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Self-Assembled Liquid Crystalline Gels Designed from the Bottom Up

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Block copolymers with long side-group liquid-crystalline (LC) midblocks and LC-phobic end-blocks form a physical network that swells readily in a small molecule LC to form model nematic gels with well-defined molecular weight between crosslinks. Ultralong (>800 kg/mol) SGLCP midblocks enable gelation at relatively low concentration (~5% polymer), which preserves the fast dynamics of small molecule LCs. Similar to LC elastomers, an initially unaligned, polydomain gel aligns under applied strain. Further, the resulting monodomain is so well oriented that it generates clear conoscopic figures. Due to the coupling between nematic order and polymer elasticity, a novel stripe pattern forms when the gels are subjected to electric fields or when the order parameter of the LC solvent changes. Meyer and coworkers have described these patterns using a linear stability analysis that connects the band formation with the spontaneous anisotropy of the SGLCP backbone. Small-angle neutron scattering (SANS) on analogous SGLCP homopolymers confirms that greater chain anisotropy favors band formation and that the sense of anisotropy (prolate or oblate) dictates the initial band orientation. The physical junctions comprised of the LC-phobic endblocks perturb the director field on a nano-scale manifested in a reduction in the mean order parameter of the LC host characterized by both refractive indices (n_e, n_o) and NMR ²H quadrupole splitting. The physical principles demonstrated for nematic gels allow rational design of gels exhibiting higher-order LC phases, such as ferroelectric gels.