Diminished Helical Character in Para-Substituted Cis-Transoidal Polyphenylacetylenes Due to Intramolecular Cyclization

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High cis content cis-transoidal and cis-cisoidal helical poly(phenylacetylene) (PPA)¹⁻³ continues to inspire novel concepts, particularly at the nanoscale.⁴ As a dynamic helical polymer,⁵ both helical screw senses exist in equilibrium.^{3,6} Selection of a particular helix sense is accomplished by appending the aromatic ring with chiral, nonracemic substituents,⁷ or noncovalent association of chiral substrates.⁸ By the latter process, a particular handedness can be induced, memorized and maintained in the presence of achiral substrates.⁹ Mutation of the helix stereochemistry upon thermal treatment¹⁰ raises questions about competing kinetic and thermodynamic preferences in helical backbone of *cis*-PPA.

Typically, the dynamic of the helical conformation is evaluated by optical rotation or circular dichroism (CD) spectra at various temperatures.¹¹ Cis-transoidal (-)-poly[4-(L-mentholoxycarbonyl)phenylacetylene]⁷ (cis-(-)-poly[4-(menthO₂C)PA]) and (-)-poly[4-(L-mentholoxycarbonylamino)phenylacetylene]^{12,13} (cis-(-)-poly[4-(menthO₂CN)PA]) (Scheme 1) exhibit large optical rotations and intense Cotton effects related to the polymer backbone up to 45 °C. Furthermore, scanning tunneling (STM)¹² and atomic force (AFM)¹³ microscopies visualize helically ordered and disordered superstructures obtained from cis-(-)-poly[4-(menthO₂CN)PA] deposited on highly ordered pyrrolytic graphite (HOPG) and mica. It was noted during STM visualization of cis-(-)-poly[4-(menthO₂CN)PA] on HOPG in air that the structures were irreversibly altered during measurements.¹²

Helical cis- and trans-poly(alkylacetylenes) exhibit different CD spectra in solution.¹⁴ In solution and in bulk, 1,3-cis-5-hexatriene sequences in PPA and its substituted analogues undergo electrocyclization to form cyclohexadiene repeat units.^{1,15-17} We expect a dramatic influence on the observed chiroptical properties of helical cis-transoidal PPAs with different cis content.¹ The mole fraction of cis (92%), trans (4%), and cyclohexadiene (4%) repeats units¹⁸ is the same in both *cis*-(-)-poly[4-(menthO₂C)PA] and cis-(-)-poly[4-(menthO₂-CN)PA]. Rearomatization of the cyclohexadiene sequences results in extrusion of 1,3,5-triarylbenzene and concomitant chain cleavage.¹ Additionally, solutions exposed to both light and O₂ undergo photooxidative chain cleavage.¹⁶ Herein we demonstrate that the electrocyclization reaction occurs in degassed solutions of cis-(-)-poly[4-(menthO₂C)PA] and cis-(-)-poly[4-(menthO₂CN)PA] (Scheme 1). This process impacts the helical asymmetry of the polyene backbone, resulting in decreased Cotton effect intensity. To circumvent this

Scheme 1. 6π Electrocyclization of Cis-Transoidal PPAs



cis-(-)-Poly[4-(menthO₂C)PA] cis-(-)-Poly[4-(menthO₂CN)PA]

complication we demonstrate dynamic helical behavior in solution at 2 and 22 $^{\circ}$ C using cis-transoidal copolymers of 4-(menthO₂C)PA and phenylacetylene (PA).

CD Spectra of cis-(-)-poly[4-(menthO₂CN)PA] in THF and benzene (C₆H₆) confirmed its dynamic helical behavior. The Cotton effect at 370 nm in THF and at 380 nm in C₆H₆ decreased with increasing temperature. Even at the highest temperature measured (75 °C, C₆H₆), a helical structure was apparent. Subsequent cooling to 10 °C did not recover the full Cotton effect intensity. Further heating to 75 °C resulted in a less intense signal in the CD spectra. Despite the diminished molar ellipticity upon heating, we did not obtain complete loss of the signal. During these experiments, we observed no changes in the corresponding UV-vis spectra, which suggests that extrusion of 1,3,5-triarylbenzene or photooxidation are minimal or non existent.

Electrocclization is the most significant reaction in anaerobic solutions of PPA at 60 °C, and the rate of cyclization is solvent independent.¹⁶ Degassed solutions cis-(-)-poly[4-(menthO₂C)PA] in CCl₄ and cis-(-)-poly-[4-(menth O_2 CN)PA] in THF (or THF $-d_8$) were monitored by ¹H NMR, CD and UV-vis spectroscopies, and gel permeation chromatography (GPC). Figure 1 illustrates the mole fraction of alkene residues $(F_{a.r.})$ accounted for as polyene, cyclohexadiene repeat units, and extruded 1,3,5-triarylbenzene in each case.¹⁶ Concurrent with the changes in polymer structure, the number-average molecular weight (M_n) decreases and molecular weight distribution (M_w/M_n) increases. These changes are separate from changes related to chain cleavage events. Inspection of the kinetic data in Figure 1 shows that both polymers undergo cyclization at a comparable rate to cis-transoidal PPA.¹⁶ Neither the steric nor the electronic influence of the para-substitutents is significant enough to impede the cyclization reaction.



Figure 1. Plots of the mole fraction of alkene residues ($F_{a.r.}$) accounted for as polyene (\blacksquare), cyclohexadiene (\bigcirc), and 1,3,5-triarylbenzene (\bullet) in solutions of (a) *cis*-(-)-poly[4-(menthO₂C)-PA] in CCl₄ and (b) *cis*-(-)-poly[4-(menthO₂CN)PA] in THF- d_8 annealed at 60 °C.



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Figure 2. (a) Plot of molar ellipticity for *cis*-poly[4-(menthO₂C)-PA] (CCl₄, 373 nm, red) and cis-(-)-poly[4-(menthO₂CN)PA] (THF, 381 nm, blue) samples annealed at 60 °C. (b) Representative CD spectra obtained at 0 and 8 h. Spectra were recorded at 2 °C.



Figure 3. Plots of (a) specific optical rotation ($[\alpha]_D$, \blacksquare) and (b) molar ellipticity ($[\theta]$) at 2 (O) and 22 °C (\blacktriangle) as a function of the mole fraction of chiral monomer (F^*) in cis-(-)-poly[4-(menthO₂C)PA-co-PA].

CD and UV-vis spectra confirm that electrocyclization results in an irreversible and diminished helical character before impacting the conjugation length of the polymer backbone. Figure 2 illustrates the decreased intensity of the negative Cotton effect associated with the polyene backbone. It is important to stress that this outcome may be particular to these specific PPAs and/ or the conditions employed. Since 6π electrocyclization is a stereospecific reaction,¹⁹ the newly formed stereocenters adjacent to the polyene backbone can either reinforce or counteract the helical handedness selected by the para-substituent. In addition to cyclization and cis-trans isomerization,^{2,16} the amount of single-handed helical character decreases at 60 °C. Both of these events contribute to the stereochemical diversity of the cyclization products.

As an alternative to the thermal analysis typically used to examine helix dynamics, we show that sergeantand-soldiers²⁰ experiments provide similar insight. The advantage of this approach is that they minimize the impact of cyclization because the polymers spend shorter times in solution and lower temperature experiments are most informative. Cis-transoidal copolymers of (-)-4-(menthO₂C)PA and PA have been prepared using a $[M_1 + M_2]/[Rh]$ ratio of 50:1. The mole fraction of chiral monomer in the polymer (F^*) was determined by ¹H NMR spectroscopy.

Figure 3 presents the Cotton effect intensity at 2 and 22 °C and optical rotation as a function of copolymer composition. The linear correlation between response and the amount of chiral comonomer indicates a dilution effect upon increasing the amount of PA in the copolymer. This is expected to occur when the excess energy of converting a helical conformation to a helical reversal $(\Delta G_{\rm r})$ is small.¹¹ Consistent with the above discussion, the measured Cotton effect for all copolymers is more intense at lower temperature. This effect is more prominent with increasing F^* because the steric bulk of the majority monomer leads to an increase of $\Delta G_{\rm r}$.²¹

Cooperative behavior is expected when $\Delta G_{\rm r}$ is large or the temperature low enough that it appears large.¹¹ This energy is about 4 kcal/mol for polyisocyanates¹¹ and on the order of 1 kcal/mol for bulky poly(propiolic ester)s.²²

In summary, we have shown that the cis-transoidal PPA helix undergoes irreversible structural changes related to 6π electrocyclization of 1,3-cis-5-hexatriene sequences in the polymer backbone. This process complicates the investigation of chiroptical properties in solution and in bulk. Since many of the anticipated applications of PPAs hinge upon the helical conformation and its dynamics, it is important to elucidate this process and it implications. We observe no electronic or steric effects on intramolecular cyclization due to parasubstituents. As an alternative to elevated temperature experiments, we show that chiroptical studies as a function of copolymer composition provide the desired qualitative picture. The results reported here demonstrate that literature data on helical PPA are only qualitative since no complete structural analysis was reported in any previous publication.

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Supporting Information Available: Text giving synthesis and characterization of monomers and polymers and details of annealing experiments, a reaction scheme, and figures showing CD and UV-vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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