

Research Article

New Polymer Syntheses Part 57: Thermally Stable New Ferrocene-Polyazomethines, Synthetic Methodology, and Characterization

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A new interesting category of higher thermally stable polyazomethines containing ferrocene in the polymers main chain **6a–e** was synthesized by solution-polycondensation reaction of 1-(*m*-formylphenyl)-1'-(5-formyl-2-methoxyphenyl)-ferrocene monomer **4** with different aliphatic and aromatic diamines. A model compound **5** was synthesized from dialdehyde monomer **4** with aniline and was characterized by elemental and spectral analyses. The desirable resulting polymers were characterized by elemental and spectral analyses, in addition to solubility measurement using different solvents. The thermal properties of these polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The redox behaviours were studied for the ferrocene polymers in comparison with both the parent ferrocene monomer and the model compound by using cyclic voltammetry (CV).

1. Introduction

Metal-containing polymers have emerged as an important category of polymeric materials. The impetus for the development of these materials is based on the premise that polymers-containing metals are expected to possess properties significantly different from those of conventional organic polymers. Ferrocene remains, after about 55 years since its discovery, a molecule of intrigue and continued interest. The sustained interest in ferrocene is in part due to the rich chemistry of iron (II) center and the variety of synthetic methods available for functionalizing the cyclopentadienyl ligands [1–9]. Ferrocene derivatives with good donor abilities (i.e., nitrogen, sulfur, oxygen, phosphorus, etc.) have attracted much interest, as the coordination of a metal to these heteroatoms generates multicenter molecules which have potential in many different areas. Amongst these N-substituted ligands ferrocenyl Schiff bases play pivotal role in the field of catalysis [10–17].

A class of the particularly attractive polymers is the aromatic polyazomethines or Schiff base polymers because they show good mechanical strength, attractive thermal stability and fiber-forming properties [18]. They are synthesized by condensation polymerization of dialdehydes or diketones with diamines to give high-molecular weight polymers. However, poor solubility in organic solvents limited their practical applications in various fields [19]. A few groups of researchers have synthesized soluble polyazomethines by introducing alkyl or alkoxy groups into the polymer chains and investigated their structure and physical properties such as electric conductivity and mechanical properties [20]. In last years, there has been increasing interest in the synthesis of new polymers with unusual thermal, optical, and mechanical properties. Among these ones, polyazomethines were investigated with respect to their properties including thermal stability [21], optical and electrical response [22–25], conductivity [26, 27], syn-anti isomerization [28], opto(electronic) and liquid crystal properties [29–31], and film or fiber

forming ability [32, 33]. The inclusion of ferrocene units into polymeric arrays has attracted much attention due to the electronic donating ability, reversible redox chemistry, steric properties, and ready functionalization of this stable fragment.

The approach chosen in this study deals with the synthesis and characterization of new polyazomethines containing ferrocene moiety in the polymers main chain. The electrochemical behaviours of these polymers were investigated by cyclic voltammetry. Moreover solubility, thermal stability, and morphology of the synthesized polymers had been examined and the data were discussed.

2. Experimental Part

2.1. Materials. All polymers are new; details of the synthesis and characterization of these compounds are given in the experimental part. All ferrocene monomers were prepared following the previously reported methods [34]. Dichloromethane (DCM) and chloroform from El-Nasr Chemical Company (Egypt) were freshly distilled before use: propane-1,3-diamine (>99%) Merck, decane-1,10-diamine (>96%) Merck, dodecane-1,12-diamine (>98%) Merck, *p*-phenylenediamine (>98%) Merck, and 4,4'-diaminodiphenyl ether (>98%) Merck. Reagents and solvents were purchased and used as received unless otherwise stated. All reactions were performed under nitrogen atmosphere. Silica gel 60 M (Macherey-Nagel, 0.04–0.063 mm/230–400 mesh) was used as a stationary phase for column chromatography. Whenever possible, reactions were monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminum plates 60F₂₅₄ (Merck).

2.2. Instrumentation. Fourier transform Infrared spectrophotometer (FT-IR) spectra were recorded on Nicolet 6700—Thermo Fisher Scientific, by using the KBr pellet technique. ¹H-NMR spectra were recorded on a Bruker AM 200 (¹H: 200 MHz) spectrometer, and chemical shifts are reported as δ values (ppm) relative to internal Me₄Si. High-resolution MALDI-TOF mass spectrometry (MS) analysis was performed by the MS-service of the Laboratorium für Organische Chemie at ETH Zürich. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. The samples were dried rigorously under vacuum prior to analysis to remove strongly-adhering solvent molecules. High-resolution thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) and differential thermal gravimetric (DTG) were carried out in air with Shimadzu DTG-60 at heating rate of 10°C/min in air. All measurements were carried out in an air-stream under the same conditions. The mass loss was plotted against increasing temperature as well as its first derivative (DTG) that represents the change in decomposition rate. Differential scanning calorimetry (DSC) measurements were performed using the DSC Q1000 differential scanning calorimeter from TA Instruments in a temperature range of –80–+200°C with a heating rate of 10°C min⁻¹. Samples of a total weight ranging

between 3 and 10 mg were closed into aluminum pans of 40 μ L, covered by a holed cap, and analyzed under a nitrogen atmosphere. The glass transition temperature (T_g) was taken in the second heating run. CV was measured on a cyclic voltammetric analyzer using glassy carbon electrode (GCE), Bioanalytical System, USA, starting potential 0.0 V and final potential +1.5 V, at Analytical Chemistry Unit ACAL, Assiut University, Egypt.

2.3. Monomers Syntheses

2.3.1. 1-(*m*-Formylphenyl)-1'-(5-formyl-2-methoxyphenyl)ferrocene (4). Monomer **4** was synthesized in our previous work [34] as follows. A mixture of ferrocene-dialcohols **3** (3.00 g, 6.70 mmol) and MnO₂ (30.00 g) in CHCl₃ was stirred at room temperature for 15 h. The reaction mixture was filtered off through glass wool and the filtrate was evaporated under reduced pressure at 30°C. The product was purified by column chromatography on silica gel (CHCl₃: hexane, 3:1 ratio) as orange red crystals: 71%; m.p.: 87–88°C.

C₂₅H₂₀FeO₃: Calcd. C, 70.77; H, 4.75; Found. C, 71.01; H, 4.51. FT-IR (KBr): ν C=O 1702 cm⁻¹. ¹H-NMR (CDCl₃): δ = 3.81 (s, 3H, OCH₃), 4.32 (s, 2H, ferrocene-H), 4.36 (s, 2H, ferrocene-H), 4.61 (s, 2H, ferrocene-H), 4.82 (s, 2H, ferrocene-CH), 6.67 (m, 1H, Ar-H), 7.18–7.62 (m, 6H, Ar-H), 9.7 (s, 1H, CHO), 9.8 (s, 1H, CHO). FABMS *m/e* (%) [M⁺, 424].

2.4. Model Compound Synthesis

2.4.1. 1-(*m*-anilinemethinephenyl)-1'-(2-methoxy-5-aniline-methinephenyl)ferrocene (5). A mixture of 1-(*m*-formylphenyl)-1'-(5-formyl-2-methoxyphenyl)ferrocene (**4**) (0.424 g, 1.000 mmol) and aniline (0.245 g, 2.200 mmol) was dissolved in 30 mL absolute EtOH in presence of few drops piperidine. The reaction mixture was stirred in oil bath at 80°C under nitrogen for 6 h. A solid product separated out during reflux, which was filtered off and dried. Purification by recrystallization from ethanol as orange red crystals yield: 75%; m.p.: 114–116°C.

C₃₇H₃₀FeN₂O: Calcd. C, 77.35; H, 5.26; N, 4.88; Found: C, 77.04; H, 5.94; N, 5.00. FT-IR (KBr): ν CH=N 1622 cm⁻¹. ¹H-NMR (CDCl₃): δ = 3.89 (s, 3H, OCH₃), 4.31 (t, 2H, ferrocene-CH), 4.35 (t, 2H, ferrocene-CH), 4.64 (t, 2H, ferrocene-CH), 4.85 (t, 2H, ferrocene-CH), 6.71 (d, 4H, Ar-H), 6.74 (d, 4H, Ar-H), 7.16–7.45 (m, 3H, Ar-H), 7.63 (d, 4H, Ar-H), 7.67 (d, 4H, Ar-H), 7.82 (d, 2H, Ar-H), 8.26 (s, 1H, CH=N), 8.31 (s, 1H, CH=N). MS (MALDI-TOF): *m/z* = 575.17 [M]⁺.

2.5. Polymer Syntheses

2.5.1. General Procedure. In a three-necked flask equipped with a condenser, dry nitrogen inlet, outlet, and dropping funnel, a mixture of 1-(*m*-formylphenyl)-1'-(5-formyl-2-methoxy-phenyl)ferrocene (**4**) (1.0 mmol) and diamine (1.1 mmol) was dissolved in 30 mL absolute EtOH in presence of few drops piperidine. The reaction mixture was stirred in an oil bath at 80°C under nitrogen for 6–10 h. A solid product

separated out during reflux, which was filtered off, washed well with hot ethanol, was dried under high vacuum.

Fc-Polyazomethine 6a. The title compound was synthesized according to general procedure of polymerization from compound **4** (0.424 g, 1.000 mmol), propane-1,3-diamine (0.081 g, 1.100 mmol), and piperidine (few drops) in absolute EtOH (30 mL) (6 h at 80°C) as an orange precipitate (68%).

$C_{28}H_{26}FeN_2O$: Calcd. C, 72.73; H, 5.67; N, 6.06; found: C, 73.72; H, 5.56; N, 5.96. FT-IR (KBr): ν CH=N 1642 cm^{-1} . 1H -NMR ($CDCl_3$): δ = 1.50 (q, 2H, CH_2), 3.73 (t, 4H, CH_2), 3.78 (s, 3H, OCH_3), 4.17–4.70 (m, 8H, ferrocene-H), 6.60–8.13 (m, 9H, Ar-H & CH=N).

Fc-Polyazomethine 6b. The title compound was synthesized according to general procedure of polymerization from compound **4** (0.424 g, 1.000 mmol), decane-1,10-diamine (0.189 g, 1.100 mmol), and piperidine (few drops) in absolute EtOH (30 mL) (6 h at 80°C) as an orange film (74%).

$C_{35}H_{40}FeN_2O$: Calcd. C, 74.99; H, 7.19; N, 5.00; found: C, 72.19; H, 6.96; N, 4.81. FT-IR (KBr): ν CH=N 1644 cm^{-1} . 1H -NMR ($CDCl_3$): δ = 1.30 (t, 16H, CH_2), 3.57 (q, 4H, CH_2), 3.79 (s, 3H, OCH_3), 4.27–4.77 (m, 8H, ferrocene-H), 6.68–8.16 (m, 9H, Ar-H & CH=N).

Fc-Polyazomethine 6c. The title compound was synthesized according to general procedure of polymerization from compound **4** (0.424 g, 1.000 mmol), dodecane-1,12-diamine (0.220 g, 1.100 mmol), and piperidine (few drops) in absolute EtOH (30 mL) (6 h at 80°C) as a reddish brown precipitate (73%).

$C_{37}H_{44}FeN_2O$: Calcd. C, 75.50; H, 7.53; N, 4.76; found: C, 71.98; H, 7.84; N, 5.05. FT-IR (KBr): ν CH=N 1646 cm^{-1} .

Fc-Polyazomethine 6d. The title compound was synthesized according to general procedure of polymerization from compound **4** (0.424 g, 1.000 mmol), *p*-phenylenediamine (0.118 g, 1.100 mmol), and piperidine (few drops) in absolute EtOH (30 mL) (10 h at 80°C) as an orange precipitate (65%).

$C_{31}H_{24}FeN_2O$: Calcd. C, 75.01; H, 4.87; N, 5.64; found: C, 73.81; H, 4.99; N, 5.61. FT-IR (KBr): ν CH=N 1619 cm^{-1} .

Fc-Polyazomethine 6e. The title compound was synthesized according to general procedure of polymerization from compound **4** (0.424 g, 1.000 mmol), 4,4'-diaminodiphenyl ether (0.118 g, 1.100 mmol), and piperidine (few drops) in absolute EtOH (30 mL) (10 h at 80°C) as an orange precipitate (69%).

$C_{37}H_{28}FeN_2O_2$: Calcd. C, 75.52; H, 4.80; N, 4.76; found: C, 74.25; H, 5.33; N, 5.09. FT-IR (KBr): ν CH=N 1621 cm^{-1} , 1H -NMR ($CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 4.34–4.97 (m, 8H, ferrocene-H), 6.43–7.79 (m, 15H, Ar-H), 8.09 (s, 2H, CH=N).

3. Results and Discussion

3.1. Monomers Syntheses. The synthetic sequences to monomers **2–4** are delineated in Scheme 1 as done in our previous work [34]. Applying Gomberg's arylation of

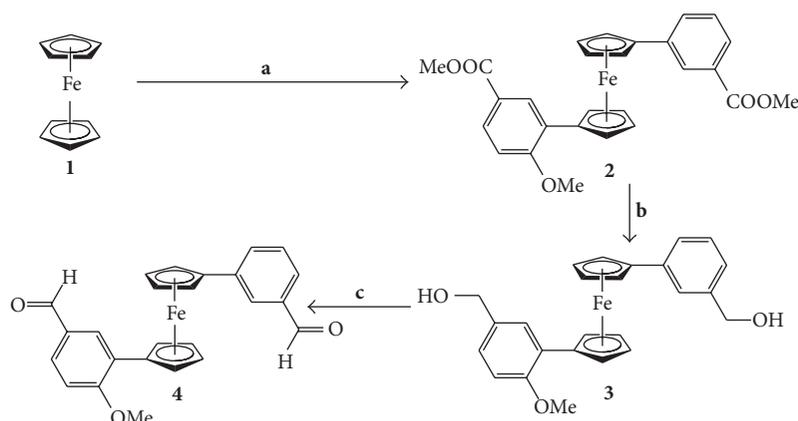
ferrocene with diazonium salt of the methyl 3-amino-4-methoxybenzoate to give the corresponding 1-(3-methoxycarbonyl-2-methoxyphenyl)ferrocene which was subjected to diazotization with diazonium salt, derived from methyl 3-aminobenzoate, to give the corresponding diester **2** then reduction with Lithium aluminium hydride (LAH) to give monomer **3**, which was oxidized with activated MnO_2 in dry $CHCl_3$ to get the target monomer 1-(*m*-formylphenyl)-1'-(5-formyl-2-methoxyphenyl)ferrocene (**4**), in 71% yield.

3.2. Synthesis of Model Compound. Before attempting polymerization, model compound **5** was synthesized by the interaction of 1 mole of monomer **4** with 2 moles of aniline in EtOH, piperidine as described in Scheme 2. The structure of this model compound was confirmed by elemental and spectral analysis. The FT-IR spectrum showed a new characteristic absorption band at 1622 cm^{-1} due to CH=N stretching in addition to other characteristic absorption bands of the Fe–Cp stretching vibrations, at 1074, 975 and 823 cm^{-1} . The 1H -NMR spectrum of model compound **5** (in $CDCl_3$) was in accordance with the proposed structure (Figure 1). It showed the molecular ion peak in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum.

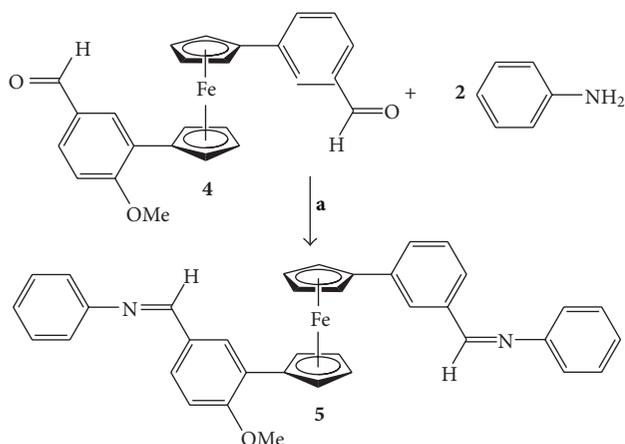
3.3. Polymerization and Polymer Characterization. Using solution polycondensation technique [35] by the interaction of one mole of monomer **4** with one mole of diamine compounds in presence of few drops piperidine give new Fc-polyazomethines **6a–e** as described in Scheme 3.

The structures of the resulting polymers were also established from elemental analyses and spectral data. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer; the data are included in the experimental part. The FT-IR spectral data of all polyazomethine derivatives showed characteristic absorption band at 3078–3085 cm^{-1} for C–H aromatic, at 2833–2926 cm^{-1} for C–H aliphatic 1619–1646 cm^{-1} due to C=N, bands of the Fe–Cp stretching vibrations at 1079, 970 and 815 cm^{-1} . In addition, other characteristic absorption bands due to specific groups present in the various polymers. Also the 1H -NMR spectra of Fc-polyazomethine **6a**, **6b**, and **6e** (in $CDCl_3$) were in accordance with the proposed structures (Figure 2, 1H -NMR of Fc-polyazomethine **6b**).

3.4. Solubility. The solubility of the Fc-polyazomethines **6a–d** was tested using solvents including dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), chloroform, benzene, hexane, and formic acid. 50 mg of the polymer were added to 1 mL of the chosen solvent and the solution analyzed by visual inspection. The results are shown in Table I. All Fc-polyazomethines **6a–e** are clearly less soluble in polar, aprotic solvents DMSO and DMF except Fc-polyazomethines which contain aliphatic moieties **6a–c** are virtually insoluble in DMSO. All Fc-polyazomethines **6a–e** are soluble in hexane and formic acid.



SCHEME 1: Synthesis procedure of ferrocene monomer 4. Reagents and conditions: **a** (i) diazonium salt of methyl 3-amino-4-methoxybenzoate, AcOH (ii) diazonium salt of methyl 3-aminobenzoate; **b** LAH, EtOH, r.t.; **c** MnO₂, CHCl₃, r.t.



SCHEME 2: Synthesis procedure of model compound 5. Reagents and conditions: (a) EtOH, piperidine, reflux.

TABLE 1: Room-temperature solubility characteristics of Fc-polyazomethines **6a**, **6b**, **6c**, **6d**, and **6e**.

Polymer number	DMF	DMSO	CHCl ₃	Benzene	Hexane	HCOOH
6a	+	-	++	++	++	++
6b	+	-	++	++	++	++
6c	+	-	+	++	++	++
6d	+	+	+	+	++	++
6e	+	+	++	+	++	++

++: soluble according to visual inspection, +: partially soluble, -: insoluble.

All Fc-polyazomethines which contain aliphatic moieties **6a–c** are freely soluble in chloroform and benzene except **6c** which is partially soluble in chloroform. All Fc-polyazomethines which contain aromatic moieties **6d–e** are partially soluble in chloroform and benzene except **6e** which is freely soluble in chloroform. The study succeeded in inserting the ferrocene moieties in the polymer main chain. As expected, the presence of such moieties in the polymer

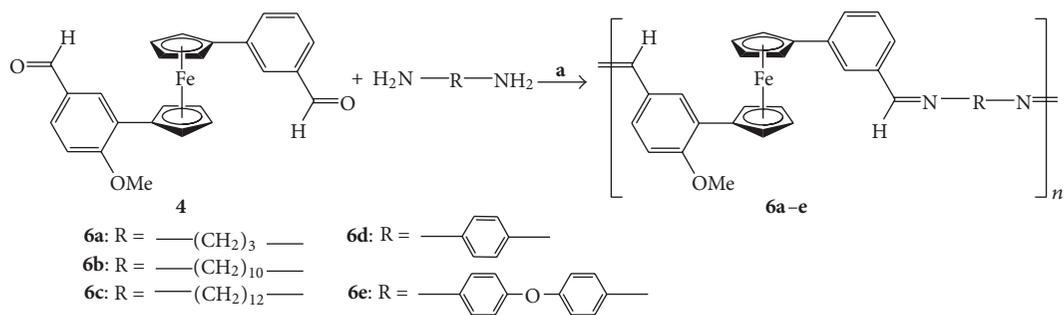
TABLE 2: Thermal properties of Fc-polyazomethines **6a**, **6b**, **6c**, **6d**, and **6e**.

Polymer number	Temperature (°C) for various decomposition levels*					
	10%	20%	30%	40%	50%	PDT _{max}
6a	140	170	385	430	440	439
6b	430	430	431	432	433	433
6c	435	450	455	480	510	516
6d	340	340	345	350	370	373
6e	395	396	397	398	400	402

*The values were determined by TGA at heating rate of 10°C min⁻¹.

backbone will lead to increasing chain packing distances and decreasing interchain interactions, such as hydrogen bonding, thereby increasing the solubility compared with other polyazomethines [36]. It can be clarified that the solubility of Fc-polyazomethines **6a–e** is based on the aliphatic or aromatic spacers in the polymer backbone. It was found that the presence of aliphatic spacers in the polymer backbone increase the flexibility of the polymer chains and allow the solvent molecules to go through them which increase the probability of solubility.

3.5. TGA and DSC Studies. The thermal behaviour of the Fc-polyazomethines **6a–d** was evaluated by TGA in air with heating rate of 10°C/min. TGA curves show a small weight-loss in the range 0.5–4.5% starting at 50°C until 235°C except Fc-polyazomethine **6a**. Table 2 shows the temperatures for the various % weight loss. The initial decomposition temperature (PDT) [35], which occurred in range 140°C to 435°C. The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred. PDT_{max} for Fc-polyazomethines **6a–d** were 439°C, 432°C, 516°C, 373°C, and 402°C, respectively. The degradation steps involve the scission of azomethine groups; scission of many bonds with the liberation of free shorter chains depending upon the



SCHEME 3: Synthesis procedure of Fc-polyazomethines **6a-e**. Reagents and conditions: (a) EtOH, piperidine, reflux.

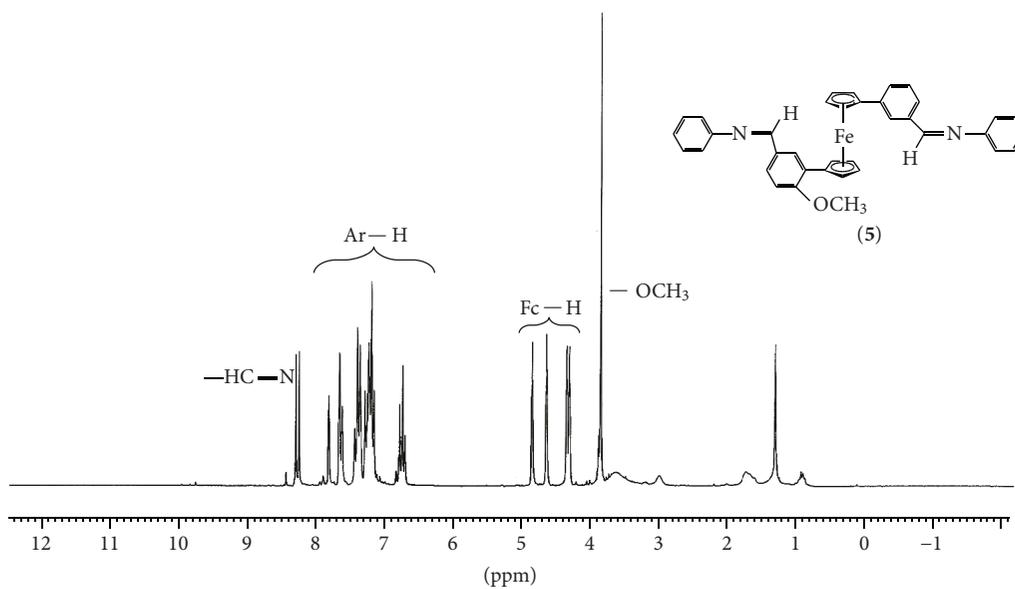


FIGURE 1: ¹H-NMR spectrum of model compound **5** in CDCl₃.

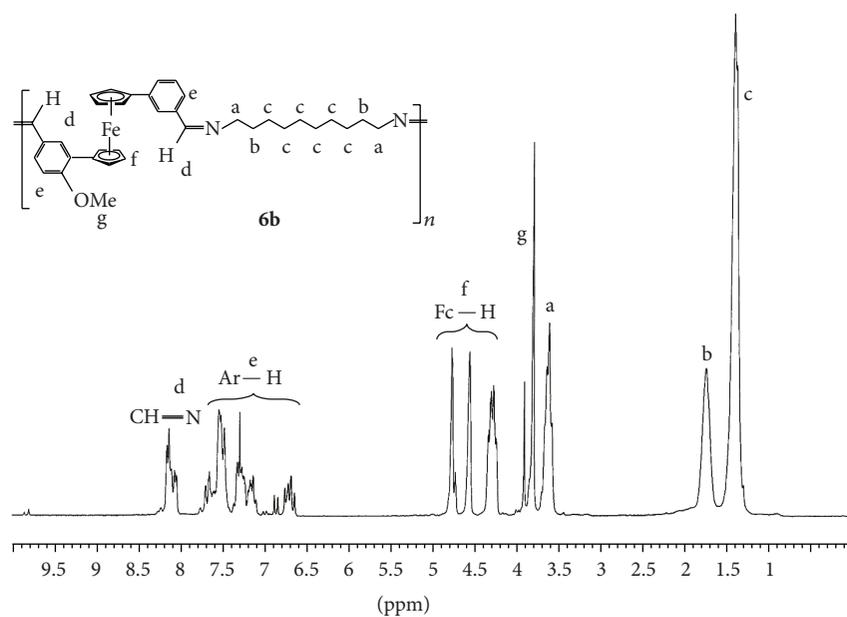


FIGURE 2: ¹H-NMR spectrum of Fc-polyazomethine **6b** in CDCl₃.

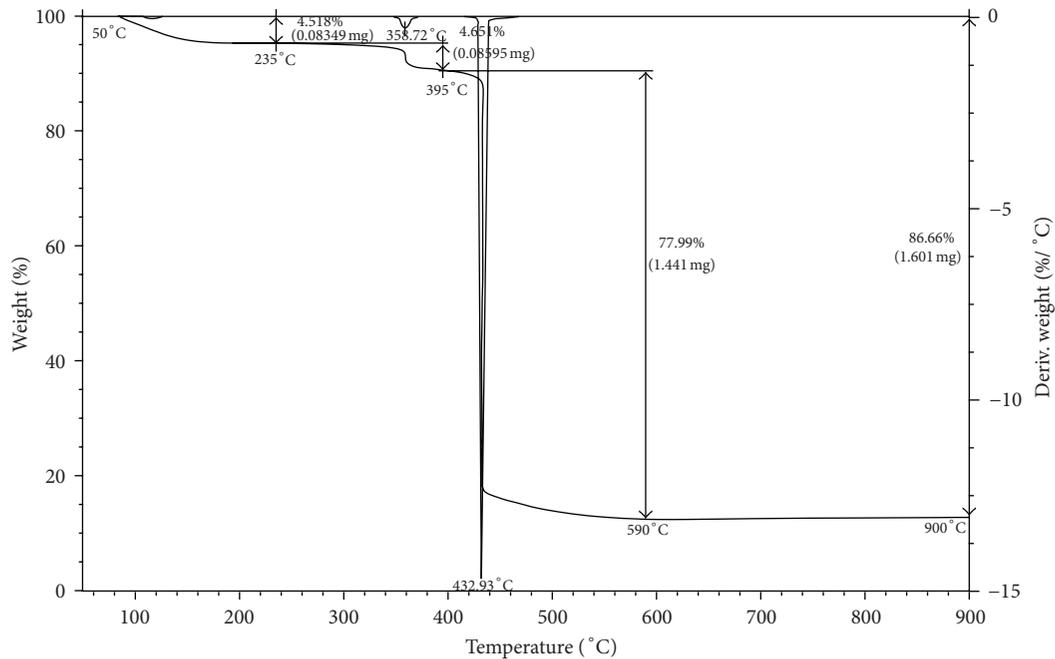


FIGURE 3: TGA curve of Fc-polyazomethine 6b.

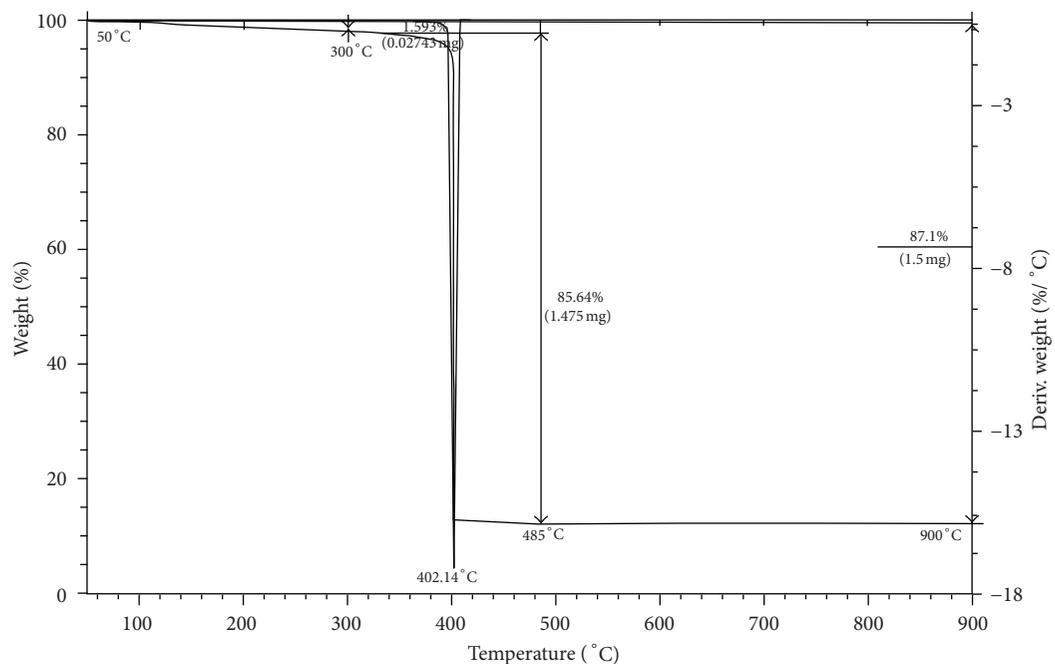


FIGURE 4: TGA curve of Fc-polyazomethine 6e.

TABLE 3: Cyclic voltammetric parameters of monomer **4**, model compound **5**, Fc-polyazomethines **6a**, **6b**, **6c**, **6d**, and **6e** at 20 mVs⁻¹.

Compound number	E_{pc} (mv)		E_{pa} (mv)		E^0 (mv)		ΔE_p (mv)		I_{pc} (μA)		I_{pa} (μA)	
	P_1	P_2	P_1	P_2	P_1	P_2	P_1	P_2	P_1	P_2	P_1	P_2
4	249	—	437	637	343	—	188	—	+1.98	—	-0.79	-2.14
5	346	—	480	565	413	—	134	—	+7.40	—	-11.27	-44.18
6a	303	—	467	540	385	—	164	—	+1.64	—	-7.58	-5.53
6b	303	—	467	—	385	—	164	—	+2.89	—	-13.28	—
6c	346	—	510	—	428	—	164	—	+1.62	—	-4.40	—
6d	358	—	528	619	443	—	170	—	+3.63	—	-9.24	-10.72
6e	382	—	419	643	401	—	37	—	+8.67	—	-2.40	-43.54

nature of these polymers. This observation is in agreement with that observed in the literature [26]. TGA curve for Fc-polyazomethine **6a** shows mass loss between 127.62 and 250.94°C (-17.03%) in first region, between 253.42 and 367.82°C (-5.90%) in the second region, and between 367.87 and 505.51°C (-58.11%) in third region. Fc-Polyazomethine **6b** shows mass loss between 358.72 and 395.00°C (-4.65%) in first region, between 395.00 and 432.93°C (-77.99%) in the second region (Figure 3). Fc-Polyazomethine **6c** shows mass loss between 219.40 and 403.31°C (-5.56%) in first region, between 404.77 and 473.25°C (-28.67%) in the second region, and between 474.23 and 569.60°C (-50.21%) in third region. Fc-Polyazomethine **6d** shows mass loss between 227.61 and 340.74°C (-37.77%) in first region, between 339.76 and 447.43°C (-46.38%) in the second region. Fc-Polyazomethine **6e** shows mass loss between 300.00 and 485.00°C (-85.64%) in one region (Figure 4). From the TGA data it is noticed that the fast degradation step in all Fc-polyazomethines **6a–e** did not start before 277.61°C. Thus, it is quite acceptable to claim that these polymers are thermally stable till high temperature.

The thermal behaviour of two selected polymers, Fc-polyazomethine **6b** and **6e** as containing different aliphatic and aromatic spacers in the main chain was studied by differential scanning calorimetry (DSC) which revealed that these compounds have T_g values at 55°C and 150°C, respectively, indicating that Fc-polyazomethine containing aromatic spacers has higher T_g values than that which contains aliphatic spacers and this may be due to the more flexibility effect of the aliphatic spacers on the polymer chains.

3.6. Electrochemical Study. The electrochemical behaviours of some ferrocene derivatives were investigated by cyclic voltammetry showing interesting behaviour [34, 37, 38], this encouraged us to study the electrochemical behaviour of some new polyazomethines with ferrocene moiety in the main chain. The electrochemical redox properties of the newly synthesized polyazomethines **6a–e** based ferrocene moiety were studied by cyclic voltammetry at room temperature in (dry CH₂Cl₂: absolute ethanol, 1:1) solutions, using glassy carbon electrode as working electrode, Pt gauze as a counter electrode and Ag/AgCl as a reference electrode, and tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. The electrochemical data of the

investigated compounds were compared with those of Fc-monomer **4** and Fc-model compound **5**, the results are summarized in Table 3. The Cyclic voltammetric behaviour of these compounds showed one cathodic peak and the corresponding oxidation peak in the potential range of 250–650 mV at the glassy carbon electrode. The separation of the anodic and the cathodic peak potentials, ΔE_p , were 188, 134, 170, 37, 164, 164, and 164 mV at 20 mVs⁻¹ for Fc-monomer **4**, Fc-model **5**, and Fc-polyazomethines **6a–e**, respectively. These values are larger than that expected for a reversible two-electron transfer reaction, which is given by $57/z$ mV, where z is the number of electrons transferred in the process [39], indicating that the irreversibility of the electron-transfer process was maintained under this condition. The formal potential, E^0 , taken as the average of E_{pc} and E_{pa} were 343, 413, 443, 401, 385, 385, and 428 mV for Fc-monomer **4**, Fc-model **5**, and Fc-polyazomethines **6a–e**, respectively. E^0 shifted to more positive potentials by ca. 100 mV for Fc-polyazomethine **6d** in comparing to Fc-monomer **4**. This revealed that the reduction of Fc-polyazomethine **6d** becomes more easily at the glassy carbon electrode. One couple of redox waves is observed clearly in the cyclic voltammograms for all compounds in the potential range ca. 0.00–1.50 V. The couple redox waves in the potential range ca. 240–530 mV is due to the redox process of ferrocene/ferrocenium⁺ system. Also, there is another anodic wave for all compounds in potential range 540–650 mV, this is due to the conjugation through the conjugated aromatic system. The second anodic wave did not appear in the case of Fc-polyazomethines **6b** and **c**, due to the increasing of methyl spacer which cut the conjugation through the conjugated aromatic system, on the other hand in case of Fc-polyazomethine **6e** this anodic wave increased because of the presence of ether aromatic linkage and the lone pairs of electron relay the conjugation through the conjugated aromatic system.

4. Conclusion

In this research a new interesting series of thermally stable Fc-polyazomethines **6a–e** was synthesized via polycondensation reactions of ferrocene-dialdehyde derivative with different diamines. The ferrocene-dialdehyde was prepared through

three- step reactions. Ferrocene was converted to ferrocene-diester derivative through Gomberg's arylation reaction. Reduction of ferrocene-diester derivative using LAH converted it to ferrocene-dialcohol derivative. The latter was oxidized with activated MnO_2 in dry CHCl_3 to get the ferrocene-dialdehyde derivative. The thermal behaviour of these new Fe-polyazomethines showed that the polymer decomposition temperature (PDT) of them did not start before 340°C except for Fe-polyazomethine **6a** at 140°C , which indicated that these new Fe-polyazomethines are thermally-stable till high temperature. Also, the electrochemical properties of these new Fe-polyazomethines were studied in comparison with both Fc-monomer **4** and Fc-model **5** by CV. SEM study of Fe-polyazomethines **6b** indicated that its surface possesses a globular structure and for Fe-polyazomethines **6d** the surface possesses a globular structure with some coalescence present. The research team is interested in modifying the chemical structure of these polymers aiming to improve their chemical and physical properties. This work is presently in progress.

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