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Synthesis of conjugated polymers with ferrocene units as pendants or as end-groups

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Abstract

Conjugated polymers with ferrocene units as pendants or as end-groups have been synthesised using the classical metathesis polymerisation catalyst $W(CO)_6$ under photo-irradiation. The polymers are characterised by spectroscopic techniques and the redox-behaviour of these complexes have been examined by cyclic voltammetry. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Synthesis of soluble, well-defined polymers containing transition elements in the main chain poses a challenge and represents a growing interest due to the unusual physical and chemical properties exhibited by these materials [1]. The team headed by Manners has reported successful polymerisation of [1] ferrocenophanes with silicon or boron bridges [2,3]. Ring-opening-metathesis polymerisation of derivatives of norbornene (NBE) containing ferrocene units has yielded polymers and block copolymers containing redox-active centres [4–6]. Buretea and Don Tilley prepared metal-containing conjugated polyferrocenylenevinylene PFV, an organometallic analogue of polyphenylenevinylene PPV. PFV was synthesised by ROMP of strained vinylene-bridged *ansa*-ferrocene using Schrock's carbene complex [7].

Another topic of active investigation is the synthesis of transition metal complexes incorporating unsaturated carbon chains between the metal centres. These complexes are generally termed as one-dimensional molecular wires, because of the possibility of charge transfer along the conjugated chain [8–11]. The investigation of through-space and through-bond redox interactions of organometallic fragments across C_n ligands is of fundamental interest and the presented organometallic carbon chains are particularly suitable for such a study [12,13]. The extent of the charge delocalisation between the two metal centres can be studied by cyclic voltammetry. The electrochemically determined oxidation potentials of the binuclear complexes and their separation in energy as a function of the chain length, is a factor worth knowing in these complexes [14,15]. Moreover, conjugated organometallic materials that contain metallocenes are believed to have some of the greatest potential for high second and third-order non-linear optical property [16,17].

In this paper we detail our efforts towards synthesis of two different polyacetylenes viz. one that contains ferrocene moieties as pendant groups and another at the chain ends by employing a classical metathesis polymerisation system based on $W(CO)_6$.

2. Experimental

2.1. General experimental conditions

The molecular weights of the polymers were analysed using Waters gel permeation chromatography (GPC) equipped with an RI detector. The analyses were done using three ultrastyragel columns (100, 10^3 and 10^5 Å) connected in series. THF was used as the eluant at the flow rate of 1 ml min^{-1} and narrow molecular weight

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polystyrene samples were used as calibration standards. Rayonet photochemical reactor equipped with a light source of 350 nm was used to carry out the photolysis. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out in a BAS 100A electrochemical analyser. Pt wire was used as a working electrode, Pt foil as a counter electrode and Ag as a reference electrode. n-Bu_4NPF_6 (0.1 M) was used as a supporting electrolyte in CH_2Cl_2. All the electrochemical studies were carried out at room temperature (r.t.) using ferrocene (0.47 V) as the standard. The solvents were purified as prescribed in Perrin and Armarego [18]. Metal carbonyls, $W(CO)_6$, $Mo(CO)_6$ and $Cr(CO)_6$ and also monomers like phenylacetylene (PA) and NBE were purchased from Aldrich Chemical Company and used as received. Ferrocenylacetylene (FA) was synthesised according to the literature reported method [19].

2.2. Synthesis of PFA

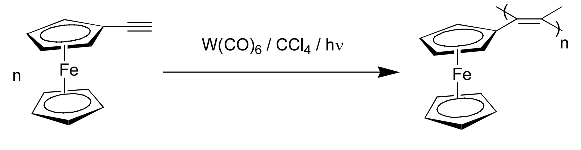
$W(CO)_6$ (0.03 g, 0.09 mmol) in 5 ml of CCl_4 was irradiated at 350 nm for 1 h to give a blue coloured solution. FA (0.5 g, 2 mmol) in 3 ml of CCl_4 was cannula-transferred into it and the reaction mixture stirred at r.t. under dark for 24 h. The progress in polymerisation was discernible from the colour change from orange to red brown. The mixture was poured into hexane, the precipitate was filtered and vacuum dried. Yield 0.45 g (90%).

2.3. Synthesis of copolymer

The active species was generated as mentioned earlier and FA (20 equivalents) was added and polymerisation was carried out as given before. PA (30 equivalents) or NBE (30 equivalents) were added and stirred at r.t. for another 24 h and the polymer that precipitated out by pouring into excess hexane was filtered and dried under vacuum.

2.4. Synthesis of polyphenylacetylene with ferrocenyl end-groups

$W(CO)_6$ (0.285 g, 0.81 mmol) and FA (0.170 g, 0.81 mmol) in 10 ml of hexane was irradiated for 2 h at 350 nm. PA (1.652 g, 16.2 mmol, 20 equivalents) was added and irradiated for 24 h. The reaction was terminated by adding ferrocenecarboxaldehyde (0.173 g, 0.81 mmol) and stirred at r.t. for 5 h. The polymers were precipitated in excess methanol, and purified by column chromatography ($CHCl_3$–hexane, 1:3)



Scheme 1. Synthesis of PFA.

Spectral data of $Fc(PA)_{20}Fc$: IR (KBr, cm^{-1}) 1590 (m) (ν, C=C), 1488 (s), 1440 (s), 398 (s), 809 (m), 752 (s), 489 (s), 448 (s) ($\nu_{asymmetric}$ C_5H_5–M) and (C_5H_5 ring tilt). The absence of a strong peak at 740 cm^{-1} could suggest a predominantly *trans* structure for the polyPA block. δ_H (400 MHz, $CDCl_3$) 4.25 (s, C_5H_5), 4.30, 4.47–4.57 (m, C_5H_4), 7.00 (m, C_6H_5 and C=C–H); δ_c ($CDCl_3$) 69.7, 70.2, 70.4, 70.5 (C_5H_5 and C_5H_4), 127.0, 127.2, 127.6, 128.3, 128.5, 128.6, 129.0, 129.5 (C_6H_5 and –C=C). Also, for instance, the molecular weight of $Fc(PA)_{20}Fc$ as calculated from ^1H-NMR, from the relative intensities of Cp and PA signals, is 2650 and compares well with the M_n obtained from GPC and the expected values (Table 3).

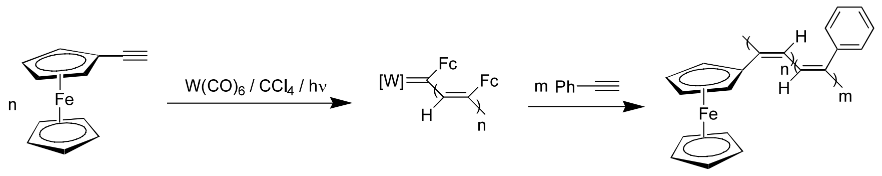
3. Results and discussion

3.1. Synthesis and studies on polyferrocenyl acetylene

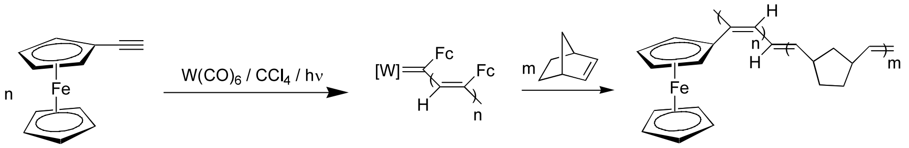
Polyferrocenylacetylene (PFA) is an electro-active polymer containing ferrocene units in the polymer backbone. A logical approach to ferrocene substituted polyenes is to polymerise FA. However, previous attempts to synthesise such conjugated polymers have yielded materials that suffer from poor solubilities and low conductivities. In most attempts, either the formation of trimers (1,3,5- and 1,2,4-triferrocenylbenzene) and oligomers with high polydispersities (PDI = 5–10) or that of insoluble, brown, partially oxidised, poorly characterised polymers were reported [20]. The poor reactivity of FA is probably due to the fact that the metallocene unit is highly electron rich and is difficult to polymerise. Buchmeiser reported successful polymerisation of FA by a well-defined molybdenum carbene complex to give a polymer with low polydispersity value [21]. From the literature it is seen that there are only a few reports available for the synthesis of PFA. Hence, we decided to study the polymerisation of FA using a well-known classical metathesis catalyst $W(CO)_6/CCl_4/h\nu$ [22–24]. With this system FA also underwent copolymerisation reaction with PA and NBE. The polymers were characterised structurally by spectroscopy and electrochemically by CV (Section 2).

3.1.1. Homopolymerisation of FA and copolymerisation of FA with NBE or PA

FA could be polymerised easily with the classical olefin metathesis system viz. $W(CO)_6/CCl_4/h\nu$ (Scheme 1). This homopolymer of FA, soluble in most common organic solvents, can thus be prepared with units up to 30 equivalents of the monomer in very high yield of 90%. Beyond that proportion, only unreacted monomer was recovered.



Scheme 2. Copolymerisation of FA with PA.



Scheme 3. Copolymerisation of FA with NBE.

Copolymerisation was carried out by adding the second monomer, PA or NBE, to the red brown solution of PFA (Schemes 2 and 3). Various stoichiometric ratios of FA and PA were copolymerised and it was found that the maximum yield of polymer was obtained in the case of $PFA_{20}PPA_{30}$ and $PFA_{20}PNBE_{30}$. If the number of equivalences of FA is increased to greater than 20 in the copolymer preparation, then unreacted FA was recovered in almost all cases. The yields obtained for all three polymers were very high.

3.1.2. Polymer properties

The molecular weights of the polymers were determined by GPC and the values are given in Table 1. The calculated molecular weight for PFA was 6300 and the obtained molecular weight was 5430. From the table it is seen that the PFA–PNBE copolymer showed the highest molecular weight of 16 000. All the three polymers are unimodal in GPC with the polydispersity value less than 1.6 indicating controlled polymerisation. The polymers were air stable at room temperature and dissolved readily in common organic solvents like CH_2Cl_2, $CHCl_3$, THF, DMF and DMSO.

PFA showed high thermal stability. Thus in the TGA the maximum weight loss occurred at 440 °C. PFA–PNBE showed two decomposition maxima, one at 220 °C and another at 490 °C, indicating the presence of two blocks in the copolymer. PFA–PPA showed decomposition maxima at 400 °C, indicating that both the blocks underwent decomposition at the same temperature.

3.1.3. Spectroscopic studies

PFA showed characteristic ferrocene absorptions at 230 and 275 nm corresponding to $\pi-\pi^*$ transition. Broad absorptions in the region of 350–550 nm with very lower intensity can be ascribed to d–d transitions. In the case of $PFA_{20}PPA_{30}$ and $PFA_{20}PNBE_{30}$ the λ_{max} was at 230 nm corresponding to $\pi-\pi^*$ transition. The IR spectra of PFA showed a band around 1667 cm^{-1} corresponding to the C=C stretching vibration of the polyene and bands around 1401, 1273, 1107, 996, 816 and 489 cm^{-1} corresponding to the stretching frequencies of ferrocene moiety. The stretching frequency at 750 cm^{-1} band indicated that the geometry of the double bond in the polymer backbone was predominantly *trans*.

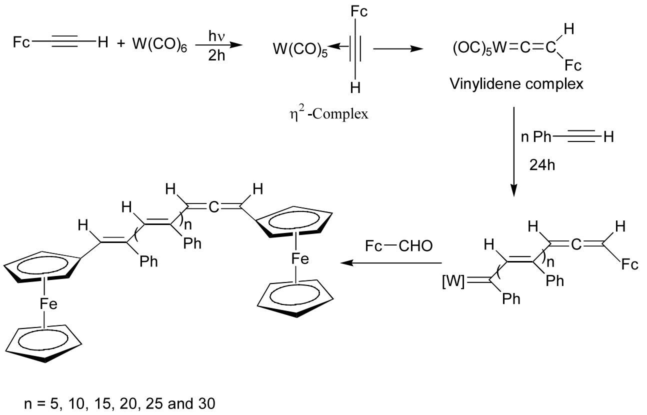
The ^1H-NMR spectrum of PFA had a broad signal around 4.0 ppm due to the protons present in the cyclopentadienyl ring of ferroence unit. $PFA_{20}PPA_{30}$ showed two types of signals one around 4.0 ppm corresponding to the ferrocene fragment and a broad signal around 6.50–7.50 ppm due to PPA unit indicating that both the blocks were present in the polymer. $PFA_{20}PNBE_{30}$ showed three types of signals, 1.40–3.0 ppm due to the alkyl protons of NBE unit, 4.0 ppm due to ferrocenyl protons and 5.30–5.40 ppm corresponding to olefinic protons. The ^{13}C-NMR spectrum of PFA showed two types of signals, one around 68 ppm corresponding to the carbons in the cyclopentadienyl ring and the other at 123 ppm corresponding to the olefinic carbon atoms. In the case of $PFA_{20}PNBE_{30}$ the carbon atoms of the cyclopentane ring of PNBE appeared around 25–40 ppm, the carbon attached to cyclopentadiene (PFA) appeared around 68 ppm and the olefinic carbon of PNBE appeared at 130 ppm. $PFA_{20}PPA_{30}$ showed two types of signals one around 68 ppm and another around 125 ppm.

Table 1
Molecular weight data of the homo and copolymers of FA

Polymer	% Yield	M_n	M_w	M_w/M_n
PFA	90	5430	8000	1.40
$PFA_{20}PPA_{30}$	85	12 450	18 300	1.47
$PFA_{20}PNBE_{30}$	80	16 000	24 600	1.53

Table 2
Third-order susceptibility values of homo and copolymers of FA

Polymer	χ^3 10^{-18} (m^2 V^{-2})
PPA	1.6
PFA	1.26
$PFA_{20}PPA_{30}$	1.61
$PFA_{20}PNBE_{30}$	0.60



Scheme 4. Synthesis of PPA with ferrocenyl end-groups.

Table 3
Details of experiments on the synthesis of PPA with ferrocenyl end-groups

Compound	% Yield	M_n		M_w	M_w/M_n
		Calc.	Obs.		
$Fc(PA)_5Fc$	90	910	1100	1260	1.13
$Fc(PA)_{10}Fc$	88	1420	1570	2100	1.32
$Fc(PA)_{15}Fc$	92	1930	2070	2800	1.36
$Fc(PA)_{20}Fc$	96	2440	2380	3280	1.37
$Fc(PA)_{25}Fc$	93	2950	2840	3870	1.36
$Fc(PA)_{30}Fc$	89	3460	3020	4530	1.50

3.1.4. CV studies

The polymers were electrochemically active and their redox behaviour was followed by CV. Initial scan in the CV of PFA from 0.0 to 1.0 V showed a broad reversible peak at 0.62 V. The broadening observed for the polymers also suggested the presence of possible electronic interaction between the Fc units. $PFA_{20}PPA_{30}$ also $PFA_{20}PNBE_{30}$ also showed waves at 0.6 V.

3.1.5. Third-order non-linear optical study

The search for new and efficient materials that can carry out non-linear optical processes has been intense [25]. As the PFA synthesised in our laboratory are conjugated, we measured the χ^3 values of PFA, $PFA_{20}PPA_{30}$ and $PFA_{20}PNBE_{30}$ by degenerate-four-wave-mixing techniques and the measured constants are listed in Table 2. Here, $PFA_{20}PPA_{30}$ gave a higher value compared to $PFA_{20}PNBE_{30}$. This is to be expected since the effective conjugation is less in the case of $PFA_{20}PNBE_{30}$ with a low χ^3 value while in $PFA_{20}PPA_{30}$ the conjugation length is more and the χ^3 value appeared higher (Table 2).

3.2. Synthesis and studies on polyphenylacetylenes containing ferrocenyl end-groups

In this study, we have synthesised PPA, a conjugated polymer, anchored with redox-active ferrocenyl moieties as the end-groups [26]. This new derivative of PPA was easily synthesised by the metathesis polymerisation of PA using $W(CO)_6$ with FA as the initiator and ferrocenecarboxaldehyde as the terminator.

3.2.1. Synthesis of ferrocene anchored polyphenylacetylene

It is known that η^2-complexes of terminal alkynes undergo vinylidene rearrangement [27] and the inherent metal–carbene unit can be used for metathesis polymerisation [28]. Thus we surmised, irradiation of equimolar amount of FA and $W(CO)_6$ would lead to the corresponding vinylidene complex that in turn can polymerise calculated amounts of PA and the growing polymer chain would leave the metal unit at the end. Removal of the metal carbene by treatment with ferrocenecarboxaldehyde should give conjugated PPAs with ferrocenyl end-groups (Scheme 4). Thus, by varying the amount of PA added, polymers with different chain lengths separating the ferrocene units can be prepared.

3.2.2. Polymer properties and characterisation

The polymers were isolated in very high yield ($>88\%$). The polymers were reddish brown, air stable and 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 obtained from GPC. The results showed that the Mn values obtained from GPC matches very well with the calculated values and the polydispersity values were also low ranging from 1.3 to 1.5 (Table 3).

The absorption characteristics of the compound obtained from the UV spectrum showed a band at 230 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, the λ_{max} shifted slightly towards the red region of the spectrum. The ^1H-NMR spectra contained signals at 4.3 ppm for the Cp protons of the ferrocenes and a broad signal at 7 ppm for the olefinic and aromatic protons of the PPA, with matching intensities. The ^{13}C-NMR spectrum of the polymer showed broad signals around 69 ppm corresponding to the carbons present in the cyclopentadienyl units of the ferrocenyl groups and around 127 ppm attributable to the olefinic and aromatic carbon atoms of PPA.

3.2.3. CV analysis

CV and differential pulse voltammetric studies performed suggest that the metal centres influence each other through the conductive polymer chain towards oxidation. The initial scan in the cyclic voltammogram of the polymers from -0.2 to $+0.7$ V displayed two reversible one electron oxidation waves as shown in Fig. 1. The voltammogram was reproducible at successive as well as delayed scans. In order to explain the observed electrochemical behaviour, we suggest that the polymer undergoes two successive one electron oxidations to yield the mono and dications, respectively. The lowering of the oxidation potential $E1$ from $+0.47$ (ferrocene) to $+0.15$ V indicated the electron donating nature of the second iron centre and carbon bridge. Subsequent oxidation of the remaining iron centre is energetically less favourable and therefore occurs at $+0.52$ V due to the electron withdrawing effect of the monocation. We could surmise that the difference in the oxidation potential values, ΔE, depends upon the separation between the two metal centres and the degree of conjugation in the bridging carbon chain linking the two metal centres.

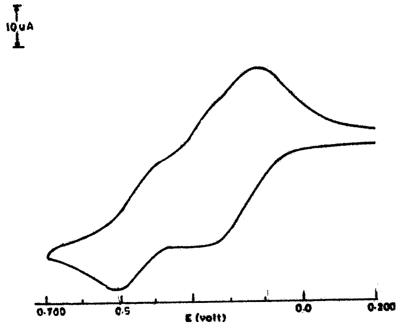


Fig. 1. Cyclic voltammogram of $Fc(PA)_{20}Fc$.

Table 4
Details of CV studies on PPA with ferrocenyl end-groups

S. no.	Compound	E_1(ox)	E_2(ox)	ΔE
1	$Fc(PA)_5Fc$	+0.15	+0.49	+0.34
2	$Fc(PA)_{10}Fc$	+0.20	+0.48	+0.28
3	$Fc(PA)_{15}Fc$	+0.22	+0.49	+0.27
4	$Fc(PA)_{20}Fc$	+0.24	+0.5	+0.26
5	$Fc(PA)_{25}Fc$	+0.30	+0.52	+0.22
6	$Fc(PA)_{30}Fc$	+0.40		

Table 5
Third-order susceptibility values of ferrocene-anchored polyphenylacetylene

Polymer	χ^3 10^{-20} (m^2 V^{-2})
$Fc(PA)_5Fc$	1.6
$Fc(PA)_{10}Fc$	2.15
$Fc(PA)_{15}Fc$	2.92
$Fc(PA)_{20}Fc$	3.05
$Fc(PA)_{25}Fc$	1.62

On lengthening the carbon chain in the system, the difference of the oxidation potentials between the metal centres determined by cyclic voltammetry becomes smaller as seen in Table 4. 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 zero, indicating that the interaction between the two Fe centres vanished and they behaved as independent but equivalent redox centres. We also find PPAs containing single ferrocenyl end like $PA_{20}Fc$ or $FcPA_{20}$ show only single peak in CV (0.45 V) indicating that the two ferrocene end-groups do influence each other.

3.2.4. Non-linear optical study

The third-order susceptibility value (χ^3) was measured. The values are listed in Table 5. The values obtained showed that as the chain length of the polymer increased, conjugation increased thereby increasing the χ^3 value.

4. Conclusion

Conjugated polymers with ferrocene units as pendant groups were synthesised from FA by employing the classical metathesis polymerisation catalyst based on $W(CO)_6$ under photo-irradiated conditions. Block copolymers of FA and PA or NBE were also synthesised and the electrochemical as well as third-order non-linear optical responses of these polymers were studied. PPAs containing ferrocenyl end-groups were synthesised in a controlled manner with a $W(CO)_6/h\nu$ catalyst system. Here, by CV studies we could establish distance-dependent communication between the two iron centres. In general, we have shown that easy-to-use classical metathesis polymerisation catalysts can be useful for controlled polymer synthesis.

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