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# Thiol-functionalized Nanogels as Reactive Plasticizers for Crosslinked Polymer Networks

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## Abstract

Significant efforts have been expended to mitigate plasticizer migration from crosslinked methacrylic and poly(vinyl chloride) polymer networks by synthesizing reactive plasticizers that can blend homogeneously within the networks to reduce polymer property change, acute toxicity and downstream environmental effects of plasticizer migration with limited and varying amount of success. We hypothesized that appropriate thiol-functionalized nanogels synthesized using the same monomers as the parent network to generate highly compact, crosslinked structures will form thermally stable, homogeneous networks and perform as optimal reactive plasticizers. Nanogels were synthesized via a thiol-Michael addition solution polymerization and incorporated at different mass ratios within a polyethylene glycol 400 urethane dimethacrylic monomer to form photo-crosslinked networks. While maintaining the inherent hydrolytic stability, thermal stability and biocompatibility of the parent matrix at ~ 99 % acrylic group conversion, the PEG400 urethane dimethacrylic -nanogel networks retained optical clarity with > 90 % visible light transmission at 20 wt % nanogel loading. The addition of the nanogels also enhanced the elongation of the parent matrix by up to 320 %, while a 37 °C reduction in glass transition temperature ( $\Delta T_g$ ) and  $\geq 50$  % reduction in modulus was observed. A 52 % reduction in the shrinkage stress of the material was also noted. The results indicate that the application of thiol-functionalized nanogels as plasticizers to alter the bulk properties of the parent matrix while mitigating plasticizer migration by covalently crosslinking the nanogels within the polymer matrix provides a simple yet efficient technique to

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