

Hierarchical Heredity on Self-Assembled Helices of Chiral Block Copolymers

The helical phase in chiral block copolymers (BCP) has been profoundly investigated in terms of homochiral evolution from molecular, to intrachain, interchain and mesodomain chirality.

The self-assembly of BCP offers a unique route to create three-dimensional nanostructures *via* bottom-up approaches, such as lamellae, double gyroid, hexagonally packed cylinders and BCC spheres in linear diblock copolymers. A chiral BCP, composed of one chiral block, can assemble into an atypically helical nanostructure, indicating that the chirality and helical entity have an inseparable relation. The design and synthesis of relevant BCP materials are, therefore, attempted actively toward a controllable domain size with cheap manufacture for varied applications in nanomaterials. The chirality is generally identified as the principal origin of the symmetry breaking. In natural systems, the transfer of chirality from protein-building blocks to twisted intermolecular arrangements—characterized by chirality on length scales much larger than those blocks—underlies functional optical and mechanical structures found in organisms from insects to mollusks. Although the chirality transfer in chiral BCP is recognized to be an interesting topic, little is known about how a chiral assembly develops from the molecular level to a mesoscale structure.

Rong-Ming Ho (National Tsing Hua University) and Jing-Cherng Tsai (National Chung Cheng University) recently devoted their efforts to the investigation of self-assembly of chiral BCP.¹ They utilized synchrotron-based small-angle X-ray scattering (SAXS) at **TLS 23A1** and tomography with a transmission electron microscope to identify the formation of a helical phase in newly synthesized chiral BCP, poly(benzyl methacrylate)-*b*-poly(D-cyclohexylglycolide) (PBnMA-PDCG) and PBnMA-*b*-poly(L-cyclohexyl glycolide) (PBnMA-PLCG). These chiral BCP, featuring a helical conformation of the chiral PLCG or PDCG blocks, can form unique helical nanostructures (a so-called helical phase), in which hexagonally packed PLCG or PDCG helices exist in the PBnMA matrix. To investigate systematically the mechanism of homochiral transfer, they reported further evidence of chiral interchain interactions with vibrational circular dichroism (VCD), consistent with some extent of handed skew configurations of chiral PLCG and PDCG segments in a melt state packing. The bulkier chiral side group of the chiral BCP (PDCG or PLCG) produces an increasingly persistent helical bias and also enhances the chiral anisotropy of intersegment forces. This condition enhances the thermodynamic stability of the helical phase relative to poly(styrene)-block-poly(L-lactide).

In summary, helical nanostructures of chiral BCP display helices at various structural levels—from the molecular to the mesodomains—are controlled by their inter- and intramolecular chi-

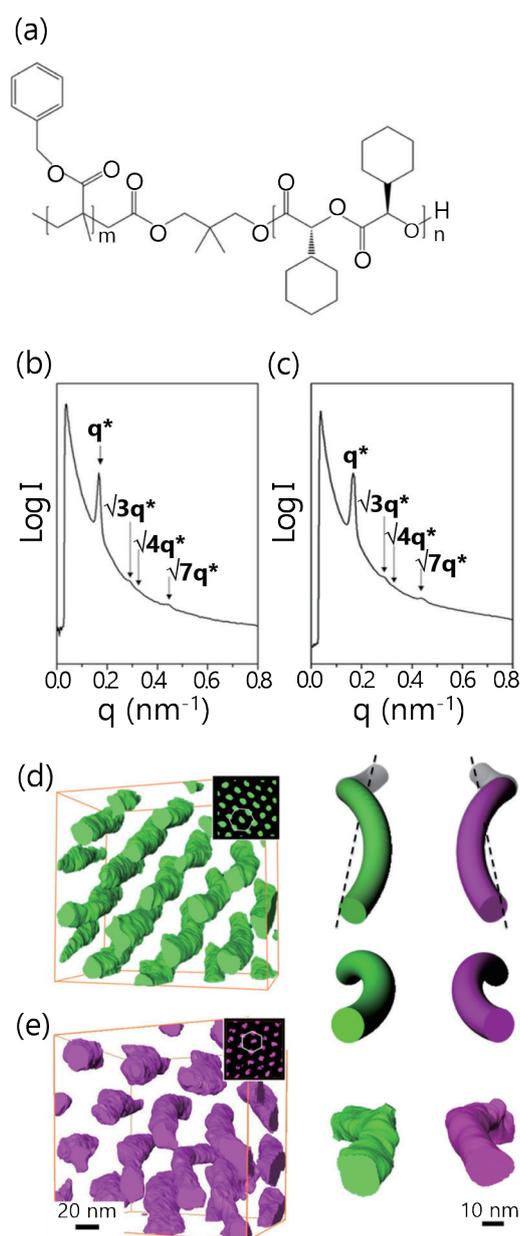


Fig. 1: (a) Chemical structure of poly(benzyl methacrylate)-*b*-poly(D-cyclohexylglycolide) (PBnMA-PDCG). (b)–(c) SAXS profiles of PBnMA-PDCG and PBnMA-PLCG, respectively. (d)–(e) Three-dimensional TEM reconstruction of helical domains from PBnMA-PLCG and PBnMA-PDCG, respectively. [Reproduced from Ref. 1]

rality. This homochiral evolution hence sheds light on the transfer mechanisms that link chiral structure across these length scales in self-assembling materials. (Reposted by Rong-Ming Ho, National Tsing Hua University)

*This report features the work of Rong-Ming Ho, Jing-Cherng Tsai and their collaborators published in Proc. Natl. Acad. Sci. USA **116**, 4080 (2019).*

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- SAXS
- Soft Matter, Block Copolymers, Self-assembly, Chirality

Reference

1. H. F. Wang, K. C. Yang, W. C. Hsu, J. Y. Lee, J. T. Hsu, G. M. Grason, E. L. Thomas, J. C. Tsai, R. M. Ho, Proc. Natl. Acad. Sci. USA **116**, 4080 (2019).

Transfomer: Self-Healing Hydrogels

Smart structures of hydrogels can automatically repair damage in varied environmental conditions according to actuation properties.

Self-healing hydrogels are artificial substances with three-dimensional networks, which have built-in smart structures to allow automatic repair of damage to themselves with neither external diagnosis of the problem nor human intervention. Self-healing hydrogels can thus adapt to varied environmental conditions according to their sensing and actuation properties, because they contain reversible dynamic bonds, such as hydrogen bonds, Schiff base, Diels–Alder reaction, boronate ester bonds, host–guest chemistry, hydrophobic interactions, ionic interactions and metal–ligand coordination. Hydrogels are able to absorb water or biological fluids in large proportions, and thus have the advantages of biocompatibility, biodegradability, injectability and porous structure to be utilized as soft scaffolds for cells in tissue engineering and for surgical operation in a minimally invasive way. Because of their poor mechanical strength and the fragile nature of the hydrogels, the feasibility of applying these hydrogels is, however, still limited. Hydrogels with desirable chemical compositions and tunable mechanical strength have been designed with various synthetic strategies.

Shan-Hai Hsu (National Taiwan University) and her collaborators has devoted to an investigation in the fields of biomaterials, polyurethane, tissue engineering and nanomaterials. Recently, that group reported chitosan-based hydrogels with an ability of self-healing for biomedical applications.¹ Chitosan is generally nontoxic, biocompatible, biodegradable and bacteriostatic, satisfactory for utilisation in many pharmaceutical and medical applications. The observation of macroscopic self-healing of the hydrogels is shown in Fig. 1. The cut semi-disc pieces of the hydrogels can merge into an integrated circular piece of the

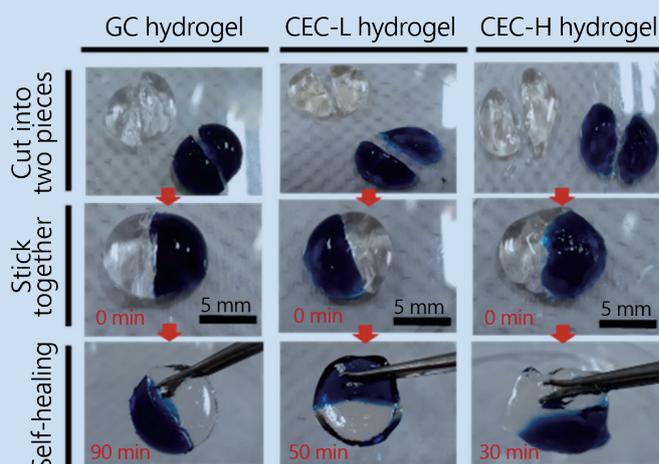


Fig. 1: Glycol chitosan (GC) and N-carboxyethyl chitosan (CEC) were cut into two pieces and stuck back next to each other. All hydrogels later recovered their shape and could be picked up with tweezers without breaking, showing the self-healing behavior. [Reproduced from Ref. 1]

hydrogels and recover the mechanical stability after several decade minutes. All healed hydrogels could be picked up and shaken with tweezers without breaking, indicating that the self-healing hydrogels retain great strength. The workers utilized small-angle X-ray scattering *in situ* combined with a rheometer (Rheo-SAXS) at **TLS 23A1** and ultra-small-angle X-ray scattering (USAXS) at **TPS 25A** to probe the structure of the hydrogels and their dynamics. From the SAXS results (Figs. 2(a), 2(c) and 2(e)), the hydrogels show a typical mechanism of nucleation and growth for the three chitosan-based hydrogels. The critical nucleation sizes of the three hydrogels were observed from the SAXS profiles. The time-resolved