

Acrylic Triblock Copolymers Incorporating Isosorbide and Glucose for Pressure Sensitive Adhesives

Mohammadreza Nasiri, Derek J. Saxon, Theresa M. Reineke *

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

Polymer chemistry has allowed for the versatile design of functional thermoplastic elastomers (TPEs) that comprised of ABA-type triblock copolymers. Their mechanical properties are due to their phase-separated morphology, which results in glassy domains dispersed in a continuous flexible network. Researchers have paid tremendous attention to fashioning sustainable feedstocks for many polymer applications such as TPEs and pressure sensitive adhesives. For example, efforts toward substituting styrene-based polymers in commodity materials with poly(lactide) (PLA) have been examined by the incorporation of PLA as the glassy component in TPEs. Previous work on sustainable TPEs has provided many examples of PLA incorporation as the hard end blocks in ABA triblock copolymers.

While PLA has been shown to provide a useful for TPEs, it has inherent drawbacks (*e.g.* low glass transition temperature), which limits its utility. Other, alternative biomass derivatives including natural polymers such as lignin, cellulose, rosin acid- and terpene-derived feedstocks have been explored. Our group has also previously reported using acrylic derivatives of acetylated glucose and isosorbide as the glassy end blocks in triblock copolymers. The previous studies showed that these sustainable building blocks provide excellent candidates for the glassy domain of an ABA triblock copolymer TPE.

In this work, the properties and performance of triblock copolymers derived from both sustainable monomers, acetylated glucose and isosorbide, have been explored. Two sustainable and glassy monomers, acetylated acrylic isosorbide (AAI) and glucose acrylate tetraacetate (GATA), were copolymerized with *n*-butyl acrylate (nBA) create high molar mass ABA triblock copolymers. We employed reversible addition–fragmentation chain transfer (RAFT) polymerization and utilizing a bifunctional chain transfer agent (CTA) that allowed synthesis of well-controlled triblock copolymers of GATA/AAI with nBA in a two-step reaction. 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy) benzoic acid (BTCBA) was used as the CTA. Poly(glucose-6-acrylate-1,2,3,4-tetraacetate) [PGATA] and poly(acetylated acrylic isosorbide) [PAAI] end blocks were chain-extended from a poly(*n*-butyl acrylate) [PnBA] midblock.

The adhesion and mechanical properties of these materials were evaluated. Adhesion testing—including loop tack, steady shear, peel adhesion, and shear failure temperature tests—revealed that the isosorbide-based copolymer possesses properties comparable or better than commercially used pressure sensitive adhesives. Structures with higher ratios of the glassy components were also prepared and examined for performance. PAAI-PnBA-PAAI exhibited excellent adhesion properties: peel = 8.74 N cm⁻¹, loop tack = 2.96 N cm⁻², no shear failure up to 100 h, and shear adhesion failure temperature (SAFT) = 60 °C. Although similar peel adhesion and higher loop tack were observed for PGATA-PnBA-PGATA, the shear strength and SAFT were moderate (18 h and 42 °C, respectively). PAAI-PnBA-PAAI are tough elastomers and

demonstrated high stress and elongation at break ($\sigma = 6.5$ MPa and $\varepsilon = 620\%$, respectively) while the GATA-based analogue exhibited weaker tensile properties ($\sigma = 0.8$ MPa and $\varepsilon = 476\%$).

We incorporated noncovalent interactions via hydrogen bonding within the GATA end blocks of the glucose-derived triblock copolymer by deacetylating the anomeric hydroxyl groups to probe the effect of non-covalent interactions on the mechanical properties. Indeed, hydrogen bonding and other non-covalent interactions can play a significant role in performance. To address this, the anomeric hydroxyl group of GATA units were deprotected to promote self-complementary hydrogen bonding in the glassy domains, resulting in 80% enhancement in the ultimate tensile stress at break ($\sigma = 1.5$ MPa). Thus, these enhanced intermolecular interactions within the glassy domains promoted stronger physical cross-links and improved the mechanical performance.

In summary, incorporation of glucose- and isosorbide-derived high T_g components in ABA triblock copolymers results in sustainable alternatives to commodity TPEs. This study demonstrates properties enhancement in sugar-derived triblock copolymers. In addition, this study aims to demonstrate effects of non-covalent interactions such as hydrogen bonding, to enhance the adhesion and mechanical performance of sugar-derived TPEs.

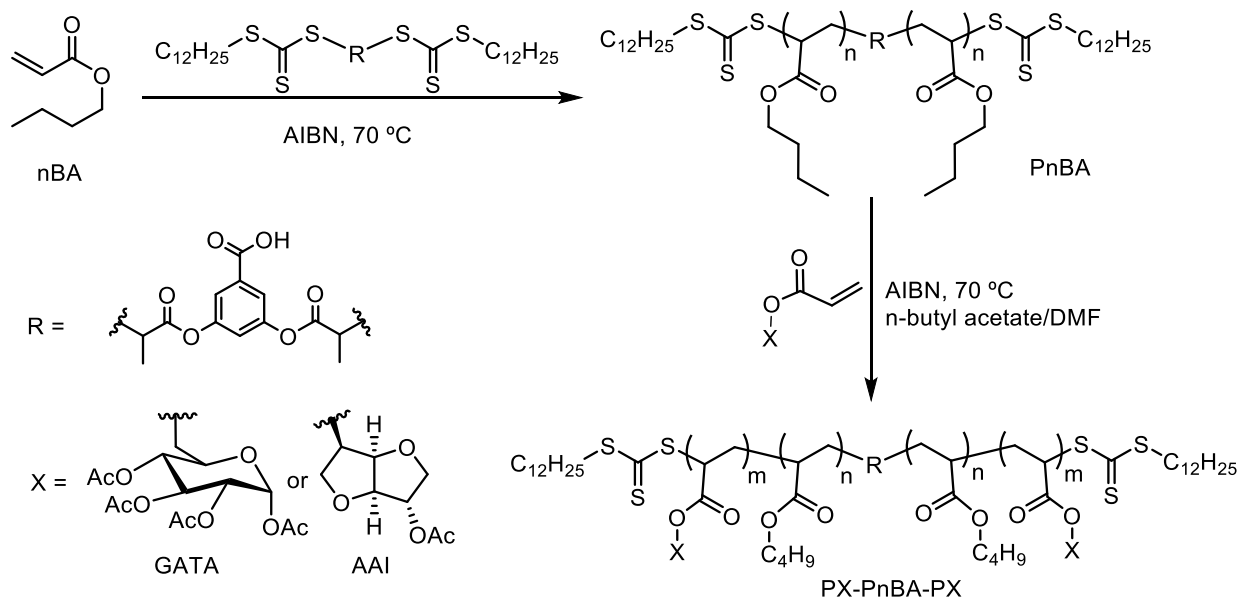


Figure 1. Schematic synthesis of the PX-PnBA-PX triblock copolymers (where X is GATA or AAI).