



Rapid limonene-induced mirror symmetry breaking in achiral polyfluorene containing pendant crown ether groups: Enhanced by ion complexation



Jingjing Liu^a, Yin Zhao^a, Hailing Chen^a, Zhengbiao Zhang^a, Wei Zhang^{a,*}, Xiulin Zhu^{a,b}

^a Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu, China

^b Silicon Lake College of Vocational Technology, International Business Zone Huaqiao, Kunshan 215332, Jiangsu, China

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ABSTRACT

A novel circular dichroism (CD)-silent π -conjugated polyfluorene bearing the bulky crown ether pendant (**PF8C4**) as the potassium ion binding site was successfully prepared by polymerization of the corresponding monomers with palladium catalyst. The polymer containing polar groups was found to form the eximious helical assembly by aggregating in chiral limonene at a lower temperature. The aggregates obtained from *R*- and *S*-limonene exhibited mirror-image CD peaks in the UV–vis region of polymer backbone. Therefore, the chirality of enantiopure limonene was successfully transferred to the optically inactive **PF8C4**, and the relative *P*- and *M*-helical supramolecules were successfully prepared. Moreover, after appending K^+ ion to the helical supramolecules, the complexation between the K^+ ion and the crown ether pendant helped to strengthen the optical activity, and thus more stable optically active supramolecular structures were achieved.

1. Introduction

Optically active π -conjugated polymers have attracted considerable attention for their potential applications in stereoscopic optical and circular polarization-based photoelectric device materials [1–2]. Among the numerous methods reported for the preparation of chiral materials, asymmetric polymerization is the earliest and most reported method [3]. Recently, many external chirality sources have been successfully used to obtain supramolecular chirality from achiral sources, such as liquid crystal chirality, [4,5] chiral solvation, [6,7] circularly polarized photon chirality, [8–11] and polymer chirality transfer [12,13]. Among these methods, chirality transfer from small chiral guest molecules to achiral host π -conjugated polymers has been one of the most environmentally friendly methods to prepare optically active materials because it requires neither a tedious synthesis process nor expensive chiral reagents. The chiral-solvation-induced chirality to induce the helical preference of achiral poly(*n*-hexyl isocyanate) was first explored by Green et al. [6] Subsequently, a series of main-chain and side-chain polymers were also found as good candidates for chiral solvation method to achieve supramolecular chirality [14–23]. Supramolecular chirality is achieved by the intermolecular interactions between chiral solvent molecules and polymer chains, including hydrogen bondings, van der Waals forces, and π – π interactions. In most of

previous studies, mix solvents (good solvent/poor solvent/chiral solvent) were used to generate polymer assemblies; however, chiral nanoparticles were observed only with transmission electron microscopy (TEM). Recently, our group successfully achieved supramolecular chirality from achiral poly(9,9-dioctylfluorene) (**PF8**) in neat limonene and clearly observed the *P*- and *M*-helical fibers by AFM technology [24].

Previous studies mostly focused on achieving supramolecular chirality using chiral small molecules as inducer by weak inter- or intramolecular interactions [25,26]. This supramolecular chirality is sometimes constitution dynamic; therefore, more attention has been paid on enhancing or fixing the supramolecular chirality [27–32]. As we know, crown ether-based molecular recognition motifs possess good reversibility and convenient enviro-responsiveness [33,34]. The host–guest interaction between the crown ethers and guest molecules has been actively involved in fabricating various topologic supramolecular polymers with novel properties and potential applications [35–39]. Li et al. reported that poly(phenylene vinylene) bearing crown ether substituent could self-assemble into wormlike nanoribbons through the complexation with K^+ in dilute chloroform solution [37]. They proposed that a 2:1 sandwich complex is formed between K^+ ions and crown ether substituents, thus enabling a closer interaction between the two polymer chains. Furthermore, Swager et al. tuned this interpolymer

* Corresponding author.

E-mail address: weizhang@suda.edu.cn (W. Zhang).

interaction induced by K^+ ions by controlling the steric bulk 15-crown-5 pendants and their distance in a single polymer main chain, which could be further functionalized as potassium sensory materials [40]. To exploit the relationships between crown ether polymers and small chiral molecules, Yashima et al. discovered that a stereoregular poly(phenylacetylene) bearing the aza-15-crown-5 ether as the pendant evidently forms a one-handed helical conformation by chirality induction from chiral amino acids, amino alcohols, and amines [41]. Notably, reports concerning the preparation of optically active crown-ether-based supramolecules from achiral polymers induced by chiral solvation are relatively rare. All these successful studies intrigued us whether supramolecular chirality could be induced in neat chiral limonene and be further enhanced or fixed by complexation with K^+ ions. Therefore, in our experiment, a novel achiral polyfluorene derivative containing polar pendant crown ether group was designed instead of traditional alkyl pendants to enhance or fix the supramolecular chirality, which was prepared by Suzuki coupling polymerization method. The supramolecular assembly processes of optically inactive **PF8C4** were then investigated in enantiopure limonene, and the relative *P*- and *M*-helical supramolecules were successfully obtained. Moreover, after appending K^+ ions to the helical supramolecules, the optical activity was further enhanced by the complexation between the K^+ ion and the crown ether pendant.

2. Experimental section

2.1. Materials

Tetrakis(triphenylphosphine)-palladium(0) (97.0%, Tokyo Chemical Industry (TCI)), 2-bromoethanol (97%, J & K Scientific), 3,4-dihydro-2*H*-pyran (99%, Acro Organics), 2,7-dibromofluorene (97%, J & K Scientific), triethylene glycol (95%, J & K Scientific), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-octylfluorene (98.0%, J & K Scientific), 2,7-dibromo-9,9-di-*n*-octylfluorene (98.0%, TCI), tricyclohexylphosphonium tetrafluoroborate (98%, Ark Pharm), cesium fluoride (99.99%, Tansoole), tetrabutylammonium bromide (99%, Aladdin), and tris(dibenzylideneacetone)dipalladium (98%, Adamas) were used as received. Potassium bis(trimethylsilyl)amide (1.0 M solution in THF, Adamas) was used after evaporating into solid powder in nitrogen atmosphere. (*R*)-(+)-limonene (1*R*, > 95%, $[\alpha]_{589}^{24} = +99.62^\circ$, TCI) and (*S*)-(-)-limonene (1*S*, > 95%, $[\alpha]_{589}^{24} = +97.72^\circ$, TCI) were used without further purification. All the other chemicals were obtained from Shanghai Chemical Reagents and used as received. Compounds 1–5 were synthesized according to the previous literature, and their purification methods were modified [42]. Polymers (**PF8C4**, **PF8**, and **PC4**) were prepared by polymerizations of the corresponding monomers with palladium catalyst (Scheme 1). **PF8C4**: $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS, 25 °C): δ (ppm) 0.53–2.24 (m, octylfluorene), 2.31–2.75 (s, crown ether), 3.29–4.04 (m, crown ether), 8.25–7.42 (m, aromatic region), $M_n = 56,000$ g/mol, $M_w/M_n = 1.96$. **PF8**: $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS, 25 °C): δ (ppm) 0.55–1.37 (m, $\text{CH}_2 + \text{CH}_3$), 1.91–2.33 (s, CH_2), 7.44–8.05 (m, aromatic region), $M_n = 54,000$ g/mol, $M_w/M_n = 1.30$. **PC4**: $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS, 25 °C): δ (ppm) 1.59–1.89 (s, CH_2), 2.30–2.71 (s, CH_2), 3.33–3.97 (m, CH_2), 7.52–8.15 (m, aromatic region), $M_n = 27,600$ g/mol, $M_w/M_n = 2.05$.

2.2. Measurements

The CD spectra were recorded on a JASCO J-815 spectropolarimeter (JASCO China, Shanghai, China) at 25 °C equipped with a Peltier-controlled housing unit, using the SQ-grade cuvette, a single accumulation, a path length of 1 cm, a bandwidth of 2 nm, a scanning rate of 200 nm min^{-1} , and a response time of 1 s. The UV–vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer (Shimadzu China, Shanghai, China). Fluorescent spectra were measured on a PerkinElmer

LS-50B spectrofluorometer with a scanning rate of 1200 nm min^{-1} , an excitation bandwidth of 2 nm, a monitoring bandwidth of 5 nm, and 352 nm as excitation wavelength at 25 °C. The proton nuclear magnetic resonance ($^1\text{H NMR}$) spectra of the samples were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. NMR samples were prepared with concentrations of 10–20 mg/mL in CDCl_3 or $\text{DMSO-}d_6$. The $^1\text{H NMR}$ spectra were referenced to δ 7.26 ppm in CDCl_3 or δ 2.50 ppm in $\text{DMSO-}d_6$. The number-average molecular weight (M_n) and polydispersity ($D = M_w/M_n$) of the polymers were measured by using a HLC-8320 size exclusion chromatograph (SEC, TOSOH) equipped with a refractive index detector and UV detectors using two TSKgel Super Multipore HZ-N columns (4.6 × 150 mm, 3 μm particle size) in series, with molecular weights ranging from 7 × 10² to 2 × 10⁵ g/mol. Tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL min^{-1} and 40 °C. The molecular weights were calculated with polystyrene standards.

2.3. Preparation of optically active **PF8C4** aggregates

PF8C4 was well dispersed in enantiopure *R*-limonene (1*R*) or *S*-limonene (1*S*) ($c = 4 \times 10^{-5}$ mol L^{-1} in repeating unit) by stirring the mixtures for 30 min at 120 °C. The solution was then cooled down to room temperature and further filtered through a 0.45- μm PTFE filter to remove dust particles. Afterwards, 3 mL solution was added into a quartz cell (optical length = 1 cm) equipped with a stopcock. The solutions were subsequently cooled for a certain period at four low temperatures (0 °C, –10 °C, –20 °C, and –30 °C), and optically active **PF8C4** aggregates in 1*R* or 1*S* at each temperature were successfully prepared.

2.4. Addition of potassium ions

Potassium bis(trimethylsilyl)amide was first well dispersed in enantiopure 1*R* or 1*S* ($c = 0.12$ mol L^{-1}), and then, 10 μL of this potassium ion solution was transferred into corresponding optically active **PF8C4** aggregates. After complete mixing with the aggregates for 6 h at room temperature, the corresponding CD spectra were subsequently measured.

3. Results and discussion

3.1. Characterization of **PF8**, **PC4**, and **PF8C4**

To accelerate the supramolecular assembly process of achiral polyfluorene in neat limonene and to optimize the assembling condition, a novel achiral polyfluorene derivative **PF8C4** containing polar crown ether pendant was prepared through Suzuki coupling polymerization between 2,7-dibromo-9,9-dioctylfluorene and crown-containing fluorene monomer (**5**). Meanwhile, homopolyfluorenes, **PF8** and **PC4**, were also prepared. Scheme 1 illustrates their synthetic routes. The monomers and polymers were synthesized according to the procedures reported previously [42]. Their structures were satisfactorily identified by the corresponding $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra (Fig. S1). Assignments of each proton and carbon agree well with the proposed molecular structures. In particular, the chemical shifts at around 3.2–4.3 ppm (b) and 2.5 ppm (c) were assigned to the methylene protons of crown ether substituents in **PF8C4** and **PC4**. The number-average molecular weights and polydispersity indices for **PF8C4**, **PF8**, and **PC4** were 56,000, 54,000, and 27,600 and 1.96, 1.30, and 2.05, respectively (Fig. S1). Glass-transition temperatures (T_g) for **PF8C4** and **PF8** were evaluated by DSC characterization as 105 °C and 84 °C, respectively (Fig. S2). The higher T_g of **PF8C4** than that of **PF8** indicates that the strong dipole–dipole interaction between side polar crown ether pendants may decrease the distance between polymer chains, which probably benefits for the intermolecular interactions between

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