New modes of self-assembly in side-chain liquid crystalline polymers

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Helical, and particularly double-helical, structures have fascinated scientists and the public since the discovery of the DNA double helix. A helix provides a topological compromise between a polymer's tendency to stay relatively straight for efficient packing and its need to twist to avoid steric clashes between side groups. In liquid crystals, however, columns self-assembled from achiral molecules rarely show long-range chiral order. Thermodynamically a one-dimensional column cannot have long-range order meaning that helices will not form unless the columns act cooperatively and this is difficult to do without crystallizing.

We have recently explored a series of side-chain liquid-crystalline polymers, in which mesogenic side groups are attached to a polysiloxane backbone (Figure CS4a), and observed the emergence of three-dimensionally ordered columnar phases in which each column adopts a double-helical structure[3]. The aromatic cores of the side groups form two strands that wind around one another. A columnar phase with high *Fddd* symmetry is obtained, comprising eight double-helical columns - four left-handed and four right-handed (Figure CS4b). The twisting of each helix is markedly non-uniform, consisting of alternating, nearly straight "splay'' segments and sharply twisted "recovery'' regions (Figure CS4b). This non-uniform torsional behaviour drives a transition to a phase of much lower triclinic symmetry, representing the first such example in liquid-crystalline systems (Figure CS4c). In compounds Si3-n, the double-helical segments connect through three-way junctions to form a complex bicontinuous four-network Gyroid (4NG) cubic structure[4]. Two networks wind around each other left-handed (blue and light blue), while the other two are right-handed (red and gold), and the equal populations of opposite handedness render the overall 4NG phase achiral (Figure CS4d). Grazing-incidence small-angle X-ray scattering (GI-SAXS) on XMaS, using oriented thin films, enabled the unequivocal indexing of the diffraction patterns associated with these highly complex 3D structures (Figure CS4e). These structural insights highlight behaviour that is strikingly different from expectations for polymeric liquid crystals which have to date been largely viewed as mirroring the phase behaviour of their low-molecular-weight counterparts, but these reports show that polymers offer new modes of self-assembly of their own. It calls for re-evaluation of some established models of self-organization in soft matter.

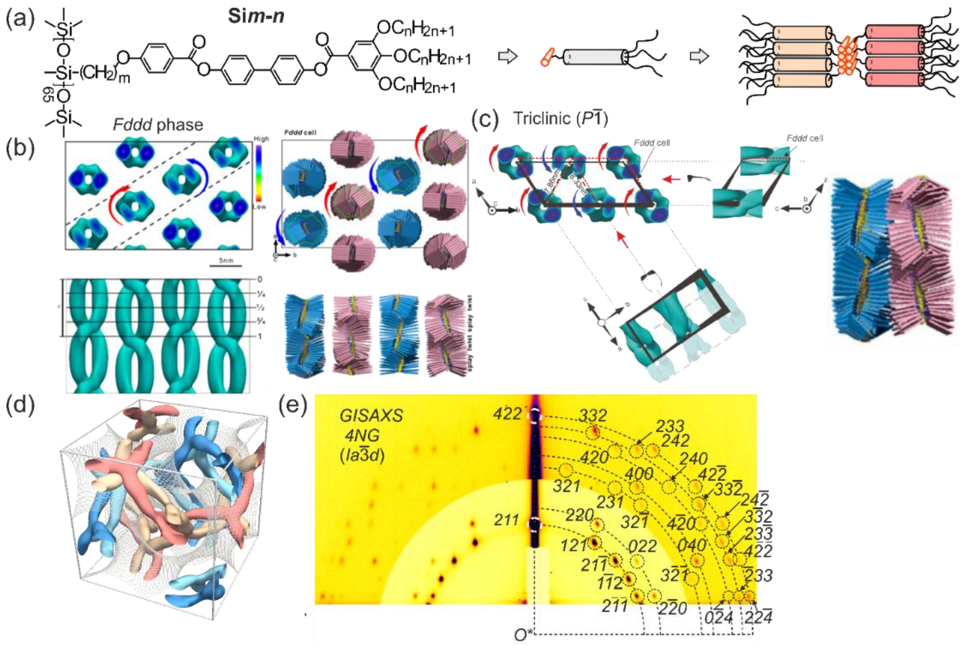

Figure CS4: (a) Chemical structure of the side-chain LC polymer. (b) Reconstructed electron density maps and the schematic molecular model of the *Fddd* phase viewed in different directions. (c) Reconstructed electron density maps viewed in different directions, and the schematic molecular model of the triclinic phase. (d) The 4NG phase with networks of double helical segments. (e) GISAXS pattern of the 4NG phase.

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[3] Y. N. Xue *et al., Angew. Chem. Int. Ed.* 64, e202505548 (2025) and Y. N. Xue *et al., J. Am. Chem. Soc.* 147, 19711 (2025).

[4] Y. M. Tang *et al, Angew. Chem. Int. Ed.* 65, e22314 (2026).