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Synthesis of conjugated polyphenylacetylenes with redox active ferrocenyl end-groups

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Summary

Metathesis polymerization has been employed for the synthesis of polyphenylacetylene (PPA) containing redox-active ferrocene groups at both ends. Two reversible one electron oxidation waves were detected in CV. The ΔE values decreased with increase in chain length of the polymer, indicating that the metal-metal interaction decreases by increasing the chain length.

Introduction

Synthesis of transition metal complexes incorporating unsaturated carbon chain between the metal centres is currently a topic of active investigation[1-8]. These complexes are generally termed as one-dimensional molecular wire[9] because of the possibility of charge transfer along the conjugated chain. The redox-active organometallic group present at the end, at times can even stabilize the conducting polymer fragment. These compounds also display enhanced electrical conductivity[10] and non-linear-optical response[11] that can be attributed to the delocalization of the metal d electrons in the carbon chain. In this study, we have synthesized PPA, a conjugated polymer, anchored with redox-active ferrocenyl moieties as the end groups. This new derivative of PPA was easily synthesized by metathesis polymerization[12] of phenylacetylene (PA) using $W(CO)_6$ with ferrocenylacetylene as the initiator and ferrocenecarboxaldehyde as the terminator.

Experimental

Chemicals

$W(CO)_6$ was obtained from Aldrich Fine Chemicals and used without any purification. The solvents hexane, methanol and dichloromethane were purified by standard procedures. PA[13], ferrocenylacetylene[14] and ferrocenecarboxaldehyde[15] were prepared according to literature methods.

Polymer Synthesis

The photochemical reaction was carried out in a Rayonet photochemical reactor. Polymerization reactions were carried out under dry, oxygen-free nitrogen atmosphere. All transfers were performed in a nitrogen filled glove bag or by standard Schlenk

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techniques. $W(CO)_6$ was taken in a flame-dried quartz tube and ferrocenylacetylene in hexane was cannulated into it under nitrogen atmosphere. The reaction mixture was irradiated for 2 h to give a brown colored solution. PA was added to it and irradiated for 24 h and the polymer was endcapped with ferrocene unit by quenching the reaction mixture with ferrocenecarboxaldehyde. The resulting polymer was purified by column chromatography using hexane/chloroform mixture (3:1).

Polymer characterization

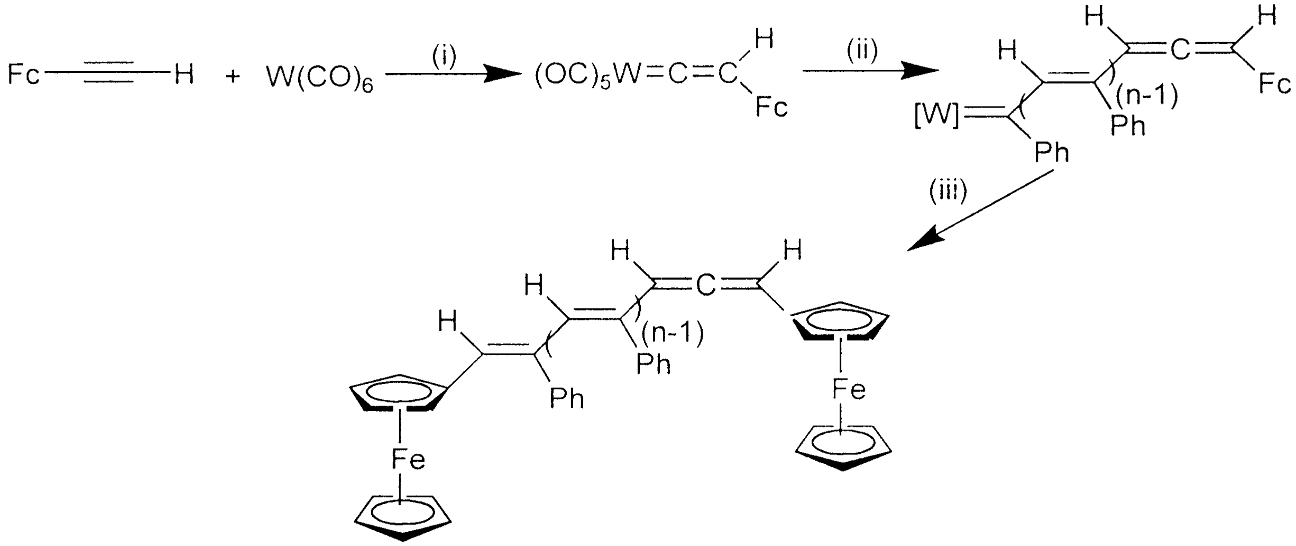
All polymers were characterized by IR, ^1H and ^{13}C NMR. The IR spectra were recorded as KBr pellets using Shimadzu (model 470) IR spectrometer. ^1H and ^{13}C NMR were recorded using JEOL model GSX 400 high resolution spectrometer. $CDCl_3$ was used as the solvent and the signals were obtained in parts per million (ppm) using tetramethylsilane as reference. Cyclic voltammetric and differential pulse voltammetric studies were carried out in a BAS 100A electrochemical analyzer. Pt wire was used as a working electrode, Pt foil as a counter electrode and Ag as a reference electrode. 0.1M Bu_4NPF_6 was used as a supporting electrolyte in 20 ml of CH_2Cl_2, All the electrochemical studies were carried out at room temperature using ferrocene (0.47 V) as the standard. The molecular weights of the polymers were determined using Waters gel permeation chromatography with a RI detector. The analyses were done using three ultrastyragel columns (100Å, 10^3 Å and 10^5 Å) connected in series. THF was used as the eluant at the flow rate of 1 ml/min and narrow molecular weight polystyrene samples were used as calibration standards.

Results and Discussion

Synthesis of Ferrocene Anchored PPA

$W(CO)_6$ in a hydrocarbon solvent forms an active alkyne polymerization catalyst in the presence of terminal alkynes under photolytic conditions[16]. It has been suggested that upon photolysis one molecule of CO is lost from $W(CO)_6$ leading to the formation of $W(CO)_5$ which immediately complexes with terminal alkynes to give a η^2 complex. Being unstable, the η^2-alkyne complex rearranges to a vinylidene complex. This vinylidene complex can lose one molecule of CO and coordinate with another alkyne unit. Cyclisation at the metal template gives rise to a metallacyclobutene intermediate, which can produce polyacetylene by successive ring opening and alkyne addition reactions. It is also presumed that this being a metathesis polymerization reaction, the growing polymer chain contains an active metal carbene terminal.

We exploited this established methodology to synthesize ferrocene anchored PPA. The technique used was as follows: Equimolar amounts of $W(CO)_6$ and ferrocenylacetylene were photolysed at 350 nm and to this calculated amounts of PA were added. The polymerization was terminated by addition of ferrocenecarboxaldehyde. This lead to the expected ferrocene anchored PPA as shown in Scheme-1. The chain length of the polymer was varied by changing the equivalence of PA added.



Scheme-1 Reagents and conditions: (i) hν/2h, (ii) PA/hν/24h
(iii) ferrocenecarboxaldehyde

Polymer Properties

The polymers were isolated in very high yields (>88%). The color of the polymers was usually reddish brown. The polymers were air-stable and highly soluble in common organic solvents like CH_2Cl_2, $CHCl_3$, THF, DMF, DMSO but insoluble in hexane and methanol. The molecular weights of the polymers were determined by GPC. The results showed that the M_n values obtained from GPC match well with the calculated values. All the polymers showed low polydispersity ranging from 1.13-1.50 as shown in Table-1. The GPC overlay of ferrocene anchored polyphenylacetylenes is given in Figure 1. In addition, the molecular weight of $Fc(PA)_{20}Fc$ as calculated from ^{1}H-NMR, from the relative intensities of Cp and PA signals, was 2652 that concurred well with the M_n value of 2450 obtained from GPC and the expected value.

Table-1
GPC data of $Fc(PA)_nFc$

Compound	% Yield	M_n		M_w	PDI
		Cal	Obs		
$Fc(PA)_5Fc$	90	918	1120	1270	1.13
$Fc(PA)_{10}Fc$	88	1428	1570	2090	1.32
$Fc(PA)_{15}Fc$	92	1938	2070	2810	1.36
$Fc(PA)_{20}Fc$	96	2448	2380	3280	1.37
$Fc(PA)_{25}Fc$	93	2958	2840	3880	1.36
$Fc(PA)_{30}Fc$	89	3468	3020	4530	1.50

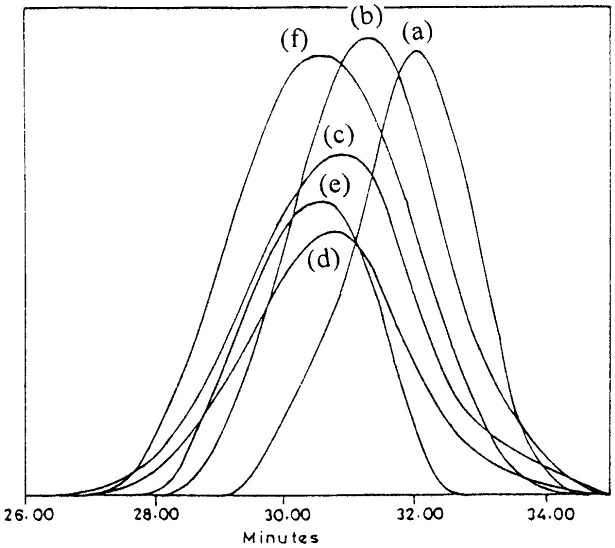


Fig. 1 GPC overlay of $Fc(PA)_nFc$

Solvent – THF, flow rate - 1ml/min, standard – narrow molecular weight polystyrene.
(b) $Fc(PA)_5Fc$ (b) $Fc(PA)_{10}Fc$ (c) $Fc(PA)_{15}Fc$ (d) $Fc(PA)_{20}Fc$ (e) $Fc(PA)_{25}Fc$
(f) $Fc(PA)_{30}Fc$

The absorption characteristics of the compound obtained from the UV-Vis spectrum showed a band at 230 nm and 275 nm corresponding to π-π^* transition of the cyclopentadienyl ring in the ferrocene unit, olefinic and aromatic units present in PPA. As the chain length of the polymer increased, a slight shift in the λ_{max} towards the red region of the spectrum was observed.

The IR spectrum of the compound revealed a strong C=C stretching vibration of olefinic and aromatic units at 1590 cm^{-1}. The band at 752 cm^{-1} was assigned to the C-H bending vibration of the olefinic unit. Also absence of band at 740 cm^{-1} suggested that the microstructure of PPA was predominantly of *trans* geometry[17]. Sharp bands at 448 cm^{-1} and 489 cm^{-1} were attributed to asymmetric ring tilt of the cyclopentadiene ring and asymmetric ring-metal stretch, indicating the presence of ferrocene units.

The ^1H NMR spectra also confirmed the presence of ferrocene unit in the polymer. Signal at 4.30 ppm corresponded to cyclopentadienyl protons of the ferrocene group. The protons attached to olefinic and aromatic unit of PPA appeared at 7.0 ppm with matching relative intensities of the protons, indicating that the polymer was anchored with ferrocenyl groups.

^{13}C NMR spectrum of the polymer showed signals at 69 ppm corresponding to carbon present in the cyclopentadienyl unit of the ferrocenyl group. The signal at 127 ppm corresponded to olefinic and aromatic carbon atoms of PPA.

Cyclic Voltammetric Studies

The electronic interaction between the two metal centres in the polymer backbone was obtained from CV and differential pulse voltammetric (DPV) studies. The initial scan in the cyclic voltammogram of the polymers from -0.2 V to +0.7 V displayed two reversible one electron oxidation waves as shown in Figure 2. The voltammogram was reproducible at successive as well as delayed scans. The oxidation potential values are listed in Table-2.

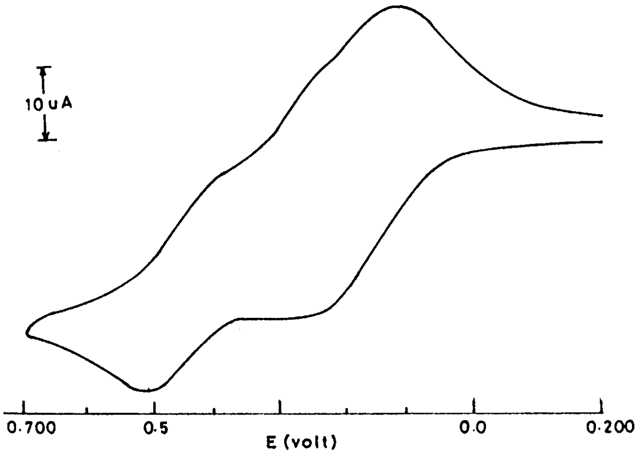


Fig. 2 CV of $Fc(PA)_{20}Fc$

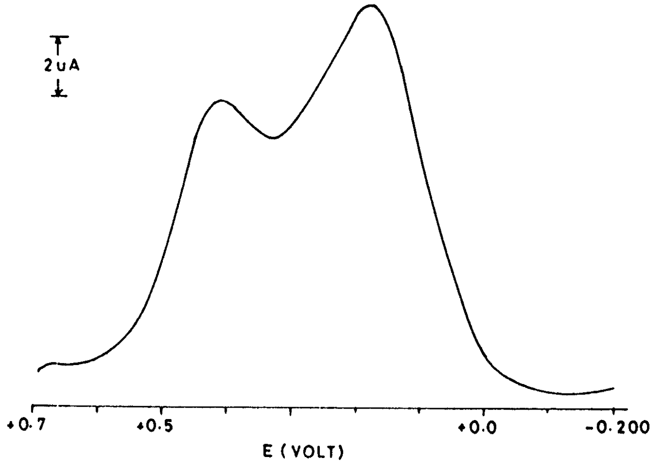


Fig. 3 DPV of $Fc(PA)_{20}Fc$

In order to explain the observed electrochemical behavior, we suggest that the polymer undergoes two successive one-electron oxidations to yield the mono and dications respectively.

Table-2
Electrochemical data for $Fc(PA)_nFc$

Compound	E_1(ox)	E_2(ox)	ΔE
$Fc(PA)_5Fc$	+0.15	+0.49	+0.34
$Fc(PA)_{10}Fc$	+0.20	+0.48	+0.28
$Fc(PA)_{15}Fc$	+0.22	+0.49	+0.27
$Fc(PA)_{20}Fc$	+0.24	+0.50	+0.26
$Fc(PA)_{25}Fc$	+0.30	+0.52	+0.22
$Fc(PA)_{30}Fc$	+0.40	-	-

Conditions: Pt wire - working electrode, Pt foil - counter electrode, Ag - reference electrode. 0.1 M Bu_4NPF_6 - supporting electrolyte, CH_2Cl_2 - solvent, scan rate - 100 mV/s

The lowering of the oxidation potential E_1 from +0.47 V (ferrocene) to +0.15 V indicated the electron donating nature of the second iron centre and that of the carbon bridge. Subsequent oxidation of the remaining iron centre is apparently less favorable and therefore occurred at +0.52 V due to the electron withdrawing effect of the first formed ferrocenyl cation. The difference in the oxidation potential value (ΔE) depended upon the separation between the two metal centres and the degree of conjugation in the bridging carbon chain linking the two metal centres.

Thus, on lengthening the carbon chain in this system, the magnitude of ΔE was found to decrease as determined by CV. In the case of $Fc(PA)_{30}Fc$, the two reversible oxidation waves merged to give a single broad reversible wave. Here, the ΔE was found to be zero, indicating that the interaction between the two Fe centres vanished and they behaved as independent and equivalent redox centres.

We also found that PPA's containing single ferrocenyl end groups like $PA_{20}Fc$ or $FcPA_{20}$ showed only single peak in CV (0.45 V) indicating that the two ferrocene end groups in $Fc(PA)_nFc$ do influence each other. DPV of $Fc(PA)_{20}Fc$ also showed two waves that implied the presence of two different iron atoms in the polymer as shown in Figure 3.

Conclusion

New type of polymer, $Fc(PA)_nFc$ with ferrocene units at both ends has been easily prepared by metathesis polymerization of PA. The polymers are found to be electro-active. The ΔE values decrease by increasing the chain length of the polymers and becomes zero when the chain length is 30.

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Notes and References

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