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Citation	Chemical Communications, 47(39), 10996-10998 https://doi.org/10.1039/c1cc13711e
Issue Date	2011-10-21
Doc URL	https://hdl.handle.net/2115/49880
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Type	journal article
File Information	CC47-39_10996-10998.pdf



A Chiral π -Stacked Vinyl Polymer Emitting White Circularly Polarized Light[†]

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

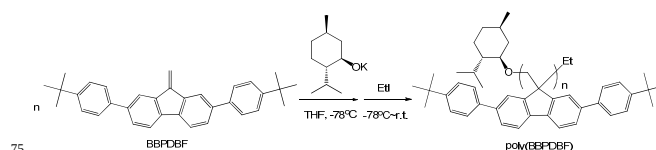
DOI: 10.1039/b000000x

An optically active, π -stacked poly[2,7-bis(4-*t*-butylphenyl)dibenzofulvene] having preferred-handed helical conformation was synthesized by anionic polymerization. A thin film sample of the polymer exhibited broad-band white circularly polarized light (CPL) emission on photo excitation.

Fluorescent and phosphorescent organic polymers are an important class of materials for organic light-emitting diodes (OLEDs) based on their advantages that emission properties can be modified through molecular designs, that they are inherently light and flexible, and that they can be readily fabricated by solution processes.¹ Among various polymers of this class, those emitting circularly polarized light (CPL) are of particular interest because of their potential for photonic devices such as 3D displays and energy-efficient backlights for LC displays.²⁻⁴ CPL-emitting polymers extensively studied so far are mainly main-chain π -conjugated ones including linear poly(*p*-phenylenevinylene) derivatives,⁵ polyfluorene derivatives,⁶ poly(*p*-phenyleneethynylene) derivatives,⁷ polysilane derivatives,⁸ and poly(*p*-phenylene) derivatives,⁹ and polymers consisting of thiophene units,¹⁰ and a hyperbranched fluorenevinylene polymer,¹¹ and no example has been reported on CPL emission of a vinyl polymer.

Although vinyl polymers are advantageous over main-chain conjugated polymers due to their higher solubility and controllability of molecular weight and block sequences, they generally exhibit significantly lower charge mobilities than conjugated polymers that may lead to a poor performance as a photo electronic material. In order to overcome this shortcoming, π -stacked vinyl polymers have been invented.^{12,13} The first example in this category is poly(dibenzofulvene) (poly(DBF)) in which the side-chain fluorene units are regularly and densely stacked on top of each other and the main-chain has a helically twisted zigzag conformation.¹⁴⁻¹⁹

Hole mobility of this polymer is in the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is higher than some main-chain conjugated polymers and is slightly less than polyfluorene derivatives.²⁰ This information combined with the fact that poly(DBF) has fluorescent fluorene units in the side-chain urged us to synthesize a chiral poly(DBF) derivative and examine its CPL-emitting properties. For this purpose, in this study, optically active poly[2,7-bis(4-*t*-butylphenyl)dibenzofulvene] (poly(BBPDBF)) possessing chiral menthyl group at the chain terminal was synthesized by anionic polymerization (Scheme 1). Prior to this work, optically active poly(DBF) bearing a chiral terminal group has been reported;¹⁹ however, the emission quantum yield of poly(DBF) is around 0.1. Hence, in order to improve emission quantum yield, the side-chain conjugation system was extended by introducing 4-*t*-butylphenyl groups at the 2- and 7-position of the fluorene backbone. *t*-Butyl group at the 4-position of phenyl group was attached to improve solubility of the BBPDBF monomer and the polymer derived therefrom.



Scheme 1. Synthesis of optically active poly(BBPDBF).

Herein, we present the synthesis and properties of optically active poly(BBPDBF). BBPDBF monomer, which can be synthesized starting from 4-*t*-bromobenzene and 2,7-dibromofluorene, was available from our recent work.²¹ BBPDBF was polymerized in tetrahydrofuran (THF) using a reaction mixture of KH and L-menthol (potassium menthoxide) as anionic initiator at -78°C at [BBPDBF]/[initiator] = 10 and 20. The polymerization was terminated by adding EtI as terminator. The reactions at [BBPDBF]/[initiator] = 10 and 20 afforded optically active products with relatively low molecular weights (molar masses) of Mn 3800 (Mw/Mn 1.07) and Mn 5200 (Mw/Mn 1.08), respectively (ESI: **Tab. 1S**). Although polymers showed circular dichroism (CD) spectra, the polymer of Mn 3800 showed a more intense CD spectrum ($[\theta]_{319} 7400 \text{ deg cm}^2 \text{ dmol}^{-1}$ for Mn 3800; $[\theta]_{319} 3300 \text{ deg cm}^2 \text{ dmol}^{-1}$ for Mn 5800) (ESI: **Fig. 1S**). This observation is ascribed to the fact that the influence of the chiral terminal group is more significant in the closer range along the chain from the initiation terminal.¹⁹ Hereafter, chiroptical properties of the

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†Electronic Supplementary Information (ESI) available: Experimental details including polymer syntheses, ¹H NMR spectra, UV and CD spectra, TGA and DSC charts, and photographs of the film sample. See DOI: 10.1039/b000000x/

polymer of Mn 3800 are discussed.

Fig. 1 shows the UV and fluorescent spectra of 2,7-bis(4-*t*-butylphenyl)fluorene as a monomeric unit model (**Scheme 1**) and the poly(BBPDBF) and the CD-UV spectra of the poly(BBPDBF). The model compound was available from our recent work.²² In the UV spectra (**Fig. 1A**), the poly(BBPDBF) exhibited a remarkable hypochromic effect and a red shift of the absorption band edge compared with the monomeric unit model, indicating that the polymer has a π -stacked conformation. A π -stacked conformation was supported by ¹H NMR spectra of the polymer and BBPDBF monomer where aromatic proton signals of the polymer were significantly up field shifted (ESI: **Fig. 2S**).

In the fluorescent spectra (**Fig. 1B**), the monomeric unit model exhibited intense emission bands at around 350-400 nm with two separate peaks at 360 nm and 375 nm and one shoulder peak at 400 nm. In sharp contrast, the poly(BBPDBF) exhibited a broad structure-less band peaking at 415 nm. This band is ascribed to excimer (dimer) emission based on the π -stacked conformation. The emission quantum yield (Φ) of the monomeric unit model was 0.79 while that of the polymer was 0.40 as determined using 9,9-diphenylanthracene as a reference compound. The quantum yield of the polymer was much higher than that of poly(DBF) ($\Phi \sim 0.1$), which can be ascribed to the extended π -conjugation system in the side chain. This observation may also mean that the π -stacked structure of the poly(BBPDBF) is not as tight as that of poly(DBF), *i.e.*, stacking of the side-chain 4-*t*-butylphenyl groups is not as rigid as that of the fluorene units due to a certain freedom of rotation around the bonds connecting the fluorene units and the 4-*t*-butylphenyl groups.

The poly(BBPDBF) exhibited intense positive Cotton effects in the CD spectrum (**Fig. 1C**). The chromophores of the polymer, therefore, are under a chiral environment by the effect of terminal menthoxy group. The polymer is proposed to possess a preferred-handed helical conformation such as that of poly(DBF) having a chiral terminal group.¹⁹ The helix of poly(BBPDBF) is thought to be dynamic in solution similarly to that of poly(DBF). This is supported by the fact that CD spectral intensity and pattern changed reversibly depending on the temperature of measurement (ESI: **Fig. 3S**).

In the light of the facts that the poly(BBPDBF) has a chiral conformation and that it effectively emits light upon photo excitation, the polymer can be regarded as a good candidate of a CPL-emitting material. In order to test this aspect, a thin-film sample of the polymer was formed on a quartz plate by a solution casting method, and CD, fluorescence, and CPL-emission spectra were measured in the solid state (**Fig. 2**).

The film sample exhibited clear bisignate CD bands over the entire wavelength range where polymer absorbs (**Fig. 2A**). The spectral shape was different from that observed in solution, and the spectral intensity was much higher than that in solution ($CD_{\max}$ 3.07 m° normalized for 1.0 UV absorbance at 319 nm in solution; $CD_{\max}$ 14.9 m° normalized for 1.0 UV absorbance at 350 nm in the solid state). These observations indicate that the polymer conformation in the solid state differs from that in solution and that helical sense excess is greater in the solid state possibly due to interchain interaction.

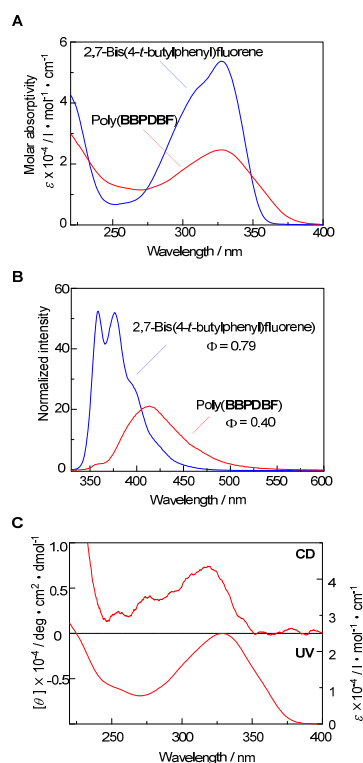


Fig. 1 Optical properties of the poly(BBPDBF) and the monomeric unit model in a THF solution. A) UV spectra of the two compounds (1.25×10^{-4} M, cell path 1 mm). B) Fluorescent spectra of the two compounds normalized to a constant absorbance at 322 nm (λ_{ex} 322 nm, 1.25×10^{-6} M, cell path 1 cm). C) CD and UV spectra of the poly(BBPDBF) (1.25×10^{-4} M, cell path 1 mm).

In order to enhance chain alignment in the solid state and to increase the CD intensity, the film sample was thermally annealed at 120°C. The annealing temperature was chosen based on differential scanning calorimetric (DSC) analyses of the polymer. DSC exhibited a clear endothermic response at around 120°C on the 1-st cooling run that might be based on chain alignment or crystallization (ESI: **Fig. 4S**). Thermal annealing has been reported to be an effective method for linear polyfluorene derivatives in enhancing chirality.⁶ However, the CD intensity of the poly(BBPDBF) film only slightly decreased, and no major change in spectral intensity and shape was observed. The anisotropy factor for the CD spectrum after annealing (the dissymmetry factor (g_{CD}) in absorption), which is defined as $g_{\text{CD}} = 2(\epsilon_{\text{L}} - \epsilon_{\text{R}}) / (\epsilon_{\text{L}} + \epsilon_{\text{R}})$ with ϵ_{L} and ϵ_{R} being the extinction coefficients for left and right circularly polarized light, respectively, was 9×10^{-4} at 350 nm.

In the fluorescence spectra of the polymer film, the emission band width was much broader than that observed for a THF solution (**Fig. 2B**). In addition to the peak at around 415 nm, a broader and more intense emission band peaking at around 500 nm emerged, and overall emission wavelength range spread from 365 nm to beyond 650 nm. The relative intensity of the longer-wavelength band increased on thermal annealing. These observations can be ascribed to the formation of inter-chain π -stacking formation in the solid state. As discussed earlier, there should be a certain degree

of rotational freedom around the single bond connecting the fluorene unit and the 4-*t*-butylphenyl group. The proposed conformational freedom may enhance interchain π -stacking formed between the phenyl groups, causing the broad emission band peaking at around 500 nm. Thus, the poly(BBPDBF) in a thin-film form exhibits a highly broad-band emission. To naked eyes, emission from a thin-film sample of poly(BBPDBF) looked almost white under irradiation using a black light (λ_{ex} 365 nm) (ESI: **Fig. 5S**). It is, to the best of our knowledge, very rare that a single organic polymer species exhibits light in such a broad range.

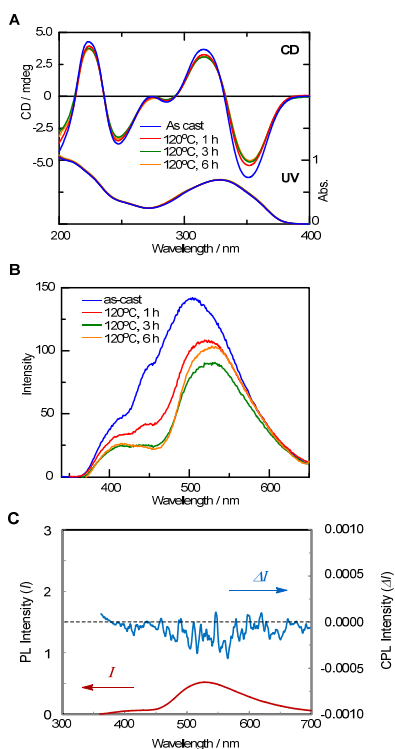


Fig. 2 Optical properties of the poly(BBPDBF) in a thin-film form. A) CD spectra recorded upon thermal annealing at 120°C. B) Fluorescent spectra recorded upon thermal annealing at 120°C (λ_{ex} 329 nm). C) CPL emission spectra of the sample annealed at 120°C for 6h.

CPL emission spectra were recorded upon excitation at 329 nm (**Fig. 2C**). Unambiguous CPL responses were observed in the entire range of emission though the intensity was moderate. The dissymmetry factor in photoluminescence (g_{PL}), which is defined as $g_{\text{PL}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$ with I_{L} and I_{R} being intensities of left and right circularly polarized light, respectively, was ca. 6×10^{-4} . The magnitude of g_{PL} coincided with that of g_{CD} .

In summary, we have demonstrated that optically active poly(BBPDBF) with a π -stacked intra- and intermolecular structure exhibits CPL emission in a broad, visible wavelength range. A broad-band CPL emitting single organic polymer species is unprecedented. Such a polymer may be applied as a backlight material for energy-efficient LCDs and a light source of 3D OLED displays. Although CPL efficiency is moderate, it will be able to be improved by enhancing helical

sense excess of the polymer. With a menthoxy group as a chirality source at the chain terminal, g_{CD} was in the order of 10^{-4} , suggesting that helical sense excess of the polymer is moderate. Helical sense excess may be largely increased by optimizing the terminal chiral group structure, leading to improved g_{CD} and g_{PL} .

This study was supported in part by the MEXT through Grants-in-Aid No. 21655037, No. 22350047, and No. 23655092 and through the Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Science) and in part by the Asahi Glass Foundation.

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