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# Self-Assembling Phenylpropyl Ether Dendronized Helical Polyphenylacetylenes

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**Abstract:** The first example of a self-assembling phenylpropyl ether based dendronized polymer has been reported and its preferred helical handedness has been determined. Dendronized polymer poly(**10**) and its nondendritic analogue poly(**8**) are high-*cis*-content polyphenylacetylenes (PPAs) prepared by using $[Rh(nbd)Cl]_2/NEt_3$ (nbd: 2,5-norbornadiene). Both polymers possess a stereocenter in their side chain, which selects a preferred helical handedness. Based on negative exciton chirality observed in the CD spectra of poly(**10**), we have designated this molecule as a right-handed helical polymer, which persists over a wide temperature range. Poly(**10**) self-organizes into both $\Phi_h^{io}$ and $\Phi_h$ lattices in bulk. The $\Phi_h^{io}$-to-$\Phi_h$ transition is associated with thermoreversible *cis*-cisoidal to *cis*-transoidal isomerization of the helical PPA, accompanied by a dramatic decrease in the column diameter and a decrease in the π-stacking correlation length along the column. A model for the right-handed helical dendronized PPA has been proposed wherein dendrons from adjacent column strata interdigitate to effectively fill space.

**Keywords:** dendrons · helical structures · polymers · self-assembly · supramolecular chemistry

## Introduction

Dendronized polymers approach the architectural complexity of biomacromolecules and provide some of the most powerful building blocks currently explored at the interface between chemistry, biology, physics, medicine, and nanoscience.[1,2] Divergent,[3] attach-to,[4,5] macromonomer,[6–8] and supramolecular[9,10] strategies to prepare these polymers facilitate tremendous diversity of structural composition. A subset of these polymers has been demonstrated to self-organize into periodic[2,4,6,7,8d,9] and quasiperiodic[11] arrays, which enable detailed understanding of the self-assembly mechanism through retrostructural analysis.[2,11] We[2,4a,b,5–7,9] and others[4,8] have developed a robust strategy to prepare self-organizing dendronized polymers by using benzyl ether based self-assembling dendrons.

We have recently expanded the palette of self-assembling dendrons from which to prepare supramolecular dendrimers and self-organizing dendronized polymers by using $(AB)_y$–$AB_3$ and constitutional isomeric $(AB)_y$–$AB_2$ building blocks,[11i] biphenyl methyl ether dendrons,[11o] hybrid dendrons,[11r] and self-assembling phenylpropyl ether dendrons.[11p] Self-assembling phenylpropyl ether based dendrons are more flexible and stable toward heat and acid than their benzyl ether based analogues. Faster dynamics of self-assembly yield larger supramolecular structures with higher order and lower transition temperatures than those observed with the corresponding benzyl ether based self-assembling dendrons. Furthermore, self-assembling phenylpropyl ether dendrons provide more examples of flat-tapered dendrons than had been encountered in previous libraries.[2,11p]

Motivated in part by the desire to improve charge-carrier mobility in complex electronic materials derived from supramolecular dendronized polymers,[9] we have investigated strategies to program the helical handedness of dendronized polymers.[2,7e] A helical arrangement of the polymer backbone that penetrates cylindrical dendronized polymers had been demonstrated previously by our group.[6f–p] We have

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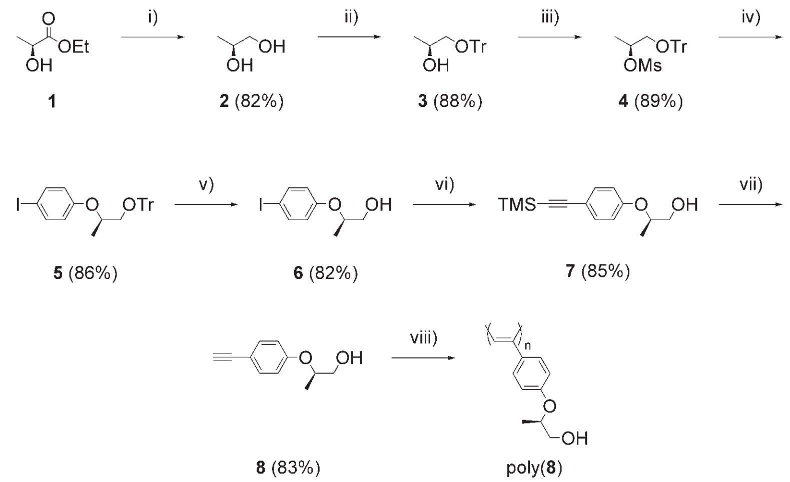

Scheme 1. Synthesis of poly(**8**): i) $LiAlH_4$, THF, 23 °C, 2 h; ii) TrCl, DMAP, DCM, $NEt_3$, 23 °C, 14 h; iii) MsCl, dichloromethane, $NEt_3$, 23 °C, 2 h; iv) *p*-iodophenol, $K_2CO_3$, DMF, 75 °C, 6 h; v) TsOH, dichloromethane, 23 °C, 8 h; vi) trimethylsilylacetylene, $[PdCl_2(PPh_3)_2]$, CuI, $PPh_3$, $NEt_3$, 50 °C, 3 h; g) $K_2CO_3$, MeOH, 23 °C, 10 h; vii) $[Rh(nbd)Cl]_2$, $NEt_3$, 1,2-dichloroethane, 23 °C. TrCl: triphenylmethylchloride; DMAP: 4-dimethylaminopyridine; MsCl: methanesulfonyl chloride; DMF: *N*,*N*-dimethylformamide; TsOH: toluenesulfonic acid; TMS: trimethylsilyl; nbd: 2,5-norbornadiene.

elucidated design principles for expressing the chirality of the peripheral tails in the backbone of self-organizing dendronized polyphenylacetylenes (PPAs) and other polyarylacetylenes.[2,7f] Additionally, we have demonstrated control over the helicity of supramolecular polymers generated from self-assembling dendrons appended with chiral apex groups.[11] These are currently used to investigate the structural origin of functions and thus create new functions through 3D tertiary and quaternary structures in accordance with biological design principles.

Herein, we report the synthesis and structural and retrostructural analysis of the first self-assembling phenylpropyl ether based dendronized polymer as well as the corresponding poly{(*R*)-4-[(2-hydroxy)propyloxy]phenylacetylene} (poly(**8**)), which lacks any dendrons. That both polymers adopt a preferred helical handedness in solution serves to distinguish helix sense selection from helix induction. Variable temperature CD and UV/Vis spectra of the dendronized polymer (poly(**10**)) demonstrate it to be a relatively stable dynamic helical polymer. Furthermore, these spectra indicate that the CD signal is due to negative exciton chirality that is consistent with a right-handed helical conformation.[12] Poly(**10**) self-organizes into a hexagonal columnar lattice with internal order ($\Phi_{\mathrm{h}}^{\mathrm{io}}$) and a hexagonal columnar liquid crystalline lattice ($\Phi_{\mathrm{h}}$). X-ray diffraction (XRD) experiments reveal that the helical polymer undergoes reversible stretching and compression during thermal cycling. Structural and retrostructural analysis of self-organized poly(**10**) culminates in a model for the internal right-handed helical order.

## Results and Discussion

**Synthesis of the monomers**: Scheme 1 outlines the synthesis of the chiral monomer (*R*)-2-(4-ethynylphenoxy)propane-1-ol (**8**). Compound **4** is prepared in a three-step sequence from ethyl L-lactate (**1**) without purification of the intermediates.[13] Ethyl L-lactate is reduced with $LiAlH_4$ and the resulting diol **2** is selectively etherified with triphenylmethyl chloride at the less sterically hindered hydroxy group. Subsequently, the remaining hydroxy group of **3** is transformed into a leaving group by using methanesulfonyl chloride. Williamson etherification of *p*-iodophenol with **4** takes place with inversion of stereochemistry to provide **5**. The aryl iodide **6** was obtained by elimination of the triphenylmethyl group of **5** with *p*TsOH. Sonogashira cross-coupling of **6** with trimethylsilylacetylene by using $Pd^0/CuI/PPh_3$ in $NEt_3$ proceeded with high yields. Base-induced elimination of the trimethylsilyl moiety provided the desired chiral monomer **8**. The $^1H$ NMR spectrum of **8** is shown in Figure 1. Characterization of **8** and its preceding intermediates confirms their molecular structure, but we have not verified their enantiomeric purity and therefore must presume that some of the racemate is present.[14]

Scheme 2 illustrates the synthesis of the dendritic monomer **10**. The dendritic carboxylic acid **9** was prepared as described previously.[11m] Esterification of **9** with **8** was accom-

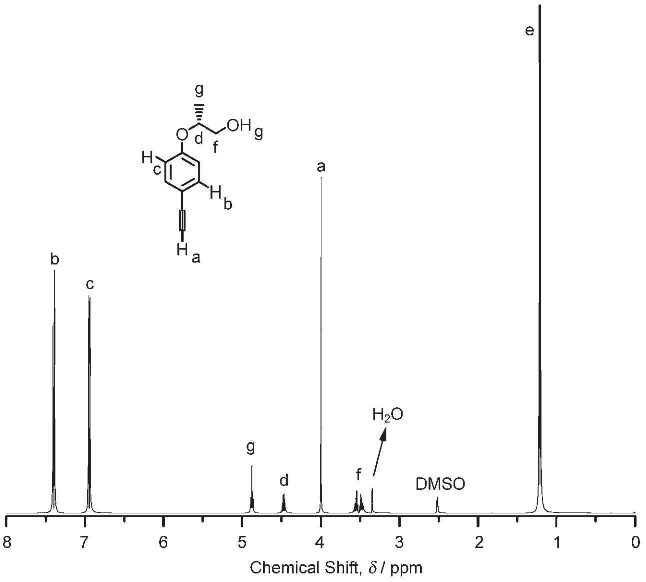

Figure 1. $^1H$ NMR spectrum of monomer **8** in $[D_6]$DMSO. The chemical structure with proton assignments is also shown.

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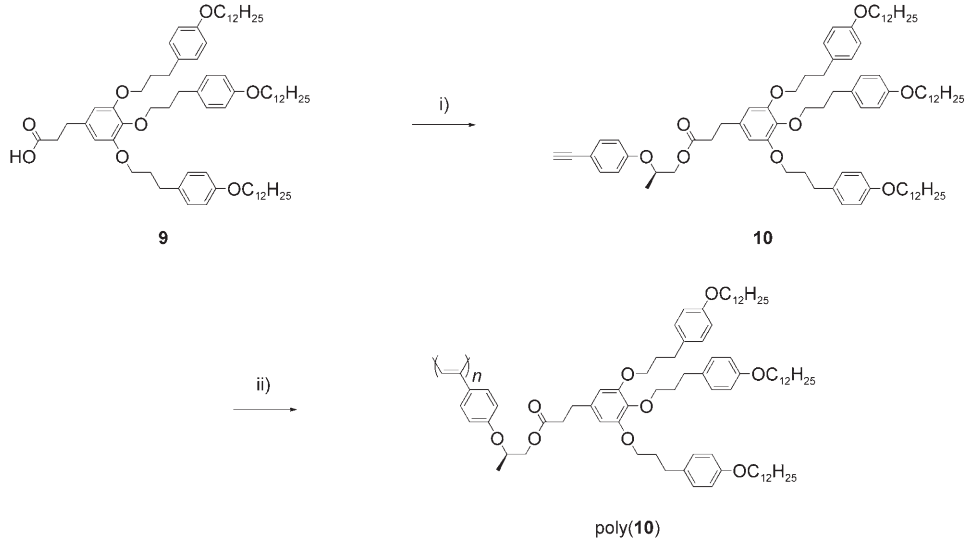

Scheme 2. Synthesis of poly(**10**): i) EDAC, DPTS, **8**, THF; ii) $[Rh(nbd)Cl]_2$, $NEt_3$, 1,2-dichloroethane, 23 °C. EDAC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride; DPTS: 4-(*N*,*N*-dimethylamino)pyridinium toluene sulfonate; nbd: 2,5-norbornadiene.

plished by using EDAC and DPTS. The dendritic monomer **10** was isolated in only 50 % yield. We have previously discussed the challenges associated with using carbodiimide coupling agents with dendritic carboxylic acids.[7b,c] The increased solubility associated with the self-assembling phenylpropyl ether based dendrons makes purification even more difficult. Nonetheless, pure **10** was obtained, as demonstrated by thorough characterization including $^1H$ and $^{13}C$ NMR spectroscopy, HPLC, and MALDI-TOF mass spectrometry. Figure 2 shows the $^1H$ NMR spectrum of **10**.

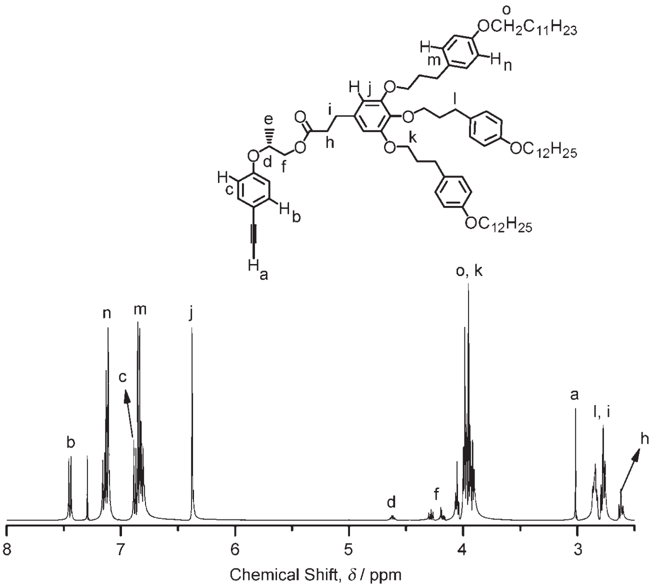

Figure 2. $^1H$ NMR spectrum of dendritic monomer **10** in $CDCl_3$. The chemical structure with proton assignments is also shown.

**Polymerization of the monomers and characterization of the polymers in solution**: As shown in Schemes 1 and 2, the polymerizations of **8** and **10** were effected by using $[Rh(nbd)Cl]_2/NEt_3$. This catalyst yields high-*cis*-content polyarylacetylenes,[15] including dendronized polyarylacetylenes.[2,7] We have previously noted that polymerizations of benzyl ether based dendritic monomers with $Rh^I$-based catalysts can be complicated by side reactions, a fact that we have attributed to cleavage of the benzyl ether linkages.[2,7c] We envision that the acid tolerance of the phenylpropyl ether based dendrons will permit access to larger and more structurally diverse libraries of dendronized polyarylacetylenes.

Table 1 reports polymerization conditions, molecular weight, molecular-weight distribution, and *cis* content for the polymers. Under dilute conditions, an extremely high-molecular-weight dendronized PPA is obtained. In the cases of dendronized polystyrenes and polymethacrylates, we have demonstrated anomalous elution during GPC of similarly high-molecular-weight polymers.[6o] In such cases, some of the extremely high-molecular-weight fraction is retarded during elution from the GPC column and thus coelutes with small polymers; the lower-molecular-weight polymers elute normally. Consequently, we expect that the $M_n$ and $M_w/M_n$ values reported in Table 1 for poly(**10**) are underestimated by this method[6o] by more than that due to hydrodynamic volume discrepancies between dendronized polymers and polystyrene calibration standards.[3c,6o,8c]

Table 1. Polymerization conditions and structural characteristics of the polymers.[a]

| Polymer | $[M]_0$ [M] | $[M]_0/[Rh]_0$ | *t* [h] | Yield [%] | $M_n\times10^{-3}$[b] | $M_w/M_n$[b] | *cis* content [%][c] |
|---|---|---|---|---|---|---|---|
| poly(**8**) | 0.182 | 40 | 14 | 50 | 3.4 | 1.36 | 91 |
| poly(**10**) | 0.041 | 58 | 14 | 69 | 231.7 | 2.14 | 88 |

[a] Polymerizations were carried out with $[Rh(nbd)Cl]_2$ in 1,2-dicloroethane/$NEt_3$ (10:1 v/v) at 23 °C. $[M]_0$: initial concentration of the monomer; $[Rh]_0$: initial concentration of the catalyst; $M_n$: number-average molecular weight; $M_w$: weight-average molecular weight. [b] Determined by GPC (THF, 1 mL min$^{-1}$) calibrated with polystyrene standards. [c] *cis* content determined by $^1H$ NMR spectroscopy by using the methods developed in our laboratory (see reference [16a]).

The *cis* content of both polymers was found to be high by using methods previously elaborated by our group (Table 1).[7b,c,e,16] The $^1H$ NMR spectra of poly(**8**) and poly(**10**) are shown in Figures 3 and 4, respectively. The proton resonance of the *cis*-polyene backbone is labeled in each as "$H_a$" for reference. Integration of this resonance versus the rest of the aromatic region of the spectrum permits quantitative determination of the *cis* content.[7b,c,e,16] The *trans*-polyene backbone resonance is overlapped by the aromatic protons of the side chain (for example, "$H_b$" and "$H_c$"); this prevents direct quantification of the *trans*-polyene content. The methylene resonances of poly(**8**) (labeled "$H_f$" in Figure 3) prevent qualitative and quantitative identification of the methine resonance that is indicative of 1,3-cyclohexadiene defect moieties in the polyene backbone.[2,7,16] Similarly, the alkyl ether methylene resonances of poly(**10**) prevent such analysis. This has been observed for previously reported examples of dendronized polyarylacetylenes.[2,7] It is worth stressing that the integration method employed for dendronized polyarylacetylenes only determines the presence of *cis*-polyene repeat units and not their conformational disposition. In PPA, the conformation (that is, cisoid versus transoid) can be determined because *cis*-cisoidal PPA is crystalline and therefore insoluble.

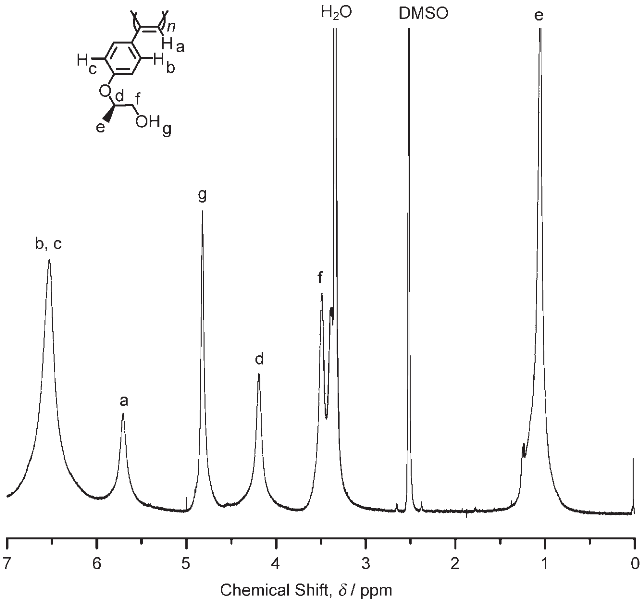

Figure 3. $^1H$ NMR spectrum of poly(**8**) in [$D_6$]DMSO. The chemical structure with proton assignments is also shown.

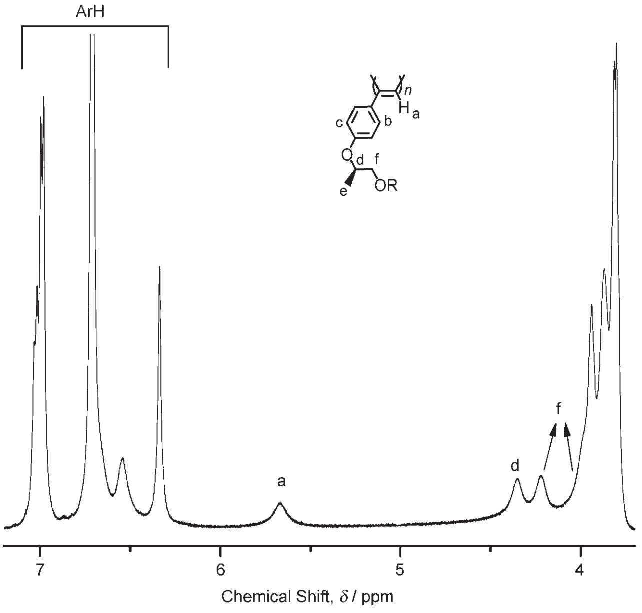

Figure 4. $^1H$ NMR spectrum of poly(**10**) in $CDCl_3$. The chemical structure of the linear polymer backbone with proton assignments is also shown.

In DMSO, poly(**8**) exhibits a strong Cotton effect associated with a long-wavelength absorption due to the conjugated polyene backbone (Figure 5). Like other examples of polyarylacetylenes with chiral, nonracemic side chains, poly(**8**) adopts a preferred helical handedness.[16g,17,18] Poly(**10**) also adopts a preferred helical handedness in methylcyclohexane (Figure 6). We have demonstrated for other self-organizing dendronized polyarylacetylenes that this occurs due to helix sense selection rather than induction of a helical conformation.[2b,7b,e] Limited comparisons of the CD spectra for poly(**8**) and poly(**10**) can be made since the spectra are recorded in such different solvents. The second Cotton effect (≈380 nm) in both polymers is comparable in magnitude and sign, a fact that leads us to speculate that these polymers adopt rather similar conformations in solution. That is to say that the dendron structure appears to have little impact on the communication of chiral information in this instance.

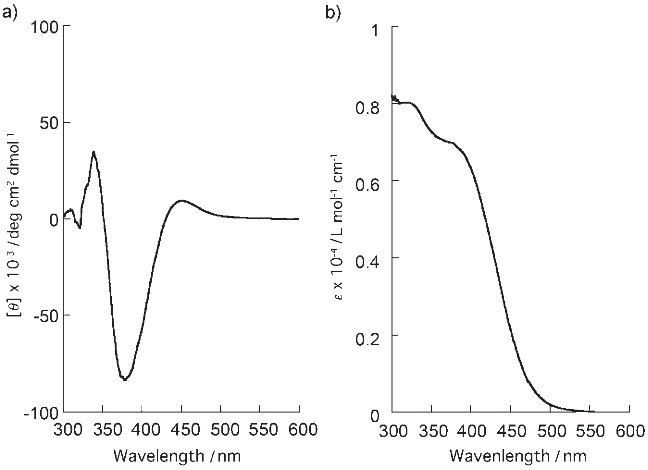

Figure 5. a) CD and b) UV/Vis spectra of poly(**8**) at 23 °C in DMSO.

Polyarylacetylenes are dynamic helical polymers,[17] and variable-temperature CD and UV/Vis spectroscopy can be used to gauge the stability of such synthetic helical polymers.[17] Longer wavelength absorption and the corresponding CD signal are due to more flat, extended conformations of the conjugate polyene backbone. Thus, we can probe the stretching/unwinding of the helical conformation. We have

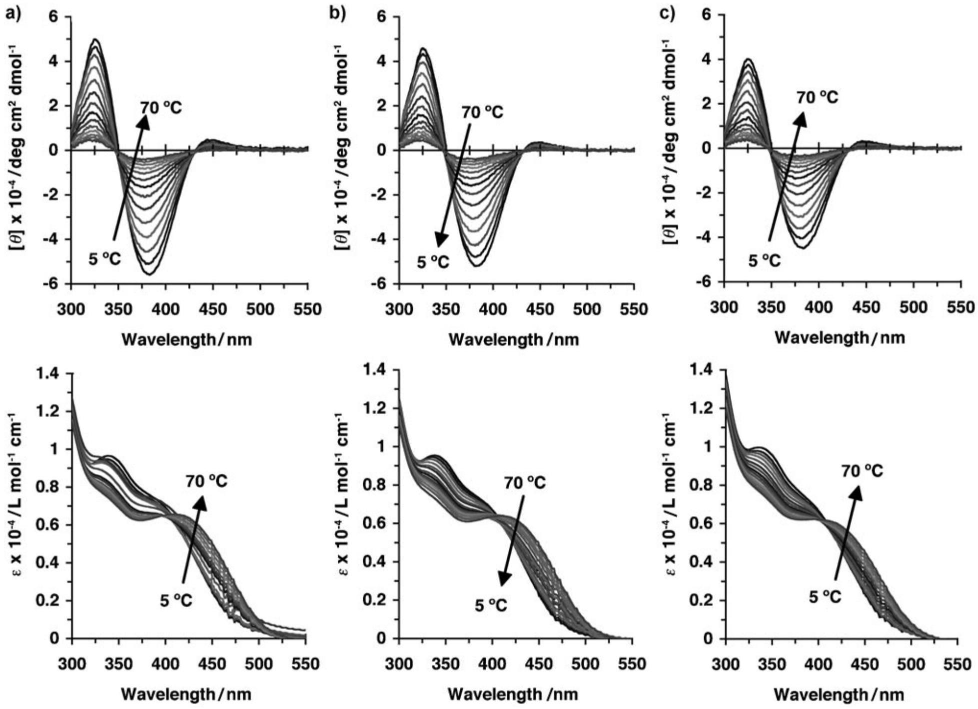

Figure 6. Variable-temperature CD (top) and UV/Vis (bottom) spectra of poly(**10**) in methylcyclohexane ([rpu] = $8.4\times10^{-4}$ M). a) First heating, b) first cooling, and c) second heating cycles are shown.

shown previously that structural transformations associated with the polyene backbone can interfere with the interpretation of such experiments.[16g] *cis–trans* isomerization, 6π electrocyclization to form 1,3-cyclohexadiene moieties, chain cleavage due to rearomatization of these moieties accompanied by extrusion of triarylbenzene, and photooxidative cleavage of the backbone are all possible transformations.[16] Nonetheless, we get a qualitative sense of the stability of the helix even when we cannot directly measure the molecular weight, molecular-weight distribution, *cis* content, and amount of 1,3-cyclohexadiene defect structures. Both the overall magnitude of the Cotton effects and the temperature range over which they can be observed decrease as the stereocenter is moved farther away from the backbone in dendronized polyarylacetylenes.[7a,b,e]

The variable-temperature CD and UV/Vis spectra for poly(**10**) in methylcyclohexane are shown in Figure 6. We show the first heating and cooling scans as well as a second heating scan. Immediately visible is the hysteresis of the Cotton effects measured at 5 °C in each scan. The initial magnitude is never recovered. We have noted this effect in menthol-derived PPAs and have shown that this is due to structural transformations of the polyene backbone.[16g] Furthermore, close inspection of the UV/Vis spectra at 70 °C reveals a gradual blue shift through the experiment. This is consistent with a reduction of the effective conjugation length of the polyene backbone.

The CD spectra of poly(**10**) show three Cotton effects of opposite sign at ≈440, ≈380, and ≈325 nm (Figure 6). Figure 7 shows overlay plots of the CD and UV/Vis spectra from the cooling scans at 10 °C and 40 °C. The identification of a negative exciton chirality[12] is demonstrated here by the second and third Cotton effects, which are both observed in the vicinity the first UV/Vis absorption maximum at ≈336 nm (Figure 7a). At the higher temperature, the second and third Cotton effects, as well the corresponding UV/Vis absorption maximum, exhibit a slight blue shift, thus making it easier to separate these from the first negative Cotton effect. The higher wavelength UV/Vis absorption maximum shifts slightly toward longer wavelengths with the temperature increase. We can assign this UV/Vis absorption maximum to a negative Cotton effect that overlaps with the one localized at 381.4–376.0 nm (Figure 7). The presence of this overlapped Cotton effect explains the asymmetry of the second peak from the CD spectra, as well the slight mismatch in the crossover of the CD spectra localized at 348 nm with the first UV/Vis maximum localized at 336.5 nm. Consequently, the negative Cotton effect considered in the exciton coupling has its true maximum at a lower wavelength than that shown in Figure 7. The negative exciton chirality identified here is commensurate with a right-handed helical structure.[12]

**Evolution of helical structure in macromolecules and supramolecules**: Phenomena by which an excess of one helical handedness is observed in polyarylacetylenes are frequently categorized as helix induction.[9,10,17b,d,f,18] This suggests that in the absence of a chiral stimulus, no helix would be found. Helix induction occurs through increased rotational barriers that prevent the polymer from accessing nonhelical confor-

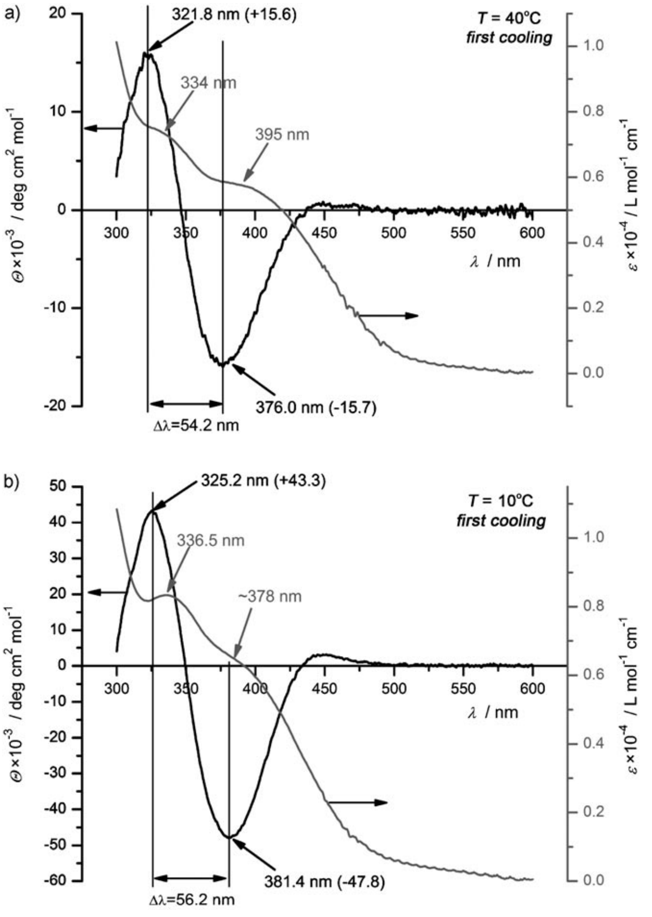

Figure 7. Overlays of CD (left axis) and UV/Vis (right axis) spectra at a) 10 °C and b) 40 °C from the first cooling of poly(**10**) in methylcyclohexane ([rpu] = $8.4\times10^{-4}$ M). The overlays highlight the negative exciton chirality.

mations,[19] such as for cylindrical, self-organizing dendronized polystyrenes and polymethacrylates.[6f–p] We proposed that polyarylacetylenes adopt a helical conformation[16a] in the absence of a chiral field (for example, a side chain, solvent, or ligand) and have shown this to be the case for dendronized polyarylacetylenes.[2b,7a,b,e] Observations of an excess of one helical handedness are due to helix sense selection by a chiral bias rather than helix induction. This is also the case for polyisocyanates[20] and polyguanidines.[21] Covalently[8,16d,17f] and noncovalently[18] attached chiral side chains program the preferred helical handedness due, in part, to infrequent helix reversals in substituted PPAs.[17]

The spectra in Figures 3 and 5 are critical to the distinction between helix sense selection[2b,7a,b,e,20,21] and helix induction.[9,10d,17b,d,f,18] In [D$_6$]DMSO, the $^1$H NMR peak shape and area are consistent with facile rotation of the backbone and side chains in poly(**8**) (Figure 3). Steric, hydrogen-bonding, and solvophobic effects are not meaningful for poly(**8**) in [D$_6$]DMSO or DMSO. The preferred helical handedness, which gives rise to the observed Cotton effects for poly(**8**) (Figure 5), is therefore due to the chiral environment associated with the side chains, rather than restricted motion due to their steric bulk.[20] The same mechanism responsible for the preferred helical handedness in poly(**8**) is likely responsible for that in poly(**10**).

**Structural and retrostructural analysis of the dendronized polymers**: Thermal optical polarized microscopy and differential scanning calorimetry (DSC) were used to identify phase transitions for poly(**10**). The scans are shown in Figure 8 and the phase-transition temperatures are reported with their corresponding enthalpies in Table 2. Similar to previously reported dendronized PPAs,[7b,c] poly(**10**) exhibits a transition between $\Phi_h^{io}$ lattices that is only found on the first heating. The highest temperature phase is $\Phi_h$. The poly-

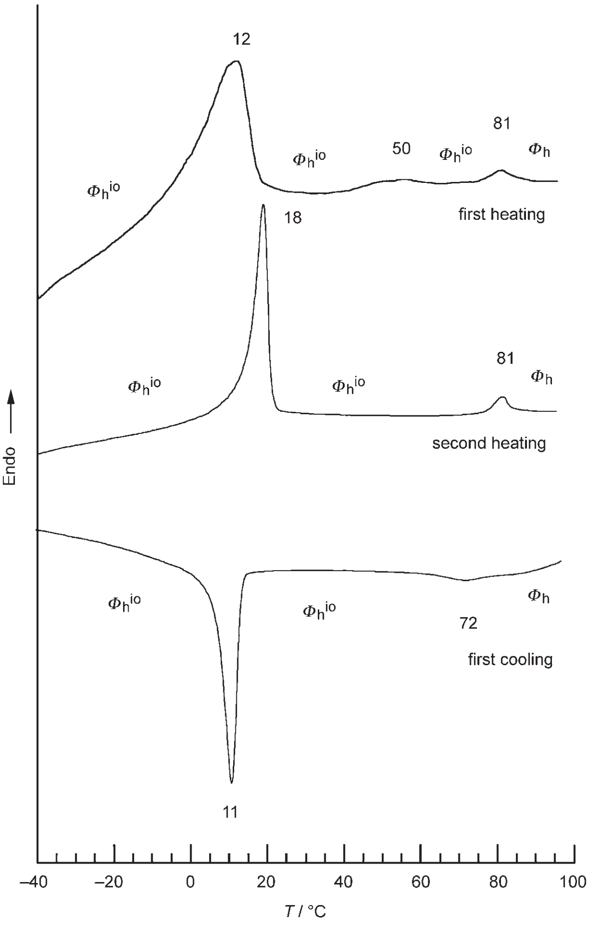

Figure 8. DSC traces (10 °C min$^{-1}$) of poly(**10**).

Table 2. Thermal transitions [°C] and corresponding enthalpy changes [kcal mol$^{-1}$] of the self-organized periodic arrays of poly(**10**).[a]

| | First and second heating scans | First cooling scan |
|---|---|---|
| 1 | $\Phi_h^{io}$ 12 (2.55) $\Phi_h^{io}$ 50 (0.12) $\Phi_h^{io}$ 81 (0.13) $\Phi_h^{c}$ | $\Phi_h$ 72 (0.27) $\Phi_h^{io}$ 11 (4.40) $\Phi_h^{io}$ |
| 2 | $\Phi_h^{io}$ 18 (4.57) $\Phi_h^{io}$ 81 (0.28) $\Phi_h$ | |

[a] Thermal transitions and enthalpy changes (in parenthesis) were determined by DSC (10 °C min$^{-1}$). $\Phi_h^{io}$: hexagonal columnar lattice with internal order; $\Phi_h$: *p6mm* hexagonal columnar lattice.

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mer decomposes before isotropization. Below the decomposition temperature, transitions in subsequent heating and cooling cycles are reversible and reproducible.

All phase assignments were confirmed by XRD. The structural and retrostructural analysis of poly(**10**) is reported in Table 3. In addition to the data in Table 3, Figure 9 reports the average column diameter measured by XRD for poly(**10**) at various temperatures above and below the $\Phi_h^{io}$-to-$\Phi_h$ transition. We have previously associated this transition with the unprecedented conversion of the PPA backbone from a *cis*-cisoidal conformation into a *cis*-transoidal conformation.[7b] The large variation of the column diameter indicates an unwinding of the helical backbone with the temperature increase, as confirmed also by the small gradual increase in the average column strata thickness observed in the wide-angle fiber experiments (Figure 10). Furthermore, wide-angle XRD from oriented fiber samples suggests long correlation lengths within the cylindrical PPAs (Figure 10).

Table 3. Structural and retrostructural analysis of the self-organized periodic arrays of poly(**10**).

| $T$ [°C] | Phase | $d$ Spacings [Å] | | | | $t$ [Å][a] | $a=D_{col}$ [Å][b] | $\mu$[c] |
|---|---|---|---|---|---|---|---|---|
| | | $d_{10}$ | $d_{11}$ | $d_{20}$ | $d_{21}$ | | | |
| −20 | *p6mm* | 46.2 | 26.9 | 23.1 | 17.5 | 4.3 | 53.5 | 4.7 |
| 30 | *p6mm* | 47.3 | 27.2 | 23.6 | 17.8 | 4.46 | 54.5 | 5.1 |
| 80 | *p6mm* | 46.1 | 26.6 | 22.9 | 17.4 | 4.56 | 53.1 | 4.9 |
| 110 | *p6mm* | 41.6 | 24.0 | 20.8 | | 4.58 | 48.0 | 4.0 |

[a] $t$: Average column stratum thickness. [b] Lattice parameter for the *p6mm* columnar hexagonal lattice; $a=2<d_{100}>3^{-0.5}$, in which $<d_{100}>=0.25(d_{10}+3^{0.5}d_{11}+2d_{20}+7^{0.5}d_{21})$ and is equal to the diameter of a column ($D_{col}$). [c] $\mu$: Number of dendrons in a column stratum $=(3^{0.5}atN_A\rho)(2M)^{-1}$, in which Avogadro's number $N_A=6.0220455\times10^{23}$, $\rho$ is the density of the polymer (assumed to be 0.93 g cm$^{-3}$), and $M$ is the molecular weight of the monomer.

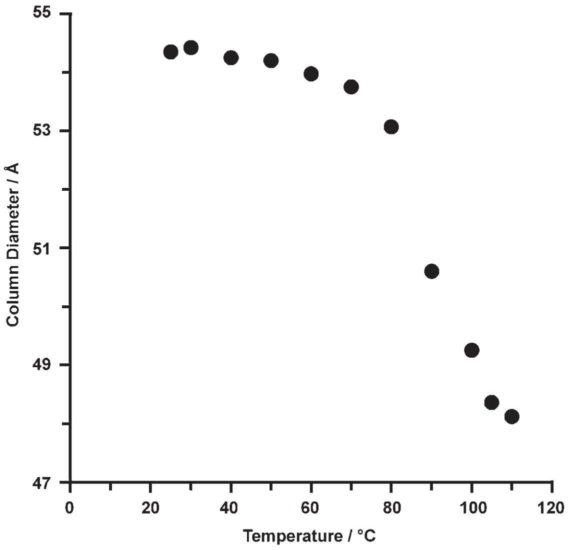

Figure 9. Plot of the average column diameter determined from XRD as a function of temperature.

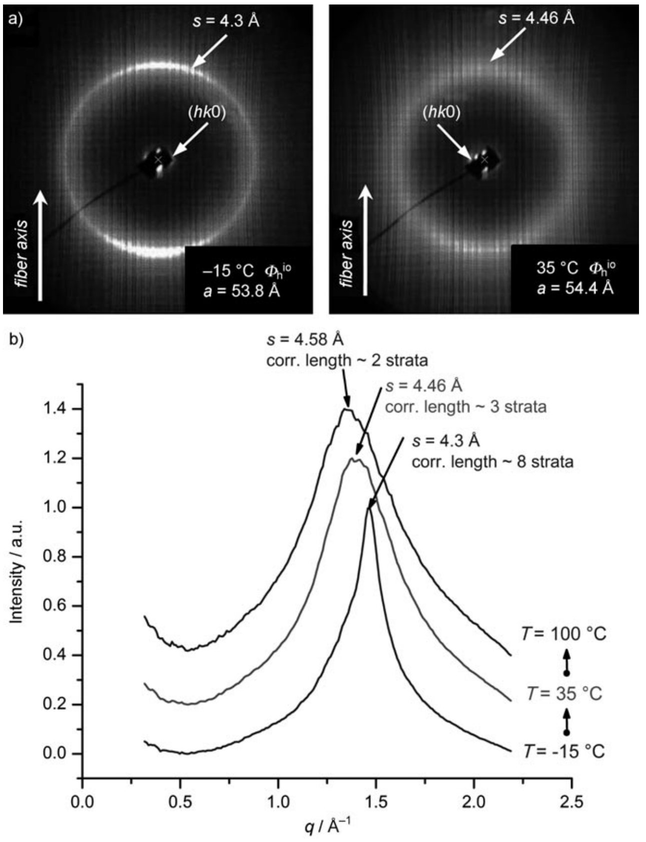

Figure 10. a) Fiber XRD patterns for poly(**10**) and b) meridional plots for poly(**10**) showing the gradual increase of the average column strata thickness, noted with the $s$ value, with the increase of temperature. Collection temperatures and correlation lengths are indicated and the plots are $y$-axis offset for clarity.

All of the above observations correlate to give a molecular model that partially (high temperatures, above 80 °C) or completely (low temperatures, below 80 °C) includes in each column stratum dendrons from the next adjacent layer, as shown in Figure 11. A plausible mechanism for this involves the relatively large empty space around the PPA backbone and dendron linkage created by the flexible self-assembling phenylpropyl ether dendrons. Thus, in order to maximize van der Waals interactions both at the nearby backbone region and at the peripheral region, the layers are thermally dynamically interdigitated, thereby causing the number of dendrons per column strata average thickness to vary from $\mu=4.7$ at 20 °C to $\mu=4.0$ at 110 °C (both numbers are calculated by assuming a constant density of $\rho=0.93$ g cm$^{-3}$).

## Conclusion

The first example of a self-assembling phenylpropyl ether based dendronized polymer has been reported and its preferred helical handedness has been determined. Poly(**10**) and its nondendritic analogue poly(**8**) are high *cis*-content PPAs prepared by using $[Rh(nbd)Cl]_2/NEt_3$. Both polymers

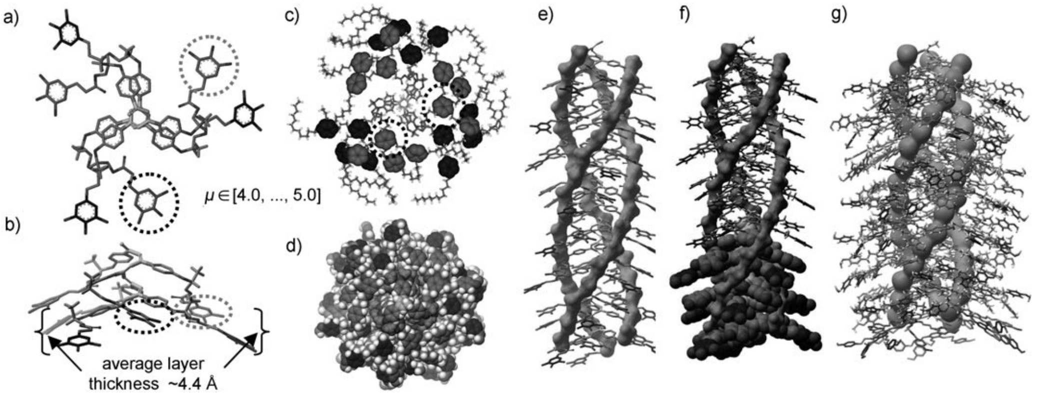

Figure 11. Structure of poly(**10**): a) Top and b) side views of the core region. The dotted circles mark the dendrons from the adjacent layer that are interdigitated to facilitate a better packing at the region close to the PPA backbone. c) Top view of two layers, d) top space-filling view of the supramolecular column, and e)–g) detailed side views of the supramolecular columns. The surface marks the right-handed helix array of aromatic rings templated by the right-handed helical polyene backbone, which is selected by the *R* chiral center.

possess a stereocenter in their side chain, which selects a preferred helical handedness. Based on negative exciton chirality observed in the CD spectra of poly(**10**), we have designated it as a right-handed helical polymer. Likely, the same helical handedness is found in poly(**8**). Due the close proximity of the stereocenter to the polyene backbone, poly(**10**) exhibits a CD signal over a wide temperature range.

Poly(**10**) self-organizes into both $\Phi_{\mathrm{h}}^{\mathrm{io}}$ and $\Phi_{\mathrm{h}}$ lattices in bulk. The $\Phi_{\mathrm{h}}^{\mathrm{io}}$-to-$\Phi_{\mathrm{h}}$ transition corresponds with a dramatic decrease in the column diameter and decrease in the $\pi$-stacking correlation length along the column. We attribute this to thermoreversible *cis*-cisoidal to *cis*-transoidal isomerization of the helical PPA. A model for the dendronized PPA has been proposed wherein dendrons from adjacent column strata interdigitate to effectively fill space. This is likely a consequence of the smaller projected molecular solid angle occupied by self-assembling phenylpropyl ether based self-assembling dendrons compared to that of benzyl ether based self-assembling dendrons.[11p]

The introduction of self-assembling phenylpropyl ether based self-assembling dendrons offers previously unobtainable possibilities for dendronized polyarylacetylenes. We have previously discussed the limitations of $\mathrm{Rh}^{\mathrm{I}}$-based polymerization catalysts with increasingly larger benzyl ether based dendritic monomers.[2b,7c] Side reactions due to cleavage of the benzyl ether linkages are obviated by the acid tolerance of self-assembling phenylpropyl ether based self-assembling dendrons.[11p] We have shown that compact helical structures more efficiently communicate chiral information from the periphery of dendronized polymers to the polymer backbone.[2b,7a,b,e] Larger dendrons will allow us to probe whether the more extended helix is fundamentally more difficult to program. Reversible, temperature-responsive extension and compression of the polyene backbone offers rudimentary sensing in both solution and in bulk. We envision further possibilities for multianalyte sensing based on the helical chirality of the polyarylacetylene.[17f,18] Furthermore, self-assembling phenylpropyl ether dendrons appended with chiral apex groups make it possible to create complex electronic materials comprising larger supramolecular dendronized polymers whose helical handedness can be defined. New concepts such as these will be the subject of future publications.

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