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# Chiral Solvation Induced Supramolecular Chiral Assembly of Achiral Polymers

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<http://dx.doi.org/10.5772/67700>

## Abstract

To date, liquid crystal chirality, mechanophysical chirality, circularly polarized photon chirality, gelation and chiral solvation are all feasible candidates to generate optically active polymers and supramolecular chirality when employing achiral molecules as starting substances. Among this, chiral-solvation-induced chirality is one of the dominant methods for construction of chirality from achiral sources, such as achiral poly(*n*-hexyl isocyanate) (PHIC),  $\pi$ -conjugated polymers, oligo(*p*-phenylenevinylene), polyacetylenes,  $\sigma$ -conjugated polysilanes and side-chain polymers. Supramolecular chirality is well established through their intra- or inter-molecular noncovalent interactions, such as van der Waals, CH/ $\pi$ , dipole-dipole interactions, hydrogen bonding and metal-ligand coordinating interactions. Compared with the traditional methods, this strategy avoids the use of expensive chiral reagents and also expands the scope towards challenging substrates. This chapter highlights a series of studies that include: (i) the development-historical background of chiral solvent induction strategy; (ii) the chiral-solvation-induced chirality in small molecules and oligomers; and (iii) recent developments in polymers, especially in  $\pi$ -conjugated polymers and  $\sigma$ -conjugated polymers.

**Keywords:** optical activity, supramolecular chirality, chiral solvation, self-assembly, circular dichroism, circularly polarized luminescence

## 1. Introduction

As early as the second half of the nineteenth century, many scientists have long thought that the intrinsic biomolecular homochirality found in the living world is the origin of life on earth, since inherent optical activity exists inside all living organisms [1–14]. For example, typical fundamental components of our body, DNA and polypeptide biopolymers, consist of *D*-ribose and *L*-amino acid building blocks with the same handedness, respectively. The

absolute enantiopurity inside living organisms is of prime importance for many biological processes involving molecular recognition and replication, enzymatic catalysis, heritable characters, and pharmaceutical and toxicological activities [15]. Therefore, the studies on chirality were actually meant to explore life itself, its origin and nature.

Lord Kelvin first coined the term chirality as 'I call any geometrical figure, or group of points, chiral, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself'. Many pioneering concepts, such as 'optical activity', 'asymmetry', 'enantiomers' and 'chirality', also have been proposed since Pasteur's discovery of handedness in molecules. Research on chirality increased the demand of chiral materials and motivated more studies on synthetic chiral materials, especially chiral polymers, which have great promising applications in asymmetric catalysis, chiral resolution, chirality sensor and optoelectronic materials [16–24]. In general, most molecules or polymers possessing handed stereogenic centres and/or handed stereogenic bonds are considered to be optically active or chiral. This kind of chirality is attributed to straightforward chiral induction biases. Nowadays, traditional methods for preparing these chiral polymers have encountered many problems like the use of expensive chiral monomers or complex asymmetric polymerization processes. It is worth noting that, even if many substances have no optical activity, it does not mean that they cannot be chiral. They may exist as racemic mixtures or exist as time-averaged structures in a mirror-symmetric potential energy surface. External influence of molecular species, including stereogenic centres and/or stereogenic bonds, may indirectly induce their chiroptical activity. What's more, optical activity should be recognized as observable and measurable chiroptical signals in the ground and photoexcited states, but not as the typical defined chirality with chiral structure itself. Introducing asymmetry into optically inactive sources to obtain supramolecular chirality has gained increasing interest due to the appeal of avoiding of tedious synthesis of chiral polymers, as well as the possibility of several chiroptical applications including memory and switching.

Nowadays, methods for introducing asymmetry have been expanded widely, for example, using asymmetric liquid crystal field, supramolecular interactions with small chiral molecules, chiral circular polarized light and chiral solvation [21, 24–28]. Among these, chiral solvation method by simply using chiral solvent molecules as chiral source provides a relatively greener way to prepare optically active polymers. In this way, achiral macromolecules are surrounded by numerous chiral solvent molecules, and noncovalent supramolecular interactions (acid-base interaction, hydrogen bond, metal-ligand interaction and van der Waals force) existing between them will probably produce optical activity. Although these chiral induction biases are weak, chirality transfer from small molecules to macromolecules could be successfully realized through this way. Also, chiral induction biases can be amplified with the help of solvent quantity, subsequently obtaining supramolecular chirality. The concept of supramolecular chemistry was first delineated by Lehn as "the chemistry of molecular assemblies and of intermolecular bond" [29]. Supramolecular chemistry is closely allied to self-assembly, which has been defined as the spontaneous organization of pre-existing disordered components into ordered structures or pattern, as a consequence of specific interactions among those components themselves without external direction. Both supramolecular chemistry and molecular self-assembly are related to noncovalent interactions. They are great

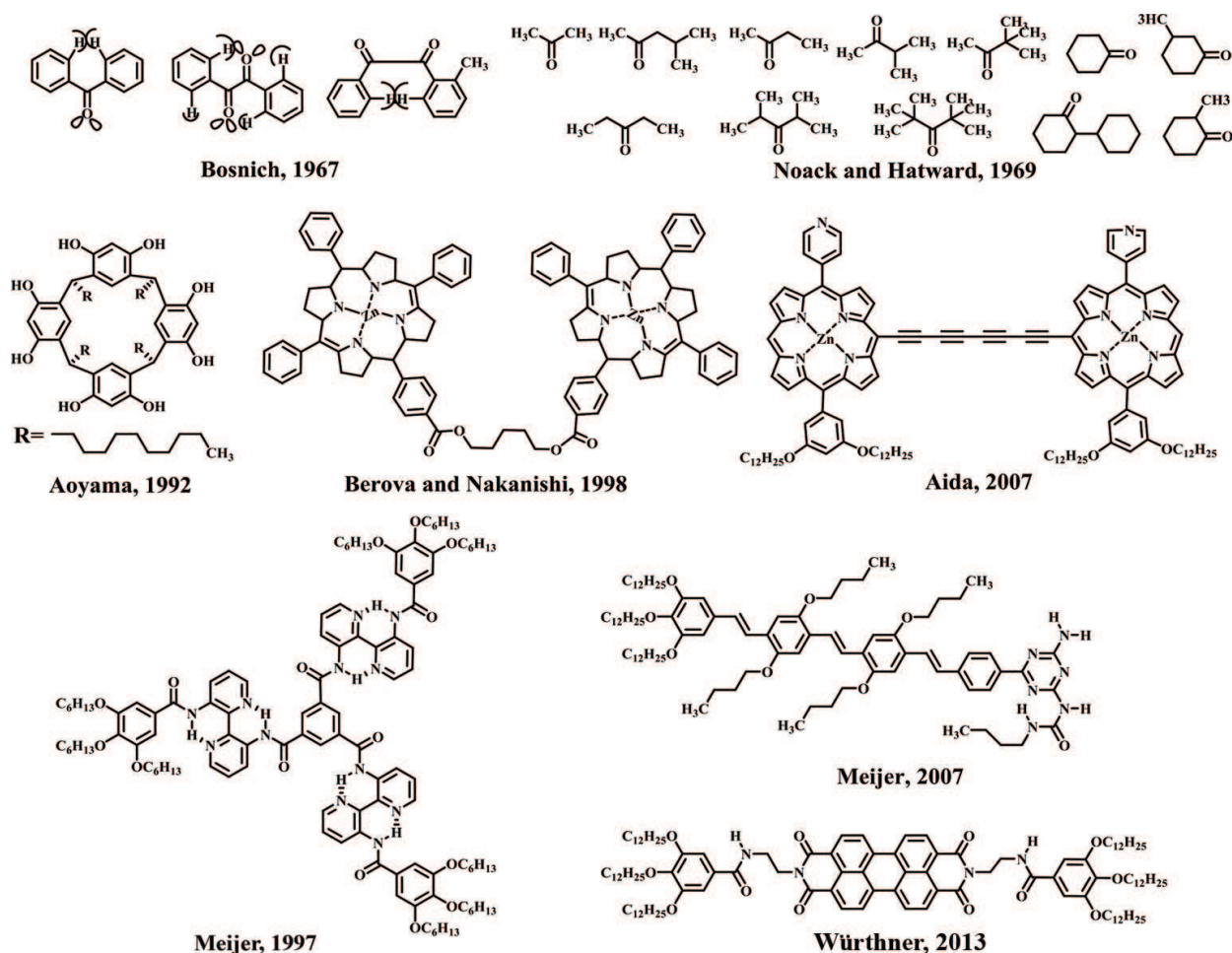
essential parts of biological systems, and exist everywhere such as the transfer and storage of genetic information in nucleic acids, and the self-folding of proteins into more functionally active molecular machines. These biological molecular self-assembly processes produce supramolecular chirality, due to the special spatial arrangements of the biological molecules. In a self-assembled system, both chiral and achiral components can be used to produce supramolecular chirality.

To detect this kind of supramolecular chirality in the ground states, circular dichroism (CD) and optical rotation dispersion (ORD) are used to investigate the electronic transition properties of the chiral species [30]. Vibrational circular dichroism (VCD) and Raman optical activity are used to investigate their vibronic transition properties [31, 32]. On the contrast, circularly polarized luminescence (CPL) provides us their structure information of chiral species in the photoexcited states [33]. These molecular structures are also predictable computationally by using the time-dependent density functional theory (DFT). The various processes of chiral supramolecular assembly can be monitored by UV-visible spectrophotometry, circular dichroism (CD) and fluorescent spectroscopy. Furthermore, their micro morphologies (nanoparticles or nanofibers) can be investigated by Atomic Force Microscopy (AFM), Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) technologies. This chapter highlights a series of studies that include: (i) the development-historical background of chiral solvent induction strategy; (ii) the chiral-solvation-induced chirality in small molecules and oligomers; and (iii) recent developments in polymers, especially in  $\pi$ -conjugated polymers and  $\sigma$ -conjugated polymers.

## 2. Chirality of small molecules and oligomers induced by chiral solvation

### 2.1. Induced circular dichroism for small molecules

It is well known that the induced optical activity for the absorption band(s) of the achiral species is defined as "induced circular dichroism (ICD)" [34]. One of the earliest observations was made when small achiral or CD-silent molecules were dissolved in chiral solvents, and the mirror symmetry of the chromophoric substrate was successfully broken by the solvation. In 1898, Kipping and Pope reported the first stirred chiral crystallization of aqueous  $\text{NaClO}_3$  solutions in *D*-dextrose, *D*-mannitol and *D*-dulcitol [35–37]. Although the aqueous solution of sodium chlorate is not optically active, the crystals obtained showed strong bias towards formation of one enantiomorphic form due to the successful chirality transfer from sugar solute. In isotropic solutions, the chiral solvation method applied in several small CD-silent molecules was then investigated [38]. As early as 1965, Mason et al. observed for the first time ICD bands for the *d-d* transitions of  $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$  in aqueous diethyl-(+)-tartrate solutions, according to the outer-sphere coordination between them [39]. What's more, Bosnich et al. found ICD effects not only for the *d-d* transitions of  $[\text{PtCl}_4]^{2-}$  but also for the *n- $\pi^*$*  transitions of benzyl and benzophenone in (*S,S*)-2,3-butanediol (**Figure 1**) [40]. The ICD effects for these aromatic groups were ascribed to the inherently twisting conformations of benzyl groups due to their H-H repulsion [41]. Further study on ICD effects has been reported by



**Figure 1.** Optically active small molecules and oligomers induced by chiral salivation.

Hayward et al. for the  $n\text{-}\pi^*$  transitions of 10 symmetric and racemic aliphatic ketones in six chiral tetrahydrofuranols (**Figure 1**) [42]. Later, a molecular complex with 1:1 molar ratio between achiral-saturated ketones and chiral *L*-menthol was proposed to exist in the solution by investigating the concentration dependence of ICD bands [43]. This was possibly ascribed to chiral OH/O interactions. Such induced CD (ICD) effects have so far been observed in a number of situations, and the intermolecular interactions such as hydrogen bonding, van der Waals interactions, or ionic coupling between chiral species and achiral ones are contributed to the induction of the optical activity for the electronic transitions of achiral species.

## 2.2. Induced circular dichroism for oligomers

Another most frequently studied type of ICD effects is between achiral or CD-silent oligomers and chiral solvents, due to their intra- or inter-molecular interactions. In 1992, Aoyama et al. prepared a hydrophobic resorcinol cyclic tetramer (host molecule) by reaction between resorcinol and dodecanal (**Figure 1**) [44, 45]. Through cooperative CH- $\pi$  and hydrogen-bonding effect, this achiral, chromophoric host molecule efficiently formed soluble complexes with chiral, nonchromophoric guest molecules, such as various glycols and sugars, (*R*)-/(*S*)-2-pentanol,



(*R*)-/(*S*)-1-phenylethanol, *D*-/*L*-menthol, epicholesterol and cholesterol. The desymmetrization of the host molecule upon host-guest complexation enabled the coupling of the transition moments generated by the aromatic rings, giving rise to not only ICD effects but also exciton-coupled CD spectra. This kind of observed couplet was also further applied to determine the absolute configuration of the guest molecules. The complexation between CD-silent zinc porphyrins and chiral amines or alcohols is another important intermolecular interaction applied to prepare optically active complexes. Berova et al. have designed an achiral zinc bis-porphyrin linked with a long pentamethylene diester (host molecule) as shown in **Figure 1** [46–48]. By relatively intense coordination interactions between zinc porphyrin and nitrogen or oxygen, the host molecules successfully bound plenty of chiral diamines, amino alcohols and amino acids and showed clear ICD effects, due to the formation of CD-active 1:1 and 1:2 host-guest complexes. Borovkov, Inoue and coworkers have synthesized a CD-silent zinc bis-porphyrin rotamer linked with a shorter 1,2-ethane spacer (**Figure 1**) [49–51]. When it binds chiral secondary amines or chiral secondary alcohols through ligand-to-metal coordination, the rotamer shows efficient switch between *syn*- and *anti*-conformations. This kind of supramolecular chirality is caused by the steric interactions between the 3,7-ethyl groups of the porphyrin and the substituents of the ligand. Tsuda and Aida designed a zinc bis-porphyrin rotamer containing a rigid linker and pyridine substituent [52]. When it is dissolved in asymmetric hydrocarbons, such as (*S*)- and (*R*)-limonene, it is capable of self-assembling into a twisted box-shaped tetramer through multipoint non-covalent interactions and gives rise to the chiral supramolecular assembly. The homochirality of the self-assembled tetramer was then characterized by analysing its CD spectra as functions of limonene enantiopurity and the time-dependent CD change in a dilute condition. Also, the obtained tetrameric assembly is enantiomerically enriched and optically active, confirming the successful preparation of supramolecular chiroptical sensor for chiral limonene. And from the CD spectra of the porphyrin box, the optical purity and absolute configuration of limonene can be determined.

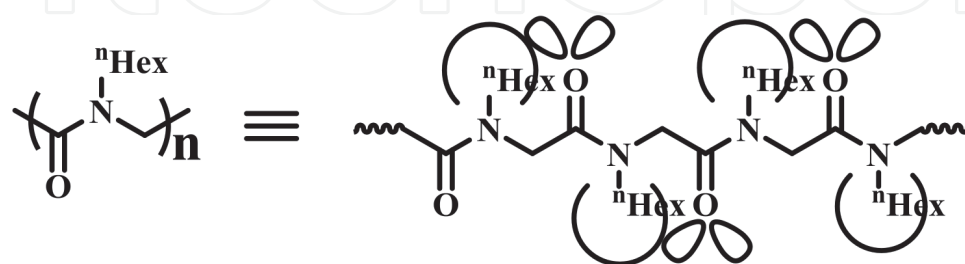
Aside from breaking the inner mirror symmetry, the induced optical activity of achiral oligomers can also be accomplished by forming supramolecular assemblies when the oligomers are aggregating in chiral solvents. Meijer et al. presented pioneering studies on the construction of supramolecular chirality for self-assembled  $C_3$  symmetric disc-shaped molecules and achiral oligo(*p*-phenylenevinylene) derivatives (OPVs) through preferential chiral solvation (**Figure 1**) [53–55]. In their work, the chiral inducers, such as (*S*)- and (*R*)-citronellic acid, (*S*)- and (*R*)-citronellol and (*S*)-2,6-dimethyloctane, showed chiroptical induction ability and promised homochirality of the assemblies through chiral OH/N, OH/O and CH/ $\pi$  interactions. For achiral OPVs equipped with ureidotriazine arrays and *n*-butoxy side chains, chiral solvation gives rise to quadruple H-bonded dimers and subsequently forms well-defined supramolecular stacks by cooperative  $\pi$ - $\pi$  stacking [54, 55]. Würthner et al. demonstrated that chiral solvent, (*S*)- and (*R*)-limonene, successfully generated one-dimensional helical nanofibres from optically inactive amide-functionalized perylene bisimide derivatives (PBI) by synergic effects of hydrogen-bonding interactions and  $\pi$ - $\pi$  stacking (**Figure 1**) [56]. The presence of reversed CD effects of this PBI gelator in (*S*)- and (*R*)-limonene reveals that helically packing of the chromophore is successfully directed by the chiral environment, which was also proven by the chiral bias towards homochiral aggregates observed by AFM studies.

### 3. Chirality of polymers induced by chiral solvation

Apparently, compared with small organic molecules, optically active polymers possess better film-processing ability, thermodynamic stability and particular physical and chemical properties. These polymers are always prepared by polymerization with chiral monomers, asymmetric polymerization with achiral monomers, or chiral self-assembly processes from optically inactive sources. The latest method has been studied intensively and been recognized as one of the most promising ways for preparing optically active polymers. Nowadays, inter- or intra-molecular interactions (like van der Waals, CH/ $\pi$ , hydrogen bonding, coulombic, charge-transfer and metal-ligand coordinating interactions) have been used to facilitate the chirality induction of optically active polymers from optically inactive polymers. As early as in 1993, Green et al. observed for the first time a macromolecular conformational change driven by a minute chiral solvation energy [26, 57]. The chirality transfer from non-racemic solvents, such as (*S*)-1-chloro-2-methylbutane and (*R*)-2-chloroalkanes, to CD-silent poly(*n*-hexyl isocyanate) (PHIC) macromolecules was successfully realized (**Figure 2**). The generation of supramolecular chirality of PHIC polymers with a preferred handed helix was also demonstrated by CD signals. After the successful chirality transfer from solvent chirality to achiral polymers, the substrate structures with different functionality, mostly based on  $\sigma$ -conjugated polymers and  $\pi$ -conjugated polymers, are also investigated.

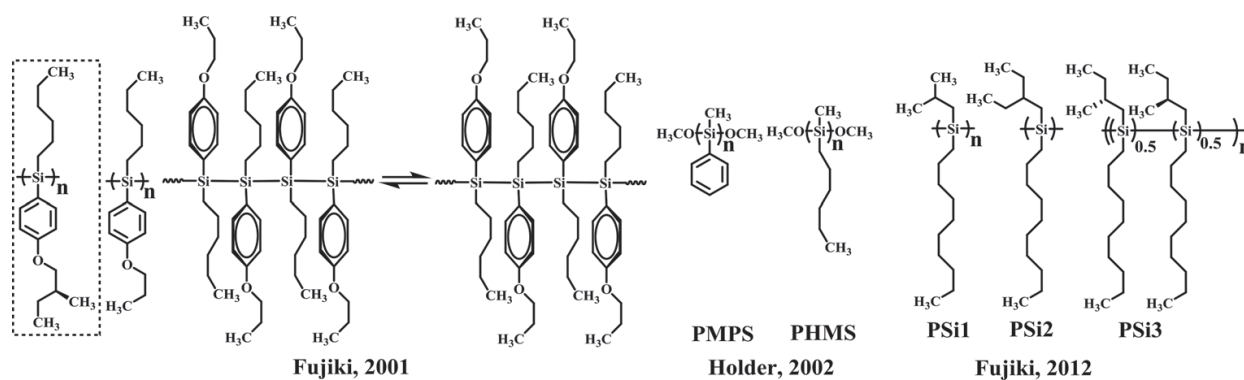
#### 3.1. Preparation for optically active $\sigma$ -conjugated polymers

Fujiki et al. found that a certain polysilane bearing remote chiral (*S*)-2-methylbutoxyphenyl groups was CD-silent when it was molecularly dispersed in tetrahydrofuran (THF) solution, due to the existence of dynamically equivalent amounts of right- and left-handed screw sense helical main chain domains. However, after addition of methanol, optically active polysilane aggregated in the good/poor cosolvents system and marked bisignate CD signals were abruptly observed in the UV region due to the  $\text{Si}\sigma\text{-Si}\sigma^*$  transition [58]. This interesting observation intrigued them to investigate the chiral-solvent-induced aggregation processes of CD-silent polysilanes bearing achiral groups in tersolvents (chiral solvent/good solvent/poor solvent) systems (**Figure 3**). Then the clear exciton couplet CD signals of  $\text{Si}\sigma\text{-Si}\sigma^*$  transitions of achiral polysilane aggregates with achiral *n*-propoxyphenyl and *n*-hexyl groups,



**Green, 1993**

**Figure 2.** Conformational change of poly(*n*-hexyl isocyanate) driven by chiral solvation.



**Figure 3.** Optically activity of  $\sigma$ -conjugated polymers induced by chiral solvation.

certificated the successful chirality transfer and amplification of the molecular chirality of 2-phenylethanol (chiral solvent) [59]. Holder et al. first reported that preferential helical sense of inherently achiral  $\sigma$ -conjugated polysilanes was successfully induced via chiral solvation, which was investigated by optical UV-visible and CD spectroscopy [60, 61]. When polysilanes, poly(methylphenylsilane) (PMPS) and poly(methyl-*n*-hexylsilane) (PHMS) are totally dissolved in good solvents, they normally exist as random coils whose segments have an equal probability of adopting either *P* or *M* helical screw senses. While dissolved in chiral solvents, such as (*S*)-(-)-2-methyl-1-propoxybutane and (*S*)-(-)-(2-methylbutoxymethyl) benzene, a preference for one helical sense is achieved. Among these diverse chiral solvents mentioned above, limonene is most widely used as a mirror-symmetry-breaking solvent due to its nontoxicity and its easy extraction process from natural fruits. Through aggregation in the limonene/methanol/THF tersolvent, Fujiki et al. also successfully prepared optically active supramolecules from the original CD-silent  $\sigma$ -conjugated polysilanes (**Figure 3**) [62]. The chiral solvent ratio and polymer molecular weight dependences were both certified as critical factors to the dissymmetry factor,  $g_{CD}$ . Also, chirality inversion was observed when different limonene solvent ratios were applied to PSi1 and PSi3. And apparent CPL signals for PSi2 and PSi3 were observed in the supramolecular aggregates formed through chiral solvation. These interesting phenomena including chirality inversion and CPL signals are all instructive for research on solvent-chirality-transfer mechanism.

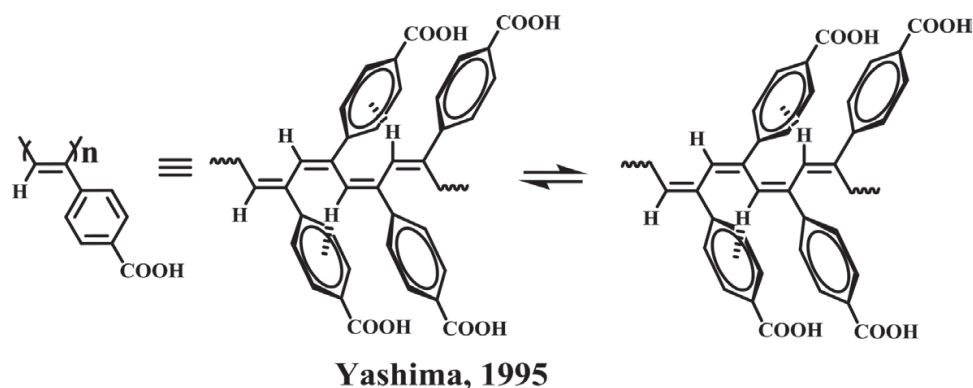
### 3.2. Preparation for optically active $\pi$ -conjugated polymer

$\pi$ -Conjugated polymers are very essential materials for applications in organic solar cells, polymeric organic light emitting diodes (OLED), thin-film transistors, lasers and photovoltaic devices. Among this, those polymers with chiroptical properties bring about perfect linearly and circularly polarized electroluminescence, which are widely applied in fields of optical switching and processing, chiral bio-imaging and metamaterials [63, 64]. As a typical  $\pi$ -conjugated polymer, achiral polyphenylacetylene possesses a plenty of short random twist segments with many helix-reversal points in the adjacent double bonds around a single bond. Yashima et al. reported that the random twist conformation can be transformed into a prevailing one-handed helical conformation upon complexation with optically active amines and amino alcohols in polar DMSO, certificated by the observation of characteristic ICD effects in the UV-vis region

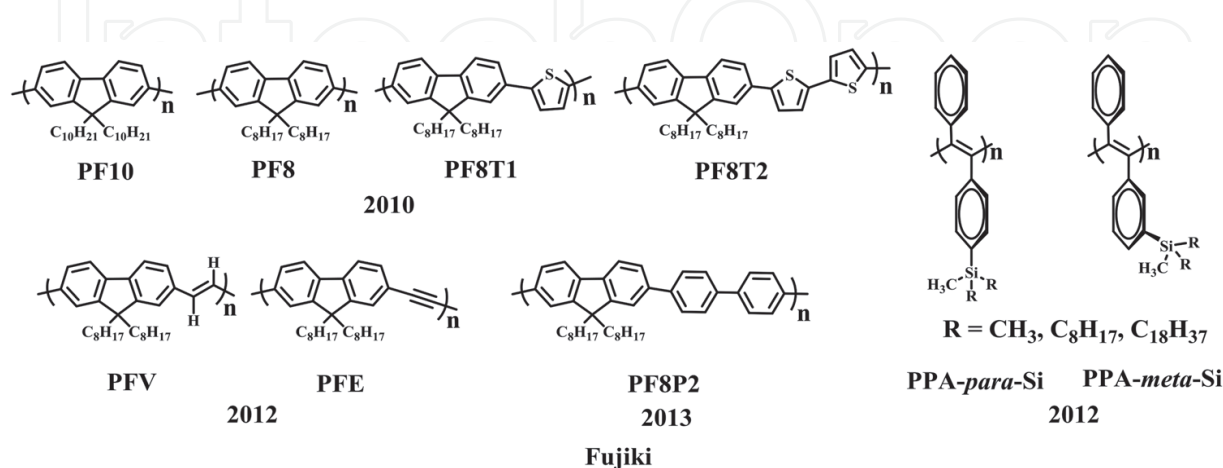


(**Figure 4**) [53, 65, 66]. The CD signs corresponding to the different helical superstructures can be used as a probe for determining the configuration of chiral amines. What's more, this helicity can be successfully memorized when the original chiral amines are removed or replaced by achiral ones, while the helical conformation is still unchanged.

Among those  $\pi$ -conjugated polymers, polyfluorenes (PFs) possessing higher photoluminescence efficiency are much easier for film-processing and structure modification, which are great promising materials for organic light emitting diodes (OLED). Traditional methods for synthesizing PFs always involve expensive chiral catalysts and complex experimental procedures. The perfect application of chiral solvation method in preparing optically active  $\sigma$ -conjugated polymers and  $\pi$ -conjugated polyphenylacetylenes gave rise to the possibility of inducing optically active PFs. First, Fujiki et al. successfully utilized terpene chirality transfer method to generate serials of CD- and/or CPL-active  $\pi$ -conjugative polymers from the corresponding achiral counterparts (**Figure 5**) [67–71]. Meanwhile, many diverse factors, such as tersolvent composition, solvent polarity, polymer molecular weight, alkyl chain length, limonene enantiopurity, solution temperature, clockwise and counter-clockwise stirring, and aggregate size are confirmed to influence the magnitude of the induced CD and/or CPL amplitude. Through theoretical calculation, they assume that the inherent twisting ability (H-H repulsion) between the near-



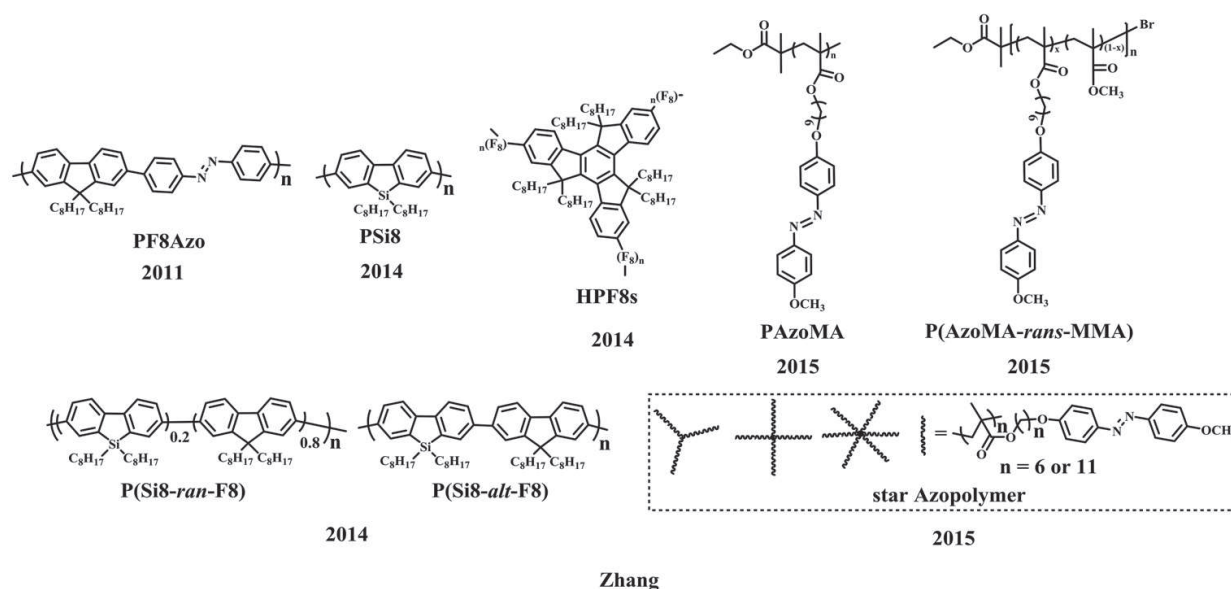
**Figure 4.** Helical poly(1-phenylacetylene) carrying carboxyl group.



**Figure 5.** Optical activity of  $\pi$ -conjugated polymers induced by chiral solvation.

est neighbouring fluorene rings within mainchains of PF8T1, PF8T2, PF8, PF10 and PF8P2 are responsible for the preferential handedness formed during aggregation process. In comparison, fluorene units linked with a C≡C triple bond (PEE) did not generate any optically active aggregate, ascribed to the lack of H-H repulsion.

Zhang et al. demonstrated that solvent chirality can be transferred to the aggregates of many optically inactive  $\pi$ -conjugated polymers with different backbone structures, such as main chain azo-containing polyfluorene (F8AZO), poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PF8), poly(9,9-di-n-octylsila-fluorenyl-2,7-diyl) (PSi8), poly(9-(1-octylnonyl)-9H-carbazole-2,7-diyl) (PCz8), P(F8-*alt*-Si8), P(F8-*alt*-Cz8), and P(Si8-*alt*-Cz8), hyperbranched PF8s, side chain azo-containing polymers PAzoMA, P(AzoMA-*rans*-MMA), and star side-chain Azo polymers (star PAzoMAs) as shown in **Figure 6** [69, 72–76]. Optically active F8AZO aggregates were successfully generated by the chirality transfer from (*S*)- and (*R*)-limonene, demonstrated by the intense ICD signals corresponding to F8AZO in the visible region [69]. Upon alternating photoirradiation at 405 (*trans* form) and 546 nm (*cis* form), a first reversible chiroptical switch for Azo-containing  $\pi$ -conjugated polymer was achieved, resulting from the switching between the *trans*-origin aggregation and *cis*-origin disaggregation of F8AZO in the limonene/2-propanol/chloroform ternsolvent system. Then, they generated the first optically active hyperbranched  $\pi$ -conjugated polymer aggregates with strong CD and CPL properties with the help of solvent chirality transfer from chiral limonene [72]. Their studies showed that degree of branching, poor solvent type, volume fraction, limonene enantiopurity and polymer concentration have obvious effects on the magnitude and sign of the CD signals. Surprisingly, further studies found chiroptical inversion during aggregation of achiral PF8 and PSi8 and chiroptical inversion between CD and CPL spectra of PSi8 aggregates [73]. The unique chiroptical inversion was probably attributed to the opposite Mulliken charges between 9-Si in Si8 and 9-C in F8 unit and between *Cipso*(1) in Si8 and *Cipso*(1) in F8 unit, or resulting from the opposite direction of dipole moments in



**Figure 6.** Optical activity of main-chain and side-chain  $\pi$ -conjugated polymers induced by chiral solvation.

three stable rotational isomers of the equatorial limonene rotamer. This novel element-dependent chiroptical inversion and structural dependence of  $\pi$ -conjugated polymers with the help of limonene chirality in aggregation states pave a new way for designing chiroptical functional polymers. Furthermore, they successfully constructed the supramolecular chirality for CD-silent PF8 by cooling its limonene solution at low temperature [74]. More interestingly, the supramolecular chirality can be transferred to solid films and be perfectly memorized. Facile generation and inversion of the CPL sign were also observed between aggregation states and film states. AFM studies clearly revealed the right- and left-handed twist helical fibres induced by nonracemic limonene, which are responsible for the CD and CPL functionality.

Although this chiral solvation strategy has been well applied in preparing many optically active main chain  $\pi$ - and  $\sigma$ -conjugated polymers, this concept has been extended to side chain polymeric systems. Guerra et al. reported that the first side chain polymer, syndiotactic polystyrene (s-PS), exhibited intense ICD signals in the polymer absorption region after exposure to nonracemic solvent vapour and thermal annealing processes in the film state [77]. The chiroptical properties obtained for racemic nanoporous  $\delta$ -phase s-PS was assumed due to the induced chiral co-crystallization with solvent molecules, and the sign of CD signals is determined by the chirality of the nonracemic guests. However, a more recent study demonstrated that the signs depend essentially only on the nature of the polymer host supramolecular chirality, but not on the *R* or *S* solvent chirality, proven by the VCD spectra of the  $\delta$ -phase s-PS film used [78]. To investigate the induction of supramolecular chirality for achiral side-chain polymers, Zhang et al. designed serials of linear and star-shaped achiral side chain azobenzene-containing polymer (PAzoMA, P(AzoMA-*rans*-MMA), and star PAzoMAs) [75, 76]. Chirality of nonracemic solvents were successfully transferred to these polymers, and well-assembled supramolecular *trans*-azobenzene aggregates are prepared in DCE/(*R*)- or (*S*)-limonene mixsolvents. The chirality obtained was ascribed to the ordered stacking of azobenzene group on the side chain when the polymer molecules were aggregating in the chiral solvents. This supramolecular chirality can also be destroyed by the *trans*–*cis* photoisomerization process due to the noncoplanar structure of the *cis*-Azo unit; however, it can be recovered by the heating-assisted reorganization process. The successful construction of a reversible chiral-achiral switch based on an achiral azobenzene-containing side chain polymer will open a new approach for production of chiroptical materials.

## 4. Conclusion

This chiral solvation approach provided herein allows the production of various CPL-/CD-functionalized polymer solutions or aggregates from CD-silent artificial polymers under mild conditions through the noncovalent interactions between small chiral molecules and achiral polymers. What's more, the chiral transfer, amplification and memory of supramolecular chirality in polymer solution and its solid polymer films were also realized, which is highly significant for the practical applications in chiroptical switch and memory, optical data storage and detection of circularly polarized luminescence (CPL). Considering the potential application of chiral materials in nonlinear optical devices, this concept paves a more convenient way for designing and constructing chiral polymer materials.

## Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (21374072 and 21574089), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions and the Program of Innovative Research Team of Soochow University.

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