

## Robust Photolabile Physically Crosslinked Polymer Networks

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**Statement of Purpose:** Molecular-scale reconfigurability of polymeric networks represents an important capability in the design of smart materials for applications ranging from microelectronics to medicine. The physical properties of light-sensitive polymers can be actively controlled using exogenous light sources by modulating chain topology and connectivity. Covalently crosslinked hydrogels and temperature-responsive aqueous micellar gels have been reported for use of dynamic cell-materials interactions studies, light-activated carriers for smart controlled release and biomolecular patterning. But few reports describe the preparation of physically crosslinked photodegradable solid films with robust macroscopic mechanical properties. Herein we describe the synthesis and characterization of a class of photolabile amphiphilic ABA triblock copolymers that can be conveniently processed into photodegradable materials by self-assembly including tough thin films and soft hydrogels.

**Methods:** ABA triblock copolymers composed of *o*-nitrobenzyl methacrylate (NBMA) and poly(ethylene glycol) (PEG) were synthesized using atom transfer radical polymerization. PEG macroinitiators of 4 kDa and 20 kDa molecular weights were used to prepare solid films and hydrogels, respectively. The formation of physical crosslinking in polymer thin films were demonstrated by means of tensile test and atomic force microscopy (AFM). The rheological properties of hydrogels were characterized before and after photo irradiation. The process of polymer disintegration by long wave UV exposure were recorded over time.

**Results:** The total degree of polymerization for the NBMA blocks was found to be 40 for poly(NBMA)-*b*-PEG4000-*b*-poly(NBMA) and 20 for poly(NBMA)-*b*-PEG20000-*b*-poly(NBMA) as measured by <sup>1</sup>H NMR. Dehydrated poly(NBMA)-*b*-PEG4000-*b*-poly(NBMA) can be prepared into highly viscous thin films with a tensile Young's modulus *E* of 0.38 MPa, a maximum stress  $\sigma_{max}$  of 6 kPa, and significant stress relaxation. Upon hydration, viscous films are transformed into tough, mechanically robust, solid films with a tensile modulus of  $76 \pm 12$  MPa, an ultimate tensile stress of  $1.35 \pm 0.14$  MPa, and a maximum elongation at break of  $10.4 \pm 3.1\%$ . This is attributed to the spontaneous formation of physical crosslinks arising from phase separation of the triblock copolymers driven by differential hydrophilicity. The formation of physical crosslinks is also inferred through AFM phase images. Little phase separation is observed in dehydrated thin films but after hydration clear phase contrast was shown by AFM.

Triblock copolymer networks can undergo rapid photodegradation by converting into water-soluble poly(methacrylic acid) (PMAA) segments upon UV-induced deprotection reactions. Exposing hydrated polymer films (60  $\mu\text{m}$  in thickness) to low intensity long wave UV irradiation ( $\lambda = 365$  nm, 10 mW/cm<sup>2</sup>) produces *o*-nitrosobenzaldehyde as a by-product of

photodeprotection. Accumulation of this species results in significant coloration of the film within 2 hours. Exposing the film to 24 hours of UV irradiation leads to complete disintegration of the film.

Triblock copolymers with 20 kDa molecular weight PEG segment can be processed directly into hydrogels at room temperature. These networks exhibit a mass swelling ratio of  $Q_m = 6.3 \pm 0.25$  and remain stable in water for more than one month over a wide temperature range from 0 °C to 60 °C. Hydrated networks exhibit a frequency independent dynamic storage modulus *G'* of  $13 \pm 0.6$  kPa, a loss modulus *G''* of  $1.1 \pm 0.17$  kPa and a much lower tan delta value of  $0.08 \pm 0.01$  compared with other physically crosslinked hydrogels. Irradiation of the hydrogels (100  $\mu\text{m}$  in thickness) with long wave UV for 1 hour reduces *G'* nearly 10-fold to 1.5 kPa. Exposing hydrogels to UV irradiation for an additional 1 hour leads to complete disintegration of the gel.

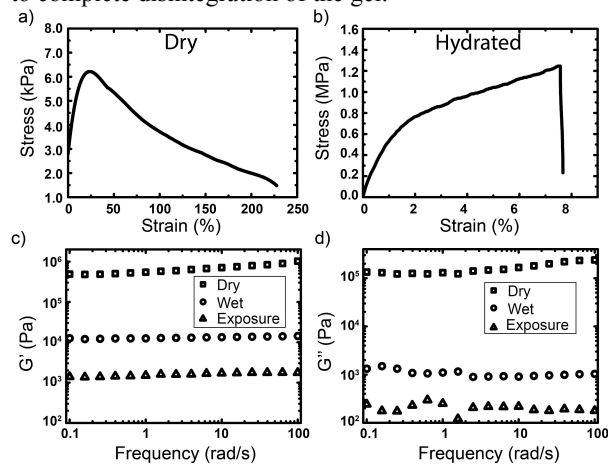


Figure 1. Photolabile poly(NBMA)-*b*-PEG4000-*b*-poly(NBMA) block copolymer films exhibit (a) highly viscous behavior in the neat state and (b) robust mechanical properties after hydration. Poly(NBMA)-*b*-PEG20000-*b*-poly(NBMA) hydrogels exhibit (c) reduced dynamic storage and (d) loss moduli after photo irradiation.

**Conclusions:** ABA triblock copolymer composed of *o*-nitrobenzyl methacrylate and poly(ethylene glycol) with varying molecular weights can be processed into photodegradable thin films and hydrogels by self-assembly. Physical crosslinks arising from phase separation of the triblock copolymers in hydrated environments contribute to the formation of robust and stable polymer networks, which undergo photodegradation upon irradiation with long wave UV light. This class of materials would be suitable for a broad range of biomedical applications such as on-demand delivery of pharmaceuticals or cell-based therapies.

**References:** (Kloxin AM. *Science*. 2009;324:59-63.); (Frey MT. *Soft Matter*. 2009;5:1918.); (Woodcock JW. *Soft Matter* 2010;6:3325-3336.).