

Review

The Chirality Induction and Modulation of Polymers by Circularly Polarized Light

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Abstract: Chirality is a natural attribute nature of living matter and plays an important role in maintaining the metabolism, evolution and functional activities of living organisms. Asymmetric conformation represents the chiral structure of biomacromolecules in living organisms on earth, such as the L-amino acids of proteins and enzymes, and the D-sugars of DNA or RNA, which exist preferentially as one enantiomer. Circularly polarized light (CPL), observed in the formation regions of the Orion constellation, has long been proposed as one of the origins of single chirality. Herein, the CPL triggered asymmetric polymerization, photo-modulation of chirality based on polymers are described. The mechanisms between CPL and polymers (including polydiacetylene, azobenzene polymers, chiral coordination polymers, and polyfluorene) are described in detail. This minireview provides a promising flexible asymmetric synthesis method for the fabrication of chiral polymer via CPL irradiation, with the hope of obtaining a better understanding of the origin of homochirality on earth.

Keywords: homochirality; circularly polarized light; asymmetric reaction; polymer

1. Introduction

Homochirality is one of the most valuable aspects of science and is an essential molecular characteristic of terrestrial life [1–4]. Asymmetric conformation represents the chiral structure of biomacromolecules in living organisms on earth. Homochirality in biomolecular building blocks almost exclusively results in the use of only one enantiomer for the molecular architecture, such as the D-sugars of nucleic acids and L-amino acids of proteins [5–11]. In the achiral environment, the chemical and physical properties of D- and L-enantiomers were not different except for tiny energy differences which can be attributed to the parity violation of the weak interactions. However, these small energy differences have been theoretically proposed, but they are hard to be detected by conventional experiments [12]. During the process of building up biopolymers such as proteins, enzymes and nucleic acids, an important requirement is the selection of one enantiomer. Therefore, the origin of homochirality in nature has been widely often exploited, and the homochirality of life remains an important subject to be researched.

The asymmetric structure of polymers plays an important role in the maintenance of life processes, metabolism and evolution, and chiral polymers have been widely used in asymmetric synthesis, chiral recognition, and enantiomeric separation [13–23]. Moreover, chiral polymers also hold potential

for application in chiral catalysts, liquid crystals, nonlinear optical materials, and the biomedical industry [24–33]. In recent years, scientists have reported several methods to synthesize chiral materials, such as the use of chiral solvents or templates, polymerization with chiral monomers, substituted achiral polymers with a chiral center, supramolecular self-assembly and circularly polarized light (CPL) irradiation. Compared with these methods, circularly polarized light (CPL), proposed to be one of the origins of homochirality in nature, is regarded as an important tool to prepare photo-active chiral materials [34].

As shown in Figure 1, CPL is one kind of electromagnetic waves with a spiral arrangement of the electric field vector along the propagation direction [35]. Right and left-handed CPL are considered to be plausible candidates to introduce the initial chiral asymmetry into biomolecular building blocks. In 1929, Kuhn conducted an experiment by irradiating a racemic organic molecule solution with CPL for the first time, and the results demonstrated that CPL could successfully induce the asymmetric photolysis of organic molecules [36]. Moreover, Kagan also prepared the helical structure of an olefin molecule with a redox reaction between diarylethene and iodine accompanied by the CPL irradiation. Interestingly, the results showed that the final obtained products behaved with chiral signals opposite to that of the external circularly polarized light [37]. In recent years, with the development of CPL technology, CPL has been widely utilized in areas such as asymmetric photolysis, asymmetric polymerization, and deracemization reaction [38–42]. Meinert and co-workers reported that the enantiomeric excess (ee) value of molecules was not only dependent on the polarization state of the CPL but also deeply affected by the wavelength of the CPL [43–45]. Although the CPL irradiation method is considered to be an important tool to synthesize helical biomolecules, the enantiomeric excess is quite a small (<4%). Therefore, how to improve the ee value based on CPL technology remains a question to be answered. In 2009, Vlieg et al. reported that with CPL irradiation, a racemic solution of amino acid derivatives could induce a small amount of chiral bias that was then amplified to give a pure chiral solid phase. The solution of racemic amino acids could be converted to single-handedness through an abrasive grinding process, and the final chirality of the solid phase could be totally controlled by the external handedness of the CPL [38]. Meanwhile, Kotov et al. demonstrated that left- (right-) handed CPL illumination of racemic CdTe nanoparticles in a dispersion state could induce the same direction twisted nanoribbons. Moreover, the chiral nanoribbons were generated in an enantiomeric excess exceeding approximately 30%, and this ee value was substantially higher than that obtained from traditional CPL-induced reactions [46]. Their results opened a pathway for the preparation of helical photonic structures and provided a scenario for the plausible origin of homochirality in biomolecules during the evolution of early earth. Kim et al prepared helical structure based on triphenylamine derivatives, and the helicity of the aggregation was totally controlled by the handedness of the CPL [47]. Therefore, the utilization of CPL irradiation technology in areas including the chirality induction, transference and amplification of liquid crystal or polymers would be of great value especially in asymmetric reaction.

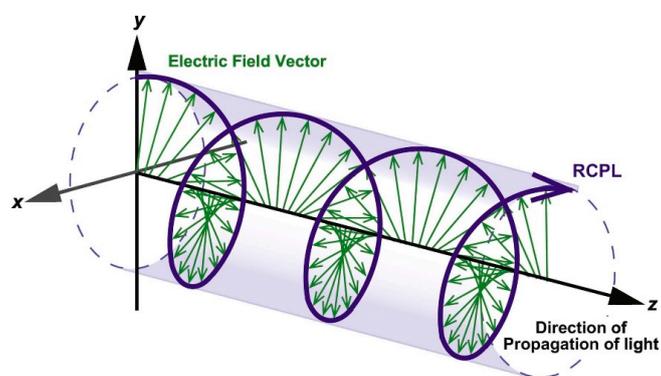


Figure 1. The schematic of right-handed circularly polarized light (R-CPL), reprinted with permission from Reference [34]. Copyright 2018 Elsevier.

In this review, the recent advances in the preparation and modulation of chiral polymers based on CPL irradiation technology are outlined, and the asymmetric mechanism and influence factors are also discussed. Our main purpose is to offer a comprehensive understanding of helical structure construction based on CPL technology which mainly focuses on polydiacetylene, polyfluorene, azobenzene, chiral coordination polymers and so on. This review provides a promising flexible asymmetric synthesis method for the preparation of chiral polymers based on CPL technology, hoping to help us obtain a deeper understanding of the plausible origin of homochirality on earth.

2. The Asymmetric Synthesis of Chiral Polymers Based on Circularly Polarized Light

2.1. The Asymmetric Polymerization of Diacetylene

Polydiacetylene (PDA) is a novel photosensitive material, which possesses conjugated backbone chains, and can be easily formed in different structures by self-assembled systems. Diacetylene (DA) monomers can be polymerized with the irradiation of UV light or γ -rays. With external stimuli (ions, pH, temperature, etc.), PDA exhibits an apparent color and fluorescence change, thereby making it an ideal material for sensing in different forms such as liposomes, vesicles, films or microtubes [48–56]. In 2006, Iwamoto et al. demonstrated the enantioselective synthesis of chiral PDA triggered by ultraviolet circularly polarized light (Figure 2). The DA monomer without any chiral centers was used to prepare the monomer film and ultra-violet CPL was the only chiral source. Interestingly, the formed films irradiated with different-handed (left or right) CPL distinguishably induced the opposite handedness of PDA films [57].

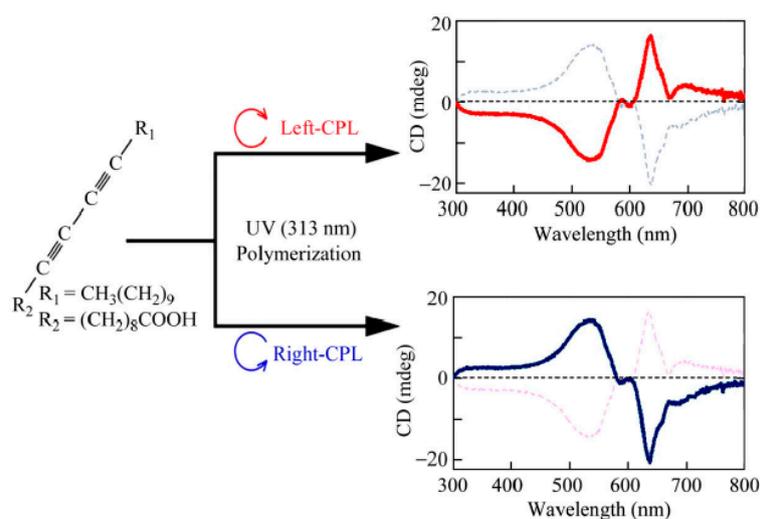


Figure 2. The preparation of chiral polydiacetylene films upon irradiation with left- or right-handed circularly polarized light (reprinted with permission from Reference [57]. Copyright 2006 the Chemical Society of Japan).

Owing to the C-C bond being able to rotate along with the direction of the CPL, a disturbance could be generated in the PDA backbone chains. Thus, the formed PDA, which was irradiated with L- or R-CPL, definitely yielded the opposite chiral polymer. However, upon irradiation with unpolarized ultraviolet light alone, no CD signals could be noticed at the corresponding absorption band for the PDA film. It was reported that visible light could also maintain the polymerization of DA monomers when the number of repeat units of PDA oligomer was more than five. In this case, the enantio-selective polymerization of diacetylene monomers triggered by circularly polarized visible light (CPVL) was realized for the first time (Figure 3). The 532 nm CPVL could effectively offer the chiral information and controlled the handedness of the final PDA chains. This work offered a new method for the synthesis of chiral optical polymers by the visible light region [58].

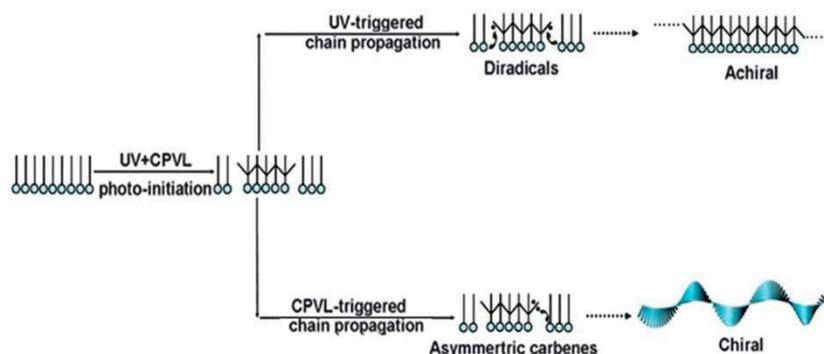


Figure 3. The mechanism of Enantio-selective polymerization of diacetylene (DA) films triggered by circularly polarized visible light (reprinted with permission from Reference [58]. Copyright 2014 The Royal Society of Chemistry).

CPL is one kind of electromagnetic waves and is considered to be a chiral form of light, which exhibits a helical trajectory propagation of the electric field vector [59–61]. However, natural CPL emitted from star formation is usually located in the long-wavelength light such as the IR region, while most chiroptical reactions were induced by ultraviolet light or visible light. Therefore, it was reasonable to extend the chirality induction to the IR region (Figure 4). It was demonstrated that by incorporating NaYF_4 up conversion particles, the enantioselective photoinduced polymerization of achiral benzaldehyde-functionalized DA monomers could be realized with the irradiation of 980 nm CPL, which based on the multiphoton up conversion mechanism. The 980 nm CPL acted as the only chiral source and the screw direction of the chiral polymer chain followed the handedness of 980 nm near CPL. This work paved the way for a deeper understanding of the possible origins of homochirality in living systems [62].

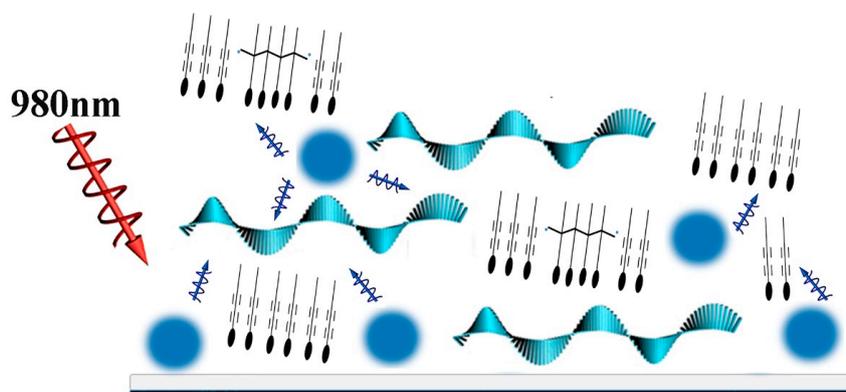


Figure 4. The mechanism of Enantio-selective polymerization of DA films triggered by 980nm circularly polarized light by doping NaYF_4 nanoparticles (reprinted with permission from Reference [62]. Copyright 2017 Wiley).

Moreover, according to the novel method for the synthesis of helical conjugated polymers in a nematic liquid crystal phase reported by Akagi et al., helical PDA structures in the liquid crystal (LC) phase could also be synthesized successfully. In 2014, Xu et al. synthesized the 1,3,5-tris(1-alkyl-1H-1,2,3-triazol-4-yl) benzene (TTB) molecule, and the HB complex was obtained by mixing DA with TTB in a 3:1 molar ratio through the self-assembly method (Figure 5). Interestingly, The DA units in the crystal phase could not form helical chains due to the restriction of the crystal lattice, while in the lamellar columnar mesophase, the molecular motion of the hydrogen-bonded complex was relatively free, and the external CPL could effectively direct the screw orientation of the final PDA chains [63]. This work offered a new method for the fabrication of helical polymers in the liquid crystal phase.

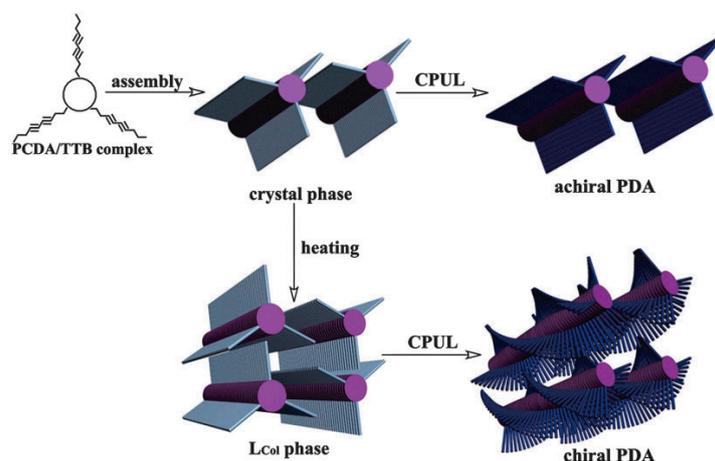


Figure 5. The mechanism of formation helical PDA films in the Lcol liquid crystal state (reprinted with permission from Reference [63]. Copyright 2014 The Royal Society of Chemistry).

In 2018, Zou and co-workers synthesized benzaldehyde-functionalized diacetylene (BSDA) monomers and demonstrated that these DA monomers could be polymerized by the visible light region. Interestingly, super-chiral light (SCL) was introduced to achieve an enhancement in the dissymmetry of BSDA molecules in this work (Figure 6). The super-chiral light was generated by the interference of two circularly polarized lights with the same wavelength, yielding opposite handedness but with a different intensity. It should be noted here that the SCL could generate a greater chiral transfer and amplification than that of the traditional circularly polarized light during the asymmetric photo-polymerization reaction of BSDA monomers. Moreover, the formed helical PDA films irradiated with SCL exhibited an excellent chiral recognition ability and could be utilized to construct a visual sensor for the discrimination of several specific enantiomers. This work offered a new method and might open a pathway for other asymmetric photochemical systems [64].

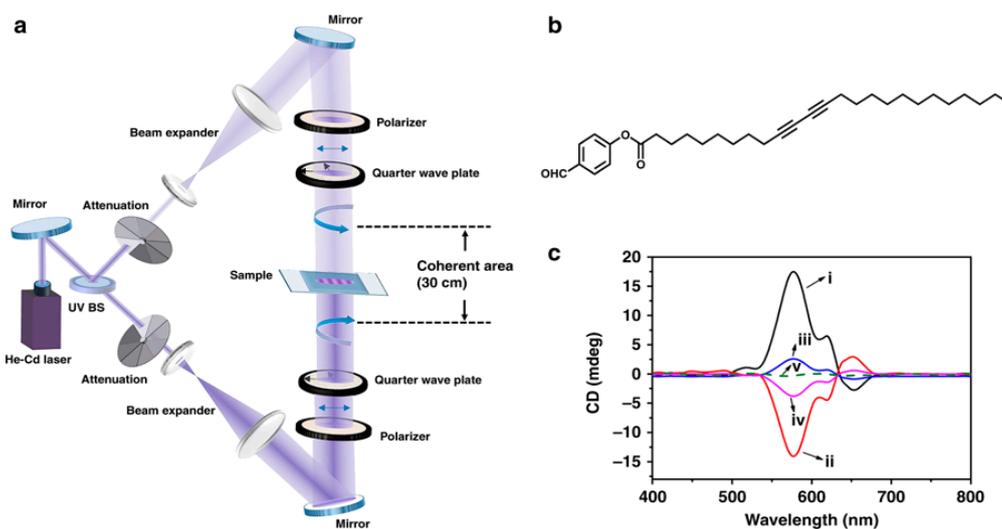


Figure 6. Experimental set-up, molecular structure and CD spectra. (a) Experimental set-up for SCL generated by two counter-propagating CPL waves with the same frequency and opposite handedness. The coherent length of the laser is 30 cm and the optical path difference of the two counter-propagating CPL waves is less than 2 cm; (b) The molecular structure of BSDA monomer; (c) CD spectra of thus-formed PDA films by application of (i) left-handed or (ii) right-handed SCL; (iii) left-handed or (iv) right-handed CPL; (v) LPL, respectively. The wavelength of SCL, CPL and LPL were all 325 nm. The irradiation time was 40 min (reprinted with permission from Reference [64]. Copyright 2018 Springer Nature).

2.2. Enantioselective Synthesis of Chiral Coordination Polymers with CPL

Helical coordination polymers have been widely used in asymmetric catalysis, ferroelectrics, nonlinear optical effects, and chiral resolution [65–67]. Scientists have developed a series of chiral coordination polymers (CCPs) from achiral materials without the doping of any chiral agents. However, it is impossible to predict the absolute configuration of CCPs and the asymmetric synthesis of CCPs remains challenging. With the inspiration of a CPL-triggered solid-liquid mixture of a racemic amino-acid derivative reported by Vlieg et al., Wu and co-workers synthesized the chiral copper (II) CCP $[[P \text{ or } M\text{-Cu}(\text{succinate})(4,4'\text{-bipyridine})]_n] \cdot (4\text{H}_2\text{O})_n$, which adopts a three-dimensional helical configuration (Figure 7), and the enantioselective synthesis of chiral coordination polymers by the visible-light region was successfully obtained (Figure 8). To discover the influence of CPL, final products were separated into two zones, bath in the CPL zone (Light-R, L) or bath in dark zone (Dark-R, L). Moreover, nearly 92 samples were selected during the experiments. In the CPL light zone, the fragment $[\text{Cu}(\text{succinate})]_x$ acted as the chiral center, which could exist in one preferential configuration and directed the helical assembly direction upon irradiating with CPL. The value of enantioselectivity was at most 80% and the helical structure of the crystalline product was the same as that obtained by the irradiation of circularly polarized light. In the visible-light region, circular dichroism effect was relatively weak, and the size of light spot was small than the cuvette, this size mismatch could not effectively offer enough light bath area, all that lead the enantioselectivity could not reach 100%. Interestingly, a similar CD signals were also discovered in the dark zone, but CD spectra demonstrated dissonance, this was attribute to the sharing of one cuvette compared with Light-zone. This work provided a good avenue to control the enantioselective synthesis of coordination polymers [66].

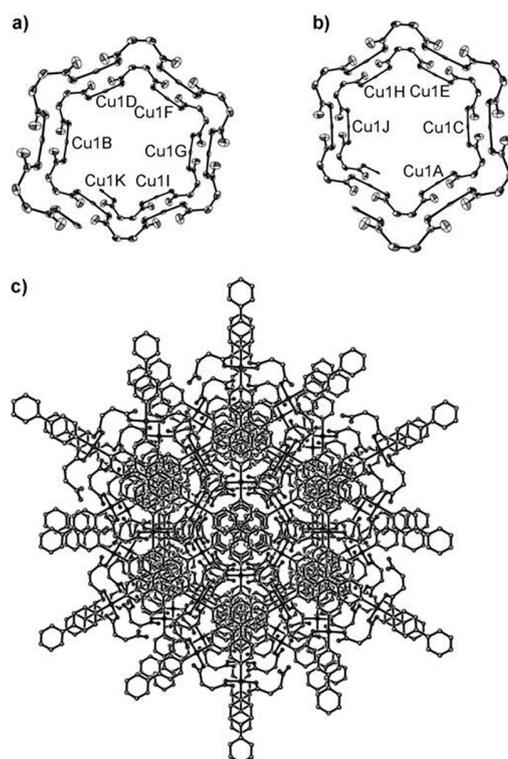


Figure 7. ORTEP plots with thermal ellipsoids set at the 30% probability level showing (a) the right-handed helix of polymeric $[\text{Cu}(\text{succinate})]_n$; (b) the left-handed helix of polymeric $[\text{Cu}(\text{succinate})]_n$, and (c) the overall structure of $[\text{Cu}(\text{succinate})(4,4'\text{-bipyridine})]_n \cdot (4\text{H}_2\text{O})_n$ viewed along the c axis (reprinted with permission from Reference [65]. Copyright 2007 Wiley).

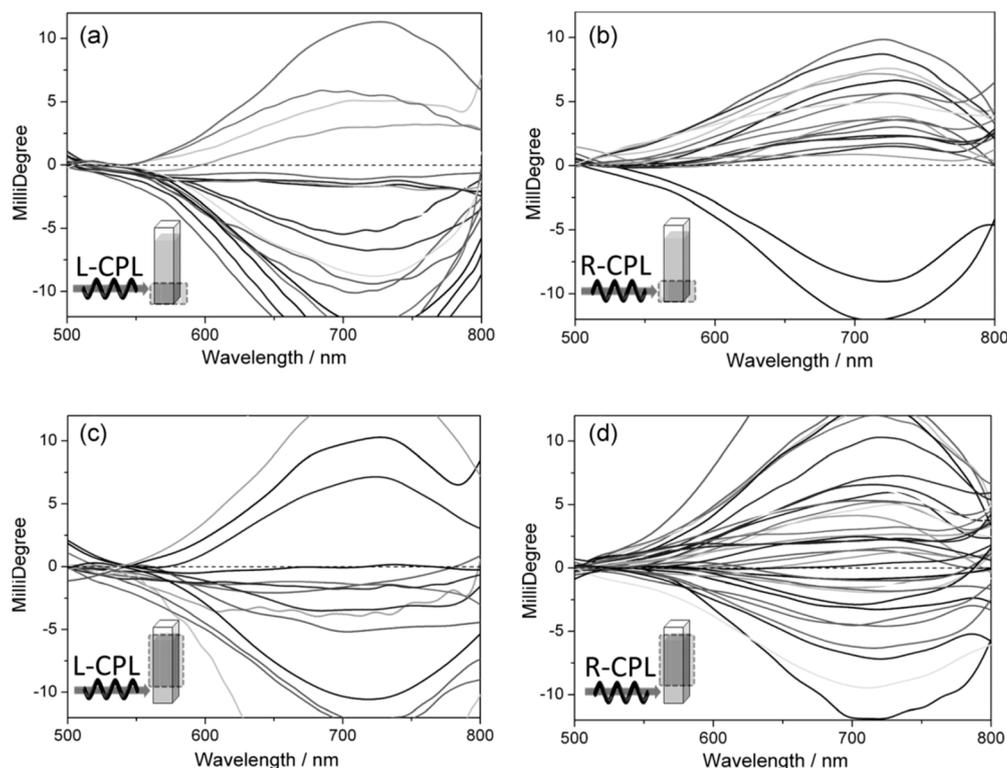


Figure 8. The CD spectra of (a) light-L; (b) light-R; (c) dark-L and (d) dark-R CCPs (reprinted with permission from Reference [66]. Copyright 2014 Wiley).

2.3. Enantioselective Thiol-ene Polymerization Reaction Triggered by CPL

The thiol-ene reaction, which given its high yield, rapid rate, and mild reaction conditions, has been widely used in the synthesis of novel organic compounds and smart functional polymers, especially in surface modification, drug-controlled release and advanced optical materials synthesis. However, how to realize the asymmetric click reaction from a racemic mixture remains a question to be solved. In 2017, the allyl-(1-((3-(dimethylamino)propyl)amino)-4-mercapto-1-oxobutan-2-yl)carbamate (DPAMOC) enantiomers were synthesized, and circularly polarized light was utilized to trigger an asymmetric polymerization reaction by our group. The results demonstrated that without any chiral dopant or catalyst, the chiral optically active polymer could also be obtained from racemic monomers with the irradiation of CPL (Figure 9). Via the CPL-triggered enantioselective polymerization click reaction, chiral linear and hyperbranched polymers were easily synthesized with the CPL acting as the only chiral source. Interestingly, the inducible chiral signals of the final polymers could be flexibly controlled by the handedness of the external CPL as well as the irradiation time. This work paved the way for expanding to other common asymmetric click reactions for the preparation of chiral polymers with controllable enantioselectivity [68].

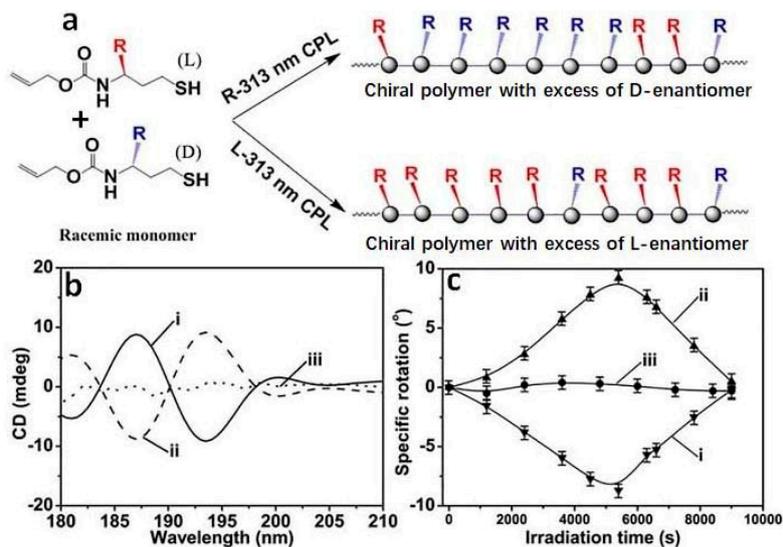


Figure 9. (a) Schematic illustration of preparing chiral polymer from racemic monomers through the asymmetric click polymerization process irradiated by 313 nm CPL irradiation. (b) CD signals and (c) Time-resolved development of the specific rotation values of the final polymer triggered by (i) L-CPL, (ii) R-CPL or (iii) normal UV light, respectively (reprinted with permission from Reference [68]. Copyright 2017 The Royal Society of Chemistry).

3. The Asymmetric Photo-Modulation of Chirality Polymers Based on Circularly Polarized Light

The photo-modulation of chiroptical properties based on functional materials has gained research interest, and the approach could lead to the rapid development of smart materials or devices for reversible information storage. It is believed that chiroptical polymers originate from the properties of natural polymers, which have a specific one-handed helical structure in living matters. However, the single-helical configuration (right- or left-handed) of chiroptical polymers was not stable. With an external physical or chemical stimuli such as light, heating, ions, pH or solvents, the helical configuration could be changed and may be reversed to opposite handedness. Recently, the circularly polarized light-triggered photo-modulation of chiroptical properties has been widely researched in many kinds of photochromophores [69–72]. Herein, the photo-modulation of the chiroptical properties of polymers based on CPL is described.

3.1. Enantioselective Photo-Modulations of Azobenzene Polymers

Polymers that contain azobenzene chromophores have been widely investigated due to their fortunate optical storage properties. Nikolova et al. first reported that with the illumination of circularly polarized light, side-chain azobenzene liquid crystalline polyesters could exhibit a very large circular anisotropy, and the CPL was the only chiral center [73]. An amorphous achiral azobenzene (Azo) liquid crystalline polymer (p4MAN) was synthesized by Iftime et al. With the irradiation of 514 nm CPL, the opposite handedness of CPL produced enantiomeric structures (Figure 10). However, upon switching the handedness of the external CPL, a reversible chiral signal switching between two enantiomeric superstructures of the azobenzene liquid crystalline polymer could be achieved successfully. While after several cycles of switching the handedness of the external CPL, the circular dichroism (CD) signals of the polymers tended to decrease, and this phenomenon was attributed to the orientation of the several azobenzene units which were perpendicular to the Azo film plane. After the photoisomerization, the azobenzene chromophores would exhibit a cis-to-trans transfer, whereby the Azo film plane underwent an angular reorientation. However, several Azo chromophores were also out of the polymer film's plane, and the final numbers of Azo units in the polymer film plane would decrease so that the Azo liquid crystalline polymers exhibited some fatigue, leading to the CD signal decrease [74].

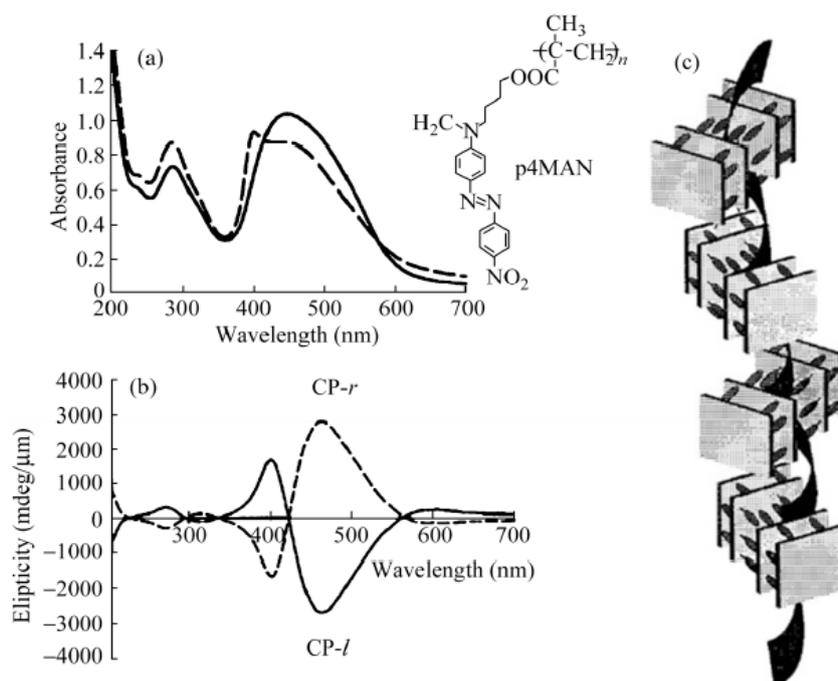


Figure 10. (a) UV-vis absorbance and (b) CD spectra of the p4MAN thin film after irradiating with circularly polarized light; (c) The model of p4MAN to demonstrate the helical arrangement after irradiation with circularly polarized light (reprinted with permission from Reference [74]. Copyright 2000 American Chemical Society).

Ivanov et al. demonstrated that not only the liquid crystalline phase but also the amorphous phase of achiral Azo polymers could form a helical structure upon illumination with CPL (Figure 11). The liquid crystalline orientation represented one of the important factors in the fabrication of chiral superstructure, as the circular momentum could transfer from the CPL to the azobenzene moiety in the polymers [75].

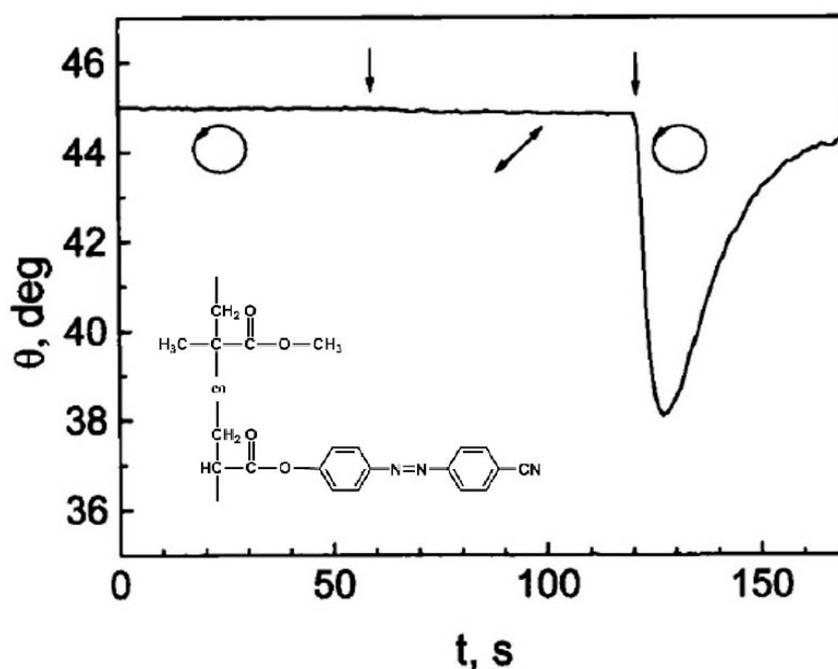


Figure 11. The structure and the rotation of the probe beam azimuth of the Azo polymers (reprinted with permission from Reference [75]. Copyright 2017 Taylor & Francis).

Kim et al. reported the CPL-driven chiral formation based on amorphous azobenzene polymer films, and achiral epoxy-substituted azobenzene polymer PDO3 was synthesized in this work [76]. The amorphous azo polymer chains in the film were in a state of several layers, upon irradiation with left circularly polarized Ar⁺ laser light, the linear polarized beam of the incident light would lead to the azobenzene chromophores orienting in one way, which was perpendicular to the main axis of the incident light (Figure 12). After passing across the first layer, the major axis of the incident light could rotate following the counterclockwise direction. Therefore, the major axis of incident light could rotate the same angle in the same direction after passing through the successive layers and the final optical rotation of the polymer would be extended, thus generating the same handedness helical structure in the amorphous azopolymer. This work not only broadened the asymmetric modulation of Azo containing materials but is of great value to the deep understanding of the mechanisms behind chirality photoinduction.

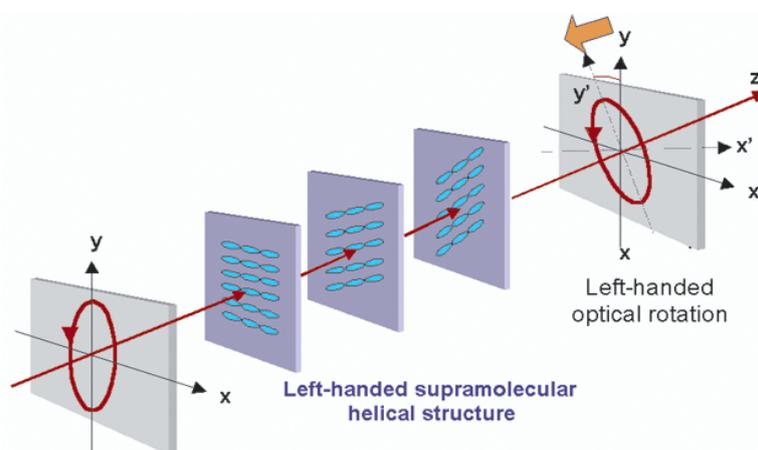


Figure 12. Schematic illumination of a proposed mechanism for the CPL induced chiral helical structure based on an amorphous azopolymer film (reprinted with permission from Reference [76]. Copyright 2000 American Chemical Society).

To further study the influences of the azobenzene chromophores structure and the spacer length during the CPL-triggered helical structure formation, several chiral azobenzene-containing homopolymers were synthesized by Zheng et al (Figure 13). The results indicated that the above samples with a short spacer length (0 or 2) did not generate any CD signals, while those with a longer spacer length (6 or 11) produced clear CD signals. Interestingly, all the films irradiated with 442 nm linearly polarized light displayed a CD signal enhancement in the azobenzene moieties absorbance region between 260 nm and 360 nm. However, the homopolymers with six methylene units demonstrated the largest level of enhancement. During the modulation of the chirality process, the cooperative dipolar interaction with the chiral side chains acted as a key factor in the arrangement of the main chains of the polymers. With longer spacers (chiral side chains), the aggregation level of chiral side chains was higher, which was convenient for the chirality transference and formation of the helical backbones. This work will be of benefit to the design of more sensitive chiral polymers for information storage and chiroptical switching [77].

The chiroptical properties of the azobenzene-substituted diacetylene (NADA) were also researched by Zou et al (Figure 14). With the irradiation of 313 nm circularly polarized ultraviolet light (CPUL), the LB films displayed supramolecular chirality, and evident CD signals were measured by the CD spectra. Consequently, the handedness of the obtained LB films was consistent with that of the CPUL. In this system, the chirality could transfer from the azobenzene units in the side chains to the PDA backbone and could determine the helical direction of the PDA chains. During the chirality transfer process, the stereoregular packing of the azobenzenes was believed to play an important role in the determination of the enantiomeric helical PDA chains. Moreover, the above

chiral LB film (irradiated with right-handed CPUL) was also irradiated with left-handed 442 nm CPL. The azobenzene chromophores first changed their stereoregular packing to the opposite helical manner (L-handed), then lead the PDA chains to form the opposite helical structure. Therefore, the modulation of poly-azobenzene-substituted diacetylene (PNADA) LB film chirality could be achieved easily by the CPL treatment. However, another finding should be noted, by changing the stereoregular packing manner of the azobenzene chromophores, a partial inhomogeneous perturbation force was generated against the chiral arrangement of the Azo chromophores, which was accompanied by generating variations in the weakness of CD signals. In this way, the CD signals would decrease after a few cycles. This research offered a novel model system for the deep understanding of the chirality transfer and modulation based on azobenzene polymers [78].

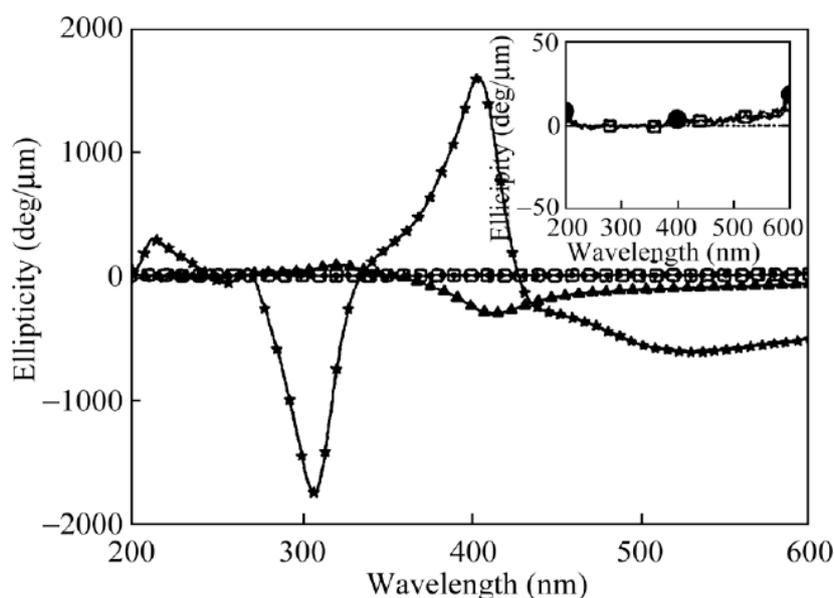


Figure 13. The CD spectra of PM x AP ($x = 0, 2, 6, 11$) film (reprinted with permission from Reference [77]. Copyright 2000 Elsevier).

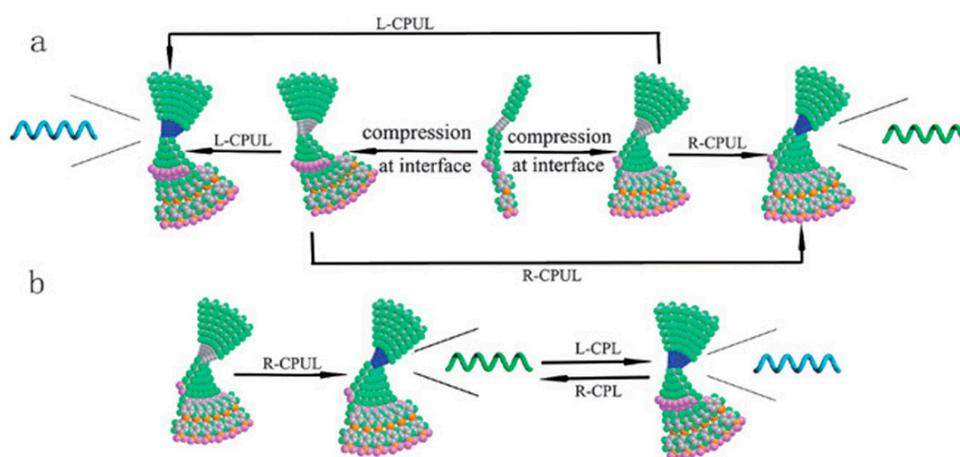


Figure 14. Schematic mechanisms of (a) chirality induced and (b) chirality modulation for PNADA films with CPL treatment (reprinted with permission from Reference [78]. Copyright 2010 The Royal Society of Chemistry).

3.2. Enantioselective Photo-Modulations of Ketone-Containing Polymers

To further study the influence of CPL during the modulation chirality process, ketone-containing polymers have also been researched by several groups. In 1999, Schuster and co-workers synthesized a racemic acrylic-substituted bicyclic ketone, and the cholesteric phase of liquid crystals based on a mixture of 4-cyano-4'-*n*-alkylbicyclohexanes could be obtained upon irradiation with CPL (Figure 15). Owing to the different absorption properties of the isomers in the presence of left- or right-handed CPL, the photoisomerization reaction of racemic acrylic-substituted bicyclic ketones could be triggered and lead to an enantiomeric excess. The chirality could be transferred through the polymer chains and induced the polymer to form the same helical structure. The enantiomeric excess (ee) value of the bicyclic ketone could be easily modulated by controlling the handedness of the CPL and the irradiation time, which could control the screw pitch and the switch from nematic to cholesteric forms of the liquid crystalline materials [79].

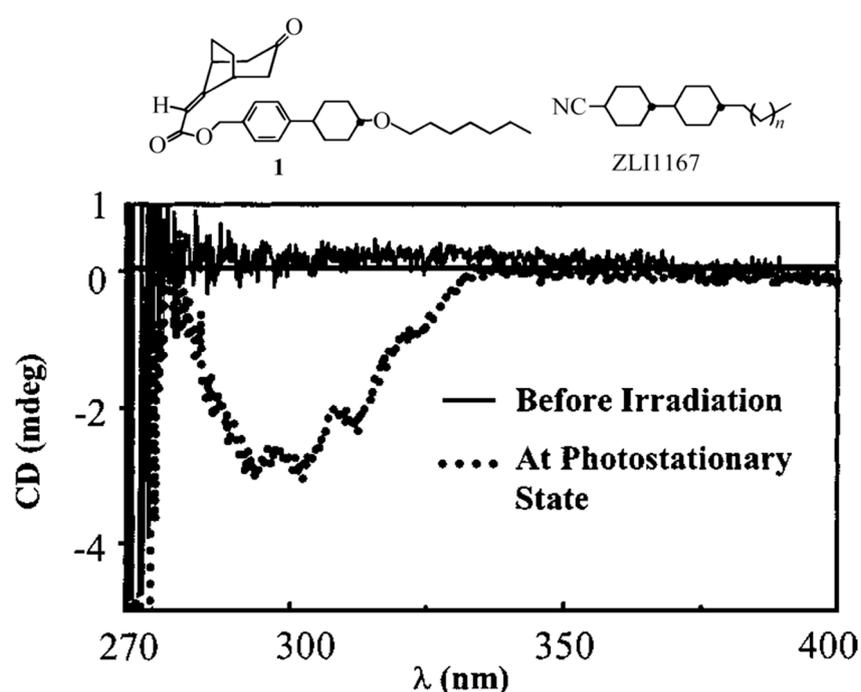


Figure 15. The molecular structure and CD spectra of the racemic samples before and after CPL irradiation (reprinted with permission from Reference [79]. Copyright 1999 American Chemical Society).

With the same idea, Selinger et Al. switched the photoresolvable polymers between mirror images with the tool of CPL in 2000 (Figure 16). The racemic mixture of the ketone-containing group was induced to the polyisocyanate matrix. The polymers first produced no CD signals due to the equal amount of isomers, however, after irradiation with CPL, the polymers could generate a small enantiomeric excess, and noticeable CD signals could be measured in the region of the ketone chromophore. This result demonstrated that circularly polarized light could enforce a disproportionate excess to form a fixed helical structure in the polymers, even with the influence of large proportions of other achiral pendants. Therefore, the helicity of the obtained polymers could be switched reversibly with the alternation of the handedness of the CPL and could also easily return to the original states without a CD signal upon irradiation by plane polarized light [80].

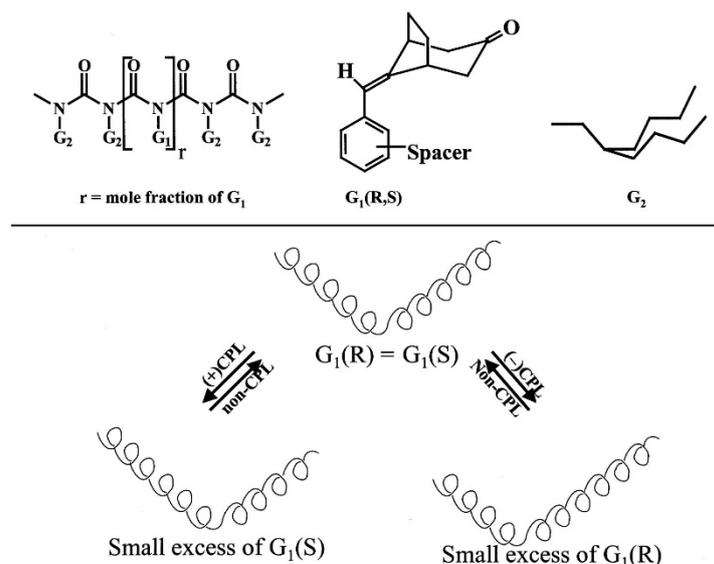


Figure 16. Schematic illumination of the switch between two-handed backbone helices for the polymers irradiated with (+) or (−) circularly polarized light (CPL) or non-circularly polarized light (non-CPL) (reprinted with permission from Reference [80]. Copyright 2000 American Chemical Society).

3.3. Enantioselective Photo-Modulations of Fluorene-Based Polymers

The preparation of optical helical polymers and asymmetric synthesis based on CPL as the only chiral source have been contributing great value and have been gaining increasing attention from researchers. Herein, the CPL-triggered optical chirality induction and asymmetric synthesis of chiral fluorene-based polymers (PDOF) have been outlined.

Similar to diacetylene, the structure of PDOF polymers also has no chiral center, due to the single bonds of the fluorene units could be rotated. Therefore, the exchange between the two conformations (P- and M-twists) can be achieved, and the enrichment of enantiomeric excess can also be obtained by external stimuli, such as CPL. In 2012, Nakano et al. prepared an achiral polymer film based on the poly(9,9-di-n-octylfluoren-2,7-diyl). After irradiating with R-CPL for 6 min, the optically active PDOF film displayed intense negative CD signals (CD-1, π - π^* transition, approximately 400 nm) (Figure 17). Interestingly, upon irradiating with L-CPL for 6 min, the CD signal of the PDOF film (CD-2) disappeared completely. After additional irradiation with L-CPL for 6 min, an intense positive CD signal could be noted at the same CD bond (CD-3), the spectra of CD-1 and CD-3 were almost symmetrical. Therefore, the helical structure could be reversibly modulated with CPL [81].

In order to obtain a better understanding the mechanism during chirality induction and the switching process of PDOF when irradiated by CPL, simulations of the chirality-switching free-energies based on poly(9,9-dioctylfluoren-2,7-diyl) (PDOF) were calculated not only on an amorphous silica surface but also in the vacuum phase by Nakano and co-workers (Figure 18). Based on the free-energy landscape analysis, the achiral-to-chiral switching of PDOF occurred easily only on the matrix of amorphous silica, where the activation free-energy was calculated to be 35 kcal mol^{-1} . The interactions between PDOF and amorphous silica played an important role during the chirality switching. Compared with PDOF in the solution state or in a suspension, the fluorene-fluorene dihedral of a PDOF film which was deposited on quartz glass could be twisted in a stepwise manner with the irradiation of external CPL [82].

In 2013, for the first time, Fujiki et al. achieved the mirror symmetry breaking of achiral azobenzene-alt-fluorene copolymer particles under the condition of optofluidic organic solvents as well as with CPL irradiation (Figure 19). It was demonstrated that the medium of optofluidic organic solvent, the wavelength, irradiation time and the ellipticity of the external CPL played important roles in the chirality generation, switching, racemization and retention of the copolymer particles. The CPL

could trigger the two conformations (P- and M-twists) with asymmetric broken, and the enrichment of one enantiomeric excess could be finally obtained. With continual switching of the CPL handedness, the reversible modulation of chirality in the fluorene-alt-azobenzene copolymer particles could be achieved successfully [83]. This research would be helpful for the design of smart memory devices with the use of the nanosized supramolecular assembly.

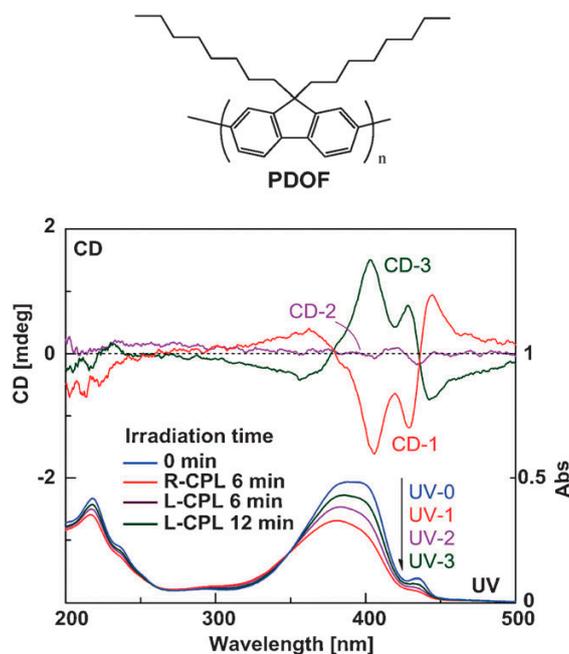


Figure 17. Molecular structure, CD and UV spectra switches of PDOF film upon irradiation with different handedness CPL for different times (reprinted with permission from Reference [81]. Copyright 2012 The Royal Society of Chemistry).

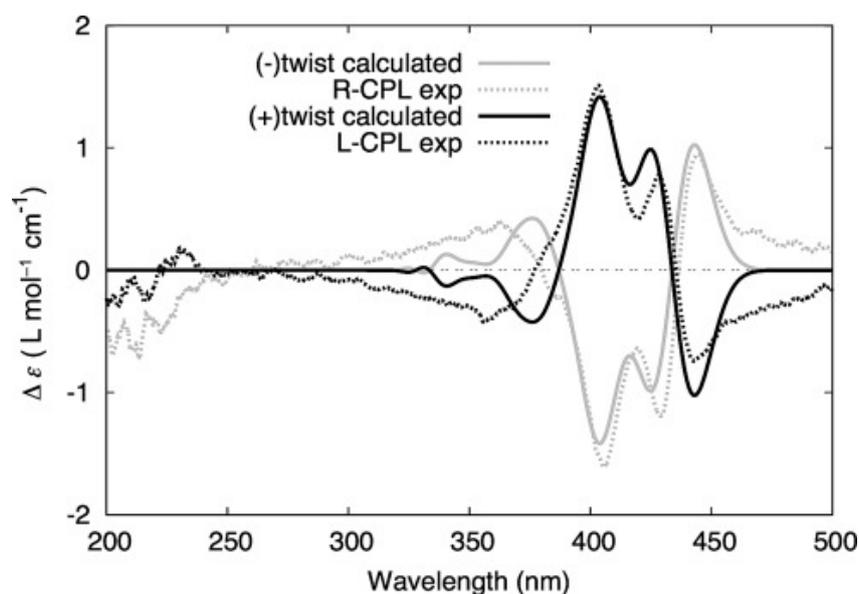


Figure 18. The ECD spectra for the calculated at the ZINDO level for the negative (–) and positive (+) twist basins of poly(fluorene-2,7-diyl) with the relating experimental spectra recorded after CPL irradiation for 6 min (reprinted with permission from Reference [82]. Copyright 2015 Wiley).

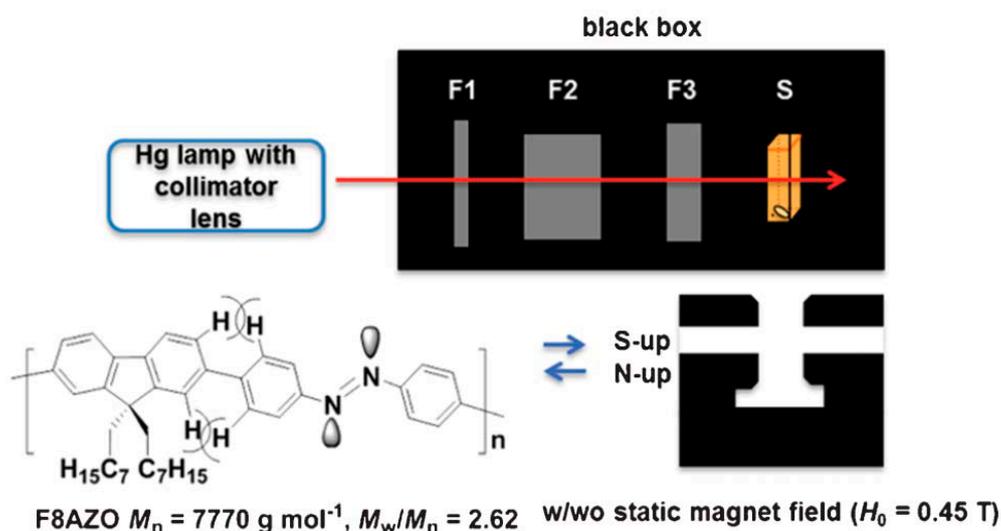


Figure 19. Schematic representation of setup for CPL triggered chirality induction and modulation in a solution of F8AZO particles by r-/l-CPL (reprinted with permission from Reference [83]. Copyright 2013 The Royal Society of Chemistry).

4. Conclusions

Homochirality is one of the universal geometric properties and has garnered remarkable interest in recent years. The circularly polarized light-triggered asymmetric polymerization and photo-modulation of chirality in polymers have gained considerable attention owing to the hypothesis that CPL could transfer single chirality signals to polymers. Moreover, the asymmetric chemical reaction based on CPL displayed several advantages including the purity of products without any chiral dopants or catalysts, and the facile adjustment of CPL parameters such as intensity, wavelength, polarization and interference. Outstanding examples of the asymmetric synthesis of homochirality in polymers, which are based on the effective CPL irradiation technique for control of the molecular asymmetry would help us acquire a better understanding of the mechanisms during single chirality formation, transfer, amplification and modulation. Although significant progress on single chirality induced by CPL has been made in recent years, the abundance of room for growth in this area also needs further research attention, including (1) the fabrication of monomers with a more efficient response to CPL with a large enantiomeric excess. (2) The utilization of CPL in the long-wavelength region to expand the number of chiral materials for potential applications, owing to the fact that CPL emitted from the universe is located in the infrared region. We hope this mini-review allows researchers to find new ways to fabricate chiral materials with more efficiency for applications of photolysis and photosynthesis as well as chiral recognition and to greater understand the probable origin of homochirality in living matter.

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