

ORIGINAL ARTICLE

Twisting poly(3-substituted thiophene)s: cyclopolymerization of gemini thiophene monomers through catalyst-transfer polycondensation

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Polythiophenes are an important class of materials in the field of organic electronics. The molecular structures of polythiophenes have a critical role in determining device performance; therefore, substantial efforts have been devoted to controlling their regioregularity, molecular weight and polydispersity. Herein, we demonstrate a new approach for controlling another structural parameter, the dihedral angle. We exploited the unique polymerization mechanism of cyclopolymerization: an alternating intramolecular–intermolecular chain propagation that produces a series of cyclic molecules along the polythiophene chain. We designed gemini thiophene monomers in which two thiophene monomers are tethered by an alkylene strap and we processed the monomers by using the catalyst-transfer polycondensation method. We found that the dihedral angle in the polythiophene is dictated by the size of the macrocycle formed.

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INTRODUCTION

In general, the polymerization of a monomer that has two polymerizable moieties results in insoluble cross-linked polymer networks. However, with an appropriate monomer design and optimized polymerization conditions, a soluble polymer can be obtained through a process called cyclopolymerization in which an alternating intramolecular–intermolecular chain propagation produces a series of cyclic molecules along the polymer chain.^{1,2} To achieve this, monomers are generally designed such that thermodynamically favored five- or six-membered rings are formed. However, with an elaborate monomer design, large macrocycles can be produced, thus resulting in polymeric materials with the capacity of molecular recognition.^{3–8} In addition, the alternating propagation process can be exploited for sequence control in a polymer main chain.^{9,10} As such, cyclopolymerization is an intriguing polymerization methodology that allows access to novel polymer structures. The aim of the present study was to apply cyclopolymerization to the synthesis of poly(3-substituted thiophene)s (P3XT).

P3XT, in which 'X' represents the substituents, are semiconducting polymers that are widely used in various organic electronic devices.^{11,12} Synthetic methodologies that produce well-defined P3XT structures have been developed in the past two decades and have contributed to the understanding of structure–property relationships.^{13,14} The structural parameters regarding P3XT include regioregularity (head-to-tail selectivity), molecular weight

and polydispersity, which are currently controllable because of recent advances in nickel catalyst-transfer polycondensation (CTP).^{15–20} In this study, we focus our attention on another structural parameter, specifically the dihedral angle of the conjugated backbone, because it governs the effective conjugation length along the polymer chain.^{21,22} Indeed, the dihedral angle has an important role in device performance. For instance, Bao and colleagues²³ have reported that a twisted polythiophene backbone, compared with a planar polymer, achieves larger open-circuit voltages in bulk heterojunction solar cells. Given the nature of chain growth, the CTP method would enable cyclopolymerization of thiophenes (Scheme 1a). We can then deduce that the dihedral angle of P3XT is dictated by the size of the macrocycles formed (Scheme 1b). To date, cyclopolymerization that produces π -conjugated polymers has been limited to the synthesis of polyacetylene by ring-closing metathesis;^{24–26} to the best of our knowledge, this study is the first report of polythiophene synthesis through cyclopolymerization.

EXPERIMENTAL PROCEDURE

General

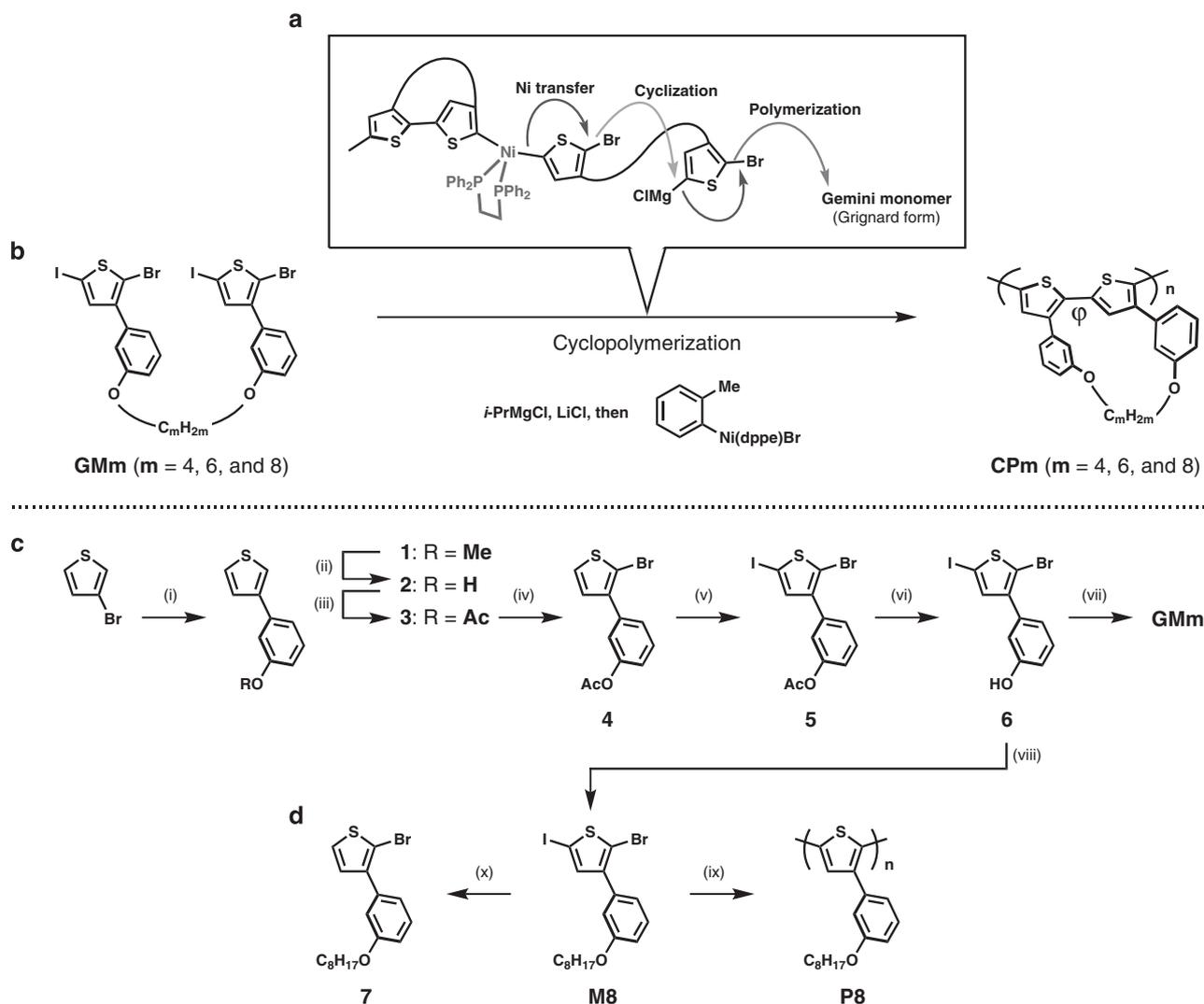
Reagents and solvents were purchased from commercial suppliers and used without further purification. Air- and/or water-sensitive reactions were conducted under argon by using dry solvents. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (Tokyo, Japan, 400 MHz) spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectra were measured by using a Shimadzu AXIMA-CFR Plus station (Kyoto,

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Scheme 1 (a) Proposed cyclopolymerization mechanism based on catalyst-transfer polycondensation. (b) Cyclopolymerization of **GMms**. (c and d) Synthetic scheme of the gemini thiophene monomer, **GMm**, **7**, **M8** and reference polymer **P8**: (i) 3-methoxyphenylmagnesium bromide, Ni(dppp)Cl₂, THF, reflux; (ii) BBr₃, DCM, 0 °C; (iii) (AcO)₂O, NaOH, THF; (iv) NBS, CHCl₃, AcOH; (v) I₂, PhI(OAc)₂, DCM; (vi) NaOH aq.; (vii) Br(C_mH_{2m})Br, Cs₂CO₃, DMF; (viii) octylbromide, Cs₂CO₃, DMF; (ix) *iso*-propylmagnesium chloride and lithium chloride, then the external catalyst; and (x) *iso*-propylmagnesium chloride and lithium chloride, then quenched with methanol. A full color version of this scheme is available at *Polymer Journal* online.

Japan). Melting points were determined with a Yanako NP-500P micro melting point apparatus (Tokyo, Japan). Ultraviolet–visible absorption and fluorescence spectra were recorded on a JASCO V-630 spectrophotometer (Tokyo, Japan) and JASCO FP-8500 spectrofluorometer, respectively. The molecular weight distribution M_n and M_w/M_n (polydispersity index, PDI) values of the polymers were determined in tetrahydrofuran (THF) at 40 °C (polystyrene standard for **CPms** and **P8**, and poly(methyl methacrylate) standard for **P6'**, where **CP** stands for cyclopolymer) using a TOSOH GPC system (Tokyo, Japan, HLC-8320GPC EcoSEC) equipped with two TSK gel super-multipore HZ-M columns and an ultraviolet detector (254 nm).

Polymerization of gemini thiophene monomers

A typical procedure for cyclopolymerization of gemini thiophene monomers is as follows.^{27,28} A round-bottomed flask was heated with a heat gun under reduced pressure. After the flask was cooled to room temperature, the gemini thiophene monomer **GM4** (113 mg, 0.138 mmol) was placed in the flask. The flask was then evacuated and re-filled with argon three times. After the addition of a solution of LiCl (0.5 mol l⁻¹ in THF, 1.108 mmol, 2.22 ml) and dry THF (20 ml), a solution of *iso*-propylmagnesium chloride (2 mol l⁻¹ in THF,

0.277 mmol, 0.138 ml) was added under 0 °C. The resulting mixture was stirred at room temperature for 1 h. Then, an external-initiator (*o*-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (1.7 mg, 5%) was added and the mixture was stirred again at room temperature overnight. The reaction mixture was quenched with 5 M HCl aqueous solution, washed with water and extracted with CHCl₃ three times. The combined organic layer was washed with brine and dried over MgSO₄. After the solvent was evaporated, the product was purified by reprecipitation two times (THF/MeOH = 1 ml/30 ml) and then THF/acetone = 1 ml/30 ml).

Ring-opening cross metathesis of CP6' with butyl acrylate

A flask was charged with **CP6'** (17.4 mg, 40 μmol), evacuated and re-filled with argon three times.²⁹ **CP6'** was dissolved in dichloromethane (DCM, 0.5 ml), into which butyl acrylate (11.3 mg, 89 μmol) and Grubbs catalyst, second generation (1.7 mg, 5%), were added in sequence. The resultant mixture was stirred at 40 °C for 8 h and then washed with water and extracted with CHCl₃ three times. The combined organic layer was washed with brine and dried over MgSO₄. After the solvent was evaporated, the product was purified by reprecipitation (THF/MeOH = 1 ml/30 ml).

RESULTS AND DISCUSSION

Synthesis of monomers

We designed and synthesized gemini thiophene monomers in which 2-bromo-5-iodo-thiophenes, which are able to be processed by CTP,^{17–19} are tethered by alkylene straps (Scheme 1b: **GMm**, where **GM** stands for ‘gemini monomer’ and **m** represents the strap length). These monomers were synthesized in seven steps, as shown in Scheme 1c. Kumada–Tamao–Corriu cross-coupling between 3-methoxyphenylmagnesium bromide and 3-bromothiophene produced compound **1**. We first conducted bromination of thiophene in **1** using *N*-bromosuccinimide; however, the reaction was not selective and the anisole moiety was also brominated. We therefore replaced the methoxy group with acetoxy group to alter the reactivity. With **3**, bromination and subsequent iodination resulted in good yield, thereby producing the 2-bromo-5-iodo-thiophene skeleton, **5**. Deprotection of the acetoxy group followed by Williamson ether synthesis produced gemini thiophene monomers, **GMm**. **M8** and **7** were also synthesized as a reference monomer and a model compound for a ‘pendant’ defect, respectively (Scheme 1d). All the compounds were ambiguously characterized, as discussed in the Supplementary Information.

Cyclopolymerization of gemini thiophene monomers

CTP of **GMm**s under common conditions ($[\text{GMm}] = 100 \text{ mM}$, $\text{Ni}(\text{dppp})\text{Cl}_2$, THF, room temperature) resulted in insoluble orange precipitates, whereas **M8** yielded a soluble regioregular polythiophene (**P8**), thus suggesting that the gemini monomers underwent cross-linking. We further optimized the concentrations and catalyst systems. Under diluted concentration conditions (6 mM) and using an external catalyst (*o*-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide^{30,31}, we obtained polythiophenes that were soluble in common organic solvents, briefly implying successful cyclopolymerization. We performed matrix-assisted laser desorption ionization time-of-flight mass spectral measurements using several matrices and additives (such as sodium trifluoroacetate); however, we did not observe the peaks of polymeric species. Size-exclusion chromatography revealed that the average molecular weights (M_n s) of the obtained polymers were in the range of 6 to 9 K with PDI values of 1.4 to 1.6 (Table 1). These values are not strong indicators of controlled polymerization, yet it is known that cyclopolymerization often results in a relatively large PDI value, in particular when a large macrocycle is designed.

¹H-NMR spectra of **CP4**, **CP6** and **CP8** together with those of **P8** and **7** are shown in Figure 1. Although the spectra are somewhat complicated to interpret, all the **CPm** spectra were similar. The integral ratios of the aromatic peaks (6.5–7.5 p.p.m.) to the OCH_2 peak in the straps (~3.9 p.p.m.) were in agreement with the expected ratio (10H:4H). Compared with **P8**, **CPm**s showed broad peaks, most probably because of slow molecular motion restricted by the strap. In addition, sharp peaks representing compound **7** were not clearly observed in **CPm**s, thus suggesting that the pendant defect, which would be formed by the failure of cyclization, is negligible.

¹³C-NMR spectra were simpler than the ¹H-NMR spectra and allowed for further characterization. Although the ¹³C-NMR spectra of the **M8** and **GM8** monomers were virtually the same (Supplementary Figure S2), the spectra of **P8** and **CP8** did not overlap (Figures 2b and c), thus indicating that these two polymers have distinct structures. ¹³C-NMR distortionless enhancement by polarization transfer experiments distinguish tertiary and quaternary carbons in the aromatic moiety. In **P8** (as well as in **M8** and **GM8**, as shown in Supplementary Figure S3), as anticipated, five tertiary carbons were

Table 1 Cyclopolymerization of **GMm** and CTP of **M8**

	M_n	M_w	PDI	DP
CP4	6.6 K	10.0 K	1.51	16
CP6	8.9 K	14.2 K	1.58	20
CP8	7.0 K	9.6 K	1.36	15
P8	6.8 K	7.5 K	1.10	23

Abbreviations: CTP, catalyst-transfer polycondensation; **GMm**, gemini monomer strap length.

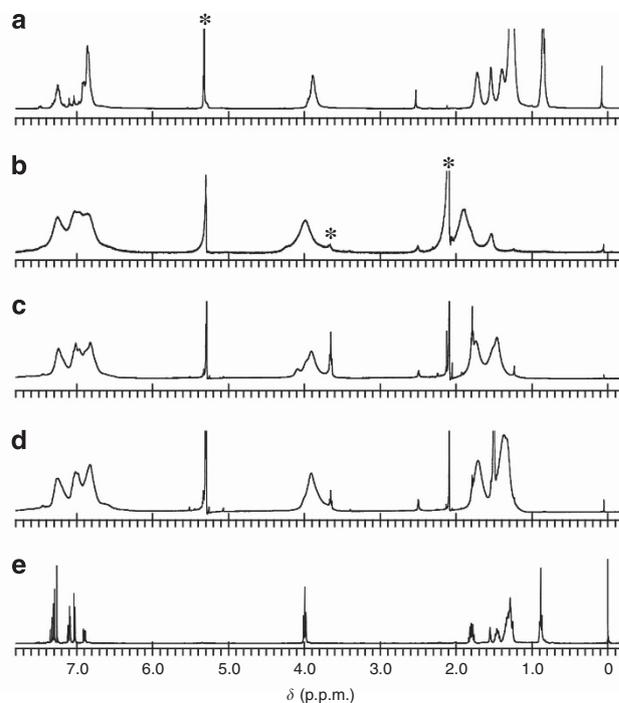


Figure 1 ¹H-NMR spectra of (a)**P8**, (b)**CP4**, (c)**CP6**, (d)**CP8** and (e)**7**. The asterisks indicate the solvent peaks: deuterated DCM for polymers and chloroform for **7**.

observed (Figure 2d), whereas **CP8** showed one additional tertiary carbon at 126.24 p.p.m. (as indicated by the arrow in Figure 2e). It is noteworthy that the two equivalent thiophenes in the gemini monomer become dissimilar after the cyclopolymerization in the linear sequence along the polymer chain (Scheme 1b). Taking the ring-current effect by the anisole moiety into account,³² we attribute the new peak to the tertiary carbon of thiophene located inside the macrocycle.

To further corroborate the cyclic structure, we synthesized **GM6'** in which the strap contains an olefin. **GM6'** was polymerized under the optimized conditions and we obtained a cyclopolymer **CP6'** ($M_n = 6.4 \text{ K}$, $\text{PDI} = 1.4$). Except for the olefin moiety, **CP6'** showed similar ¹H- and ¹³C-NMR spectra to those of **CP6**. However, treating **CP6'** with butyl acrylate in the presence of a second-generation Grubbs catalyst significantly changed the spectra; as shown in Figure 3c, the ¹H-NMR spectrum became sharper, thus suggesting that the conformational restriction was released. The peak of tertiary carbon at 126 p.p.m., which is characteristic of the cyclic structure (see above), disappeared after the metathesis reaction (Figures 3c and d). In addition, the ¹H- and ¹³C-NMR spectra of **CP6'** after the cross-metathesis reaction resembled those of **P8**. These results indicate that the cross-metathesis reaction opened the macrocycles, thus producing **P6'** (Figure 3e). Importantly, the molecular weight did not change

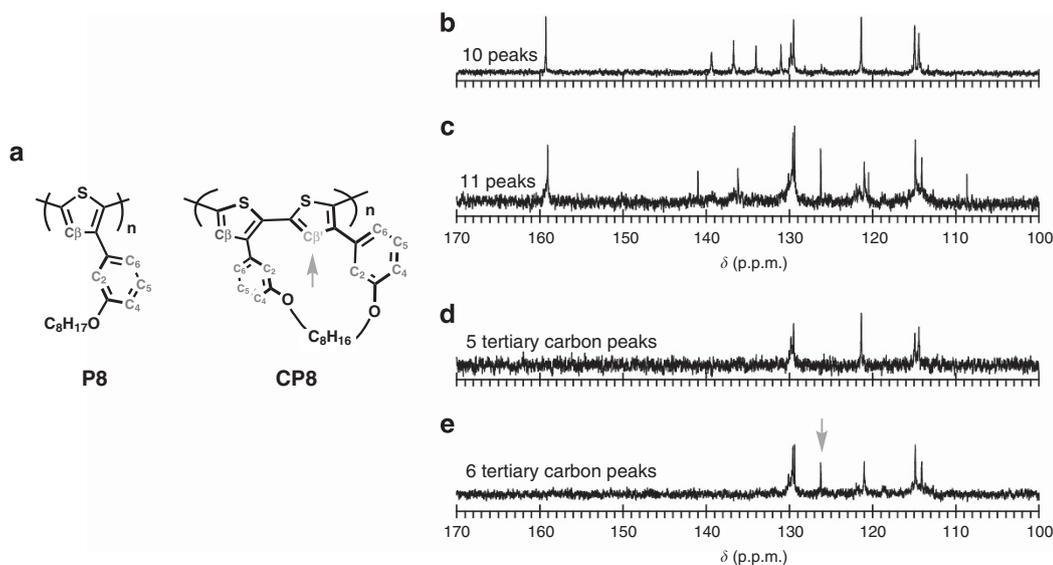


Figure 2 (a) Structures of **P8** and **CP8**. ¹³C-NMR spectra of (b) **P8** and (c) **CP8**, and ¹³C-NMR distortionless enhancement by polarization transfer (DEPT) spectra of (d) **P8** and (e) **CP8**. A full color version of this figure is available at *Polymer Journal* online.

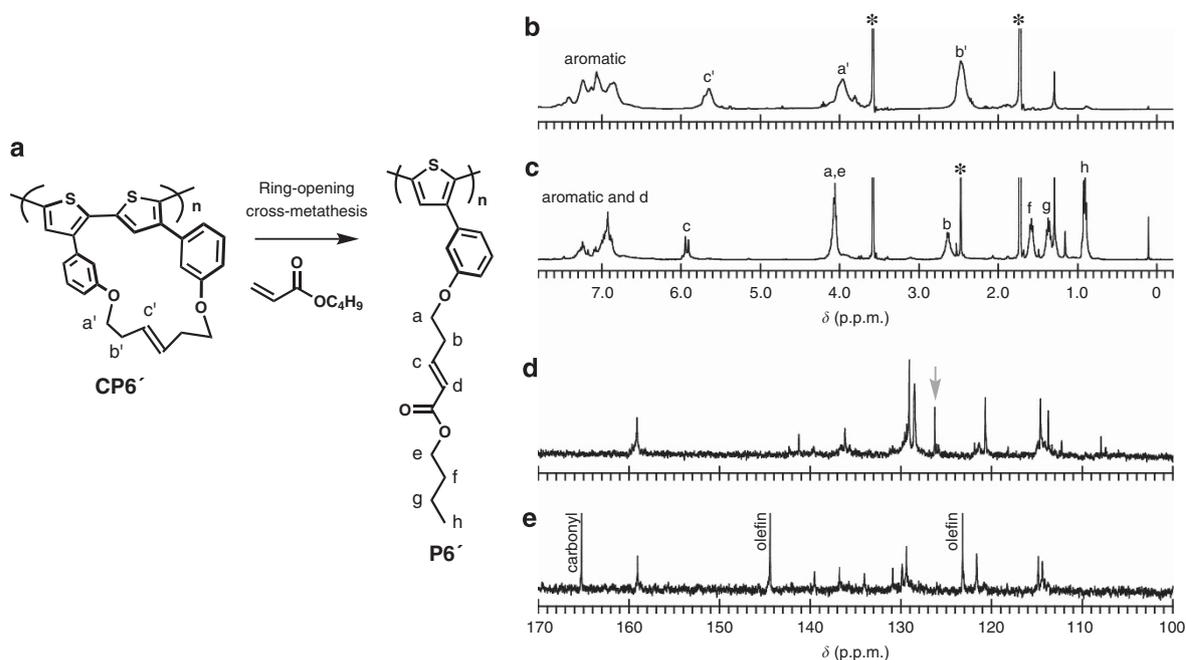


Figure 3 (a) Ring-opening cross-metathesis reaction of **CP6'** with butyl acrylate. (b and c) ¹H- and (d and e) ¹³C-NMR of **CP6'** (a and d) before and (c and e) after the metathesis reaction. The peak indicated by the arrow in **d** disappears after the metathesis reaction. The asterisks indicate the solvent and residual water peaks in deuterated THF. A full color version of this figure is available at *Polymer Journal* online.

significantly after the metathesis reaction ($M_n = 5.3$ K, PDI = 1.9), thus suggesting that the cross-link defect, if any, in **CP6'** was insignificant. These results provide further indirect evidence of the proposed structure of the cyclopolymers.

Structure–property relationship of cyclopolymers

Figure 4a compares the absorption spectra of **CP4**, **CP6**, **CP8** and **P8**. Interestingly, the absorption maxima gradually blue-shifted as the strap length increased. Although the peak shift was not significant, we

also observed a similar tendency in the fluorescence spectra (Figures 4b and c). The absorption spectra of **CPms** measured in the film state were similar to those measured in solution, a result that we believe corroborates the cyclic structure, because it should prohibit conformational changes on film formation. To gain insight into the structure–property relationship, we performed density functional theory calculations (B3LYP/6-31+G(d,p)) for the repeating units of **CPm**: cyclized bithiophenes (Figure 5). As the strap length increased, the dihedral angle became larger. By using the energy-minimized

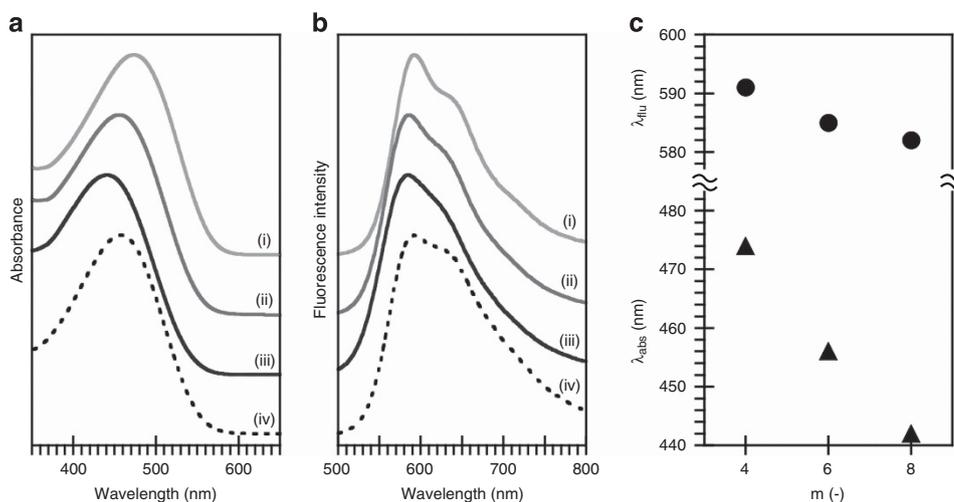


Figure 4 (a) Absorption and (b) fluorescence spectra of CP4 (i), CP6 (ii), CP8 (iii) and P8 (iv). (c) Plots of (triangle) absorption maxima and (circle) fluorescence maxima as a function of the strap length. A full color version of this figure is available at *Polymer Journal* online.

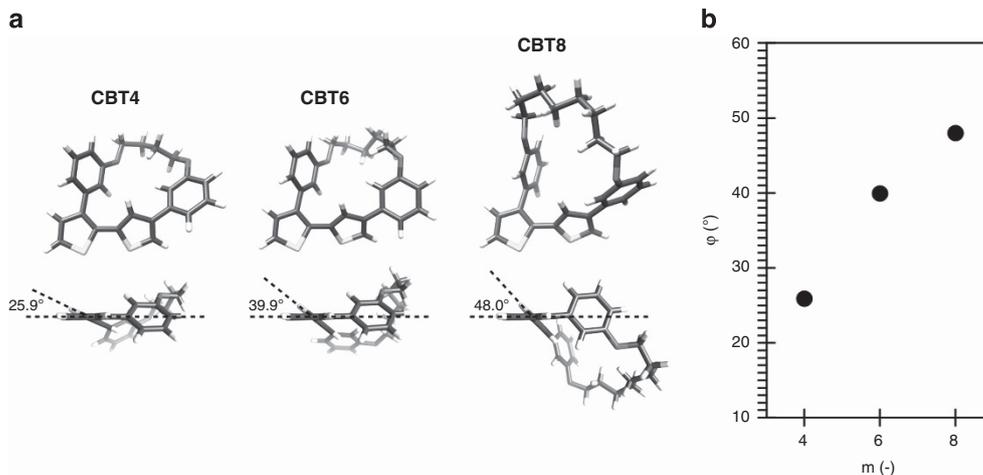


Figure 5 (a) Top and side views of the optimized structures of cyclic bithiophenes at the B3LYP/6-31+G(d,p) level. (b) Plot of the dihedral angle of the bithiophene unit as a function of the strap length. A full color version of this figure is available at *Polymer Journal* online.

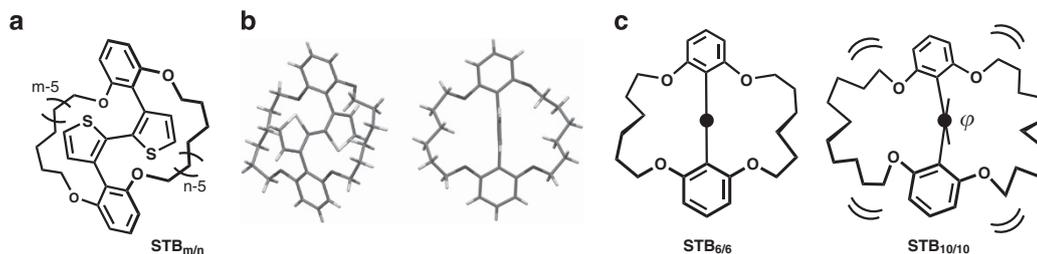
structures of cyclized bithiophenes (Figure 5 and Supplementary Figure S4), we conducted additional time-dependent density functional theory calculations for their trimers (that is, sexithiophene conjugation) (B3LYP/6-31G(d)//B3LYP/6-31(d)). Although the excitation energies were slightly overestimated, the highest occupied molecular orbital–lowest unoccupied molecular orbital gap increased as the strap length increased, a tendency that agrees well with the experimental results (Supplementary Figure S5).³³

A previous study by our group, conceptually related to the present study, has demonstrated that the dihedral angle of bithiophene is affected by cyclic side chains.^{34–37} In STBm/n (Scheme 2), the movable range of the dihedral angle of the bithiophene backbone was defined by the length of the strap. The longer the strap, the larger the fluctuation of the dihedral angle (Scheme 2c). However, the change in absorption spectra induced by this approach was not significant.³⁶ The present study adds another example of ‘strapped’ polythiophenes, which appear to be more effective than our previous molecular design concept in terms of controlling the dihedral angle.

CONCLUSIONS

In conclusion, we present a proof-of-concept example of the synthesis of polythiophene through cyclopolymerization. To date, structural parameters, such as regioregularity, molecular weight and polydispersity, have been controlled using the CTP method. We demonstrate that another important structural parameter, the dihedral angle, can also be controlled by the monomer design. Therefore, the photo-physical properties of polythiophene can be modulated.

The present study expands the scope of the CTP method in terms of the intramonomer condensation process; such an acrobatic CTP is expected to lead to the production of novel conjugated polymer structures.^{38,39} Although the concept is still preliminary, optimization of the monomer structure as well as the polymerization conditions (for example, catalyst systems) should improve the controllability of quasi-living CTP and provide the ability to synthesize block and gradient polymers.^{30,40–42} We are also interested in controlling the axial chirality of the bithiophene dihedral angle by using a chiral ligand; this research is now in progress in our laboratory.



Scheme 2 (a) Structure of $STB_{m/n}$. (b) X-ray crystallographic structure of $STB_{6/6}$. (c) Schematic illustration of the side views of $STB_{6/6}$ and $STB_{10/10}$, representing the control of the dihedral angle of the bithiophene backbone by changing the strap length. A full color version of this scheme is available at *Polymer Journal* online.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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