Effect of Block Number on the Order-Disorder Transition, Viscoelastic Properties and Shear Alignment Behavior of Linear $(AB)_n$ Multiblock Copolymers

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERISITY OF MINNESOTA
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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October 2004

ABSTRACT

This thesis reports the consequence of varying block number on the order-disorder transition (ODT), viscoelastic properties and shear alignment behavior for lamellar multiblock copolymers. A series of symmetric poly(styrene-*b*-isoprene) multiblocks ($(SI)_n$, n = 1 to 10) were synthesized by anionic polymerization. As n increases, the order-disorder transition temperature (T_{ODT}) approaches an asymptotic value, consistent with random phase approximation calculations. A systematic difference between the experimental and theoretical results is attributable to the effects of fluctuations, independent of block number (or n). Addition of a non-selective solvent into $(SI)_n$ copolymers results in a non-mean-field behavior for the ODT, independent of n. In contrast, binary blends of $(SI)_n$ copolymers exhibit a mean-field mixing behavior for the ODT, independent of n.

Increasing block number leads to a dramatic enhancement of melt relaxation times: the crossover frequency ω_x, demarcating the transition from block/chain- to domain-dominated relaxation, scales as $\omega_x \sim n^{-7.5}$ in the ordered (lamellar) state, whereas the steady flow viscosity depends on the molecular weight as $\eta_0 \sim M^{4.2}$ in the disordered state, both exceeding the conventional power for entangled homopolymers. Nevertheless, all samples cooled from the disordered state developed a distinct lamellar morphology, from diblocks to undecablocks, although the resulting ellipsoidal multilamellae grains decreased in size with increasing n.

As *n* increases, randomly oriented lamellae are more easily aligned to a perpendicular orientation with the lamellae normal along the vorticity direction under oscillatory shear. Surprisingly, a parallel orientation with the normal along the gradient direction, which is "forbidden" for $n > 2$, can be achieved even for heptablocks ($n = 6$) in the region of low shear frequencies and large strain amplitudes. We demonstrated that the internal blocks adopt predominant looping conformations in parallel-arranged lamellae, in order to accommodate large deformation by layer sliding. The alignment kinetics under steady shear reveals that the large strain shear facilitates the formation of parallel orientation and the transformation from bridging to looping conformation, while low shear rates ensure a high conversion of the transformation, thereby stabilizing the parallel orientation.