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Effect of chain architecture and surface energies on the microdomain orientation in block copolymer films V. KHANNA, E. J. KRAMER, E. W. COCHRAN, G. H. FREDRICKSON, UCSB, X. LI, J. WANG, Argonne National Lab, S. F. HAHN, Dow Chemical Company — We investigate the effect of surface energy and chain architecture on the orientation of microdomains in relatively thick films (600nm) of lamellar and cylindrical block copolymers of poly(vinylcyclohexane)(C) and poly(ethylene)(E). The E block has 26 ethyl branches per 1000 backbone carbon atoms. Melt surface energies of the C and E blocks are 22.3 and 20.9 mJ/m^2 , respectively. GISAXS, SFM and cross sectional TEM show that cylindrical and lamellar CEC triblock copolymers orient their microdomains normal to the surface through the film thickness. However, a lamellar CE diblock prefers a parallel orientation of the sheets with an E surface. Moreover, a cylindrical CEBC triblock copolymer where the EB block has 125 ethyl branches per 1000 backbone carbon atoms leads to EB cylinders that always orient parallel to the surface. In this case the lower surface energy EB block dominates the surface. Self-consistent field theory calculations allow us to interpret the experimental results in terms of the entropic cost of forming a wetting layer comprised entirely of looping blocks. Thus in triblock copolymers, parallel orientations are only stabilized when the surface energy of the midblock is low enough to compensate for this conformational penalty, which is absent in diblock copolymers.

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