

Poly(Trimethylene Carbonate)/Poly(ϵ -Caprolactone) Phase-Separated Triblock Copolymers with Advanced Properties

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Abstract : Biodegradable and biocompatible block copolymers have risen as the golden materials in both medical and environmental applications. Moreover, if their architecture is of controlled manner, higher applications can be foreseen. In the meantime, organocatalytic ROP has been promoted as more rapid and immaculate route, compared to the traditional organometallic catalysis, towards efficient synthesis of block copolymer architectures. Therefore, herein we report novel organocatalytic pathway with guanidine molecules (TBD) for supported synthesis of trimethylene carbonate initiated by poly(caprolactone) as pre-polymer. Pristine PTMC-b-PCL-b-PTMC block copolymer structure, without any residual products and clear desired block proportions, was achieved under 1.5 hours at room temperature and verified by NMR spectroscopies and size-exclusion chromatography. Besides, when elaborating block copolymer films, further stability and amelioration of mechanical properties can be achieved via additional reticulation step of precedently methacrylated block copolymers. Subsequently, stimulated by the insufficient studies on the phase-separation/crystallinity relationship in these semi-crystalline block copolymer systems, their intrinsic thermal and morphology properties were investigated by differential scanning calorimetry and atomic force microscopy. Firstly, by DSC measurements, the block copolymers with χ_{ABN} values superior to 20 presented two distinct glass transition temperatures, close to the ones of the respecting homopolymers, demonstrating an initial indication of a phase-separated system. In the interim, the existence of the crystalline phase was supported by the presence of melting temperature. As expected, the crystallinity driven phase-separated morphology predominated in the AFM analysis of the block copolymers. Neither crosslinking at melted state, hence creation of a dense polymer network, disturbed the crystallinity phenomena. However, the later revealed as sensible to rapid liquid nitrogen quenching directly from the melted state. Therefore, AFM analysis of liquid nitrogen quenched and crosslinked block copolymer films demonstrated a thermodynamically driven phase-separation clearly predominating over the originally crystalline one. These AFM films remained stable with their morphology unchanged even after 4 months at room temperature. However, as demonstrated by DSC analysis once rising the temperature above the melting temperature of the PCL block, neither the crosslinking nor the liquid nitrogen quenching shattered the semi-crystalline network, while the access to thermodynamical phase-separated structures was possible for temperatures under the poly (caprolactone) melting point. Precisely this coexistence of dual crosslinked/crystalline networks in the same copolymer structure allowed us to establish, for the first time, the shape-memory properties in such materials, as verified by thermomechanical analysis. Moreover, the response temperature to the material original shape depended on the block copolymer emplacement, hence PTMC or PCL as end-block. Therefore, it has been possible to reach a block copolymer with transition temperature around 40°C thus opening potential real-life medical applications. In conclusion, the initial study of phase-separation/crystallinity relationship in PTMC-b-PCL-b-PTMC block copolymers lead to the discovery of novel shape memory materials with superior properties, widely demanded in modern-life applications.

Keywords : biodegradable block copolymers, organocatalytic ROP, self-assembly, shape-memory

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