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Polycyclooctatetraene (Polyacetylene): Synthesis and Properties

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Abstract: Addition of metathesis catalysts to "neat" 1,3,5,7-cyclooctatetraene (COT) provides a unique synthesis of the conducting polymer polyacetylene. No solvent is required, and the transformation from liquid to lustrous, silver film occurs in several seconds under ambient temperature and pressure. Properties of the poly-COT film are compared with properties of polyacetylene synthesized through acetylene polymerization. Morphology and processing modes for poly-COT are described. Linear copolymers are prepared in both random and block fashion from the metathesis polymerization of COT with other cycloolefins. Preliminary results from the metathesis polymerization of bromocyclooctatetraene are reported. The mechanism of polymerization and its consequences upon benzene formation and stereochemistry are discussed.

The morphology of polyacetylene has been demonstrated to have a decided influence upon such properties as density,[1] conductivity,[1,2] electrical and optical anisotropy,[3] and tensile strength.[4] Polyacetylene morphology is likewise an important consideration in the design of solar cells[5] or solid-state batteries.[6] Due to the intractable nature of polyacetylene, its morphology is largely fixed during the polymerization process. New modes of preparation that generate novel morphologies and allow facile fabrication are therefore instrumental in understanding and exploiting this conducting polymer.

Initial research efforts in this field, procedures that involved bubbling acetylene through various catalyst solutions, produced polyacetylene only in powder form.[7] A major breakthrough occurred in 1971 when Shirakawa and co-workers succeeded in preparing free-standing films by polymerizing acetylene at the gas/liquid interface of a concentrated catalyst solution.[8] Adaptations of the Shirakawa method have resulted in polyacetylene as a low-density gel,[1] polymerizations in liquid-crystalline media,[9] and polymerizations conducted under shear flow conditions to induce chain alignment.[10] Edwards and Feast have produced polyacetylene from a processable precursor polymer.[11] More recently, Naarmann's modification of the Shirakawa method has led to high-density polyacetylene with a conductivity approaching that of copper metal.[12]

Several research groups have targeted the metathesis polymerization of 1,3,5,7-cyclooctatetraene (COT) as a route to polyacetylene (Figure 1). In 1985, Höcker et al. reported the polymerization of COT with the "classic" metathesis catalyst system $WCl_6/AlEt_2Cl$.[13] Dilute solution conditions resulted in very low yields of insoluble powder, and vapor deposition of COT onto a catalyst slurry over a period of days produced films containing chlorination and saturation defects. No conductivities were reported for any of the samples.

We now present a versatile and convenient route to polyacetylene through the condensed-phase metathesis polymerization of 1,3,5,7-cyclooctatetraene. Dissolution of catalyst in "neat" COT provides a means of transforming the liquid into a high-quality film. Properties of these poly-COT films are nearly identical with those of polyacetylene produced by the Shirakawa method. Linear copolymers of varying conjugation lengths can be prepared by the addition of a second monomer, and new derivatives of polyacetylene can be prepared from substituted COT. This previously unpromising approach now appears to be an excellent route to conducting organic materials.

Experimental Section

General Considerations. All work involving air- or moisture-sensitive compounds was performed by using standard high-vacuum or Schlenk techniques under Argon purified by passage through BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. Solids manipulation and "neat" polymerizations were conducted in a nitrogen-filled Vacuum Atmospheres drybox equipped with refrigeration unit. Solution NMR spectra were recorded on a JEOL FX-90Q (89.60-MHz ^1H) or a JEOL GX-400 (399.65-MHz ^1H). Analytical gas chromatography was performed on a Shimadzu GC-mini 2 flame ionization instrument equipped with a 0.24 mm × 25 m SE-30 capillary column. Low-resolution GC–MS analysis was obtained with Hewlett-Packard 5890/5970 instrumentation. Conductivities were measured in an inert atmosphere by use of a four-point probe arrangement in order to negate contact resistance. Surface area measurements employed BET analysis with nitrogen as the chemical sorbate. Scanning electron microscopy of gold-coated samples (10-nm coating, sputtered deposition) was performed using 20-KeV electrons (micrographs taken in the back-scattering mode). X-ray diffraction was measured by wide-angle scattering from a Guinier camera employing monochromatic Cu Kα radiation. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7 instrument under nitrogen purge, at a scanning rate of 30 °C/min. Elemental analysis of pentane/MeOH-washed films was performed by Spang Laboratories.

Materials. Cyclooctatetraene was prepared by Reppe cyclotetramerization of acetylene.[14] COT was fractionally distilled (45 °C, 25 mmHg), filtered through neutral alumina, and vacuum distilled from CaH_2. Purity was confirmed by GC analysis before use (>99.9%). Purified COT was stored under nitrogen, below its melting point, protected from light. Norbornene (Aldrich; 99%), 1,5-cyclooctadiene (Aldrich; 99%), 1,3-cyclooctadiene (Aldrich; 98%), 1,3,5-cyclooctatriene (Organometallics; 97%), and bromocyclooctatetraene[15] were purified by vacuum distillation from CaH_2. Solvents were vacuum distilled from benzophenone ketyls, except for methylene chloride which was vacuum

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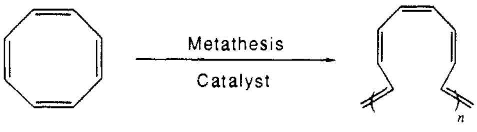

Figure 1.

distilled from P_2O_5. All polymerization substrates were cleaned thoroughly and subjected to vacuum before use. Catalysts $\mathbf{1}^{16}$ and $\mathbf{2}^{17}$ were synthesized as previously described. Cyclooctatetraene-d_8 was synthesized by a method similar to that previously reported.[18] Isotopic purity (percent deuterium incorporation) of this COT was determined by mass spectroscopy to be between 90 and 95%. Comonomer solutions were prepared by mixing appropriate amounts of COT with the second monomer (1,5-cyclooctadiene or norbornene) in stoppered glass vials. Mixing and subsequent storage were carried out in the drybox. Procedure for polymerization of these comonomer solutions is as described for neat COT.

Table I

property	poly-COT	Shirakawa PA	ref
appearance	shiny, silver; smooth surface	shiny, silver; fibrillar surface	19
surface area, m^2/g	31 ± 3	66	20
density (bulk), g/mL	0.40 ± 0.04	0.4–0.5	21
density (flotation), g/mL	1.12 ± 0.01	1.13	21
X-ray spacing *d*, Å	3.90 ± 0.05	3.80–3.85 (cis)	8
conductivity (undoped), Ω^{-1}/cm	$<10^{-8}$	10^{-5} (trans) 10^{-9} (cis)	22
conductivity (iodine-doped), Ω^{-1}/cm	50–350	160 (trans) 550 (cis)	22
solid-state CP-MAS ^{13}C NMR, ppm	126.4, 132.2	126–129 (cis)	23
thermal isomerization	135.9	136–139 (trans)	
IR major, peaks, cm^{-1}	930, 980 765	1015 (trans) 740 (cis)	8
thermal isomerization	1015	1015 (trans)	
DSC exotherm temp, °C	150	150	24
elemental anal.: found (expected)			
carbon	91.95 (92.26)	C and H	25
hydrogen	7.66 (7.74)	99%+	

Table II

COT in mix, %	film appearance	Raman C=C stretch (half-height range), cm^{-1}
0	colorless	1659–1673
20	orange	1517–1538
40	red	1509–1544
60	dark red	1494–1544
80	red-black	1483–1542
90	dark silver	1479–1545
100	silver	1463–1531

Polymerization of Neat COT. Films are prepared routinely by dissolution of catalyst **1** in 50–150 equiv of COT and subsequent polymerization on a glass surface at ambient temperature and pressure. As example: 4.2 mg (0.0053 mmol) of catalyst **1** is dissolved in 50 μL of pentane, dropped by syringe onto a glass slide over an area of $\sim$1 cm^2, and the pentane allowed to evaporate to provide a thin film of catalyst. COT (60 μL, 0.53 mmol, 100 equiv) is added all at once by syringe on top of the catalyst film. Immediately, the liquid is stirred with the flat end of a glass rod for several seconds to dissolve the catalyst. The color proceeds from the initial yellow hue of COT through orange, red, and magenta to a highly reflective silver. Viscosity gradually increases during the polymerization. At room temperature and with the above conditions, the transformation from a liquid to solid film occurs in 10–30 s. Lower monomer/catalyst ratios produce films exothermically within a few seconds. Much higher monomer/catalyst ratios result in a black powder precipitated in a pool of unreacted COT.

Films are removed from the glass slide and rinsed generously with pentane ($\sim$3 mL total) and then methanol ($\sim$1 mL). Typical film thickness is 150 μm, as measured with a micrometer. The polymerization can be conducted on substrates other than glass: metal, plastics, and cellulose have proven to be suitable. During the liquid stage of the neat polymerization, the polymer can literally be painted onto substrates.

Films Prepared by Vapor Deposition of COT. A 50-mL cylindrical Schlenk tube is loaded with 25 mg of catalyst **1** and 0.5 mL of toluene. The solution of catalyst is constantly swirled around the inner walls of the tube while being pumped upon at pressure 0.05 mmHg. As the toluene evaporates, a thin film of catalyst forms. This Schlenk tube is connected by a glass bridge to a reservoir of 2 mL of purified COT and the entire apparatus evacuated to 0.05 mmHg. After 24 h, the black film formed on the inner wall of the Schlenk tube is washed with pentane and then methanol and dried by vacuum. Pieces of the relatively brittle film were removed from the Schlenk tube (in drybox) for SEM analysis.

Polymerization on Cellulose. Ordinary postal string (composed of intertwined strands each 4–5 μm thick as determined by SEM) was subjected to 1-μm vacuum for 24 h and then submersed in a 0.01 M pentane solution of catalyst **1**. The string was removed and pentane allowed to evaporate. The string was then dipped in neat COT, upon which polymerization occurred (exothermicity apparent) immediately. Poly-COT on a string, when cut with a razor blade, "snaps" as would fiberglass. Figure 9 shows the interior of poly-COT on a string after one such cut. If after soaking in a catalyst solution the string was rinsed several times with pentane before dipping in neat COT, no polymerization occurred.

Dilute-Solution Polymerization. Catalyst **1** (2.1 mg, 2.7 μmol) was dissolved in toluene-d_8 (0.50 mL) in an NMR tube before capping with a septum. ^1H NMR shifts vs residual solvent: δ 8.84 (s, 1 H, carbene), 7.06 (s, 1 H, p-aromatic), 6.95 (s, 2 H, m-aromatic), 3.52 (septet, 2 H, C*H*Me$_2$), 1.35 (s, 6 H, alkoxide) 1.23 (s, 6 H, CH*Me*$_2$), 1.15 (s, 6 H, CH*Me*$_2$), 1.06 (s, 9 H, t-Bu). COT (3.0 μL, 26.5 μmol) was injected from a septum-capped vial via syringe into the NMR tube, and after brief vigorous shaking, a spectrum was promptly recorded ($\sim$30 s) to obtain an initial COT integration ratio. The COT peak [δ 5.61, (s)] diminished

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(34) Catalyst **1** ring-opens neither benzene nor 1,3-cyclohexadiene, nor readily reacts with cyclohexene (unpublished results, this laboratory).

(35) The synthetic precursor to catalyst **1** contains an ether ligand (dimethoxyethane) which is removed in vacuo.

(36) Cis-to-trans thermal isomerization at room temperature is relatively slow: Chien, J. C.; Karasz, F. E.; Wnek, G. E. *Nature (London)* **1980**, *285*, 390. However, local exothermicities involved in the polymerization of neat COT may be sufficient to induce some isomerization.

(37) It is unknown at this time whether or not the ring-opening of the tungstacyclobutane to form the new carbene involves associative coordination of COT.

(38) Final stereochemistry may be in part due to thermal isomerization.

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(41) Catalysts **1** and **2** have been shown to polymerize a wide variety of cycloolefins, including those with heteroatom functionalities: Unpublished results in this laboratory; communications with Prof. Richard R. Schrock.

(absent after 30 min), and a new peak [δ 7.13 (s)], assigned to benzene, grew in. Sharp singlets in the aliphatic region appeared, δ 1.63 and 0.96, tentatively assigned to the alkoxide and *tert*-butyl protons of activated catalyst, respectively. Activated/unactivated catalyst was determined by integration δ 1.63/δ 1.35. COT and benzene integrations were referenced to the residual proton concentration of toluene.

For the bromocyclooctatetraene kinetics, 0.50 mL of a stock solution—10.0 mg of **1** in 2.50 mL of CD_2Cl_2—was placed in a septum-capped NMR tube. Approximately 3 μL of Br-COT was injected, and after brief shaking, a spectrum was taken immediately for an initial Br-COT/catalyst ratio. All integrations were referenced to the residual proton concentration of methylene chloride.

Solid-State CP-MAS ^{13}C NMR Experiments. Spectra were recorded at 50.36 MHz on a home-built spectrometer described elsewhere,[42] using a contact time of 2 ms and a recycle time of 2 s. Samples were subjected to magic angle spinning at 4.0–4.5 KHz in a high-pressure stream of pure nitrogen gas, which also served to protect the samples from atmospheric oxidation. Poly-COT film was powdered with dried KBr (mortar and pestle in a drybox) and loaded (~20 mg) into a sapphire rotor with polyethylene caps (Doty Scientific). To isomerize the pristine sample, the rotor was removed from the spectrometer, heated to ~150 °C for 15 min, and returned to the spectrometer for additional analysis. Spectra shown consist of 1000–1200 averaged scans. Reported shifts (see Table I) are referenced to TMS.

Raman Experiments. Spectra were obtained for excitation wavelength 488 nm from a Argon ion laser source. One to three scans (reflected from the film's surface) were taken with a power source of 300–330 mW; signal-to-background was ~40:1. Reproducibility was within 3 cm^{-1}, and each sample was referenced to the known absorption frequencies of a CCl_4 sample. Optical filters were placed in front of the target sample so as to limit external dispersion effects. Samples were polymer films enveloped between two thin glass plates (biological cover slips). No attempt was made to cool the sample during analysis. In the range of 600–2200 cm^{-1}, two major peaks with maximums at 1113 and 1491 cm^{-1} are observed. The frequencies of COD/COT copolymer C=C absorption are reported in Table II.

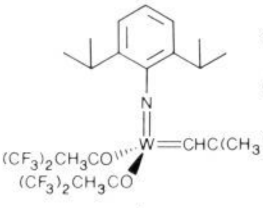
Infrared Experiments. Spectra were obtained between 4000 and 400 cm^{-1} on a Shimadzu IR-435 continuous-wave infrared spectrometer. Polymer films (~150 μm) were sandwiched between NaCl plates and placed in the infrared beam path. Some such samples were subsequently heated at ~150 °C for 15 min to induce isomerization and then reinvestigated by IR. Major absorption frequencies for poly-COT are reported in Table I. IR absorptions for films prepared from COT-d_8 are given (in cm^{-1}): 2230 (w), 960 (s), 905 (s), and 740 (s).

Microprobe Analysis and Sample Preparation. Quantitative analyses were performed with a JEOL 733 electron microprobe equipped with wavelength-dispersive X-ray detectors. The W Mα line was used for measurement relative to a tungsten metal standard. Analyses were performed at 15 KeV. Data were corrected by the ZAF correction procedures of Love and Scott and Packwood and Brown as modified by Armstrong.[43] Standard deviations for the data are estimated to be within 1% relative to the absolute amount.

Films were mounted in epoxy (Colpot; resins 12A and 12B). After being cured, the epoxy was cut with a slow-speed diamond blade rotary saw perpendicular to the film's surface, producing thin epoxy wafers each containing cross sections of the poly-COT film. Samples were prepared from poly-COT film (100 equiv of COT/catalyst **1**) that was not washed with solvent (Figure 4) and from poly-COT film washed with 0.1 M HCl in methanol.

Results

The well-defined metathesis catalysts **1** and **2** were found to be effective in the polymerization of COT into films:



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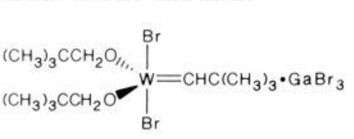

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Our experience is that catalyst **1**, readily soluble in hydrocarbon solvents such as COT, produces the highest quality poly-COT films. In Table I, properties of these poly-COT films are compared with those of polyacetylene prepared by the widely used Shirakawa method. All films were prepared by using 100 equiv of COT to catalyst **1**, as described in the Experimental Section.

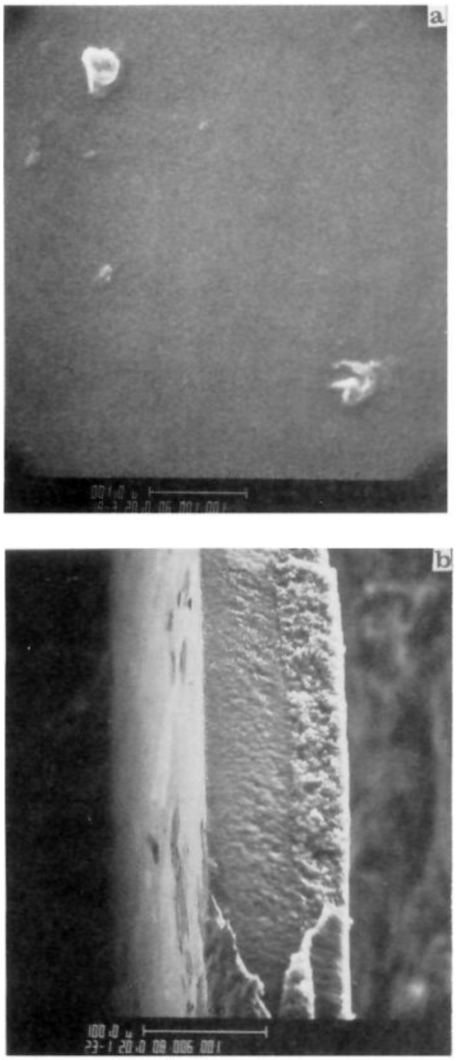

Figure 2. (a) Surface of poly-COT film (magnification 18 000×). Dust grains included in micrograph to aid focusing. (b) Cross section of poly-COT film (magnification 230×). Film standing on edge, tilted to right.

Physical Properties of Films. Whereas polyacetylene films prepared by the standard Shirakawa technique have fibrillar or globular morphology,[26] scanning electron microscopy (SEM) of poly-COT films reveals a smooth surface morphology (Figure 2a). Surface area measurements imply a more compact structure for poly-COT, in accord with SEM observations. However, the bulk density (determined by M/V) of poly-COT film is similar to that of Shirakawa polyacetylene. A more compact structure would be expected to have a higher density. The results are rationalized by examining the cross section of a thin poly-COT film. As shown in Figure 2b, the interior of the film is considerably more fibrillar than is the surface. Thus, what begins as a homogeneous polymerization solution develops into a heterogeneous material, in the absence of external perturbations.

Smoothness of morphology is largely dependent upon compactness of polymer chains, which in turn depends upon local catalyst concentration. The smooth surface morphology of poly-COT is understood to be the result of a *uniform* concentration of active catalyst species at the surface. By adopting the polymerization conditions of the Shirakawa technique (vapor deposition of monomer onto a layer of catalyst **1**), the same globular texture

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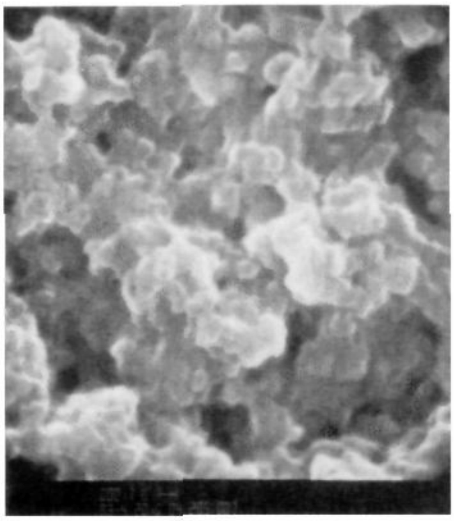

Figure 3. Surface of film produced by vapor deposition of COT (Magnification 30000×).

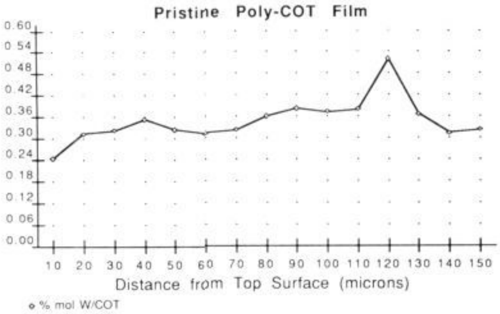

Figure 4. Cross-sectional microprobe analysis. A profile of tungsten from the top (surface away from polymerization surface) to the bottom (surface in contact with polymerization surface) of an unwashed poly-COT film. Thickness of film was determined by SEM to be 180 μm.

present in Shirakawa PA develops in poly-COT (Figure 3).

Electron microprobe analysis of residual catalyst in unwashed poly-COT film is shown in Figure 4. Depicted is a profile of tungsten concentration throughout the cross section of a thin poly-COT film. The analysis indicates that during polymerization the catalyst is indeed getting dispersed throughout the COT liquid, from "top to bottom". In poly-COT film that has been rinsed with methanolic HCl, electron microprobe analysis reveals no residual tungsten.

The crystallinity of poly-COT films has been investigated by wide-angle X-ray scattering. The only major reflection in poly-COT corresponds to $d = 3.90$ Å, whereas the only major reflection of Shirakawa *cis*-polyacetylene has a spacing of 3.80 Å.[8] The width at peak's half-height of this reflection in both PA and poly-COT is ~1.1° in θ, indicating similar degrees of crystallinity.

Poly-COT films are oxidatively doped by exposure to iodine vapor or submersion in saturated solutions of I_2 in CCl_4[12] to conductivities greater than $10^2\ \Omega^{-1}$/cm. Final composition of the film determined by weight uptake of iodine is $(CHI_{0.17-0.20})$, the mole fraction of iodine varying slightly from sample to sample. This corresponds to saturative doping, based on the model of one I_3^- dopant molecule for every 15–16 carbon atoms as seen in Shirakawa polyacetylene.[12]

Structure of Films. There are four pure isomeric structures available for polyacetylenes (Figure 5). Acetylene polymerization at low temperatures (Shirakawa method) results in isomer II. Heating II produces the thermodynamically favored isomer IV. Even though the cis–cisoid helical structure I prevents extended planarity, there is X-ray evidence for its existence in soluble diblock copolymers.[27]

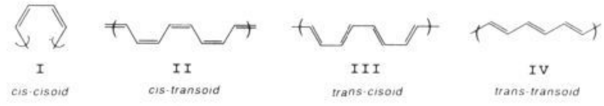

Figure 5. Isomers of polyacetylene.

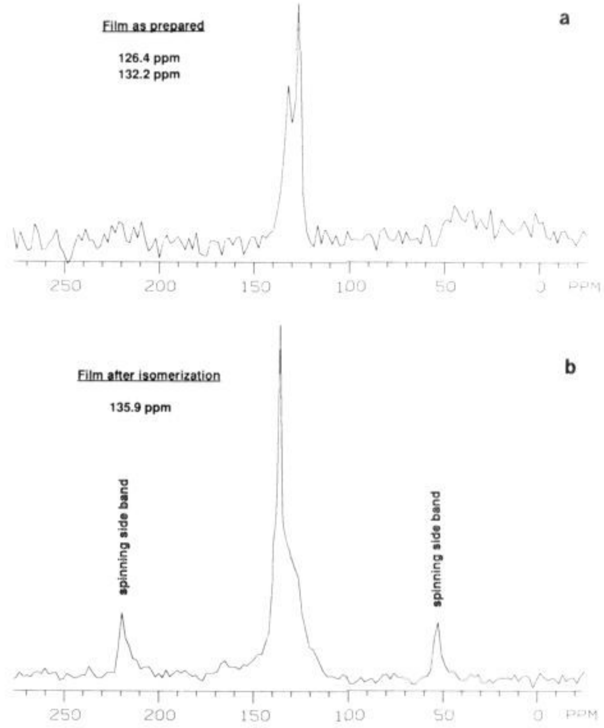

Figure 6. Solid-state CP-MAS ^{13}C NMR of poly-COT.

The structure of poly-COT film as prepared contains two distinct sp^2 carbon types as shown by solid-state CP-MAS ^{13}C NMR (Figure 6a). The low-field peak at 126.4 ppm can be attributed to carbons situated in cis double bonds. The high-field peak at 132.2 ppm is assigned to trans double-bond carbons. The ^{13}C NMR shifts of structures II and IV have previously been reported as ~126 and ~136 ppm, respectively. Whereas the NMR shifts of carbons in conjugated cis double bonds are largely insensitive to the surrounding cis–trans sequencing, carbons in conjugated trans double bonds are known to shift up to 5–6 ppm depending upon the configuration of surrounding double bonds.[28] Upon heating the sample, one peak with shift 135.9 ppm is observed (Figure 6b). As expected, heating induces thermal isomerization to produce long segments of trans–transoid structure (IV) within the polymer chains. The low-field shoulder reveals that the sample was not completely isomerized.

Infrared spectra also indicate the presence of cis (745 cm^{-1}) and trans (915, 985 cm^{-1}) conjugated double bonds. Heating the film produces the new peak (1005 cm^{-1}) in the trans region at the expense of the cis peak.

Finally, an exotherm centered at 150 °C is observed for poly-COT by differential scanning calorimetry (DSC). Integration of the exotherm indicates the enthalpy change for poly-COT is -50 ± 1 cal/g. Tober and Ferraris have found that the heat evolved during isomerization (h) is linear with respect to cis content:[44]

$$\%\ \text{cis} = (1.3\ \text{g/cal})h + 1$$

The observed value of −50 cal/g for poly-COT corresponds to a cis content of 66% for the pristine[45] film.

Conjugated Analogues. Two types of linear copolymers containing COT can be prepared through metathesis polymerization

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(44) Tober, R. L.; Ferraris, J. P. *Polymer Commun.* **1987**, *28*(12), 342.

(45) Upon cooling the sample and reheating through 200 °C no exotherm is observed, as the sample has already undergone cis–trans thermal isomerization during the first scan.

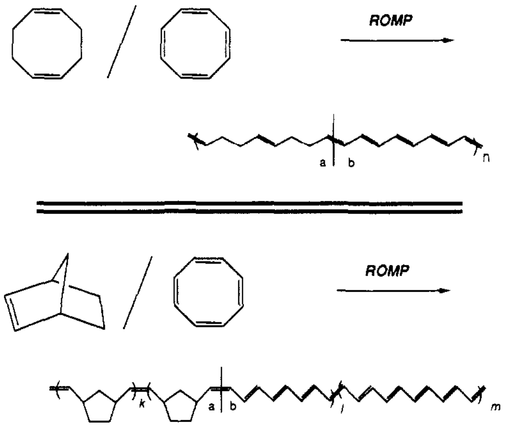


Figure 7. COT copolymerization. Ring-opening metathesis polymerization (ROMP) of COD/COT mixtures yields a random copolymer of (formally) polybutadiene and polyacetylene. Various sequence lengths a (COD unit) and b (COT unit) are distributed within the polymer chain containing *n* monomer units. In the NBE/COT copolymerization, the near-instantaneous polymerization of norbornene produces first a long block (repeat length k) of norbornene. As the norbornene concentration rapidly tapers off, COT begins to polymerize. The much slower polymerization of COT produces the final block (repeat length *m*). Polymer chain length is $k + l + m$.

(Figure 7). A *random* copolymer results when a mixture of two monomers having similar reactivities, such as 1,5-cyclooctadiene and COT, is polymerized. The graduation in color and Raman shift at peak's half-height (Table II) show that the conjugation length of polyene sequences[29] in these films increases with increasing COT content. Maximum conductivities of I_2-doped random copolymers range from 10^{-10} to over 10^2 Ω^{-1}/cm, just by varying the COT content in the COD/COT mixture from 60 to 100%. When norbornene, a much more reactive monomer, is copolymerized with COT, a tapered *block* copolymer is produced. As evidenced by the shiny golden surface and Raman absorption (half-height C=C stretch, 1480–1540 cm^{-1}) in films produced from 20% COT/80% norbornene mixtures, these block copolymers exhibit extended conjugation even when norbornene is present as the predominant monomer.

Bromocyclooctatetraene has been polymerized to a strong, flexible golden film. The film is swollen in THF to a blue-black material. Upon removal of THF, the polymer shrinks and the gold luster returns. Though the pristine film is an insulator, exposure to iodine increases the conductivity to 0.5 Ω^{-1}/cm. The final composition of the film as determined through weight uptake of iodine is $(C_8H_7BrI_{0.34})_n$, or $(CH_{0.88}X_{0.17})_n$. Again, this corresponds to saturative doping.

Dilute-Solution Polymerization. In a dilute solution of catalyst **1**, COT is completely consumed affording a 75% yield of benzene,[30] as observed by ^{1}H NMR. Benzene is confirmed by ^{13}C NMR and also by gas chromatography. During the disappearance of monomer and simultaneous appearance of benzene, the solution changes from its initial color of yellow to orange, red, magenta, and finally to a fine suspension of black particles. In an NMR tube where spinning tends to compact the particles against the inner wall, a highly reflective silvery sheen develops. A 0.005 M concentration of catalyst **1** in benzene consumes 10 equiv of COT in ~20 min. Only 30–40% of **1** is active in the polymerization, as revealed by ^{1}H NMR. The polymerization has been conducted in toluene, benzene, methylene chloride, tetrahydrofuran, diethyl ether, and pentane.

Solvent effects play an important role in the rate of these solution polymerizations. In pentane, a 0.03 M concentration of catalyst **1**, upon addition of 25 equiv of COT, forms an insoluble black powder within seconds. Similar conditions with toluene extends the reaction time to 2–3 min. In THF at these concentrations the polymerization occurs over 1–2 h. These kinetic effects may be the result of solvent molecules competing for active catalyst sites, as explained in the Discussion. No attempt was made to determine kinetic rate constants for the various solvents.

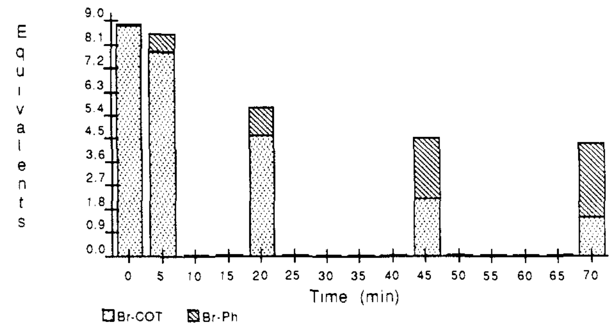
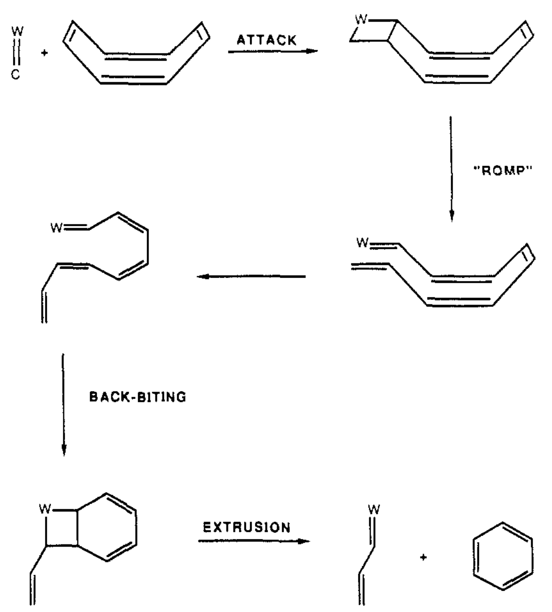


Figure 8. Dilute-solution polymerization of Br-COT.

Scheme I. Dilute-Solution Polymerization of COT

A KEKULEAN NIGHTMARE



Based on the accepted mechanisms of other carbene metathesis reactions,[31,32] the mechanism of Scheme I is proposed for ring-opening metathesis polymerization (ROMP) of COT in dilute solution. The cyclooctatetraene molecule first enters into a 2 + 2 cycloaddition reaction with the tungsten carbene (W=CR) to form a metallocyclobutane and then undergoes ring-opening cleavage to produce a new tungsten carbene. After rearrangement, the carbene proceeds to back-bite the chain and then extrudes benzene. If the proposed mechanism is correct, then analogous results should be obtained with structures similar to COT.

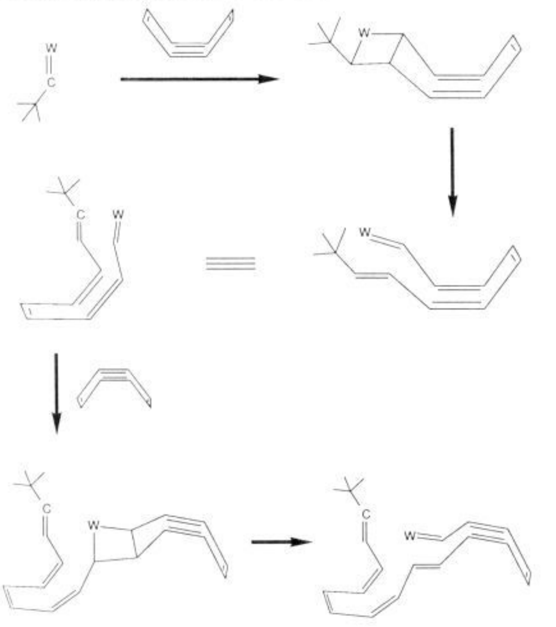
Consistent with the proposed mechanism, 1,3-cyclohexadiene is produced during dilute-solution polymerization of 1,3,5-cyclooctatriene, and cyclohexene is produced during polymerization of 1,3-cyclooctadiene. Bromobenzene (Br-Ph) is formed during the polymerization of Br-COT (Figure 8). "Equivalents" is defined by $[M]/C_0$, where [M] is the cycloolefin concentration and C_0 is the *initial* catalyst concentration. The decrease in total equivalents of Br-COT plus Br-Ph reflects the formation of polymer (precipitated—NMR silent) during the reaction.

Discussion

Mechanism. In the dilute-solution polymerization of COT the cycloextrusion of benzene dominates the reaction. CPK models reveal that the 127° C–C–C bond angles of COT[33] readily assume 120° bond angles once the ring is opened. "Driving forces" are the relief of strain, as well as increased pπ–pπ overlap. Once this rearrangement has occurred, the tungsten carbene is in position to add to the γ double bond and then extrude benzene. As benzene is inert to the metathesis catalyst,[34] the cycloextrusion reaction is irreversible.

Cycloextrusion competes with ROMP. In dilute solution, the rearrangement process necessary for cycloextrusion has time to

Scheme II. Polymerization of "Neat" COT



occur. However, in the neat polymerization of COT the tungsten carbene is surrounded by a pool of reactive sites (double bonds) at all times. The addition of COT to the catalyst reaction site is rapid, and consequently, chain growth (polymerization) is favored over the slower cycloextrusion.

In the dilute-solution polymerization of bromocyclooctatetraene it is interesting to note that no benzene is formed, as would be possible if the tungsten carbene were to attack the double bond containing bromine. Steric hindrance of the bromine toward the bulky catalyst is probably sufficient reason that attack does not occur on this double bond. The dependence of cycloextrusion statistics upon concentration, solvent, and eight-membered ring undergoing metathesis is currently being investigated.

The rate of COT polymerization spans several orders of magnitude, depending upon the choice of solvent. The more donating (Lewis basic) the solvent is to the tungsten site, the less active the catalyst. In the case of THF and other coordinating solvents, the solvent molecule behaves as a reversibly binding ligand.[35] This extra ligand serves not only to crowd the coordination sphere where reaction occurs but also reduces the electrophilicity—the metathesis activity—of the tungsten catalyst. Recently, this knowledge has been applied to improve the processability during the neat polymerization. Addition of THF to COT (~10%) lengthens the liquid stage of polymerization to several minutes, thus allowing more time for fabrication.

Structure. During the polymerization of neat COT, one of the double bonds undergoes metathesis reaction to form a new double bond having either cis or trans stereochemistry. *If it is assumed* that no isomerization occurs during polymerization,[36] three of the four cis double bonds originally present in COT remain cis, so that the final polymer should contain no less than 75% cis stereochemistry. Scheme II illustrates the formation of isolated trans double bonds during the polymerization.[37] The cis–trans structure that develops in these chains is consistent with ^{13}C NMR, IR, and DSC data. Not shown in Scheme II is the relaxation process that allows extended $p\pi$–$p\pi$ planarity in poly-COT, as is evidenced by Raman spectroscopy. A study of cis–trans content vs degree of cycloextrusion (controlled by dilution factor) will help to delineate mechanistic influence upon observed stereochemistry,[38] since extrusion of benzene eliminates the three "uninvolved" cis double bonds. Large rings resulting from *macrocyclic* extrusion may be present in the films, possibly accounting for the incomplete isomerization observed by NMR and IR.

At the terminus of each polymer chain should be a *tert*-butyl group, originally part of the carbene catalyst. Assuming that each catalyst molecule is active in the polymerization with an initial monomer/catalyst ratio of 100:1, chains should be ~100 monomer units (800 carbon atoms) in length. Since not all the catalyst initiates as seen in dilute-solution studies, chain lengths should be even greater. This large number of sp^2 carbons per *tert*-butyl group ($sp^2/sp^3 > 200$) explains why the appended *tert*-butyl group (neohexene-like) is not detected in solid-state ^{13}C NMR, IR, or elemental analysis. It is emphasized that while sp^3 carbons are expected to be present due to these *tert*-butyl groups, they are the residual functionality of catalyst **1** and do not interrupt backbone conjugation.

Figure 9. "Poly-COT on a string" (magnification 1500×).

Copolymers. As the conjugation length of a polyene sequence increases, the energy difference between the π and π^* orbitals decreases. Consequently, energies of UV–visible electronic transitions and the coupled vibrational transitions are useful indicators of conjugation length. The resonance Raman spectroscopy of polyacetylene (an "infinite" polyene) and low-conjugation-length polyenes has been intensely studied.[39,40] Profiles of the C=C vibronic absorption for polyene sequences depend upon (1) the distribution of conjugation lengths within the sample and (2) the excitation wavelength.[39] For the study of these COT copolymers, a laser excitation wavelength of relatively high energy (488 nm) was used so as to accentuate absorption of the finite (moderately short) conjugation lengths. Spectra show that, upon increasing COT content in the COD/COT polymerization mixtures, Raman C=C peaks of the resulting copolymer films broaden due to additional low-energy absorption; that is, more long conjugation segments are being formed.

Morphology. Interchain meshing seems to be important for the formation of films with good mechanical properties. In dilute-solution polymerizations of COT (also at high monomer/catalyst ratios) where the tungsten centers are far apart, the rigid chains being formed become insoluble and precipitate as a powder before the chain–chain meshing necessary for film formation can occur. As mentioned in Results, however, highly lustrous films can be prepared from dilute-solution polymerizations by in situ compression of the growing chains, thus allowing a new option for the processing of polyacetylene.

Much of the ingenious morphology research dedicated to improving the properties of polyacetylene—including shear flow polymerization conditions, polymerizations in liquid-crystalline media, and film stretching to align chains—should be applicable to the polymerization of neat COT. During the liquid stage of the neat polymerization, it should be possible to induce the morphology of preformed substrates onto poly-COT. A preliminary survey of COT polymerizations conducted within various host materials reveals (by SEM analysis) some intriguing results. Figure 9 is an electron micrograph of "poly-COT on a string". The ultimate goal in controlling morphology of organic conductors would be to grow single-crystalline material in sheets or in bulk, so as to maximize the electrical/optical properties and allow for the possible fabrication of superlattices.

Summary

Cyclooctatraene can now be polymerized to give high-quality films with iodine-doped conductivities in the metallic regime. Physical and spectral characteristics indicate that polycyclooctatetraene *is* polyacetylene. The one outstanding feature of poly-COT films is an extremely smooth surface, understood to be a consequence of polymerization conditions.

In addition to polymerizing cyclooctatetraene neat on a variety of substrates, highly lustrous films can also be produced at a slower rate by centrifugal compression of polymer during polymerization of a dilute solution of COT. Furthermore, during the liquid stage of neat polymerizations, the polymer can be painted onto substrates, a significant advance in the processability of polyacetylene.

Cyclooctatetraene is endowed with a rich history of chemistry[33]—its derivatives are varied and plentiful. As evidenced by the example of bromocyclooctatetraene, metathesis polymerization of the readily available mono- and polyhalogenated COT derivatives is expected to yield a series of novel polyacetylene analogues.

An advantage of this polymerization methodology lies in the variety of copolymers that can be prepared.[41] Depending on the relative reactivities of cycloolefins, random or block copolymers are formed. The COD/COT random copolymerizations produce materials having varied degrees of $p\pi$–$p\pi$ conjugation, determined by mole fraction COT. *This approach* to the synthesis of polyene sequences spanning the range of conjugations lengths maintains a high degree of experimental control. We are currently addressing research toward both nonlinear optical properties and electronic conduction as a function of conjugation length. Continued investigation into these new materials should lead to a greater understanding of finite conjugation sequences and conducting polymers in general.

Acknowledgment. We appreciate financial support of the National Science Foundation through Grant CHE8520517 and acknowledge the NSF Southern Californian Regional NMR facility for the CP-MAS ^{13}C spectrum. We thank Scott Virgil for his assistance and helpful instruction during catalyst preparation. F.L.K. gratefully acknowledges NSF for a graduate fellowship.

Registry No. 1, 101249-40-5; **2**, 86993-74-0; (COT)(1,5-cyclooctadiene) (copolymer), 116531-80-7; (COT)(norbornene) (block copolymer), 116531-81-8; I_2, 7553-56-2; BrCOT, 116531-82-9; cyclooctatetraene, 629-20-9; benzene, 71-43-2; cyclooctatetraene (homopolymer), 30374-82-4; cyclooctatetraene (SRU), 116531-79-4.

Supplementary Material Available: Raman, solution NMR, DSC, and IR spectra (9 pages). Ordering information is given on any current masthead page.

Lipoxygenase Inhibitors from the Essential Oil of Garlic. Markovnikov Addition of the Allyldithio Radical to Olefins[1a]

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Abstract: Brief pyrolysis of diallyl disulfide (**2**) at 150 °C affords diallyl trisulfide (**3**), thioacrolein dimers 3-vinyl-4*H*-[1,2]-dithiin (**4**) and 2-vinyl-4*H*-[1,3]-dithiin (**5**), diallyl sulfide (**6**), diallyl tetrasulfide (**7**), 6-methyl-4,5,8,9-tetrathiadodeca-1,11-diene (**8**), a mixture of 2- and 3-(2′,3′-dithia-5′-hexenyl)-3,4-dihydro-2*H*-thiopyran (**9** and **10**), and 4,5,9,10-tetrathiatrideca-1,12-diene (**11**, minor). Further heating resulted in loss or gain of sulfur, disproportionation, and cyclization affording 6- and 7-methyl-4,5,8-trithiaundeca-1,10-diene (**12** and **13**), 5-methyl-4,7-dithiadeca-1,9-diene (**14**), 7- and 8-methyl-4,5,6,9,10-pentathiatrideca-1,12-diene (**15** and **16**), 2- and 3-(2′-thia-4′-pentenyl)-3,4-dihydro-2*H*-thiopyran (**17** and **18**), 2- and 3-(2′,3′,4′-trithia-6′-heptenyl)-3,4-dihydro-2*H*-thiopyran (**19** and **20**), 4,5,9-trithiadodeca-1,11-diene (**21**), 4-methyl-1,2,3-trithiolane (**22**), 5-methyl-1,2,3,4-tetrathiane (**23**), *cis*/*trans*-3,7- and *cis*/*trans*-3,8-dimethyl-1,2,5,6-tetrathiacyclooctane (**24** and **25**), 2-(2′-[3′,4′-dihydro-2*H*-thiopyranyl])-4*H*-[1,3]-dithiin (**26**), bis[2-(3,4-dihydro-2*H*-thiopyranyl)methyl] sulfide (**27**), bis-[3-(3,4-dihydro-2*H*-thiopyranyl)methyl] sulfide (**28**), 2-(3,4-dihydro-2*H*-thiopyranyl)methyl 3-(3,4-dihydro-2*H*-thiopyranyl)methyl sulfide (**29**), bis[2-(3,4-dihydro-2*H*-thiopyranyl)methyl] disulfide (**30**), bis[3-(3,4-dihydro-2*H*-thiopyranyl)methyl] disulfide (**31**), and 2-(3,4-dihydro-2*H*-thiopyranyl)methyl 3-(3,4-dihydro-2*H*-thiopyranyl)methyl disulfide (**32**). We have also detected many of these products in commercial samples of the essential oil of garlic. They are postulated to account for the antioxidant and lipoxygenase inhibitory activity of this oil. A general mechanism is proposed for formation of these products based on C–S homolysis of diallyl disulfide and reversible terminal and internal addition of the allyldithio radical to diallyl disulfide. Intramolecular hydrogen atom abstraction–fragmentation of the intermediate formed by internal (Markovnikov) addition of the allyldithio radical is favored, affording thioacrolein and the 1-(allyldithio)-2-propylthio radical. Pyrolysis of neat diallyl sulfide in a sealed tube at 200 °C affords **17** and **18**.

While the first detailed chemical report of the preparation and analysis of the essential oil of garlic (*Allium sativum*) appeared in 1844,[2] it is likely that many centuries earlier alchemists and pharmacists distilled garlic bulbs to produce potions for a plethora of ailments.[3] The 1844 paper attributes garlic's appeal to the presence of a "sulfur-containing, liquid body, the so-called garlic oil. All that is known about the material is limited to some meager facts about the pure product which is obtained by steam distillation of bulbs of *Allium sativum*. Since sulfur bonding has been little investigated so far, a study of this material promises to supply

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(1) (a) Portions of this work have been presented at the 11th International Congress of Heterocyclic Chemistry, Heidelberg, West Germany, Aug 16, 1987, and the Third Chemical Congress of North America, Toronto, Canada, June 5-10, 1988 (Abstract ORGN 417). (b) SUNY—Albany. (c) NYU. (d) University of Ottawa.

(2) Wertheim, T. *Justus Liebigs Ann. Chem.* **1844**, *51*, 289.

(3) (a) Block, E. *Sci. Am.* **1985**, *252*. 114. (b) Block, E. In *Folk Medicine: The Art and the Science*; Steiner, R. P., Ed.; American Chemical Society: Washington, DC, 1986; pp 125-137.

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