Chapter 2

Polycyclooctatetraene (Polyacetylene) Produced with a Ruthenium Olefin Metathesis Catalyst

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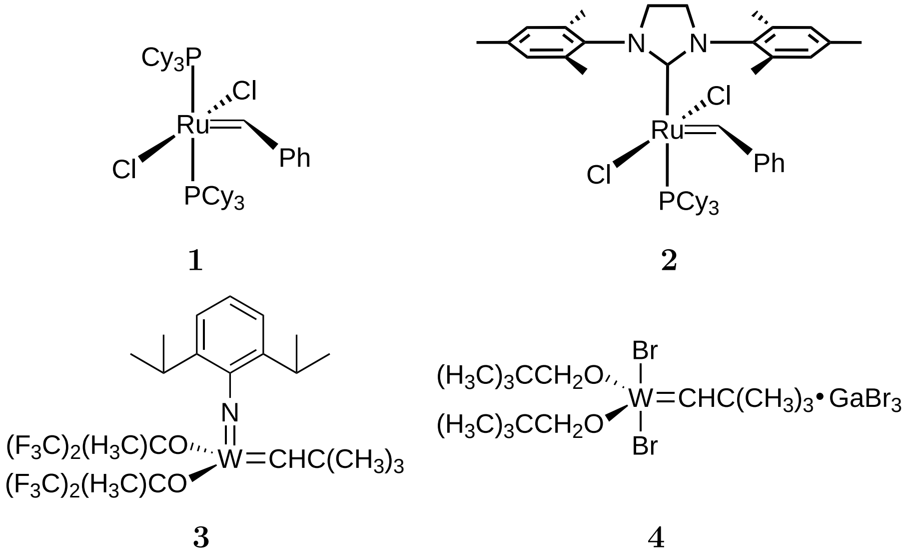
2.1 Abstract

Ring-opening metathesis polymerization (ROMP) of 1,3,5,7-cyclooctatetraene to form poly(COT), which is structurally polyacetylene (PA), has been accomplished using a well-defined ruthenium olefin metathesis catalyst. Physical and spectral properties of poly(COT) films are similar to PA obtained with previously published synthetic methodology.

2.2 Introduction

The area of highly conjugated organic polymers has commanded interest for quite some time. Polyacetylene (PA) is the (structurally) simplest conjugated organic polymer; however, its intractable nature has made its characterization quite difficult. The first successful PA film was produced in 1971 by Shirakawa and Ikeda from acetylene monomer and a highly concentrated Ziegler-Natta catalyst.[1] Over the last thirty years several methods have been introduced which allow for the synthesis of a precursor polymer that can subsequently be transformed into PA.[2, 3] Unfortunately, many of these techniques either involve the extrusion of large molecular fragments that can limit the processing of these polymers or produce very sensitive and even explosive materials.[4] Therefore, a forgiving and direct route to PA and substituted PA, such as ring opening metathesis polymerization (ROMP), which might lead to new substrates and amenable processing conditions is worth pursuing.

The metathesis polymerization of 1,3,5,7-cyclooctatetraene (COT) has been reported previously,[5–7] however the only successful routes to date have focused on early transition metal catalysts (tungsten) which are sensitive to air, moisture, and functional groups. It would be advantageous to use a late transition metal catalyst (ruthenium) which is more tolerant towards air, moisture and functional groups. Unfortunately, the $RuCl_2(=CHPh)(PCy_3)_2$, catalyst **1**, was not able to polymerize COT presumably due to its lower activity. Here we report the ROMP of COT by a highly active well defined ruthenium olefin metathesis catalyst, $RuCl_2(=CHPh)(PCy_3)(IMesH_2)$,



1

2

3

4

Figure 2.1: Several olefin metathesis active catalysts.

catalyst **2**, to produce films of polyacetylene (PA) with conductivities comparable to those first produced by Shirakawa.

2.3 Results and Discussion

Several years ago the ROMP of COT was reported using early metal tungsten catalysts, catalysts **3** and **4** (Figure 2.1).[6] Late metal metathesis catalysts have been developed in an effort to eliminate the rigorous conditions required by the early transition metal catalysts. Monomers such as norbornene and 1,5-cyclooctadiene which possess high to moderate ring strains of 27.2 kcal/mol[8] and 13.28 kcal/mol,[9] respectively, are well suited to ROMP with catalyst **1**, while COT has only 2.5 kcal/mol[8] ring strain and does not polymerize with **1**. Recently, it was reported that replacement of one of the phosphine ligands on catalyst **1** by a N-heterocyclic carbene ligand dramatically increases the activity of catalyst **2** towards ROMP.[10] Catalyst **2** is effective in the ROMP of COT to produce polyCOT (PA) (Figure 2.2).

Table 2.1 compares the properties of the polyCOT films produced by catalyst **2** to those produced with catalyst **3** and the standard Shirakawa method.[6] The most robust PA films were prepared by using 500 equivalents of COT to catalyst **2**, however up to

Table 2.1: Comparison of polyacetylenes properties produced by different routes and catalysts.

Property	Shirakawa PA	Poly(COT) from catalyst **3**	Poly(COT) from catalyst **2**
appearance	shiny, silver	shiny, silver	shiny, gold[a]
X-ray spacing *d*, Å	3.80-3.85 (*cis*)	3.90±0.05	3.79
σ (undoped)	10^{-5} (*trans*) 10^{-8} (*cis*)	$<10^{-8}$	$<10^{-8}$
σ (doped)	160 (*trans*) 550 (*cis*)	50-350	>25
SS CP-MAS ^{13}C NMR	126-9 ppm (*cis*)	126 (*cis*) 132 (*trans*)	127 (*cis*) 133 (*trans*)
IR major peaks	1015 (*trans*) 740 (*cis*)	930, 980, 765	1010, 992, 773, 745

[a] The shiny, gold appearance of poly(COT) produced from catalyst **2** is most likely due to the high *trans* content of the polymer.

2000 equivalents of COT also produced a film. The robust polyCOT films could be folded without cracking while films produced with higher monomer to catalyst ratios were quite fragile and often exhibited cracking. The undoped films are insulators,[6] however, exposure to iodine increased the conductivity in the range of 10^1 to 10^2 S/cm.

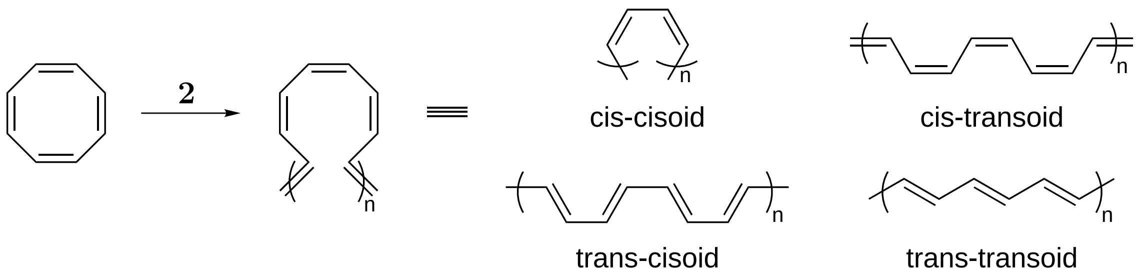


Figure 2.2: ROMP of COT and four isomeric microstructures of PA.

Four major isomeric structures exist for PA (Figure 2.2). The *cis* and *trans* isomers can be observed by solid-state ^{13}C NMR.[11, 12] Previous reports indicate that the thermodynamically favored all *trans* form of PA can be obtained upon heating of the polymer.[11] Catalyst **3** produced polyCOT with two sp^2 carbon types observed by solid-state CP-MAS ^{13}C NMR.[6] Upon heating of the sample, only one peak at 135.9

ppm was observed consistent with large trans-transoid segments in the sample.[6] The polyCOT produced by catalyst **2** also showed two sp^2 carbon types in the same region with shifts of 127 ppm (*cis*) and 133 ppm (*trans*), respectively. Bloch-decay MAS ^{13}C NMR indicates a *cis*:*trans* ratio of approximately 60:40. However, after one week the small amount of catalyst remaining in the solid sample appears active enough to isomerize the polyCOT to the thermodynamic all *trans* form, with a ^{13}C shift of 136 ppm, at room temperature (see Figure 2.3 a and b). This is consistent with previous reports for catalyst **2** to be long-lived and yielding the thermodynamic reaction product.[10]*

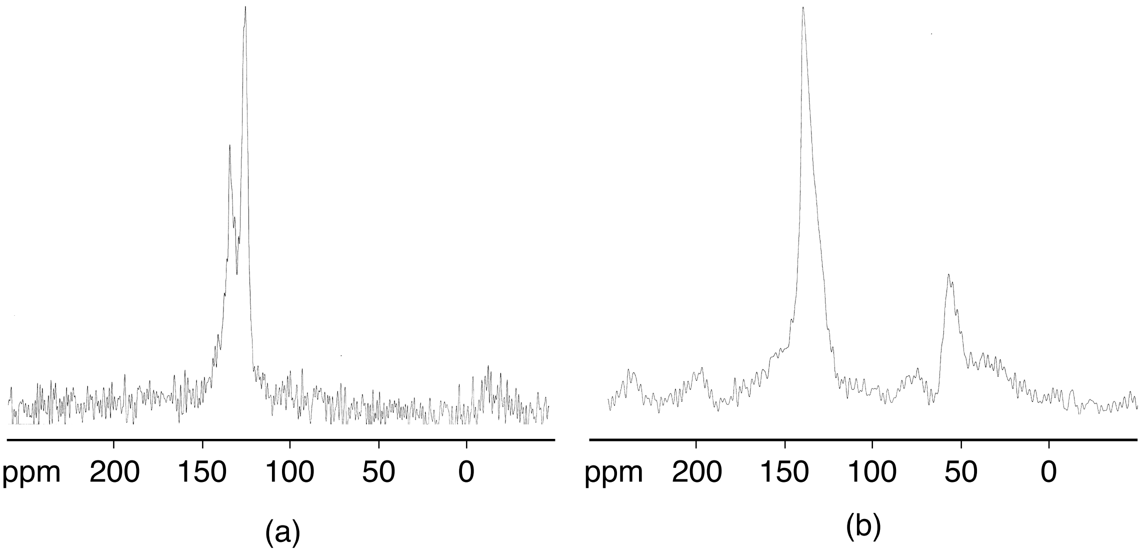


Figure 2.3: Solid-state ^{13}C NMR of poly(COT). (a) Bloch-decay MAS ^{13}C NMR of poly(COT), *cis*:*trans* ratio approximately 60:40. (b) Same sample after 1 week stored in the dark, under a nitrogen atmosphere. A small amount of oxidation is apparent, however, the large peak at ~50 ppm falls at a spinning side band.

Vibrational spectroscopies also indicate a fair amount of *trans* double bond content in the polyCOT produced from catalyst **2**, as is evident by the large peak at 1010 cm^{-1} in the IR spectrum. As Table 2.1 suggests, the IR peaks observed for polyCOT correspond nicely with Shirakawa PA. Strangely FT-Raman results indicate only *trans* double bonds with a sharp C-C stretch between 1060–1090 cm^{-1} (maximum at 1070 cm^{-1}) and a sharp C=C stretch between 1450–1480 cm^{-1} (maximum at

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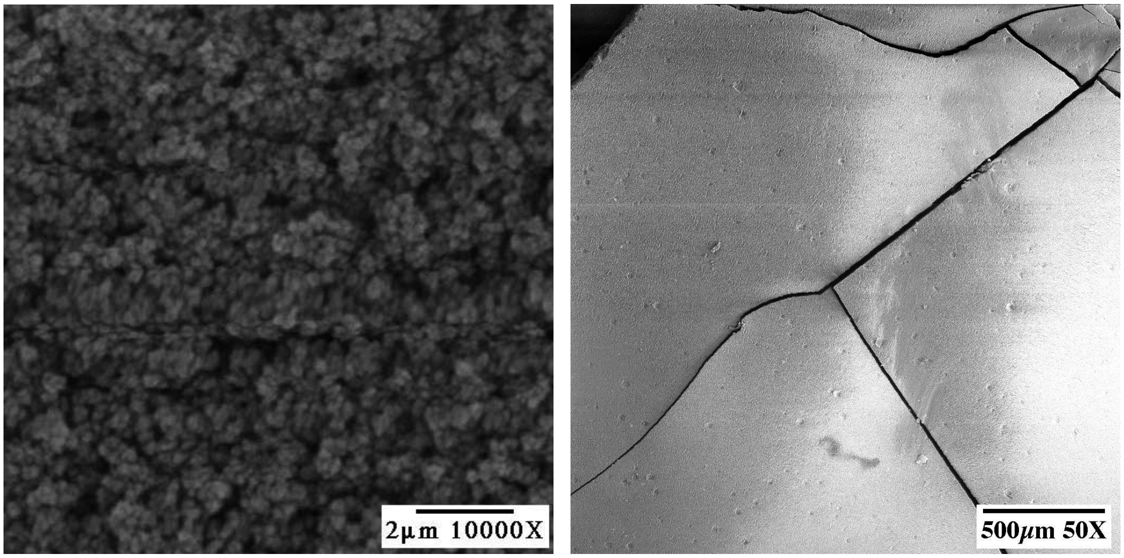
*The original monomer to catalyst ratio for this sample was 500:1. The sample was kept out of the light and remained in a nitrogen atmosphere dry box for one week between NMR experiments.

1460 cm^{-1}). This lower Raman shift for the C=C stretch is indicative of longer average conjugation length as compared to polyCOT produced by **3** which Klavetter *et al.* observed between 1463–1531 cm^{-1}.[6, 13] FT-IR and solid-state ^{13}C NMR certainly indicate ample *cis* double bond content in the polyCOT while the FT-Raman spectrum is virtually void of *cis* character. While this may be due to selective resonance enhancements that can obscure the *cis* peak around 1250 cm^{-1}, we are unable to definitively say why the *cis* peak is omitted in the raman spectra.[14]

Unlike polyCOT produced with catalyst **3**,[6] scanning electron microscopy (SEM) images of polyCOT produced with catalyst **2** more closely resemble Shirakawa PA. Figure 2.4a illustrates the globular texture of polyCOT produced from **2**, which is similar to Shirakawa PA. It is interesting to note the cracking seen in Figure 2.4b. During the polymerization of COT a film forms on the polymerization substrate and after approximately 30 minutes, it begins to crack until fully dry. We believe that the highly active **2** backbites and extrudes small molecules, i.e., benzene, from the growing polymer chains in a similar fashion as is observed by ROMP of COT with **3**.[6] The cracking may be attributed to the shrinkage of the film during polymerization possibly due to the packing of trans segments in the polymer chains combined with the escaping of volatile small molecules such as benzene. The loss of benzene can also help explain the low yields of solid polyCOT obtained in the polymerization reactions (see general polymerization procedures in experimental section).

The ROMP of COT with catalyst **2** affords a direct synthetic route to PA with a late transition metal catalyst. The properties of polyCOT produced from **2** are nearly identical to PA produced from early transition metal catalysts. The high functional group tolerance exhibited by **2** combined with its high activity should allow for the synthesis of PA and other polyene substrates with controlled molecular weight and end-group functional handles. Furthermore, the processing of these materials will likely become easier as less rigorous techniques are required by the robust catalyst **2**. We are currently investigating the synthesis of telechelic polyenes by previously published methodology.[15]



(a) (b)

Figure 2.4: SEM of poly(COT). (a) SEM of poly(COT) made from catalyst **2** magnified 10000x. (b) SEM of the same sample magnified 50x, depicting the cracking some poly(COT) films exhibit.

2.4 Experimental Section

General Procedures. Polymerization reactions were carried out in a nitrogen-filled dry box. COT was filtered through neutral alumina and distilled prior to use (45 °C, 25 mmHg). Purity was confirmed by GC analysis ($>$ 99.9%). Purified COT was stored under argon in a -75 °C freezer. All solvents were passed through purification columns composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant).[16] Polymerization substrates (glass microscope slides and overhead transparencies) were cleaned thoroughly before use. Catalyst **2** was synthesized as previously described.[17] Solid-state CP-MAS ^{13}C NMR experiments were carried out on a Bruker 200 MHz spectrometer. Samples were subjected to magic angle spinning at 8.0 KHz in a high-pressure stream of nitrogen to protect the samples from atmospheric oxidation. FT-IR spectra (KBr pellet) obtained on a Perkin Elmer Paragon 1000. FT-Raman spectra were obtained on a Nicolet Raman 950 in a sample cell modified to hold a sealed NMR tube. Conductivity was measured by the four-point probe method with a Signatone apparatus. Film thickness was measured with a Mitutoyo electronic micrometer. Doping of PA films by I_2 vapor were carried out in a glass schlenk tube which was evacuated and then closed, the films were allowed to sit under static vacuum for several hours.

Polymerization of COT. In a typical polymerization, approximately 5 mg of catalyst was placed in a 3 mL vial. 0.5 mL of COT (approximately 500 equivalents) was then added to the vial by syringe and the solution was swirled gently. Within 10–30 seconds the yellow solution suddenly turned dark red and subsequently purple. The purplish solution was then transferred to a pre-weighed polymerization substrate by pipet and allowed to polymerize under ambient temperature and pressure. The solution gelled and hardened within minutes yielding a shiny, black film, intractable in common solvents. The film was gently washed with a small amount of methanol to remove any unreacted monomer. The yields in these polymerization reactions ranged from 15-30% based on weight differential of the polymer substrate before and after deposition of the polyCOT.

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