Tunable Cis-cisoid Helical Conformation of Poly(3,5-disubstituted phenylacetylene)s Stabilized by $n\rightarrow\pi^*$ Interaction

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Abstract A series of novel cis poly(phenylacetylene)s (PPAs) substituted at meta-position(s) by two alkoxycarbonyl pendants, i.e., sP-Me-C8/rP-Me-C8, P-Me-C12, sP-Et-C4, sP-2C4, and sP-Oct-C4, were synthesized under the catalysis of [Rh(nbd)Cl]2 (nbd = norbornadiene). The dependence of elongation, screw sense, and stimuli response of helical polyyne backbone on the structure of pendant, solvent, and temperature was systematically investigated in both solution and solid states. Because of $n\rightarrow\pi^*$ interaction between vicinal carbonyl groups, sP-Me-C8/rP-Me-C8 could adopt contracted cis-cisoid helix in THF, toluene, CH2Cl2, and CHCl3. Such an intramolecular interaction was sensitive to the hydrogen bond donating ability of solvent and temperature, but insensitive to the dielectric constant and polarity of solvent. In poly(3-methoxycarbonyl-5-alkoxycarbonylphenylacetylene), the longer the chiral alkyl chain was, the easier the stable cis-cisoid helix could be achieved. However, when the methoxycarbonyl was changed to ethoxycarbonyl, sec-butylxycarbonyl, and octyloxycarbonyl pendant groups, only cis-transoid helix was obtained at room temperature due to the increased steric hindrance. Moreover, lowering temperature was found to facilitate the stabilization of $n\rightarrow\pi^*$ interactions, and reversible temperature-dependent stereomutations were achieved in sP-Me-C8 and sP-Et-C4 depending on the solvent where they were dissolved. These results suggested that the long alkyl chain, small pendant size, and lower temperature favored the stabilization of intramolecular $n\rightarrow\pi^*$ interactions and the formation of contracted, cis-cisoid helices for poly(3,5-diester substituted phenylacetylene)s.

Keywords Polyphenylacetylenes; Cis-cisoid; Cis-transoid; $n\rightarrow\pi^*$ Interactions; Helical conformation

INTRODUCTION

Noncovalent interactions are the backbone of hierarchical biomacromolecular structures, as well as biological processes. In the past ten years, scientists have tried to recognize the $n\rightarrow\pi^*$ interaction in biomacromolecules such as nucleic acids and proteins through extensive search of the X-ray crystal structures. Although the strength of this interaction is weaker than hydrogen bonds, it plays a vital role in stabilizing biomolecular structures and propelling life processes. For example, collagen, the most important structural protein in vertebrates, consists of three parallel left-handed polyproline type II (PPII) chains stabilized by $n\rightarrow\pi^*$ interactions between carbonyl groups. Many protein-ligand complexes, such as a serine protease-inhibitor complex and the histamine N-methyltransferase-quinarine complex, are stabilized by analogous C─X···C═O interactions, where X is a halogen located on the ligand. The $n\rightarrow\pi^*$ interaction between two carbonyl groups can be described as a lone pair (n) of electrons on the donor oxygen of a carbonyl group delocalized into the antibonding orbital (n*) of a neighbouring acceptor carbonyl group, which follows the Bürgi-Dunitz trajectory of approach of a nucleophile to an electrophilic system, requiring an O···C═O distance (d) of ≤3.2 Å and O···C═O angle (θ) of 109° ± 10°. Hitherto, the $n\rightarrow\pi^*$ interaction has been found in many proteins, peptides, nucleic acids, and small molecules. However, in artificial helical polymers, it has only been revealed in α-PLA and some peptoids. In other common artificial helical polymers such as polysloxanes, polysicyanes, polyguanidines, polyacetylenes, polysilanes, poly(methyl methacrylate), polystyrenes, and foldmers, this weak interaction has rarely been applied to stabilize the helical structures.

Polyphenylacetylene (PPA) is an important quintessential type of dynamic helical polymers and has attracted scientists’ research interests for its various tunable conformations and unique optoelectronic properties. Most PPAs are known as cis-transoid helices, whereas cis-cisoid PPAs are very limited for the strong steric repulsion between vicinal pendants.
Especially in solution, intramolecular hydrogen bonds are generally indispensable to obtain cis-cisoid helical PPAs.\cite{46–50} In low-polar or apolar solvents, Freire\cite{51–53} and Aoki\cite{54–56} groups successfully constructed cis-cisoid helical PPAs stabilized by strong intramolecular hydrogen bonds. In poly(3,5-disubstituted phenylacetylene)s bearing an achiral ester and a chiral amide pendant group,\cite{57,58} or two amide pendant groups,\cite{59} we also have succeeded in achieving cis-cisoid helical conformations by utilizing intramolecular hydrogen bonds. In a recent publication,\cite{60} we first obtained cis-cisoid helix in poly(3,5-diester substituted phenylacetylene) without hydrogen bonding but stabilized by six intramolecular \(n\rightarrow\pi^*\) interaction bands between carbonyl groups of the \(n\)th and the \((n+3)\)th pendant groups. It was revealed that disubstitution was indispensable to supply strong enough \(n\rightarrow\pi^*\) interactions, whereas effects of other structural factors and external conditions have not been systematically investigated.

To further understand the effect of the structure and external conditions on the elongation, screw sense, and stimuli response of helical polyene backbones, herein six novel 3,5-disubstituted PPAs, \textit{i.e.}, sP-Me-C8/rP-Me-C8, P-Me-C12, sP-Et-C4, sP-2C4, and sP-Oct-C4, were synthesized (Chart 1). The effects of alkyl chain length, steric hindrance of pendants, solvent nature, and temperature on the formation and transition of chiral secondary structure were systematically characterized by a combination of methods including \(^1\text{H}-\text{NMR}, \text{Raman}, \text{UV-Vis}, \text{CD}, \text{FTIR}, \text{DSC}, \text{DLS}, \text{and SLS in solution and solid states.}\) Long alkyl chain length, small pendants, weak hydrogen bond donating (HBD) ability of solvent, and low temperature were found to play key roles in forming contracted cis-cisoid helix.

**EXPERIMENTAL**

**Materials**

All reagents were purchased from Adamas-beta, Accela, Aladdin, Alfa Aesar, InnoChem, J&K, or TCI Chemicals and used without further purification unless otherwise noted.

**Instrumentation and Analysis**

\(^1\text{H/}^{13}\text{C}-\text{NMR} \) spectra were recorded on a Bruker ARX 400 instrument using CDCl\(_3\) or THF-d\(_6\) as the solvent and tetramethylsilane as the internal standard. High-resolution mass spectra were recorded on a Bruker BIFLEX III mass spectrometer. The number-averaged molecular weight \((M_n)\), weight-averaged molecular weight \((M_w)\), and polydispersity index \((M_w/M_n)\) of polymer were estimated on a gel permeation chromatography (GPC) apparatus equipped with a Waters 2410 refractive index detector and a Waters 515 pump. THF was employed as the eluent at a flow rate of 1.0 mL min\(^{-1}\) at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. UV-Vis absorption measurements were performed on a Varian Cary 1E UV-Vis spectrometer. Circular dichroism (CD) spectra were measured on a JASCO J-810 spectrometer. The light path length of the quartz cell used was 10 mm. The samples were dissolved in THF, CHCl\(_3\), or DMF at a concentration of around 5 × 10\(^{-5}\) mol L\(^{-1}\). Optical rotations were recorded on a JASCO Model P-1030 digital polarimeter.

Dynamic light scattering (DLS) and static light scattering (SLS) measurements were carried out on a commercialized spectrometer from Brookhaven Instrument Corporation (BI-200SM Goniometer, Holtsville, NY) with a vertically polarized, 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operated at 633 nm and a BITurboCo digital correlator (Brookhaven Instruments Co.). The sample was filtered through a 0.2 μm filter. Thermogravimetric analyses (TGA) were run on a TA Instrument Q600 analyzer under a N\(_2\) flow rate of 100 mL min\(^{-1}\). Differential scanning calorimetry (DSC) was conducted on a TA DSC Q100 instrument at a heating or cooling rate of 10 °C min\(^{-1}\) under a nitrogen atmosphere. Infrared spectra were recorded on a Nicolet Fourier transform Magna-IR 750 spectrophotometer.

**Synthesis of Monomers**

**Synthesis of sM-Me-C8**

To a 100 mL round bottom flask containing 3-ethyl-5-(methoxycarbonyl)benzoic acid (2.4 mmol, 0.50 g), \((S)-(+)\)-2-octanol (2.9 mmol, 0.38 g) and CH\(_2\)Cl\(_2\) (30 mL), 4-(dimethylamino)pyridine (DMAP, 0.4 mmol, 45 mg) and 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC-HCl, 3.7 mmol, 0.66 g) were added. The reaction mixture was stirred at room temperature for 24 h. The crude product was obtained after evaporation of solvent and purified by column chroma-
to yield 0.53 g of colorless liquids. Yield: 70%. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.63 (s, Ar, 1H), 8.31 (s, Ar, 2H), 5.23–5.13 (m, CH, 1H), 3.96 (s, OCH2, 3H), 3.18 (s, C=CH, 1H), 1.82–1.70 and 1.67–1.55 (m, CH2, 2H), 1.41–1.23 (m, CH3 and (CH2)3, 11H), 0.88 (t, CH3, 3H). 13C-NMR (101 MHz, CDCl3, δ, ppm): 165.58, 164.58, 137.01, 136.87, 131.78, 130.90, 130.65, 123.04, 81.70, 79.04, 72.72, 52.56, 35.97, 31.72, 29.12, 25.42, 22.59, 20.05, 14.07. HRMS (m/z): [M+N]+ Calc. for C15H19NaO3: 339.1567; found, 339.1568.

**Synthesis of m-Me-C8**

Using the method described for sM-Me-C8. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.63 (s, Ar, 1H), 8.34–8.30 (m, Ar, 2H), 4.35 (t, OCH2, 2H), 3.96 (s, OCH3, 3H), 3.18 (s, C=CH, 1H), 1.85–1.68 (m, CH2, 2H), 1.47–1.17 (m, CH3, 18H), 0.88 (t, CH3, 3H). 13C-NMR (101 MHz, CDCl3, δ, ppm): 165.51, 165.03, 133.07, 130.14, 130.78, 130.11, 130.64, 123.05, 81.70, 79.03, 72.71, 52.55, 35.97, 31.71, 29.11, 25.41, 22.58, 20.04, 14.06. HRMS (m/z): [M+N]+ Calc. for C14H17ClO4: 333.1367; found, 333.1369.

**Synthesis of M-Me-C12**

Using the method described for sM-Me-C8. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.64 (t, Ar, 1H), 8.34–8.30 (m, Ar, 2H), 4.35 (t, OCH2, 2H), 3.96 (s, OCH3, 3H), 3.18 (s, C=CH, 1H), 1.85–1.68 (m, CH2, 2H), 1.47–1.17 (m, CH3, 18H), 0.88 (t, CH3, 3H). 13C-NMR (101 MHz, CDCl3, δ, ppm): 165.51, 165.03, 133.07, 130.14, 130.78, 130.11, 130.64, 123.05, 81.70, 79.03, 72.71, 52.55, 35.97, 31.71, 29.11, 25.41, 22.58, 20.04, 14.06. HRMS (m/z): [M+N]+ Calc. for C13H15ClO3: 327.2373; found, 327.2383.

**Synthesis of M2C-C2**

To a 250 mL round bottom flask containing dimethyl-5-((trimethylsilyl)ethyl)isophthalate (17.2 mmol, 5.0 g) and 30 mL of THF, and 30 mL of CH2Cl2 of 5.7 mL of LiCl. acetate/petroleum ether = 1/15, V/V) to yield 0.40 g of white solids. Yield: 55%. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.64 (t, Ar, 1H), 8.30 (m, Ar, 2H), 5.19–5.05 (m, CH, 2H), 3.18 (s, C=CH, 1H), 1.74 (ddt, CH2, 4H), 1.35 (t, CH3, 6H), 0.98 (t, CH3, 6H). 13C-NMR (101 MHz, CDCl3, δ, ppm): 164.68, 163.73, 131.72, 131.05, 122.91, 81.85, 78.87, 73.77, 28.87, 19.48, 9.70. HRMS (m/z): [M+H]+ Calc. for C8H15O2: 131.0519; found, 131.0517.

https://doi.org/10.1007/s10118-020-2376-z
(CH$_2$)$_n$ 8H), 0.96 (t, CH$_3$, 2H), 0.88 (t, CH$_3$, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$, 6 ppm): 165.16, 164.65, 136.90, 136.81, 131.71, 131.30, 130.68, 122.96, 78.98, 73.81, 65.82, 31.80, 29.25, 29.20, 28.89, 28.66, 26.01, 22.66, 19.54, 14.12, 9.78. [M+NH$_4$]$^+$ Calcd. for C$_{22}$H$_4$_3NO$_4$, 376.2482; found, 376.2473.

**Polymerization**

Take sM-Me-C8 as an example. Monomer sM-Me-C8 (120 mg, 0.38 mmol) and THF (3 mL) were added to a dry ampule, which was then frozen by liquid nitrogen and evacuated on a vacuum line. After three freeze-pump-thaw cycles, to the ampule was added 1 mL of THF solution containing catalyst [Rh(nbd)Cl]$_2$ (4.0 mg, 0.007 mmol) and 1 drop of TEA. The concentrations of monomer and the rhodium catalyst were 0.10 and 0.0015 mol L$^{-1}$, respectively. The mixture solution was stirred at 25 °C for 12 h. The color of the reaction mixture changed to dark red within 15 min and the viscosity became very large quickly. After 12 h, 20 mL of THF was added and the resulting polymer was precipitated into a large amount of methanol, collected by filtration, and washed by methanol. After drying under vacuum was precipitated into a large amount of methanol, collected by filtration, and washed by methanol. After drying under vacuum at 50 °C for 3 h, 108 mg of dark red solids was obtained. Yield: 90%.

**RESULTS AND DISCUSSION**

In the present work, six novel Ppas, i.e., sP-Me-C8/rP-Me-C8, P-Me-C12, sP-Et-C4, sP-2C4, and sP-Oct-C4, were designed to gain deep insights into the crucial rules of generating and tuning cis-cisoid helical structures in poly(3,5-diester substituted phenylacetylene). We previously reported that intramolecular n–n interactions and two ester substituents played important roles in the formation of cis-cisoid helix in poly(3-methoxycarbonyl-5-[(S)-sec-butyl]oxy)carbonyl)phenylacetylene) (sP-Me-C4).$^{[60]}$ sP-Me-C8/rP-Me-C8 and P-Me-C12 with longer alkoxy carbonyl pendants would help clarify the effect of alky chain length on formation and stabilization of cis-cisoid helix. sP-Et-C4, sP-2C4, and sP-Oct-C4 in which small methyl ester was replaced by larger ester pendants were designed to discover the steric hindrance of ester pendant.

**Synthesis and Polymerization**

The monomers, sM-Me-C8/rM-Me-C8, M-Me-C12, sM-Et-C4, sM-2C4, and sM-Oct-C4 were prepared with moderate yields according to the synthetic route shown in Schemes 51–53 (in electronic supplementary information, ESI). 3-Methoxy carbonyl-5-carboxyphenylacetylene was obtained following the previously reported method.$^{[50]}$ It underwent esterification with chiral (S)/(R)-2-ocetal or achiral dodecanol under the catalysis of 1-ethyl-3-(3-dimethyaminopropyl)carbodiimide hydrochloride (EDC-HCl) and 4-(dimethylamino)pyridine (DMAP) to yield the target monomers, sM-Me-C8/rM-Me-C8 and M-Me-C12, respectively. Complete hydrolysis of dimethyl 5-(trimethylsilyl) ethynyl)isophthlate, followed by the esterification with ethanol and (S)-2-butanol, produced M-2C2 and sM-2C4, respectively (Scheme S2 in ESI). Then through partial hydrolysis of M-2C2 followed by the esterification with (S)-2-butanol, sM-2C4 would be obtained. Acyl chloride reaction of 5-ethynylisophthalic acid, followed by the esterification with 1 equiv. of n-octanol, produced 3-ethyl-5-(octyloxy)carbonyl benzoic acid. Then it underwent esterification with chiral (S)-2-butanol to yield sM-Oct-C4. These monomers were identified by $^{1}H/^{13}C$-NMR as well as high-resolution mass spectroscopy. All the data agreed well with the expected structures (Figs. S1–52 in ESI).

The polymerizations of these six monomers were carried out in THF at 25 °C using [Rh(nbd)Cl]$_2$ (nbd = norbornadiene) as a catalyst with a fixed monomer to catalyst molar ratio of 40:1. In THF, the reaction mixture turned a little viscous once the catalyst was added. The resulting polymers were obtained with CH$_2$OH as the precipitant and collected by filtration.$^{[59,60]}$ Interestingly, red polymer film was obtained for sP-Me-C8/rP-Me-C8 and P-Me-C12, whereas other three polymers existed as yellow or brown powders, probably due to the distinct intermolecular packings of the polymer chains with different stereostructures as observed in previous works.$^{[57–60]}$ All the monomers were converted to the corresponding polymers, sP-Me-C8/rP-Me-C8, P-Me-C12, sP-Et-C4, sP-2C4, and sP-Oct-C4, with high yields and molar masses (Table 1). Moreover, these polymers presented high thermal stability and possessed the temperature of 5% weight loss under inert atmosphere above 300 °C (Fig. S21 in ESI).

**$^1H$-NMR Spectra**

The chemical and stereo-structures of the resultant polymers were first characterized by $^1H$-NMR spectroscopy. Fig. 1 shows the $^1H$-NMR spectra of sM-Me-C8 and sP-Me-C8 in CDCl$_3$ and THF-d$_2$. The resonance signals of sM-Me-C8 at δ = 5.18, 3.96, and 3.18 ppm are ascribed to the resonance absorptions of methane (HC=), methoxycarbonyl (CO$_2$CH$_3$), and ethynyl (C≡CH) protons, respectively (Fig. 1a). As for sP-Me-C8, only the proton signals of long alkyl chains are observed in pure CDCl$_3$ (Fig. 1b) and THF-d$_2$ (Fig. 1d), whereas the other proton signals are very weak or badly resolved, making it impossible to analyze its structure. Given the good solubility of sP-Me-C8 in CHCl$_3$ and THF, the poor resolution of its $^1H$-NMR spectrum is probably due to its contracted helix, which will be addressed again in the

**Table 1**

| Monomer   | $[a]_{D}^{20} (\circ)$ | Conv. (%) | $M_n$ ($\times 10^{-4}$) | PDI | $\%\alpha$ | $T_g (\circ)$ |
|-----------|----------------------|-----------|-------------------------|-----|------------|--------------|
| sM-Me-C8  | +35                  | 90        | 1.44                    | 1.91 | 98         | -30          |
| rM-Me-C8  | -39                  | 91        | 19.4                    | 1.47 | 99         | +213         |
| M-Me-C12  | 0                    | 95        | 10.7                    | 2.46 | 94         | 0            |
| sM-Et-C4  | +28                  | 89        | 26.4                    | 1.30 | 96         | +85          |
| sM-2C4    | +51                  | 92        | 30.3                    | 1.30 | 97         | +208         |
| sM-Oct-C4 | +20                  | 88        | 30.1                    | 1.28 | 91         | +106         |

*Carried out in THF at 25 °C under nitrogen for 12 h; [M] = 0.06 mol L$^{-1}$, [cat.] = 1.5 mmol L$^{-1}$. $^a$ Specific optical rotations measured in THF, concentration: 0.2 g dL$^{-1}$. $^b$ For monomers: 0.02 g dL$^{-1}$ for polymers. $^c$ Methanol-insoluble part. $^d$ Estimated by GPC in THF on the basis of a polystyrene calibration. $^e$ Determined by $^1H$-NMR analysis. $^f$ Temperature at which 5% weight loss was observed under nitrogen with a heating rate of 10 °C min$^{-1}$. [64]"
following section. To obtain a better resolved spectrum, 10 vol% 2,2,2-trifluoroacetic acid (TFA) was added into the CDCl₃ solution. As expected, all important resonance signals become clearer. It is evident that the ethynyl proton signal of sM-Me-C8 disappears after polymerization. Instead, a new olefinic C₈ bond vibration of contracted cis-cisoid helix. Interestingly, in Raman spectra, sP-Et-C₄ presents three obvious Raman shifts at 1617, 1597, and 1570 cm⁻¹. The former two signals are ascribed to the cis C=C bond vibrations of cis-transoid polyene backbone which overlaps with that of the phenyl rings, implying the coexistence of cis-cisoid and cis-transoid helices in the solid state of sP-Et-C₄.

**DSC Curves**

DSC is commonly used to study cis-cisoid to cis-transoid helical transitions of polyacetylenes.[60,61] Fig. 3 depicts the DSC traces of the polymers measured under a nitrogen atmosphere at a heating rate of 10 °C·min⁻¹. All the polymers present an obvious exothermic peak above 190 °C, which is attributed to the cis-transoid to trans-transoid isomerization. This transition temperature in solid correlates with the polymer structure. As for sP-Me-C₈, P-Me-C₁₂, and sP-Oct-C₄, this transition occurs at around 196 °C, while this isomerization temperature appears at 208 and 216 °C for sP-Et-C₄ and sP-2C₄, respectively. Moreover, unlike sP-2C₄ and sP-Oct-C₄, sP-Me-C₈ and P-Me-C₁₂ exhibit a sharp endothermic peak at 172 and 192 °C, respectively, before the cis-transoid to trans-transoid isomerization, corresponding to the thermal transition from cis-cisoid to cis-transoid helix. These results further convince that sP-Me-C₈ and P-Me-C₁₂ take a contracted cis-cisoid helix in solid, whereas a stretched cis-transoid helix is adopted by sP-2C₄ and sP-Oct-C₄. For sP-Et-C₄, its DSC curve presents a small endothermic peak at 103 °C ascribed to cis-cisoid to cis-transoid transition, suggesting that it consists of both contracted cis-cisoid and extended cis-transoid helices, which concurs well with its Raman spectrum.

https://doi.org/10.1007/s10118-020-2376-z
Effect of the Length of Alkyl Chain

In previous work, the polymer sP-Me-C4 presented a contracted cis-cisoid helix in THF, toluene, and weak HBD solvents like CHCl$_3$ and ClCH$_2$CH$_2$Cl stabilized by strong intramolecular $n$→$n^*$ interactions, but a stretched cis-transoid helix in CHCl$_3$ and Cl$_2$CHCHCl$_2$ at 25 °C. sP-Me-C8/rP-Me-C8 and P-Me-C12 with the longer alkyl chains were prepared to study effect of the length of alkyl chains on the formation of cis-cisoid helix. As shown in Fig. 4, sP-Me-C8 presents the same absorption spectra as THF, toluene, CH$_2$Cl$_2$, and CHCl$_3$, which are similar to that of sP-Me-C4 in THF, suggesting a similar contracted cis-cisoid helix formed in these solvents. The Cotton effects of sP-Me-C8 in CHCl$_3$ and CH$_2$Cl$_2$ are slightly stronger than those in THF and toluene, probably ascribed to the weak interaction between HBD solvents and carbonyl groups, which lowers the inversion barriers and makes the polyene backbone more flexible. So better chirality transfer can be achieved in CH$_2$Cl$_2$ and CHCl$_3$ in the presence of intramolecular $n$→$n^*$ interaction. In comparison to sP-Me-C4, the contracted cis-cisoid helix also can form in CHCl$_3$ for sP-Me-C8 at room temperature, which is ascribed to the possible reason that the long alkyl chain may hinder the interaction between the ester C=O and CHCl$_3$ molecules, and thereby favor the stability of $n$→$n^*$ interaction. Moreover, the secondary structure of sP-Me-C8 in various mixed solvents with different polarities and dielectric constants was also examined. As shown in Figs. S28 and S29 (in ESI), the contracted cis-cisoid helix is also maintained by sP-Me-C8 when DMF, acetone, CH$_3$CN, EtOAc, and dioxane are added into the CHCl$_3$ or THF solution. This demonstrates that the formation of cis-cisoid helix in poly(3,5-diestere substituted phenylacetylene) does not correlate with the polarity and dielectric constant of solvents, which is in accordance with the nature of $n$→$n^*$ interaction. $n$→$n^*$ interaction is the delocalization of an electron pair of the oxygen of the donor carbonyl group into the antibonding orbital ($n^*$) of the acceptor carbonyl group, instead of the Coulombic interaction or dipolar interaction. These results well explain the above solvent effect, further suggesting the existence of $n$→$n^*$ interaction around the tight cis-cisoid polyene backbone.

For rP-Me-C8, it presents the same absorption spectra with sP-Me-C8. Their Cotton effects show a perfect mirror image in THF and CHCl$_3$ (Fig. S30 in ESI), suggesting a contracted cis-cisoid helix with opposite screw sense adopted by rP-Me-C8.

What should be mentioned is that in CHCl$_3$, a very weak shoulder peak at ~440 nm is observed in the absorption spectra of sP-Me-C8 ascribed to the existence of small quantity of stretched polyene backbone, probably because the alkyl chain is still not long enough. Therefore, P-Me-C12 with the dodecyl pendant was prepared and their absorption spectra are depicted in Fig. 5. As expected, with the increasing length of alkyl chain, the absorption intensity at 440 nm decreases gradually. For P-Me-C12, it presents a better cis-cisoid helix with nearly no obvious absorption at ~440 nm, compared to sP-Me-C4 and sP-Me-C8, clearly evincing that the long alkyl chain can efficiently stabilize the $n$→$n^*$ interaction and favor the formation of contracted cis-cisoid structure.

Effect of HBD Solvent

Considering CHCl$_3$ is a weaker HBD solvent which may be not able to efficiently interact with C=O group in sP-Me-C8, trifluoroacetic acid (TFA), hexafluorisopropanol (HFP), and 2,2,2-trifluoroethanol (TFE) were chosen as additives to
modulate the helical conformation for their higher HBD ability.[64,65] As shown in Fig. 6(a), with the addition of TFA, an obvious 75 nm redshift in the main-chain absorption is observed. Meanwhile, the Cotton effect at 370 nm gradually disappears, while a weak positive signal at around 450 nm emerges in the visible spectra region, reflecting the transition from cis-cisoid to cis-transoid helix. Moreover, the addition of HFP (Fig. S31 in ESI) and TFE (Fig. S32 in ESI) also exhibits the same induction like TFA. The stronger the HBD ability is, the smaller the quantity of HBD solvent is needed to realize this conformation transition. This stereomutation can be attributed to the hydrogen bonding interaction between HBD solvents and carbonyl groups, which destroys the initial intramolecular n→π* interaction. Considering halogen atom also can interact with C=O through n→π* interaction, which may compete with hydrogen bonding, CF₃COOCH₃ was used to manipulate the conformation for comparison. As shown in Fig. S33 (in ESI), sP-Me-C8 still keeps a good cis-cisoid helix even when 10 vol% CF₃COOCH₃ was added, further convincing that the previous destruction of n→π* interaction between carbonyl groups is mainly ascribed to the hydrogen bond interaction rather than the interaction between fluorine atom and C=O group.

Figs. 6(b) and Fig. S34 (in ESI) depict the conformation transition of P-Me-C12 in CHCl₃ triggered with the addition of TFA and HFP, respectively. The adding amount of TFA or HFP to realize the complete stereomutation is much larger than that in sP-Me-C8. Only when 1.20 vol% of TFA is added can cis-cisoid helix completely transfer to cis-transoid helix (Fig. 6b). However, only 0.15 vol% of TFA is needed to realize this transition for sP-Me-C8 and no TFA is needed for sP-Me-C4 with the shortest alkyl chain. By comparison, these results coincide well with our previous results that the long alkyl chain can prevent carbonyl groups from interacting with HBD solvents to some extent and stabilize the intramolecular n→π* interactions.

**Effect of Steric Hindrance**

In sP-Me-C4, sP-Me-C8, and P-Me-C12, the methyl ester kept unchanged. We also examined the effect of steric hindrance on helical conformation of sP-Et-C4, sP-2C₄, and sP-Oct-C₄ in which the methyl ester is replaced by ethyl, (S)-2-butyl, and octyl ester, respectively. Fig. 7 shows their UV-Vis absorption and CD spectra. In THF, sP-Et-C4 and sP-Oct-C₄ present strong main-chain absorption peaked at around 430 nm, and that of sP-2C₄ appears at 440 nm, indicating an extended cis-transoid helix. In CD spectra, they exhibit weak positive Cotton effects at about 440 nm ascribed to the polycene backbone, suggesting the existence of helical reversals as well as the presence of helices with opposite screw senses in cis-transoid helix. In CHCl₃, they exhibit similar absorption and CD spectra like those in THF (Figs. S37–S39 in ESI), unable to adopt cis-cisoid helix as well. These results clearly indicate that the helical structure in poly[3,5-diester substituted phenylacetylene]s is sensitive to the substituent size. Slight changes in the substituent size may increase the steric hindrance between monomer units, which would destroy the intramolecular n→π* interaction and impede the formation of cis-cisoid helix.

**Thermo-responsive Stereomutation**

The helical structures of polyacetylenes are easily influenced by external stimuli such as heating and addition of polar solvents. To examine the thermal stability of the helical structures, we measured the CD and UV-Vis spectra in toluene (Fig. S35 in ESI) and CHCl₃ (Fig. 8) at various temperatures. As shown in Fig. S35 (in ESI), the cis-cisoid helix of sP-Me-C8 in toluene exhibits outstanding thermo-stability, and no obvious changes are observed in UV and CD spectra even heated to 80 °C, ascribed to the strong intramolecular n→π* interactions and its striking
stability in non-HBD solvent. Nevertheless, the helix of sP-Me-C8 present good modulation in CHCl3 and can be reversibly switched by altering solution temperature. As depicted in Fig. 8a, the weak absorption at around 440 nm gradually disappears with the temperature decreasing, indicating that the small quantity of cis-transoid polyene backbone completely transfers to cis-cisoid structure. Moreover, sP-Me-C8 in CHCl3 at 30 °C mainly takes a contracted cis-cisoid helix, but presents a stretched cis-transoid helix with a strong absorption at 440 nm when temperature is lifted to 40 °C. The Cotton effect of main chain changes from −2.4 × 10^4 deg·cm^2·dmol^−1 (at 367 nm) to 1.7 × 10^3 deg·cm^2·dmol^−1 (at 450 nm), suggesting the screw-sense reversion. If the solution temperature returns to 30 °C, the spectra also recover to the initial curve. The spectra can be reversibly modulated by alternating temperature changes at least for three cycles (Fig. 8b), endowing sP-Me-C8 with an excellent thermo-response. Temperature increment may enhance flexibility of polymer and open a window for solvent molecules to interact with carbonyl groups leading to the destruction of n→π* interactions. Once the temperature decreases, the solvent molecules are excluded out again by the long alkyl chains, and the cis-transoid helix transfers to the original contracted helix. For P-Me-C12, its absorption spectra in CHCl3 (Fig. S36 in ESI) keep unchanged at various temperatures. It further evinces that long alkyl chain is beneficial to the stabilization of intramolecular n→π* interactions and the formation of cis-cisoid helix.

To gain deep insights into the steric effect and temperature-dependent stereomutation, the UV-Vis absorption and CD spectra of sP-Et-C4 and sP-C8-C4 in THF at various temperatures were recorded. As shown in Fig. 9, sP-Et-C4 at 25 °C adopts a stretched cis-transoid helix in THF, with a long main-chain absorption at ~430 nm. However, the absorption peaked at 430 nm shifts to 360 nm, and the solution changed from yellow to colorless with decreasing temperature, indicating the formation of cis-cisoid helix. Meanwhile, the weak positive CD signal at 450 nm disappears, and a new strong negative Cotton effect at about 360 nm is observed. The whole CD curve at −10 °C is almost the same with that of sP-Me-C4 in THF. It further implies that lower temperature benefits the stabilization of n→π* interactions and the formation of cis-cisoid helix. Moreover, this thermal responsive stereomutation is only observed in THF solution. In CHCl3 solution, sP-Et-C4 is unable to form cis-cisoid helix even at ~30 °C (Fig. S40 in ESI). It is probably attributed to the combined effects of HBD and steric hindrance, which enhance the difficulty in forming cis-cisoid helix. As for sP-Oct-C4, it still keeps cis-transoid helix in THF even when the temperature decreases to ~30 °C (Fig. S41 in ESI) ascribed to its larger steric hindrance.

DLS and SLS
Above mentioned temperature- and solvent-sensitive stereomutations are also reflected in the variation of overall dimensions of these polymers in THF or CHCl3 revealed by dynamic light scattering (DLS) and static light scattering (SLS) (Table 2 and Figs. S42–50 in ESI). The corresponding hydrodynamic radius (R_d) value is 18 nm for sP-Me-C8 in THF and CHCl3 at 25 °C, and the root-mean-square radius of gyration R_g obtained from SLS measurement is 54 and 50 nm for sP-Me-C8 in THF and CHCl3 respectively. So the prefactor (R_g/R_d) of sP-Me-C8 is 3.0 and 2.8 in THF and CHCl3 respectively, suggesting sP-Me-C8 adopts a rigid conformation in both THF and CHCl3 at 25 °C. At 50 °C, R_d and R_g values of sP-Me-C8 in CHCl3 decrease to 13 and 26 nm, respectively. At this time, p

![Fig. 9](https://doi.org/10.1007/s10118-020-2376-z)
equals 2.0, indicating a much more flexible structure in accordance with the results of temperature-dependent UV-Vis and CD spectra. However, the ρ value of sP-Me-C8 in THF at 50 °C still keeps > 3.0, implying a rigid cis-cisoid structure, which helps convincing the thermal stability of n→n’ interaction in THF. Moreover, the ρ value of sP-Et-C4 is 1.9 at 25 °C, but 2.8 at 5 °C, further evincing that flexible cis-transoid helix at 25 °C transfers to a rigid cis-cisoid structure with temperature decreasing. For sP-Oct-C4, at either 25 or 5 °C, its ρ value in THF is 2.0, exhibiting a stretched cis-transoid helix with a larger flexibility due to its larger steric hindrance.

### Table 2 DLS and SLS results of PPAs. *

| Polymer     | Solvent | T (°C) | Rg (nm) | Rh (nm) | Rg/Rh |
|-------------|---------|--------|---------|---------|--------|
| sP-Me-C8    | THF     | 25     | 18      | 54      | 3.0    |
| sP-Me-C8    | THF     | 50     | 15      | 52      | 3.5    |
| sP-Me-C8    | CHCl3   | 25     | 18      | 50      | 2.8    |
| sP-Me-C8    | CHCl3   | 50     | 13      | 26      | 2.0    |
| sP-Et-C4    | THF     | 25     | 14      | 27      | 1.9    |
| sP-Et-C4    | THF     | 5      | 23      | 65      | 2.8    |
| sP-Et-C4    | THF     | 25     | 21      | 41      | 2.0    |
| sP-Oct-C4   | THF     | 25     | 14      | 28      | 2.0    |
| sP-Oct-C4   | THF     | 5      | 15      | 30      | 2.0    |

* The test concentration was ~ 0.5 mg·mL⁻¹.

### Solution-state FTIR

Considering 1H-NMR was unable to clearly characterize the structure of cis-cisoid helix due to the poor resolution in rigid conformation, solution-state FTIR was performed to understand the n→n’ interaction as well as its solvent and temperature effects. As shown in Fig. 10, a strong vibration at 1732 cm⁻¹ and a shoulder peak at 1724 cm⁻¹ ascribed to the ester C=O signal were observed in the THF solution of sM-Me-C8, whereas sP-Me-C8 presented two C=O absorption bands at 1732 and 1716 cm⁻¹ in THF. Compared to sM-Me-C8, the second C=O vibration band shifted remarkably to the lower wavenumber, ascribed to the intramolecular n→n’ interaction, which increases the length of C=O bond in the carbonyl acceptor. A similar IR spectrum was observed in the CHCl3 solution of sP-Me-C8, but when 1.0 vol% HFP was added, this bimodal band in CHCl3 fused to a single vibration band at 1722 cm⁻¹ (Fig. 10d) due to the hydrogen bond interactions between carbonyl group and HFP molecules, which destroyed the initial carbonyl-carbonyl interactions. The same change in IR spectrum can also be observed when temperature was lifted to 45 °C (Fig. 10e), attributed to the thermal instability of n→n’ interaction. The results of solution-state FTIR spectra further convinced the existence of n→n’ interaction between C=O groups, which played a vital role in stabilizing the contracted cis-cisoid helical conformation.

### CONCLUSIONS

Six novel poly(3,5-diester substituted phenylacetylene)s, sP-Me-C8/rP-Me-C8, P-Me-C12, sP-Et-C4, sP-2C4, and sP-Oct-C4, bearing various alkoxycarbonyl pendants at meta positions were synthesized. A comprehensive characterization of ¹H-NMR, UV-Vis absorption, CD, Raman, DSC, IR, DLS and SLS indicated that the structure of pendant, the nature of solvents, and temperature remarkably affected the helical structures of polypene backbones in solution. The construction of cis-cisoid helix in poly(3,5-diester substituted phenylacetylene) exhibited a restrict requirement in the chemical structure of pendants. The long alkyl chain, small pendant, and disubstitution favored the stabilization of n→n’ interactions and the formation of contracted cis-cisoid helix. The reversible helix-helix transition could be triggered by changing solvent or varying temperature. Non-HBD solvents and lower temperature were more beneficial to forming cis-cisoid helix. Not only chain rigidity and interactions between neighboring units but also electronic structure are distinct in contracted and stretched helical conjugated polypene, which may influence their liquid crystallinity, chiral amplification, and optoelectronic property. Gaining deep insights into the construction rule of cis-cisoid will help us design novel chiral materials better. The related work is under way.

### Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2376-z.

### ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51833001 and 21674002).

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