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Poly(2,7-di-*n*-pentyldibenzofulvene) showing chiroptical properties in the solid state based purely on a chiral conformation†

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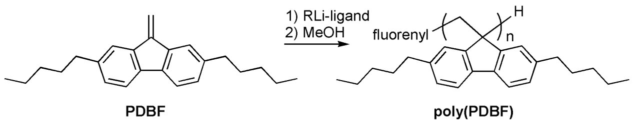
Poly(2,7-di-*n*-pentyldibenzofulvene)s with no stereocenters, obtained by anionic polymerization using chiral 9-fluorenyllithium ligand complexes, showed intense circular dichroism in film form due purely to the chiral conformation of the main chain, while no chiroptical properties were detectable in solution.

Optically active synthetic polymers with conformational chirality have become a research field of widespread interest in recent years.[1] Although a wide range of synthetic polymers with conformational chirality have been synthesized from various types of monomers, a vinyl polymer with conformational chirality bearing no stereocenters in the main and side chains is not known. The existing examples of optically active vinyl polymers with conformational chirality include isotactic, helical polyolefins bearing asymmetric side chains[2] and isotactic, helical polymethacrylates bearing bulky, achiral side chains.[1a,b,3]

Here we present the new asymmetric synthesis leading to an optically active vinyl polymer whose chiroptical properties arise only from a chiral conformation (Scheme 1). Such a synthesis was realized by the anionic polymerization of 2,7-di-*n*-pentyldibenzofulvene (PDBF) in which the monomer and the polymer have no stereocenters. The parent monomer of this system, dibenzofulvene (DBF), is known to afford a polymer having a constrained conformation characterized by densely stacked side-chain chromophores.[4,5] The poly(PDBF) showed intense circular dichroism (CD) absorptions in film or in suspension but not in solution.

PDBF was anionically polymerized using the complexes of 9-fluorenyllithium (FlLi) with (−)-sparteine (Sp) and (+)- and (−)-1,4-bis(dimethylamino)-2,3-dimethoxybutane (DDB) in toluene or using *n*-BuLi in tetrahydrofuran (THF) under N_2 atmosphere at −78 °C ($[\mathrm{PDBF}]_o$ = 0.20 ~ 0.21 M, [PDBF]/[Li] = 20, [ligand]/[Li] = 1.2). The chiral complexes have been effectively used in the helix-inducing polymerization of methacrylates.[3] The obtained polymers were washed with methanol to remove ligand residue. The ligand residue contents in the MeOH-insoluble polymers were less than 0.01 mol% (per monomeric residue) as determined by ^{1}H NMR.[6] The polymers were partially insoluble in tetrahydrofuran (THF) and chloroform. The THF-insoluble part seems to have the same chemical structure as that of the THF-soluble part based on IR spectra (see ESI†); the insoluble part probably has a higher molecular weight. The number-average-molecular weights of the THF-soluble polymers were 4750 ~ 5950 (molecular weight distribution ≤ 1.20) as determined by size-exclusion chromatography using viscometric, rectangular light scattering, and RI detectors (a Viscotek TDA300 detector system).



Scheme 1 Synthesis of poly(PDBF).

The THF-soluble PDBF polymers prepared using the optically active initiators did not show detectable circular dichroism (CD) absorption bands or optical rotation in THF solution. No CD absorption was observed in solution even at −50 °C. However, thin films cast on a quartz plate from a hexane solution of the polymers (conc. 3 g L^{-1}) showed intense CD bands (Fig. 1, A–C).[7] The spectra of films of the polymers obtained using (+)-DDB-FlLi and (−)-DDB-FlLi were almost mirror images (A and B). The polymer obtained using (−)-Sp-FlLi showed an intense spectrum with a spectral pattern similar to that of the polymer obtained with (+)-DDB-FlLi. The polymer obtained by polymerization with achiral *n*-BuLi did not show CD absorptions in film (D).

The spectral intensity varied from film to film prepared in repeated experiments. However, the signs and patterns of the CD spectra were unchanged for a specific polymer. In addition, changing the direction and orientation of the film sample did not significantly affect the spectral intensity and pattern. Furthermore, the films did not show birefringence in polarized optical microscopy analysis. These observations rule out the possibility that the CD spectra are due to linear dichroism based on film anisotropy and support the idea that the film spectra reflect molecular chirality.

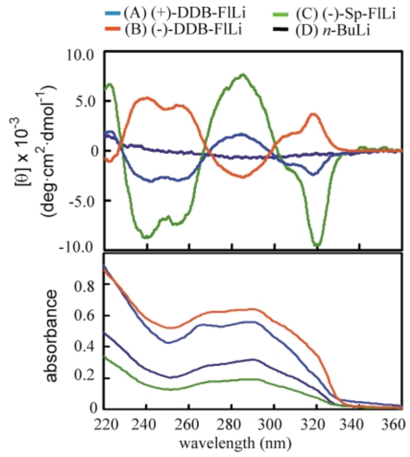


Fig. 1 CD (top) and absorption (bottom) spectra of THF-soluble poly(PDBF)s prepared using (+)-DDB-FlLi (M_n 5290, M_w/M_n 1.03) (A), (−)-DDB-FlLi (M_n 5710, M_w/M_n 1.16) (B), (−)-Sp-FlLi (M_n 5950, M_w/M_n 1.05) (C), and *n*-BuLi (M_n 4750, M_w/M_n 1.20) (D) measured using a JASCO J-820 spectrometer. Concentration of the film samples for molar elipticity calculation was determined by comparing absorbance of a film at 290 nm with that of a solution in THF (conc. 1.10 × 10^{-2} M, cell length 0.1 mm, absorbance at 290 nm = 0.983). The thickness of film B was 0.10 ~ 0.16 μm as measured using a Keyence VK9500 Laser microscope.

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† Electronic supplementary information (ESI) available: experimental details and selected spectra. See http://www.rsc.org/suppdata/cc/b3/b312027a/

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CD absorptions similar to those indicated in film were also observed for a decalin suspension of THF-insoluble polymer (fine powder ground with a mortar) synthesized using (−)-Sp-FlLi (see ESI†). This further supports the idea that the CD spectra in film (Fig. 1) do not arise from sample anisotropy.

The chemical structure of the polymers shown in Scheme 1 was confirmed by MALDI-MS analysis of THF-soluble polymers (Fig. 2). Therefore, the polymers obtained in this study have no chiral ligand fragment attached to the chain and have no stereocenters in the main- or side-chain. Hence, the CD absorptions are unambiguously ascribed to a chiral conformation induced during the polymerization process.

Poly(DBF), the parent polymer of poly(PDBF), has been shown to have a π-stacked, single-handed helical conformation in crystal.[5] A π-stacked structure was also indicated for poly(PDBF) by remarkable hypochromicity[8] in absorption and exclusive dimer emission[9] in fluorescene spectra (see ESI†). Therefore, it will be reasonably assumed that the CD absorptions observed in this work are based on a helical conformation of poly(PDBF) with excess single handedness. Because the polymers showing clear CD bands in film did not show chiroptical properties in solution, molecular aggregation[10] may amplify and stabilize the single-handed helical conformation induced by the asymmetric polymerization possibly due to intermolecular cooperative effects[1f] in the solid state.

The molecular dynamics (MD) simulation[11] at 300 K for 8.6 ns of a PDBF 20-mer model created on the basis of the DBF oligomer conformation[5] afforded the structure shown in Fig. 3 in which the neighboring fluorene moieties stack on top of each other in a chiral, slightly twisted arrangement. The entire chain formed a relatively long-pitched helical structure in the simulation. Hence, the local twist and the helix may contribute to the CD spectra.

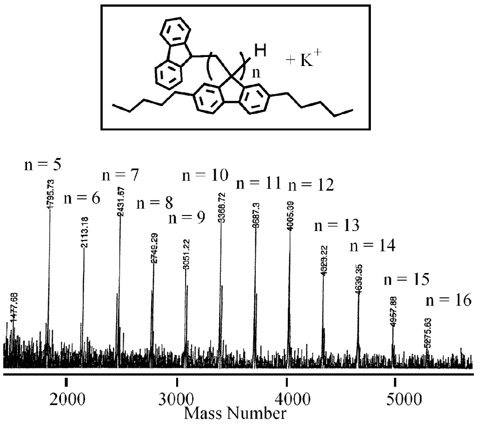

Fig. 2 MALDI-Mass spectrum of poly(PDBF) synthesized using (−)-Sp-FlLi (THF-soluble, MeOH-insoluble part, M_n 5950 as determined by size exclusion chromatography) [matrix: 2,5-dihydroxybenzoic acid].

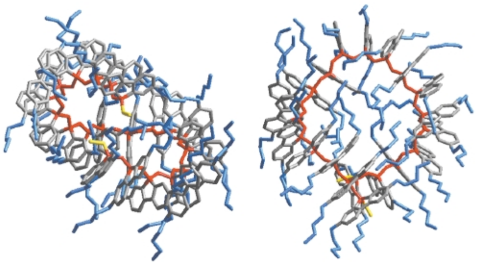

Fig. 3 The conformation of a PDBF 20-mer unit having terminal ethyl groups generated through MD simulation (NVT, 300 K, 8 ns): side and top views. The main chain is shown in red, fluorene moieties in gray, pentyl groups in light blue, and terminal ethyl groups in yellow.

The poly(PDBF)s prepared using chiral initiators have a chiral conformation in solution although their chiroptical properties are below detectable levels, *i.e.*, they are cryptochiral.[12] In order to test conformational stability in solution, THF-soluble polymer synthesized using (−)-Sp-FlLi was heated in a toluene solution at 110 °C for 16 h. A film made from the polymer after the heat treatment still showed intense CD bands, indicating that the conformation induced in polymerization was stable in a solution under these conditions.

In summary, PDBF polymers showing significant CD absorptions in film form have been synthesized by anionic polymerization although the intensity of chiroptical properties is below instrumental noise level in solution. The polymers belong to a new class of optically active vinyl polymers whose chiroptical properties originate only from a chiral conformation in the absence of any configurational information. More detailed structural analyses on the molecules and the aggregates are now under way. In addition, the effects of conformational chirality on photophysical and electronic properties of π-stacked polymer systems are being studied.

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Notes and references

1 (*a*) T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013; (*b*) Y. Okamoto and T. Nakano, *Chem. Rev.*, 1994, **94**, 349; (*c*) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem. Rev.*, 2001, **101**, 3893; (*d*) J. J. L. M. Crnelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039; (*e*) T. Nakano and Y. Okamoto, *Macromol. Rapid Commun.*, 2000, **21**, 603; (*f*) M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger and J. V. Selinger, *Angew. Chem., Int. Ed.*, 1999, **38**, 3138; (*g*) A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed.*, 1998, **37**, 63; (*h*) S. H. Gelman, *Acc. Chem. Res.*, 1998, **31**, 173.

2 (*a*) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Nazzanti and G. Moraglio, *J. Am. Chem. Soc.*, 1955, **77**, 1708; (*b*) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, 1960, **82**, 4745; (*c*) P. Pino, G. P. Lorenzi and L. Lardicci, *Chim. Ind. (Milan)*, 1960, **42**, 712.

3 (*a*) Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada and H. Yuki, *J. Am. Chem. Soc.*, 1979, **101**, 4763; (*b*) T. Nakano, Y. Okamoto and K. Hatada, *J. Am. Chem. Soc.*, 1992, **114**, 1318.

4 T. Nakano, K. Takewaki, T. Yade and Y. Okamoto, *J. Am. Chem. Soc.*, 2001, **123**, 9182.

5 T. Nakano and T. Yade, *J. Am. Chem. Soc.*, 2003, DOI: 10.1021/ja037836x.

6 A film made from the polymer synthesized using *n*-BuLi by adding 0.01 mol% of (−)-Sp did not show clear CD. This rules out the possibility that residual ligand induced the CD spectra in Fig. 1.

7 The film of poly(PDBF) synthesized using (−)-DDB-FlLi showed optical rotatory dispersion (ORD) in the wavelength range shorter than 330 nm: $[\alpha]_{295}$ −25° (see ESI†).

8 For other π-stacked polymers: (*a*) I. Tinoco, *J. Am. Chem. Soc.*, 1960, **82**, 4785; (*b*) W. Rohdes, *J. Am. Chem. Soc.*, 1961, **83**, 3609; (*c*) J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, *Science*, 1997, **277**, 1793; (*d*) K.-I. Okamoto, A. Itaya and S. Kusabayashi, *Chem. Lett.*, 1974, 1167.

9 F. Brouwer, in *Conformational Analysis of Molecules in Excited States*, J. Waluk, ed., Wiley-VCH, New York, 2000, p. 177.

10 Atomic force microscopic analyses indicated that the polymer synthesized using (−)-Sp-FlLi indicated a tendency to form aggregate while the one prepared using *n*-BuLi did not (see ESI†).

11 MD simulations were performed under a constant NVT condition using a Materials Studio software package (Accelrys) with a COMPASS force field: H. Sun, *J. Phys. Chem.*, 1998, **102**, 7338.

12 K. Mislow and P. Bickart, *Isr. J. Chem.*, 1976/1977, **15**, 1.