HOKKAIDO UNIVERSITY

Title	Molecular chirality induction to an achiral π-conjugated polymer by circularly polarized light
Author(s)	Wang, Yue; Sakamoto, Takeshi; Nakano, Tamaki
Citation	Chemical Communications, 48(13), 1871-1873 https://doi.org/10.1039/c2cc17027b
Issue Date	2012-02-11
Doc URL	https://hdl.handle.net/2115/50988
Rights	Chem. Commun., 2012, 48, 1871-1873 - Reproduced by permission of The Royal Society of Chemistry (RSC)
Type	journal article
File Information	CC48-13_1871-1873.pdf

Molecular Chirality Induction to an Achiral π-Conjugated Polymer by Circularly Polarized Light **

Yue Wang,[a] Takeshi Sakamoto,[b] and Tamaki Nakano*[b]

A preferred-handed helical conformation was induced to poly(9.9-dioctylfluren-2,7-diyl) (PDOF) in a thin film form upon irradiation with single-handed circularly polarized light (CPL) where the induction was reversible.

Chiral polymers create important materials exhibiting valuable functions. Polymers with helical chirality, in particular, are known to feature excellent functions, including chiral recognition ability.[1,2] Optically active helical polymers have been synthesized by asymmetric polymerization using complexes of chiral ligands and metallic species or by supramolecular interactions between polymer chains and external chiral molecules.[3-5] Herein, we report a novel method of preparation of an optically active artificial polymer with molecular chirality from an achiral source material using single-handed circularly polarized light (CPL).

The potential for use of CPL for the production of optically active materials was recognized as early as the 19th century,[6,7] and there have been examples of CPL–assisted asymmetric syntheses.[8,9] There has, however, been no clear example of turning an optically inactive, achiral polymer with no specific conformation into an optically active form with a preferred-handed helical strcture. In this work, we have succeeded in preparing optically active poly(9,9-di-*n*-octylfluoren-2,7-diyl) (PDOF) in thin film using CPL as the only source of chirality.

PDOF has been applied as a light-emitting and hole-transport material for organic light-emitting diodes (OLEDs).[10,11] This polymer has no center of chirality. Although axial chirality around single bonds connecting fluorene units is possible, due to the extremely fast conformational dynamics, this polymer can virtually be regarded achiral in solution. In the solid state, where conformational dynamics are retarded, however, exchange between P- and M-twists around single bonds may be remarkably slow, and enrichment of either of the mirror image twists may be conducted by external stimuli. PDOF in the solid state consists of chiral twisted sequences and planar-zigzag or 2_1 helical sequences forming the achiral β-phase.[12]

[a] *Graduate School of Chemistry and Chemical Sciences, Hokkaido University, Sapporo 060-8628, Japan.*
[b] *Division of Biotechnology and Macromolecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan. E-mail: nakanot@eng.hokudai.ac.jp; Fax: +81 11 706 6869*
† This communication is dedicated to Professor Dr Tatsuki Kitayama on the occasion of his 60th birthday ("Kanreki").
‡Electronic Supplementary Information (ESI) available: Experimental details, ^{1}H NMR, UV, CD, FT-IR spectra, SEC curves, DSC charts, XRD profiles, and polarized optical micrographs of the film sample.

Based on this concept, PDOF was irradiated with CPL in a thin-film form under N_2 atmosphere. Film samples were prepared by a solution cast method (thickness ca. 0.05 μm).

Intense bisignate Cotton effects due to a π–π* transition were observed in circular dichroism (CD) spectra for a PDOF film upon CPL irradiation (**Fig. 1**). Upon irradiation using a 500-W Hg-Xe lamp-based R-CPL for 6 min at 23°C, a clear negative Cotton band emerged at around 400 nm (**Fig. 1** CD-1). This band almost completely disappeared upon L-CPL irradiation for 6 min (**Fig. 1** CD-2). Further irradiation with L-CPL for an additional 6 min (total duration = 12 min) gave rise to a positive CD band at around 400 nm (**Fig. 1** CD-3). The first and last spectra were almost symmetrical. Thus, clear chiral induction and chiral switching were attained for PDOF using CPL. Similar chiral induction was also attained by sunlight (ESI: **Fig. S1**).
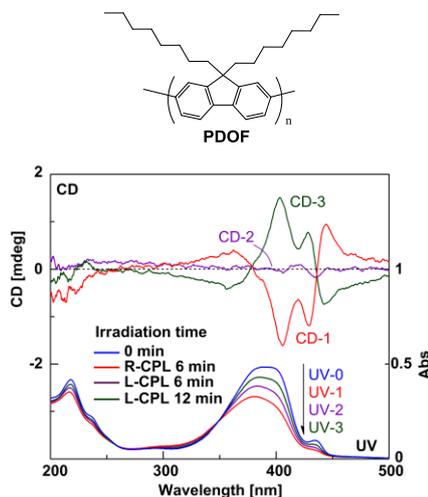

Fig. 1. CD and UV spectral changes of PDOF in film on irradiation with R-CPL for 0 min (blue, UV-0) and 6 min (red, UV-1 and CD-1) and on irradiation with L-CPL for 6 min (purple, UV-2 and CD-2) and for additional 12 min (green, UV-3 and CD-3). CD spectra were obtained by averaging those recorded at different film orientations (angles) with the film face positioned vertically to the incident light beam for measurement.

The CD spectral patterns are closely similar to those reported for optically active polyfluorenes bearing chiral side-chain groups with a preferred-handed twisted, helical conformation.[13,14] The CD spectra shown in **Fig. 1** consequently indicate that PDOF irradiated with CPL has a bias of P- or M-twist and that the entire polymer chain is in a preferred-handed helical conformation. Although the CD patterns observed in this study were not completely indentical

to those in literature,[13,14] the slight discrepancies may be based on differences in helical pitch. The relation between the absolute configuration of the helix and the sign of the CD spectra has been theoretically investigated: for a model trimer of fluorene, a positive Cotton effect at 410 nm due to the S_0-S_1 transition has been predicted to be based on an M-twist.[13b] Hence, L-CPL induces an M-helical sense for PDOF.

When the irradiated polymer was dissolved in tetrahydrofuran, it did not indicate Cotton effects anymore. This indicates that the induced conformation is stable only in the solid state. In addition, racemization in the solid state also took place on heating film at 160°C (ESI: **Fig. S2**).
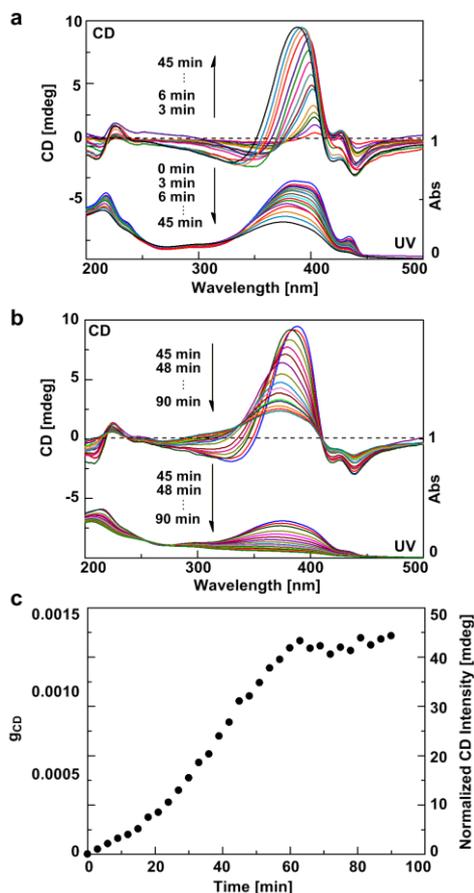

Fig. 2. CD and UV spectra of PDOF measured every 3 min during L-CPL irradiation for a 0-45 min duration at ambient temperature (22-23°C) (a), those measured every 3 min during L-CPL irradiation for a 45-90 min duration at ambient temperature (22-23°C) (b), and g_{CD} (normalized CD intensity)-vs.-irradiation time plot based on the data from **a** and **b** (c). g_{CD} in **c** was estimated for the CD signal at around 380 nm. CD intensity in **c** was normalized for 1.0-UV absorbance.

The intensity of the induced CD spectra varied with the irradiation time with L-CPL in extended irradiation durations (**Fig. 2a** and **b**). The apparent CD intensity first increased and then decreased with the irradiation time, and, at the same time, the UV absorption intensity decreased and slightly blue shifted continuously with the irradiation time. The anisotropy factor (g_{CD}) increased with the irradiation time and eventually leveled off after ca. 60-min irradiation (**Fig. 2c**). The maximum g_{CD} was 0.0013 (44m° for 1.0 absorbance at 374 nm) after 90-min irradiation.

The decrease in intensity and blue shifts in UV spectra are ascribed in part to the hypochromic effect due to interchain $\pi-\pi$ stacking in an H-type aggregation form. π-Stacking leads to a pronounced hypochromicity,[15] and H-aggregation results in blue shifts.[16] This assumption is supported by the fluorescent spectra. While the PDOF film before irradiation indicated emission bands peaking around 440 nm, 470 nm, and 500 nm, the film after L-CPL irradiation for 12 min at 23°C indicated a broad emission band peaking at around 530 nm in addition to the aforementioned bands (ESI: **Fig. S3**). The broad emission is ascribed mainly to excimer emission and partially to oxidized units (vide infra). Increased conformational homogeneity induced by CPL may possibly have made close interchain interaction more feasible, although the interaction seems to be limited to relatively short-distance ranges, as no apparent liquid crystallinity was confirmed for the irradiated film sample.

In addition, the decrease in intensity of the UV band at around 435 nm due to the β-phase seems more obvious than at around 400 nm, suggesting that the molecular motion of twisted sequences on excitation and deactivation (twist-coplanar transition, vide infra) induces conformational transition of planar-zigzag sequences contained in the β-phase in the vicinity into twisted forms by steric interactions.

Effect of CPL on chemical structure of PDOF was investigated by means of FT-IR, ^{1}H NMR, and SEC analyses (ESI: **Fig. S4-S6**). Although the apparent molecular weight estimated by SEC was almost unchanged before and after irradiation, unambigously indicating that no chain session took place, FT-IR spectra suggested the formation of fluorenone units (keto defects).[17a] The amount of fluorenone units was asummed to be only ca. 0.3% and ca. 0.5% after irradiation for 6 min and 90 min, respectively, based on ^{1}H NMR spectra.[17b] Therefore, they would not significantly contribute to the observed CD spectra. Whether the formation of a small amount of fluorenone units is correlated to chirality induction is not yet clear at this stage.

Although chirality induction mechanism is not completely clear yet, it is proposed to be as follows. Biaryl compounds are known to undergo a conformational transition on photo excitation, where a twist conformation in the ground state is transformed into a coplanar form in excited states.[18] This transition would be plausible for the fluorene-fluorene units in PDOF. When P- and M-twists have different molar absorptivities toward single-handed CPL, either the P- or M-twist will be preferentially excited. The excited enantiomeric twist will form P- and M-twists, resulting in an excess concentration of a twist with less likelihood of excitation by the single-handed CPL used for irradiation (a reversible photo racemization process[9]). This mechasnism is supported by the facts that chemical structural change of PDOF was only slight and that the chiral induction was reversible.

The proposed mechanism of chiral induction is partially supported by the facts that intensity of the induced CD spectra largely decreased on linearly polarized light (LPL) irradiation (ESI: **Fig. S7**). These results suggest that LPL, racemic CPL, induces racemization of the induced preferred-handed helix.

Achievable extent of chiral induction is related to the

difference in molar absorptivity toward single-handed CPL between enantiomers. However, it is generally subtle for organic molecules with a $\pi-\pi^*$ transition.[9a] The difference is evaluated by Kuhn's g_γ value[19] which is on the order of less than 10^{-3} for typical aromatic organic molecules. Hence, the enantiomeric excess achievable by CPL in the photostationary state ($\gamma_{PSS} = 1/2\ g_\gamma$) is extremely small, and the chiroptical properties of reversible photo racemization products are often negligible.

Although the g_γ of PDOF is unknown because the polymer is usually recognized as an achiral compound and its optically pure form is therefore unavailable, the intense CD may suggest a significant extent of chiral induction. The CD intensity of 44m^{o} for 1.0-UV absorbance achieved by 90-min CPL irradiation is comparable to that of optically pure poly(9,9-bis((*S*)-5-methylheptyl)fluoren-2,7-diyl) with chiral side-chain groups (ca. 50 m^{o} at 400 nm), and it is ca. 1/45 that of poly(9,9-bis((3*S*)-3,7-dimethyloctyl)fluoren-2,7-diyl).[13b]

The significant chiral induction observed in this study may be due in part to an amplification effect[20] in the solid state. In the solid state, deactivation of an excited twist may not be a complete racemization process but, rather, an enriching process, where the chances of obtaining P-twist and M-twist from a coplanar excited chromophore are unequal due to the steric effects of single-handed twists in the vicinity that have been formed previously in earlier excitation-deactivation events. This effect should be more obvious when the difference in the populations of P- and M-twists is larger, bringing about an apparent amplification. This proposal is supported by the plots of effective CD intensity against irradiation time in **Fig. 2c**, where the slope of the curve tends to increase with increases in irradiation time. This is especially obvious in the early stages of irradiation, where levelling-off of the plots does not hide the increase in slope.

The PDOF film samples studied in this work seemed to be mostly glassy as supported by polarized-microscopic observations, thermal analyses, and X-ray diffraction experiments (ESI: **Fig. S8-S10**). Neither polarized-microscopic observations of film samples before nor after irradiation at ambient temperature indicated a clear texture that might be related to crystalline or LC phases. In differential scanning calorimetric (DSC) analyses, moreover, films before and after irradiation indicated exothermic and endothermic responses at around 100-120°C and 130-150°C, respectively. These behaviors are typical of glassy, amorphous PDOF.[21] Further, X-ray diffraction profiles before and after irradiation did not show responses due to crystalline domains. Hence, chirality induction by CPL under the conditions employed in this study took place mainly in an amorphous solid state, and it mainly caused molecular conformational chirality.

In summary, we have successfully induced chirality to PDOF by CPL obtained from an artificial light source and the sun. This is the first report on preferred handed-helical conformation induction to a virtually achiral main-chain conjugated polymer without the use of chemical substances but with only the aid of light. Polymer chirality induction by CPL has been demonstrated for a helical polyisocyanate

bearing CPL-sensitive side-chain groups.[22] In addition, CPL-induced chirality to film samples of vinyl polymers bearing photochromic azo moieties has been reported where observed chiroptical properties are assigned to formation of chiral liquid crystalline phases.[23] Our work on PDOF is distinguished from these examples by the facts that the source polymer is virtually achiral, that it has no photochromic groups and that it is not a specially designed polymer dedicated to CPL experiments. Induction of preferred-handed helix by CPL presented here may be extended to a wide variety of main-chain conjugated polymers.

Notes and references

1   Y. Okamoto and K. Hatada, *J. Liq. Chromatogr.*, 1986, **9**, 369-384.

2   T. Nakano, *J. Chromatogr.,* 2001, **A 906**, 205–225.

3   Y. Okamoto and T. Nakano, *Chem. Rev.,* 1994, **94**, 349-372.

4   T. Nakano, Y. Okamoto, *Chem. Rev.,* 2001, **101**, 4013-4038.

5   E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.,* 2009, **109**, 6102–6211.

6   J. A. Le Bell, *Bull. Soc. Chim. Fr.,* 1874, **22**, 337- 347.

7   J. H. Van't Hoff, Pamphlet, Utrecht, September 3, 1874.

8   (a) A. Moradpour, J. F. Nicoud, G. Balavoine, H. Kagan, *J. Am. Chem. Soc.*, **1971**, *93*, 2353-2354; (b) W. J. Bernstein, M. Calvin, O. Buchardt, *J. Am. Chem. Soc.*, **1972**, *94*, 494-498.

9   (a) Y. Inoue, *Chem. Rev.,* 1992, *92*, 741-770; (b) B. L. Feringa and R. A. Delden, *Angew. Chem. Int. Ed.,* 1999, **38**, 3418-3438.

10 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.,* 2000, **12**, 1737-1750.

11 U. Scherf and E. List, *Adv. Mater.,* 2000, **14**, 477-487.

12 M. Grell, D. D. C. Bradley, G. Ungar, J. Hill and K. S. Whitehead, *Macromolecules,* 1999, **32**, 5810-5817.

13 (a) M. Oda, H.-G. Nothofer, G. Lieser, U. Scherf, S. C. J. Meskers and D. Neher, *Adv. Mater.*, 2000, **12**, 362-365; (b) M. Oda, H.-G. Nothofer, U. Scherf, V. Sunjic, D. Richter, W. Regenstein and D. Neher, *Macromolecules,* 2002, **35**, 6792-6798.

14 M. R. Craig, P. Jonkheijm, S. C., J. Meskers, A. P. J. J. Schenning and E. W. Meijer, *Adv. Mater.,* 2003, **15**, 1435-1438.

15 (a) T. Nakano and T. Yade, *J. Am. Chem. Soc., J. Am. Chem. Soc.*, **2003**, *125,* 15475-15484; (b) T. Nakano, K. Takewaki, T. Yade and Y. Okamoto, *J. Am. Chem. Soc.,* **2001**, *123*, 9182-9183.

16 A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *Chem. Rev.,* **2000**, *100,* 1973-2011.

17 (a) E. J. W. List and R Guentner, *Adv. Mater.,* 2002, **14**, 374-378; (b) C. Chi, C. Im, V. Enkelmann, A. Ziegler, G. Lieser and G. Wegner, *Chem. Eur. J.*, 2005, **11**, 6833-6845.

18 A. Imamura and R. Hoffmann, *J. Am. Chem. Soc.,* 1968, **90**, 5379-5385.

19 W. Kuhn, *Trans. Faraday Soc.,* 1930, **26**, 293-308.

20 (a) T. Kawasaki, M. Sato, S. Ishiguro, T. Saito, Y. Morishita, I. Sato, H. Nishino, Y. Inoue and K. Soai, *J. Am. Chem. Soc.,* 2005, **127**, 3274-3275; (b) K. Soai, T. Shibata, H. Morioka, K. Choji, *Nature*, 1995, **378**, 767-768.

21 M. Grell, D. D. C. Bradley, M. Inhasekarun and E. P. Woo, *Adv. Mater.*, 1997, **9**, 798-802.

22 J. Li, G. B. Schuster, K.-S. Cheon, M. M. Green and J. V. Selinger, *J. Am. Chem. Soc.,* 2000, *122*, 2603-2612.

23 (a) L. Nikolova, T. Todorov, M. Ivanov, F. Andruzzi, S. Hvilsted, P. S. Ramanujam, *Opt. Mater.*, 1997, **8**, 255-258 ; (b) G. Iftime, F. L. Labarthet, A. Natansohn and P. Rochon, *J. Am. Chem. Soc.,* 2000, **122**, 12646-12650; (c) A. Natansohn and P. Rochon, *Adv. Mater.* **1999**, *11*, 1387-1391.