

Novel linear and tri-branched polymers with redox-active end-groups via $W(CO)_6$ initiated metathesis polymerisation

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General procedures:

All the reactions were carried out strictly under nitrogen atmosphere using standard Schlenk line techniques, unless otherwise noted. Nitrogen was purified by passage through columns of MnO anchored on silica gel catalyst and 4 Å molecular sieves.¹² Solid organometallic compounds were transferred in a nitrogen-filled glove bag. All glasswares, syringes and needles were oven-dried at 120 °C and cooled to room temperature under nitrogen purging before use. Hexane solvent was dried by distilling from sodium-benzophenone ketyl while dichloromethane, acetonitrile and acetophenone were distilled from calcium hydride prior to use. Ferrocenylacetylene (FA), ferrocenecarboxaldehyde, 1, 3, 5-triethynylbenzene and (acetophenone)Cr(CO)₃ complexes were prepared by known literature procedures. $W(CO)_6$, Cr(CO)₆ and terephthalaldehyde were purchased from Aldrich and used as received. Heber Heop systems UV photochemical reactor equipped with a light source of 350 nm was used to carry out UV assisted polymerisation. Molecular weights of the polymers were determined by Waters GPC instrument with Styragel[®] columns (10⁶, 10⁵ and 10³ Å columns connected in series) equipped with an RI detector using THF as solvent at a flow rate of 1.0 mL/min and were calibrated using narrow polystyrene standards. NMR experiments were carried out in Bruker AVANCE 400 spectrometer using CDCl₃ as a solvent. The IR spectra were recorded on Perkin-Elmer spectrum one FT-IR spectrometer model L120. The electrochemical experiments were carried out in CH Instruments version 3.31 using Pt wire as working electrode, Pt foil as counter electrode and Ag as a reference electrode. *n*-Bu₄NPF₆ (0.1 M) was used as a supporting electrolyte in CH₃CN. All the electrochemical studies were carried out at room temperature (r.t.) using ferrocene (0.47 V) as the standard at a scan rate of 100mv/s. Elemental analysis was carried out in Perkin-Elmer CHNS analyzer. TGA was carried out in Perkin Elmer TGA 2400.

Synthesis of linear polyPA having ferrocene and (arene)Cr(CO)₃ as end-groups Fc(PA)₁₅[Cr]

$W(CO)_6$ (0.285, 0.81 mmol) and FA (0.170, 0.81 mmol) in 10ml of hexane was irradiated for 2h at 350nm. PA (1.652g, 12.5 mmol, 15 equiv) was added and irradiated for 24h. The reaction was terminated by adding one equiv of (arene)Cr(CO)₃. (0.207g, 0.81mmol) and stirred at room temperature for 5h. The polymers were precipitated in excess methanol, and purified by column chromatography (CHCl₃/hexane, 1:3) to give polymer Fc(PA)₁₅[Cr].

Synthesis of linear polyPA having ferrocene end-groups 1,4-Ar[(PA)₃Fc]₂

W(CO)₆ (0.285g, 0.81 mmol) and FA (0.170g, 0.81 mmol) in 10ml of hexane was irradiated for 2h at 350nm. PA (1.652g, 2.43 mmol, 3 equiv) was added over a period of 1h and irradiated for further 24h. The reaction was terminated by adding one equiv of terephthalaldehyde. (0.108g, 0.81mmol) and stirred at room temperature for 5h. The polymers were precipitated in excess methanol, and purified by column chromatography (CHCl₃/hexane, 1:3). This polymer was then used to end-cap another growing polymer of PPA having FA at one end giving linear polyPA with ferrocene end-groups after purification by column chromatography (CHCl₃/hexane, 1:3) 1,4-Ar[(PA)₃Fc]₂

Synthesis of tri-branched polyPA having ferrocene end-groups

W(CO)₆ (0.285g, 0.81 mmol) and triethynylbenzene (0.04g, 0.27 mmol) in 20ml of hexane was irradiated for 2h at 350 nm. PA (0.247g, 2.43 mmol, 3 equiv) was added and irradiated for further 24h. The reaction was terminated by adding three equiv. of ferrocenecarboxaldehyde. (0.52g, 2.43mmol) and stirred at room temperature for 5h. The polymers were precipitated in excess methanol, and purified by column chromatography (CHCl₃/hexane, 1:3) giving tri-branched polyPA 1,3,5-Ar[(PA)₃Fc]₃ with ferrocene end-groups.

The ¹H NMR of the linear 1,4-Ar[(PA)_nFc]₂ and branched 1,3,5-Ar[(PA)_nFc]₃ having ferrocene end-groups showed signals at 4.3 ppm attributable to ferrocene moiety and a broad signal at around 7 ppm due to olefinic and aromatic protons of the intervening PolyPA chain with matching intensities. The ¹³C NMR showed broad signals around 69 ppm corresponding to the ferrocene unit and around 127 ppm attributable to the olefinic and aromatic carbons of the PolyPA chain. The ¹H NMR of the polymers having ferrocene and (arene)Cr(CO)₃ as end-groups, (Fc(PA)_n[Cr]), contained signal due to methyl protons at 2.1 ppm, signals at 5.3-5.8 ppm due to aromatic ring attached to Cr(CO)₃ fragment, in addition to signals due to ferrocene moiety at 4.3 ppm and a broad signal at around 7 ppm due to the olefinic and aromatic protons with matching intensities. The ¹³C NMR of these polymers also showed signals due to methyl carbon at 23 ppm in addition to broad signals around 69 ppm corresponding to the ferrocene unit and around 127 ppm attributable to the olefinic and aromatic carbons of the PolyPA chain. The carbonyl group attached to the chromium center appeared at 225 ppm.

Elemental analysis of selected oligomers is as given below

Fc(PA)₁₅[Cr] Calculated C 86.5% H 5.5% Experimental C 76.3% H 5.5%

1,3,5-Ar[(PA)₃Fc]₃ Calculated C 84.3% H 5.4% Experimental C 80.9% H 5.2%

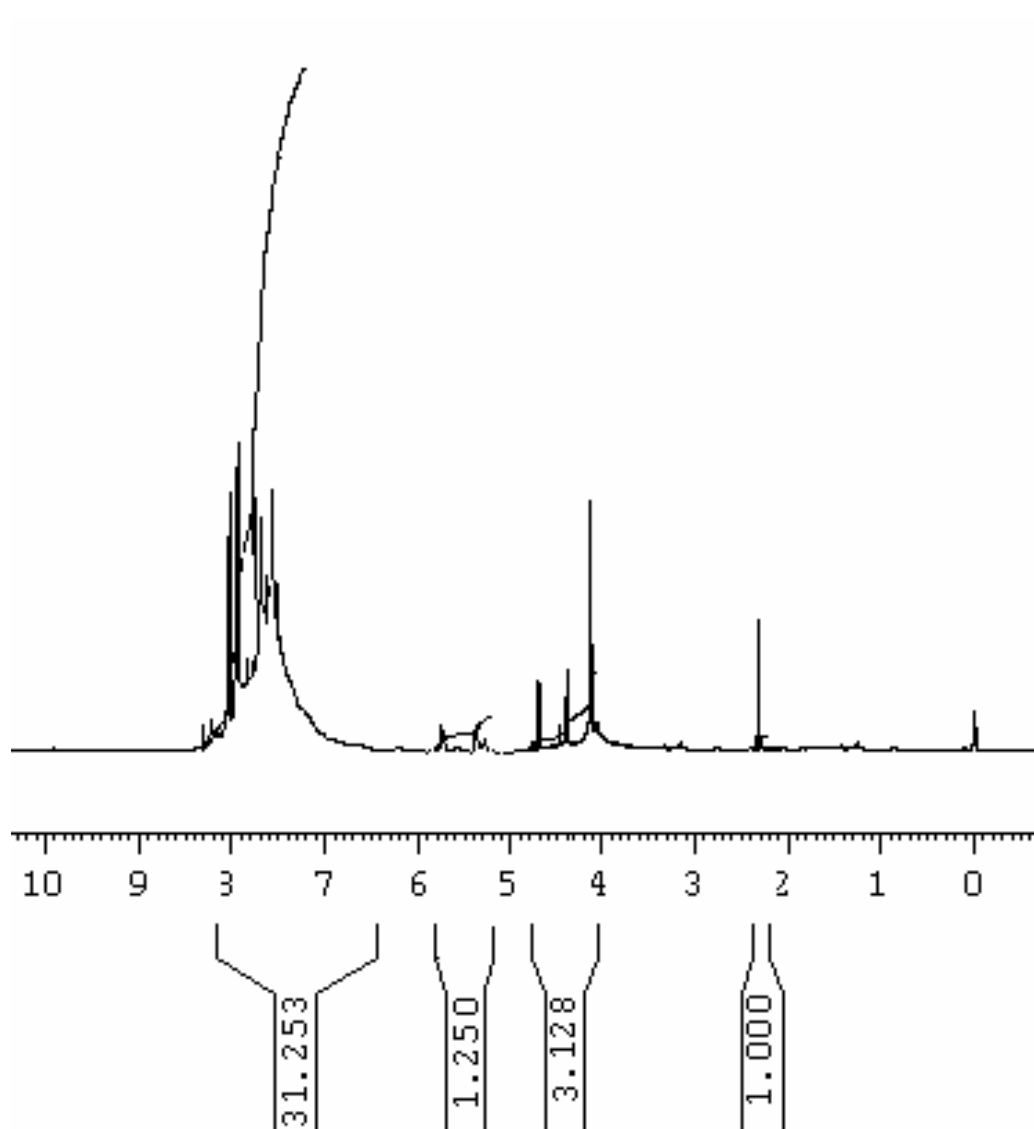


Figure 1. ^1H NMR of $\text{Fc(PA)}_{15}[\text{Cr}]$

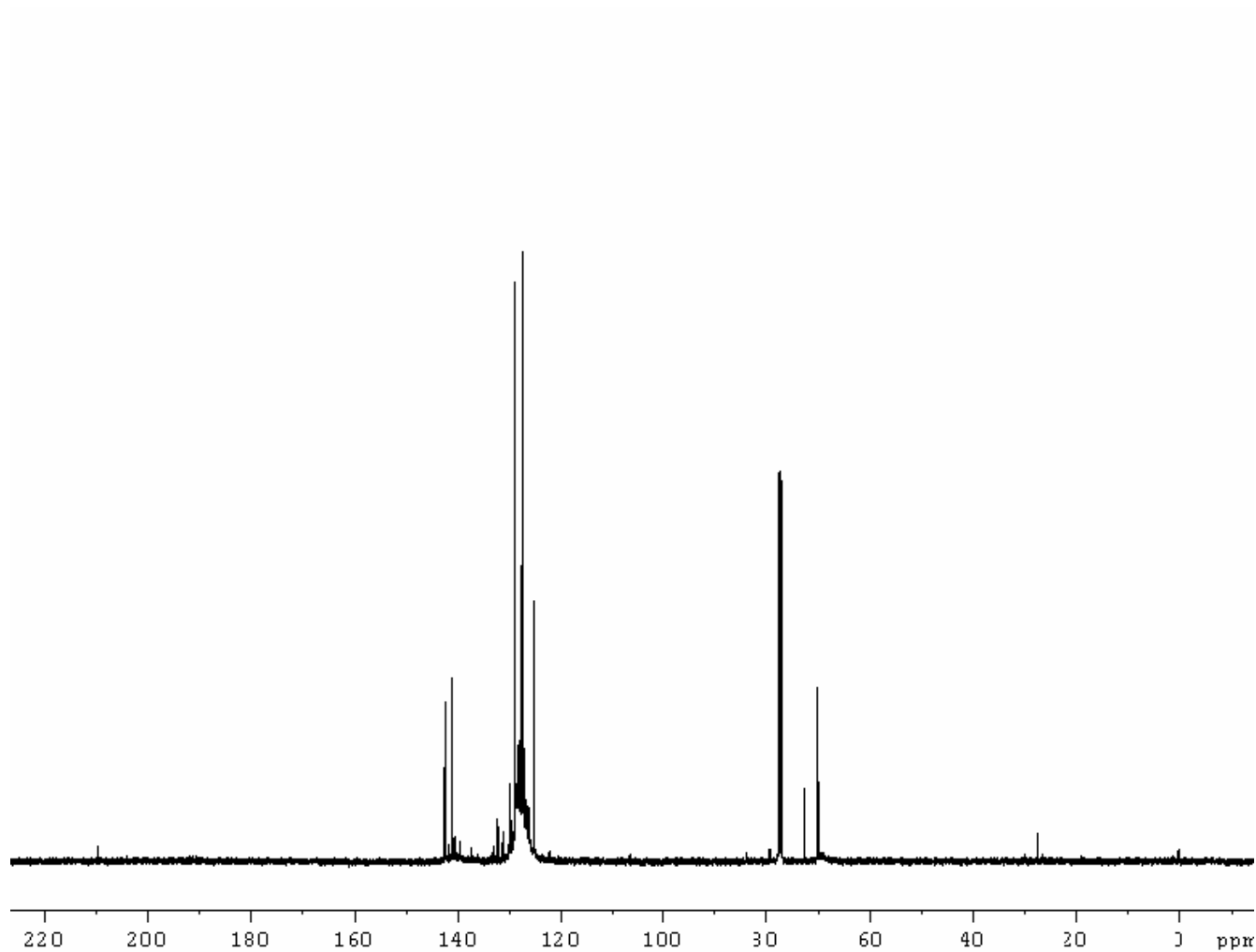


Figure 2. ^{13}C NMR of $\text{Fc(PA)}_{15}[\text{Cr}]$

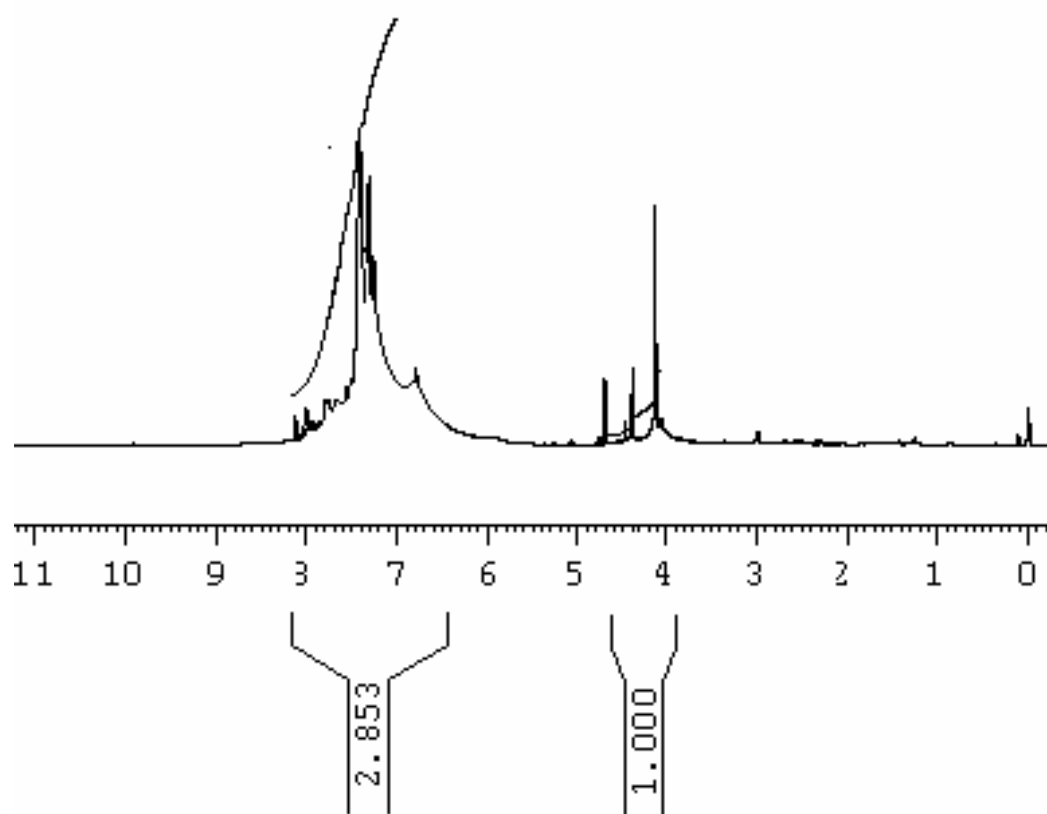


Figure 3. ^1H NMR of 1,4-Ar[(PA)₃Fc]₂

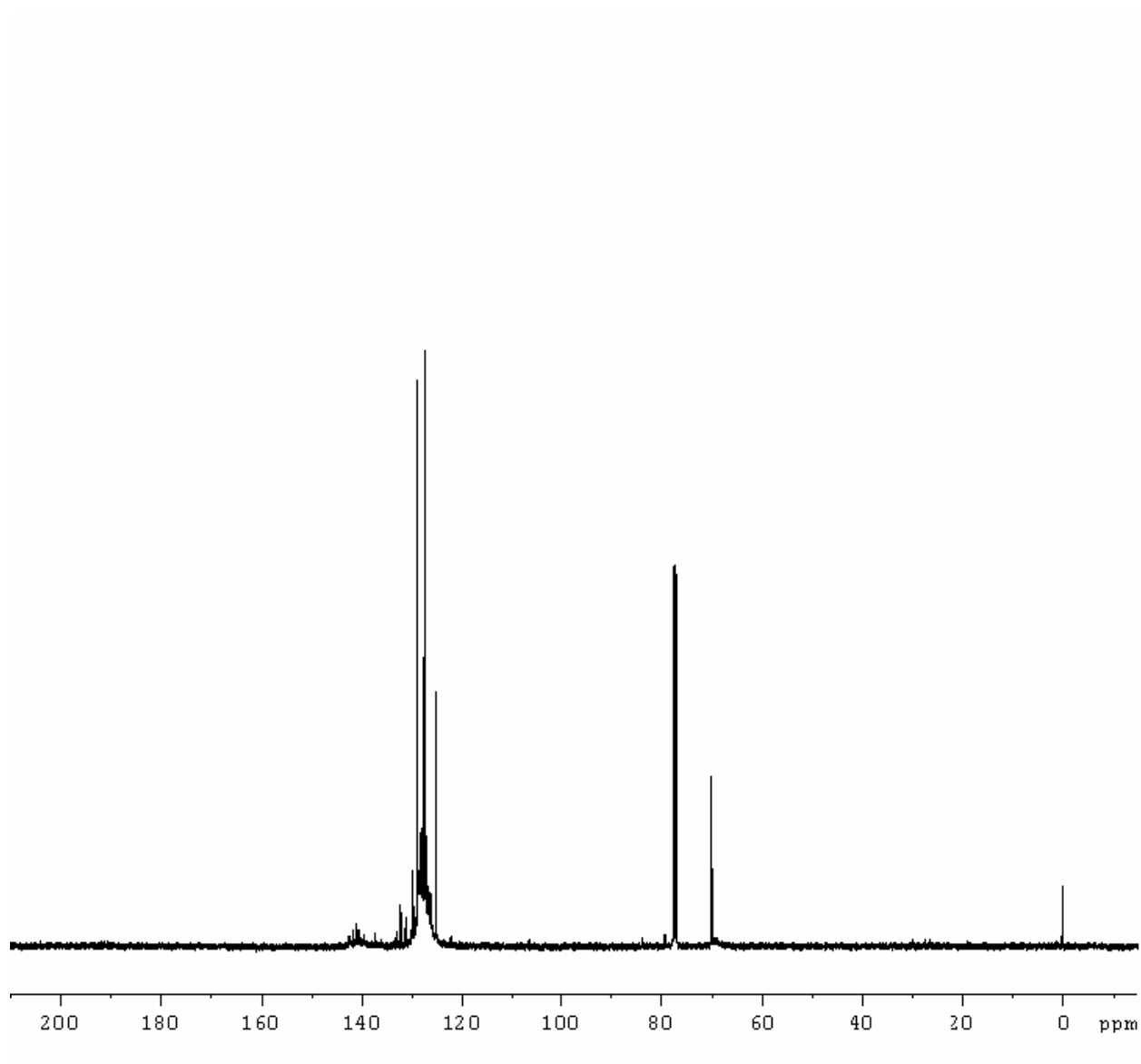


Figure 4. ^{13}C NMR of 1,4-Ar[(PA)₃Fc]₂

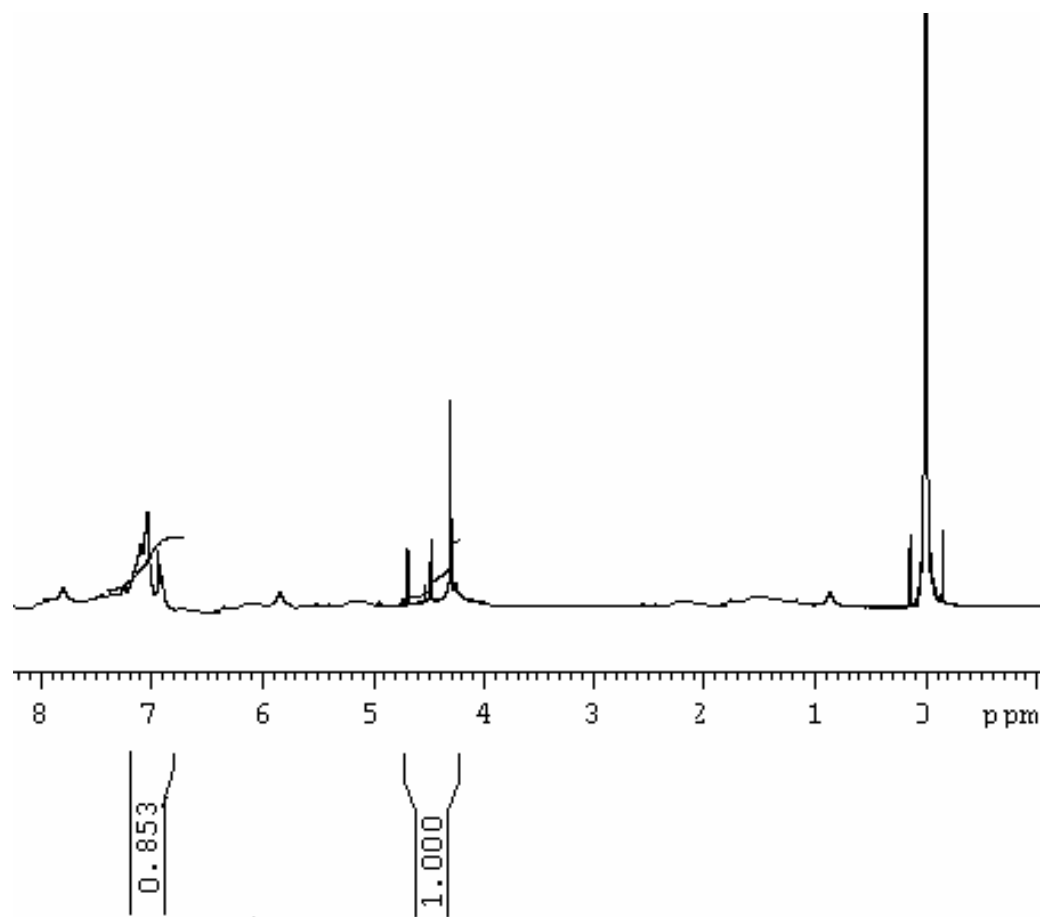


Figure 5. ^1H NMR of 1,3,5-Ar[(PA)₃Fc]₃

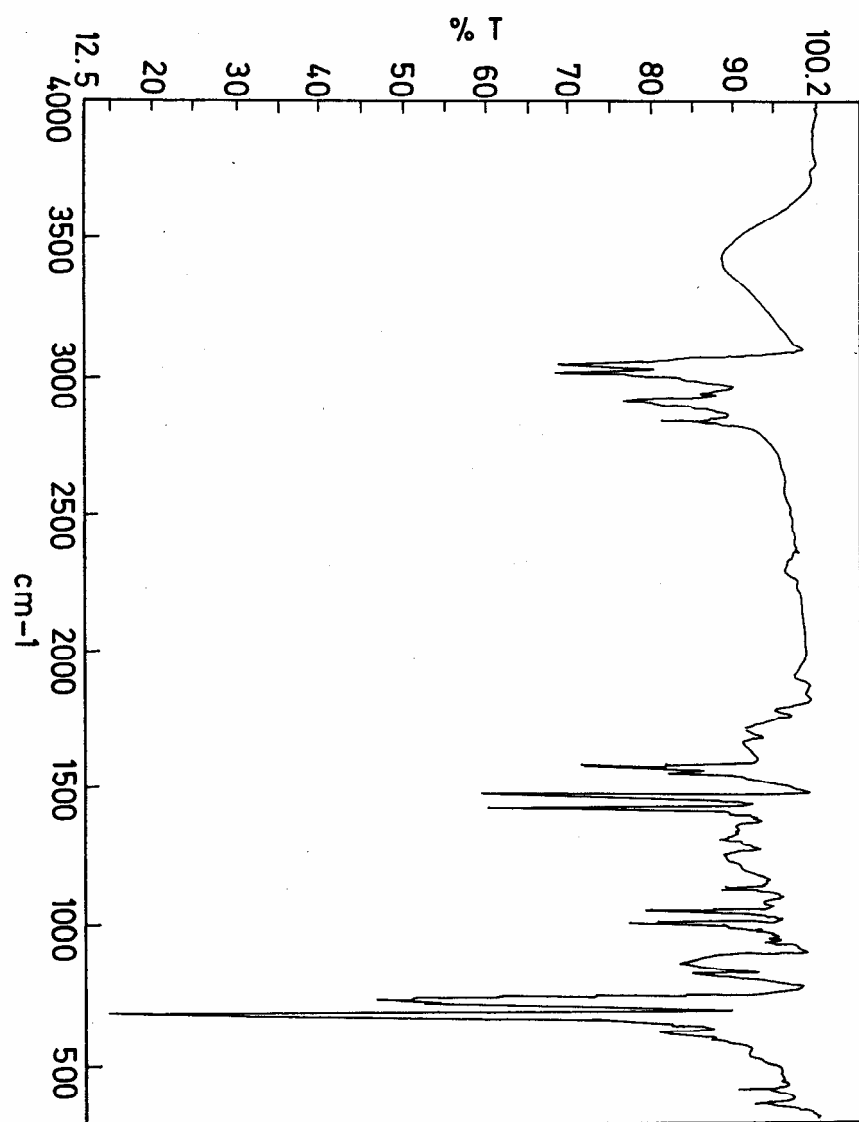


Figure 6. IR of $\text{Fc(PA)}_5[\text{Cr}]$

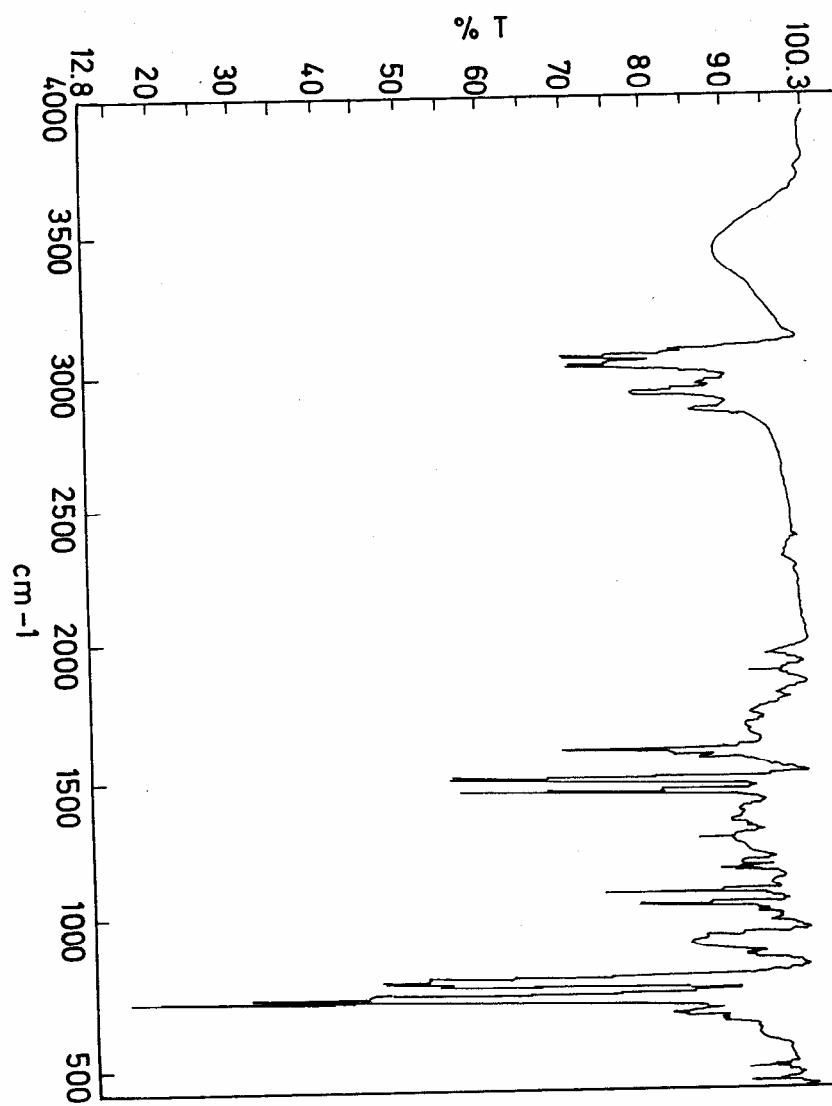


Figure 7. IR of 1,4-Ar[(PA)₃Fc]₂

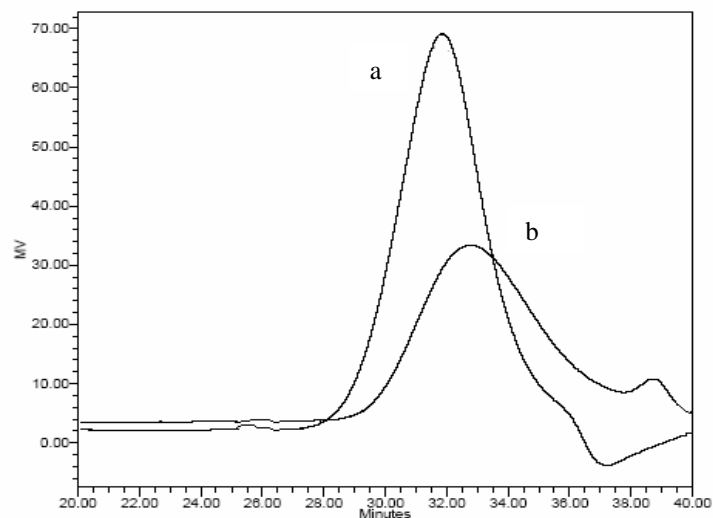


Figure 8. GPC overlay of (a) 1,3,5-Ar[(PA)₃Fc]₃ and (b) Fc(PA)₃

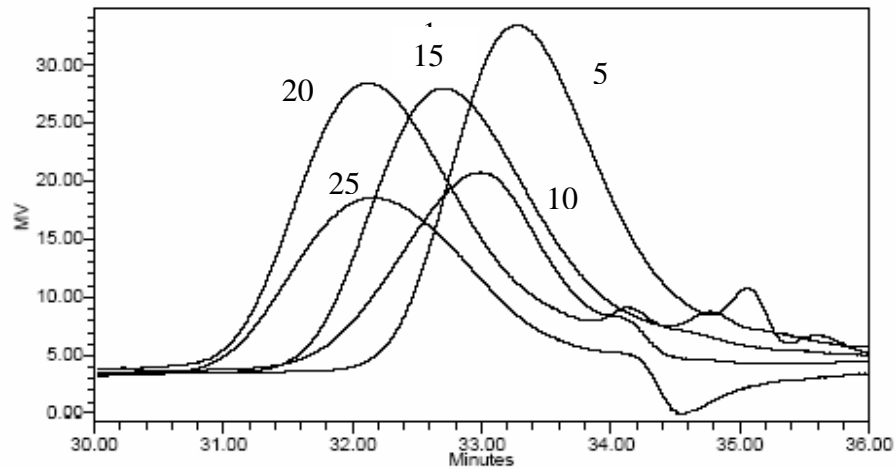


Figure 9. GPC overlay of polymers Fc(PA)_n[Cr], where n = 5, 10, 15, 20, 25.

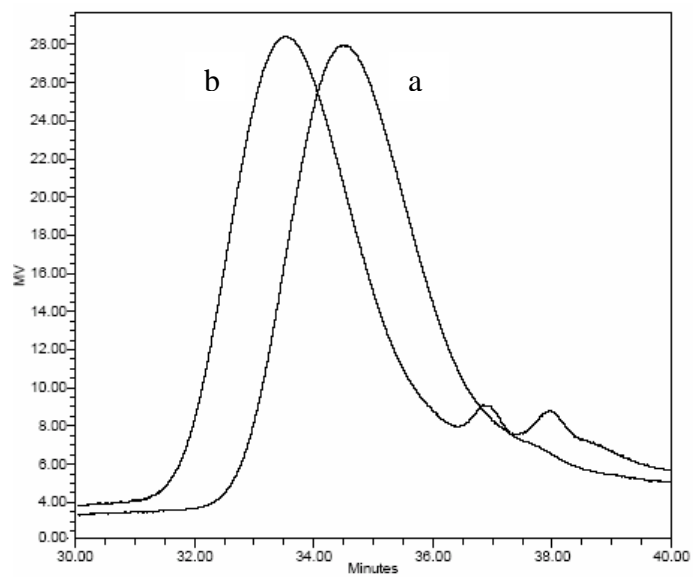


Figure 10. GPC overlay of (a) 1,4-Ar[(PA)₃Fc]₂ and (b) 1,4-Ar[(PA)₆Fc]₂

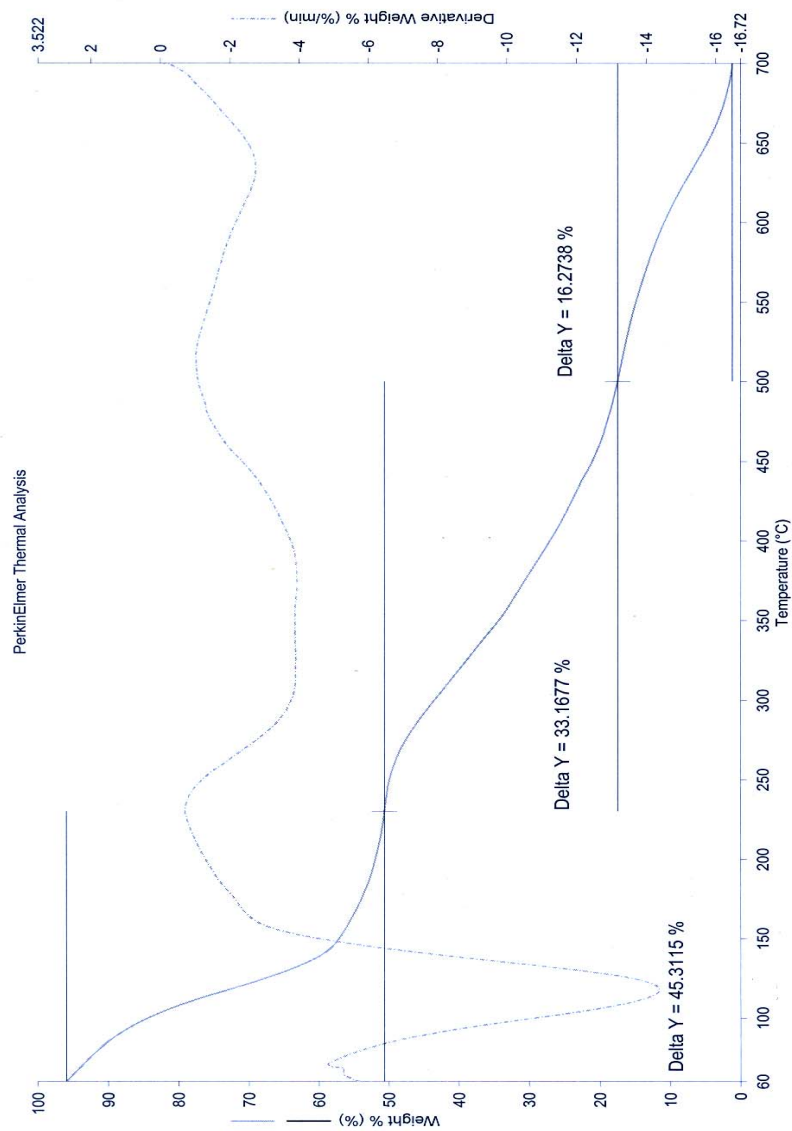


Figure 11. TGA of 1,3,5-Ar[(PA)₃Fc]₃

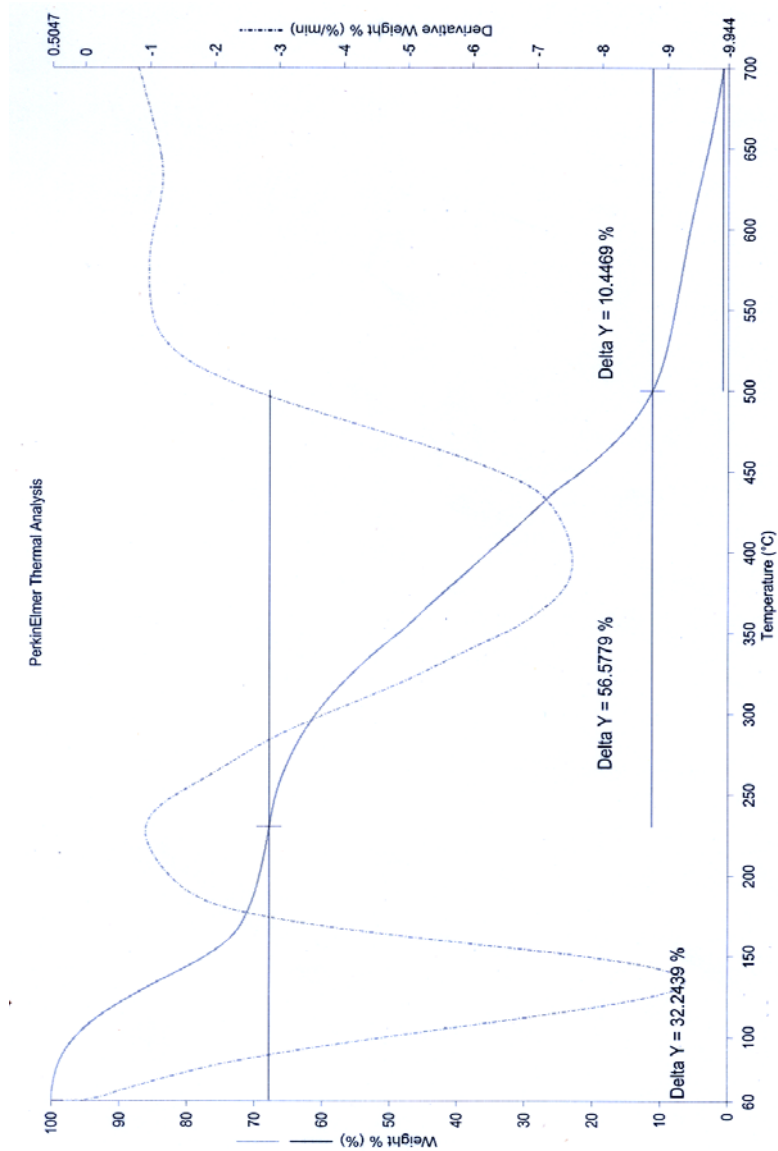


Figure 12. TGA of 1,4-Ar[(PA)₃Fc]₂

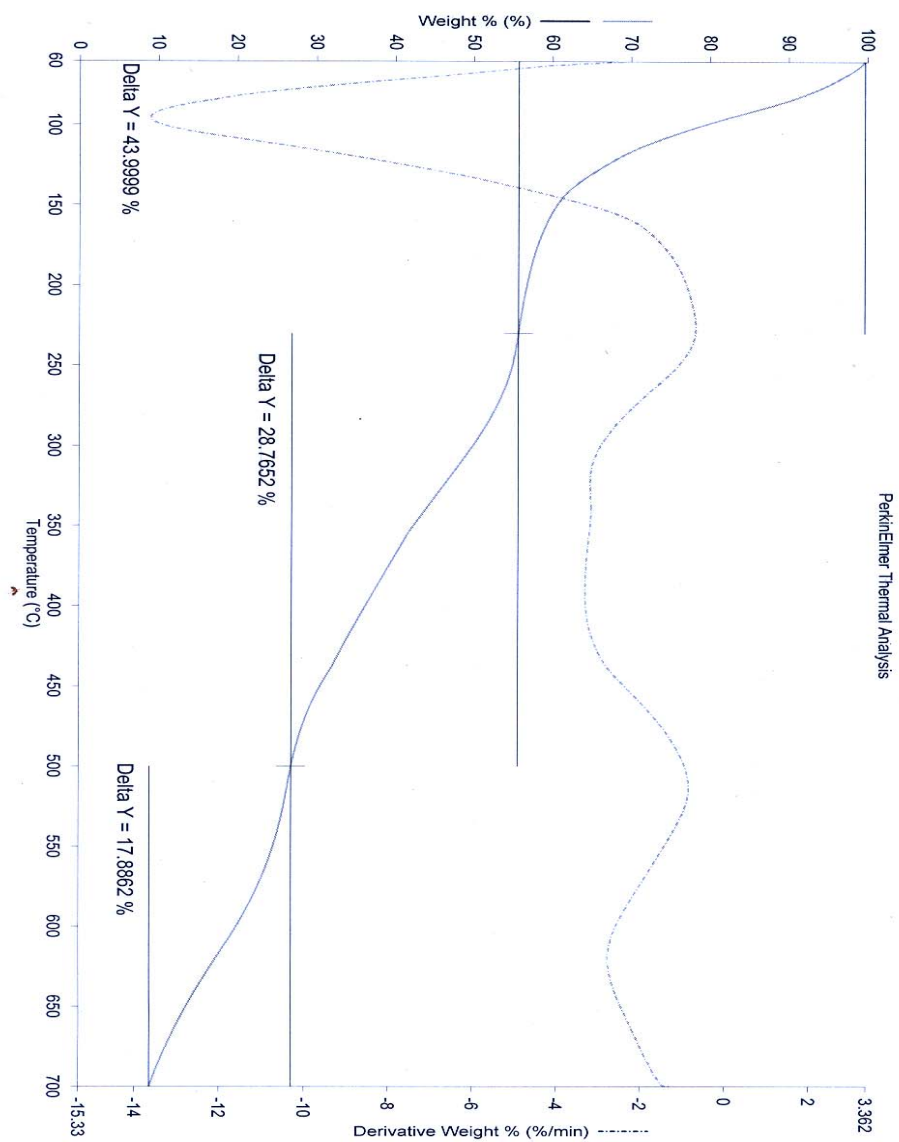


Figure 13. TGA of Fc(PA)₁₅[Cr]