Self-Assembly of Block Copolymers in a Liquid Crystal Solvent: Consequences of "Switchable Quality"

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The usual phase behavior of block copolymers in solution is modified when the solvent is a liquid crystal (LC) because the quality of the solvent for the component blocks changes discontinuously across the LC phase transitions. The orientational order of the LC in the nematic phase presents a large entropic penalty to solvation of a random coil polymer (e.g. polystyrene, PS), but in the isotropic phase the solvent's spherical symmetry imposes no such solubility constraints. Attaching mesogenic side groups to a polymer can provide a side-group liquid crystalline polymer (SGLCP) that is soluble in both the nematic and isotropic phases of the LC solvent. In a coil-SGLCP block copolymer, the LC solvent switches from being strongly selective toward the SGLCP block to being a good solvent for both blocks at the nematic to isotropic phase transition. This transition takes place over a very narrow temperature range (1 °C or less) and we term the phenomenon "switchable solvent quality." Such abrupt changes in solvent quality do not occur in non-LC solvent. Pairwise thermodynamic interactions between a LC solvent (4-pentyl-4'-cyanobiphenyl, 5CB), a coil homopolymer (PS), and a SGLCP homopolymer are inferred from their ternary phase diagram. These interactions provide multiple driving forces for self-assembly that are exceptionally sensitive to species concentrations and temperature. Unfavorable 5CB-PS interactions dominate at all concentrations in the nematic phase, unfavorable PS-SGLCP interactions dominate at high concentrations in the isotropic phase, and an "asymmetric solvent effect" deriving from the slight preference of 5CB for SGLCP dominates at moderate concentration in the isotropic phase. An understanding of these driving forces explains structural transitions observed by small-angle neutron scattering (SANS) and rheology in PS-SGLCP diblock solutions and PS-SGLCP-PS triblock copolymer gels.