Solvent assisted rapid thermal treatment in low molecular weight asymmetric and symmetric PS-b-PMMA thin films

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The self-assembly of block copolymers (BCPs) into a nanometric ordered structure and the chemical similarity with the photoresist materials employed in standard photolithographic processes have triggered the application of BCPs as template masks. Poly(styrene-block-methylmethacrylate) (PS-b-PMMA) can form nanodomains perpendicularly oriented with respect to the substrate since the weakly unbalanced surface interactions are easily neutralized by grafting the appropriate functional poly(styrene-random-methylmethacrylate) (PS-r-MMA) random copolymer (RCP) to the surface. In this work, the self-assembly and the lateral organization of a cylinder forming asymmetric and of a lamellar forming symmetric PS-b-PMMA BCP over a PS-r-MMA RCP grafted layer is accomplished by a fine tuning of the annealing temperature \( T_{\text{ann}} \) and time \( t_{\text{ann}} \) using a Rapid Thermal Process (RTP) machine.

The lower edge of the grey area (it corresponds to processing leading to inhomogeneous polymeric films) indicates the combination of processing parameters: \( t_{\text{ann}} = 10/30 \) s, \( T_{\text{ann}} = 330 \) °C, \( t_{\text{SPS}} = 60/500 \) s, \( T_{\text{SPS}} = 310 \) °C, corresponding to the highest \( \xi \) values.

- Fast and slow coarsening regimes of the lamellar structures.

The TTS procedure generates a single master curve \( \langle t_{\text{inv}} \rangle \) at \( T_{\text{inv}} = 250 \) °C describing the evolution of \( \langle t_{\text{inv}} \rangle \).

- The occurrence of inhomogeneous regions in the polymeric film hampers the investigation of lateral order evolution at high temperature for long \( t_{\text{inv}} \).
- The exponential growth of \( \xi \) turns into the plateau values indicating the system is entering a slow coarsening regime.

The residual amount of trappedtoluenefor the thick RCP even at the longest \( t_{\text{inv}} \) (900 s) is higher than that for thin RCP even at the shortest \( t_{\text{inv}} \) (1 s).

The competition between self-assembly and polymer degradation processes was investigated through the quantification of the lateral ordering. This systematic analysis indicates that the two processes occur on a different time scale.

RTP takes advantages of very fast heating rate that allows reaching the target temperature in a very short amount of time, preventing any kind of degradation during the transient regime. The ordering evolution depends on capacity of the solvent reservoir in the total RCP + BCP system. Indeed, this content increases with the RCP thickness. The combination of solvent reservoir and RTP thermal processing allows reaching micrometer scale correlation lengths.

Patent protection related to this work is pending.