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Distinctive Chiral Conformations Induced to Poly(naphthalene-1,4-diyl) by Helix-sense-selective Polymerization and Circularly Polarized Light Irradiation

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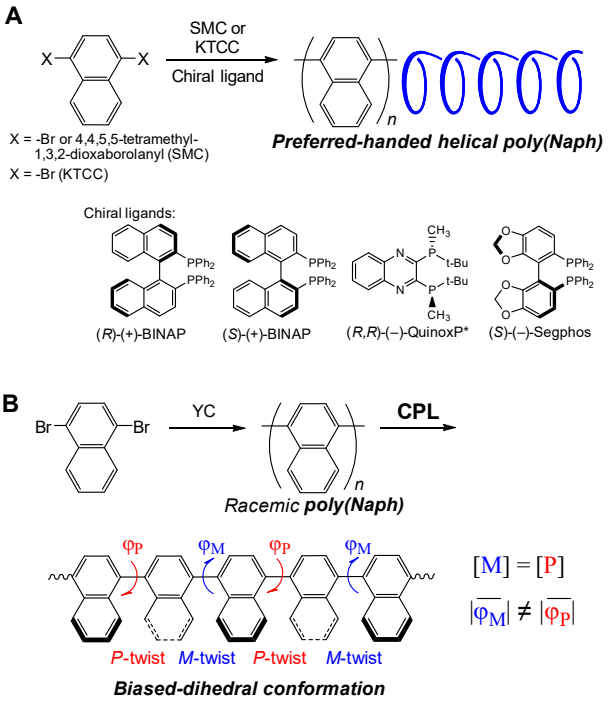
Abstract: Optically active poly(naphthalene-1,4-diyl) was prepared through helix-sense-selective polymerization of the corresponding monomers and also through circularly polarized light (CPL) irradiation, resulting in distinctive circular dichroism (CD) spectral patterns. Chirality of the helix-sense-selective polymerization -based polymer is ascribed to preferred-handed helicity while that of the CPL-based polymer to a non-helical, chiral conformation ('biased-dihedral conformation') with preferred-handedness which was stable only in the solid state. The helix of the helix-sense-selective polymerization-based polymer gradually racemized in tetrahydrofuran while it was stabilized by aggregate formation in a hexane-dichloromethane solution. Both helix-sense-selective polymerization- and CPL-based polymers exhibited efficient circularly polarized luminescence.

Macromolecules having a single-handed helical structure are useful sources of optically active polymeric materials showing functions including resolution of racemic compounds, asymmetric catalysis, and circularly polarized luminescence (CPLm).[1-4] One of the most established methods of polymer helix synthesis is helix-sense-selective polymerization (asymmetric polymerization, asymmetric helix-chirogenic polymerization) where single-handedness arises from chirality of ligands used in the polymerization or of monomeric units.[3-4] In addition, single-handed helix can be dynamically controlled through interactions of polymer chain with external, chiral molecules.[1,2] Apart from these established methodologies, a newer way to create single-handed helices has been developed employing circularly polarized light (CPL) as the chirality source. By this method, single-handed helicity was introduced to polyfluorene derivatives as well as related small- to medium-sized molecules.[5-9] In addition, various azobenzene-containing polymers[10-17] as well as supramolecular systems[18] have been made optically active using CPL. While there have been a number of reports on asymmetric polymerization resulting in helical polymers and also reports on CPL-driven chirality induction to polymers, direct comparison between the two method using the same macromolecular species has never been conducted. This work, for the first time, makes direct comparison between the helix-sense-selective polymerization and the CPL method in the preparation of optically active poly(naphthalene-1,4-diyl) (poly(Naph)).

Helix-sense-selective polymerization was carried out by Suzuki-Miyaura cross coupling[19] (SMC) with Pd catalysis and Kumada-Tamao-Corriu cross coupling[20,21] (KTCC) with Ni catalysis using bis(diphenylphosphino)-1,1'-binaphthyl (BINAP),[22] 5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole (Segphos),[23] and 2,3-bis(tert-butylmethylphosphino)quinoxaline (QuinoxP*)[24] as chiral ligands (Scheme 1A), and the CPL-method was conducted for an optically inactive, racemic sample prepared by SMC and Yamamoto coupling (YC)[25] using Ni species without any chiral ligands (Scheme 1B).



Scheme 1. Synthesis of preferred-handed helical poly(Naph) by helix-sense-selective polymerization (A) and preparation of optically active poly(Naph) having 'biased-dihedral conformation' by CPL irradiation (B).

The SMC copolymerization of 1,4-dibromonaphthalene with 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)naphthalene (Scheme S3 in SI) and the KC and YC polymerization of 1,4-dibromonaphthalene (Schemes S1 and S2 in SI) produced polymers at high conversions. The products were composed of tetrahydrofuran (THF)-soluble poly(Naph)s with M_n's as high as about 3800 and THF-insoluble parts (Table S1 in SI). The insoluble polymers may have higher molar masses. The rather low M_n's of the soluble products means that poly(Naph)s generally have low solubility. The soluble polymers showed ^{1}H NNR and mass spectra consistent with the expected polymer structure (Figures S2-S4 in SI).

The polymers prepared by SMC and KC using chiral ligands showed circular dichroism (CD) spectra (Figure 1). Because poly(Naph) does not have any centers or planes of chirality, the chiroptical properties are ascribed to preferred-handed helical conformation based on preferred-handed twist hand between neighboring monomeric units. The polymers prepared by SMC with (*R*)- and (*S*)-BINAP showed the mirror image CD spectra (Figure 1 A-a,b), confirming that the enantiomers of BINAP lead to opposite handed helices.

The polymers prepared by SMC using (*R*)- and (S)-BINAP and by KTCC using (*R,R*)-QuinoxP* showed clearer CD spectra with higher intensities than the other polymers (Figure 1 A-a,b B-c). These polymers showed clear positive Cotton splitting patterns in the range below 250nm which resemble the CD spectra of enantiomers of 1,1'-binaphthyl obtained by HPLC resolution as a model dimer compound prepared in racemic form by SMC between 1-bromonapthalene and 1-napthaleneboronic acid (Figure 1 C). Based on the spectral resemblance, the absolute configurations in excess of the helical poly(Naph)s prepared by SMC using (*R*)- and (S)-BINAP may be assigned to be S and R, respectively.[26]

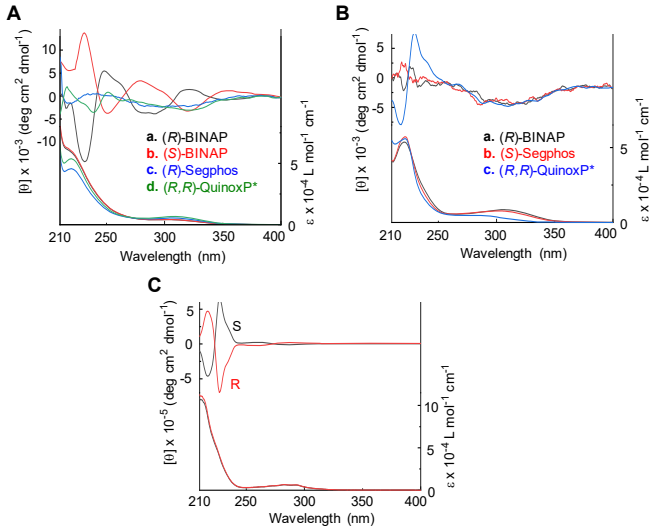


Figure 1. CD-UV spectra of poly(Naph)s prepared by SMC (A) and KC (B) with chiral ligands and enantiomers of 1,1'-binaphtyl as model dimer obtained by HPLC resolution (C). [conc. = 2.3 x 10-3 M (per residue) (A,B), 1.0 x 10-3 M (C); cell path = 1 mm].

In addition, it is noteworthy that the polymers made by SMC with BINAP and the one prepared by KTCC with (*R,R*)-QuinoxP* showed different spectral patterns in the range of 270-400 nm, where the polymers prepared by SMC with BINAP showed the additional Cotton splitting patterns which were absent for the one prepared by KTCC with (*R,R*)-QuinoxP* (Figure 1 A-a,b B-c). Such spectral differences may arise from different tacticities.

Also, based on the spectral intensities of the enantiomers of 1,1'-binaphthyl and the polymers, helix-sense-excess is estimated to be about 3% and 1% in SMC with (*R*)-BINAP and KTCC with (*R,R*)-QuinoxP*, respectively. The polymers prepared by SMC with Segphos and QuinoxP* and those by KTCC with BINAP and Seghos showed weaker CD signals, indicating that they have much lower helix-sense excesses (Figure 1 A-c,d B-b,c). Poly(Naph)s are expected to assume stretched, rigid conformations on the basis of molecular mechanics calculations (Figure S17 in SI).

It should be noted that experimental determination of helix-sense excess is generally difficult.[27,28] The CD-intensity based method employed here requires the conditions that the e.e. of the standard compound is unambiguously determined and that the chemical structure of the standard compound is similar enough to the units of polymer.[28] 1,1'-Binaphthyl as the standard compound fulfills both conditions, and the above results are hence reliable.

Furthermore, the polymers prepared by SMC with (*R*)- and (*S*)-BINAP indicated mirror image CD spectra also in thin film form (Figure S14 in SI) where the spectra showed greater intensities for longer-wavelength signals compared with the solution spectra. The shape of the preferred-handed helix of poly(Naph) may be altered by solidifying where the average dihedral angle between neighboring monomeric units in helix may be reduced through inter-chain packing.

Stability of the polymer helix obtained by SMC with (*R*)-BINAP as well as that of (*R*)-1,1'-binaphthyl as a dimer model was assessed by monitoring changes in CD spectra in solution. (*R*)-1,1'-binaphthyl (e.e. >99%) obtained by HPLC resolution showed a gradual decrease in CD intensity in hexane-dichloromethane (1/1, v/v) solution at 25 °C (Figure 2 A), which is based on racemization as evidenced by HPLC resolution (Figures S5 in SI). On the other hand, the polymer showed only negligible spectral changes in hexane-dichloromethane (1/1, v/v) solution (Figure 2 B) while it lost its CD signals in THF solution in 6 h (Figure 2 C) due to racemization. These clear solvent effects on helix stability of poly(Naph) is explained in terms of aggregate formation of the polymer. Dynamic light scattering (DLS) measurements of the polymer in hexane-dichloromethane (1/1, v/v) solution indicated the presence of aggregates with a mean diameter of 33 nm while aggregate formation was not confirmed in THF under the same analytical conditions (Figure S15 in SI). Inter-chain interactions through aggregate formation seems to prevent racemization of the helix. Aggregate structure was assessed by transmission electron microscopy (TEM) and molecular dynamics (MD) simulations (Figures S17 and S18, respectively, in SI). However, no specific aggregate structures were found in either way.

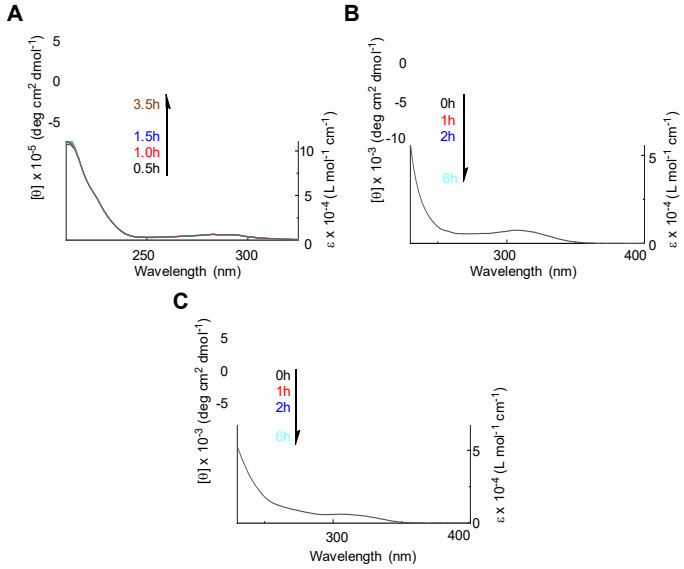


Figure 2. Changes in CD-UV spectra of (R)-1,1'-binaphthyl in hexane-dichloformethane (1/1, v/v) (A) and those of poly(Naph) prepared by SMC with (R)-BINAP in hexane-dichloformethane (B) and in THF (C). [conc. = 1.0 x 10-3 M (A), 1.0 x 10-3 M (per residue) (B, C) cell path = 1 mm, temp. 25 °C].

This conclusion was further supported by calculations of energy-barriers of rotation around the single bond connecting the two naphthyl groups of 1,1'-binaphthyl (2-mer model) and around the single bond connecting the neighboring naphthyl groups at the center of 4-mer and 10-mer models. The three species were predicted to have very similar barriers (around 23~25 kcal/mol) at the semiempirical PM6 level (Figure S16 in SI), indicating that extending of the length of single chain itself does not contribute to helix stability. However, a longer chain may tend to form aggregates that hamper helix reversal.

Next, chirality induction by the CPL irradiation method was studied for the optically inactive, racemic polymer prepared by YC without using chiral ligands (run 7 in Table S1 in SI). This method was applied to film samples of the polymer prepared by casting a THF solution to quartz glass plate. In order to minimize the effects of linear dichroism, CD spectra were obtained by averaging the data recorded at four different film orientations (angles) at an interval of 90° with the film face positioned vertically to the incident light beam for measurement. The CPL-irradiated films showed clear and intense CD spectra where L- and R-CPL irradiation resulted in the mirror image spectra (Figure 3 A), indicating that oppositely handed chiral conformations were induced by using oppositely handed CPL for irradiation. IR spectral studies indicated that no remarkable changes in the chemical structure of poly(Naph) was caused by irradiation (Figure S6 in SI), supporting that the mirror image CD spectra arise from conformational chirality. However, the CD spectra are not based on preferred-handed helices because the spectra were immediately lost when the CPL-irradiated films were dissolved in hexane-dichloromethane (1/1, v/v) in which helix can be stable as discussed for the polymer prepared by SMC with (*R*)-BINAP and also because the CD spectral shapes are clearly different between the CPL-irradiates samples and the helical samples (Figure 1 A B, Figure 3 A).

'Biased-dihedral conformation' is proposed as a non-helical, chiral structure of poly(Naph) induced by CPL (Scheme 1 B). This conformation is composed of diads having right- and left-handed twists of the same population (equimolar mixture of left- and right-handed twists) in which the right- and left-handed twists are not mirror images having different dihedral angles. While CPL irradiation to polyfluorene derivatives and related molecules caused full rotation around their aryl-aryl junctions,[5-10] CPL appears not to induce full rotation modifying right-handed twist into left-handed twist in poly(Naph) but to change dihedral to different extents for right- and left-handed twists. The CPL-induced molecular motion may be based on twisted-coplanar transition known for polyfluorene derivatives and related molecules including biphenyl.[5-10,29-31]

Chirality induction by CPL was reversible. The positive CD signals induced by L-CPL were changed to the negative ones by additional R-CPL irradiation, and the positive signals were recovered by through further irradiation by L-CPL (Figure 3 B).

Maximum CD intensities were reached within about 15 min of irradiation, which was much faster than helix induction to polyfluorene derivatives and related molecules[5-10] (Figure 3 C). Further, a decrease in UV intensity was observed upon CPL irradiation. This is ascribed not to chemical modifications but to a decrease in the dihedral angle between neighboring naphthalene-1,4-diyl units which has been reported for biphenyl.[32,33] Chirality induction rate was evaluated by plotting g_{CD} against the irradiation energy sum where data points were well approximated with an exponential function in increasing form [$g_{CD} = -4.2 \times 10^{-4} \times \exp(-[\text{relative irradiation energy sum}]/33.1) + 4.2 \times 10^{-4}$] (Figure 3 D). This result is in a sharp contrast to that the helix induction to polyfluorene derivatives by CPL irradiation was approximated by a power function implying chirality amplification through helix formation.[6] The present results further support that the CPL-based chirality induction to poly(Naph) is distinguished from the helix formation of polyfluorene derivatives and related molecules.[5-10]

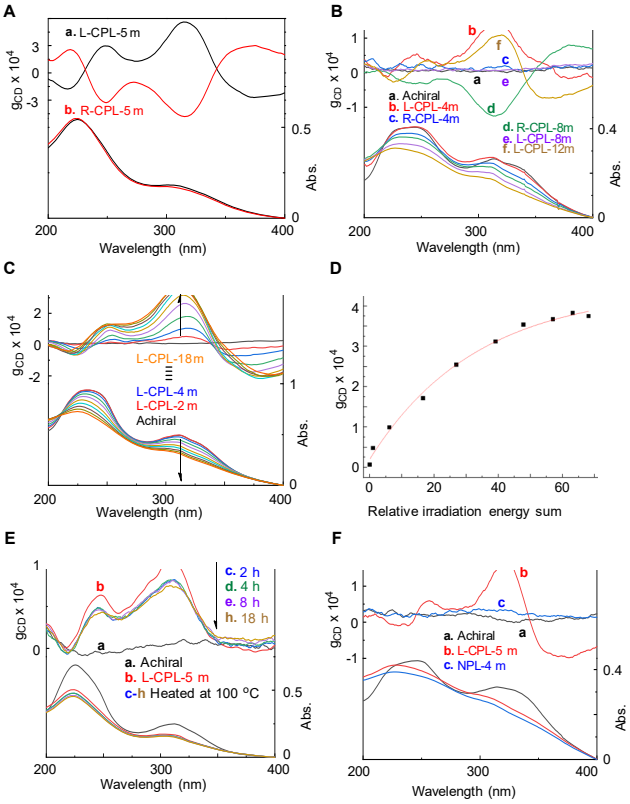


Figure 3. CD-UV spectra of poly(Naph) films prepared by L- and R-CPL irradiation (A), chirality switching by alternating L- and R-CPL irradiation (B), time-course of CD-UV spectra on L-CPL irradiation (C), g_{CD}-vs.-relative irradiation energy sum plot for chirality induction with CPL irradiation (D), and changes in CD-UV spectra of the film prepared by L-CPL irradiation on heating (E) and on achiral NPL irradiation (F).

The chiral structure of poly(Naph) induced by CPL was rather stable on heating (Figure 3 E and Figure S13 in SI). On heating at 100 deg, the CD intensity of the film irradiated with L-CPL initially decreased by about 15% and thereafter almost unchanged in 18 h (Figure 3 E). The loss of CD was only 5% in 18 h when the heating temperature was 60 °C (Figure S13 in SI). On the other hand, irradiation with intense linearly polarized light (LPL) made the CD spectrum swiftly erased (Figure 3 F).

Biased-dihedral conformation was supported by theoretical CD calculations of 5-mer models at the ZINDO level (Figure 4). The single-handed helical models with dihedral angles of 50° and 60° resulted in an intense exciton coupling in the range of 200-250 nm that well corresponded to the Cotton splitting in Figure 1 A-a,b and Figure 1 B-c of the helical poly(Naph)s (Figure 4 A). On the other hand, the 5-models having biased-dihedral conformations composed two diads having *P*-twist and two diads having *M*-twist having different sequential orders and dihedral angles shown in Figure 4 B were predicted to have much less remarkable exciton couplings (Figure 4 C. D). In addition, the relative intensity of the signal at around 300 nm was higher when the absolute dihedrals of *P*- and *M*-twists are closer such as 40°-45° and 40°-50° (Figure 4 D) than 40°-60°, 70°-30°, 70°-40°, and 70°-50° (Figure 4 C), and the predicted CD for the model having dihedral angles of +45°, -40°, +45° and -40° (Figure 4 C-d) was rather similar to the experimental spectrum of the film irradiated with L-CPL (Figure 3 A-a). These results support that CPL irradiation induced a biased-dihedral conformation to poly(Naph) whose difference in dihedral angle between *P*- and *M*-twists is rather small.

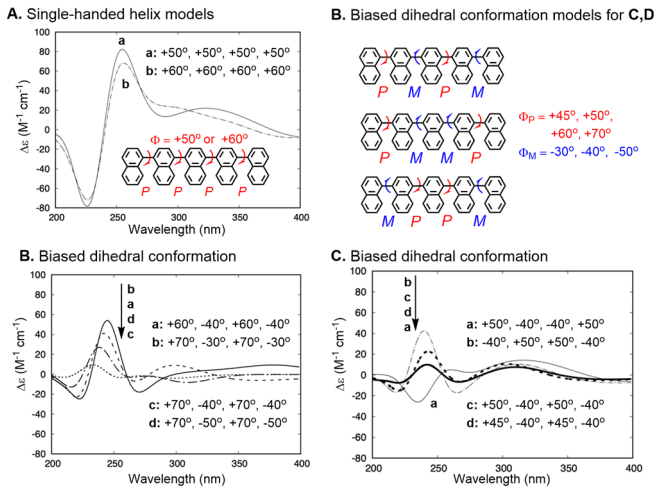


Figure 4. Predicted CD spectra of 5-mer models of single-handed helical poly(Naph) (A), 5-mer models with biased-dihedral conformations (B), and predicted CD spectra of biased-dihedral 5-mer models (C, D). [ZINDO level calculations].

Both preferred-handed helical and biased-dihedral poly(Naph) samples prepared by the helix-sense-selective polymerizaiton and the CPL irradiation, respectively, exhibited efficient circularly polarized luminescence (CPLm). The helical polymers synthesized by SMC with (*R*)- and (*S*)-BINAP showed the CPLm spectra centered at around 390 nm with positive and negative signs, respectively, of g_{lum} of the 10^{-3} order in film (Figure 5 A B), suggesting that the helical structrure induced through the polymerization is preserved in excite states. In addition, the films of the polymers synthesized by YC without chiral ligand and irradiated by CPL also indicated CPLm spectra of g_{lum} of the 10^{-3} order where the films irradited with L- and R-CPL exhibited positive and negative CPLm, respectively, indicating that the polymers irradiated with L- and R-CPL have enantiomeric structures in excited states as well as in the ground state (Figure 5 C D). The present results clearly indicate that handedness of CPLm of poly(Naph) can be tuned by chosing the absolute configuration of chiral ligand in helix-sense-selective polymerization or by chosing the handedness CPL in inducing the biased-dihedral conformation.

The polymers prepared by SMC with (*R*)- and (*S*)-BINAP also showed CPLm having positive and negative signes, respectively, in THF solution (Figure S12 in SI) although g_{lum} values were much lower than in film. The helical conformations may be stabilized in the solid state through inter-chain interations in excited states.

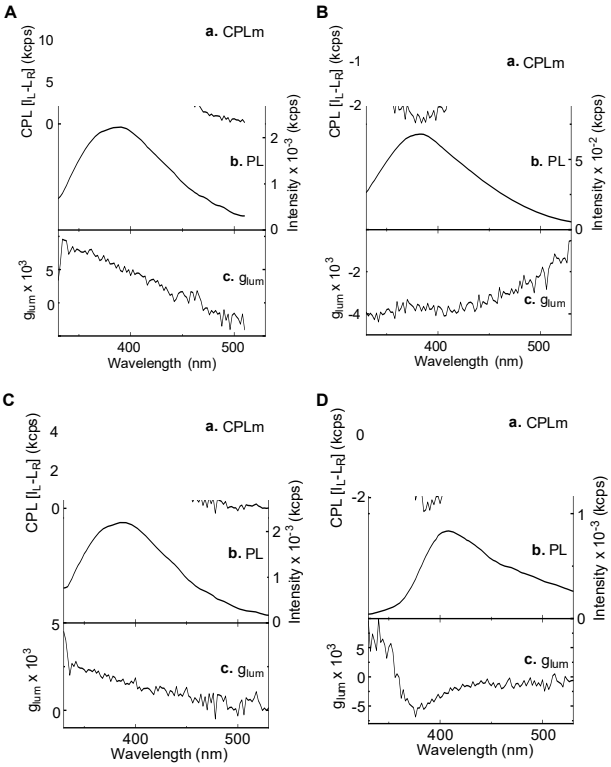


Figure 5. CPLm (a), total emission (PL) (b), and g_{lum} (c) spectra of cast film samples of poly(Naph)s prepared by SMC with (*R*)-BINAP (A) and with (*S*)-BINAP (B) and films of optically inactive poly(Naph) prepared by YC and irradiated with L-CPL for 5 min (C) and with R-CPL for 5 min (D). [λ_{ex} 260 nm]

In conclusion, this work presented chirality induction to poly(Naph) by helix-sense-selective polymerization and by CPL irradiation resulting in two different types of chiral conformation, *i.e.*, single-handed helical conformation and biased-dihedral conformation, respectively. The comparison between the two methods in the ground state and in excited states about the same

polymer is unprecedented to the best of our knowledge. The preferred-handed helix made by helix-sense-selective polymerization was stabilized by chain aggregation. Although helix can be stabilized through steric interactions between bulky side-chain groups in solution as best presented for optically active vinyl polymers,[3,4] and helical conformation is discussed assuming single chain in solution for most synthetic helical polymers, the results of the present work implicate the importance of chain aggregation in building helix. The biased-dihedral conformation proposed for the CPL-irradiated polymers may be regarded as a novel class of chiral structure of polymers with non-helical, axial chirality in the main chain. Studies are underway to clarify the details of this conformation. The information disclosed here may open a way to the synthesis and utilization of optically active polymers with conformational chirality whose scope focuses not only conventional helices but also encompasses non-helical, unforeseen structures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Chirality· Circular dichroism· Polymers · Circularly polarized light · Supramolecular chemistry

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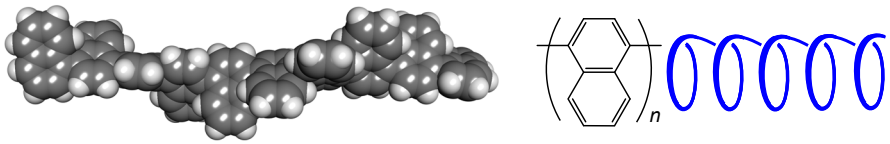
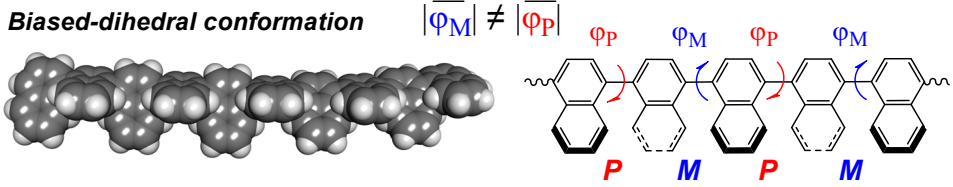
Signle-handed helical conformation



Biased-dihedral conformation

$|\overline{\varphi_M}| \neq |\overline{\varphi_P}|$



Distinctive chiral structures, *i.e.*, single-handed helical conformation and non-helical “biased-dihedral” conformation, were induced to poly(naphthalene-1,4-diyl) by asymmetric polymerization and circularly polarized light irradiation, respectively.

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