COPLING POLYMER THERMODYNAMICS AND VISCOELASTICITY TO LIQUID CRYSTALLINE ORDER: SELF-ASSEMBLY AND RELAXATION DYNAMICS OF BLOCK COPOLYMERS IN A NEMATIC SOLVENT

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Neal R. Scruggs

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-Sir Isaac Newton

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ABSTRACT

The discontinuous change in solvent quality of a liquid crystal (LC) solvent, 5CB, at the nematic-isotropic phase transition produces abrupt changes in the phase behavior of solutions of coil and LC-polymers and in the self-assembly of coil-LC block copolymers. Nematic 5CB is strongly selective for a side-group liquid crystal polymer (SGLCP) and isotropic 5CB is a good solvent for both SGLCP and a random coil (polystyrene, PS). In nematic 5CB, unfavorable LC-PS interactions drive phase separation in SGLCP-PS-LC ternary solutions and drive micellization of PS-SGLCP diblocks. In isotropic 5CB, rich phase behavior occurs in both ternary solutions and block copolymer solutions. Despite the fact that isotropic 5CB is a good solvent for both SGLCP and PS, segregation can occur due to the asymmetric solvent effect (i.e., the preference of the solvent for the SGLCP). In concentrated isotropic solutions, unfavorable SGLCP-PS interactions become dominant.

In binary solutions of SGLCP and 5CB, the delicate thermodynamic balance between LC order and polymer entropy manifests itself in a non-monotonic concentration dependence of the solutions' clearing points. The frustration between LC order and polymer entropy in an SGLCP melt is partially relieved by the addition of small molecule LC, greatly increasing the polymer's configurational freedom and stabilizing the nematic phase. In dilute solutions, the polymer adopts an anisotropic conformation because of its coupling to the LC solvent's prevailing director field; the sense and the magnitude of the anisotropy depend on the architecture of the SGLCP (end-on or side-on mesogens).

Coil-SGLCP-coil triblock copolymers self-assemble in 5CB to form liquid crystalline gels in which nematic order is coupled to an associative polymer network. The network's dynamic restructuring couples to fluctuations in the LC's local order to provide an additional relaxation process that is not present in SGLCP solutions or LC elastomers, and the importance of this process is highly dependent on the underlying anisotropy of the SGLCP-based network. The network furthermore provides a memory of the LC orientation state: when the LC is reoriented by electric-magnetic fields or mechanical

shear, the network structure prevents the orientation from relaxing back to a random distribution when the aligning force is removed.

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