Thermoplastic Elastomers Containing Crystalline and Glassy Components from Single-Phase Melts

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Thermoplastic elastomers (TPEs) are typically symmetric ABA triblock copolymers made up of a majority component rubbery midblock (B) and minority component glassy endblocks (A) [1]. In this system, interblock repulsion between the hard glassy segments and the rubbery midblocks causes microphase separation, creating a physical crosslinking of the rubbery midblock chains, thus producing elastomeric behavior. In these types of TPEs where both the hard and soft blocks are amorphous, it is desirable to have a strong degree of incompatibility between the blocks so microphase separation can occur. However, the microphase-separated structure persists into the melt for these materials causing an adverse effect on the processability as the segregated melts have a high viscosity. If instead the hard segments were crystalline, microphase separation can be driven by crystallization itself from a lower viscosity single-phase melt and therefore strong interblock repulsion is not required. The use of crystalline endblocks in TPEs can also confer properties such as solvent resistance to the material [2]. Indeed, there has been a considerable amount of research on TPEs from single-phase melts containing crystalline endblocks, primarily using hydrogenated high-1,4 polybutadiene as the crystalline component [2,3]. Unfortunately, these crystalline TPEs were plagued by poor tensile strengths and high hysteresis relative to their amorphous counterparts.

Here, we report the synthesis of TPEs formed from single-phase melts containing both crystalline and hard segments to combine the superior tensile strengths of glassy components with the solvent resistance of a crystalline component, and allow microphase separation to be driven solely by crystallization. To accomplish this, we used living ring-opening metathesis polymerization (ROMP) and subsequent hydrogenation to synthesize symmetric pentablock copolymers with the architecture crystalline-glassy-rubbery-glassy-crystalline. With this architecture and appropriate selection of block lengths, crystallization from a single-phase melt will cause a glassy block-rich layer to form around the crystalline lamellae, forming an effective hard block with both crystalline and glassy components. The synthesized pentablocks show the desired strain-hardening mechanical behavior typically seen in TPEs with only glassy endblocks that have higher viscosity microphase-separated melts. In contrast, we synthesized a TPE with only crystalline endblocks, which showed undesirable plastic deformation at only moderate strains.

[1] N.R. Legge, *Rubber Chem. Technol.* 60, G83 (1987).
[2] M. Morton, *Rubber Chem. Technol.* 56, 1096 (1983).
[3] R. Seguela and J. Prud'homme, *Polymer* 30, 1446 (1989).