NB-DHP407 before (dark green) and after (light green) exposure to green light (525 nm, 80000 Lux, 10 min). Continuous and dashed lines represent the storage ( $G'$ ) and loss ( $G''$ ) moduli, respectively.

## The role exerted by the co-initiator in the thiol-ene photo-crosslinking process



**Figure S4.** Frequency sweep tests performed at 25 °C, 30 °C and 37 °C (from left to right) on S-DHP407/A-DHP407 (A) and S-DHP407/NB-DHP407 (B) formulations before (dark colors) and after (light colors) exposure to visible light (525 nm, 80000 Lux, 10 min) upon the addition of a co-initiator (i.e., TEOA and TYR for thiol-acrylate and thiol-norbornene systems, respectively). For higher clarity,  $G'$  and  $G''$  values of control samples were divided by a factor of 100. Irrespective of considered formulation and temperature, the addition of a co-initiator did not alter formulation capability to undergo a temperature-driven gelation both pre- and post-irradiation. Moreover, the comparison between each light-irradiated formulation and its corresponding control suggested the successful thiol-ene interaction through the  $\omega_{crossover}$  shift towards lower frequencies. (C) Strain sweep test performed at 37 °C on S-DHP407/A-DHP407\_TEOA (left) and S-DHP407/NB-DHP407\_TYR (right) formulations before (dark colors) and after (light colors) light-irradiation.