Highly Responsive Self-Assembled Gels from Block Copolymers in Liquid Crystal Solvent

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Polymeric gels formed by the self-assembly of block copolymers in a liquid crystal (LC) solvent are highly responsive materials having novel properties resulting from the synergistic coupling between polymer and solvent. The orientational order of the LC solvent imparts electo-optic and mechano-optic properties that are forbidden by symmetry in isotropic gels, and the polymer network provides memory via long-time relaxation processes that do not exist in the bulk LC. Triblock copolymers having an ultralong (>1,000 kg/mol), LC-philic side-group liquid crystal polymer (SGLCP) midblock and LC-phobic polystyrene (PS) endblocks form gels at low concentrations (~5 % polymer) when dissolved in the nematic LC 4-pentyl-4'-cyanobiphenyl (5CB); the physically associated PS endblocks constitute the network's crosslinks which are spanned by the dissolved midblock. At dilute polymer concentrations the LC solvent's transition from the nematic to the isotropic phase is accompanied by the solubilization of the PS endblocks, and the gel transitions to a Newtonian solution of free polymer chains. Gels can be aligned into a single-crystal monodomain by applied shear, electric fields, magnetic fields, or surface effects, and the alignment state is preserved by the network's elastic restoring force. This results in slower electric field-induced reorientation time but faster field-off relaxation, relative to the bulk LC. When confined to a fixed gap, under an applied torque on the director (electric field) or a change in the order parameter (temperature) the system minimizes the elastic free energy cost by forming "stripe patterns"- periodic variation of director orientation and network strain. The molecular basis for macroscopic properties is inferred from a variety of characterization techniques. Small-angle neutron scattering (SANS) reveals the anisotropic conformation of the SGLCP midblock; the sense of the anisotropy determines the direction of shear-alignment and influences stripe pattern formation. Memory effects imparted by the network connectivity are demonstrated by comparing the electro-optic switching between triblock copolymer gels and an analogous diblock solution.