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Donor-Acceptor Conjugated Block Copolymer of Poly(arylenevinylene)s by Ring-Opening Metathesis Polymerization †

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Novel conjugated cyclophanes comprising electron donating cyclopentadithiophene-vinylene and accepting dithienobenzothiadiazole-vinylene have been synthesized by McMurry coupling. Ring-opening metathesis polymerization (ROMP) of the acceptor monomer and the subsequent addition of the donor monomer allows the preparation of a fully conjugated diblock copolymer. The diblock copolymer exhibits multiple optical and electrochemical functions.

Conjugated polymers have been investigated intensively for applications in opto-electronic devices, such as organic light emitting diodes (OLEDs),[1] organic photovoltaics (OPVs)[2] and organic field effect transistors (OFETs).[3] For these applications, typical high-performing p-type polymers are composed of electron donor-acceptor alternating structures, most of which have been synthesized by step-growth polymerization, such as Pd-complex catalyzed Suzuki or Stille coupling polymerizations.[1-3] Fully conjugated block copolymers have been of great interest as these polymers can incorporate multiple photo- and electronically-active blocks.[4-7] Among them, precision synthesis of such block copolymers with low polydispersity is particular challenging. Such synthesis can be achieved by chain-growth polymerization with subsequent addition of different monomers after completion of the first polymerization.[4-6] However, these monomers must have asymmetric functional groups, such as bromide and boronic acid groups. Synthesis of such monomers is generally difficult, leading to limited versatility of monomers. Other typical methods to synthesizing fully conjugated block copolymers are end-functional polymer copolymerization and end-functional polymer coupling.[5,7] In both methods, one-sided brominated poly(3-hexylthiophene) (P3HT-Br) with low PDI is often used as a macromolecular end-capping reagent.

Ring-opening metathesis polymerization (ROMP) is a type of olefin metathesis polymerization of cyclic olefin monomers.[8] It offers well-defined conjugated polymers with low polydispersity and few structural defects. Furthermore, it has potential to prepare fully conjugated block copolymers. Yu and Turner et al. reported the synthesis of homopolymers[9] and block copolymers[10] of poly(phenylenevinylene)s (PPVs) with precise molecular weights by ROMP of cyclophanedienes using the Grubbs initiator. In addition, this method was applied to the synthesis of poly(thienylenevinylene) (PTV) from annulene-trisulfide monomers.[11] Despite good controllability of polymerization by ROMP, the monomers are limited to relatively simple structures due to multiple-step synthesis with low overall yield.[12]

The fully conjugated block copolymers incorporating multiple photoactive blocks are of great interest as these polymers can absorb a wide range of sunlight when they are used in OPV. Here, we report the synthesis of a donor-acceptor conjugated block copolymer of poly(arylenevinylene)s comprising electron donating cyclopentadithiophene (CPDT) and accepting bis(thienyl)benzothiadiazole (TBT) by ROMP of cyclophanetriene using a ruthenium-based Grubbs initiator.

Monomers **M1a**, **M2a**, and **M3a** with branched alkyl chains of 2-ethylhexyl groups were synthesized by McMurry coupling of dialdehydes of CPDT and TBT, using TiCl$_4$/Zn, as shown in Scheme 1. Yields of these monomers were relatively low (21% for **M1a**, 9% for **M2a**, and 12% for **M3a**) as the reactions produce larger cycles and linear oligomers; however, isolation of **M1a** was facile by column chromatography with hexane eluent because **M1a** can be eluted as a first fraction without other oligomers, whereas purification of **M2a** and **M3a** required preparative gel permeation chromatography (GPC) due to their similar polarity but different molecular size. The obtained monomers were characterized by ^{1}H NMR spectroscopy and fast atom bombardment mass spectrometry (FABMS).

To confirm the molecular structure of the cyclophanes, analogues of the monomers with shorter alkyl chains were also synthesized. Single crystals of **M1c** were prepared from chloroform/diethyl ether solution, and X-ray crystallography was performed (Figure 1a). In the crystal, **M1c** has a well-strained structure because three CPDT groups are tethered with vinylenes to form an absolutely conjugated macrocycle with 30-π electrons. The angles between two planes of thiophene rings in CPDTs are 13.9°, 9.7°, and 7.9°. In contrast,

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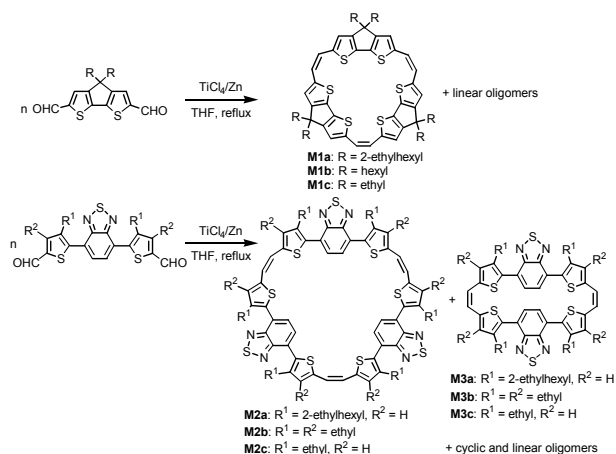
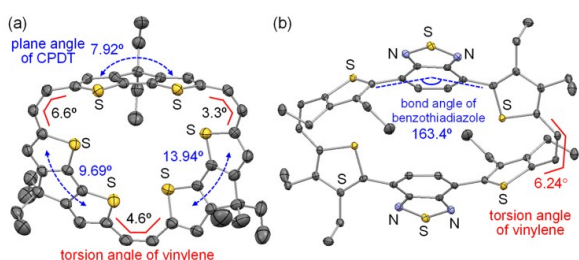Scheme 1. Synthesis of cyclic monomers by McMurry coupling

Fig. 1 Molecular structures of (a) M1c and (b) M3b in the single crystal. ORTEP drawn with 50% probability. Hydrogen atoms and chloroform molecule in (a) are omitted for clarity.

in a linear molecule of (CPDT)-(benzothiadiazole)-(CPDT), CPDT is absolutely planar, according to our previous report.[13] In addition, the torsion angles of the *cis*-vinyl part of M1c are 6.6°, 3.3°, and 4.6°. Such strained structure is adequate for ROMP.

The molecular structure of M3b was analyzed in our previous study[14] and is shown in Figure 1b for comparison. The crystal structure of M3b also shows a strained structure with torsion angles of 163.4° at the 4,7-positions of benzothiadiazole and 6.2° at the vinyl parts. This molecule has π–π interactions at the central benzothiadiazole units, which may interrupt the ring-opening of the cyclophanedienes by the Grubbs initiator. Other compounds did not form suitable crystals for X-ray crystallography, probably due to the existence of too many conformations derived from bond rotation.

As shown in Scheme 2, M1a, M2a, and M3a were polymerized by ROMP applying a second-generation Grubbs catalyst in *p*-xylene at 120 °C for 6 min. The reaction mixture was then quenched by ethyl vinyl ether. Further heating for an hour transformed the polymers with *cis*- and *trans*-vinylene backbones to an all-*trans*-vinylene backbone. Finally, the polymers were purified by reprecipitation in methanol. Despite the relatively strained structure of M3a, ROMP of M3a was slower and less active than that of M1a or M2a, affording low molecular weight P2 under same reaction conditions as other monomers.[15] Therefore, we used M1a and M2a for later analysis and the synthesis of a block copolymer rather than M3a. The diblock copolymer P3 was prepared by ROMP of M2a followed by subsequent addition of M1a. Addition of monomers in the opposite order can also produce almost the same block copolymer due to the similar reactivity of M1a and M2a.

The molecular weights of the polymers were determined by GPC using a UV-vis detector at 254 nm and polystyrene standards in THF solution. As shown in Figure 2a, the number-averaged molecular weights (M_n) of P1 and P2 are proportional to the initial
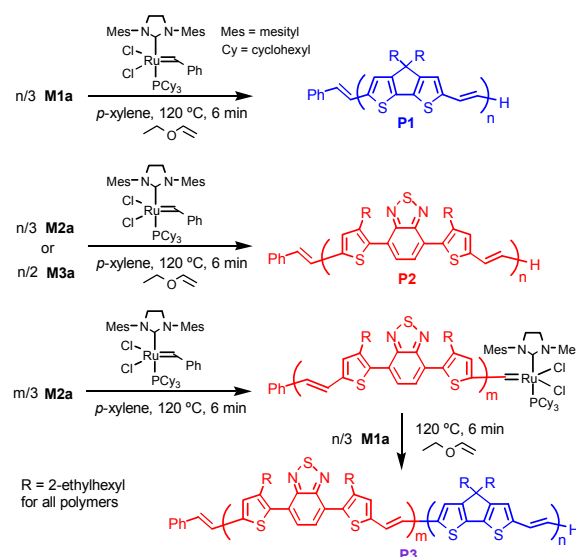
Scheme 2. Synthesis of polymers by ROMP of cyclophanes

monomer-to-catalyst ratios with a correlation coefficient of 0.96 and 0.97, respectively, suggesting living-like polymerization. These values are in a range of 8600–16000 (n = 20–37) for P1 and 17600–23700 (n = 32–43) for P2; however, the values are slightly higher than expected (M_n = 7700–13000 with n = 18–30 for P1 and M_n = 8200–18100 with n = 15–33 for P2). A plausible explanation for the higher M_n is that these polymers have a larger hydrodynamic radius than that of polystyrene calibration standards resulting in a larger polystyrene equivalent molecular weight when determined by GPC. This trend is more significant after isomerization from *cis*- to *trans*-vinylene form.[9b] P1 and P2 are both expected to have *trans* form, as described later. Polydispersity indexes (PDI) of these polymers were in a range of 1.64–1.85 for P1 and 1.51–1.82 for P2. These PDIs are lower than or similar to that of PTV by ROMP of annulene-trisulfide (PDI = 1.8 for M_n = 10400)[11], but higher than PPVs by ROMP of cyclophanedienes (PDI = 1.2–1.5 for similar M_n polymers).[9,10] The higher PDIs of P1 and P2 may be attributed to the lower ring strain of M1a and M2a compared to the cyclophanedienes with higher strain used for PPVs synthesis.
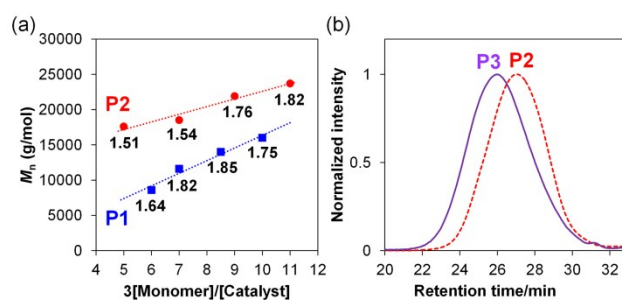

Fig. 2 (a) Dependence of the molecular weight (M_n) of P1 and P2 on the monomer-to-catalyst ratio. The polydispersities are also shown. (b) GPC traces of P2 and P3 detected using a UV-vis detector at 254 nm (THF eluent, flow rate = 1.0 mL/min).

In the block copolymer synthesis, TBT-vinylene monomer M2a was polymerized first with an initial monomer-catalyst ratio of 3[M2a]$_0$/[catalyst]$_0$ = 5.0 in *p*-xylene at 120 °C for 6 min to give P2 (M_n = 17600, PDI = 1.51). CPDT-vinylene monomer M1a with monomer-catalyst ratio of 3[M1a]$_0$/[catalyst]$_0$ = 7.0 was then added

to the reaction mixture, and the second block growth was conducted at 120 °C for another 6 min to give **P3**. As shown in Figure 2b, the GPC elution curve shifts to a higher molecular weight region with $M_n = 35600$ and PDI = 2.10. These values are consistent with those obtained using the UV-vis detector at 490 nm and 650 nm and using a refractive index (RI) detector (Figure S-35). These results show that the second monomer was polymerized under a chain-growth mechanism from the polymer terminal group of the first polymer **P2** to give diblock copolymer **P3** comprising TBT-vinylene and CPDT-vinylene.

The polymerization is driven by the release of ring strain in the cyclophane-triene monomers by opening only one of the 3 double bonds; therefore, the resulting polymers are expected to have a backbone of alternating two *cis*- and one *trans*-vinylene linkages.[9,10] However, the ^{1}H NMR spectrum of **P1** ($M_n = 19100$, PDI = 1.94) simply shows two prominent signals in an aromatic region: one is assigned to the *trans*-vinylene group at 6.95 ppm and the other is assigned to the 3-position of CPDT at 6.83 ppm (Figure 3a). These peaks were assigned by synthesizing a model compound of CPDT-CH=CH-CPDT, and its 2D NMR analysis. The ^{1}H NMR spectrum of **P1** suggests the disappearance of the *cis*-vinylene group, presumably due to thermal isomerization of the *cis*, *trans*-microstructure to an all-*trans*-vinylene backbone after the end-capping reaction at 120 °C for an hour. This property is advantageous because further treatment of as-synthesized polymers is unnecessary. When PPVs were synthesized by ROMP, UV-irradiation to PPV solutions was required to obtain the all-*trans*-vinylene backbone.[9,10]

The ^{1}H NMR spectrum of **P2** ($M_n = 18600$, PDI = 1.74) shows three peaks at 7.67, 7.09, and 7.01 ppm, which are assigned to the proton on benzothiadiazole, thiophene, and all *trans*-vinylene groups, respectively, without a *cis*-vinylene signal (Figure 3b). Block copolymer **P3** shows the superimposed spectrum of **P1** and **P2**, representing the existence of two blocks (Figure 3c). From the integration of the peaks, the ratio between **P1** and **P2** is estimated to be 1:0.87 in mol and 1:0.68 in weight, and is consistent with the growth of molecular weight in GPC.

To estimate conversion of monomers, ^{1}H NMR spectra of the reaction mixture were measured immediately after the polymerization without purification (Figure S-34). Monomer peaks in **P2** were completely disappeared, showing completion of the first ROMP reaction. This result presumably suggests that the second block should not contain **P2** unit (not gradient) in **P3**.
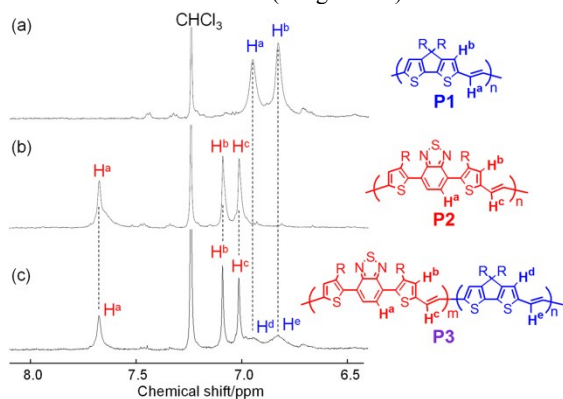

Fig. 3 ^{1}H NMR spectra of (a) **P1**, (b) **P2**, and (c) **P3** in CDCl$_3$ solution

The obtained polymers show quite different colors; **P1**, **P2**, and **P3** are blue, red-orange, and purple, respectively. UV-vis absorption spectra of **P1** ($M_n = 19100$, PDI = 1.94), **P2** ($M_n = 18600$, PDI = 1.74), and **P3** were recorded in CHCl$_3$ solutions and films, and are shown in Figure 4. **P1** shows absorption peaks in the long-

wavelength region (609 and 655 nm), whereas **P2** shows peaks at in the short-wavelength region (374 and 490 nm) in CHCl$_3$ solution. This can be attributed to different backbone structures that result in different conjugation systems: CPDT-vinylene is composed of a fused ring with high planarity, leading to extended conjugation, whereas TBT-vinylene has rotatable bonds between benzothiadiazole and thiophenes with sterically hindered alkyl chains on the thiophene rings.[17] Block copolymer **P3** shows a wide visible absorption spectrum from 300 to 700 nm with peaks at 370, 515, 602, and 650 nm in a CHCl$_3$ solution. This absorption spectrum is the superposition of the **P1** and **P2** absorption spectra. Such a conjugated block copolymer is potentially useful as an efficient light-harvesting material in OPV devices. The superimposed absorption spectrum of **P3** and the similarity of the GPC traces obtained at 254 nm, 490 nm, and 650 nm also provide evidence of yielding the block copolymer. From the absorption intensities, the molar ratio between **P1** block and **P2** block is approximately the same, which is consistent with the GPC and NMR analysis.

UV-vis spectra of the polymers were also measured in films. **P1** shows a broader absorption spectrum than that in the CHCl$_3$ solution, possibly due to stronger intermolecular interaction in the solid state. The absorption spectrum of **P2** in film is similar to that in a solution, indicating less intermolecular interaction. The absorption spectrum of **P3** consists of the spectra of **P1** and **P2**. From the onset of the absorption spectra in film, optical band gaps of the polymers were estimated to be $E_{opt} = 2.00$ eV for **P1**, 1.71 eV for **P2**, and 1.72 eV for **P3**.
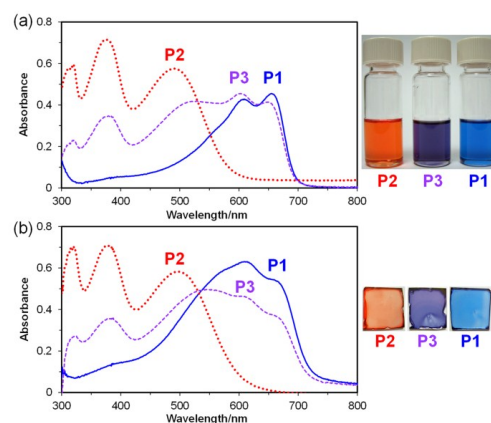

Fig. 4 UV-vis spectra of **P1**, **P2** and **P3** (a) in CHCl$_3$ and (b) in films. Photos of solutions and films are inserted.

The electrochemical properties of the polymers were investigated by cyclic voltammetry, as shown in Figure 5a. The cyclic voltammogram (CV) of **P1** shows a reversible anodic peak at 0.95 V (vs AgCl/Ag) and a cathodic shoulder at −1.63 V. These relatively low potential positions are due to the presence of the electron donating CPDT group. In contrast, the CV of **P2** shows a quasi-reversible oxidation shoulder at 1.62 V and a reversible reduction peak at −1.36 V. These relatively high potential positions are due to the presence of the electron accepting benzothiadiazole group. **P3** shows a superimposed CV composed of **P1** and **P2**, which is similar to the UV-vis spectrum for **P3**.

HOMO and LUMO levels of the polymers were estimated from the onset of oxidation and reduction signals in the CVs and are summarized in Figure 5b. The HOMO and LUMO levels are calculated to be −4.83 and −2.79 eV for **P1** and −5.44 and −3.18 eV for **P2**. As **P3** exhibits a superimposed CV, HOMO and LUMO levels of **P3** show similar values as **P1** and **P2**. In the film of **P3**, the **P1** block and **P2** block do not disrupt individual block properties.
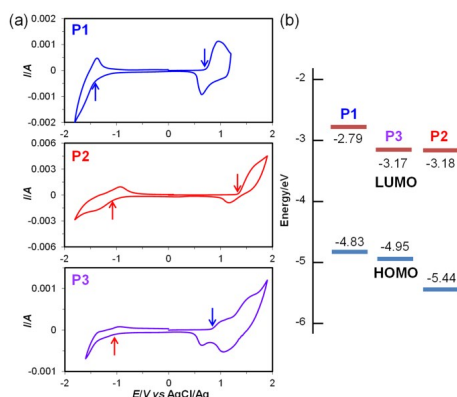
Fig. 5 (a) Cyclic voltammograms of **P1** (top), **P2** (middle), and **P3** (bottom) on Pt electrode in acetonitrile solution containing 0.1 M *n*-Bu$_4$NPF$_6$. (b) Energy diagrams of polymers. HOMO-LUMO levels were estimated from onset of oxidation and reduction peaks in CVs (shown as arrows in (a)).

In summary, we have demonstrated the synthesis of a fully conjugated block copolymer comprising donor and acceptor poly(arylenevinylene)s by ROMP of cyclophanes. The block copolymer exhibits multiple functions derived from each block, e.g., wide-range UV-vis absorption and high and low HOMO-LUMO levels. This method can be applied to the synthesis of conjugated block copolymers with versatile backbone structures. In addition, such block copolymers can potentially self-assemble into a variety of interesting morphologies (e.g., microphase separation). Such morphologies are currently under investigation.

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