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Journal Name

New fluorene-based chiral copolymers with unusually high optical activity in pristine and annealed thin films

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Polyfluorene (PF)-based chiral alternating copolymers, i.e., PFPh and PFTh, were successfully synthesized to obtain high circular dichroism (CD) in pristine thin films. By tethering chiral side-chains to the fluorene moiety, the resultant PFPh and PFTh films intriguingly exhibited high CD even in pristine films, which was attributed to the relatively low steric hindrance between the repeating units and intermolecular interactions between the polymer chains. Compared to PFTh bearing a five-membered heteroaromatic thiophene monomer, PFPh containing a six-membered aromatic benzene monomer, showed significantly enhanced CD in an annealed film. Of particular importance, results of optical microscopy and atomic force microscopy can be used to assess the CD of a chiral polymer thin film after thermal annealing.

Introduction

Although chiroptical properties are often observed in biomaterials and organic small molecules, optically active π-conjugated polymers have attracted significant attention because of their high chiroptical properties in thin films.[1-16] The highly transparent and homogeneous thin films of these polymers are easily formed using solution-processing techniques such as dip-coating, spin-coating, and drop-casting. Moreover, the circular dichroism (CD) of these thin films could be significantly enhanced through typical thermal annealing, which is better than other methods such as self-assembly or gelation in the solution state.[17,18] These conjugated polymers exhibit strong absorption and CD signals in the visible-wavelength range, which is in contrast to many naturally occurring chiroptical polymers such as proteins, DNA, and cellulose.

To achieve conjugated polymers with high chirality, many kinds of conjugated polymers have been designed, synthesized, and characterized through the introduction of optically active side-chain moieties. For example, a general approach involves the incorporation of phenylene-*alt*-phenylene or phenylene-*alt*-acetylene units into polymer chains such as poly(*p*-phenylene),[2] poly(*p*-phenylacetylene),[3,4] and polythiophene derivatives.[5-8]

Although the molecular structures of those polymers were modified using various chiral alkyl side-chains and repeating groups to ensure the chiral properties, they still suffered from low CD in the film state. Exceptionally, fluorene-based polymers with chiral alkyl side-chains are one of the more successful chiroptical materials. Fluorene-based homopolymers or copolymers have been reported to exhibit better chiroptical properties in thin films than other polymers.[9-16]
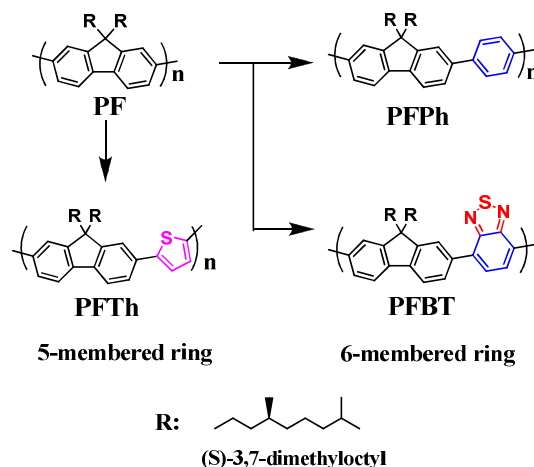

Figure 1. Molecular structures of π-extended fluorene-based chiroptical copolymers.

However, compared to fluorene-based conjugated homopolymers containing various chiral alkyl side-groups, copolymers with π-bridges such as five- or six-membered aromatic rings in the repeating unit have been less studied. Additionally, it has been suggested that the chirality of fluorene-based polymers in film states significantly depends on the annealing temperature and time.

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Electronic Supplementary Information (ESI) available: [DSC curves, PL spectra, absorption and CD spectra, and torsional potential energies of all polymers]. See DOI: 10.1039/x0xx00000x
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Therefore, it is worth determining if the chirality of polymers both in pristine and annealed films can be controlled through the incorporation of aromatic units in the backbone of a fluorene-based copolymer.

In this work, we synthesized a series of fluorene-based chiroptical copolymers with various π-extended bridges, such as thiophene, benzene, and benzo[*c*][1,2,5]thiadiazole (BT), which are expected to reduce the steric hindrance between the chiral alkyl-substituted fluorenes in the polymer backbone, as shown in **Figure 1**. All copolymers (i.e., **PFPh**, **PFTh**, and **PFBT**) showed significantly different UV-vis absorption and CD spectra in the visible region between 300 and 550 nm. It is very intriguing that the relatively high CD of the **PFPh** and **PFTh** copolymers was observed even in pristine films. In particular, the CD of the **PFPh** polymer bearing six-membered benzene rings was significantly enhanced in annealed film. It is very different from that of **PFTh** containing five-membered thiophene rings. Additionally, the chirality observed in a PFTh:HAuCl$_4$ blend film was recovered after exposure to hydrazine vapor; this reveals the possibility of new applications for vapor phase–sensing in the solid state.
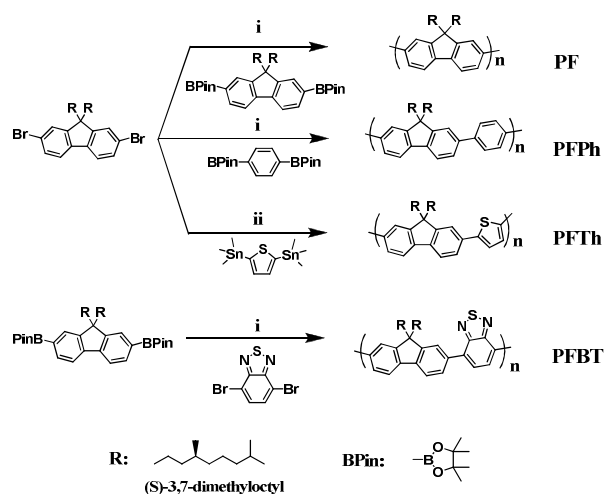
Scheme 1. Synthetic procedure for PF-based chiroptical polymers: i) Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_3$, Aliquat 336, toluene, 100 °C, 12 h and ii) Pd(PPh$_3$)$_4$, toluene, 100 °C, 5 h.

Results and discussion

Synthesis and characterization

The general synthetic procedures for the homopolymer and copolymers are outlined in **Scheme 1**. **PF** and **PFBT** were synthesized following the reported procedure.[11] The **PFPh** copolymer was prepared *via* Suzuki coupling polymerization of 2,7-dibromo-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene with 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. The **PFTh** copolymers were synthesized *via* Stille coupling of 2,7-dibromo-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene with 2,5-bis-(trimethylstannyl)thiophene. To remove the low mass compounds and byproducts, the crude polymers were purified *via* successive Soxhlet extraction using

methanol, acetone, hexanes, and chloroform. All polymers showed good solubility in methylene chloride, tetrahydrofuran (THF), chloroform, and halogenated aromatic solvents. Gel permeation chromatography (GPC) was employed to measure the molecular weights and polydispersity indices (PDIs) of the synthesized polymers. The number average molecular weight (M_n) values of **PF**, **PFPh**, **PFTh**, and **PFBT** were 7.7, 9.2, 7.7, and 8.7 kDa, respectively. Other measured and calculated parameters are tabulated in **Table 1**. The endothermic transition temperature (T_{trans}) values obtained from differential scanning calorimetry were 56, 64, 57, and 73 °C for **PF**, **PFPh**, **PFTh**, and **PFBT**, respectively (**Figure S1**). The T_{trans} values of PF and PFBT were slightly higher than those in literature because of their larger molecular weight. Additionally, the T_{trans} values of the copolymers were higher than that of **PF** as a homopolymer. It is probable that the copolymers have relatively small molar ratios of alkyl groups to the aromatic backbone per repeating unit.

Optical properties and theoretical calculations

To investigate the optical and chiroptical properties of PF-based polymers, thin films were prepared by spin-coating a solution of the polymer in chloroform/monochlorobenzene (9:1 v/v). A co-solvent system comprising both low and high boiling-point solvents was employed to generate smooth homogeneous films.[11] Optical properties of polymer films made with chloroform and monochlorobenzene solutions were measured and the results were illustrated in **Figure S2**-**S5**. The UV-vis absorption spectra of the PF-based polymer solutions and thin films are illustrated in **Figure 2**, and the measured parameters are summarized in **Table 1**.
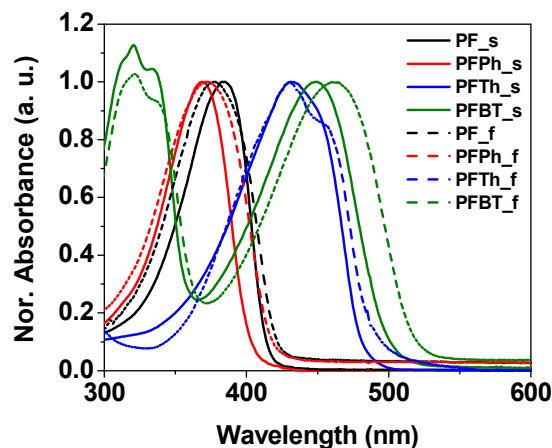

Figure 2. UV-Vis absorption spectra of PF-based chiroptical polymers in solution (solid line) and as thin-films (dashed line).

Compared to those of the **PF** homopolymer, the absorption bands of copolymers **PFTh** and **PFBT** showed large bathochromic spectral shifts; this indicates that thiophene, as a strongly electron-donating unit, and BT, as an electron-withdrawing unit, effectively modulated the HOMO/LUMO levels and reduced the energy band-gap.
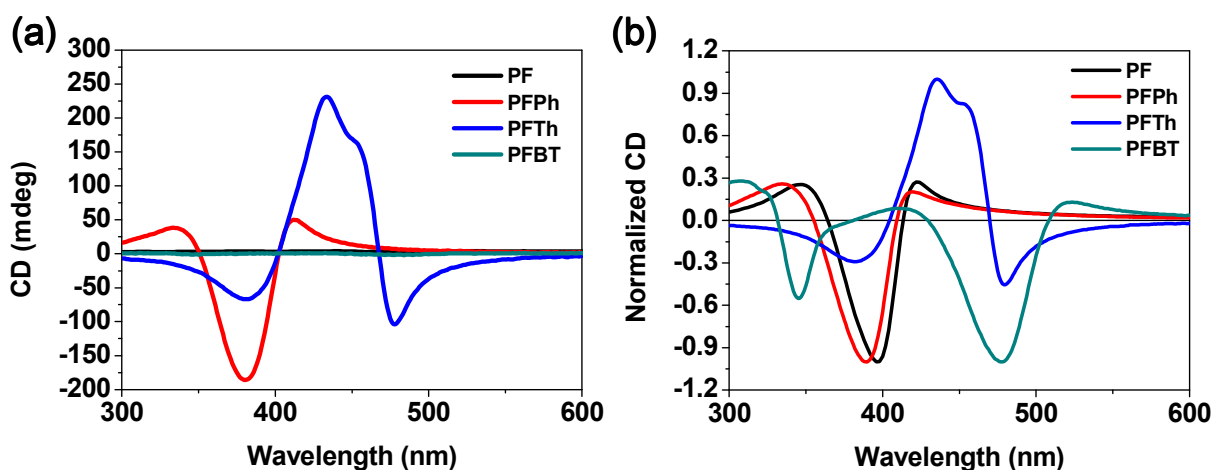
Figure 3. CD spectra of **PF**-based chiroptical polymers in (a) pristine and (b) annealed films.

Table 1. Physical and optical properties of the synthesized chiral polymers.

Polymer	M_n (kDa)	PDI	Pristine film			Annealed film (120 °C)		
			Abs (nm)	CD (nm)	FOM [a] (deg)	Abs (nm)	CD (nm)	FOM [a] (deg)
PF	7.7	1.98	379	-	-	379	403 (n)	-8.30 (409nm)
PFPh	9.2	1.74	375	380 (n)	-0.42 (383 nm)	375	388 (n)	-4.80 (393 nm)
PFTh	7.7	2.69	432	434 (p)	+0.44 (434 nm)	453, 429	436 (p)	+0.67 (436 nm)
				478 (n)	-0.58 (478 nm)		480 (n)	-0.90 (480 nm)
PFBT	8.7	1.85	459, 321	-	-	459, 321	477 (n)	-11.9 (485 nm)
							346 (n)	-5.90 (351 nm)

[a] FOM is figure of merit (FOM = CD(deg)/absorbance). *(n) and (p) are the negative and positive bands, respectively.

These results indicate that the optical properties of **PF**-based copolymers can be easily tuned by introducing aromatic units with different electron densities. The photoluminescence spectra of four chiral polymers are displayed in **Figure S6**.

In past studies, it was usually found that chiral alkyl chains containing polyfluorene derivatives displayed high CD in annealed thin films but weak or no CD in the pristine films.[19] Additionally, to generate fairly high CD, some **PF**-based chiral polymers had to be thermally annealed at a high temperature for a long time.

Figure 3 shows the CD spectra of **PF**-based chiroptical polymers in pristine and annealed film states. **PF** and **PFBT** exhibited the same CD, which is consistent with previously reported results.[11] In contrast, **PFPh** and **PFTh** displayed high CD in both pristine and annealed films. The CD spectrum of **PFPh** shows a strong negative band at 380 nm while that of **PFTh** exhibits medium-intensity negative and high-intensity positive CD bands at 390 and 467 nm, respectively. Compared to the **PF** homopolymer, the **PFPh** copolymer bearing benzene showed similar absorption and CD spectra while the **PFTh** copolymer, which contains thiophene, exhibited different CD; this indicates that the CD signal changes sign approximately at the center wavelength of the main $\pi-\pi*$ transition, which is called the Cotton effect.

In order to ensure that the CD spectra really reflect chirality of the films, linear dichroism (LD) spectra of polymer films were measured. It was found that four polymers did not show significant linear dichroism effects in pristine and annealed films (**Figure S7**).

The high chiral activity of **PFPh** and **PFTh** in pristine films could not be explained through the typical characteristics of planarity and the dihedral angles between the repeating units in the polymer backbone. As shown in **Figure 4a**, the optimized geometries of the simplified molecular structures had out-of-plane geometries with high twist angles of around 25.43–38.67°; these results do not correlate well with the optical activity.
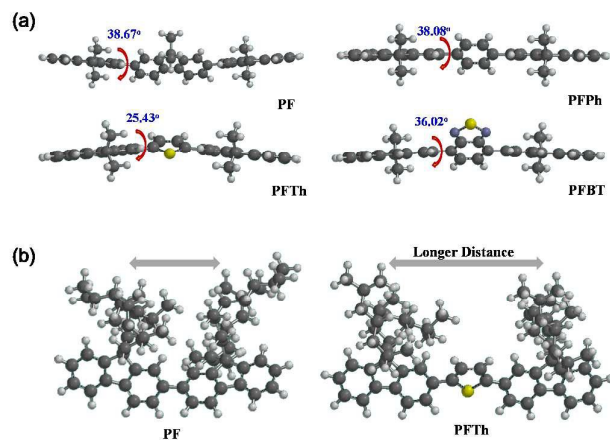

Figure 4. (a) Optimized molecular geometries of the PF-based chiroptical polymers with dihedral angles, and (b) the effect of the alkyl chain distance of PF and PFTh (DFT method, B3LYP/6-31G*).

Therefore, these unusual phenomena must be explained in an alternate way. The potential energies of the simplified structures as a function of the torsion angles were obtained *via* theoretical calculations and are shown in **Figures S8** and **S9**. There are significant differences in the torsional potentials of the four simplified structures: F-Ph in **PFPh** has the lowest torsional potential; in contrast, F-BT in **PFBT** has the highest torsional potential. This indicates that the formation of a helix structure is more favorable for **PFPh** in pristine films. The high torsional potential of **PFBT** could be due to charge transfer from F to the BT unit. Additionally, the **PF** homopolymer was composed of closely connected fluorenes bearing two bulky chiral alkyl chains; these interrupt the uniform orientation of the polymer main chain through higher steric hindrance between the chiral alkyl groups than that in **PFPh** and **PFTh**, as shown in **Figure 4b**. **PFBT**, which contains bulky and electron-deficient BT units, had higher steric hindrance between F and the BT units, which induced strong intermolecular interactions between polymer chains. Therefore, the **PF** and **PFBT** films must be treated thermally to generate helix structures. In contrast, the molecular structures of **PFPh** and **PFTh** have less steric hindrance and fewer intermolecular interactions. Therefore, the polymer chains could re-organize to generate optical activity during spin-coating and drying.
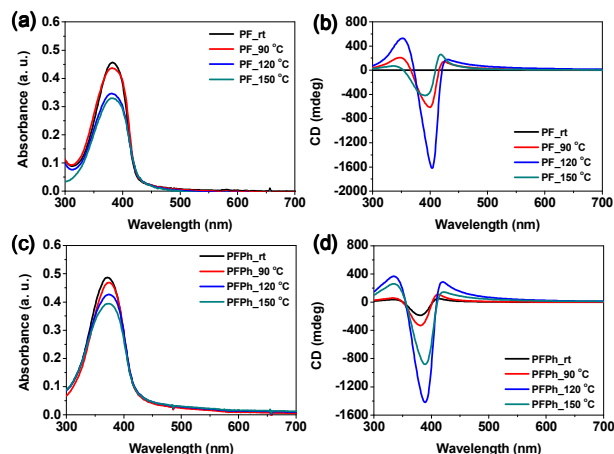

Figure 5. (a, c) UV-Vis absorption and (b, d) CD spectra of (a, b) PF and (c, d) PFPh in thin films. The film thicknesses of PF and PFPh were 45 and 50 nm, respectively.
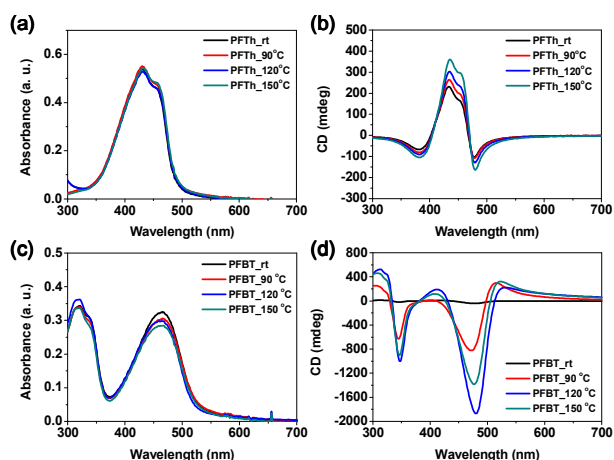

Figure 6. (a, c) UV-Vis absorption and (b, d) CD spectra of (a, b) PFTh and (c, d) PFBT in thin films. The film thicknesses of PFTh and PFBT were 80 and 60 nm, respectively.

Temperature dependence of the optical activity of the polymer films

As mentioned above, the CD of **PF**-based chiral copolymers significantly depend on certain factors such as annealing temperature and time, geometry of the molecular structure, and molecular weight. Among the many parameters, we mainly focused on the annealing temperature at a fixed annealing time (15 min) to observe the resultant variation of CD in this work. The four polymers showed significantly enhanced CD and reduced absorbance after annealing at different temperatures, as shown in **Figures 5** and **6**. Interestingly, **PF**, **PFPh**, and **PFBT** exhibited larger CD than **PFTh**, which bears five-membered heteroaromatic thiophene units. Moreover, **PFTh** showed no change in CD when annealed above 90 °C even though high CD was observed in the

pristine film. This was indirectly observed from the intensity of the absorption spectra at different annealing temperatures, as shown in **Figures 5** and **6**.
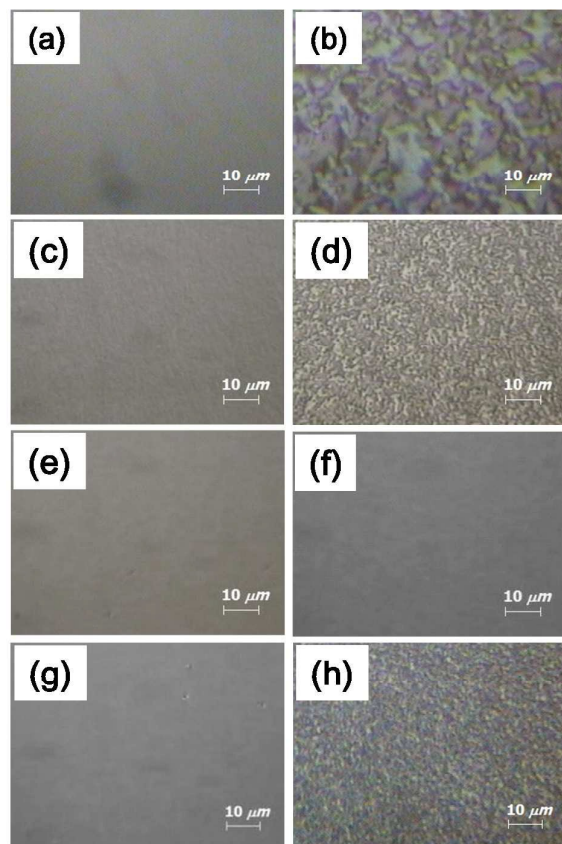

Figure 7. Cross-polarized optical microscopy images of (a, b) **PF**, (c, d) **PFPh**, (e, f) **PFTh**, and (g, h) **PFBT** in pristine films (left) and films annealed at 120 °C for 15 min (right).

To investigate the morphological variations, the surfaces of the polymer films before and after annealing were observed using polarized optical microscopy (OM), and their images are displayed in **Figure 7**. Among the polymers, the annealed film of **PFPh** showed significantly different OM images: the annealed film was coarser than the pristine film and those of the other polymers. These results indicate that the CD of chiral polymers could be easily predicted by only measuring the OM image. However, the OM images did not provide sufficiently resolved images to investigate the changes of morphology in the **PF**, **PFTh**, and **PFBT** films. Using atomic force microscopy (AFM), highly resolved images of the surface topography of the **PF**-based polymer films before and after annealing were observed. All polymer films after thermal annealing showed coarser surfaces and larger domains than those of pristine films as shown **Figure 8**. In particular, the thermally annealed **PF**, **PFPh**, and **PFBT** films exhibited markedly large island domains; this indicates that three polymers underwent significant macroscopic chain re-organization to generate the enhanced chiroptical properties.
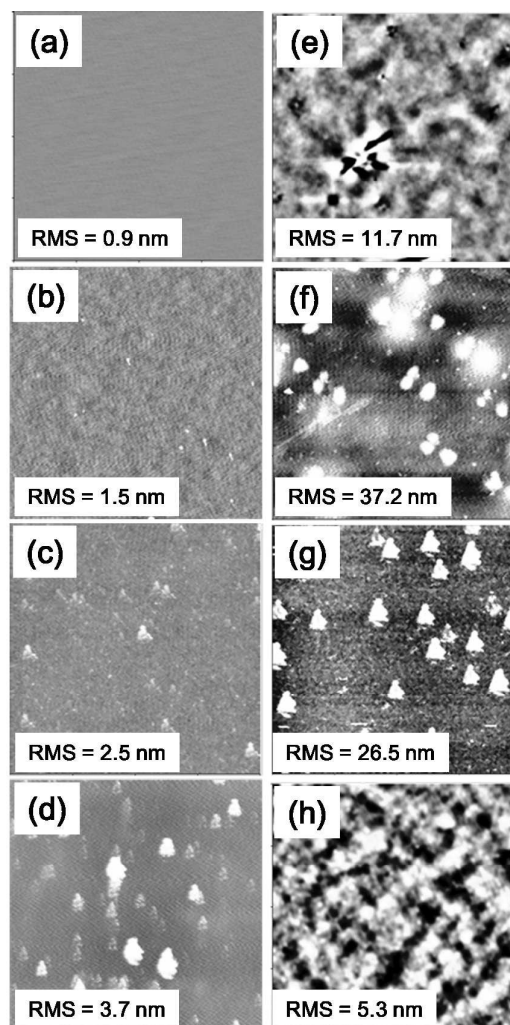

Figure 8. AFM height images (10 μm × 10 μm) of the chiral polymer films before (left) and after thermal annealing (right): (a, e) **PF**; (b, f) **PFPh**; (c, g) **PFTh**; and (d, h) **PFBT**.

Film-thickness dependence of CD in PFPh copolymers

The CD of **PF**-based chiral polymers is known to depend on the film thickness. Among the four polymers, these effects have already been well-studied for **PF** and **PFBT**.[11] To investigate the film-thickness dependence of CD in **PFPh**, various samples of **PFPh** with different film thicknesses were prepared by varying the spin-coating speed. As shown in **Figure 9a**, the CD of **PFPh** increased significantly with increasing film thickness. Intriguingly, we could not measure the full CD of the sample when the film thickness was greater than 56 nm because of the limited measurement range of instrument. These non-linear increases of CD made it difficult to determine the relationship between the linear increase of absorption in the pristine film and linear decrease of absorption in the annealed films, as shown in **Figure 9b**. These unusual behaviors have also been mentioned in literature.[11]
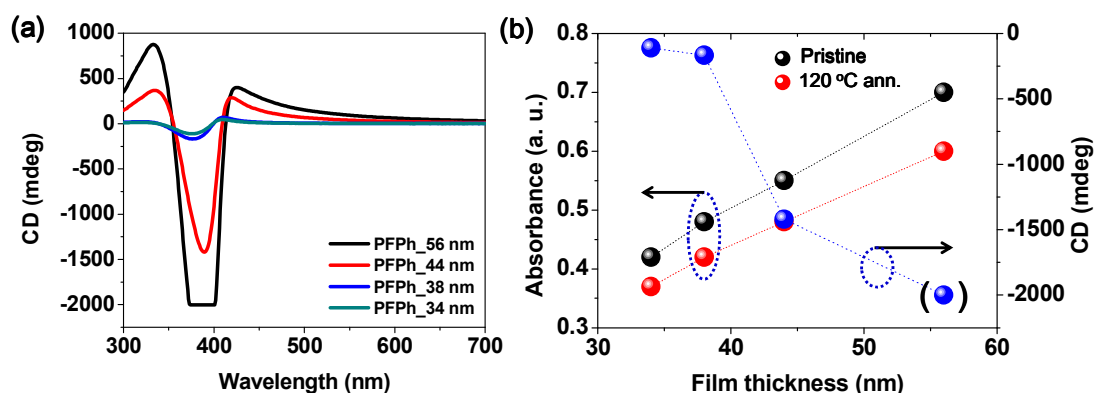
Figure 9. (a) CD spectra and (b) dependence of the absorption spectra and CD values of **PFPh** in different film thicknesses. The data point in brackets is outside the measuring range of the CD spectrometer.
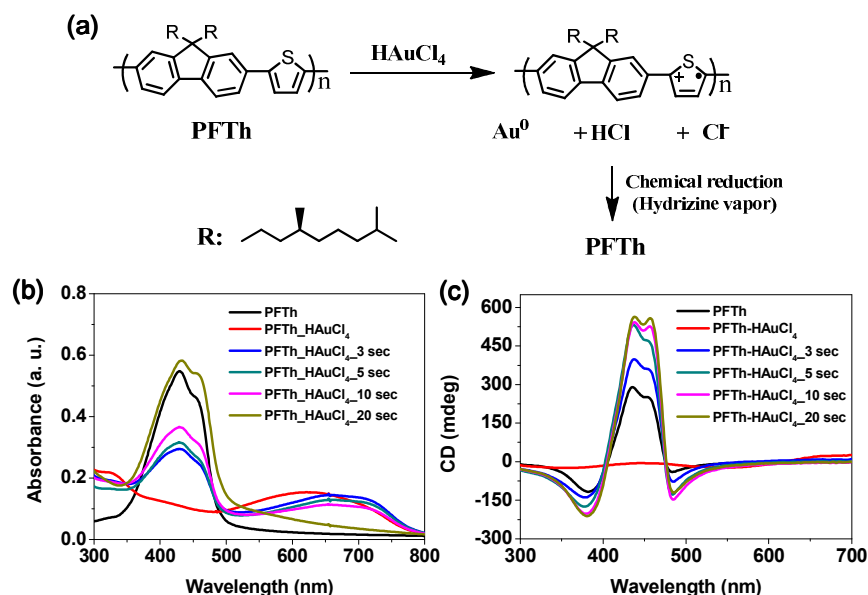

Figure 10. (a) Reaction mechanism for the oxidation and reduction of **PFTh** by HAuCl$_4$ and hydrazine vapor, respectively. (b) UV-Vis absorption and (c) CD spectra of **PFTh**, **PFTh**:HAuCl$_4$ blend films with exposure time of hydrazine vapor.

Oxidation and reduction of the HAuCl$_4$-doped PFTh film

To investigate the effect of oxidation and reduction on the optical properties of **PFTh**, **PFTh** was doped by HAuCl$_4$ as an oxidizing agent. Cho's group demonstrated that a HAuCl$_4$-doped poly(3-hexylthiophene) (P3HT) thin film could be formed *via* a solution process.[20] Accordingly, **PFTh** and HAuCl$_4$ (1:3 molar HAuCl$_4$/polymer ratio) were dissolved in THF, and the resulting solution was spin-coated onto a glass substrate. The oxidized **PFTh**:HAuCl$_4$ blend film was reduced by exposure to hydrazine

vapor. The reaction mechanism for the oxidation and reduction of **PFTh** by HAuCl$_4$ and hydrazine vapor is shown in **Figure 10a**. After oxidation, thiophene moiety was positively polarized. Therefore, by adding sufficient hydrazine vapor, the lone pair electrons in hydrazine were donated to the relatively electron deficient thiophene moiety. As shown in **Figures 10b** and **10c**, the absorption spectrum of the HAuCl$_4$-doped **PFTh** film is significantly different from that of the **PFTh** film, and the corresponding CD signals also disappeared. However, the absorption and CD spectra of the

HAuCl$_4$-doped **PFTh** film were interestingly recovered when the film was exposed to hydrazine vapor as a reduction agent.

Conclusions

We synthesized new **PF**-based chiral copolymers to investigate their optical and chiroptical behavior in pristine and thermally annealed films. The absorption and CD spectra of the copolymers were easily tuned *via* the introduction of five- and six-membered aromatics such as benzene, thiophene, and BT. Among the copolymers, **PFPh** and **PFTh** showed high CD in pristine-film states, which might be because of the small torsional potential energy between the repeating units and low intermolecular interactions between polymer chains. In particular, it should be emphasized that optical microscopy and atomic-force microscopy enable prediction of the CD of chiral polymer thin films after annealing. Additionally, the chirality observed in a PFTh:HAuCl$_4$ blend film was recovered via exposure to hydrazine vapor, which might support the sustainable chiral structure under oxidation and reduction at ambient conditions.

Experimental

Materials

All commercially available materials were purchased from Aldrich, Tokyo Chemical Industry (TCI), and ACROS Co. 2,7-Dibromo-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene, 2,7-bispinacoyl-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene boronic ester, **PF**, and **PFBT** were prepared according to literature.[11]

Synthesis of PFPh

To a solution of 2,7-dibromo-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene (0.25 g, 0.4 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.132 g, 0.4 mmol) in toluene (15 mL) was added 2 M K$_2$CO$_3$ (5 mL), Pd(PPh$_3$)$_4$ (22.8 mg, 20.0 μmol), and a trace amount of Aliquat 336 under an argon atmosphere. The mixture was allowed to stir at 100 °C for 12 h. The cooled mixture was added to vigorously stirred methanol (200 mL), and the resulting precipitate was filtered. The crude product was purified by successive Soxhlet extraction with acetone, hexane, and chloroform. The chloroform fraction was evaporated completely and then precipitated from methanol to afford the product as a light yellow solid (0.15 g, 74%). (M_n = 9.2 kDa, PDI = 1.74). Anal. Calcd for (C$_{37}$H$_{50}$S$_2$)$_n$: C, 84.35; H, 9.57; S, 6.09. Found: C, 84.13; H, 9.81; S, 6.32.

Synthesis of PFTh

To a solution of 2,7-dibromo-9,9-bis((*S*)-3,7-dimethyloctyl)fluorene (0.31 g, 0.5 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.164 g, 0.4 mmol) in toluene (15 mL) was added Pd(PPh$_3$)$_4$ (22.8 mg, 20.0 μmol) under an argon atmosphere. The mixture was stirred at 100 °C for 5 h. After cooling the mixture, it was added to vigorously stirred

methanol (200 mL), and the resulting polymer precipitate was filtered. The crude product was purified by successive Soxhlet extraction with acetone, hexane, and chloroform. The chloroform fraction was evaporated completely and then precipitated from methanol to afford the product as a yellow solid (0.15 g, 74%). (M_n = 7.7 kDa, PDI = 2.69). Anal. Calcd for (C$_{39}$H$_{52}$)$_n$: C, 89.94; H, 10.06. Found: C, 89.83; H, 10.13.

Instrumentation

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 MHz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses for determining the C, H, and N composition were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. The molecular weights of the polymers were determined by gel permeation chromatography (Waters GPC, Waters 515 pump, Waters 410 RI, 2x PLgel Mixed-B) using polystyrene as the standard and chloroform as an eluent (T = 35 °C). Atomic force microscopy (Advanced Scanning Probe Microscope, XE-100, PSIA) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the polymer films. Absorption spectra of the samples in film and solution states were obtained using a UV-vis spectrometer (HP 8453). Photoluminescence spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer. The CD spectra were measured using a spectropolarimeter (Jasco, J-815, Japan). Polarized optical microscopy was carried out using a SAMWON (SW-011863)

Film sample preparation

To investigate the optical properties of the films, such as absorption and chiroptical behavior and film morphology, the film samples of the **PF**-based chiral polymers were deposited on glass substrates using the spin-coating method. Transparent thin films were fabricated by spin-coating with a co-solvent system, i.e., chloroform/chlorobenzene (9:1 v/v %). The samples were annealed at 90, 120, or 150 °C for 15 min under ambient conditions. **PFTh** and HAuCl$_4$ (1:3 molar HAuCl$_4$/polymer ratio) were dissolved in THF, and the resulting solution was spin-coated onto a glass substrate.

Acknowledgements

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Graphical Abstract

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