

# Electro-Induced Early Transition Metal Metathesis Catalyst Systems for the Production of Polyacetylene

By Solmaz KARABULUT\*

The use of electro-induced Mo and W-based catalysts has been investigated in the ring opening metathesis polymerization (ROMP) of 1,3,5,7-cyclooctatetraene (COT). The soluble and conjugated polyacetylene (PA) was obtained under ambient temperature and pressure without employing any secondary reagent (comonomer, chain transfer agent) or substituted monomer (R-COT). NMR analysis results show that the electrochemical Mo-based system leads to a completely (100%) trans product, however, mainly (80%) trans polymer was obtained with W-based analogue for PA.

KEY WORDS: Ring Opening Metathesis Polymerization (ROMP) / 1,3,5,7-Cyclooctatetraene (COT) / Polyacetylene (PA) / Transition Metal Catalyst / Electrochemistry /

Conjugated polymers, the simplest being polyacetylene, are of current interest because the substantial electronic delocalization along their backbones gives rise to interesting optical and nonlinear optical properties and allows them to become good electrical conductors. These properties might lead to a variety of applications including optical signal processing and information storage, lightweight substitutes for metals in batteries and materials for solar energy conversion.<sup>1</sup>

In 1958, polyacetylene (PA) was first synthesized by Natta and coworkers as a black powder.<sup>2</sup> This compound remained as a scientific curiosity until 1967. An explosion of interest in polyacetylene and related conjugated organic polymers followed Ikeda and Shrikawa's report.<sup>3</sup> It was found that 1000 times too much of the Ziegler-Natta catalyst,  $\text{Ti}(\text{O}-n\text{-But})_4\text{-Et}_3\text{Al}$ , had been used.<sup>4,5</sup> When this film was investigated it was found to be semiconducting. Over the last three decades, a variety of strategies have been developed to synthesize precursor polymers that can be transformed into PA.<sup>6-10</sup> Unfortunately, many of these strategies have some limits such as using a second step. Ring opening metathesis polymerization (ROMP) is an appropriate route to PA and other conjugated polymers from various monomers.<sup>11</sup> Recently, many catalysts such as "classic" metathesis catalyst system  $\text{WCl}_6/\text{AlEt}_2\text{Cl}$ ,<sup>12</sup> "well-defined" W<sup>13,14</sup> and Ru-based catalysts<sup>15,16</sup> have been used in the direct synthesis of PA *via* ROMP of 1,3,5,7-cyclooctatetraene (COT) (Scheme 1). Unfortunately, most of these conjugated polymers are unprocessable because of their insolubility in organic solvents. Several techniques have been adopted to overcome these problems. One common method is to attach substituents along the polymer backbone.<sup>14,17,18</sup> Another synthetic method used is to produce copolymers by introducing a second monomer with good solubility properties.<sup>14,16,19,20</sup> In the second approach, block copolymer composition is limited because both monomers must be polymerizable by the same method. Furthermore, many of these PA exhibit decreased conjugation in comparison to parent PA.

In this study, the direct synthesis of soluble and highly conjugated polyacetylene from ROMP of COT was aimed in the presence of the electrochemically induced W and Mo-based catalysts without employing any co-monomer, chain transfer agent (CTA) or substituted monomer (R-COT).

Gilet and coworkers reported that the electrochemical reduction of  $\text{WCl}_6$  and  $\text{MoCl}_5$  produces metathetical active species.<sup>21,22</sup> We previously reported many scientific studies on the application of  $\text{WCl}_6\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  catalyst system to olefin metathesis reactions<sup>23-29</sup> but only one study on  $\text{MoCl}_5\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  catalyst system to ROMP of norbornene.<sup>30</sup> In this paper we described the synthesis of ROMP of COT with the electrochemically generated W and Mo-based catalyst. The major advantages of these catalyst systems ( $\text{WCl}_6\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  and  $\text{MoCl}_5\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$ ) electrochemically generated are easily preparation and higher selectivity. These systems are easily obtained and distinguished from the well-known molybdenum and tungsten alkylidenes by being less sensitive to atmospheric oxygen and retaining its activity for about 10 h.<sup>24</sup>

## EXPERIMENTAL

### Materials

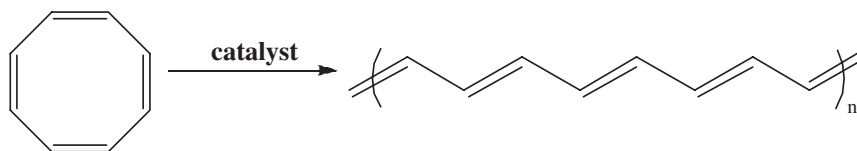
$\text{MoCl}_5$  was supplied from Aldrich (>99.9%) and used as received.  $\text{WCl}_6$  was purified by sublimation of the more volatile impurities ( $\text{WO}_2\text{Cl}_2$  and  $\text{WCl}_4\text{O}$ ) under nitrogen at about 200 °C. COT was supplied from Aldrich and distilled prior to use and stored at freezer. Dichloromethane (Aldrich) was distilled over  $\text{P}_2\text{O}_5$  under nitrogen. Pentane and methanol were supplied from Fluka and used as received.

### Electrochemical Instrumentation

The electrochemical instrumentation consisted of an EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. The measurements were carried out under a

Department of Chemistry, Hacettepe University, 06800 Beytepe, Ankara, Turkey

\*To whom correspondence should be addressed (Tel: +903122976082, Fax: +903122992163, E-mail: solmazk@hacettepe.edu.tr).



Scheme 1. ROMP of 1,3,5,7-cyclooctatetraene (COT).

nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant temperature bath was circulated. In the electrochemical experiments, the reference electrode consisted of AgCl coated on a silver wire in  $\text{CH}_2\text{Cl}_2$ /0.1 M tetra-*n*-butyl ammonium tetrafluoroborate (TBABF<sub>4</sub>), which was separated from the electrolysis solution by a sintered glass disc. Experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm<sup>2</sup>) and aluminium foil (2.0 cm<sup>2</sup>) counter electrode. Electrolysis was carried out without a supporting electrode because of its deleterious effect on the catalyst system. For this reason, the distance between the platinum working and aluminium counter electrode was kept constant and as small as possible (*i.e.*, 2.0 mm) in order to keep the solution resistance to a minimum.

#### Preparation of Catalyst

Electrochemical experiments were performed under a nitrogen atmosphere.  $\text{WCl}_6$  (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing  $\text{CH}_2\text{Cl}_2$  (25 mL) and a red solution was observed. The electrodes were introduced into the deep red solution and reductive electrolysis at +0.9 V was applied to the solution for 3 h. The colour of the solution darkened progressively. Aliquots from this catalytic solution were used in copolymerization reactions.

#### Polymerization of COT

All reactions were initiated in the solution ( $\text{CH}_2\text{Cl}_2$ ), at room temperature and under nitrogen atmosphere with Schlenk techniques. To optimize the reaction conditions, a series of experiments was performed by varying the olefin/catalyst ratio (30:1 to 300:1), reaction time (0.5 to 60 min.). COT was purified by distillation and analyzed by GC-MS to confirm the purity. 1 mL of the catalytic solution was added to a 50 mL cylindrical Schlenk tube. The solution of catalyst is constantly swirled around the inner walls of the tube at reduced pressure. Certain amount of purified COT is added to catalyst. After 30 min, the black film formed on the inner wall of the Schlenk tube is washed with pentane and then methanol and dried under vacuum. The pieces of the relatively brittle film were removed from the Schlenk tube for analysis.

#### Analysis

GC-MS analyses were performed with a Shimadzu GCMS-QP5050A using an optima column, 5–10  $\mu\text{m}$  (50 m  $\times$  0.32 mm), in a temperature range of 80–250 °C (20 °C min<sup>-1</sup>) and the carrier gas was helium at a flow rate 1 mL min<sup>-1</sup>. <sup>13</sup>C NMR spectra were recorded using a Bruker GmbH 400 MHz high-

performance digital FT NMR spectrometer.  $\text{CDCl}_3$  was used as the solvent with TMS as internal standard. Infrared spectra were obtained from KBr pellets using a Perkin-Elmer FT-IR spectrometer. GPC analyses were performed using a Shimadzu SPD-10ADVP UV detector, relative to polystyrene standards. The sample solutions (concentrations 1%) were prepared in THF as eluent and passed through a  $\mu$ -styrogel column. A constant flow rate of 1 mL min<sup>-1</sup> was maintained at 25 °C. Differential scanning calorimetry was carried out using a Shimadzu DSC 60 over the temperature range of 25/500 °C at a heating rate of 10 °C min<sup>-1</sup>. UV-visible spectra were obtained on a PG Instrument T80 spectrophotometer in THF. Conductivity was measured by the four-point probe method. Film thickness was measured by electronic micrometer.

## RESULTS AND DISCUSSION

A series of polymerizations was conducted at ambient temperature in order to estimate the polymer yield quantitatively. Conversion to polymer was obtained in maximum yield when the olefin/catalyst ratio was 160 for the molybdenum-based catalyst system. This ratio has been found as 80 for the tungsten-based catalyst system. We found that the catalytically active species formed from  $\text{WCl}_6$  during electrolysis retain their activity for nearly 3 d when kept under nitrogen atmosphere. With the  $\text{MoCl}_5\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  system was completely lost after 2 d.

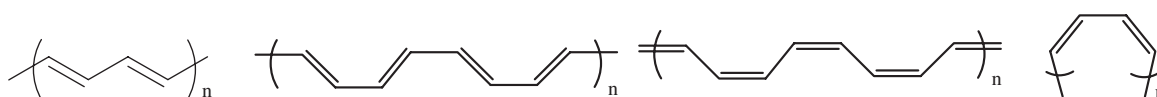
A comparison of the polymerization results of PA films produced by various catalyst systems to those produced with electrochemically generated W and Mo-based catalyst systems are shown in Table I.

Four major isomeric structures exist for PA (Scheme 2). The *cis* and *trans* isomers can be observed by NMR. The peak positions for the <sup>13</sup>C NMR spectra of PA obtained by Mo and W-based catalysts are given in Table I. Figure 1 gives the expanded <sup>13</sup>C NMR spectra of the PA obtained in the presence of Mo and W-based catalyst systems. In the olefinic region of the <sup>13</sup>C NMR spectra of the PA using electro-induced W-based catalyst systems, two groups of peaks can be observed. The more intense signal belongs to *trans* isomer occurring at 132 ppm, with a weaker signal for the *cis* isomer at 128 ppm. Based on the intensities of these signals, PA is assigned to have mainly *trans* (80%) stereochemistry obtained by W analogue. No significant peak between 128 and 133 ppm due to *cis* double bonds was observed in the <sup>13</sup>C NMR spectrum of PA obtained by Mo-based catalyst systems. However, the peak at 133 ppm due to *trans* double bonds indicates that the polymer is

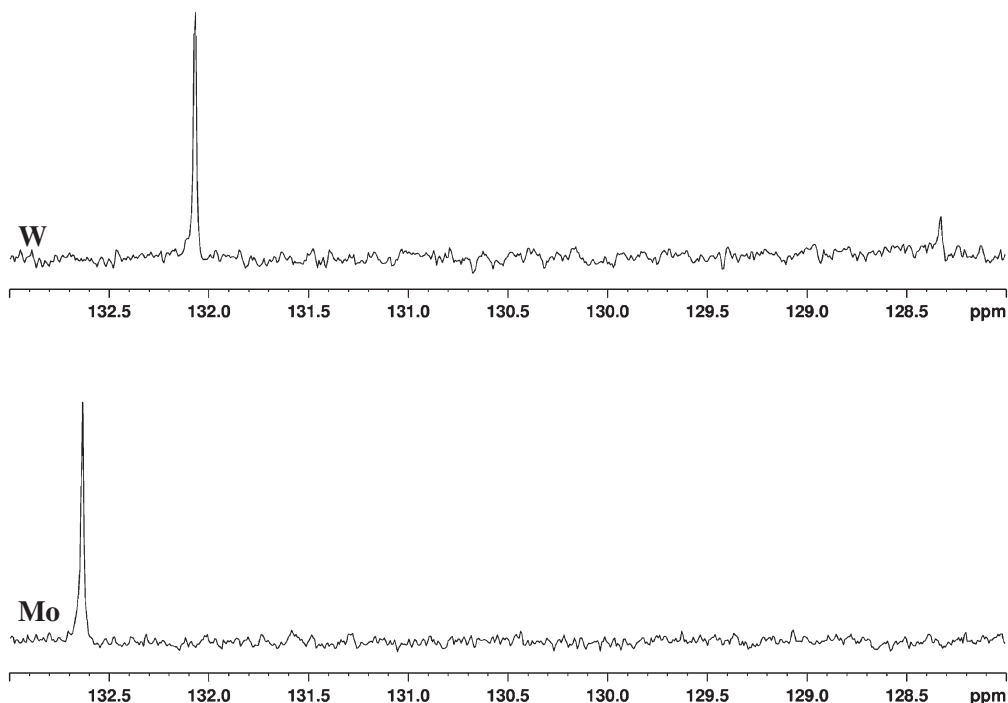
**Table I.** A comparison of the polymerization results and reaction conditions using various catalyst systems for PA

	Monomer/ catalyst	Reaction time	<sup>a</sup> Yield (%)	NMR ( $\delta$ , ppm)	<sup>b</sup> % trans	IR ( $\text{cm}^{-1}$ )	$\sigma$ (S/cm)	$\lambda_{\text{max}}$ (nm)	<sup>c</sup> $M_n$ ( $\times 10^{-3}$ )	PDI	$T_{\text{isomerization}}$ ( $^{\circ}\text{C}$ )
Ziegler-Natta catalyst <sup>4,5</sup>	1000:1	—	—	126, cis 129, cis		1015 740	$10^{-5}$ – $10^{-8}$	—	—		150
Well-defined W-based catalyst <sup>14,15</sup>	100:1	10–30 s.	—	126, cis 132, trans		930 980 765	$<10^{-8}$	—	—		150
Well-defined Ru-based catalyst <sup>15</sup>	500:1	30 min.	15–30	127, cis 133, trans	40	1010 992 930 773 745	$<10^{-8}$	—	—		—
$\text{MoCl}_5\text{-e}^-$ -Al- $\text{CH}_2\text{Cl}_2$	160:1	5 min.	35	133, trans	100	980 912 723	$<10^{-6}$	526	2.8	1.2	—
$\text{WCl}_6\text{-e}^-$ -Al- $\text{CH}_2\text{Cl}_2$	80:1	30 min.	28	128, cis 132, trans	80	990 915 730	$<10^{-6}$	500, trans 320, cis	1.3	1.7	128

<sup>a</sup>Determined by gravimetrically. <sup>b</sup>Calculated from  $^{13}\text{C}$  NMR spectra. <sup>c</sup>Determined by GPC, relative to polystyrene standard.



**Scheme 2.** The isomers of polyacetylene.



**Figure 1.** Olefinic region of  $^{13}\text{C}$  NMR spectra of the PA obtained by electrochemically generated Mo and W-based catalyst systems.

completely (100%) trans. These results correlate well with the literature, where the polymers produced from  $\text{WCl}_6$ -based systems are of intermediate cis content.<sup>31–34</sup> According to Ivin

*et al.*<sup>31</sup> steric interactions around the active centre and the higher oxidation state of the metal favor the formation of cis double bonds. The mechanism proposed in the  $\text{WCl}_6\text{-e}^-$ -Al-

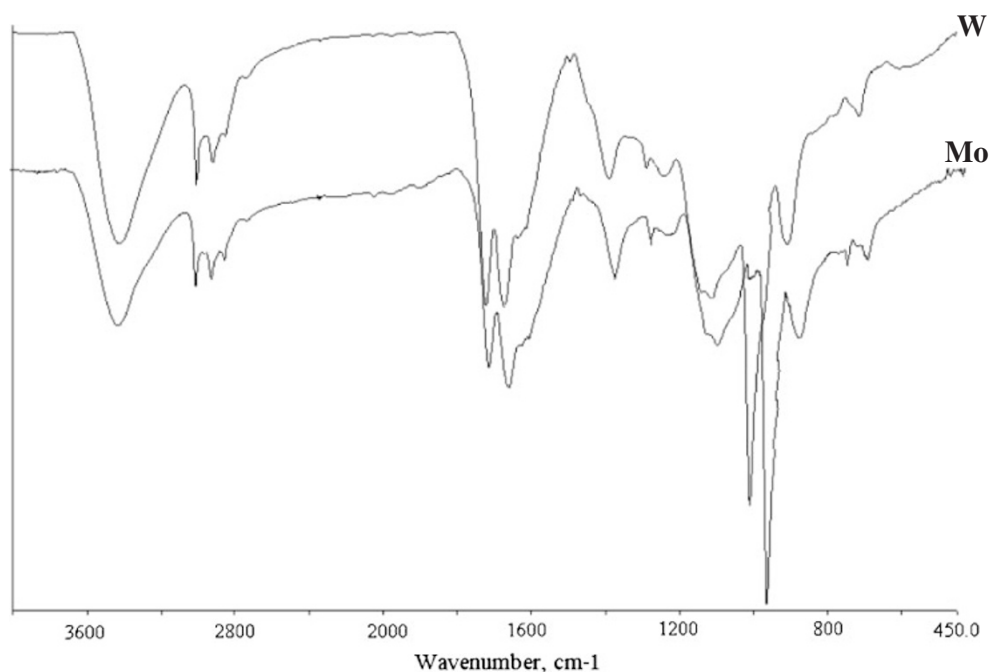


Figure 2. Partial FT-IR spectrum of PA obtained by electrochemically generated Mo and W-based catalyst systems.

$\text{CH}_2\text{Cl}_2$  catalyst system involves the initial formation of the olefin adduct with the  $\text{WCl}_5^+$  species.<sup>23</sup> The observed higher cis fraction of the polymer obtained with  $\text{WCl}_6\text{-e}^-$ - $\text{Al-CH}_2\text{Cl}_2$  catalyst system conforms to the suggested mechanism that the olefin entering the cage around tungsten (VI) prefers the cis orientation, leading to cis double bonds in the polymer.

Figure 2 illustrates the FT-IR spectra of PA prepared by  $\text{MoCl}_5$  and  $\text{WCl}_6$ . The high amount of trans double bonds of polymer is confirmed by, the FT-IR results of PA prepared by  $\text{WCl}_6\text{-e}^-$ - $\text{Al-CH}_2\text{Cl}_2$ , the stronger absorption of the trans  $=\text{CH}$  out-of-plane bending at  $915$  and  $990\text{ cm}^{-1}$  compared with the absorption at  $730\text{ cm}^{-1}$  for the cis  $=\text{CH}$  out-of-plane-bending. The absorption at  $1650\text{ cm}^{-1}$  belongs to the  $\text{C}=\text{C}$  stretching. This absorption shows that the unsaturation in the polymers is retained, which is an indication for the ring-opening metathesis mechanism (Table I).

The *cis-trans* structure developed in these chains is consistent with  $^{13}\text{C}$  NMR, IR and DSC data. Figure 3 displays the DSC thermogram of PA obtained by  $\text{WCl}_6\text{-e}^-$ - $\text{Al-CH}_2\text{Cl}_2$ . An exotherm is observed related to *cis-trans* isomerization of polymer at  $128^\circ\text{C}$ . Integration of this curve shows the enthalpy change for PA as  $-16\text{ cal/g}$ . The heat evolved during isomerization (h) is linear with respect to cis content having been reported by Tober and Ferraris.<sup>35</sup> According to this equation cis content of PA prepared by  $\text{WCl}_6$ -based catalyst is calculated as 22%.

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

After the first scan, the sample was cooled and reheated to  $300^\circ\text{C}$ . No observable exotherm was obtained in the second scan, as the sample has already undergone *cis-trans* thermal isomerization during the first scan.

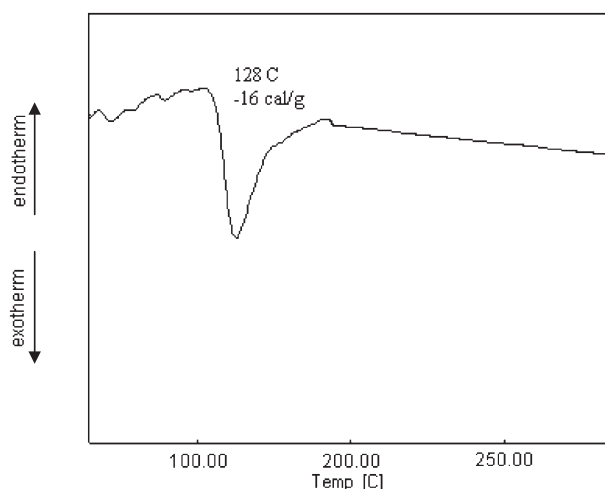
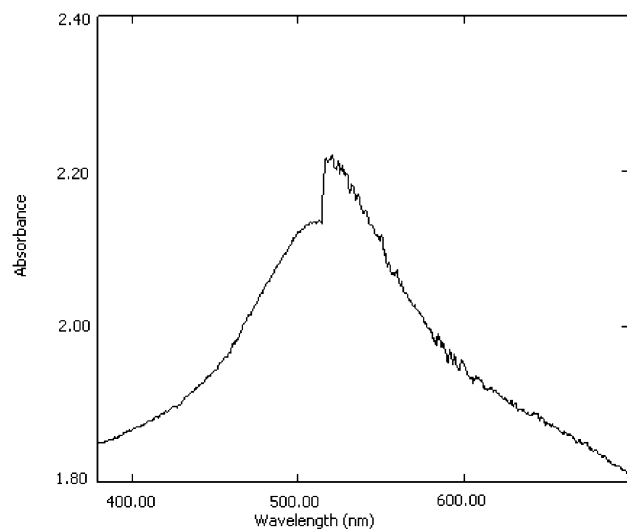


Figure 3. Partial DSC curves for the PA obtained by  $\text{WCl}_6\text{-e}^-$ - $\text{Al-CH}_2\text{Cl}_2$ .

GPC data shows that the 1,3,5,7 cyclooctatetraene has been polymerized into low molecular weight polymer with a narrow polydispersity using the electrochemically active species (Table I). As shown in Table I, the electrochemical molybdenum-based system leads to polymers of higher molecular weight ( $M_n = 2.8 \times 10^3$ ) and lower polydispersity ( $\text{PDI} = 1.2$ ) in comparison with the electrochemical tungsten-based system ( $M_n = 1.3 \times 10^3$ ,  $\text{PDI} = 1.7$ ).

The energies of UV-visible electronic transitions are useful indicators of conjugation length. As the energy differences between  $\pi$  and  $\pi^*$  orbital decreases, the number of conjugated double bonds increases. For this purpose, the absorption maxima of the polymer can be used as an indication of the effective conjugation length of the double bonds in the main



**Figure 4.** Absorption spectra of trans PA obtained by  $\text{MoCl}_5\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  in THF.

chain. The UV-visible spectrum of the resulting polymer obtained by  $\text{MoCl}_5\text{-e}^- \text{-Al-CH}_2\text{Cl}_2$  in THF is shown in Figure 4. The transition at 526 nm is consistent with a polymer composed of 10–15 double bonds.

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