ORGANIC
LETTERS

2006
Vol. 8, No. 4
605−608

Novel Linear and Tribranched Polymers with Redox-Active End Groups via W(CO)$_6$-Initiated Metathesis Polymerization

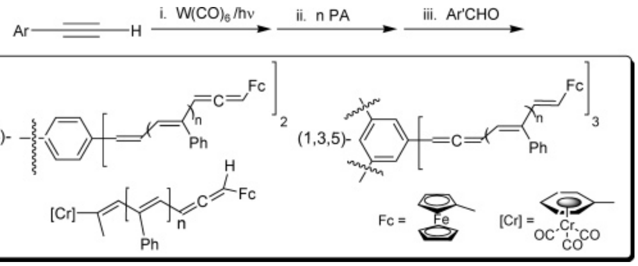
N. S. Santhosh and G. Sundararajan*

Department of Chemistry, Indian Institute of Technology Madras,
Chennai- 600 036, India

gsundar@iitm.ac.in

Received November 16, 2005

ABSTRACT



Synthesis, characterization, and electrochemistry of linear and tribranched polyphenylacetylenes having redox-active ferrocene and/or (arene)-chromiumtricarbonyl as end groups are reported in this study. The methodology adopts polymerization of phenylacetylene by a metathesis pathway, initiated by W(CO)$_6$ when photolyzed. A distance-dependent electronic communication between the metal centers is demonstrated in these polymers by means of cyclic voltammetry.

The synthesis of compounds having an organometallic end group is an area of active interest because of their anticipated applications as electronic or nonlinear optical materials.[1] Ferrocenes, with their iron center, have captured the center stage in organic synthesis and catalysis because they are a versatile building block.[2] There are numerous examples of carbon-bridged homobimetallic complexes of iron holding interesting physical and chemical properties.[3] Such oligometallic ferrocenyl and mixed metal complexes deserve attention because the electronic communication that exists between the metal centers is a notable feature.[4]

The chemistry community, especially the synthetic organic and polymer chemists, has recognized the importance and utility of olefin metathesis.[5] Our interest in this area began when we synthesized novel polyphenylacetylenes (polyPAs) having ferrocene end groups through the metathesis route using a simpler catalyst system.[6] The two ferrocene end groups showed a distance-dependent communication. As an

---

(1) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (b) Insuasty, B.; Atienza, C.; Seonane, C.; Martin, N.; Garin, J.; Orduna, J.; Alcala, R.; Villacampa, B. *J. Org. Chem.* **2004**, *69*, 6986.

(2) (a) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH Publishers: New York, 1995. (b) *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(3) (a) Amshumali, M. K.; Chavez, I.; Arancibia, V.; Burgos, O. F.; Manriquez, J. M.; Molins, E.; Roig, A. *J. Organomet. Chem.* **2005**, *690*, 1340. (b) Rodriguez, J. G.; Gayo, M.; Fonseca, I. *J. Organomet. Chem.* **1997**, *534*, 35. (c) Schwarz, M.; Vollmann, M.; Wartchow, R.; Butenscho, H. *J. Organomet. Chem.* **2005**, *690*, 2263.

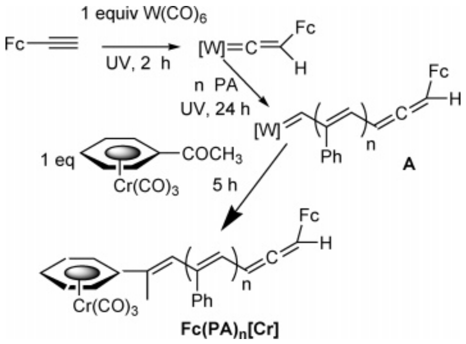
(4) (a) Gonzalo, V.; Coudret, C.; Patoux, C.; Launay, J. P. *Comptes Rendus de l'Académie des Sciences, Series IIC, Chemistry*, **1999**, *2*, 321. (b) Sato, M.; Fukui, K.; Sakamoto, M.; Kashiwagi, S.; Hiroi, M. *Thin Solid Films* **2001**, *393*, 210.

(5) (a) The Chemistry Nobel Prize 2005 being awarded to scientists working in the field of Olefin Metathesis is a crowning glory. (b) For a general introduction to olefin metathesis chemistry, see: Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997.

(6) (a) Dhanalakshmi, K.; Sundararajan, G. *J. Organomet. Chem.* **2002**, *645*, 27. (b) Dhanalakshmi, K.; Sundararajan, G. *Polym. Bull.* **1999**, *42*, 683.

10.1021/ol052774w CCC: $33.50

Scheme 1. Synthesis of PolyPA with Redox-Active Ferrocene and (Arene)$Cr(CO)_3$ End Groups



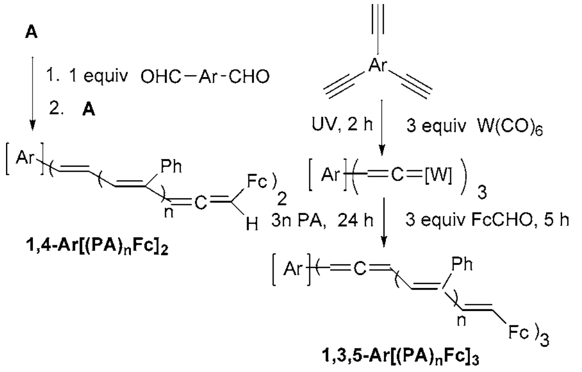
extrapolation, we opted to study intermetallic interactions in (i) a polyPA chain having (arene)$Cr(CO)_3$ and ferrocene end groups and (ii) an aromatic ring core with linear and tribranched polyPAs having ferrocene end groups.

It is well-documented that $W(CO)_6$ could polymerize terminal alkynes through a metathesis pathway when irradiated with UV light, wherein the metal alkynes could rearrange to a metal−vinylidine complex, the active-metal carbenic species.[7] Thus, we construed that 1 equiv of ferrocenylacetylene could form a vinylidine at the metal center when photolyzed at 350 nm in the presence of 1 equiv of $W(CO)_6$, with the intervening chains being formed by reacting with appropriate stoichiometric amounts of phenylacetylene (PA). Because in a metathesis polymerization the growing polymer always contained a metal carbene at the end, we surmised that it could be end capped by (acetophenone)$Cr(CO)_3$ in a Wittig-type olefination reaction to give linear polyPA with redox-active ferrocene and chromiumtricarbonyl as end groups ($Fc(PA)_n[Cr]$) (Scheme 1).

There have been literature reports of compounds having more than one ferrocene unit that are spanned by aromatic moieties. To generate such complexes with the present catalytic system, terephthalaldehyde (1 equiv) was used as an end-capping reagent to obtain a polyPA with aldehyde and ferrocene end groups. This polymer could then be used to end cap another growing polyPA chain having metal carbene at one end and ferrocene at the other end to give linear polymers with an intervening aromatic moiety, 1,4-$Ar[(PA)_nFc]_2$ (Scheme 2).

A modification of the methodology has been used to make tribranched polyPA having redox-active ferrocene end groups. Thus, irradiating triethynylbenzene (1 equiv) with $W(CO)_6$ (3 equiv), followed by addition of the required stoichiometry of PA (n equiv), generated polymers of required length. End capping these growing polymers by ferrocenecarboxaldehyde (3 equiv) gave the corresponding tribranched polymer 1,3,5-$Ar[(PA)_nFc]_3$ (Scheme 2).

Scheme 2. Synthesis of Linear and Tribranched PolyPA Having Redox-Active Ferrocene End Groups



In all experiments, the polymers were isolated in moderate yields (60−65%). The polymers were reddish-brown and soluble in most common organic solvents but insoluble in hexane and methanol. The molecular weights of all the polymers determined by GPC matched reasonably well with calculated values (Table 1), and the polydispersity values (M_w/M_n) in most cases ranged from 1.3 to 1.7, suggesting a moderately controlled nature of polymerization. Moreover, the molecular weight of ($Fc(PA)_{15}[Cr]$), as calculated from ^1H NMR from the relative intensities of Cp and PA signals, is 2130 and strikes close to the M_n value of 1970 obtained from GPC and the expected value of 2140.

Table 1. Calculated and Observed Molecular Weights of the Polymer

polymer	calcd M_n[a]	obsd M_n[b]	PDI
$Fc(PA)_5[Cr]$	1160	970	1.33
$Fc(PA)_{10}[Cr]$	1630	1460	1.47
$Fc(PA)_{15}[Cr]$	2140	1970	1.36
$Fc(PA)_{20}[Cr]$	2650	2610	1.65
$Fc(PA)_{25}[Cr]$	3160	3390	1.50
1,4-$Ar[(PA)_3Fc]_2$	930	1070	1.68
1,4-$Ar[(PA)_6Fc]_2$	1540	1550	1.59
1,3,5-$Ar[(PA)_3Fc]_3$	1750	1080	1.45
1,3,5-$Ar[(PA)_6Fc]_3$	2670	1550	1.70

[a] Calculated from the formula of the compound. [b] From GPC using THF as eluent and calibrated to polystyrene standards.

The IR (in cm^{-1}) of all the polymers showed peaks at 1590 ($\nu_{C=C}$), 1490 (s), 1440 (s), 809 (m), 754 (s), 489 (s, $\nu_{asymmetric}$, C_5H_5−Fe), and 443 (s, $\nu_{ring\ tilt}$, C_5H_5). The polymers, ($Fc(PA)_n[Cr]$), also showed symmetric and asymmetric carbonyl stretching at 1880 and 1940. In all of the polymers, the absence of a strong peak at 740 cm^{-1} could suggest a predominantly trans structure of the polyPA backbone.

As expected, the molecular weights for the tribranched polymers determined from GPC were lower than the calculated values. The narrow polydispersity values suggest the branched nature of the polymer and also satisfy the formula $PDI_{branched} = 1 + [PDI_{linear} - 1]/f$, where PDI_{linear} is the polydispersity index for the linear analogues and f (=3) is the functionality of the branched polymer (Table 2).[8]

---

(7) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

Table 2. Comparison of PDI of the Branched Polymers and Their Linear Analogues

chain length	PDI_{linear}	$PDI_{branched}$[a]	calcd PDI[b]
$Fc(PA)_3$	1.45	1.07	1.05
$Fc(PA)_6$	1.70	1.10	1.02
$Fc(PA)_9$	1.60	1.10	1.02

[a] Determined from GPC. [b] Calculated using the formula $PDI_{branched} = 1 + [PDI_{linear} - 1]/3$.

The cyclic voltammogram (CV) of the linear polymer, like 1,4-Ar$[(PA)_3Fc]_2$, showed two single electronic oxidation waves. The initial scan in the CV of the polymers from -0.2 to $+0.7$ V displayed two reversible one-electron oxidation waves (Figure 1, Table 3). The CV was reproducible at successive as well as delayed scans. The differential pulse voltammogram (DPV) is in line with the observation made with the CV.

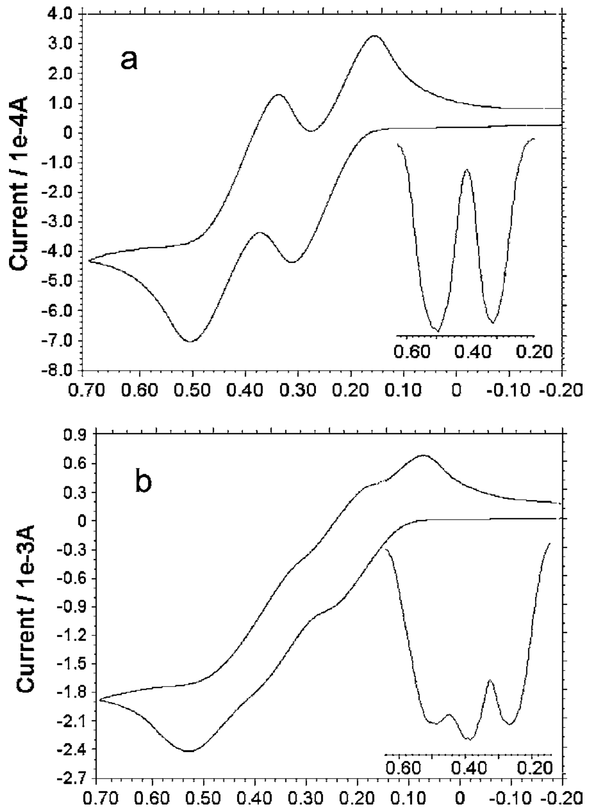


Figure 1. CV and DPV (inset) of polymers (a) 1,4-Ar$[(PA)_3Fc]_2$ and (b) 1,3,5-Ar$[(PA)_3Fc]_3$.

Table 3. Electrochemical Studies of Linear and Branched PolyPA with Ferrocene End Groups[a]

polymer	E_1	E_2	E_3
1,4-Ar$[(PA)_3Fc]_2$	0.30	0.50	
1,4-Ar$[(PA)_6Fc]_2$	0.48		
1,3,5-Ar$[(PA)_3Fc]_3$	0.28	0.39	0.51
1,3,5-Ar$[(PA)_6Fc]_3$	0.49		

[a] E_1, E_2, and E_3 are the first, second, and third oxidation waves, respectively, seen in the CV of the polymers.

The CV of 1,4-Ar$[(PA)_3Fc]_2$ indicates the occurrence of two successive one-electron transfer processes customarily denoted as the EE mechanism.[9] The formal potentials for each process (E_1 and E_2) are well separated from each other with the difference in potentials (ΔE) providing a measure of the extent of the Nernstian behavior.

The presence of two monoelectronic processes in the present case occurs despite the intervening aromatic nucleus, which is contrary to the one observed by others for iron-containing compounds.[10] Here, one of the oxidation potentials occurs at a lower value when compared to ferrocene, suggesting that the second ferrocene moiety in the polymer is electron donating in nature. This allows us to calculate the comproportionation constant for the equilibrium

$$Fc - Fc + Fc^+ - Fc^+ \leftrightarrows 2Fc - Fc^+$$

using the formula $K_c = 10^{\Delta E//0.059}$, which is 58.88. On further increasing the length of the polymer chain, the redox behaviors of the ferrocene centers become independent of each other, giving only a single oxidation wave at 0.48 V in the CV.[11]

The redox behavior of the branched polymer, 1,3,5-Ar-$[(PA)_3Fc]_3$, showed three oxidation waves in the respective CV (Figure 1) and in the DPV, attributable to the three different iron centers. As expected, the higher polymers in this series do not show any interaction, showing only a single oxidation wave in the CV.

Interestingly, in the case of 1,4-Ar$[(PA)_6Fc]_2$ and 1,3,5-Ar$[(PA)_6Fc]_3$, the waves merge implying that the ΔE is sufficiently small, thereby leading to the observation of a single peak in the corresponding voltammogram (Table 3). However, the compound 1,3,5-Ar$[(PA)_3Fc]_3$ exhibits three successive one-electron transfer processes wherein the difference in potential ($E_2 - E_1$) is nearly equal to ($E_3 - E_2$), viz. 0.12 V, indicating that the intrinsic Gibbs free-energy changes for the two processes are similar. Another important observation would be that the difference potential, ($E_2 - E_1$), of 1,4-Ar$[(PA)_3Fc]_2$ (para connectivity) is 100 mV larger than the difference potential, ($E_2 - E_1$), for 1,3,5-Ar$[(PA)_3$-$Fc]_3$ (meta connectivity). In our opinion, this could be

---

(8) Dounis, P.; Feast, W. J. *Polymer* **1996**, *37*, 2547.

(9) Geiger, W. E. In *Laboratory techniques in electroanalytical chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.;. Marcel Dekker: New York, 1996; p 683.

(10) (a) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646. (b) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.

(11) It should also be noted that polyPAs containing single ferrocenyl end groups such as $PA_{20}Fc$ or $FcPA_{20}$ show only a single peak in CV (0.47 V).

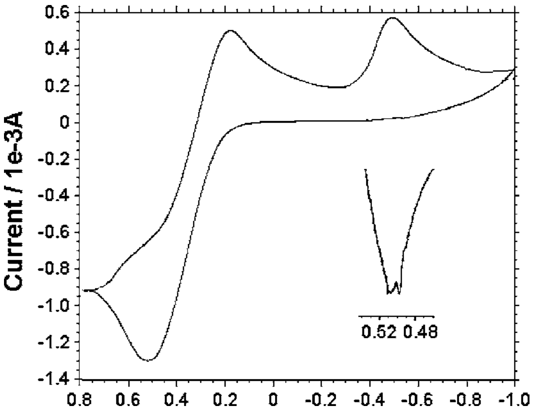


Figure 2. CV and DPV (inset) of $Fc(PA)_5[Cr]$.

indicative of a stronger communication between the metal centers in the former polymer invoking inductive and mesomeric effects, whereas in the latter case, only the inductive effect operates.

Electrochemical studies of $(Fc(PA)_n[Cr])$ polymers showed an interesting trend. The CV (Figure 2) for the polymer $(Fc(PA)_5[Cr])$ shows a reversible oxidation wave due to ferrocene at 0.51 (E_{Fc}) and an irreversible reduction process for the chromium metal center at a potential of −0.51 V (E_{Cr}). The observed higher value for the oxidation potential of ferrocene incorporated in the polymer, when compared to free ferrocene, could be attributed to the result of the electron-withdrawing nature of $(arene)Cr(CO)_3$ attached at the far end of the polymer chain.

On increasing the chain length by increasing the number of intervening PA molecules, it was found that the oxidation potential due to the ferrocene center almost remained constant in all the cases and the irreversible reduction potential increased and reached the value of −0.31 V for the polymers $(Fc(PA)_{25}[Cr])$ and $(Fc(PA)_{30}[Cr])$ (Table 4). The presence of electronic synergism between the two metal centers having similar electronic configurations has been suggested earlier.[12] According to these authors, the initial oxidation of the ferrocene unit is followed by an electron transfer from the chromium center to the ferrocene through the intervening conjugated carbon chain, for which the equilibrium constant is 2.4×10^3. Therefore, the second oxidation again occurs at the iron center. The electrochemical studies revealed that polymers $(Fc(PA)_n[Cr])$ showed similar behavior. The CV of $(Fc(PA)_5[Cr])$ showed a broad oxidation wave due to the ferrocene center. The irreversible reduction at −0.51 V, in all probability, is due to the chromium center. However, the DPV showed two single electronic oxidation processes occurring, albeit closely placed, due to the iron center. These two ferrocene-centered successive oxidations are in good agreement with that previously reported. It is important to appreciate at this point that the electron transfer from chromium to the iron center was found to depend on the length of the intervening conjugation chain; vide the cathodic reduction potentials of the chromium center in the polymer chain as shown in Table 4.

Table 4. Electrochemical Studies of Linear PolyPA with Ferrocene and $(Arene)Cr(CO)_3$ as End Groups

polymer	E_{Cr}[a]	E_{Fc}[b]
$Fc(PA)_5[Cr]$	−0.51	0.51
$Fc(PA)_{10}[Cr]$	−0.45	0.51
$Fc(PA)_{15}[Cr]$	−0.40	0.52
$Fc(PA)_{20}[Cr]$	−0.38	0.52
$Fc(PA)_{25}[Cr]$	−0.31	0.50
$Fc(PA)_{30}[Cr]$	−0.31	0.51

[a] E_{Cr} is the irreversible reduction potential due to the chromium center. [b] E_{Fc} is the oxidation potential due to the ferrocene center.

To conclude, we were able to synthesize linear and tribranched polymers with redox-active ferrocene and/or $(arene)Cr(CO)_3$ groups, spanned by polyPA, through a simple metathesis route by a judicious choice of the starting materials and end-capping reagents. Through electrochemical studies, we were able to demonstrate the existence of an electronic communication between the iron centers in the case of linear and tribranched polymers and that the presence of the aromatic ring in the intervening carbon chain does not impede an interaction between the iron centers. In the case of linear polyPA having ferrocene and $(arene)Cr(CO)_3$ as redox-active end groups, we have demonstrated a distance-dependent communication between the metal centers.

Acknowledgment. Financial support from Department of Science and Technology is greatly acknowledged (No.: SP/S-1/G-08/99). N.S.S. thanks CSIR, New Delhi, for financial support.

Supporting Information Available: Experimental details, ^1H and ^{13}C NMR spectra, and TGA and GPC traces of selected polymers are given. This material is available free of charge via the Internet at http://pubs.acs.org.

OL052774W

---

[12] (a) Yeung, L. K.; Kim, J. E.; Chung, Y. K.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1996**, *15*, 3891. (b) Muller, T. J. J. *J. Organomet. Chem*. **1999**, *578*, 95.