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Chiral Recognition and Resolution Based on Helical Polymers

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Abstract Helical polymers have attracted a great deal of attention and been extensively investigated due to their various applications. One of the most important applications of helical polymers is chiral recognition and resolution of enantiomers for the reason that a pair of enantiomers is commonly with different physiological and toxicological behaviors in biological systems. Helical polymers usually present unexpected high chiral recognition ability to a variety of racemic compounds. What's more, the chiral recognition and resolution abilities of the system are dependent on the highly ordered helical structures of the helical polymers. This mini review mainly focuses on the recent progress in chiral recognition and resolution based on helical polymers. The synthetic methodology for helical polymers is firstly discussed briefly. Then recent advances of chiral recognition and resolution systems based on helical polymers, especially polyacetylenes and polyisocyanides, are described. We hope this mini review will inspire more interest in developing helical polymers and encourage further advances in chiral-related disciplines.

Keywords Helical polymer; Chiral recognition; Chiral resolution; Polyacetylenes; Polyisocyanides

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1. INRTODUCTION

Helix is not only one of the essential and important structural moieties in biological macromolecules, but also a universal object in nature from microscope to macroscope.[1–3] Inspired by nature, scientists, especially chemists, have done enormous efforts to design and prepare artificial helical materials, including molecules,[4,5] oligomers,[6,7] polymers,[8,9] as well as supramolecular aggregates,[10,11] *etc*. Among them, helical polymers have attracted a great deal of attention due to their theoretical and practical significance.[12–15] Lots of helical polymers have been developed, such as vinyl polymers bearing large pendent groups,[16] polyacetylenes,[17] polyisocyanides,[18] polyamides,[19] polyguanidines,[20] *etc*. as shown in Fig. 1. These helical polymers present some interesting and distinctive properties. For example, helical polymer can be obtained through copolymerization of an achiral monomer with a small amount of optically active monomer, which is known as "chiral amplification" effect. Meanwhile, since the helical conformation is chiral in nature, *i.e.* the right helices are with mirroring relationship to the left ones, helical polymers are inherently chiral. What's more, benefitting from the development of synthetic chemistry, novel helical polymers with excellent performance can be elaborately prepared and investigated, with more still under rapid development currently.

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One of the most distinguished applications of helical polymers is the chiral recognition and resolution of enantiomers.[21–24] Since a pair of enantiomers is usually with different physiological and toxicological behaviors in biological systems, the development of chiral drugs with a single enantiomer is of great significance on people's life. This means that the selective preparation and chiral resolution of racemates are essential in this field. As for the chiral recognition and resolution of racemates, helical polymers are commonly used as chiral stationary phase (CSP) of high-performance liquid chromatography (HPLC), as well as to fabricate membrane.[25–27] Moreover, the chiral recognition and resolution abilities of the system depend on the highly ordered helical structures of the helical polymers.

Here, the methodology for the preparation of helical polymers will be firstly introduced. Then, the significant research progress (from 2010 to 2021) of the synthetic helical polymers, such as polyacetylenes, polyisocyanides, *etc*. in the fields of chiral recognition and resolution will be described.

2. METHODOLOGY FOR THE SYNTHESIS OF HELICAL POLYMERS

In general, the most forthright and easy method to synthesize chiral helical polymer is through the polymerization of chiral monomers directly. However, chiral monomers are usually expensive and their kinds are limited. Therefore, the helix-sense-selective polymerization (HSSP) of achiral monomers with the help of chiral initiators, catalysts, or additives to afford chiral helical polymers becomes important. In the meantime, chiral

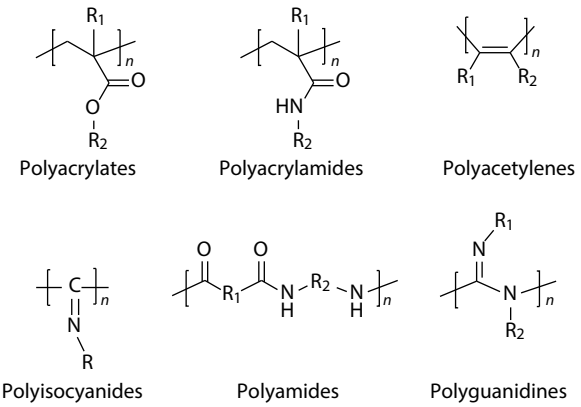

Fig. 1 Chemical structures of synthetic helical polymers.

induction of racemic helical polymers, or copolymerization of achiral monomer with a small amount of chiral monomers can afford chiral helical polymers, too. This part will mainly introduce HSSP of achiral monomers (Section 2.1) and chiral induction of racemic helical polymers (Section 2.2).

2.1 Synthesis of Helical Polymers by HSSP of Achiral Monomers

Owing to the advantages of using achiral monomers to afford chiral helical polymers with desired optical activity, HSSP strategies attract a great deal of attention and have been extensively employed recently. The HSSPs are mainly conducted with the help of chiral initiators, chiral catalysts, chiral additives, and so forth.

2.1.1 HSSPs with chiral catalysts

HSSPs of achiral monomers using chiral catalytic system are an easy and effective method for preparing chiral helical polymers.[28–35] Generally, a chiral catalytic system contains an achiral transition metal complex and chiral molecular ligands, and they together can offer a chiral active species. Helical polymers with optical activity will be obtained *via* HSSPs of achiral monomers in the presence of chiral active species. Teraguchi *et al.* explored the HSSP of achiral phenylacetylene monomers bearing two *N*-alkylamide groups using the chiral catalyst of $[Rh(nbd)Cl]_2$-(*R*)-(+)-1-phenylethylamine (nbd = norbornadiene) as shown in Fig. 2.[28] The resulted polymers presented Cotton signals at the absorption regions of the polymeric backbone, indicating that the excess of one-handed helical structure was induced. What's more, benefiting from intramolecular hydrogen bonds, the induced helical conformations could be maintained for a long time in the solution of toluene at room temperature. By using $[Rh(nbd)Cl]_2$ and chiral amine as the binary catalyst, Aoki's group achieved HSSP of achiral phenylacetylene monomer with bulky *tert*-butyl substituents.[29] The degree of polymerization was controlled, and the obtained optically active helical polymer could act as the macroinitiator for the polymerization of the second monomer to afford a block copolymer.

Optically active helical polyisocyanides can also be obtained *via* HSSPs using chiral catalysts.[30,31] Schraff *et al.* investigated the polymerization of fulvenyl-functionalized isocyanide monomers using nickel(II)-aryl complexes with chiral chelating phosphine ligands or a chiral aryl-group as the catalyst.[30] The two catalysts both presented HSSP of the isocyanide monomers to afford optically active polyisocyanides in poor solvent, which prevented the racemization of polyisocyanides in solution.

2.1.2 HSSPs with chiral additive

In addition to chiral catalysts, chiral additives are usually used as chiral source in the HSSPs to synthesize helical polymers too.[36–39] Deng and coworkers have done wonderful research of chiral additive-assisted HSSPs to prepare different chiral materials.[36,37] They constructed optically active physical gels by one-handed helical polyacetylene through HSSPs of achiral substituted acetylene monomer with (*R*)- or (*S*)-1-phenylethylamine as chiral additive.[36] The results showed that the obtained substituted polyacetylenes were with one-handed helical conformations, and the optically active physical gels were constructed *via* helical nanofibers which presented prominent one-handed screw sense. Because of the strong intra- and intermolecular π-π interaction between the phenyl groups along the polymer chains, the gels were with excellent chiral memory ability and still maintained the optical activity after removal of all the chiral additives. Meanwhile, they achieved the preparation of chiral polymeric particles by HSSP of achiral acetylenic monomer bearing bulky adamantyl group catalyzed by $(nbd)Rh^+B^-(C_6H_5)_4$ with Boc-L- or Boc-D-alanine as chiral additive.[37] The obtained chiral particles were regular spherical and with an average diameter of ~300 nm. The authors suggested that the formation of stable helical structures might result from double hydrogen bonds of the chiral additive molecules with the neighboring two amide structures of the polymer's pendant groups.

Zhang's group designed and constructed photoresponsive

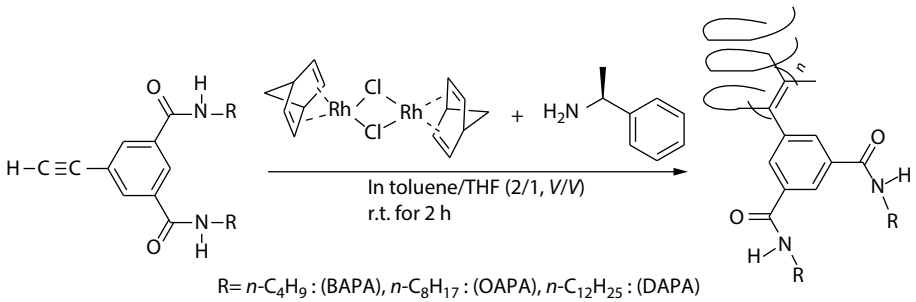

Fig. 2 HSSP of phenylacetylene monomers bearing two *N*-alkylamide groups. (Reprinted with permission from Ref. [28]; Copyright (2012) American Chemical Society).

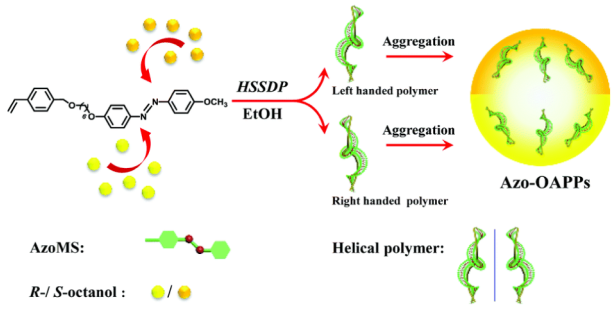

Fig. 3 A schematic illustration of the preparation of Azobenzeng-OAPPs by HSSP. (Reprinted with permission from Ref. [38]; Copyright (2020) The Royal Society of Chemistry).

polymeric particles with supramolecular helicity from achiral monomers through HSSP of achiral azobenzene-functional monomer with the addition of *R*- or *S*-octanol (Fig. 3).[38] The optical activity of the supramolecular particles was from the *π*-*π* stacking of achiral side *trans*-azobenzene groups and it was dependent on the volume fraction of the added chiral solvent, the time of polymerization, as well as the time of UV irradiation. What's more, the chirality of the polymeric particles could be completely maintained in dispersions for more than two months.

2.2 Synthesis of Chiral Helical Polymers by Chiral Induction of Racemic Helical Polymers

Chiral helical polymers can also be obtained by the induction of racemic helical polymers using chiral guest molecules. This is because noncovalent interactions can be formed between guest molecules and the polymers. The optical activity of the induced helical polymers may be retained on occasion after the removal of chiral guest molecules. Lots of research work have been done in the chiral induction of racemic polyacetylenes.[40,41] For example, Yashima and co-workers prepared optically inactive polyacetylene bearing 2,2′-biphenolderived pendants.[40] The helicity of the polymeric backbone, as well as the axial chirality of the side chains, could be induced by chiral alcohol. Moreover, the induced macromolecular helicity and axial chirality were memorized automatically and could be further switched in the solid state.

Except for polyacetylenes, vinyl polymers can be induced to form one-handed helix too.[42,43] Wan's group facilely and efficiently constructed the helical structure with diverse and tunable chiral amplification through the macromolecular acid-base complex of highly isotactic poly(2-vinylpyridine), (+)-camphorsulfonic acid ((+)-CSA), and dodecylbenzensulfonic acid (Fig. 4).[42] They found that the backbone of poly(2-vinylpyridine) would be twisted in a preferred direction driven by the ionic interactions of pyridinium pendants with the acid ions of (+)-CSA in the solution of $CHCl_3$ or $CHCl_3$/CH_3CN mixtures. Moreover, the sign and intensity of induced circular dichroism depended on the composition of the solvents.

3. CHIRAL RECOGNITION AND RESOLUTION OF HELICAL POLYMERS

Chiral recognition is an essential feature of living organisms, and

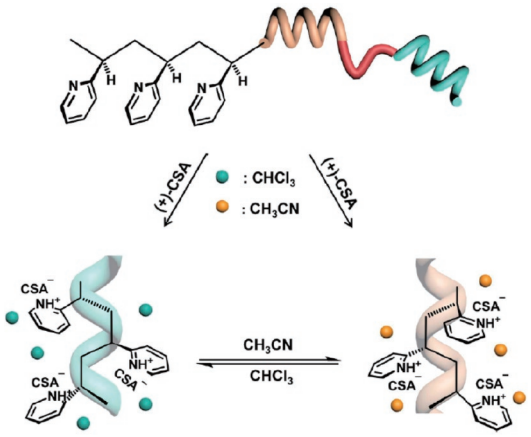

Fig. 4 Schematic illustration of helicity induction and different solvation states of iP2VP-(+)-CSA complex in $CHCl_3$ and CH_3CN. (Reprinted with permission from Ref. [42]; Copyright (2019) American Chemical Society).

a pair of enantiomers usually presents different physiological and toxicological behaviors in biological systems. Therefore, chiral resolution of enantiomers is necessary and of great significance. The helical polymer-based chiral resolution system has been widely investigated because of their high resolution abilities for an array of racemates. A variety of helical polymers, *e.g.*, polyacetylenes, polyisocyanides, poly(methacrylate)s, *etc.* have been explored to be applied in the field of chiral recognition and resolution. The part will be mainly divided into three sections according to the type of helical polymers, *i.e.* helical polyacetylenes (Section 3.1), helical polyisocyanides (Section 3.2), and other helical polymers out of the above scope (Section 3.3).

3.1 Chiral Recognition and Resolution of Helical Polyacetylenes

Polyacetylenes have attracted much attention and been extensively investigated for chiral recognition and resolution of racemates for the reason that their rigid conjugated backbone could be induced into a regular helical conformation *via* the covalent or non-covalent interaction of the backbone with chiral compounds.[44–47] Polyacetylenes synthesized directly by polymerization of chiral acetylene monomers are usually optically active and commonly to be used to separate racemates. Zhang and Okamoto *et al.* synthesized optically active helical poly(phenylacetylene)s with L-phenylalanine or L-phenylglycine ethyl ester pendants.[44] The chiral recognition ability of the polymers was influenced by the coating solvents, molecular weight, optical rotations, as well as the substituted groups in the chiral pendants. Shen and Wan *et al.* prepared chiral helical polyacetylenes *via* the polymerization of proline-modified acetylene monomers catalyzed by Rh-diene complexes.[45] The obtained polymers presented remarkable chiral resolution ability when they were used as the CSPs of HPLC for racemates of hydrogen-bond donors and cobalt(III) acetylace, and the chiral resolution performance was affected by the strength of the hydrogen bond and *π*-*π* interactions of racemates with CSPs. Freire and Maeda *et al.* reported three-state switchable CSP for high-performance HPLC based on the racemic poly(phenylacetylene) with a chiral (*R*)-*α*-

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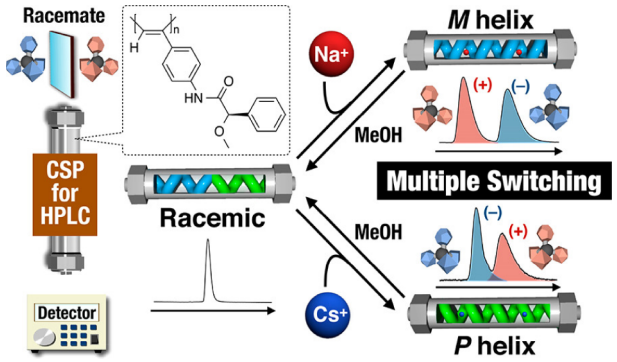

Fig. 5 Schematic illustration of macromolecular helicity modulation in poly-**1** through conformational switching of the MPA pendants using metal cations in solution. (Reprinted with permission from Ref. [46]; Copyright (2019) American Chemical Society).

methoxyphenylacetic acid (MPA) pendants (Fig. 5).[46] The helical sense of the racemic poly(phenylacetylene)-based CSP was dynamic and it could be induced to left- and right-handed upon a trace addition of soluble sodium or cesium salts in the system. Moreover, the transition of the two different helical conformations for racemic poly(phenylacetylene) could be facilely realized through rinsing the CSP with methanol and the successive addition of the proper salt.

Chiral induction strategy can also afford optically active helical polyacetylenes that present excellent performance in chiral recognition and resolution. Ishidate *et al.* prepared poly(biphenylylacetylene)s (PBPAs) with a variety of functional units at the 4′-position of the biphenyl pendants.[47] The helicity of the polymeric backbone, as well as the axial chirality of the biphenyl pendants could be induced *via* chiral 1-phenylethanol. Moreover, the helical conformation of PBPA-based CPS could be switched by alternate column treatment with a (*R*)- or (*S*)-1-phenylethanol containing solution after immobilization of PBPA chains onto silica gel.

3.2 Chiral Recognition and Resolution of Helical Polyisocyanides

Polyisocyanides have attracted a great deal of attention because of their unique rigid rod helical structure and broad applications, including chiral recognition and resolution of racemic molecules. Recently, Wu's group designed and synthesized a variety of stereoregular helical poly(phenyl isocyanide)s and explored their chiral recognition and resolution ability.[48–53] For example, they prepared block copolymers and miktoarm star polymers consisted of optically active helical poly(phenyl isocyanide)s bearing chiral pendants and random-coil poly(ethylene glycol).[48] The obtained copolymers were amphiphilic and could form supramolecular spherical self-assemblies in aqueous solutions. Moreover, the supramolecular self-assemblies presented excellent chiral recognition ability to fluorescent dansyl modified L- and D-phenylalanine (L- or D-Phe-DNSP). The fluorescent intensity of D-Phe-DNSP was about 5.4 times larger than that of L-Phe-DNSP at the same condition (Fig. 6). In another work, Zhang *et al.* prepared chiral helical poly(phenyl isocyanide)-contained hyperbranched copolymers by the combination of the ring-opening polymerization of L-lactic acid with Pd(II)-catalyzed

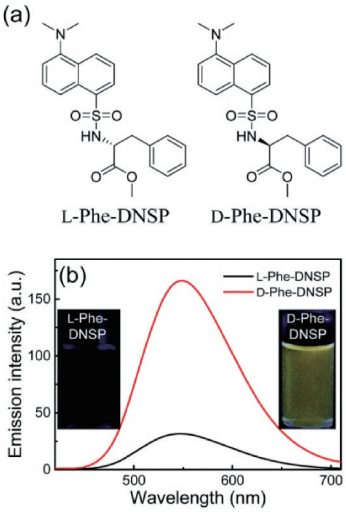

Fig. 6 (a) The structure of L- and D-Phe-DNSP. (b) Emission spectra of the L- and D-Phe-DNSP encapsulated aggregates of miktoarm star polymer measured in water at 25 °C (λ_{exc}=390 nm). Inserts are the photographs of the respective solutions under UV light of 365 nm. (Reprinted with permission from Ref. [48]; Copyright (2017) The Royal Society of Chemistry).

polymerization of phenyl isocyanide monomers bearing chiral pendants.[49] The obtained hyperbranched copolymers were optically active and showed good chiral recognition and resolution ability to racemic threonine in aqueous solutions. The enantiomeric excess (ee) value of the induced crystals could achieve 92%.

Apart from optically active helical polymers, Wu and co-workers also prepared optically active hybrid materials consisted of poly(phenyl isocyanide) with Fe_3O_4, silicon wafer, grapheme oxide (GO), *etc*.[54–56] For example, They immobilized chiral helical poly(phenyl isocyanide)s onto GO nanosheets *via* "grafting from" method and followed by hydrolysis to enhance the hydrophilicity of the hybrid GO/poly(phenyl isocyanide)s.[54] The chiral recognition and resolution ability of the obtained hybrid composite was investigated, and it turned out that L-alanine crystals could be induced *via* the composites containing the helical polymers with right-handedness. Meanwhile, they synthesized hybrid magnetic nanoparticles consisting of Fe_3O_4 as the core and helical poly(phenyl isocyanide) bearing chiral pendants as arms.[55] Benefitting from the handedness of helical poly(phenyl isocyanide), the hybrid nanoparticles were optically active and presented good performance in chiral resolution of threonine racemates. The ee value of the induced crystal could achieve 93% (Fig. 7a). Owing to the magnetic property, the chiral hybrid particles could be easily recovered *via* magnetic field, and they were still with chiral resolution ability after recover (Fig. 7b).

3.3 Chiral Recognition and Resolution of Other Helical Polymers

Besides helical polyacetylenes and polyisocyanides, helical vinyl polymers,[57] polyfluorene,[58,59] as well as supramolecular polymers[60] have also been studied in the chiral recognition

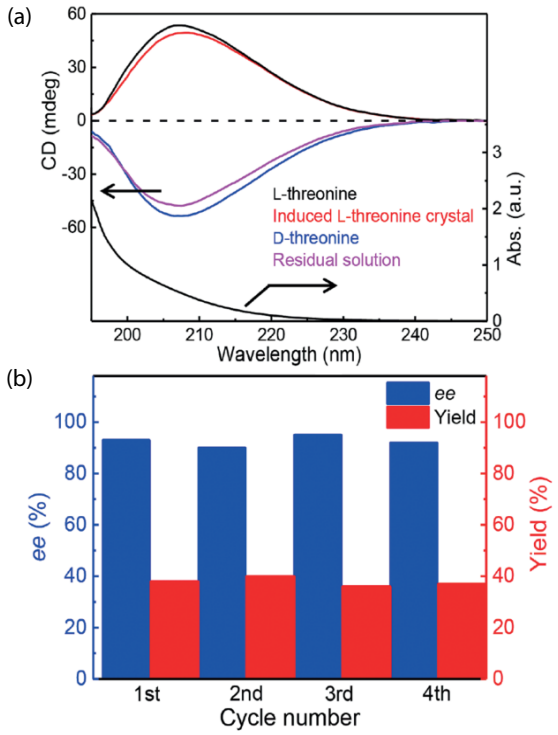

Fig. 7 (a) CD and UV-Vis spectra of the induced crystal, the rest solution, as well as the enantiopure D- and L-threonine in water. (b) The ee and yield of L-threonine induced by recycle using of hybrid nanoparticles. (Reprinted with permission from Ref. [55]; Copyright (2018) Wiley).

and resolution of racemic compounds. Lu *et al.* prepared optically active polymers through the radical polymerization of acrylamide derivatives with chiral oxazoline chromophore units using $Ln(OTf)_3$ (Ln = La, Nd, Sm, and Y, OTf = fluoromethanesulfonate) as catalysts.[57] The optical activity was affected by the stereoregularity of the polymers, and the isotactic-rich polymers showed chiral recognition ability to racemic 1,1′-bi-2-naphthol. Valášek, Kappes and Mayor *et al.* reported the chiral recognition and resolution of semiconducting single-walled carbon nanotubes (s-SWCNTs).[58] They prepared a pair of chiral acid cleavable polyfluorenes which presented exciting recognition ability to left- or right-handed s-SWCNTs and could be used for handedness sorting of s-SWCNTs. What's more, polyfluorenes could be removed to afford handedness sorted s-SWNTs by treating polymers with acids, which would cause the degradation of the polymers into recyclable fluorine monomers.

4. CONCLUSIONS AND PROSPECTS

This mini review summarized recent advances in the preparation of helical polymers and their application in chiral recognition and resolution. Preparations of optically active helical polymers from achiral monomers through chiral catalyst-assisted HSSP, chiral additive-assisted HSSP, as well as chiral induction of racemic helical polymers, were firstly described. Then, the chiral recognition and resolution of racemates based on helical polymers, particularly polyacetylene, polyisocyanide, were reviewed.

Despite the numerous remarkable achievements made to date, there are still some issues need to be further explored. For example, helical polymers with highly efficient chiral recognition and resolution ability were rare. Meanwhile, the reported helical polymers usually could separate a limited kinds of racemates, while helical polymers which can separate a wide range of racemates are seldom. In addition, mechanical performance of most synthetic helical polymers is usually poor, which may prevent them from being fabricated into optically active polymeric membrane that can be used in chiral resolution at industrial level. These are the directions for the research work in the future.

BIOGRAPHY

Zong-Quan Wu received his Ph.D. degree from Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences in 2006. He did postdoctoral research at the Nagoya University with Prof. Eiji Yashima supported by Japan Society for the Promotion of Science (JSPS) and University of Texas at Austin with Prof. Christopher W. Bielawski. He joined the Department of Polymer Science and Engineering, Hefei University of Technology, in 2011 as a full professor. He leads a group working on helical polymers, conjugated polymers, and supramolecular assembly.

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REFERENCES

1 Shen, J.; Okamoto, Y. Efficient separation of enantiomers using stereoregular chiral polymers. *Chem. Rev.* **2016**, *116*, 1094–1138.
2 Sun, T.; Qing, G.; Su, B.; Jiang, L. Functional biointerface materials inspired from nature. *Chem. Soc. Rev.* **2011**, *40*, 2909–2921.
3 Spinks, G. M. Advanced actuator materials powered by biomimetic helical fiber topologies. *Adv. Mater.* **2020**, *32*, 1904093.
4 Naaman, R.; Paltiel, Y.; Waldeck, D. H. Chiral molecules and the spin selectivity effect. *J. Phys. Chem. Lett.* **2020**, *11*, 3660–3666.
5 Akine, S.; Sairenji, S.; Taniguchi, T.; Nabeshima, T. Stepwise helicity inversions by multisequential metal exchange. *J. Am. Chem. Soc.* **2013**, *135*, 12948–12951.
6 Rogers, J. M.; Kwon, S.; Dawson, S. J.; Mandal, P. K.; Suga, H.; Huc, I. Ribosomal synthesis and folding of peptide-helical aromatic foldamer hybrids. *Nat. Chem.* **2018**, *10*, 795–795.
7 Lang, C.; Deng, X.; Yang, F.; Yang, B.; Wang, W.; Qi, S.; Zhang, X.; Zhang, C.; Dong, Z.; Liu, J. Highly selective artificial potassium ion channels constructed from pore-containing helical oligomers. *Angew. Chem. Int. Ed.* **2017**, *56*, 12668–12671.
8 Hu, G.; Li, W.; Hu, Y.; Xu, A.; Yan, J.; Liu, L.; Zhang, X.; Liu, K.; Zhang, A. Water-soluble chiral polyisocyanides showing thermoresponsive behavior. *Macromolecules* **2013**, *46*, 1124–1132.
9 Xu, Y.; Yang, G.; Xia, H.; Zou, G.; Zhang, Q.; Gao, J. Enantioselective synthesis of helical polydiacetylene by application of linearly

polarized light and magnetic field. *Nat. Commun.* **2014**, *5*, 5050.
10 Zeng, C.; Zhang, C. Y.; Zhu, J. Y.; Dong, Z. Y. Supramolecular polymerization driven by the dimerization of single-stranded helix to double-stranded helix. *Chinese J. Polym. Sci.* **2018**, *36*, 261–265.
11 Ye, Q.; Zheng, F.; Zhang, E.; Bisoyi, H.; Zheng, S.; Zhu, D.; Lu, Q.; Zhang, H.; Li, Q. Solvent polarity driven helicity inversion and circularly polarized luminescence in chiral aggregation induced emission fluorophores. *Chem. Sci.* **2020**, *11*, 9989–9993.
12 Leigh, T.; Fernandez-Trillo, P. Helical polymers for biological and medical applications. *Nat. Rev. Chem.* **2020**, *4*, 291–310.
13 Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. Supramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. *Chem. Rev.* **2016**, *116*, 13752–13990.
14 Zhang, Y.; Deng, J. Chiral helical polymer materials derived from achiral monomers and their chiral applications. *Polym. Chem.* **2020**, *11*, 5407–5423.
15 Ho, R. M.; Chiang, Y. W.; Lin, S. C.; Chen, C. K. Helical architectures from self-assembly of chiral polymers and block copolymers. *Prog. Polym. Sci.* **2011**, *36*, 376–453.
16 Zhu, Z.; Cui, J.; Zhang, J.; Wan, X. Hydrogen bonding of helical vinyl polymers containing alanine moieties: a stabilized interaction of helical conformation sensitive to solvents and pH. *Polym. Chem.* **2012**, *3*, 668–678.
17 Zhao, B.; Deng, J. Emulsion polymerization of acetylenics for constructing optically active helical polymer nanoparticles. *Polym. Rev.* **2017**, *57*, 119–137.
18 Wang, Y. Q.; Chen, Y.; Jiang, Z. Q.; Liu, F.; Liu, F.; Zhu, Y. Y.; Liang, Y.; Wu, Z. Q. Halogen effects on phenylethynyl palladium(II) complexes for living polymerization of isocyanides: a combined experimental and computational investigation. *Sci. China Chem.* **2019**, *62*, 491–499.
19 Lu, Y. X.; Shi, Z. M.; Li, Z. T.; Guan, Z. Helical polymers based on intramolecularly hydrogen-bonded aromatic polyamides. *Chem. Commun.* **2010**, *46*, 9019–9021.
20 Kennemur, J. G.; Novak, B. M. Advances in polycarbodiimide chemistry. *Polymer* **2011**, *52*, 1693–1710.
21 Yang, L.; Tang, Y.; Liu, N.; Liu, C. H.; Ding, Y.; Wu, Z. Q. Facile synthesis of hybrid silica nanoparticles grafted with helical poly(phenyl isocyanide)s and their enantioselective crystallization ability. *Macromolecules* **2016**, *49*, 7692–7702.
22 Akazaki, K.; Toshimitsu, F.; Ozawa, H.; Fujigaya, T.; Nakashima, N. Recognition and one-pot extraction of right- and left-handed semiconducting single-walled carbon nanotube enantiomers using fluorene-binaphthol chiral copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 12700–12707.
23 Zhang, Y.; Qin, M.; Zhao, C.; Dou, X.; Xing, C.; Sun, M.; Ma, X.; Feng, C. Controlled chiral transcription and efficient separation *via* graphene oxide encapsulated helical supramolecular assembly. *Carbon* **2020**, *165*, 82–89.
24 Zhang, C.; Liu, L.; Okamoto, Y. Enantioseparation using helical polyacetylene derivatives. *Trends Analyt. Chem.* **2020**, *123*, 115762.
25 Tamura, K.; Miyabe, T.; Iida, H.; Yashima, E. Separation of enantiomers on diastereomeric right- and left-handed helical poly(phenyl isocyanide)s bearing L-alanine pendants immobilized on silica gel by HPLC. *Polym. Chem.* **2011**, *2*, 91–98.
26 Shi, G.; Dai, X.; Zhou, Y.; Zhang, J.; Shen, J.; Wan, X. Synthesis and enantioseparation of proline-derived helical polyacetylenes as chiral stationary phases for HPLC. *Polym. Chem.* **2020**, *11*, 3179–3187.
27 Zhou, Y.; Zhang, C.; Zhou, Z.; Zhu, R.; Liu, L.; Bai, J.; Dong, H.; Satoh, T.; Okamoto, Y. Influence of different sequences of L-proline dipeptide derivatives in the pendants on the helix of poly(phenylacetylene)s and their enantioseparation properties. *Polym. Chem.* **2019**, *10*, 4810–4817.
28 Teraguchi, M.; Tanioka, D.; Kaneko, T.; Aoki, T. Helix-sense-selective polymerization of achiral phenylacetylenes with two *N*-alkylamide groups to generate the one-handed helical polymers stabilized by intramolecular hydrogen bonds. *ACS Macro Lett.* **2012**, *1*, 1258–1261.
29 Zang, Y.; Nakao, K.; Yotsuyanagi, H.; Aoki, T.; Namikoshi, T.; Tsutsuba, T.; Teraguchi, M.; Kaneko, T. Living-like helix-sense-selective polymerization of an achiral substituted acetylene having bulky substituents. *Polymer* **2013**, *54*, 1729–1733.
30 Schraff, S.; Kreienborg, N.; Trampert, J.; Sun, Y.; Orthaber, A.; Merten, C.; Pammer F. Asymmetric chain-growth synthesis of polyisocyanide with chiral nickel precatalysts. *J. Polym. Sci.* **2020**, *58*, 2221–2233.
31 Huang, J.; Shen, L.; Zou, H.; Liu, N. Enantiomer-selective living polymerization of *rac*-phenyl isocyanide using chiral palladium catalyst. *Chinese J. Polym. Sci.* **2018**, *36*, 799–804.
32 Zhu, H.; Luo, S. Z.; Wu, Z. Q. Living and enantiomer- selective polymerization of allene initiated by Ni complex containing chiral phosphine. *Chinese Chem. Lett.* **2019**, *30*, 153–156.
33 Hu, W.; Cao, J.; Huang, Y. L.; Liang, S. Asymmetric polymerization of *N*-vinylcarbazole with optically active anionic initiators. *Chinese J. Polym. Sci.* **2015**, *33*, 1618–1624.
34 Chu, J. H.; Xu, X. H.; Kang, S. M.; Liu, N.; Wu, Z. Q. Fast living polymerization and helix-sense-selective polymerization of diazoacetates using air-stable palladium(II) catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 17773–17781.
35 Liu, N.; Shi, L.; Han, X.; Qi, Q.-Y.; Wu, Z. Q.; Zhao, X. A heteropore covalent organic framework for adsorptive removal of Cd(II) from aqueous solutions with high efficiency. *Chinese Chem. Lett.* **2020**, *31*, 386–390.
36 Huang, H.; Deng, J.; Shi, Y. Optically active physical gels with chiral memory ability: directly prepared by helix-sense-selective polymerization. *Macromolecules* **2016**, *49*, 2948–2956.
37 Huang, H.; Yuan, Y.; Deng, J. Helix-sense-selective precipitation polymerization of achiral monomer for preparing optically active helical polymer particles. *Macromolecules* **2015**, *48*, 3406–3413.
38 Cheng, X.; Miao, T.; Ma, H.; Yin, L.; Zhang, W.; Zhang, Z.; Zhu, X. The construction of photoresponsive polymer particles with supramolecular helicity from achiral monomers by helix-sense-selective polymerization. *Polym. Chem.* **2020**, *11*, 2089–2097.
39 Chen, J. L.; Yang, L.; Wang, Q.; Jiang Z. Q., Liu, N.; Yin, J.; Ding, Y.; Wu, Z. Q. Helix-sense-selective and enantiomer-selective living polymerization of phenyl isocyanide induced by reusable chiral lactide using achiral palladium initiator. *Macromolecules* **2015**, *48*, 7737–7746.
40 Shimomura, K.; Ikai, T.; Kanoh, S.; Yashima, E.; Maeda, K. Switchable enantioseparation based on macromolecular memory of a helical polyacetylene in the solid state. *Nat. Chem.* **2014**, *6*, 429–434.
41 Seo, K. U.; Jin, Y. J.; Kim, H.; Sakaguchi, T.; Kwak, G. Kinetic study on achiral-to-chiral transformation of achiral poly(diphenylacetylene)s via thermal annealing in chiral solvent: molecular design guideline for conformational change toward optically dissymmetric structures. *Macromolecules* **2018**, *51*, 34–41.
42 Yan, Z.; Cai, S.; Tan, J.; Zhang, J.; Yan, C.; Xu, T.; Wan, X. Induced circular dichroism of isotactic poly(2-vinylpyridine) with diverse and tunable "sergeants-and-soldiers" type chiral amplification. *ACS Macro Lett.* **2019**, *8*, 789–794.
43 Jiang, S.; Zhao, Y.; Wang, L.; Yin, L.; Zhang, Z.; Zhu, J.; Zhang, W.; Zhu, X. Photocontrollable induction of supramolecular chirality in achiral side chain Azo-containing polymers through preferential chiral solvation. *Polym. Chem.* **2015**, *6*, 4230–4239.

https://doi.org/10.1007/s10118-021-2615-y

44 Zhang, C.; Wang, H.; Geng, Q.; Yang, T.; Liu, L.; Sakai, R.; Satoh, T.; Kakuchi, T.; Okamoto, Y. Synthesis of helical poly(phenylacetylene)s with amide linkage bearing l-phenylalanine and l-phenylglycine ethyl ester pendants and their applications as chiral stationary phases for HPLC. *Macromolecules* **2013**, *46*, 8406–8415.

45 Shi, G.; Dai, X.; Xu, Q.; Shen, J.; Wan, X. Enantioseparation by high-performance liquid chromatography on proline-derived helical polyacetylenes. *Polym. Chem.* **2021**, *12*, 242–253.

46 Hirose, D.; Isobe, A.; Quinoa, E.; Freire, F.; Maeda, K. Three-state switchable chiral stationary phase based on helicity control of an optically active poly(phenylacetylene) derivative by using metal cations in the solid state. *J. Am. Chem. Soc.* **2019**, *141*, 8592–8598.

47 Ishidate, R.; Sato, T.; Ikai, T.; Kanoh, S.; Yashima, E.; Maeda, K. Helicity induction and memory effect in poly(biphenylylacetylene)s bearing various functional groups and their use as switchable chiral stationary phases for HPLC. *Polym. Chem.* **2019**, *10*, 6260–6268.

48 Liu, N.; Ma, C. H.; Sun, R. W.; Huang, J.; Li, C.; Wu, Z. Q. Facile synthesis and chiral recognition of block and star copolymers containing stereoregular helical poly(phenyl isocyanide) and polyethylene glycol blocks. *Polym. Chem.* **2017**, *8*, 2152–2163.

49 Zhang, Z. H.; Qiao, C. Y.; Zhang, J.; Zhang, W. M.; Yin, J.; Wu, Z. Q. Synthesis of unimolecular micelles with incorporated hyperbranched Boltorn H30 polyester modified with hyperbranched helical poly(phenyl isocyanide) chains and their enantioselective crystallization performance. *Macromol. Rapid Commun.* **2017**, *38*, 1700315.

50 Wang, Q.; Chu, B. F.; Chu, J. H.; Liu, N.; Wu, Z. Q. Facile synthesis of optically active and thermoresponsive star block copolymers carrying helical polyisocyanide arms and their thermo-triggered chiral resolution ability. *ACS Macro Lett.* **2018**, *7*, 127–131.

51 Liu, N.; Sun, R. W.; Lu, H. J.; Li, X. L.; Liu, C. H.; Wu, Z. Q. Synthesis and chiroptical properties of helical polystyrenes stabilized by intramolecular hydrogen bonding. *Polym. Chem.* **2017**, *8*, 7069–7075.

52 Liu, N.; Lu, H. J.; Jiang, Z. Q.; Lu, Y. B.; Zou, H.; Zhou, L.; Wu, Z. Q. Facile synthesis of helical rod-coil block polymers by the combination of ATRP and Pd(II)-initiated isocyanides polymerizations. *Macromol. Chem. Phys.* **2019**, *220*, 1800574.

53 Wang, Q.; Huang, J.; Jiang, Z. Q.; Zhou, L.; Liu, N.; Wu, Z. Q. Synthesis of core cross-linked star polymers carrying helical poly(phenyl isocyanide) arms *via* "core-first" strategy and their surface chiral recognition ability. *Polymer* **2018**, *136*, 92–100.

54 Xiao, Y.; Wang, H. Q.; Zhang, H.; Jiang, Z. Q.; Wang, Y. Q.; Li, H.; Yin, J.; Zhu, Y. Y.; Wu, Z. Q. Grafting polymerization of single-handed helical poly(phenyl isocyanide)s on graphene oxide and their application in enantioselective separation. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 2092–2103.

55 Lin, Y. L.; Chu, J. H.; Lu, H. J.; Liu, N.; Wu, Z. Q. Facile synthesis of optically active and magnetic nanoparticles carrying helical poly(phenyl isocyanide) arms and their application in enantioselective crystallization. *Macromol. Rapid Commun.* **2018**, *39*, 1700685.

56 Chu, B. F.; Chu, J. H.; Zhao, S. Q.; Liu, N.; Wu, Z. Q. Facile synthesis of optically active helical poly(phenyl isocyanide) brushes on a silicon surface and their chiral resolution ability. *Polym. Chem.* **2018**, *9*, 1379–1384.

57 Lu, W.; Lou, L.; Hu, F.; Jiang, L.; Shen, Z. Optically active polyacrylamides bearing an oxazoline pendant: influence of stereoregularity on both chiroptical properties and chiral recognition. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5411–5418.

58 Xu, L.; Valasek, M.; Hennrich, F.; Sedghamiz, E.; Penaloza-Amion, M.; Haussinger, D.; Wenzel, W.; Kappes, M.; Mayor, M. Nantiomeric separation of semiconducting single-walled carbon nanotubes by acid cleavable chiral polyfluorene. *ACS Nano* **2021**, *15*, 4699–4709.

59 Senthilkumar, T.; Asha, S. K. An easy 'Filter-and-Separate' method for enantioselective separation and chiral sensing of substrates using a biomimetic homochiral polymer. *Chem. Commun.* **2015**, *51*, 8931–8934.

60 Salikolimi, K.; Praveen, V. K.; Sudhakar, A. A.; Yamada, K.; Horimoto, N. N.; Ishida, Y. Helical supramolecular polymers with rationally designed binding sites for chiral guest recognition. *Nat. Commun.* **2020**, *11*, 2311.

https://doi.org/10.1007/s10118-021-2615-y