

Triple Shape Memory Polymers Based on Self-Complimentary Hydrogen

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Statement of Purpose: Triple shape polymers (TSPs) are a growing subset of the class of smart biomaterials known as shape memory polymers. Because TSPs can store one permanent and two metastable shapes, they have been proposed for numerous biomedical device applications that call for complex deployment of medical devices after insertion in the body. Previous work has described TSPs that utilize glass transitions and crystalline melt transitions to effect triple shape behavior(1). In this study, we describe a novel TSP system that utilizes the glass transition of (meth)acrylate copolymers and the dissociation of self-complimentary hydrogen bonding moieties to enable triple shape behavior. The inspiration of this novel polymer system arises from the modular structure of the muscle protein titin, which has been previously replicated in synthetic polymers that utilize hydrogen bonding motifs(2). This novel TSP system is comprised of both permanent covalent crosslinks and supramolecular hydrogen bonding moieties, which enable broad and independent control of both glass transition temperature and crosslink density.

Methods: This novel class of TSPs is based on lightly crosslinked, random copolymers of various alkyl acrylates and 2-ureido-4[1H]-pyrimidone (UPy) functionalized monomers. UPy methacrylate (UPyMA) and UPy acrylate (UPyA), which allow for quadruple self-complementary hydrogen bonding, were synthesized through the reaction of 6-methylisocytosine and 2-isocyanatoethyl (meth)acrylate at 150 °C for 20 min in anhydrous DMSO. 50x75 mm, 1 mm-thick polymer sheets were prepared by photopolymerization between glass slides of various combinations of methyl, ethyl, propyl, and butyl acrylate, bisphenol A ethoxylate diacrylate ($M_n \sim 512$) (BPAEDA), and the novel UPy(M)A monomers in 25% DMSO solutions. After drying at 110 °C for 24 h under vacuum, the polymer samples were characterized through dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), tensile testing, and shape memory analysis.

Results: Series of copolymers were synthesized and characterized to explore the effect of three key variables on mechanical properties: covalent crosslink density, T_g and hydrogen bonding crosslink density.

Copolymers of 20% UPyMA, 5% BPAEDA, and butyl, propyl, ethyl, and methyl acrylate were synthesized to demonstrate control of T_g . T_g , as determined by $\tan \delta$ peak, was tailorable from 10 – 70 °C. In these samples two distinct transitions were present, with the $\tan \delta$ peak associated with the second transition (T_D) at 110 °C.

A copolymer of methyl acrylate and butyl acrylate (1:1) crosslinked with 5% BPAEDA was selected to assess the effects of varying UPy(M)A on T_g , T_D , and effective crosslink density as a function of temperature. Both UPyA and UPyMA were varied from 0-40%. DMA

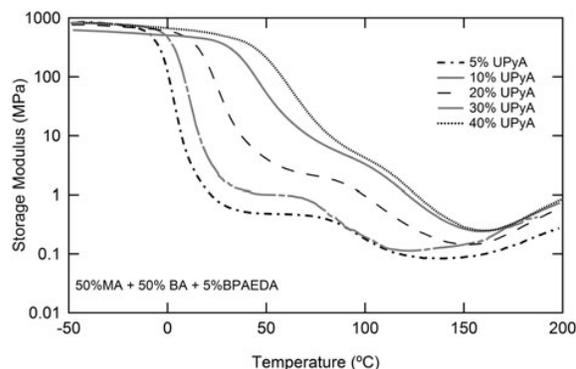


Figure 1 – DMA of copolymers containing UPyA ranging from 0-40% of copolymers of UPyA is presented in **Figure 1**. Both T_g and T_D increased with increasing UPy(M)A content, but T_g increased more dramatically. Consequently, an overlap of the two transitions at compositions above 20% UPy(M)A was observed. Modulus drop between the two transitions also increases with increasing UPy(M)A. Tensile testing of samples at the onset of T_g showed increased strength and decreased strain-to-failure with increased UPyMA content. Toughness was found to peak near 20% UPyMA.

A third series of copolymers was synthesized to explore the effect of increasing covalent crosslink density. Samples consisted of 10% UPyMA and a (1:1-X:X) ratio of butyl acrylate, methyl acrylate and BPAEDA. The concentration of BPAEDA was varied between 0-30%. DMA of the resulting copolymers demonstrated a decrease in T_D with increased crosslink density.

Conclusions: A novel TSP system has been developed based on the incorporation of bioinspired, synthetic monomers that introduce self-complimentary hydrogen bonding motifs into poly(meth)acrylates. These polymers show two distinct transitions in the useful range of 0-120 °C that could be applicable for biomedical devices(3). Wide control of thermomechanical properties such as T_g , T_D , and crosslink density has been demonstrated. This control will enable device-based research for applications requiring wide range of activation temperatures and recoverable stress.

Current research is focusing on evaluating specific shape memory properties such as shape fixity and recovery around each transition as a function of covalent and supramolecular crosslink density. Future research must determine the response of these materials to physiological conditions and develop processing methods conducive to complex medical device designs.

References:

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