Thiol-Norbornene Photopolymer for Two-Photon Photopolymerization

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Primary CNF Tools Used: Nanoscribe Photonic Professional GT2 Two-Photon Lithography System

Abstract:

Carbic anhydride is an underappreciated starting material for 3D-printable, non-hydrogel photopolymers. Compared with other norbornene precursors, carbic anhydride is cheaper and reactive via aminolysis. As a result, the generalized and efficient functionalization with carbic anhydride can increase the utilization of thiol-norbornene photopolymers. Here, we report carbic anhydride's catalyst-free condensation with two commodity polymers: amine-functionalized polypropylene glycol and polydimethylsiloxane. The reaction completes in 1h, produces water as the only byproduct, and does not require purification. It is therefore affordable, facile, and green. Mixing the product with thiol cross-linkers and the appropriate photo-additives produces photopolymers, which have the potential to be used for microfabrication with two-photon photopolymerization (2PP). The simple yet versatile platform will benefit additive manufacturing of soft materials and beyond.

Summary of Research:

Thiol-norbornene photopolymers are excellent for additive manufacturing. Nevertheless, scalable thiol-norbornene photopolymers need a more affordable starting material and a more scalable synthesis. Among the norbornene precursors, carbic anhydride (CA) is the cheapest and greenest. CA reacts via alcoholysis or aminolysis, thermodynamically favorable processes that can occur without a catalyst. If water is removed from the reaction mixture, CA's reaction with amine yields norbornene dicarboximide [1-3]. Adapting this strategy will make the synthesis of thiol-norbornene photopolymers greener and more economical.

The norbornene dicarboximide-functionalized polymers are synthesized from amine-functionalized PPG and PDMS (Figure 1). Proton nuclear magnetic resonance (1H-NMR) indicates the clean formation of norbornene dicarboximide from the singlet at 6.0-6.1 ppm (Figure 2). Except for 7kPDMS-5CA, all products are transparent liquids. 7kPDMS-5CA's opacity potentially arises from the partial crystallinity of the pendant norbornene dicarboximide propyl side chains.

Two thiol cross-linkers, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and 4.6% (mercaptopropyl)methylsiloxane]-dimethylsiloxane copolymer (polySH), are used to study photopolymerization. PETMP is miscible with PPG-based polymers but not with PDMS-based polymers. As a result, 0.9kPDMS-2CA:PETMP is a milky-white mixture. We attempted to solubilize PDMS-based polymers with polySH. However, only 5kPDMS-2CA:polySH is transparent. All immiscible mixtures remain stable emulsions after overnight storage without agitation. Aggregate formation may lead to a heterogeneous network and affect the mechanical properties of 3D-printed materials [4].

To assess the printability of norbornene dicarboximide photopolymers, we investigated their photorheology with 400-500 nm light to capture the effect of 2PP cross-linking. Judging by the cross-over point of loss and storage modulus, only 5kPPG-3CA:PETMP cross-links too slowly (385 nm or 405 nm). Cross-linked 5kPPG-3CA:PETMP is also extremely soft and tacky, indicative of a weak network not suitable for additive manufacturing. All other photopolymers cross-link quickly, with various cross-over points (Figure 3) reflecting the structure-property relationships.

After rheological studies identified four printable formulations, they were tested for 2PP. PDMS-based photopolymers are unsuitable for 2PP due to light scattering resulting from the heterogeneous mixture. 2kPPG-2CA:PETMP shows the best solubility in isopropyl alcohol, and thus is used as a proof-of-concept for 2PP (Figure 4). The cured photopolymer in the camera view suggests the photopolymer's feasibility.

The catalyst-free condensation between amine-functionalized PPG or PDMS and CA affords a family of

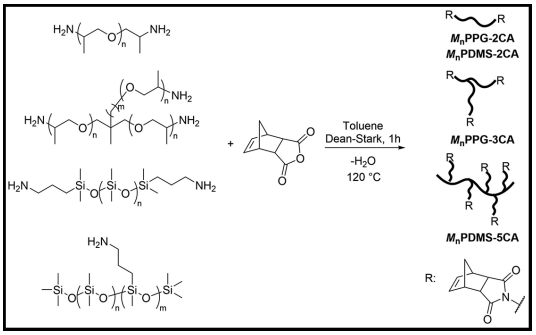

Figure 1: Synthesis of norbornene dicarboximide polymers from amine-functionalized polypropylene glycol (PPG) or polydimethylsiloxane (PDMS). The prefix Mn represents the average molecular weight of the amine-functionalized starting material. The number preceding CA represents the number of norbornene dicarboximide groups in a single chain. For example, amine-terminated PPG (Mn = 2 kDa) affords 2kPPG-2CA.

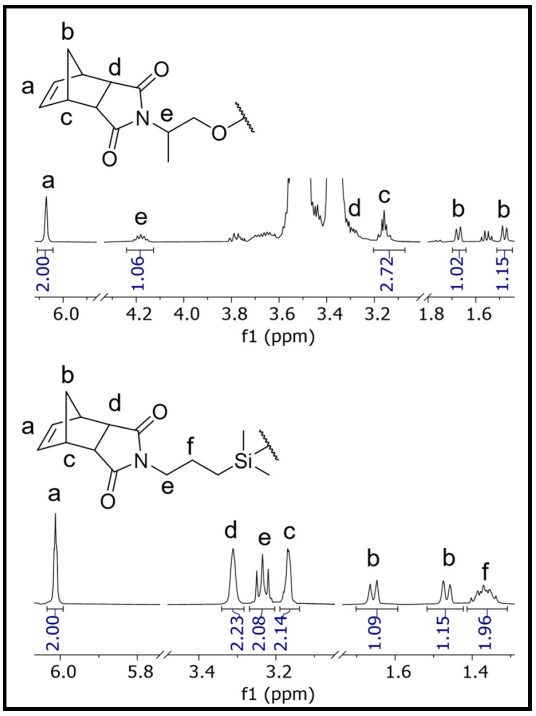

Figure 2: 1H-NMR spectra of norbornene dicarboximide-functionalized polymers showing their end group structure (500 MHz, CDCl3).

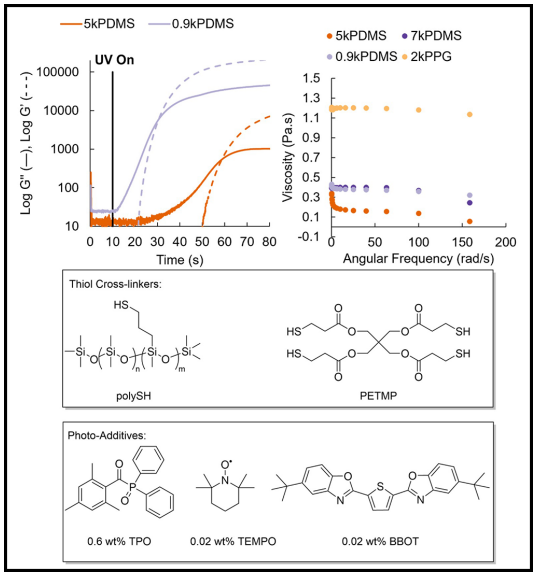

Figure 3: Photorheology and viscosity of representative photopolymers (names are abbreviated to their respective backbone). The photorheology data of 2kPPG and 7kPDMS are in Figure S3. Ultraviolet (UV) radiation (400-500 nm, 10 mW/cm^2) is switched on at 10 s (G': storage modulus; G" loss modulus).

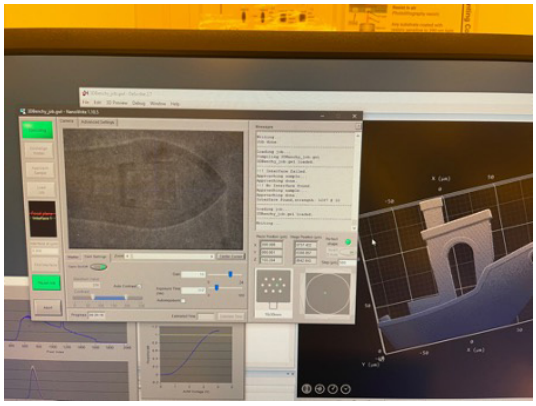

Figure 4: 2PP on Nanoscribe Photonic Professional GT2 Two-photon Lithography System with 2kPPG-2CA:PETMP showing cured 3D object on the substrate. Solvent washing during post-printing obliterated the object, potentially due to rapid solvent swelling of the partially cured photopolymer.

norbornene dicarboximide functionalized polymers—with water as the only byproduct. The reaction is affordable and green and occurs at a 100-g scale without purification. The resultant photopolymers have potential in microfabrication with 2PP. Cheap but versatile, our method can benefit additive manufacturing of soft materials and beyond. In the future, the 2PP parameter should be systematically fine-tuned for successful fabrication.

References:

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