UNIVERSITY OF HOUSTON

Cullen College of Engineering

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PhD Dissertation Defense

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ENHANCING THE ORIENTATIONAL ORDER IN BCPs USING IONIC LIQUID AND SOLVENT PROCESSING

Block copolymers (BCPs) self-assembly into periodic patterns can have potential applications in nanolithography, membranes, energy storage, high density data storage, optoelectronics, metamaterials and many other applications. Their potential however are limited due to challenges of slow kinetics and structural issues. The research develops strategies for faster and defect free annealing of BCPs such as PS-b-PMMA using an additive called Ionic Liquid (IL) and annealing techniques such as thermal annealing, solvent vapor annealing and our recently developed, direct immersion annealing (DIA). We report, long range stratification in lamellar films on a planar substrate using IL and thermal annealing. Moreover, addition of IL enhances the kinetics of ordering in these films, and can order BCP systems up to 5-7 times the entanglement Mw, not otherwise possible. Neutron Reflectivity (NR) and depth profile using ToF-SIMS analyses show the sharpening of interfacial widths by up to 41%, implying the segregation coefficient, χ in IL filled BCPs increases between 3-6 times. Solvent annealing also revealed some interesting phenomenon including the attainment of vertically oriented BCPs on Silicon substrate using a neutral solvent DIA mixture, in conjunction with IL. AFM and GISAXS analysis reveal the formation of the vertical lamellae, and the attainment of larger grain size. Selective DIA, also reveals some very interesting phenomenon including domain size shrinkage by up to 50% for the same number of segments compared to thermal annealing, and interfacial width shrinkage of up to 50% found using Tof-SIMS and NR analysis. In cylindrical morphology, very long rage order has been achieved using DIA and PDMS soft shear validated using AFM and grain size and orientation color map analysis. Solvent vapor annealing (SVA) was also performed on lamellar BCP system. Generally, for low χ polymers, solvent vapor environment tends to dewet the films. Such dewetting phenomenon was suppressed using IL, an outcome of enhance χ. Robust ordering was also attained in these films using selective and neutral solvent mixtures. NR confirmed domain length reduction of up to 60% and interfacial sharpening by up to 50%. These findings are critical advances in realizing the potential of BCPs for future applications.