ORIGINAL ARTICLE

Double screw-sense inversions of helical chiral-achiral random copolymers of fluorene derivatives in phase separating solutions

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The addition of methanol to dilute THF solutions of chiral-achiral random copolymers of fluorene derivatives and the chiral homopolymer showed thermo-reversible circular dichroism (CD) induction in the main-chain fluorene absorption region. This finding demonstrated the uneven population of the right- and left-handed helical conformations in the polymer chains. From the sign of the induced CD, two helical screw-sense inversions were found by changing the chiral monomer content. The Ising model for chirally interacting chiral-achiral random copolymers can explain the double screw-sense inversions. *Polymer Journal* (2011) 43, 832–837; doi:10.1038/pj.2011.75; published online 3 August 2011

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INTRODUCTION

Recently, π - and σ -conjugated polymers, which possess interesting electrical and optical properties, have attracted much interest as candidates for organic light-emitting diodes^{1–3} and chemical sensors.⁴ Chiroptical properties, such as circular dichroism (CD), optical rotation, and circular polarized luminescence, enrich the applications of these organic semiconductors as optical devices or sensors.^{5–9} Optically active side chains may introduce chiroptical properties into conjugated polymers, but some polymers exhibit these properties only in films or phase separating solutions,^{10–13} which indicates that intermolecular chiral interactions are necessary to induce the chiroptical properties in such conjugated polymers.

Polyfluorene derivatives are π -conjugated polymers. From electron and X-ray diffraction,^{14,15} as well as molecular modeling,^{14, 16} these polymers are known to take a helical conformation, but chirality introduced to the side chain of the polymers was not found to induce circular dichroism (CD) on their backbone chain in dilute solution. This finding probably results from weak intramolecular chiral interactions that cannot discriminate against the handedness of the backbone helical conformation.

In a previous study,¹⁷ the CD induction of an optically active homopolymer of fluorene derivative, poly(2,7-[9,9-bis((S)-citronellyl)]fluorene) (PCF), in dilute THF solutions was found by the addition of a non-solvent methanol. Although the methanol-added solutions were almost transparent because of low polymer concentrations ($\sim 10^{-6}$ g cm⁻³), static light scattering measurements indicated a liquid-liquid phase separation to form concentrated droplet phases,

and it was concluded that this induction arises from the intermolecular chiral interaction of polyfluorene chains in the concentrated droplet phases separated from the dilute solution.

Helical chiral-achiral random copolymers often exhibit interesting chiroptical properties, for example, sergeants-and-soldiers behavior,^{18–20} composition-driven helical screw-sense inversion,^{21,22} and so on. Therefore, the CD induction study in phase separating solution was recently extended to a helical chiral-achiral random copolymer of fluorene derivatives, poly(2,7-[9,9-bis((S)-citronellyl)]fluorene-*random*-9,9-di-*n*-octyl fluorene), as shown in Scheme 1, and double screw-sense inversions were found by changing the chiral monomer content x . To the best of our knowledge, this is the first observation of composition-driven double sense inversions in helical chiral-achiral random copolymers. In this paper, this finding is reported along with the theoretical argument of its origin.

EXPERIMENTAL PROCEDURE

Samples

Mixtures of the chiral and achiral dibromofluorene monomers of different compositions were copolymerized in a hot mixture of toluene and *N,N*-dimethylformamide (DMF) using a zero-valent nickel reagent by the Yamamoto coupling reaction.⁷ Each copolymer sample was divided into three fractions by fractional precipitation using THF as the solvent and methanol as the precipitant, and the middle main fraction was chosen for the following experiments.

The chiral monomer content x of five middle copolymer fractions was estimated from the ratio of the integrated intensities of the proton signals of the chiral side chains and aromatic rings. The results, listed in Table 1, are very

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Scheme 1 Chemical structure of the chiral-achiral random copolymer studied.**Table 1** Characteristics of polymer fractions used in this study and of concentrated droplet phases in methanol-added THF solutions of fractions PC505 and PCF

Fraction	X	$M_w/10^4$	$N_{0,w}$	M_w/M_n^a	R_w/nm^b	R_w/R_n^b	c_c/gcm^{-3b}
PC802	0.80 (0.8) ^{c,d}	11.5 ^a	267	1.5			
PC604	0.60 (0.6) ^{c,d}	4.1 ^a	98	1.3			
PC505	0.50 (0.5) ^{c,d}	7.0 ^a	169	1.4	110 ^e (83) ^f	1.4 ^e (1.3) ^f	0.60 ^e (0.59) ^f
PC208	0.19 (0.2) ^{c,d}	10.5 ^a	264	1.5			
PCF	1.0 (1.0) ^d	13.4 ^a	305	—	150 ^e (170) ^f	1.8 ^e (1.8) ^f	0.50 ^e (0.50) ^f

^aDetermined by SEC-MALS.^bDetermined by SLS.^cDetermined by ¹H NMR.^dChiral monomer initial composition fed at the polymerization.^eat 15 °C.^fat 40 °C.

close to the initial compositions fed at the copolymerization (the numbers in the parentheses in the second column of Table 1). The weight average molecular weights, M_w , and the ratios of M_w to the number average, M_n , of the five fractions were determined by size-exclusion chromatography with a multi-angle light scattering detector (SEC-MALS).²³ Table 1 lists the results and weight average degree of polymerization $N_{0,w}$ calculated from the M_w determined. The values of M_w/M_n indicate the relatively narrow molecular weight distributions of the fractions used in this study. One fraction of the chiral homopolymer PCF prepared in the previous study was added to the copolymer fractions for the following CD induction study, and its M_w was determined by static light scattering (SLS).¹⁷ The values of $N_{0,w}$ of all the fractions were within the range of ca. 100–300.

Measurements

Each fraction was first dissolved in THF ($8 \times 10^{-7} g cm^{-3}$), and then, methanol was added to the THF solution at room temperature. The methanol volume fraction ϕ_{MeOH} in the mixed solvent and the final polymer concentration c in the THF-methanol solution were adjusted to 0.5 and $4 \times 10^{-6} g cm^{-3}$, respectively. CD and SLS measurements were conducted using the THF-methanol solutions prepared using a JASCO J-720WO spectropolarimeter and a Fica 50 light scattering photogoniometer with 546 nm incident light, respectively, at 40 and 15 °C.

RESULTS

Static light scattering

Figure 1 shows the light scattering profiles of THF-methanol solutions of fractions PC505 ($x=0.50$) and PCF ($x=1$) at 40 °C and 15 °C (300 min after quenching from 40 °C). Here, K is the optical constant, c is the polymer mass concentration, R_θ is the excess Rayleigh ratio at the scattering angle θ , and k^2 is the square of the scattering vector. All of the profiles exhibit very strong angular dependences, demonstrating the existence of large particles in the solutions. The phase diagram obtained previously¹⁷ for the methanol-added THF solution of

Figure 1 Berry plots for methanol-added THF solutions of fractions PC505 ($x=0.50$) and PCF ($x=1$) at 40 °C and 15 °C (300 min after quenching from 40 °C); $\phi_{MeOH}=0.5$ and $c=4 \times 10^{-6} g cm^{-3}$. Solid and dotted curves, theoretical values for polydisperse spheres fitted to the data at 15 and 40 °C, respectively (see the main text).

PCF indicates that the solutions may be in the biphasic region, and the large particles are the concentrated droplet phases separated from the dilute solutions.

For dilute solutions of polydisperse spheres, $(Kc/R_\theta)^{1/2}$ can be calculated by¹⁷

$$\frac{R_\theta}{Kc} = \frac{12\pi N_A c}{k^3} \int_0^\infty \frac{[\sin(kR) - kR \cos(kR)]^2}{(kR)^3} w(R) dR \quad (1)$$

where R is the radius of the sphere, $w(R)$ is the weight fraction of a sphere of radius R , c_c is the polymer mass concentration in the spherical concentrated phase, and N_A is the Avogadro constant. Assuming that the size distribution $w(R)$ obeys the log-normal distribution,¹⁷ equation (1) was fitted to the experimental results to obtain the weight-average radius R_w , the ratio of R_w to the number-average R_n of the droplet phase and c_c . The solid and dotted curves in Figure 1 show the fitting results, and the parameters obtained are listed in columns 5–8 in Table 1. Droplet sizes are on order of 100 nm. The concentrations of the droplet phases are as high as 0.6 g cm^{-3} for both fractions and almost independent of temperature. The results of c_c for fractions PC5O5 and PCF indicate the similar affinities of the chiral and achiral monomer units to the mixed solvent.

Circular dichroism induction

None of the copolymer fractions exhibited CD in dilute THF solution, as in the case of the chiral homopolymer PCF,¹⁷ which indicates that the *intramolecular* chiral interaction between the main and side chains of the copolymers is too weak to energetically discriminate the right- and left-handed helical conformations in the fluorene main chain.

Figure 2 shows UV-visible absorption and CD spectra of the phase separating solution of PC5O5 quenched from 40 to 15 °C. In Panel a, the main peak of the UV-visible absorption, arising from the π – π^* transition in the fluorene main chain, is essentially unchanged over time since quenching, but the peak height decreases, the peak wavelength slightly increases, and a new side-peak appears at 426 nm. On the other hand, a bisign CD signal is induced in the fluorene main-chain absorption region by quenching in Panel b, just as in the case of fraction PCF reported previously.¹⁷ The induced CD disappeared upon heating to 40 °C and reappeared by quenching again to 15 °C, which is similar to PCF and demonstrates the thermal reversibility of the CD induction. The phase-separating solutions were verified to have no optical anisotropy,¹⁷ which means that the induced CD does not arise from a liquid crystal phase. The polyfluorene chain is known to take 5/2 or 5/1 helical conformations favorably^{14,16} so that the CD induction indicates uneven population of the right- and left-handed helical conformations of the copolymer main-chain. The Kuhn dissymmetry factor $g_c \equiv \Delta\epsilon/\epsilon$ at 410 nm (the CD peak position) reaches the asymptotic value at approximately 60 min (cf. Insert of Figure 1), which is slightly faster than g_c of the PCF solution.¹⁷

The new side peak at 426 nm in Panel a corresponds to the so-called ‘ β -phase’ observed for poly(9,9-di-*n*-octylfluorene) films,^{24,25} which is assigned to an almost planar conformation of the fluorene main chain with the torsional angle $\approx 160^\circ$ stabilized by the *n*-octyl side chains.²⁶ A more pronounced side-peak was observed in the methanol-added THF solution of fraction PC2O8, indicating that some of achiral monomer units take similar planer conformations in the concentrated droplet phase. Interestingly, a side-peak also grows in the CD spectrum (Panel b) at the same wavelength, which may arise from the achiral monomer unit in the copolymer chain taking the ‘ β -phase’ conformation.

In the methanol-added THF solution with the same ϕ_{MeOH} and c , a similar CD induction was observed for PC6O4 quenched from 40 to 15 °C, but a CD signal appeared for PC2O8 even at 40 °C and did not change with time after quenching to 15 °C. The CD induction experiments were examined twice for fraction PC2O8, and nearly the same CD spectra were obtained, confirming the reproducibility of the CD induction for this fraction.

Figure 3 shows the asymptotic CD absorption spectra for all chiral-achiral random copolymers and the chiral homopolymer PCF in methanol-added THF solutions ($\phi_{\text{MeOH}}=0.5$, $c=4 \times 10^{-7} \text{ g cm}^{-3}$).

Figure 2 Spectra of the molar circular dichroism $\Delta\epsilon$ (a) and the average molar extinction coefficient ϵ (b) for methanol-added THF solution of fraction PC5O5; inset in Panel b: time dependence of the Kuhn dissymmetry factor at 410 nm. A full color version of this figure is available at *Polymer Journal* online.

The bisign CD main signals induced in PCF and PC2O8 solutions are positive in the longer wavelength region but opposite in PC6O4 and PC5O5 solutions, and PC8O2 exhibits almost no CD. The sign of the side peak of PC2O8 (at 429 nm) is also opposite to that of PC5O5 (at 426 nm). The insert in Figure 3 shows the x dependence of the Kuhn dissymmetry factor at the CD peak in the region of 400–420 nm. These results demonstrate that the helical screw sense of the chiral-achiral random copolymer is inverted twice with changing x . To the best of our knowledge, this is the first observation of the double sense inversions in helical chiral-achiral random copolymers.

DISCUSSION

Consider the origin of the double sense inversions in helical chiral-achiral random copolymers. For simplicity, assume that the main-chain bond (for example the internal rotation angle) of the helical polymer chain takes P- or M-states (a two-state model). The P-helix (M-helix) means the sequence of main-chain bonds taking the P-state (M-state). In a concentrated solution, a bond taking the P-state (M-state) feels the chiral molecular field $\bar{w}^*(\text{P})$ ($\bar{w}^*(\text{M})$) generated by neighboring polymer molecules.²⁷ If the solution contains P- and

Figure 3 Asymptotic CD absorption spectra for all chiral-achiral random copolymers and the chiral homopolymer PCF in methanol-added THF solutions; inset: the x dependence of the Kuhn dissymmetry factor at the CD peak in the region of 400–420 nm. A full color version of this figure is available at *Polymer Journal* online.

M-state bonds of fractions f_P and f_M , respectively, the molecular fields, $\bar{w}^*(P)$ and $\bar{w}^*(M)$, may be given by

$$\bar{w}^*(P) = w_{PP}^* f_P + w_{PM}^* f_M, \quad \bar{w}^*(M) = w_{PM}^* f_P + w_{MM}^* f_M \quad (2)$$

where w_{PP}^* , w_{MM}^* , and w_{PM}^* are the chiral interactions between two pairs of adjacent monomer units connected by the bonds both taking the P-state, both taking the M-state, and taking the P- and M-states, respectively. Because the molecular field may include both enthalpic and entropic contributions, $\bar{w}^*(P) - \bar{w}^*(M)$ can be regarded as the free energy difference $2\Delta G_h$ of a bond when taking the P-state and M-state in the concentrated solution. From equation (2), ΔG_h is a linear function of the enantiomer excess $2f_P - 1$, for example, $\Delta G_h = \kappa(2f_P - 1) + \lambda$ where κ and λ are parameters related to the chiral interactions. In the previous study,¹⁷ it was assumed that $\lambda = 0$, but w_{PP}^* and w_{MM}^* are not necessarily identical unless the interacting monomer units are both achiral.

In the case of a chiral-achiral random copolymer solution, ΔG_h may depend on the kinds of adjacent monomer units connected by the bond under consideration:²⁸

$$\begin{aligned} \Delta G_{h,CC} &= \kappa_{CC}(2f_P - 1) + \lambda_{CC}, \\ \Delta G_{h,CA} &= \kappa_{CA}(2f_P - 1) + \lambda_{CA}, \\ \Delta G_{h,AA} &= \kappa_{AA}(2f_P - 1) \end{aligned} \quad (3)$$

where the subscripts C and A denote the chiral and achiral monomer units, respectively. Because the achiral homopolymer should be racemic at $2f_P - 1 = 0$, λ_{AA} must be zero. Helical polymers must have long sequences of the one-sense helical state along the main chain, or the helix reversal must be a rare event. Thus, the free energy ΔG_r of the helix reversal, where the adjacent bonds take the opposite helical state, must be quite high.²⁹ In what follows, the dependence of ΔG_r on the kinds of adjacent monomer units connected by the bond under consideration is not considered, which should have a minor effect on the helical screw sense inversion.

The enantiomer excess $2f_P - 1$ of the chiral-achiral random copolymer chain can be calculated by the matrix method for the Ising model.^{28,30,31} The matrix includes the statistical weights of the P- and

M-states and the helix reversal, which are respectively written as

$$\begin{cases} u_{P,i(k)i(k+1)} = \exp(\Delta G_{h,i(k)i(k+1)}/RT) \\ u_{M,i(k)i(k+1)} = \exp(-\Delta G_{h,i(k)i(k+1)}/RT) \\ v = \exp(-\Delta G_r/RT) \end{cases} \quad (4)$$

where the subscripts $i(k)$ ($1 \leq k \leq N$), taking C (the chiral monomer unit) or A (the achiral monomer unit), specify the copolymer sequence and RT is the gas constant multiplied by the absolute temperature. (This R should be distinguished from the radius R in equation (1)) Generating 100 sequences of chiral-achiral random copolymers with a given N and mole fraction x of the chiral unit on a computer, $2f_P - 1$ can be calculated numerically for the given values of $\Delta G_{h,CC}$, $\Delta G_{h,CA}$, $\Delta G_{h,AA}$, and ΔG_r in the routine procedure.

The calculated $2f_P - 1$ must fulfill equation (3) for $\Delta G_{h,CC}$, $\Delta G_{h,CA}$, and $\Delta G_{h,AA}$. This self-consistent calculation can be performed as follows. From equation (3), the relations among $\Delta G_{h,CC}$, $\Delta G_{h,CA}$, and $\Delta G_{h,AA}$ are obtained:

$$\begin{aligned} \Delta G_{h,CA} &= \frac{\kappa_{CA}}{\kappa_{CC}} (\Delta G_{h,CC} - \lambda_{CC}) + \lambda_{CA}, \\ \Delta G_{h,AA} &= \frac{\kappa_{AA}}{\kappa_{CC}} (\Delta G_{h,CC} - \lambda_{CC}) \end{aligned} \quad (5)$$

A trial value of $\Delta G_{h,CC}$ is chosen first, and $\Delta G_{h,CA}$ and $\Delta G_{h,AA}$ are calculated from equation (5) using a given set of the parameters κ_{CA}/κ_{CC} , κ_{AA}/κ_{CC} , λ_{CC} , and λ_{CA} . Then, $2f_P - 1$ is calculated by the matrix method using those values of ΔG_h and a given value of ΔG_r , and the resulting $2f_P - 1$ is substituted into the first equation of equation (3) to check the equality. The self-consistent value of $\Delta G_{h,CC}$ that fulfills the equation is sought.

The previous result indicated that $2f_P - 1$ for PCF in the phase-separating solution is close to zero at 40 °C but takes a positive finite value at 15 °C.¹⁷ To reproduce these results, $\kappa_{CC} = 40 \text{ J mol}^{-1}$ and $\lambda_{CC} = 2 \text{ J mol}^{-1}$ were selected (using these parameters, $2f_P - 1$ for PCF becomes 0.09 at 40 °C and 0.38 at 15 °C). Furthermore, $N = 220$ (the average value of our five polymer fractions) and $\Delta G_r = 10 \text{ kJ mol}^{-1}$ (a typical value for helical polymers such as polyacetylene or polyisocyanate derivatives^{32,33}). The remaining parameters in equation (2), κ_{CA} , κ_{AA} , and λ_{CA} , were taken as adjustable parameters. (The κ and λ parameters may depend on the polymer concentration c_c in the concentrated phase, but here it is assumed that these parameters are independent of x because c_c may be insensitive to x due to similar affinities of the chiral and achiral monomer units to the mixed solvent, mentioned above.)

Figure 4 shows the results of $2f_P - 1$ at 15 °C as a function of $\Delta G_{h,CC}$ and x for $\kappa_{CA}/\kappa_{CC} = -2.5$, $\kappa_{AA}/\kappa_{CC} = 3.5$, $\lambda_{CC} = 2 \text{ J mol}^{-1}$, and $\lambda_{CA} = -4 \text{ J mol}^{-1}$. Slight fluctuations in the calculated $2f_P - 1$ values arise from statistical errors in the chiral monomer content generated. The straight line in Figure 4 represents the linear relation of $2f_P - 1 = (\Delta G_{h,CC} - \lambda_{CC})/\kappa_{CC}$ with $\kappa_{CC} = 40 \text{ J mol}^{-1}$. The intersecting point of this line and the curve for each x fulfills equation (3). At large x , the curve intersects with the line once, but, in the small x region, there are three intersecting points.

Figure 5 shows the self-consistent solution of $2f_P - 1$ at 15 °C, obtained from Figure 4, as a function of x . At large x (> 0.227), the calculation gives the unique self-consistent solution of $2f_P - 1$. When x decreases from unity, $2f_P - 1$ changes from positive to negative (the solution of branch 1), corresponding to the first helical screw sense inversion. However, one negative and two positive solutions appear at $x < 0.227$. Among these solutions, the positive one reaching the origin (labeled as the branch 2) should be the real solution because the achiral homopolymer must be racemic. Therefore, a transition

Figure 4 Enantiomer excess as a function of $\Delta G_{h,CC}$ and x , calculated by the matrix method for the Ising model of the random copolymer with $\kappa_{CA}/\kappa_{CC} = -2.5$, $\kappa_{AA}/\kappa_{CC} = 3.5$, $\lambda_{CC} = 2 \text{ J mol}^{-1}$, $\lambda_{CA} = -4 \text{ J mol}^{-1}$, $\Delta G_r = 10 \text{ kJ mol}^{-1}$, $N = 220$, and $T = 288 \text{ K}$ (15°C).

Figure 5 Self-consistent solutions of the enantiomer excess $2f_P - 1$ as a function of x for the parameters listed in the text.

from branch 1 to 2 is expected with decreasing x , which corresponds to the second helical screw sense inversion. This *discontinuous* transition is an interesting phenomenon. The CD induction at x between 0.2 and 0.5 will be studied experimentally in more detail in the near future.

CONCLUSIONS

Methanol-added THF solutions of chiral-achiral random copolymers of fluorene derivatives with different chiral monomer content x were studied. The addition of methanol to dilute THF solutions of the copolymers and the chiral homopolymer induced a liquid-liquid phase separation that produced concentrated phase droplets with a polymer concentration as high as 0.6 g cm^{-3} and a size of the order of 100 nm. In the concentrated phase, the copolymers and homopolymer exhibited mostly thermo-reversible circular dichroism (CD) induction after quenching in the main-chain fluorene absorption region, demonstrating the uneven population of the right- and left-handed helical conformation in the polymer chains. From the sign of the

induced CD, two helical screw-sense inversions were found by changing x . The Ising model for chirally interacting chiral-achiral random copolymers can explain the double screw-sense inversions.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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