



N-Carboxyanhydride-Derived Polypeptides as Programmable Platforms for Hierarchical Chiral Assembly and Chiroptical Materials

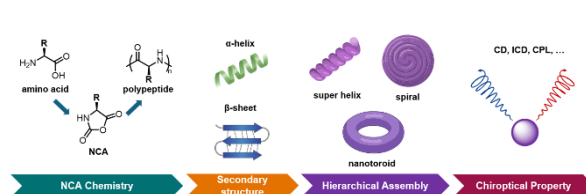
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Abstract: N-carboxyanhydride (NCA)-derived polypeptides are programmable platforms for hierarchical chiral assembly and chiroptical materials. Their controlled stereochemistry, chain length, architecture, and functionality regulate secondary structures such as α -helices and β -sheets, which further guide assembly into nanostructures, liquid-crystalline phases, and bulk ordered materials. This review summarizes how polymer structure and secondary conformation govern chiral assembly, chirality transfer, and chiroptical responses, including circular dichroism, induced circular dichroism, and circularly polarized luminescence. Recent examples of liquid-crystalline polypeptides, homopolypeptide nanotoroids, chromophore co-assemblies, and phosphorescent aggregates are discussed. Challenges and opportunities in structural diversity, performance, and block copolypeptide platforms are also highlighted.



Keywords: NCA polymerization; synthetic polypeptides; chiral assembly; chiroptical materials; chirality transfer; circularly polarized luminescence

1. Introduction

In recent years, chiroptical polymer materials have attracted increasing research interest as they organically integrate optical asymmetry with the processability, robustness, and structural hierarchy of macromolecules [1–4]. By interacting differently with left- and right-handed circularly polarized light, chiral materials can display circular dichroism, induced circular dichroism, circularly polarized luminescence, and other polarization-dependent responses. These properties are relevant to chiral sensing, optical encryption, bioimaging, photonic materials, and polarized optoelectronic devices [5]. Compared with small-molecule chiroptical systems, polymers help amplify molecular chirality into mesoscopic and macroscopic order through chain conformation, self-assembly, phase separation, and processing, opening opportunities to better chiroptical performance, flexibility, and scalability [3].

As structural analogues of natural proteins and peptides, synthetic polypeptides are uniquely suited for translating molecular chirality into hierarchical chiral structures and chiroptical responses. Composed of chiral amino acid residues linked by peptide bonds, polypeptides possess intrinsic stereochemical information and can adopt well-defined secondary structures, including α -helix, β -sheet, polyproline helix, and coil-like conformations [6–8]. These secondary structures serve as intermediate chiral motifs that bridge molecular stereochemistry and higher-order assembly. Depending on chain length, side-chain structure, monomer sequence, tacticity, and polymer topology, as well as solvent, temperature, and pH, polypeptides can further organize into micelles [9], vesicles [10], fibers [11,12], ribbons [13], toroids [14–20], liquid-crystalline phases [21–25], and thin films [26–29]. Such structural hierarchy provides a pathway for amplifying the molecular chirality of amino acid into material-level chiroptical responses.

Ring-opening polymerization (ROP) of amino acid N-carboxyanhydrides (NCAs) is one of the most efficient methods for preparing high-molecular-weight synthetic polypeptides with tunable molecular and architectural features [6,30]. Together with post-polymerization modification (PPM), NCA ROP enables access to homopolypeptides, statistical copolypeptides, block copolypeptides, hybrid block copolymers, and end- or side-chain-functionalized polypeptides [31]. Key parameters such as L/D configuration, degree of polymerization,



dispersity, block sequence, side-chain functionality, and terminal groups can be adjusted to regulate secondary structure and assembly. Thus, NCA-derived polypeptides represent programmable platforms for hierarchical chiral assembly [32].

This review focuses on NCA-derived polypeptides as synthetic platforms for hierarchical chiral assembly and chiroptical materials (Figure 1). Particular attention is given to the relationship between polymer architecture, secondary structure, hierarchical assembly, chirality transfer, and chiroptical properties. The discussion covers homopolypeptides, copolypeptides, block copolypeptides, and selected polypeptide-containing hybrids, while short peptides, proteins, and purely small-molecule systems are not the main focus. A wide range of intriguing chiroptical properties, including circular dichroism (CD), induced circular dichroism (ICD), and circularly polarized luminescence (CPL), and their relationship with the chiral structures will be examined.

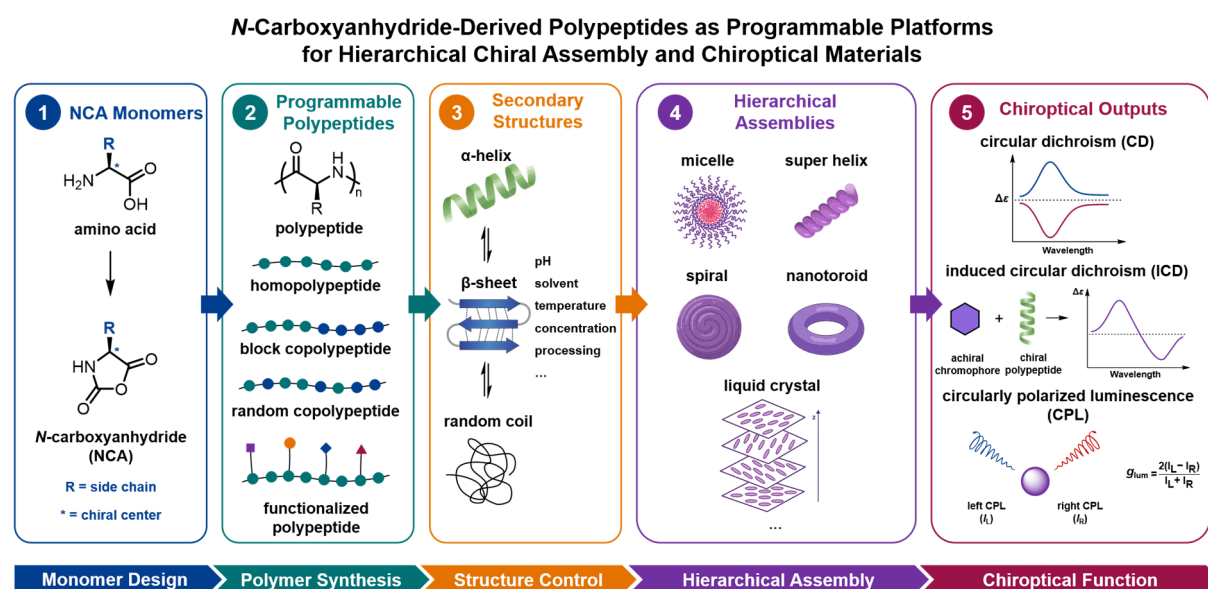


Figure 1. Schematic overview of NCA-derived polypeptides as programmable platforms for hierarchical chiral assembly and chiroptical materials.

2. NCA Polymerization and Secondary Structures of Polypeptides

The chemistry of NCA ROP has been comprehensively reviewed in several review and perspective articles (Figure 2) [6,30,33–36]. Typically, the five-member ring NCA monomers are first synthesized from the corresponding amino acid derivatives by a cyclization reaction (Figure 2a) [37], after which nucleophilic initiators such as amines are added to open the NCA ring and generate a growing polypeptide chain. The chain propagation is known to follow the normal amine mechanism with chain-end amines as the living species and give carbon dioxide as a byproduct (Figure 2b). Under optimized conditions, NCA ROP can proceed in a living/controlled manner, yielding polypeptides with predetermined degrees of polymerization defined by the monomer-to-initiator ratio, while retaining the stereochemical configuration of the amino acid precursor. Sequential monomer addition enables the synthesis of block copolypeptides, whereas copolymerization of monomer mixtures produces statistical or gradient copolypeptides depending on the monomer reactivity ratios (Figure 2c). Additionally, when multifunctional initiators are used, polymers with nonlinear topologies, such as star-like or bottlebrush-like, can also be prepared.

Beyond these primary structural parameters, one of the most distinctive features of NCA-derived polypeptides is their ability to adopt ordered secondary structures (Figure 3) [7,8,38]. Unlike many conventional synthetic polymers whose chain conformations are highly flexible and statistically disordered, polypeptides can form α -helices, β -sheets, polypyrrolone-type I or II helices, and random-coil conformations depending on molecular design parameters and external conditions, including monomer structure, degree of polymerization, side-chain functionality, polymer topology, solvent environment, pH, and temperature. Among these secondary structures, the α -helix is particularly important for chiral assembly and chiroptical materials (Figure 3a). Typical examples include poly(γ -benzyl-L-glutamate) (PBLG), poly(γ -benzyl-D-glutamate) (PBDG), poly(L-lysine), and poly(L-glutamic acid) under appropriate conditions [39–42]. The α -helical conformation possesses a well-defined handedness and a macrodipole along the helical axis, which can influence interchain packing, liquid-crystalline ordering, and the spatial arrangement of attached or co-assembled chromophores [8,25].

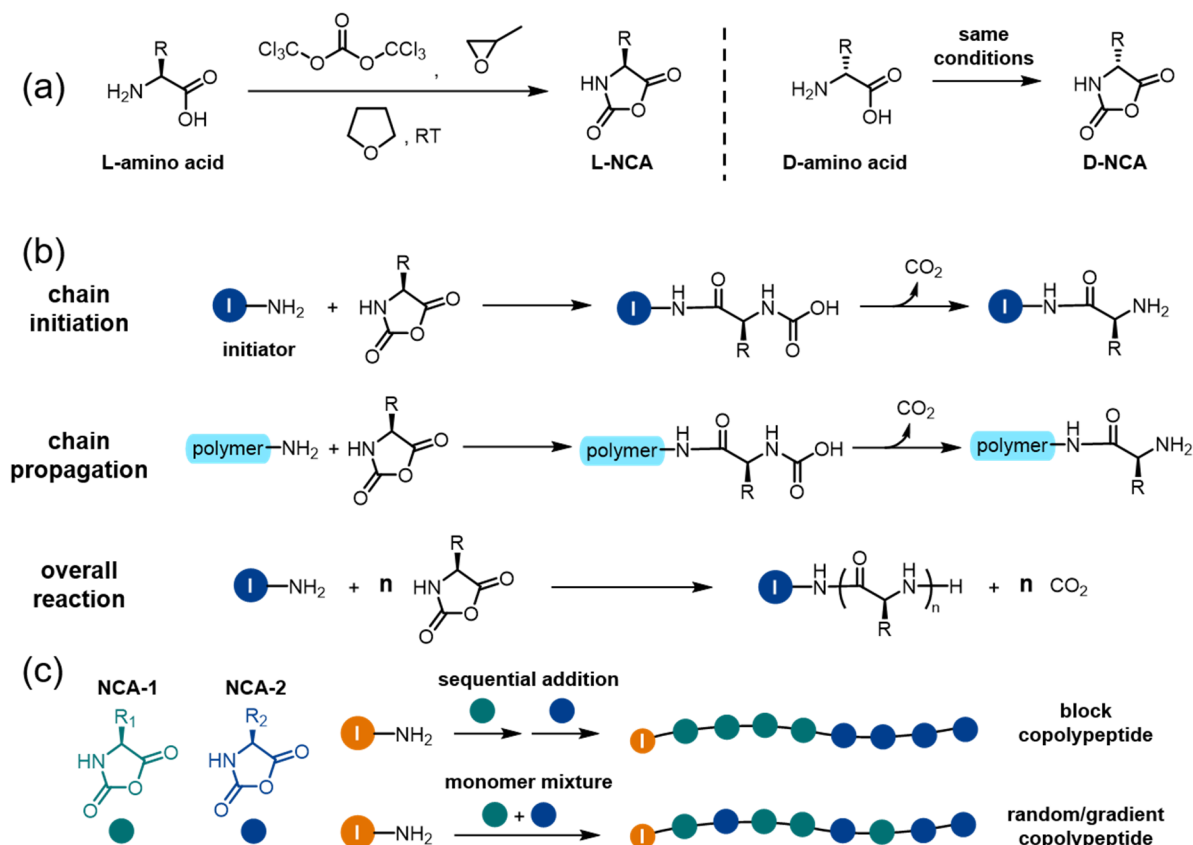


Figure 2. Chemistry of NCA ROP. (a) Representative method for preparation of NCA monomers. (b) Mechanism for primary amine-initiated ROP of NCAs. (c) The synthesis of block and random/gradient copolypeptides.

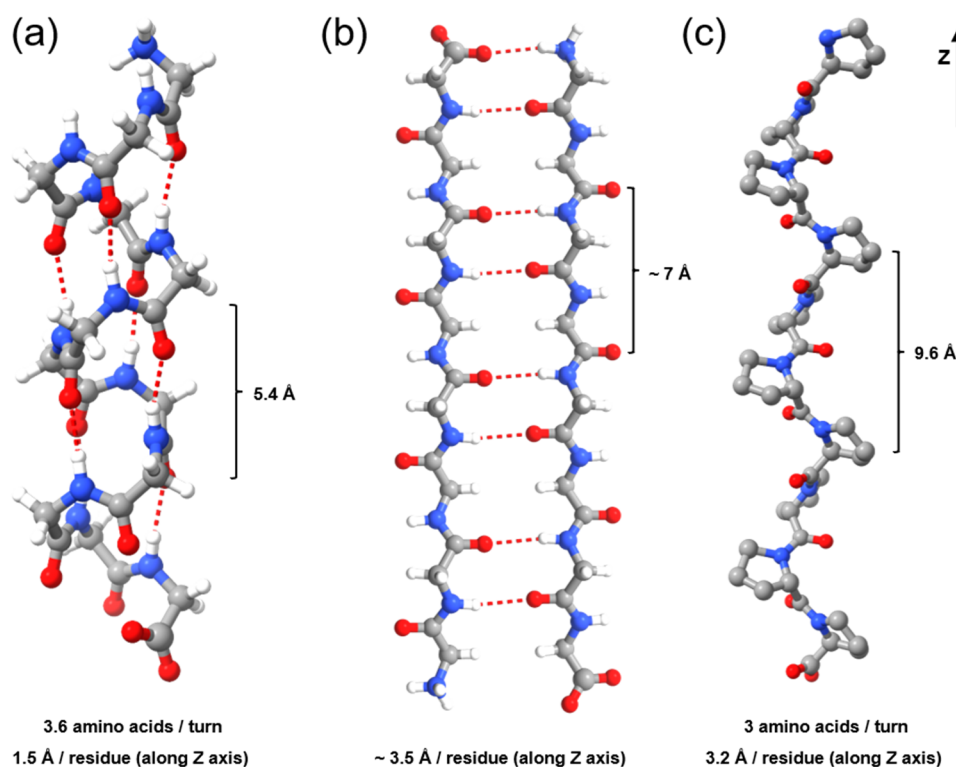


Figure 3. Representative secondary structures of polypeptides. (a) α -Helix. (b) β -Sheet. (c) Polyproline type-II helix. Carbon, hydrogen, oxygen, nitrogen atoms are in gray, white, red, and blue colors, respectively. For (a) and (b), oligomers of glycine are used for simplicity. Hydrogen bonds are represented by red dotted lines. For (c), hydrogen atoms are omitted for simplicity.

β -Sheet-forming polypeptides represent another important class of chiral structural motifs (Figure 3b). Unlike α -helices, which are mainly stabilized by intrachain hydrogen bonding, β -sheet structures are often stabilized by strong interchain hydrogen bonding and can promote the formation of fibrils, ribbons, lamellae, and other anisotropic assemblies [33,43,44]. In these systems, chirality is expressed not only through the configuration of individual amino acid residues but also through the twist, lateral packing, and long-range organization of β -sheet-rich domains [13].

Importantly, polypeptide secondary structures are not static after formation; they can undergo reversible and stimulus-responsive transitions governed by molecular design and external conditions. Depending on the processing method, the same polypeptide may form materials with different secondary structures, as conformational transitions can be kinetically hindered and metastable states may be preserved [40]. Charged polypeptides such as poly(L-lysine) and poly(L-glutamic acid) can undergo pH-dependent coil–helix transitions, while solvent polarity, ionic strength, temperature, and counterions further regulate hydrogen bonding, electrostatic interactions, and interchain association [39,42,45]. In block copolypeptides, secondary structures are coupled with amphiphilicity and phase separation; for example, a helix-forming block can act as a rigid rod, whereas a hydrophilic or coil-like block can form a flexible corona, enabling rod–coil self-assembly [46].

3. Hierarchical Chiral Assembly of Polypeptides

3.1. Solution Assemblies

Solution self-assembly of polypeptides and polypeptide-containing block copolymers often follows principles similar to conventional amphiphilic block copolymers. In selective solvents, the morphology is mainly governed by the balance between core-forming and corona-forming blocks, solvent quality, ionic strength, temperature, and the interfacial curvature of the aggregate [47]. Reviews on polypeptide-based block copolymer amphiphiles summarized that typical solution morphologies include spherical micelles, cylindrical micelles, and vesicles, with the curvature of the core–corona interface largely determined by block volume fractions and environmental conditions [46,48].

Representative experimental systems include polypeptide-based diblock copolymers that form well-defined micelles or vesicles after direct dissolution in water or organic solvents [49–52]. Notably, in these solution assemblies, the strong tendency of polypeptides to form secondary structures still shows significant effects on the final morphology, which distinguishes polypeptides from random coil polymers. In this regard, a landmark example was reported in 2004, which developed diblock copolypeptide vesicles through conformation-specific assembly (Figure 4a) [51]. The copolypeptides, named $K^p_xL_y$, contain a longer block of hydrophilic side chain-modified poly(L-lysine) and a shorter block of hydrophobic poly(L-leucine). As both blocks favor α -helical conformation, the copolypeptides prefer alignment of helical axes, giving well defined micrometer-scale vesicles with tunable sizes. In contrast, when racemic monomers were used to disrupt the ordered helical conformations, no vesicle was observed.

Recent polymerization-induced self-assembly (PISA) approaches further couple NCA chain growth with self-assembly. For example, the research groups of Du and Bonduelle/Lecommandoux independently reported the ring-opening polymerization-induced self-assembly of NCA monomers, often referred to as ROPISA or NCA-PISA, yielding biodegradable polypeptide vesicles or well-dispersed nanoparticles (Figure 4b,c) [53–56]. Poly(L-proline)-stabilized polypeptide nanostructures have also been prepared by consecutive NCA polymerization through a ROPISA process, producing rod-like, worm-like, or vesicular morphologies [57]. These examples establish solution self-assembly as a versatile route to polypeptide nanoobjects, although in many cases the observed micelles or vesicles mainly reflect amphiphilic packing rather than a direct morphological expression of chirality.

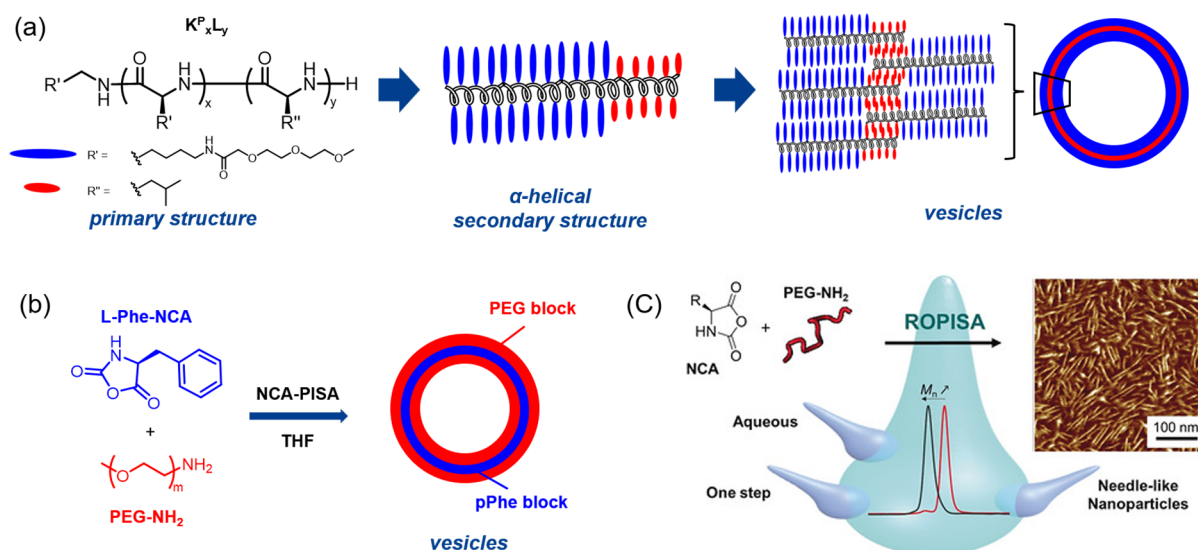


Figure 4. Solution assemblies of polypeptides. (a) Schematic showing the formation of polypeptide vesicles by conformation-specific assembly. (b) Schematic overview of NCA-PISA system developed by Du et al. using L-phenylalanine NCA as the monomer and polyethylene glycol amine (PEG-NH₂) as the initiator. (c) Schematic of ROPISA developed by Bonduelle/Lecommandoux research group. Reproduced with permission [55]. Copyright 2020, Wiley-VCH.

3.2. Discrete Chiral Nano- and Microstructures

In addition to conventional micelles and vesicles, NCA-derived polypeptides can form discrete nano- and microstructures with pronounced anisotropy, curvature, or chiral shape expression [32]. These structures are often generated in solution or at interfaces, but they are different from ordinary amphiphilic aggregates because their morphologies include super-helices, spirals, fibers, rings, and toroids rather than simple core–corona objects.

Early examples were reported in 2009 using a binary system containing amphiphilic polypeptide block copolymers (PBLG-*b*-PEG) and polypeptide homopolymers (PBLG). Super-helical rods and rings were observed when the polymer solution in a mixed solvent of THF-DMF was precipitated by water, with the polypeptide chains forming the core and PEG chains forming the shell (Figure 5a) [58]. Mechanistic study suggested that PBLG-*b*-PEG and PBLG tended to co-assemble into rod-like structures in THF-DMF as a result of tendency of PBLG to adopt a liquid crystal alignment. When water was added, interfacial tension of the surface of the hydrophobic PBLG rod core increased, causing the PBLG chains to shrink and twist to minimize the total free energy. This work demonstrated that multicomponent polypeptide systems can generate helical supramolecular objects through co-assembly, rather than only spherical or vesicular aggregates. A later study extended this strategy by combining experiments with computer simulations. Through simulation-assisted self-assembly of polypeptide-based block copolymers and homopolymers, hierarchical nanostructures with designed morphologies were developed, which could be tuned by adjusting parameters such as temperature, block rigidity, and component molar ratio [59,60].

A different class of discrete chiral structures was reported in 2018, which described the self-assembly of α -helical polypeptides into microscopic and enantiomorphic spirals by direct emulsification (Figure 5b) [61]. The final objects were micrometer-scale spiral particles with clear handedness, providing a direct morphological expression of chiral α -helical polypeptide assembly. A fiber-bundling-mediated mechanism was proposed for the transfer of helicity and chirality from α -helical chains to higher hierarchical levels. The α -helical polypeptides first assemble into fibers, which then bundle within a confined spherical geometry to generate micrometer-sized spiral particles, as supported by SEM analysis. Rather than treating the polypeptide simply as an amphiphilic block, this work highlighted the ability of α -helical chains to organize hierarchically into visible chiral shapes.

Recent studies have further connected discrete chiral morphology with the process of polymerization. A fast catalyst-free synthesis of stereoselective polypeptides was achieved through hierarchical chiral assembly in water (Figure 5c) [62]. In this system, ϵ -benzyloxycarbonyl-L/D-lysine NCAs underwent ultrasonication-assisted ROPISA initiated by PEG-NH₂ in an aqueous medium. The polymerization of L- and D-enantiomers produced predominantly right- and left-handed superhelical assemblies, respectively, in a one-pot process. Racemic monomers could also give stereoselective polypeptide segments through assembly-driven polymerization. This example differs from post-polymerization self-assembly because chain growth and hierarchical chiral assembly are coupled during polymer formation.

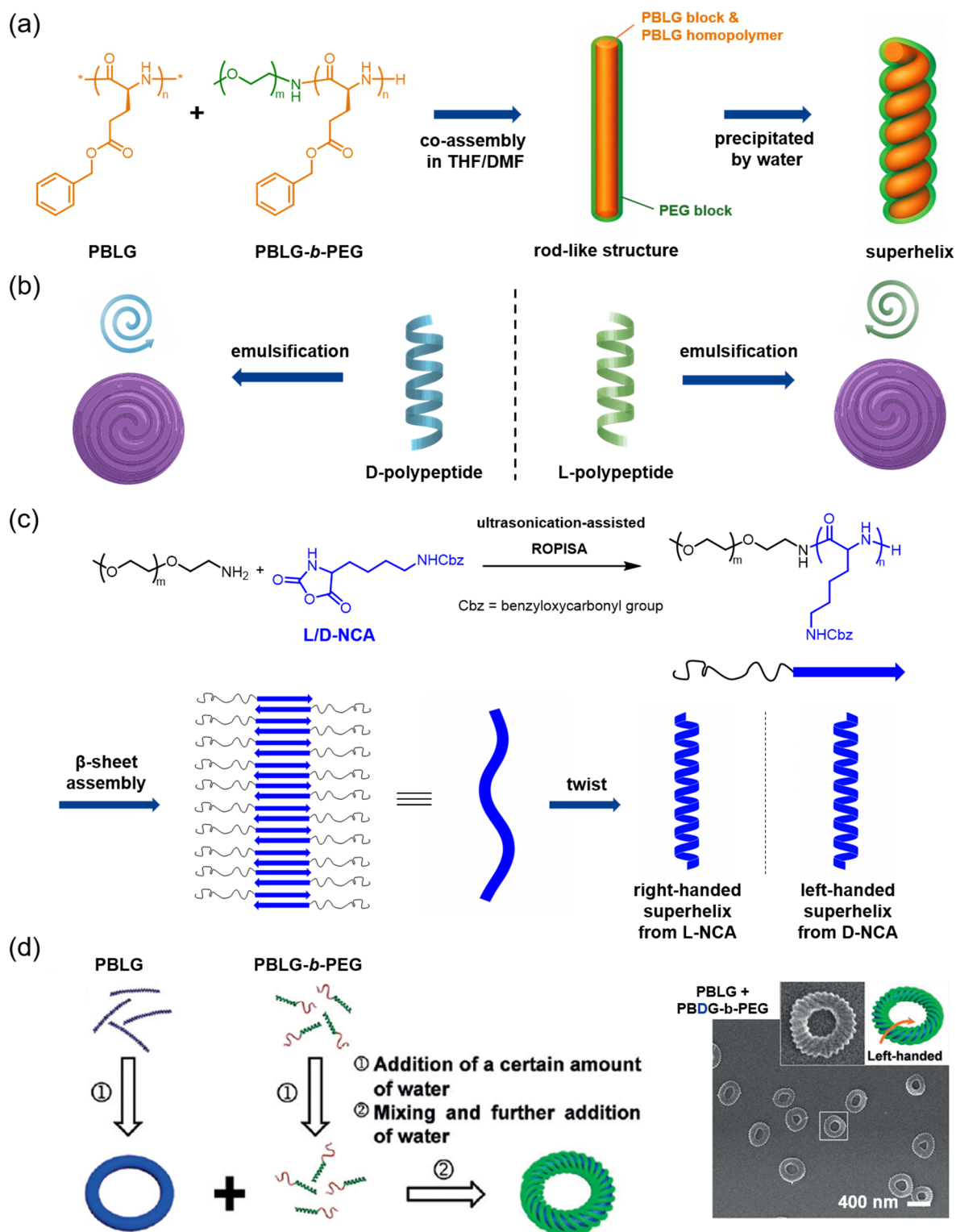


Figure 5. Discrete chiral nano-/microstructures of NCA-derived polypeptides. (a) Co-assembly of PBLG and PBLG-*b*-PEG into superhelices. (b) Fiber bundling into enantiomeric spirals. (c) Polymerization-coupled superhelical assembly. (d) Toroids formed by a two-step self-assembly of PBLG and PBL(D)G-*b*-PEG. Reproduced with permission [17]. Copyright 2020, Wiley-VCH.

Toroidal nanostructures represent another distinctive class of chiral morphology in polypeptide hierarchical assembly. An early mechanistic example described toroid formation through a supramolecular “cyclization reaction” of rodlike micelles, showing how one-dimensional polypeptide-containing micellar precursors can bend and close into ring-shaped objects [63]. Helical toroids were later reported from a two-step self-assembly of the binary system of PBLG and PBLG-*b*-PEG, further demonstrating that co-assembly can transform rodlike packing into closed, twisted, and helically organized toroidal structures (Figure 5d) [17]. These works suggest that toroids

are not merely geometric rings; their formation involves anisotropic packing and curvature of chiral polypeptide segments, providing a pathway for amplifying molecular and conformational chirality into nanoscale morphology. Subsequent studies expanded this family to fluorescent homopolypeptide toroids [64], homochiral “8”-shaped nanotoroids [19], triangular nanotoroids [15], substrate-induced nanotoroids [14], and hierarchical helical toroids obtained through one-pot controllable assembly [16].

Together, these studies show that homopolypeptides and block copolypeptides can access discrete chiral nano- and microstructures beyond conventional amphiphilic packing. Super-helices, microscopic spirals, nanofibers, nanotoroids all illustrate how polypeptide secondary structure, rod-like packing, or multicomponent co-assembly can generate anisotropic and curved morphologies. Although not every report fully resolves the mechanism of chirality transfer, these discrete structures provide an important morphological bridge between molecular chirality and material-level chiroptical responses, which will be discussed in the next section.

3.3. Liquid-Crystalline and Bulk Assemblies

At higher concentrations, in the bulk state, or under film-forming conditions, polypeptide assembly can extend from discrete nanoobjects to continuous ordered materials. Classical α -helical polypeptides such as poly(γ -benzyl-L-glutamate) (PBLG) are known to behave as rigid-rod-like macromolecules with macrodipoles rather than flexible polymer coils. Above certain concentrations, these rod-like chains can align with each other and form liquid-crystalline phases, including nematic and cholesteric phases (Figure 6a) [21–24,65–69]. The ability to form liquid crystal phase, again, emphasizes the importance of secondary structures of polypeptides for the construction of long-range ordered materials. As a processing-related example, PBLG nanofibers were prepared by electrospinning from isotropic and biphasic liquid-crystalline solutions, showing that liquid-crystalline order in α -helical polypeptides can be further transferred into solid anisotropic fibers [70].

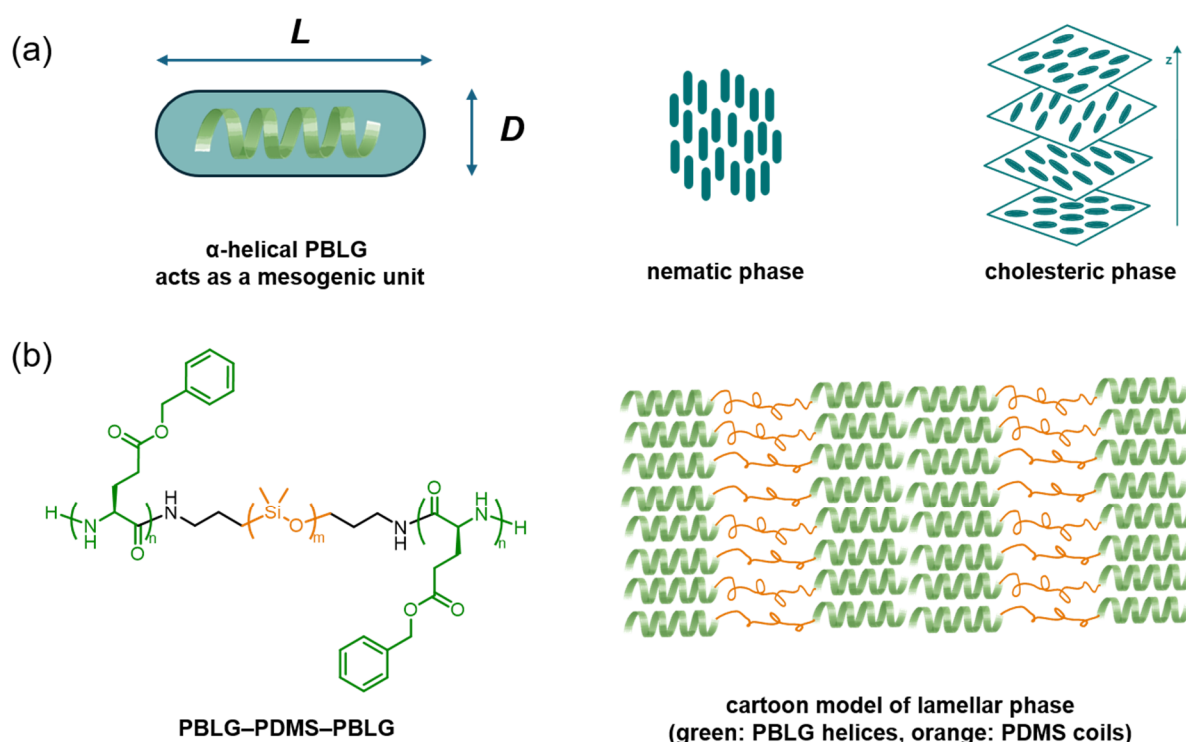


Figure 6. Liquid-crystalline and bulk assemblies of NCA-derived polypeptides. (a) α -Helical PBLG chains behave as chiral rigid rods to form liquid crystal phases. (b) Bulk assembly of PBLG-PDMS-PBLG.

This liquid-crystalline tendency also strongly affects the self-assembly of polypeptide-containing block copolymers. In ordinary flexible block copolymers, the final morphology is mainly controlled by block incompatibility and volume fraction [71]. In α -helical polypeptide-based block copolymers, however, the helical block introduces an additional factor: rod-like packing. Utilizing this property, a lot of rod-coil and rod-rod block copolymer assembly systems has been designed and investigated [72–75]. PBLG-PDMS-PBLG triblock copolymers provide a representative example: these materials combine two rigid PBLG blocks with a soft polydimethylsiloxane (PDMS) middle block, and their nano-organization depends strongly on the length and

conformation of the PBLG segments. PBLG chains with up to 23 repeating units adopt β -sheet while longer ones favor α -helical conformations, which in turn affects the supramolecular structure in the condensed state, leading to hexagonal and lamellar phase, respectively (Figure 6b) [76,77]. When the temperature changes, the block copolymers show reversible transitions relevant to the thermotropic liquid crystal behavior. These suggest that block copolypeptide assembly should be understood as a balance between two effects: the usual phase separation of block copolymers and the intrinsic ordering tendency of α -helical polypeptides.

Taken together, the hierarchical assembly of NCA-derived polypeptides spans from solution nanoobjects to discrete chiral nano-/microstructures and liquid-crystalline or bulk ordered phases. In these systems, secondary structures are not passive conformations; they influence chain stiffness, packing directionality, interchain association, and long-range ordering. While conventional amphiphilic packing often dominates simple micelles and vesicles, more complex morphologies such as spirals, helical toroids, nanotoroids, liquid-crystalline phases, and ordered block copolymer domains more clearly reflect the role of polypeptide conformation and chirality. These hierarchical structures provide the physical basis for chiroptical behavior, because optical activity depends not only on molecular stereochemistry but also on how chains, domains, and chromophores are arranged across length scales. The following section therefore discusses how these assembled polypeptide architectures are translated into chiroptical properties.

4. Chiroptical Properties of Polypeptide Materials

4.1. Circular Dichroism and Vibrational Circular Dichroism

Circular dichroism (CD) is the most basic chiroptical signal of polypeptides. In dilute solution, CD is commonly used to identify secondary structures such as α -helices, β -sheets, and random coils [78]. Representative CD curves are shown in Figure 7 [8]. However, CD spectra of polypeptide materials should not always be interpreted only as single-chain conformational signals. Once polypeptide chains aggregate, align, or form liquid-crystalline phases, the CD response can also be influenced by interchain packing and mesoscale order. For example, in lyotropic cholesteric polyglutamate solutions, Tsuchihashi and co-workers showed that CD signals at around 800 nm can arise from selective reflection of circularly polarized light by the cholesteric pitch [79].

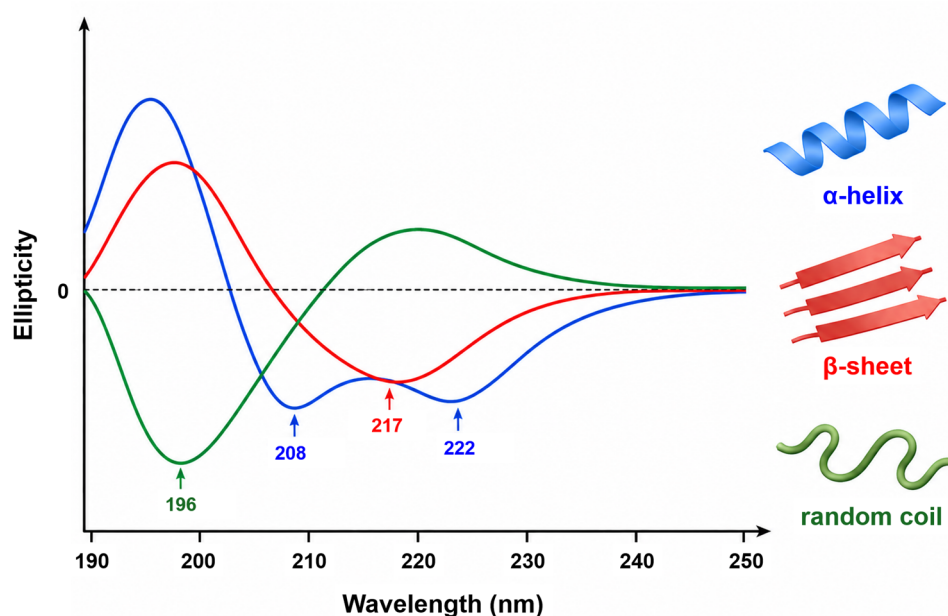


Figure 7. Representative CD responses of different conformations of polypeptides.

Vibrational circular dichroism (VCD) provides complementary chiroptical information by measuring the differential absorption of left- and right-circularly polarized infrared light. While electronic CD probes backbone and side-chain electronic transitions in the UV region, VCD is sensitive to vibrational modes such as the amide I and amide II bands, making it a useful tool for distinguishing α -helices, β -sheets, and disordered conformations in the infrared region [80]. For NCA-derived polypeptides, VCD has been used to study how solvent composition, temperature, and aggregation state affect secondary structure, as demonstrated by works on PBLG, poly(L-glutamic acid), and poly(L-lysine) [44,81,82].

4.2. Induced Circular Dichroism through Chromophore Organization

Achiral molecules can display induced circular dichroism (ICD) within their absorption bands when interacting with chiral inducing molecules [83]. ICD signals, in turn, provide evidence for interaction or chiral transfer between interested chiral-achiral pairs. For polypeptide systems, far-UV CD mainly reflects the peptide secondary structure. By contrast, when a CD signal appears in the absorption region of a chromophore, it indicates that the chromophore has been placed in a chiral electronic environment or arranged in a chiral manner. Therefore, ICD is particularly useful for evaluating whether the chirality of a polypeptide scaffold has been transferred to side-chain, terminal, or noncovalently incorporated chromophores (Table 1).

For chromophores attached to the side chains of polypeptides, the α -helical backbone can transfer its chirality to the pendant groups by providing a stereoregular environment. For example, in 1975, achiral side-chain chromophores in helical polypeptides were shown to exhibit extrinsic chiroptical activities in dilute solutions or liquid crystalline phases. Poly- β -benzyl-L-aspartate, poly- β -p-nitrobenzyl-L-aspartate, and poly- γ -p-nitrobenzyl-L-glutamate gave ICD signals in the absorption regions of the benzyl or p-nitrobenzyl chromophores, which resulted from the loss of rotational freedom of the chromophores after connecting to the helical backbone [84]. Similarly, helically arranged azobenzene chromophores with distinct ICD signals were prepared by attaching azobenzene to the side chain of NCA monomers and then polymerization [85–87]. Other side-chain chromophores studied include naphthalene, anthracene, and pyrene [88–93].

Terminal chromophore functionalization provides another useful approach. Compared with side-chain modification, end-group labeling introduces fewer chromophores and usually perturbs the polypeptide secondary structure less strongly. In 1980, the ICD signals of α -helical PBLG with covalently attached terminal chromophores were utilized to probe the local conformation of peptide units near the chain ends. The terminal chromophores were shown to sense both local helical conformation and interchain assembly, giving responses in ICD signals when external stimuli were applied [94].

A third route is to place achiral chromophores into chiral polypeptide assemblies through noncovalent interactions. In this case, the chromophore does not need to be chemically attached to the polymer. Instead, it can be organized by confinement within a chiral liquid-crystalline or supramolecular environment [95]. Sisido and co-workers provided several important examples of this strategy. Poly(α -amino acid)s bearing amphiphilic side chains were shown to bind hydrophobic guests and induce CD in the guest absorption region [96], while dye-doped PBLG gels enabled reversible cholesteric ordering of guest molecules [97,98]. In cholesteric polypeptide films doped with azobenzene derivatives, induced CD arose from the organization of the achiral dye within the chiral PBLG matrix [99]. Related liquid-crystalline gels and films further showed that dye orientation could be controlled by light, indicating that noncovalent chromophore loading can lead to dynamic and stimuli-responsive chiroptical behavior [100]. These studies establish chiral polypeptide assemblies as host matrices capable of transferring chirality to guest chromophores without covalent modification.

Table 1. Strategies for ICD in polypeptide–chromophore systems.

Strategy	Chromophore Organization	Representative Examples	Origin of ICD	Design Value
Side-chain attachment	Chromophores are covalently installed along the polypeptide side chains	Benzyl-, p-nitrobenzyl-, azobenzene-, naphthalene-, and pyrene-containing polypeptides	The α -helical backbone restricts chromophore motion and arranges pendant groups in a stereoregular environment	Provides high chromophore density and can generate strong chromophore-region CD, but may perturb secondary structure
Terminal functionalization	Chromophores are attached to one or both chain ends	Terminal chromophore-functionalized PBLG	Chain-end chromophores sense local helical conformation and interchain association	Offers a clean probe of local chirality with minimal modification of the backbone
Noncovalent guest incorporation	Achiral dyes are embedded in polypeptide assemblies, gels, or liquid-crystalline phases	Hydrophobic guests in amphiphilic poly(α -amino acid)s, dye-doped PBLG gels, azobenzene-doped cholesteric films	Chiral supramolecular or liquid-crystalline environments orient guest chromophores and induce CD in their absorption bands	Enables modular, reversible, and stimuli-responsive chiroptical materials without covalent dye attachment

From a materials-design viewpoint, these examples suggest three levels of chirality transfer. At the molecular level, the local secondary structure of the polypeptide controls the conformation and electronic environment of covalently attached chromophores. At the supramolecular level, interchain packing and ordered domains can

organize multiple chromophores into chiral arrangements. At the mesoscopic level, liquid-crystalline or other hierarchical assemblies can provide chiral fields that induce optical activity in guest dyes. The ICD signal therefore serves as a bridge between structural chirality and optical function. For the development of chiroptical polypeptide materials, ICD is also an important design criterion, which is especially relevant for emissive systems as chromophore-level chirality is often a prerequisite for circularly polarized luminescence.

4.3. Circularly Polarized Luminescence from Emissive Polypeptide Assemblies

Circularly polarized luminescence (CPL) represents a higher level of chiroptical function than CD or ICD because it requires the emissive excited state to possess chiral asymmetry. For systems without significant interchromophoric coupling, CPL generally arises when the individual emissive chromophore is intrinsically chiral or located in a chiral local environment. For systems involving coupled chromophores or aggregate/excimer emission, CPL requires a chiral spatial arrangement of the emissive units, which gives rise to chiral excitonic or aggregate excited states [101,102]. For polypeptide-based materials, this is challenging but attractive. The polypeptide backbone provides intrinsic chirality and secondary structures, but most polypeptides themselves are not strong luminophores. Therefore, emissive polypeptide CPL systems usually rely on one of three strategies: introducing luminescent side chains or terminal groups, organizing emissive chromophores in a chiral polypeptide assembly, or using liquid-crystalline or aggregated structures to amplify the dissymmetry of emission.

An early representative example is the circularly polarized fluorescence (CPF) of polypeptides with side-chain aromatic rings. Developed by Sisido and coworkers in 1980s, aromatic polypeptides, such as poly(L- and 2-naphthylalanine) (poly(1- and 2-NapAla), poly(anthrylmethyl L-aspartate) (poly[Asp(OCH₂-9-Ant)]), and poly(L-1-pyrenylalanine) (poly(L-1-PyrAla), showed different levels of CPF signals in their solution states [91,93,103]. With the highest luminescent dissymmetry factor (g_{lum}) values recorded at the level of 10^{-3} , these early studies undoubtedly supported the chirality transfer from backbone amino acids to the excited states of side-chain fluorophores.

In 2020, luminescent liquid-crystal polyglutamates bearing cyanostilbene-based mesogenic emissive side chains (named as PGAC-m) showed a more recent example of CPL-active polypeptide materials (Figure 8a) [25]. In PGACs, the polypeptide backbone supplied the chiral scaffold, while the side-chain liquid-crystalline units acted as the emissive components with aggregation-induced emission enhancement (AIEE) characteristics. The authors showed that the PGACs can form a lamellar-ordered chiral smectic C phase (Figure 8b) and the properties could be tuned by manipulating the spacer length between the backbone and cyanostilbene. In glassy liquid crystal film state, the samples exhibited striking ICD signals at around 350 nm, indicating successful chiral transfer from polypeptide backbone to cyanostilbene. The system finally showed peaked CPL signals at 458 nm, as well as a maximum solid fluorescence quantum yield and the g_{lum} of PGAC-m of 34.1% and 4.5×10^{-2} , respectively. This work therefore provides a useful example of how side-chain engineering and liquid-crystalline ordering can be combined in polypeptides to produce efficient CPL-active materials.

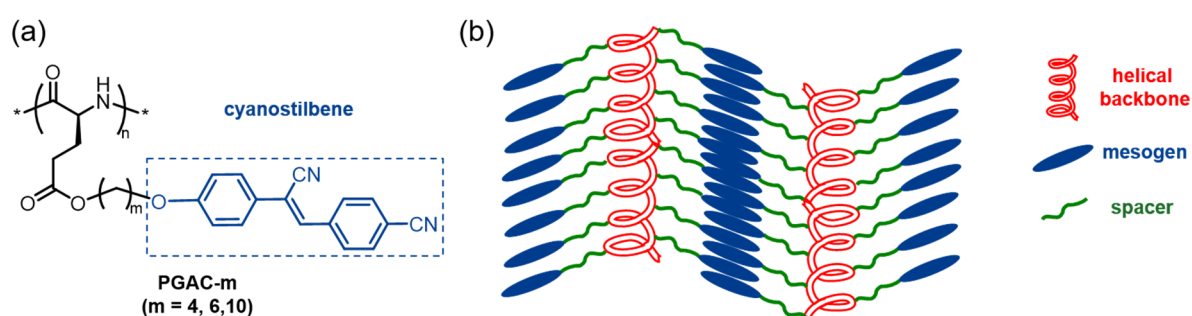


Figure 8. Luminescent liquid-crystal polyglutamates bearing emissive side chains. (a) Chemical structure of PGAC-m. (b) Proposed molecular stacking of PGAC-m.

In 2023, aqueous CPL of polypeptide materials was achieved by the chiral self-assembly of end group-functionalized α -helical PBLG (Figure 9) [104]. By attaching an aggregation induced emission (AIE) luminogen, named TNB, at the terminal group of linear PBLG homopolypeptides (the conjugate is named as TN-PBLG), the chirality of PBLG chains efficiently transferred into an emissive chiral aggregate state through hierarchical assembly (Figure 9). Specifically, the TN-PBLG was first dissolved in good solvents including tetrahydrofuran (THF) and dioxane (DOA), after which water as a poor solvent was added to give the nanotoroid or nanorod-dispersed aqueous solutions, respectively. CD measurements revealed distinct CD signals of the nanotoroid assemblies in the range of 240–480 nm, supporting the chiral arrangement of pendant phenyl groups. Typical mirror-image CPL profiles were observed for L-

and D-type nanotoroid samples with g_{lum} values at 5×10^{-4} . By contrast, the DOA-resulted nanorod control group gave no CPL response, indicating a morphology dependence. Further hierarchical co-assembly of TN-PBLG and the free TNB luminogen gave nanotoroids with much higher g_{lum} of 7×10^{-3} .

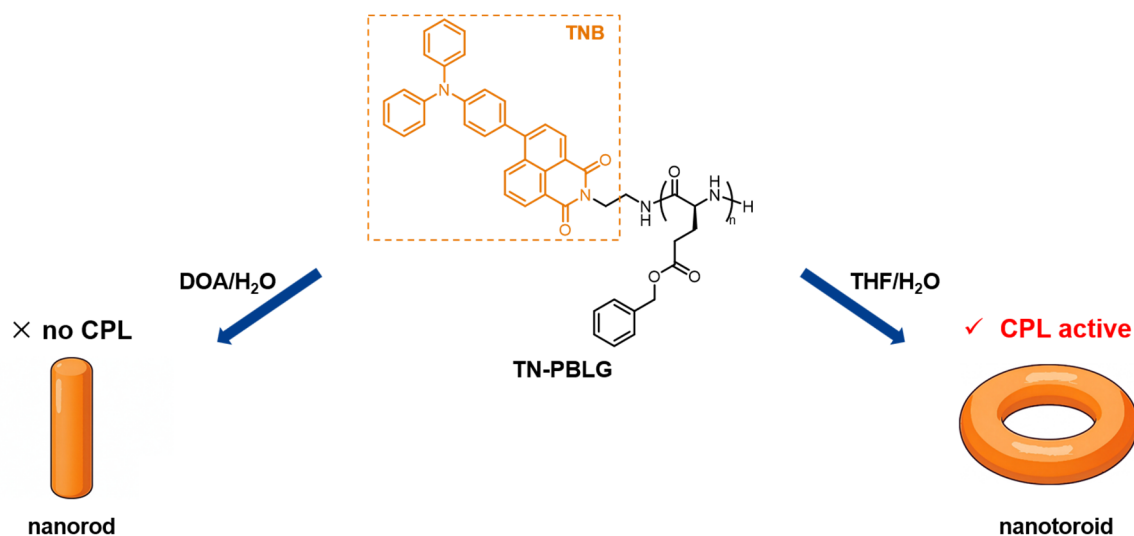


Figure 9. Aqueous CPL from α -helical homopolypeptide nanotoroids.

The role of α -helical structure was further clarified in a follow-up research by correlating the CPL behavior with parameters such as degree of polymerization, self-assembly temperature, and α -helix stability [105]. By directly linking polypeptide secondary structure to CPL performance, it is indicated that the α -helix is not only a structural motif observed by CD but also actively regulates how chirality is transferred to the emissive aggregate. Longer or more stable helical segments can strengthen the chiral environment, while changes in assembly conditions can alter the final CPL response. This work therefore provides a useful framework for designing future homopolypeptide CPL systems: control over chain length and helical stability should be considered as important as the choice of luminophore.

Another system of aqueously dispersed homopolypeptide nanotoroids with CPL properties was from the non-covalent co-assembly of helical polypeptides (PBLGs) with achiral triphenylamine (TPA) derivatives (Figure 10) [18]. This work is different from the above studies as the chiral transfer between luminogens all relies on non-covalent interactions and luminogens do not need to be pre-installed covalently at the chain end of polypeptides. This advantage allows the facile introduction of several luminogens with different structures and colors, including blue, yellow, and red. Notably, a deep-red CPL can be achieved with a record g_{lum} of 1.1×10^{-2} among aqueously polypeptide-based nanoparticles by tuning the doping content. The strong CPL from achiral luminophores, again, indicates that the nanotoroidal homopolypeptide assembly can efficiently induce chiral organization of guest chromophores. This work therefore expands homopolypeptide nanotoroids from a single emissive assembly motif to a more modular platform for color-tunable aqueous CPL.

More recently, the scope of polypeptide chiroptical emission has been extended from fluorescence to room-temperature phosphorescence (RTP). Poly(glutamic acid) aggregates with circularly polarized room-temperature phosphorescence (CP RTP) were reported with highlighted roles of poly(vinyl alcohol) (PVA) in chirality inversion and amplification (Figure 11) [106]. Specifically, poly(L-glutamic acid)s (PLGAs) with achiral phosphorescent end groups were first synthesized and assembled into vesicular architectures that showed weak CP RTP (Figure 11a). When a second polymer matrix, PVA, was added, however, the authors observed both inversion and amplification of the CP RTP signal, with the g_{lum} improved from 10^{-4} to 10^{-2} level (Figure 11b–d). Mechanism study reveals the extensive hydrogen bonding networks between polypeptide and PVA contributes to the stronger chiral transfer and inversed chiral packing pattern of the chromophores. The scope of phosphorescent end groups was finally extended to achieve multicolor afterglow from blue to red (Figure 11e). This work suggests that polypeptide CPL materials do not need to rely only on the primary polypeptide scaffold; secondary matrices and hydrogen-bonding networks may provide additional handles for tuning emission handedness and intensity.

Above research works share two common features: they all employ a polyglutamic acid-based backbone, and they all rely on organic chromophores. In principle, the chiral environment of polyglutamic acid could also induce chiral absorption and/or emission from metal complexes. In this regard, the CPL of lanthanide complexes induced by PLGA reported in 2019 showed a representative example [107]. Detailly, the europium compounds, EuCl₃ or Na₃[Eu(DPA)₃] (DPA = pyridine-2,6-dicarboxylic acid), were mixed with fibrils of PLGA in aqueous solutions

and incubated, leading to strong CPL signals at ~590 nm and g_{lum} values up to 2×10^{-2} . With higher sensitivity than VCD, the induced CPL was proposed as a new method for probing protein fibrils.

In addition to polyglutamic acid, poly(L-lysine) (PLL) represents another powerful backbone in the design of CPL-active polypeptide materials. In neutral state, PLL also favors the formation of α -helical conformation, while the side-chain free amines provide handrails for hydrogen bonding or forming ion pairs. Utilizing this property, chirality was transferred from PLL templates to disulfonic fluorescent dyes, such as NK 2571, giving large Stokes shift of 230 nm and g_{lum} of 2×10^{-3} (Figure 12a) [108]. Moreover, CPL from clusterization-triggered emission (CTE) was achieved by solid phase co-assembly of PLL and oleate ion (OL) (Figure 12b). Under mechanical pressure, PLL aligned well on the interface of self-assembled oleate bilayers, giving transparent films with ordered multilayer structures. Without the addition of external luminophores, the film generated significant CPL signals at 462 nm with the g_{lum} of 1.6×10^{-2} via the CTE mechanism [109].

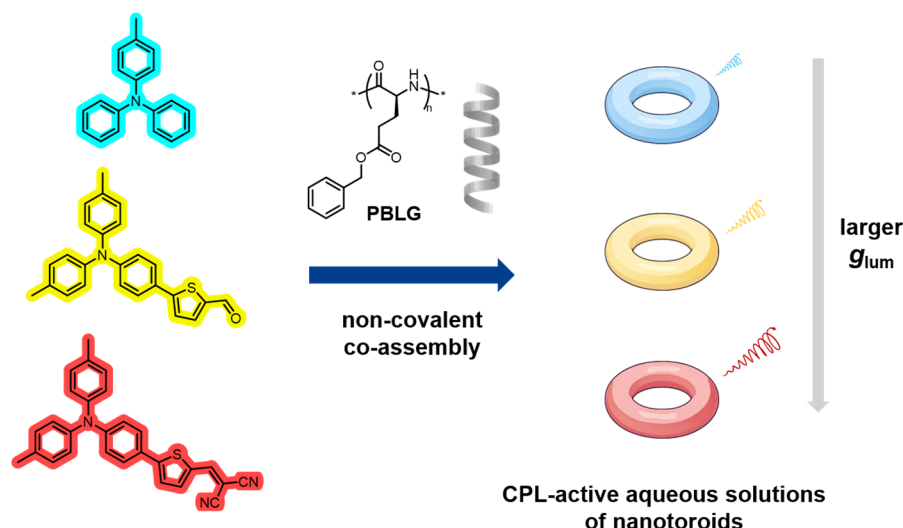


Figure 10. Noncovalent co-assembly of PBLG with achiral triphenylamine derivatives.

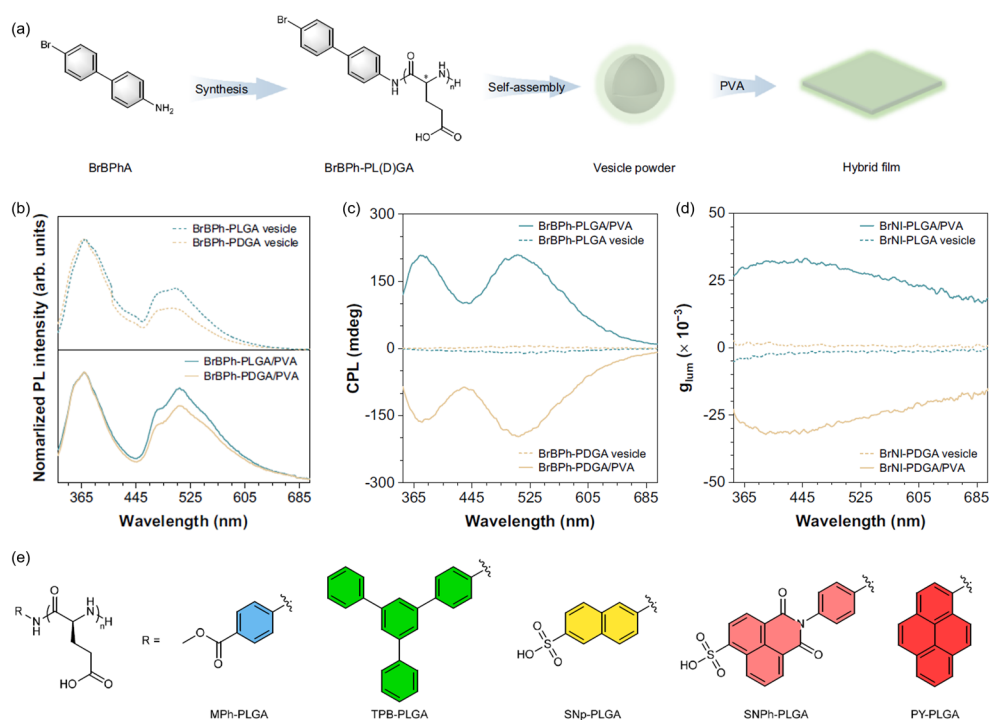


Figure 11. PVA matrix-induced chirality inversion and amplification of CPRTP. (a) Representative synthesis of 4-bromobiphenyl (BrBPh)-functionalized PLGA or PDGA and their co-assembly with PVA. (b–d) Photoluminescence (PL) spectra, CPRTP spectra, and g_{lum} curves for BrBPh-PL(D)GA samples with or without the co-assembly of PVA. (e) Scope of phosphorescent end groups studied. (a–e) Reproduced with permission [106]. Copyright 2026, Springer Nature.

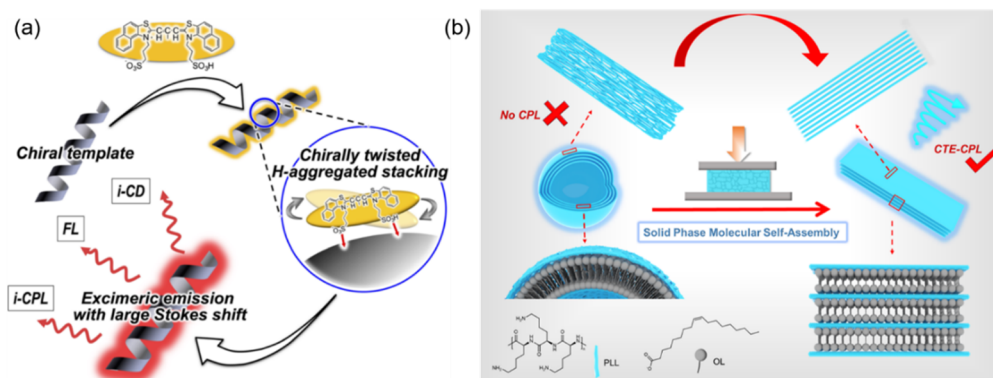


Figure 12. PLL-based CPL-active polypeptide systems. (a) Co-assembly of NK 2571 with PLL for CPL and large Stokes shift. Reproduced with permission [108]. Copyright 2023, Wiley-VCH. (b) CPL-active films formed by the co-assembly of PLL and sodium oleate. Reproduced with permission [109]. Copyright 2021, Springer Nature.

Taken together, these studies reveal several design principles in common (Table 2). First, chromophore-level chirality is essential. Whether the emissive unit is covalently attached, terminally introduced, or noncovalently co-assembled, it must experience a chiral environment that can be detected by ICD or translated into CPL. Second, α -helical secondary structure is a recurring structural origin of chirality transfer. It provides chain stiffness, stereoregularity, and a persistent chiral field. Third, hierarchical assembly is usually required to amplify the optical response. Liquid-crystalline ordering, aqueous aggregation, nanotoroid formation, and polymer-matrix confinement all help convert local chirality into an emissive chiral arrangement.

Table 2. Representative CPL-active NCA-derived polypeptide materials in recent years and their design principles.

System	Scaffold	Luminophore	Incorporation Mode	Assembly/Phase	Key CPL Feature	g_{lum}	Design Principle	Refs.
PGAC	Polyglutamate	Cyanostilbene	Side chain	Chiral smectic C liquid-crystal phase	High solid-state CPL	4.5×10^{-2} (458 nm)	Liquid-crystal organization of emissive mesogens	[25]
TN-PBLG (+TNB)	PBLG	TNB	Terminal (+co-assembly)	Nanotoroids	Aqueous CPL; morphology-dependent	7×10^{-3} (~600 nm)	Terminal AIEgen organized by PBLG nanotoroid (hierarchical co-assembly)	[104,105]
PBLG + TPA	PBLG	TPA derivatives	Noncovalent	Nanotoroids	Multicolor/deep-red CPL	up to 1×10^{-2} (multicolor)	Achiral luminophores organized by PBLG nanotoroid	[18]
PLGA + PVA	PLGA	Phosphorescent unit	Terminal	Aggregates	CP RTP; inversion/amplification; multicolor	up to 3×10^{-2} (multicolor)	Polymer matrix regulates chiral transfer	[106]
PLGA + Eu(III)	PLGA	Eu(III) complex	Coordination	Fibril assembly in aqueous solution	CPL of Lanthanide metal ion	2×10^{-2} (~590 nm)	Chirality transfer from fibril to Eu(III) by coordination	[107]
PLL + disulfonic dyes	PLL	disulfonic dyes	Noncovalent (electrostatic interaction)	Methanol solution	Large Stokes shift	2×10^{-3} (~700 nm)	Dyes organized by α -helical PLL	[108]
PLL + OL	PLL	PLL-OL	Noncovalent (electrostatic interaction)	Film	Clusterization-triggered emission	1.6×10^{-2} (462 nm)	Mechanical pressure-driven solid phase co-assembly	[109]

5. Conclusions and Outlook

NCA-derived polypeptides provide a unique polymer platform for hierarchical chiral assembly and chiroptical materials. Their value comes from the combination of synthetic programmability and biomolecule-inspired conformational order. Through NCA ROP, the stereochemistry, chain length, block sequence, topology, side-chain functionality, and terminal groups of polypeptides can be adjusted. These molecular parameters further determine secondary structures such as α -helices, β -sheets, and coil-like conformations, which serve as the first level of chiral organization. From there, polypeptides can assemble into micelles, vesicles, fibers, spirals, nanotoroids, liquid-crystalline phases, and bulk ordered structures. These hierarchical assemblies provide the structural basis for transferring molecular chirality into optical asymmetry [32].

In chiroptical materials, CD and VCD remain essential tools for probing polypeptide secondary structures, aggregation, and higher-order ordering. ICD further shows whether chirality has been transferred from the

polypeptide scaffold to side-chain, terminal, or noncovalently incorporated chromophores. CPL represents a more demanding function, because emissive chromophores must be arranged in a chiral excited-state environment. Recent examples, including liquid-crystalline polyglutamates, aqueous homopolypeptide nanotoroids, and circularly polarized room-temperature phosphorescent aggregates, demonstrate that NCA-derived polypeptides can indeed serve as programmable scaffolds for emissive chiroptical materials.

Despite these advances, the field of chiroptical NCA-derived polypeptide materials remains at an early stage. Synthetic polypeptides have a long history [33], and chromophore-functionalized, or even CPL-active polypeptides have been studied for decades [85,93]. Nevertheless, the reported systems still rely on a relatively limited set of polypeptide scaffolds, luminophores, and assembly motifs, and general structure–property relationships remain difficult to establish. A particular challenge is that the polypeptide scaffold primarily provides conformational and supramolecular chirality rather than strong emission itself. Efficient chiroptical emission therefore requires the simultaneous optimization of chirality transfer, chromophore organization, photoluminescence quantum yield, and luminescence dissymmetry, which do not necessarily improve in parallel. In addition, hierarchical polypeptide assemblies can be sensitive to concentration, solvent composition, pH, ionic strength, temperature, and processing history. Such responsiveness is attractive for sensing and adaptive materials, but it also presents challenges for long-term structural stability and reproducibility.

Further development is therefore highly desired in both chiroptical performance and material format. Current polypeptide-based CPL materials still have room for improvement in brightness, dissymmetry factor, processability, long-term stability, and batch-to-batch reproducibility. Future studies would benefit from reporting g_{lum} together with quantum yield, lifetime, morphology distribution, concentration dependence, and preparation reproducibility, thereby enabling more meaningful comparison between different material platforms. In addition, most examples are based on solution assemblies, aqueous dispersions, liquid-crystalline phases, or polymer aggregates, whereas processable films, coatings, fibers, elastomers, and device-compatible solid materials remain less developed.

The structural toolbox can be expanded beyond α -helical PBLG-derived systems. β -Sheet-forming polypeptides are comparatively underexplored for CPL materials, even though peptide and amyloid-like assemblies often form twisted ribbons, fibrils, and helical nanostructures. Extending these concepts to NCA-derived β -sheet-rich polypeptides may provide new routes to chromophore organization and CPL generation. Block copolypeptides are another promising direction, because they can couple secondary-structure chirality with nanoscale phase separation and polymer processability. Topology is also an interesting variant to study with. By designing polypeptide materials with topology beyond linear, we may benefit from the unique connectivity of cyclic, star-like, or bottlebrush-like polymers and achieve unrevealed self-assembly structures and chiroptical properties.

Importantly, the most compelling applications of NCA-derived chiroptical materials may not necessarily lie in competing directly with established inorganic, organic small-molecule, or liquid-crystalline materials in conventional optoelectronic devices. Instead, the distinctive combination of molecular chirality, chemical programmability, self-assembly, biodegradability, and potential biocompatibility may create opportunities where the material itself interacts with biological environments or disappear after completing its function. Water-dispersible CPL-active polypeptide nanoparticles, for example, could potentially provide a basis for polarization-resolved bioimaging and chiral biosensing, in which circularly polarized emission offers an additional optical dimension beyond fluorescence intensity or wavelength [110–112]. Environment-responsive changes in polypeptide conformation and assembly could further be translated into changes in CD, CPL intensity, handedness, or emission wavelength, enabling optical reporting of local chemical or biological environments [113,114].

One particularly attractive direction is the development of transient chiroptical materials. Biodegradable CPL-active nanoparticles, fibers, or coatings could potentially serve as temporary optical probes, implantable or wearable sensors, degradable optical tags, or polarization-encoded information materials that function for a defined period and subsequently undergo degradation [115]. In such applications, biocompatibility and biodegradability may distinguish polypeptide-based systems from many persistent inorganic or organic chiroptical materials, especially when direct contact with cells and tissues is necessary. At the same time, these advantages should not be assumed solely from the polypeptide backbone: the toxicity and degradation products of incorporated chromophores and other components must also be evaluated. Moreover, the degradability that is desirable for biomedical or transient applications may conflict with the long-term photochemical and mechanical stability required for displays and conventional optoelectronic devices. Application-specific control over degradation and stability will therefore be essential.

Looking forward, progress will require moving from the demonstration of chiroptical activity toward application-oriented molecular and materials design. Combining NCA polymerization with post-polymerization chromophore installation can broaden the accessible emissive structures, while noncovalent co-assembly with

achiral dyes can enable modular tuning of emission color and excited-state organization. Block copolypeptides and topological polypeptides may provide routes to robust, hierarchically ordered CPL-active materials, whereas hybrid matrices and responsive environments could allow dynamic control over handedness, intensity, lifetime, and emission wavelength. Ultimately, establishing quantitative connections among polymer sequence and topology, secondary structure, hierarchical assembly, chromophore organization, and chiroptical output will be necessary to transform NCA-derived polypeptides from model systems into functional chiroptical materials. Their strongest future opportunities may lie where this structural programmability is combined with properties that conventional chiroptical materials do not readily provide—particularly aqueous compatibility, biodegradability, and transient functionality.

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