# Soluble, Chiral Polyacetylenes: Syntheses and Investigation of Their Solution Conformation

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**Abstract:** Soluble and highly conjugated polyacetylene derivatives bearing chiral appendages have been synthesized and characterized. The backbone $\pi \rightarrow \pi^*$ transition of these polymers showed substantial circular dichroism (CD). The magnitude of the CD for the polymers is characteristic of a disymmetric chromophore. Thus, the chiral side groups twist the main chain in predominantly one sense rather than just electronically perturbing that chromophore. The ellipticity observed for the polyacetylenes studied here, having an $\alpha$-branched substituent on only one of every eight backbone atoms, is of the order of magnitude observed for previously studied chiral polyacetylenes that had $\alpha$-branched substituents on every other backbone atom. This observation suggests that the chirality imparted to the backbone by the substituent is not greatly influenced by the proximity of neighboring substituents. Decreasing temperature had much more influence on the CD of the cis polymers than on the CD of the trans polymers in their respective $\pi \rightarrow \pi^*$ regions. *cis*-Poly-RCOTs (where RCOT is substituted cyclooctatetraene) are much more conformationally flexible and may be helical, although the CD data do not provide conclusive evidence of this conformation.

## Introduction

Polyacetylene has been the subject of intensive experimental and theoretical study.[1] Its extended $\pi$ system is highly polarizable and capable of supporting mobile carriers created by oxidizing or reducing the polymer, and these phenomena lead to a variety of interesting optical and electrical properties. One of the most important features of a highly conjugated system is the low-energy $\pi \rightarrow \pi^*$ electronic absorption (1.8 eV for *trans*-polyacetylene[2]). The electronic absorption spectrum provides a probe of backbone conformation, since any deviation from planarity in the backbone will disrupt the conjugation of the olefins and increase the energy of the electronic absorption. Polymerization of substituted acetylenes, for example, results in materials with low effective conjugation lengths as shown by their high-energy visible absorption spectra and comparatively low iodine-doped conductivities.[3] This low conjugation length is presumably due to twisting around the single bonds in polyacetylene as a result of steric repulsions between the side groups (Figure 1a).[4]

Recently, the synthesis of polyacetylene by the ring-opening metathesis polymerization (ROMP) of cyclooctatetraene (COT) was reported.[5,6] This chemistry has been extended to the ROMP of substituted cyclooctatetraenes, providing a convenient route to a variety of partially substituted polyacetylenes (Figure 2).[7] With the side group spaced, on the average, every eight carbons apart rather than two, the dominant steric interaction is between the side group and a $\beta$-hydrogen, reducing the amount of twisting and allowing for a soluble polymer with a much higher conjugation length (Figure 1b). Empirically, secondary or tertiary substituents immediately adjacent to the main chain render the polymer soluble in both the predominantly cis and trans forms. The polymer backbone is thought to twist around single bonds in the main chain adjacent to the substituent. This twist increases disorder in the polymer, imparting solubility. Yet, compared to the parent unsubstituted polyacetylene, the $\pi$ system is only minimally perturbed in most cases.[8]

Ciardelli et al. have concluded that the polymerization of acetylenes with chiral substituents produces chiral, nonplanar polyacetylenes in which the rotation angle between successive double bonds has predominantly a single sense of twist.[9] These workers further concluded that the nonplanar conformation of the polyene must be a helix with a predominant screw sense. However, the high-energy $\pi \rightarrow \pi^*$ absorptions reported for these polymers (290–325 nm in *n*-heptane) indicates that their effective conjugation lengths are very short. Moreover, the polyacetylenes synthesized in this study had a cis configuration with respect to the main chain, and there is no discussion of the properties of these polymers in the trans form. Nevertheless, these polymers are very susceptible to twisting that can be influenced by the chiral side groups.

The magnitude of the CD of a molecule can be used to differentiate between a sterically perturbed disymmetric chromophore in which the chromophore itself is chiral and an asymmetric chromophore that is merely a symmetric chromophore electronically perturbed by an asymmetric center in the same molecule.[10] An example is the difference in magnitude of CD of nonplanar conjugated dienes[11] and benzenes with asymmetric substituents.[12]

In the present work, a new class of chiral polyacetylenes are synthesized by ROMP of monosubstituted COT derivatives with chiral side groups. These polymers differ from those discussed above in that they have fewer side groups and are more conjugated as indicated by their higher wavelength electronic absorption maxima. Both of these properties impede geometric distortion of the main chain. However, to the extent that each side group twists the main chain, each should contribute to the formation of a disymmetric chromophore, rather than merely acting as a chiral perturbation on an inherently symmetric (flat) chromophore. The magnitude of the CD should indicate the degree of disymmetry of the main chain. Other chiral conductive polymers have

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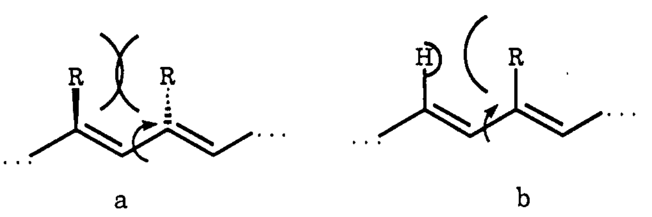


**Figure 1.** Chain twisting in polyacetylene.

been synthesized[13] with the goal of producing, for example, asymmetric electrodes for chiral electrosynthesis and ferroelectric liquid crystals. These ideas all fall into the realm of potential applications for the polymers discussed here.

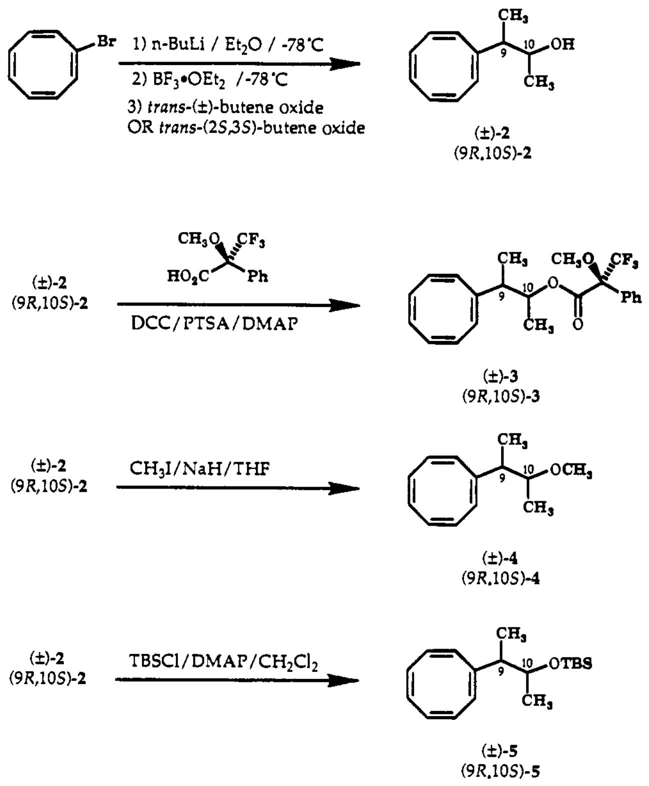
## Results and Discussion

If side groups twist the main chain of the polymer, it is of interest to determine if a chiral side group twists the main chain in predominantly one direction. Computer modeling and experimental evidence suggest that the twisting arises from the steric bulk at only the $\alpha$ carbon of the side chain. For example, the soluble polymer *trans*-poly(*tert*-butylcyclooctatetraene) is substantially twisted as indicated by its orange-red color ($\lambda_{max}$ = 432 nm in THF). *trans*-Poly(neopentylcyclooctatetraene) in which the *tert*-butyl group is displaced from the main chain by a methylene linkage is almost completely insoluble. The small amount of this polymer that is soluble in THF is intensely blue, indicative of a highly conjugated main chain with very little twisting ($\lambda_{max}$ = 634 nm in THF).[7b] In light of this observation, we designed a chiral polymer with the stereogenic center $\alpha$ to the main chain. A polymer with the stereogenic center spaced further away from the main chain was synthesized as a control. Ciardelli et al.[9] note that, in polymers of chiral acetylenes, the magnitude of circular dichroism is substantially higher in a polymer with the stereogenic center $\alpha$ to the main chain than in polymers with the stereogenic center spaced further away from the main chain. This observation suggests that the steric effects in substituted acetylene polymers are similar to those postulated for poly-RCOTs. It also suggests that the magnitude of the CD spectra of the poly-R*COTs should be very difficult for the different spacings noted previously.

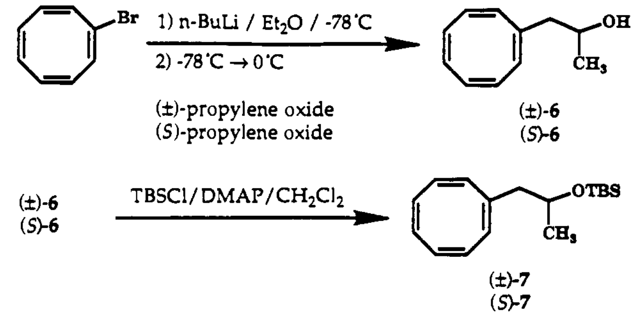
**A. Monomers.** Monomers were synthesized as outlined in Schemes I and II. The opening of ethylene oxide with LiCOT has been reported in the literature,[14] but $BF_3\cdot Et_2O$ is necessary for the opening of the sterically more encumbered *trans*-2-butene oxide.[15] Propylene oxide can be opened with or without $BF_3\cdot Et_2O$, giving the same product in each case as determined by NMR and GC/MS.

Proof that the configuration about the two stereogenic centers is retained during the ring-opening of the epoxide is furnished by synthesizing the MTPA esters[16] ((±)-**3** and (9*R*,10*S*)-**3**) of the resulting alcohols. Two well-resolved peaks, corresponding to the methoxy groups of two diastereomers, are observed in the $^1$H NMR spectra of the reaction mixture using (±)-**2**, and only one peak is observed in the reaction mixture using (9*R*,10*S*)-**2**. Thus, the chiral alcohol is enantiomerically pure within the limits of $^1$H NMR detection (>95% enantiomeric excess (ee)).

**Scheme I.** Syntheses of **2–5**



**Scheme II.** Syntheses of **6** and **7**



NMR signals were doubled in the spectra of some monomers. In particular, the 125-MHz $^{13}$C NMR spectrum of **2** showed two resonances for each of the methine carbons on the side chain, and the 125-MHz $^{13}$C NMR spectrum of **4** showed a doubling of one of the upfield methine resonances. The NMR spectra of **5** showed no unusual behavior. Compounds **2** and **4** are undergoing a dynamic process to produce two conformers that are distinguishable in the $^{13}$C NMR spectra. $^{13}$C NMR spectra of **2** and **4** at 22.5 MHz do not show this behavior, although a decoupled $^{13}$C NMR spectrum of **2** at 22.5 MHz shows resonances 4–7 ppm wide for the carbons in the side chain. On the basis of extensive work by Paquette and co-workers,[17] we assume that a dynamic ring inversion between the two forms of this molecule is occurring (Figure 3). Variable-temperature $^1$H NMR spectra of the monomers are consistent with these conclusions. For example, the $\beta$-methyl group in alcohol **2** is a broad singlet at 90 MHz and 20 °C but resolves into a sharp doublet at 90 °C. Apparently, the size of the TBS group of **5** sterically inhibits formation of one of the conformers. Thus, except for **5** and **7**, $^{13}$C NMR spectra were recorded at 22.5 MHz.

Both **4** and **5** display CD, the magnitude of which increases monotonically with decreasing temperature (Figures 4 and 5). This behavior is consistent with the "freezing out" of one COT tub conformation. In both monomers, the maximum CD effect is observed at 306 nm (THF) although the absorbance maximum of the molecule in the near-UV is at approximately 280 nm (**4**, $\lambda_{max}$ 282 nm, $\epsilon$ 348 M$^{-1}$ cm$^{-1}$; **5**, $\lambda_{max}$ 284 nm, $\epsilon$ 360 M$^{-1}$ cm$^{-1}$).

**B. Polymers.** In the syntheses of these polymers, a monomer to catalyst ratio of 150:1 was found to be ideal. Both **4** and **5**

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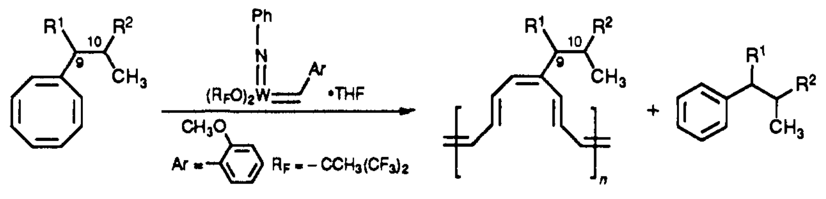
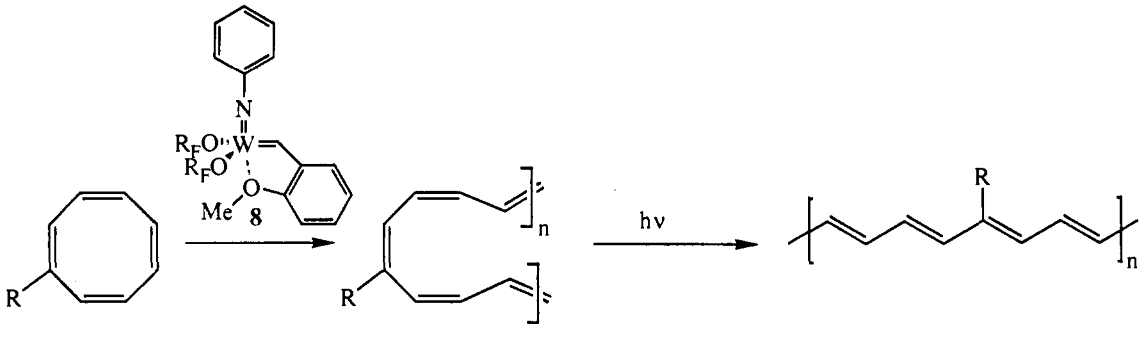
**Table I.** ROMP of Chiral COT Monomers[a]



| polymer | $R^1$ | $R^2$ | stereochem | polymerizn time (min) | polymerizn temp (°C) | % conv[b] | % backbiting[b] | GPC mol wt[c] cis ($M_w/M_n$) | GPC mol wt[c] trans ($M_w/M_n$) |
|---|---|---|---|---|---|---|---|---|---|
| **5** | $CH_3$ | O(TBS)[d] | 9*R*,10*S* | 90 | 20 | 82 | 4.9 | 499/233 | 817/626 |
| **5** | $CH_3$ | O(TBS)[d] | racemic | 60 | 20 | 66 | 3.1 | 820/497 | 889/630 |
| **4** | $CH_3$ | $OCH_3$ | 9*R*,10*S* | 65 | 20 | 12 | 6.6 | | |
| **4** | $CH_3$ | $OCH_3$ | 9*R*,10*S* | 45 | 55 | 75 | 2.8 | *e* | 485/330 |
| **4** | $CH_3$ | $OCH_3$ | racemic | 25 | 55 | 93 | 4.1 | 323/154 | 404/272 |
| **7** | H | O(TBS) | 10*S* | 60 | 20 | 93 | 7.9 | 1240/746 | 3.9/2.2[f] |
| **7** | H | O(TBS) | racemic | 60 | 20 | 83 | <5 | 995/727 | |

[a] All polymerizations were performed with a monomer to catalyst ratio of 150:1. [b] See Appendix I. [c] Molecular weight relative to polystyrene. All values listed are × $10^{-3}$. Cis and trans refer to backbone olefin geometry (see text). [d] O(TBS) = (*tert*-butyldimethylsilyl)oxy. [e] The "as polymerized" material was highly trans, and thus no cis molecular weight data could be obtained. [f] Material obtained after filtration (see text).



$R_FO = OC(CF_3)_2CH_3$, R = see text

**Figure 2.** ROMP of COT derivatives.

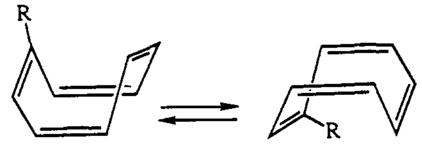


**Figure 3.** Ring inversion in monosubstituted COTs.

were polymerized at lower (50:1) and higher (300:1) ratios. At a 50:1 ratio, the molecular weight versus polystyrene as determined by GPC was $M_n$ = 28 000 for *cis*-poly-**5**. Since the correction factor versus polystyrene could conceivably be large and we wanted to use high polymer, a higher monomer to catalyst ratio was employed. At a 300:1 ratio, molecular weights were no higher than using a 150:1 monomer to catalyst ratio ($M_n$ = 110 000 for *cis*-poly-**5**), and molecular weight distributions were bimodal in some cases. The tungsten alkylidene catalyst used in this study ($W(CH\text{-}o\text{-}(OCH_3)C_6H_4)(NPh)(OCMe(CF_3)_2)_2(THF)$) (**8**, Figure 2) was prepared by a recently described procedure[18] and is similar in many ways to the catalysts first described by Schrock and co-workers[19] that were used in previous poly-RCOT work.[7] Among other features, the catalyst used here is easily synthesized and has a molecule of THF precoordinated to the metal center. The THF coordinates reversibly and slows down the polymerization so that the reaction mixture can be handled easily. This catalyst allows us to avoid adding THF to the reaction mixture as was done previously, resulting in a controlled, reproducible polymerization rate and the formation of high-quality poly-RCOT films. All COT polymerizations involve some metathesis of olefins

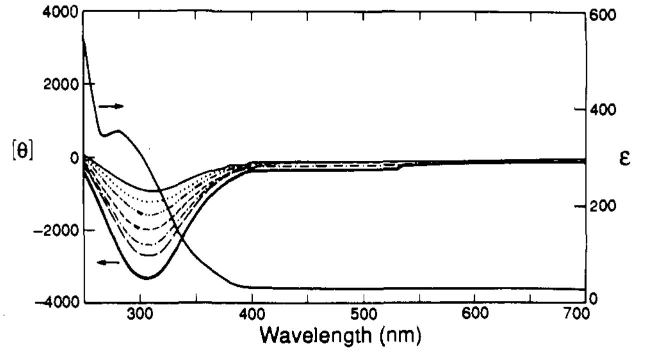


**Figure 4.** Variable temperature CD of (9*R*,10*S*)-**4**: (—) 20 °C, (···) 0 °C, (-··-) -20 °C, (---) -35 °C, (-·-) -50 °C, (-- -65 °C, (—) -75 °C.

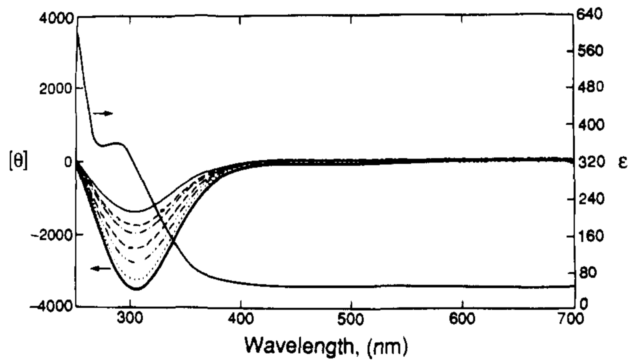


**Figure 5.** Variable temperature CD of (9*R*,10*S*)-**5**: (—) 20 °C, (---) 0 °C, (-·-) -20 °C, (--) -35 °C, (-··-) -50 °C, (···) -65 °C, (—) -73 °C.

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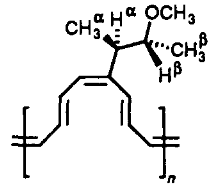
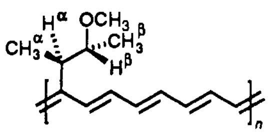
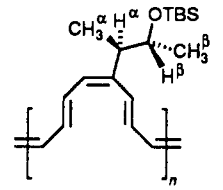
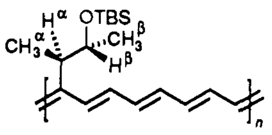
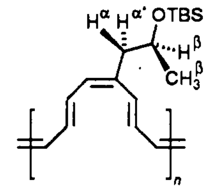
Table II. $^1H$ NMR Chemical Shift Data of Substituted Poly-COTs[a]

| reson |  |  |  |  |  |
|---|---|---|---|---|---|
| olefin[b] | 5.6–7.0 (5.91, 6.31, 6.68) | 6.1–7.1 (6.39, 6.61, 6.76, 6.95) | 5.6–7.0 (5.93, 6.29, 6.65) | 6.1–7.1 (6.41, 6.77, 6.95) | 5.7–7.0 (6.01, 6.36, 6.64) |
| $H^\beta$ | c | 3.28, 3.51 | 3.74 | 3.94, 4.16 | 3.94 |
| $H^\alpha$ | 2.36 | 2.82, 3.02 | 2.33 | 2.79, 3.11 | 2.52 ($H^{\alpha\prime}$)<br>2.31 ($H^\alpha$) |
| $CH_3^\beta$ | 1.28 | 1.41, 1.51 | 1.24 | 1.35, 1.46 | 1.16 |
| $CH_3^\alpha$ | 1.07 | 1.12 | 1.16 | 1.23 | |
| OR | 3.13 ($OCH_3$) | 3.20 ($OCH_3$) | 1.03 ($SiC(CH_3)_3$)<br>0.06 ($SiCH_3$) | 1.04 ($SiC(CH_3)_3$)<br>0.18, 0.11 ($SiCH_3$) | 1.01 ($SiC(CH_3)_3$)<br>0.08 ($SiCH_3$) |

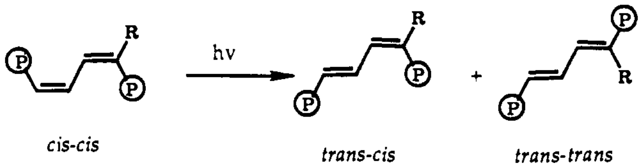
[a] Chemical shift values in ppm. Spectra were recorded at 400 MHz in benzene-$d_6$. [b] Olefin region was broad, and peaks were poorly resolved. The range of olefin chemical shift values is reported. Peak maxima are listed in parentheses. [c] $H^\beta$ for this polymer was coalesced with the methoxy resonance.

in the polymer chain, mostly to produce benzene, and the extent of this process can be determined as shown in Appendix I and is accounted for in Table I.

Although the electronic absorption spectra, Raman and infrared spectra, and molecular weights (gel permeation chromatography (GPC)) of these polymer films and solutions did not measurably change over the course of 2–3 h in air, samples decomposed visibly overnight in air, so air exposure was avoided. The films produced were flexible, but tough, indicative of high polymer. Dissolution of polymer films in an organic solvent initially produced green-brown solutions that converted to purple solutions during photolysis or over the course of several hours to days in the light under inert atmosphere. In the dark, this conversion is much slower, although the only way to prevent it is to store solutions below −20 °C in the dark. This change in color is thought to be due to a cis/trans isomerization of the double bonds in the main chain.[7] NMR evidence suggests that this isomerization is more complicated than initially thought (vide infra), but in the body of this paper, references to cis polymer or a cis structure denote the initially synthesized, predominantly cis polymer and trans refers to the predominantly trans polymer. Both isomers of poly-**4** and poly-**5** are completely soluble as is observed in all poly-RCOTs with a secondary or tertiary substituent in the position $\alpha$ to the main chain. Poly-**7** is soluble in the initially synthesized (cis) form but precipitates or aggregates (vide infra) as it isomerizes to the predominantly trans form, characteristic of all poly-RCOT polymers with a methylene (primary) substituent in the position $\alpha$ to the main chain.

There is a dramatic difference in reactivity between **4** and **5**. Qualitatively, the rate of polymerization of **5** is roughly the same as that of all other COT monomers. The polymerization of **4**, however, occurs very slowly at room temperature and requires a temperature of 50–60 °C to proceed at a rate comparable to the other monomers (Table I). This elevated polymerization temperature isomerizes the polymer to some extent, making characterization of predominantly *cis*-poly-**4** impossible. One rationale for this rate difference is that the OMe group in **4** can reversibly bind to the catalyst, slowing polymerization, but the O(TBS) group in **5** is too bulky to bind.

GPC indicates that these polymers have high molecular weights. Molecular weights are reproducible within approximately 20% from polymerization to polymerization and are comparable for homochiral versus racemic polymers (Table I). Retention times decreased upon isomerization to the trans polymer. This decrease is presumably because the polymer becomes stiffer and more rodlike upon isomerization to the trans form with a concomitant increase in hydrodynamic radius ($R_H$). This increase in $R_H$ will increase the apparent molecular weight versus polystyrene. Polydispersity also decreases upon photoisomerization, possibly because the microstructure is becoming more homogeneous. This decrease in polydispersity also indicates that photoisomerization is not accompanied by cross-linking or chain scission reactions. When the molecular weights of two polymers are compared, it is most useful to compare the numbers for the trans forms since any given cis sample has a polymer size that is changing due to isomerization at room temperature.



Designation of olefin geometry is with respect to the main chain

Figure 6. Possible species formed during isomerization of *cis*-poly-RCOTs.

A blue solution of *trans*-poly-**7** in toluene was produced by allowing a red toluene solution of *cis*-poly-**7** to isomerize for 2 days in ambient light under inert atmosphere. Some of the material had precipitated out of solution onto the sides of the vial during the isomerization. Upon filtration (0.5-μm Millex-SR filter), blue material remained behind in the filter and a purple solution was produced. This solution was too dilute for GPC analysis with refractive index (RI) detection. However, GPC with UV detection at the $\lambda_{max}$ of the solution (575 nm) showed the solution to contain substantially lower molecular weight material ($M_n$ 700; $M_w$ 733). Thus, the bulk of *trans*-poly-**7** is insoluble.

$^1H$ NMR data of the polymers are summarized in Table II. The NMR spectra for the racemic and homochiral forms of each polymer are identical. A series of broad resonances are observed downfield, bordering on the aromatic region, indicative of a polymeric olefinic chain. Backbone isomerization can be followed by NMR spectroscopy. The peaks due to protons in the side chain of the cis polymer gradually disappear, and new peaks due to trans polymer grow in as the sample isomerizes. It is noticed, however, that two peaks grow in for some protons, most notably, $H^\alpha$ and $H^\beta$. This behavior has been noticed first in these polymers, possibly because of the ample separation of the chemical shifts of the protons in the side chain. These two chemical species formed upon isomerization are tentatively assigned as detailed in Figure 6. It is possible that trisubstituted olefins do not display an overwhelming preference to be trans with respect to the main chain and that the two resonances are indicative of two diads. Further investigation of this behavior is warranted before definitive conclusions can be drawn.

In unsubstituted polyacetylene, the infrared C–H stretching vibrations at 740 and 1015 $cm^{-1}$ are diagnostic for cis and trans material, respectively.[1b] The infrared spectra of the substituted polyacetylenes are not as useful, as the vibrations of the side chains obscure those of the main chain. Raman spectroscopy, however, provides structural proof for a polyconjugated chain. Two peaks, assigned as the $A_g$ C—C stretch ($\nu_1$) and $A_g$ C=C stretch ($\nu_2$) in *trans*-polyacetylene, are observed in spectra of all the polymers (Table III). No peaks are observed that correspond to the cis form of polyacetylene, probably since no precautions were taken

**Table III.** Raman Data, 488-nm Excitation

| polymer | $\nu_1$ (Ag C—C stretch)[a] | $\nu_2$ (Ag C=C stretch)[a] |
|---|---|---|
| polyacetylene | 1090–1120 | 1500 |
| poly-(±)-**4** | 1132 | 1522 |
| poly-(9*R*,10*S*)-**4** | 1133 | 1522 |
| poly-(±)-**5** | 1131 | 1518 |
| poly-(9*R*,10*S*)-**5** | 1132 | 1519 |
| poly-(±)-**7** | 1120 | 1491 |
| poly-(9*R*,10*S*)-**7** | 1124 | 1495 |

[a] In $\mathrm{cm^{-1}}$.

to prevent isomerization by the 488-nm laser light employed. The position of $\nu_2$ is indicative of the conjugation length of the chain and indicates that the conjugation is reduced compared to polyacetylene.[20,21] The value of $A_g$ C=C in polyacetylene is dependent on excitation frequency. It has been suggested that different excitation wavelengths selectively resonance enhance different conjugation lengths in the polymer.[22] The exact nature of the conformational and/or chemical defects that give rise to this conjugation length dispersion is still an unresolved issue. The Raman spectra of these polymers are thus compared with a spectrum of polyacetylene recorded with a 488-nm excitation source. In this spectrum, the $A_g$ C=C peak is observed at approximately 1500 $\mathrm{cm^{-1}}$.[22b]

**C. Electronic Transitions and CD.** UV/vis spectra were acquired for both the cis and trans forms of both the racemic (±) and optically active (9*R*,10*S*) forms of **4**, **5**, and **7**. Absorption maxima and extinction coefficients for the optically active polymers are reported in Table IV and are similar within experimental error to the racemic polymers. Extinction coefficients for the cis polymers are only of value as empirical numbers since there is little control over their cis/trans content. One can notice, however, the shift to higher wavelength (lower energy) upon isomerization and the increase in extinction coefficient. Both of these effects have been observed in cis/trans isomerizations of polyenes.[23] *trans*-Poly-**7** has both a lower energy absorption and higher extinction coefficient than poly-**4** or poly-**5**, indicative of the higher conjugation that is expected for a polymer with $-\mathrm{CH_2R}$ versus $-\mathrm{CHRR'}$ in the position $\alpha$ to the main chain.

Both the UV/vis and CD transitions reported in Table IV are assigned to $\pi \rightarrow \pi^*$ transitions and represent the absorption with the highest extinction coefficient in the UV/vis spectrum. Transitions of higher energy than the ones reported remained unassigned but could be attributed to excitations into orbitals of higher energy than the LUMO, absorptions of parts of the polymer with lower effective conjugation due to more severe twisting, photolytic or chemical degradation, or any other defect that reduces conjugation.

CD data for the polymers prepared from **4** and **5** are reported in Table IV. CD spectra for all racemic polymers were obtained, and no CD activity was found. The magnitude of the CD effect (molar ellipticity, $[\theta]$) at the UV/vis $\lambda_{max}$ in both *cis*- and *trans*-poly-(9*R*,10*S*)-**5** is of the order of magnitude for disymmetric chromophores.[11] *Thus, the side group acts as a disymmetric perturbation on the main chain by twisting it with a preference for one-screw sense.* Moreover, the magnitude of the CD effect observed for these polymers is on the same order as that observed for polymers of chiral acetylenes.[9] Thus, the chirality imparted to the backbone by the substituent is not greatly influenced by the proximity of neighboring substituents. CD examination of *cis*-(9*R*,10*S*)-**4** was not possible since the higher temperature of polymerization resulted in a material that, as mentioned before, had a low cis content. However, *trans*-(9*R*,10*S*)-**4** and *trans*-(9*R*,10*S*)-**5** both display substantial CD at their UV/vis $\lambda_{max}$ (Figure 7).

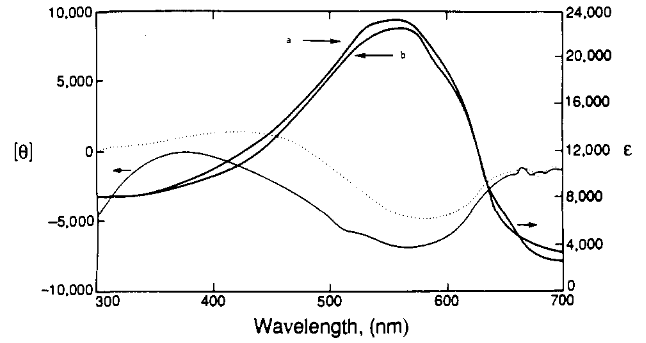


Figure 7. CD of poly-trans-(9*R*,10*S*)-**4** and poly-*trans*-(9*R*,10*S*)-**5**: (a) absorption spectrum of **4**, (b) absorption spectrum of **5**, (···) CD spectrum of **4**, (—) CD spectrum of **5**.

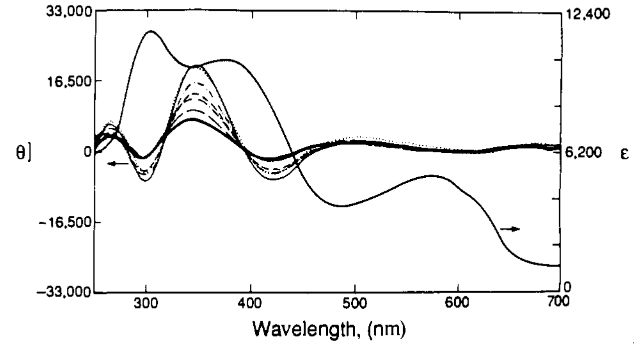


Figure 8. Variable temperature CD of poly-*cis*-(9*R*,10*S*)-**5**: (—) 20 °C, (– –) 0 °C, (–·–) -20 °C, (---) -35 °C, (–··–) -50 °C, (···) -65 °C, (—) -73 °C.

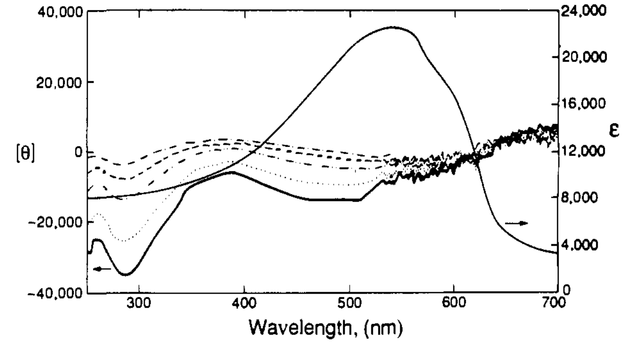


Figure 9. Variable temperature CD of poly-*trans*-(9*R*,10*S*)-**5**: (–·–) 20 °C, (---) 0 °C, (–··–) -20 °C, (···) -35 °C, (—) -50 °C.

CD spectra were recorded of both *cis*- and *trans*-poly-(9*R*,10*S*)-**5** in hexane and toluene as well as THF. Solvatochromic shifts in the UV/vis and CD spectra were minimal between these solvents. Additionally, poly-(9*S*,10*R*)-**5** was synthesized, and its CD spectra were recorded and compared to that of its enantiomer. Although the enantiomeric excess of the former was lower (see Experimental Section) and the monomer to catalyst ratio was different (50:1 and 300:1), the spectra were mirror images over the 300–700-nm wavelength range studied.

Thermochromic behavior was observed in the UV/vis spectra of these polymers. For example, upon cooling to −196 °C (2-$\mathrm{CH_3THF}$ glass), poly-*cis*-**5** shows a red shift of approximately 25 nm and an approximately 20% increase in extinction coefficient. Poly-*trans*-**5** also shows a 20–25-nm red shift upon cooling to −196 °C but, more dramatically, shows a 300% increase in extinction coefficient. An approximately 200% increase in extinction coefficient is observed upon cooling from room temperature to −78 °C.

Figures 8–10 show the variable-temperature CD spectra over the temperature range of 20 to −78 °C of poly-*cis*-(9*R*,10*S*)-**5**,

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**Table IV.**[a] Electronic Transition Data of Poly-COTs

| | cis | | | | trans | | | |
|---|---|---|---|---|---|---|---|---|
| | UV/vis | | CD | | UV/vis | | CD | |
| polymer | $\lambda_{max}$ | $\epsilon_{max}$ | $\lambda_{CD}$ | $[\theta]_{max}$ | $\lambda_{max}$ | $\epsilon_{max}$ | $\lambda_{CD}$ | $[\theta]_{max}$ |
| (9*R*,10*S*)-**5** | 302 | 11 400 | 297 | -2100 | 560 | 22 400 | 563 | -7100 |
| | 376 | 10 100 | 341 | +8000 | | | | |
| | | | 417 | -2400 | | | | |
| | | | 495 | +2100 | | | | |
| (9*R*,10*S*)-**4** | *b* | *b* | *b* | *b* | 560 | 23 100 | 587 | -5100 |
| | | | | | | | 425 | +1500 |
| (10*S*)-**7** | 306 | 12 000 | | | 594 | 35 600 | | |
| | 416 | 14 800 | | | | | | |

[a] Spectra were recorded in THF at 20 °C. [b] The "as polymerized" material was highly trans, and thus no data on the cis polymer could be obtained.

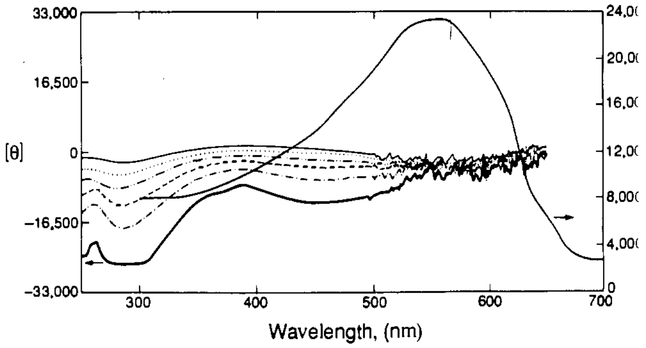

Figure 10. Variable temperature CD of poly-*trans*-(9*R*,10*S*)-**4**: (—) 15 °C, (···) -5 °C, (-··-) -20 °C, (---) -35 °C, (-·-) -50 °C, (--) -65 °C.

poly-*trans*-(9*R*,10*S*)-**5**, and poly-*trans*-(9*R*,10*S*)-**4**, respectively. Attempts to observe the electronic spectra of similar polymers at elevated temperatures failed due to decomposition of the polymer, so examination of CD above room temperature was not attempted. In each case, the magnitude of $[\theta]$ increases smoothly with decreasing temperature. Moreover, over this temperature range, the magnitude of $[\theta]$ for poly-*cis*-(9*R*,10*S*)-**5** increases with decreasing temperature far more dramatically than does the extinction coefficient, $\epsilon$. In contrast, although the CD spectrum of the poly-*trans*-(9*R*,10*S*)-**5** shows a great deal of temperature dependence below 300 nm, $[\theta]$ is much less temperature dependent at its $\lambda_{CD}$—certainly less temperature dependent than the magnitude of $\epsilon$ in the UV/vis spectrum. This behavior, coupled with the knowledge that *cis*-*n*-alkyl-poly-COTs are soluble although the trans forms of these polymers are not, suggests that cis polyacetylene units are more conformationally flexible than trans units. Although there is experimental evidence that *cis*-polyacetylene is planar in the solid state,[24] both experiments[25] and calculations[26] suggest that it can be helical in an amorphous form or in solution, although calculations disagree on the energy required to untwist and flatten the helix. Uncertainty as to the exact nature of the electronic transitions in this polymer discourages us from speculating on the helical nature of the cis form of **5**.

Since the nature of the electronic transitions below 550 nm in the trans polymers are not known with certainty, one can only say that the chromophores responsible for these transitions are much more conformationally mobile and are considerably influenced by the chiral perturbation. This behavior suggests that, rather than seeing transitions to higher energy states, we are observing less conjugated segments of the polymer. The idea that polyacetylene consists of a dispersion of conjugation lengths has been promoted in the literature (vide supra).[22b]

Within the signal to noise ratio of the spectrophotometer employed, no CD was observed for poly-(10*S*)-**7**. One problem encountered is the poor solubility of this polymer. Its CD spectra often had background signal that could not be subtracted simply with a solvent blank. The background artifact may have been caused by insoluble particulate. Filtering of these solutions did not correct the problem. The second problem encountered with the CD of poly-(10*S*)-**7** is the poor signal to noise ratio that could have arisen from two sources. First, the magnitude of the extinction coefficient for poly-*trans*-**7** is much larger than for poly-*trans*-**4** or -**5** (Table IV). Second, on the basis of the work of Ciardelli et al.,[9] we suspect that the magnitude of CD decreases as the stereocenter is moved away from the chain. The combination of increasing $\epsilon$ and decreasing magnitude of CD dramatically reduces the ratio of $[\theta]$ to $\epsilon$ and, hence, the signal to noise ratio.[27]

## Conclusions

Soluble and highly conjugated polyacetylene derivatives bearing chiral appendages have been synthesized and characterized. The backbone $\pi \rightarrow \pi^*$ transition of these polymers showed substantial CD. The magnitude of the CD for the polymers is characteristic of a disymmetric chromophore. Thus, the chiral side groups twist the main chain in predominantly one sense rather than just electronically perturbing that chromophore. The data are consistent with a model described for similar, achiral polymers in which the polymer main chain is comprised of flat, conjugated segments disturbed by kinks produced by twists about the single bonds adjacent to the side-chain substituent.[8] However, on the basis of the optical absorption maximum for the polymer (560 nm for both *trans*-poly-**4** and -**5**) and extrapolations of the absorption maxima of discreet polyenes as the number of conjugated double bonds in the molecule increases,[28] the chromophores of these polymers have effective conjugation lengths of at least 20 double bonds.

No significant solvatochromism was observed in the UV/vis or CD of the polymers. Small differences in CD were observed between polymers having $\beta$-methoxy and the more bulky $\beta$-silyloxy substituents. The ellipticity observed for the polyacetylenes studied here, having an $\alpha$-branched substituent on only one of every eight backbone atoms, is of the order of magnitude observed for previously studied chiral polyacetylenes that had $\alpha$-branched substituents on every other backbone atom. This observation suggests that the chirality imparted to the backbone by the substituent is not greatly influenced by the proximity of neighboring substituents. These polymers also offered the opportunity to examine both the cis and trans isomers of the backbone, a comparison not addressed in the past. Decreasing temperature had much more influence on the CD of the cis polymers than on the CD of the trans polymers in their respective $\pi \rightarrow \pi^*$ regions. *cis*-Poly-RCOTs are much more conformationally flexible and may contain helical regions, although the CD data do not provide conclusive evidence

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[26] (a) Cernia, E.; D'ilario, L. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, 2163. (b) Rao, B. K.; Darsey, J. A.; Kestner, N. R. *Phys. Rev. B* **1985**, *31*, 1187. (c) Elert, M. L.; White, C. T. *Phys. Rev. B* **1983**, *28*, 7387.

[27] Verbit, L.; Rao, A. S.; Clark-Lewis, J. W. *Tetrahedron* **1968**, *24*, 5839. These authors refer to $\Delta\epsilon/\epsilon$. However, $\Delta\epsilon$ is related to $[\theta]$: $[\theta] \approx 3300\Delta\epsilon$.

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of this conformation. $^1$H NMR of the polymers suggests that the olefinic units are probably not entirely cis or trans with respect to the main chain of the polymers studied, and this irregularity might prevent long-range (helical) order. These conclusions are consistent with previous results from our laboratory on solubility behavior of substituted polyCOTs.

## Experimental Section

**Instrumentation.** All syntheses are air- and moisture-sensitive and were performed with use of standard Schlenk techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. Polymerizations and subsequent handling of polymer films and preparation of polymer solutions were done in a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with either a JEOL FX-90Q (89.60-MHz $^1$H; 22.51-MHz $^{13}$C), a Bruker AM-500 (500.14-MHz $^1$H, 125.13-MHz $^{13}$C), or a JEOL GX-400 (399.65-MHz $^1$H, 100.40-MHz $^{13}$C) spectrometer. Optical rotations were determined with use of a Jasco DIP-181 digital polarimeter. Low-resolution mass spectra were obtained with a Hewlett-Packard 5890/5970 GC/MS. Gas chromatographic analysis was performed on a Hewlett-Packard 5890 using an Alltech Chirasil-Val III column. UV/vis absorption spectroscopy was performed on an HP 8451A diode array spectrophotometer. CD was performed on a Jasco J-600 CD spectrophotometer. GPC was performed on a Waters 150C ALC/GPC with differential refractometer detector and five styragel columns with use of toluene at a flow rate of 1.5 mL/min except for the GPC of *trans*-poly-**7** (vide infra), which was performed on an instrument employing an Altex 110A pump, three Shodex KF columns (KF-803, KF-804, KF-805) and a Kratos spectroflow 757 UV detector (detection at 575 nm). The toluene solution was diluted by a factor of 4 into the GPC solvent ($CH_2Cl_2$), and simultaneous RI detection showed that the oligomeric material (detected by UV) was separated from the toluene in which it was originally dissolved (detected by RI). Molecular weights are reported relative to narrow molecular weight polystyrene standards (RI or UV at 254 nm). Raman spectra were obtained from a 488-nm excitation wavelength provided by an argon ion laser source. Spectra were obtained of the light scattered off of the surface of polymer films.

**Materials.** Pentane, tetrahydrofuran, toluene, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride and chloroform were vacuum transferred off of calcium hydride. COT was purchased from Strem and was distilled from calcium hydride before use. Bromocyclooctatetraene was synthesized by the method of Gasteiger et al.[29] All reagents, including racemic *trans*-2,3-butene oxide, racemic propene oxide, (*S*)-(−)-propylene oxide ($[\alpha]^{25}_{D}$ −13.34°, 99% ee), (2*S*,3*S*)-(+)-butanediol ($[\alpha]^{25}_{D}$ +13.28°, 99% ee), and (2*R*,3*R*)-(−)-butanediol ($[\alpha]^{25}_{D}$ −12.08, 90% ee) were purchased from Aldrich unless otherwise noted. Tungsten catalyst **8** was synthesized as described in the literature.[19]

**Syntheses.** All procedures are identical for both the homochiral and the racemic forms of the monomer unless indicated otherwise.

***trans*-(2*S*,3*S*)-2,3-Epoxybutane and *trans*-(2*R*,3*R*)-2,3-Epoxybutane (1).** Synthesis was done by the method of Schurig et al.[30] except that, when complete, methyl ethyl ketone was discovered as an impurity (IR 1719 cm$^{-1}$, NMR 1.05 (t), 2.12 (s), 2.43 (q)). A representative procedure for removal of the ketone follows. A mixture of the epoxide/ketone (8.08 g, ~3% ketone impurity by GC) was vacuum transferred onto an excess of solid methyllithium (375 mg) at liquid-nitrogen temperature, and the solution was allowed to warm to −10 °C with stirring over the course of 1 h. While the solution was kept below 0 °C, the volatile material was returned to the original flask by vacuum transfer: (2*S*,3*S*) $\alpha^{25}_{D}$ −47.17°, % ee ≈ 100%; (2*R*,3*R*) $\alpha^{25}_{D}$ +44.28°, % ee ≈ 94%.

**(3-Hydroxy-*sec*-butyl)cyclooctatetraene (2).** *n*-Butyllithium (11.5 mL, 37.4 mmol, 3.25 M solution in ether, titrated before use) was added dropwise via cannula to 6.49 g (35.5 mmol) of bromocyclooctatetraene and 100 mL of diethyl ether in a 500-mL Schlenk flask at −78 °C with efficient stirring. An orange solution resulted that was stirred at −78 °C for an additional 2 h. $BF_3{\cdot}Et_2O$ (4.4 mL, 5.03 g, 35.5 mmol, Aldrich Gold Label, distilled from calcium hydride at atmospheric pressure and vacuum transferred before use) was added slowly via syringe. Immediately afterward, 2.38 mL (1.91 g, 26.5 mmol, 0.75 equiv) of *trans*-2,3-epoxybutane that had been vacuum transferred into a graduated tube with a Teflon screw top was added via cannula with efficient stirring. A color change from dark orange to yellow was observed with this addition. The reaction mixture was stirred for an additional 30 min at −78 °C, 30 mL of a saturated $NaHCO_3$ solution was added, and the mixture was allowed to warm to room temperature. Water was added, and the mixture was transferred to a separatory funnel and extracted with diethyl ether (3 × 100 mL). The organics were dried ($MgSO_4$) and concentrated. The residue was flash chromatographed over silica ($CH_2Cl_2$ and then 5% $Et_2O/CH_2Cl_2$ eluents). The yellow band was collected and concentrated. The resulting oil was distilled (short-path distillation, 55–60 °C (0.01 mmHg), first fraction discarded) to produce 2.35 g (50.2% based on epoxide) of the alcohol: $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 5.70, 5.49 (m, 7 H, COT), 3.54 (br, 1 H, (COT)C*H*−), 2.21 (bs, 1 H, −OH, (m 2.09 in toluene-$d_8$)), 2.02 (m, 1 H, −CHOH), 1.10 (d, $J$ = 6.3 Hz, 3 H, (COT)CHC$H_3$), 0.96 (d, $J$ = 7.2 Hz, 3 H, HOCHC$H_3$); $^{13}$C NMR (22.5 MHz $CDCl_3$, dec) $\delta$ 146.21, 132.5–131.2 (br, m), 69.5, 47.8, 21.3, 14.6; MS *m/z* 176 (parent), 143, 131, 117 (base), 103, 91; (9*R*,10*S*) $[\alpha]^{20}_{D}$ ($CDCl_3$) +75.5°; *m/e* calcd 176.1201, found 176.1193.

**Ester of (*R*)-(+)-$\alpha$-Methoxy-$\alpha$-(trifluoromethyl)phenylacetic Acid and (3-Hydroxy-*sec*-butyl)cyclooctatetraene (3).** A total of 59 mg (0.33 mmol) of **2**, 34 mg (0.28 mmol) of (dimethylamino)pyridine, 130 mg (0.56 mmol) of (*R*)-(+)-$\alpha$-methoxy-$\alpha$-(trifluoromethyl)phenylacetic acid, and 20 mg (0.11 mmol) of *p*-toluenesulfonic acid was combined in a round-bottomed flask, and the flask was purged with argon. A 275-mg (1.33-mmol) portion of dicyclohexylcarbodiimide in 2 mL of methylene chloride was added, and the reaction was monitored by TLC (5% $Et_2O/CH_2Cl_2$). After 20 h, no alcohol remained. The reaction mixture was passed through a 10 cm × 10 mm plug of silica and concentrated. $^1$H NMR ($CDCl_3$) of the racemic ester showed two peaks of equal intensity at $\delta$ 3.55 and 3.51. Only the peak at $\delta$ 3.55 was observed in the $^1$H NMR spectrum of the ester synthesized with the chiral alcohol.

**(3-Methoxy-*sec*-butyl)cyclooctatetraene (4).** A three-necked 50-mL round-bottomed flask was charged in the drybox with 520 mg (1.75 equiv) of NaH and fitted with a septum, stopper, and reflux condenser topped with a Teflon valve. The flask was removed from the drybox, and 20 mL of tetrahydrofuran was added via cannula. The suspension was cooled to −78 °C with stirring, and a solution of 2.18 g (12.37 mmol) of **2** and 7.5 mL of methyl iodide was added. The flask was warmed to 35 °C and stirred for 5 h under argon. A white suspension developed over this time. After being cooled to room temperature, the reaction mixture was cautiously added to a separatory funnel containing 100 mL of diethyl ether, 100 mL of a saturated sodium hydrogen carbonate solution, and 50 g of ice. The mixture was cautiously shaken and separated, and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The organic layers were combined, dried ($MgSO_4$), concentrated, and purified by flash chromatography on silica (5% $Et_2O$/petroleum ether eluent). The yellow band was collected, concentrated, and fractionally distilled from calcium hydride into a flask with a Teflon screw top (52 °C (0.03 mmHg)) to produce 1.70 g (72%): $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 5.73, 5.54 (m, 7 H, COT), 3.25 (s, 3 H, OC$H_3$), 3.00 (br, 1 H, COTC*H*), 2.14 (m, 1 H, $CH_3$OC*H*), 1.13 (d, $J$ = 6.3 Hz, 3 H, COTCHC$H_3$), 1.04 (d, $J$ = 6.3 Hz, 3 H, $CH_3$OCHC$H_3$); $^{13}$C NMR (22.5 MHz, $CDCl_3$) $\delta$ 146.5, 135.1 (br), 130.0, 128.2 (br), 123.3, 79.5 (d, $CH_3$O*C*H−, $J_{CH}$ = 137.5 Hz), 56.1 (qd, −O*C*$H_3$, $J_{CH}$ = 140.0 Hz, $^3J_{CCH}$ = 4.4 Hz), 48.0 (d, $C_8H_7$*C*H−, $J_{CH}$ = 122.9 Hz), 17.0 (qd, −$C^{\beta}HC^{\beta}H_3$, $J_{CH}$ = 125.7 Hz, $^3J_{CCH}$ = 2.9 Hz), 15.8 (q, −$C^{\alpha}HC^{\alpha}H_3$, $J_{CH}$ = 125.7 Hz); MS *m/z* 190 (parent), 158, 131, 115, 91, 77, 59 (base); $d_{20}$ 0.962; (9*R*,10*S*) $[\alpha]^{20}_{D}$ ($CH_2Cl_2$) +28.6°. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.01; H, 9.58.

**[3-(*tert*-Butyldimethylsiloxy)-*sec*-butyl]cyclooctatetraene (5).** A three-necked 50-mL round-bottomed flask was charged with 1.64 g (9.28 mmol) of **2**, 20 mL of methylene chloride, and 1.70 g (13.9 mmol) of (dimethylamino)pyridine. A solution of 2.25 g (14.9 mmol) of (TBS)Cl (Petrarch) in 5 mL of methylene chloride was added, and the contents were stirred overnight at room temperature. After 14 h, TLC (4% $Et_2O$ in petroleum ether followed by elution with 5% $Et_2O$ in $CH_2Cl_2$) showed that nearly all starting material had reacted. Contents were poured into 2 M HCl/water (50:50, 100-mL total volume) and extracted with methylene chloride (3 × 50 mL). Organic layers were dried ($MgSO_4$) and concentrated, and the residue was flash chromatographed over silica gel (3% $Et_2O$ in petroleum ether). The yellow band is collected, concentrated, and distilled (72–75 °C (0.01 mmHg) to give 2.29 g (85%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.77, 5.56 (m, 7 H, m COT), 3.47 (br, 1 H, (COT)C*H*), 2.13 (m, 1 H, O(TBS)C*H*), 1.18 (br, 3 H, (COT)-CHC$H_3$), 1.03 (d, 3 H, O(TBS)CHC$H_3$), 0.87 (s, 9 H, SiC(C$H_3$)$_3$), 0.01 (s, 6 H, Si(C$H_3$)$_2$); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.9, 132.7, 132.5, 132.3, 132.0, 131.6, 131.5, 131.3, 131.1, 130.1, 130.0, 127.6 (br), 126.2 (br), 71.4 (dq, −*C*HO(TBS), $J_{CH}$ = 139.0 Hz, $^3J_{CCH}$ = 4.9 Hz), 50.7 (d, $C_8H_7$*C*H−, $J_{CH}$ = 125.8 Hz), 25.8 (qsep, −SiC(*C*$H_3$)$_3$, $J_{CH}$ = 124.9 Hz, $^4J_{CSiCH}$ = 5.6 Hz), 22.6 (q, −$C^{\beta}HC^{\beta}H_3$, $J_{CH}$ = 125.8 Hz), 17.9 (s, −Si*C*($CH_3$)$_3$), 16.9 (q, −$C^{\alpha}HC^{\alpha}H_3$, $J_{CH}$ = 126.5), −4.19 (q, Si*C*$H_3$, $J_{CH}$ = 118.1 Hz), −4.79 (q, Si*C*$H_3'$, $J_{CH}$ = 118.8 Hz); MS *m/z* 290 (parent), 233, 189, 159, 115, 103, 73 (base); $d_{20}$ 0.932; (9*R*,10*S*) $[\alpha]^{20}_{D}$ ($CDCl_3$)

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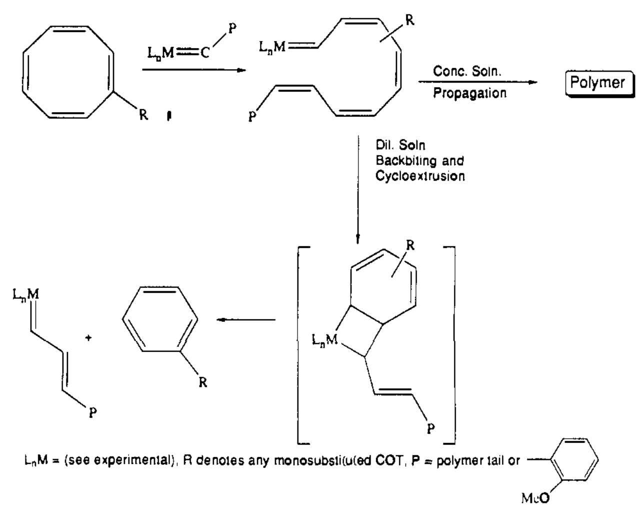
**Scheme III.** Competitive Cycloextrusion in COT Polymerizations



L$_n$M = (see experimental), R denotes any monosubstituted COT, P = polymer tail or

+13.44°. Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.41; H, 10.41. Found: C, 74.06; H, 10.39.

**(2-Hydroxy-*n*-propyl)cyclooctatetraene (6).** *n*-Butyllithium (12.8 mL, 33.9 mmol, 2.65 M solution in ether, titrated before use) is added dropwise via cannula to 5.91 g (32.3 mmol) of bromocyclooctatetraene and 100 mL diethyl ether in a 500-mL Schlenk flask at −78 °C with efficient stirring. An orange solution resulted that was stirred at −78 °C for an additional 2 h. Propylene oxide (3.4 mL, 2.8 g, 48.2 mmol) was added via syringe at −78 °C, and the solution was allowed to warm to room temperature over the course of 2 h. The solution was cooled to −78 °C, 50 mL of a saturated $NaHCO_3$ solution was added, and the solution was again allowed to warm. The solution was transferred to a separatory funnel, and the organic layer was separated. The aqueous layer was washed with diethyl ether (3 × 50 mL). The organics were combined, dried ($MgSO_4$), and concentrated. Flash chromatography over silica (3% $Et_2O/CH_2Cl_2$) yielded 1.7 g (32.5%): $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.77, 5.55 (m, 7 H, COT), 3.71 (br, 1 H, $-CH-$), 2.19 (br, 1 H, $-OH$), 2.10 (br, 2 H, $-CH_2-$), 1.14 (d, $J$ = 6.4 Hz, 3 H, $-CH_3$); $^{13}C$ NMR (22.5 MHz, $CDCl_3$) $\delta$ 140.6, 137.3, 135.0, 132.8, 130.4, 128.0, 125.9 (br), 65.6 (d, $-CH_2CHOH$, $J_{CH}$ = 139.1 Hz), 47.3 (t, $-CH_2-$, $J_{CH}$ = 128.7 Hz), 21.2 (q, $-CH_3$, $J_{CH}$ = 125.8 Hz); MS *m/z* 162 (parent), 144, 117 (base), 91, 78, 65; 10*S* $[\alpha]^{20}{}_D$ ($CDCl_3$) +8.03°, *m/e* calcd 164.1045, found 162.1034.

**[2-(*tert*-Butyldimethylsiloxy)-*n*-propyl]cyclooctatetraene (7).** A 1.96-g (12.1-mmol) portion of 6 and 35 mL of methylene chloride were placed in a round-bottomed flask and purged with argon. A 2.44-g (20-mmol) portion of (dimethylamino)pyridine and 3.02 g (20 mmol) of *tert*-butyldimethylsilyl chloride (Petrarch) (solution in 10 mL of methylene chloride) were added. The reaction was stirred overnight at room temperature under argon and washed with 5% HCl (3 × 50 mL) and water (1 × 50 mL). Aqueous layers were washed with methylene chloride, and all organic layers were combined, dried ($MgSO_4$), and concentrated. The residue was flash chromatographed over silica (3% $Et_2O$/petroleum ether), discarding the first yellow fraction. The remainder of the yellow solution was collected, concentrated, and distilled (74–79 °C (0.01 mmHg), forerun discarded) to produce 1.96 g (58%): $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.75, 5.54 (m, 7 H, COT), 3.83 (m, 1 H, $-CH-$), 2.23 (m, 1 H, $-CH_2-$ (dias)), 2.06 (dd, $J_2$ = 13.1 Hz, $J_3$ = 7.6 Hz, 1 H, $-CH_2-$ (dias)), 1.16 (d, $J$ = 5.9 Hz, 3 H, $-CH_3$), 0.86 (s, 9 H, $SiC(CH_3)_3$), 0.28 (s, 6 H, $Si(CH_3)_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 141.3 (s), 135.4 (br), 133.8 (br), 132.5 (m), 131.4 (m), 130.3 (s), 129.3 (s), 128.1 (s), 67.6 (d, $-CHO(TBS)$, $J_{CH}$ = 144.7 Hz), 48.2 (t, $C_8H_7CH-$, $J_{CH}$ = 127.5 Hz), 25.8 (qsep, $-SiC(CH_3)_3$, $J_{CH}$ = 124.8 Hz, $^4J_{CSiCH}$ = 5.7 Hz), 23.3 (q, $-CHCH_3$, $J_{CH}$ = 126.8 Hz), 18.0 (s, $-SiC(CH_3)_3$), −4.56 (q, $-SiCH_3$, $J_{CH}$ = 118.4 Hz), −4.71 (q, $-SiCH_3'$, $J_{CH}$ = 118.5 Hz); MS *m/z* 276 (parent), 261, 219, 175, 159, 103, 73 (base); $d_{20}$ 0.923; 10*S* $[\alpha]^{20}{}_D$ −24.70°. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.52; H, 10.01.

**Polymerization of 4, 5, and 7.** All polymerizations were done in the drybox. **5** and **7** were polymerized at drybox temperature (20 °C), but **4** was polymerized at 60 °C as described in the following text. The procedure was identical for the chiral and racemic monomers. In a typical polymerization, 4.3 mg of **8** was placed in a vial and dissolved in a minimum of pentane (2–3 drops). A 151.4-mg (154-equiv) portion of (±)-**4** was then added. The contents of the vial were stirred with a pipette tip, and after ca. 15 s, the solution was transferred by pipette to a glass slide sitting on a hot plate that had been thermally equilibrated to 60 °C. Over the course of 1–2 min, the mixture turned from yellow-brown to orange, red, and finally black. The film that was produced was peeled off of the slide after 25–90 min (see Table I). Polymerization at 20 °C was accomplished in the same manner, but the slide was on the drybox floor during the polymerization instead.

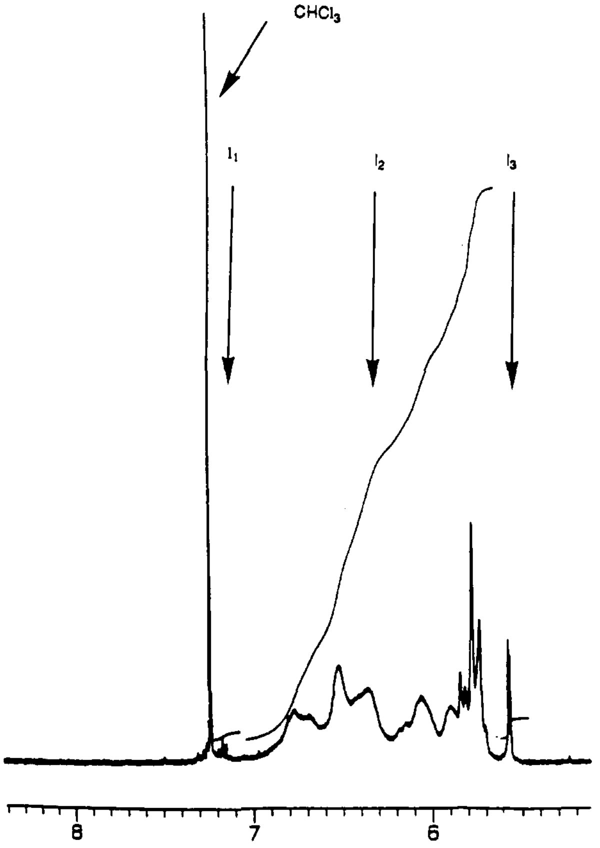


**Figure 11.** $^1H$ NMR ($CDCl_3$) olefin region of poly-**5**.

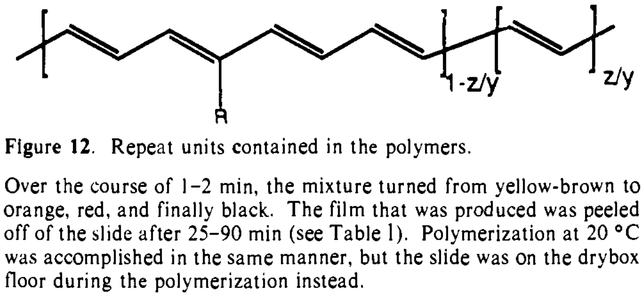


**Figure 12.** Repeat units contained in the polymers.

**Cis/Trans Isomerization of Poly-4, -5, and -7.** Isomerization could be accomplished over time by allowing solutions to sit in the light at room temperature under inert atmosphere. However, this procedure describes the photolysis used to convert predominantly cis polymer into predominantely trans material to be used for UV/vis and CD measurements. The procedure was identical for all polymers. In a typical photolysis, 3.8 mg of poly-(9*R*,10*S*)-**5** was dissolved in 5 mL of THF. A 190-$\mu$L portion of this solution was diluted to a total volume of 10 mL of THF to produce a 5 × $10^{-5}$ M (per monomer repeat unit) solution. The sample was exposed to light from a Pyrex-filtered, 350-W, medium-pressure mercury Hanovia lamp for a total of four 2-min intervals until the visible absorption spectrum showed no change. The number of exposures can vary depending on the concentration of the solution, efficiency of the lamp, etc. Overexposure resulted in a decrease in color, indicating decomposition of the material in solution. THF, toluene, and benzene were suitable solvents for this experiment, but chlorinated solvents were not acceptable.

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## Appendix I. Calculation of Percent Conversion and Percent Cycloextrusion (Backbiting) for Polymers in This Study

A more detailed look at the ROMP reaction reveals a process that affects the molecular weight of the polymer: cycloextrusion of substituted benzenes (Scheme III).[11] At any propagation step, there exists the possibility that the propagating carbene will "bite back" on the growing polymer tail, resulting in the formation of substituted benzenes. Since trisubstituted olefins undergo metathesis much more slowly, if at all,[32] it is assumed that they will not react and any cycloextrusion process will produce only substituted benzene. This action does not stop the polymerization, but it does reduce the molecular weight of the polymer and alters the polymer composition. Consequently, elemental analysis data for an as synthesized polymer film only reveals that no monomer or catalyst was lost to the environment during the polymerization. It is possible to wash the film to remove the catalyst,[6] but this act also removes the (*R*)-benzene, thus changing the side chain/main chain mass ratio of the mixture in an unpredictable way. While the amount of backbiting in the polymer can be determined by $^1$H NMR integration, this procedure is not accurate enough to calculate a meaningful elemental composition. Polymerizations in neat monomer minimize cycloextrusion, but it still occurs. For the polymers studied here, backbiting accounted for 3–8% of all metathesized monomer (Table I).

Figure 11 shows the olefinic region of the $^1$H NMR spectrum of the product of the polymerization of **5**. This spectrum is of the predominantly cis form of the polymer in the mixture, and although the shape of the olefinic polymer peak changes during isomerization to the predominantly trans form, it does not change the calculation shown here. The olefin region here is similar for any soluble polyacetylene derivative reaction mixture, and the calculation of percent conversion and percent cycloextrusion is done in an identical manner for all polymers.

One can identify three resolved integrals in Figure 11: $I_1$, $I_2$, and $I_3$. They are the integration of the following: $I_1$, cycloextrusion product (5 H) [We do not consider the contribution by the phenylimido group in the catalyst or the *o*-methoxybenzylidene group on the tail of the polymer, which also display resonances in this region. Thus, we get a higher estimate of percent cycloextrusion.]; $I_2$, integration of all protons on the polymer backbone plus six protons of the residual monomer (sharp peaks upfield); $I_3$, one proton of the residual monomer, on the basis of comparison with the $^1$H NMR spectrum of the monomer.

We define three variables: $X$, moles of unreacted monomer; $Y$, moles of monomer that reacted with the catalyst; and $Z$, moles of cycloextrusion product.

Thus, the polymers in this study are effectively copolymers of the repeat units shown in Figure 12. In this figure, repeat units are shown in the all-trans form. The isomeric content of the polymers is irrelevant for the calculations shown here.

Now, we can express the three integrals in terms of $X$, $Y$, and $Z$:

$$I_1 = 5Z \qquad I_2 = 6X + (7Y - 5Z) \qquad I_3 = X$$

In the treatment above, the quantity $7Y - 5Z$ is all the olefin protons in the polymer, i.e., all the olefin protons in the monomer minus those lost to cycloextrusion product.

Given, $I_1$, $I_2$, and $I_3$, we can solve for $X$, $Y$, and $Z$. Then,

$$\%\ \text{conversion} = \frac{Y}{Y + X}$$

$$\%\ \text{backbiting} = \frac{Z}{Y}$$

**Registry No.** *trans*-(*S*,*S*)-**1**, 63864-69-7; *trans*-(*R*,*R*)-**1**, 21490-63-1; (*R*,*S*)-**2**, 131235-98-8; **2**, 131235-97-7; **3**, 131235-99-9; (*R*,*S*)-**3**, 131346-28-6; **4**, 131236-00-5; **4** (homopolymer), 131236-06-1; (*R*,*S*)-**4**, 131236-01-6; (*R*,*S*)-**4** (homopolymer), 131236-07-2; **5**, 131236-02-7; **5** (homopolymer), 131236-08-3; (*R*,*S*)-**5**, 131236-03-8; (*R*,*S*)-**5** (homopolymer), 131236-09-4; (±)-**6**, 131236-04-9; (*S*)-**6**, 131321-26-1; (±)-**7**, 131236-05-0; (±)-**7** (homopolymer), 131236-10-7; (*S*)-**7**, 131321-27-2; (*S*)-**7** (homopolymer), 131321-28-3; **8**, 131249-95-1; (*R*)-$HO_2CC(Ph)(CF_3)OCH_3$, 20445-31-2; $CH_3I$, 74-88-4; TBSCl, 18162-48-6; (±)-propylene oxide, 75-56-9; (*S*)-propylene oxide, 16088-62-3; bromocyclooctatetraene, 7567-22-8.

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