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Synthesis and physicochemical studies of ferrocene-containing materials

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Low-temperature solution-phase polycondensation of 1,1′-ferrocenedicarboxylic acid chloride with newly synthesized aromatic diamines was carried out in tetrahydrofuran in the presence of triethylamine to form several new organometallic aromatic polyamides containing ferrocene units. The organometallic aromatic polyamides derived were in good yields ranging from 75 to 80%, amorphous with melting temperatures of >350 °C. The monomers and the resulting polymers were characterized by their physical properties, elemental analysis, ^{1}H NMR and FTIR spectroscopy. The differential scanning calorimetry and thermogravimetric studies of the resulting aramids were also carried out. All the polymers were insoluble in common organic solvents. However, all dissolved in concentrated H_2SO_4 forming reddish brown solutions. Their glass transition temperatures were quite high, which is characteristic of aramids. They were also stable up to 450 °C with 10% mass losses (14–23%) recorded in the range 400–470 °C. The activation energies for decomposition of each aramid were also calculated using the Horowitz and Metzger method. All polymers showed reduced solution viscosities in concentrated sulphuric acid, which may be attributed to non-Newtonian behavior.

KEYWORDS: ferrocene; organometallic aramids; polyamides

INTRODUCTION

Aromatic polyamides also known as ‘aramids’ are based on aromatic diamines[1] and characterized as very high temperature resistant materials with a favorable balance of other physical and chemical properties.[2] Recently, many studies[3–6] have focused on introducing ether-containing and bulky pendant groups along the aramid backbone to minimize the tradeoff between the processability and properties. The introduction of ether linkages enhances the processability and toughness without a significant reduction in thermal stability. The incorporation of a bulky pendant group decreases interchain hydrogen bonding interactions and generally disturbs the co-planarity of aromatic units to reduce packing densities and crystallinity. This should enhance solubility and maintain high glass-transition temperatures (T_g) through controlled segmental mobility.[7]

Ferrocene, among organometallic compounds, is the most promising candidate for incorporation of metal into polymer structures due to its well-characterized redox behavior and excellent photochemical and thermal stability.[8–12] Ferrocene polymers are useful for several applications, e.g. manufacture of electronic devices like microelectrochemical diodes,[13] formation of redox gels that show charge transfer properties,[14] modification of electrodes,[15] construction of amperometric biosensors[16] and more recently in the area of non-linear optical (NLO) materials.[17]

In a continuation of our previous work,[18] we report here the effects of different amines with ferrocene into the aramid backbone using low-temperature solution polycondensation. We have synthesized three new aromatic diamines having flexible ether linkages along with sterically bulky groups to determine the effects of chain flexibility and bulkiness of the side groups on the basic properties of these organometallic aramids. Solubilities in common organic solvents, thermal stability and thermal degradation kinetics were studied, along with elemental and Fourier transform IR (FTIR) spectroscopic characterization. Solubility

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behavior in concentrated sulfuric acid was also studied, in which the products were found to form red-colored solutions.

EXPERIMENTAL

Materials

All chemicals and reagents used were of highest purity. Ferrocene, aluminum chloride, potassium carbonate, 2,6-dihydroxytoluene, bisphenol-A, 4,4′dihydroxybiphenyl and *p*-nitrochlorobenzene were purchased from Fluka, Switzerland and used as received. Hydrazine and thionyl chloride were obtained from Merck, Germany. Sodium hypochlorite was obtained from a commercial source and the strength was determined before use. Solvents (dichloromethane, chloroform, *n*-hexane, acetone, ethanol, diethyl ether and methanol) were obtained from Merck, Germany, ethyl acetate from Fluka, Switzerland and tetrahydrofuran (THF) from Riedel-deHaën, Germany, and were freshly distilled and dried as required.[19]

The organic monomers were synthesized in the laboratory and purified in ethanol. Unless stated otherwise, all the manipulations were conducted under vacuum conditions in dry He/N_2. The purity of the products was monitored by thin-layer chromatography using pre-coated TLC plates.

Measurements

Elemental analyses

Elemental, C, H, N analyses were carried out on an Elementar Model Vario-EL (Germany). Melting temperatures of the starting materials and the polymers were determined on a Mel-Temp, Mitamura Riken Kogyo Inc., Tokyo, Japan, using open capillary tubes.

^{1}H-NMR analyses

^{1}H-NMR spectra were measured on Bruker Spectrometer operating at 250 MHz in DMSO-d_6 using tetramethylsilane as an internal reference.

FTIR analyses

The solid-state Fourier transform infrared spectra (KBr pellets, 4000–400 cm^{-1}) were recorded on BioRad Excalibur FTIR Model FTS 3000 MX.

Thermogravimetric analyses

Thermogravimetric (TG) measurements were conducted using a Perkin Elmer TGA 7 thermo balance at a heating rate of 20 °C/min in a nitrogen atmosphere with a hold for 1 min at 50 °C.

DSC analyses

DSC curves were recorded at a heating rate of 20 °C/min in nitrogen with sapphire as standard, on a differential scanning calorimeter, Perkin Elmer models DSC 7 and DSC 404C.

Viscometry

Viscosimetric studies in concentrated H_2SO_4 were carried out with the help of a U-tube (Ostwald's) viscometer having 1 mm capillary tube, at 25.0 ± 0.1 °C.

MONOMER SYNTHESIS

Preparation of ferrocene monomers

1,1′-ferrocenedicarboxylic acid (FcDA) was synthesized from ferrocene according to a published procedure.[20,21] Ferrocenedicarbonyl chloride (FcDAC) was prepared using thionyl chloride as chlorinating agent in dichloromethane with triethylamine as catalyst.[22]

Synthesis of aromatic monomers (diamines)

General procedure

Step 1: A mixture of the corresponding aromatic diol, anhydrous K_2CO_3 and *p*-nitrochlorobenzene in (1 : 2:2) molar ratio in 70 ml of DMF was heated at 120 °C for 12 h under nitrogen atmosphere. The color of the solution was changed as the reaction proceeded. After cooling to room temperature the reaction mixture was poured into 500 ml of water to form colored precipitates, which were washed thoroughly with water and then collected by filtration. The crude product was recrystallized from ethanol and the purity was tested by TLC using hexane, ethylacetate and methanol in 8 : 2:1 ratio. The products were characterized by their melting point, physical state, color, solubility, FT-IR spectroscopy and elemental analyses.

Step 2: A two-neck flask was charged with the dinitro-specie prepared in the previous step, 10 ml of hydrazine monohydrate, 80 ml ethanol and 0.1 g of 5% palladium on carbon (Pd–C). The mixture was refluxed for 24 h and then filtered to remove the Pd–C catalyst. The filtrate was concentrated on a rotatory vacuum evaporator; the solid colored precipitates were then recrystallized from ethanol and purity was tested by the solvent system as above. The products were characterized by their melting point, physical state, color, solubility, FT-IR, ^{1}H NMR spectroscopy and elemental analyses.

Preparation of 2,6-di (4-aminophenyloxy) toluene (A)

The general procedure was followed using a mixture of 2 g (0.016 mol) 2,6-dihydroxytoluene, 2.25 g (0.032 mol) anhydrous K_2CO_3 and 2.53 g (0.032 mol) *p*-nitrochlorobenzene. The color of the solution was changed from dark brown to greenish black as the reaction proceeded and the product was isolated as a yellow solid. Yield 83%, m.p. 125 °C. Elemental analyses for $C_{19}H_{14}N_2O_6$ (MW = 366) in wt% calculated: C = 62.32, H = 3.82, N = 7.65; and found C = 62.15,

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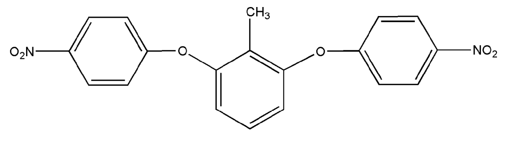


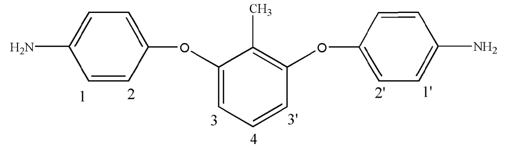
Scheme 1. 2,6-Di-(4-nitrophenyloxy) toluene (a).

H = 3.75, N = 7.40, IR (KBr pellet) in cm^{-1}: 1538, 1325 (NO_2), 1251 (C –O –C), and 1454, 1365 (CH_3 st).

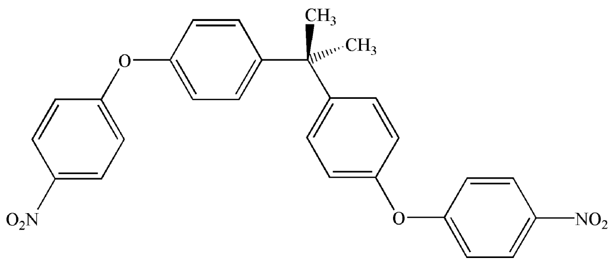
The reduction was carried out following step 2 of the general procedure using 2,6-di (4-nitrophenyloxy) toluene (a), 2 g (0.005 mol), and 10 ml of hydrazine monohydrate, 80 ml ethanol and 0.1 g of 5% palladium on carbon (Pd–C). The solid dark brown-colored precipitates were recrystallized from ethanol. Yield 80%, m.p. 148 °C. Elemental analyses for $C_{19}H_{18}N_2O_2$ (MW = 306) in wt% calculated: C = 74.54 H = 5.88, N = 9.15; and found: C = 74.21, H = 5.65, N = 8.97; IR (KBr pellet) in cm^{-1}: 3377, 3333 (NH_2 st), 1632 (NH_2 bend) 1323 (aromatic CN st), 1232 (C –O –C st) and 1461, 1370 (CH_3 st). ^{1}H-NMR (DMSO-d$_6$) in δ (ppm) and J (Hz): 2.15 (3H, s, CH_3), 3.39 (4H, s, NH_2), 6.41 (4H, d, $J_1 = J_{1'} = 8.20$), 6.54 (4H, d, $J_2 = J_{2'} = 6.76$), 6.74 (2H, dd, $J_3 = J_{3'} = 8.72$), 6.87 (1H, t, $J_4 = J_{3,3'} = 8.17$).

2,2′-Di-[4-(4-aminophenyloxy) phenyl] propane (B)

The general procedure was followed using a mixture of 5 g (0.0219 mol) bisphenol-A, 6.5 g (0.0438 mol) anhydrous K_2CO_3 and 6.9 g (0.0438 mol) *p*-nitrochlorobenzene in 70 ml of DMF. The color of the solution changed from white to yellow as the reaction proceeded. Yellow precipitates obtained were washed thoroughly with water and collected by filtration and recrystallized from ethanol. Yield 81%, m.p. 92 °C. Elemental analyses for $C_{27}H_{22}N_2O_6$ (MW = 470) in wt% calculated: C = 69.00, H = 4.68, N = 5.95; and found C = 69.45, H = 4.65, N = 6.05; IR (KBr pellet) in cm^{-1}: 1568, 1335 (NO_2), 1235 (C –O –C), and 1434, 1385 (CH_3 st).



Scheme 2. 2,6-Di-(4-aminophenyloxy) toluene (A).



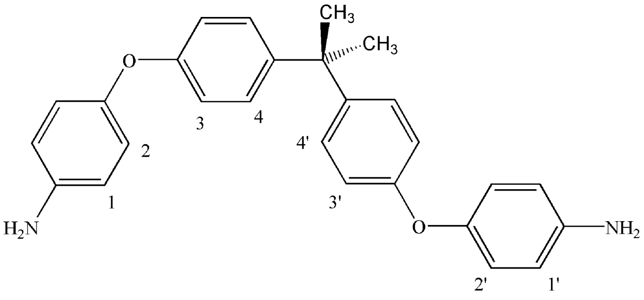
Scheme 3. 2,2′-Di-[4-(4-nitrophenyloxy) phenyl] - propane (b).

Step 2 of general procedure was followed using 2,2′-di-[4-(4-nitrophenyloxy) phenyl] propane (b) 2 g (0.004 mol), 10 ml of hydrazine monohydrate, 80 ml ethanol and 0.1 g of 5% palladium on carbon (Pd–C). The solid pale yellow colored precipitates formed were then recrystallized from ethanol. Yield 78%, m.p. 78 °C. Elemental analyses for $C_{27}H_{26}N_2O_2$ (MW = 410) in wt% calculated: C = 78.60 H = 6.79, N = 6.79; and found C = 77.90, H = 6.77, N = 6.75; IR (KBr pellet) in cm^{-1}: 3335, 3343 (NH_2 st), 1611 (NH_2 bend), 1342 (aromatic CN st), 1224 (C –O –C st), and 1358, 1342 (CH_3 st). ^{1}H-NMR (DMSO-d$_6$) in δ (ppm) and J (Hz): 1.56 (6H, s, CH_3), 3.59 (4H, s, NH_2), 6.76 (4H, dd, $J_1 = J_{1'} = 8.73$), 7.03 (4H, dd, $J_{2,3} = J_{2',3'} = 8.34$), 6.58 (4H, d, $J_4 = J_{4'} = 8.23$).

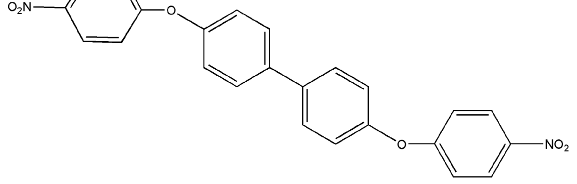
4,4′ -di (4-aminophenyloxy) biphenyl (C)

The general procedure was followed using 3 g (0.0161 mol) of 4,4′-dihydroxybiphenyl, 4.76 g (0.0322 mol) anhydrous K_2CO_3 and 5.08 g (0.0322 mol) *p*-nitrochlorobenzene in 70 ml of DMF. The initial color of the solution changed from white to greenish white as the reaction proceeded and the greenish white precipitates obtained were washed thoroughly with water, filtered and recrystallized from ethanol. Yield 80%, decomposition temperature >200 °C. Elemental analyses for $C_{24}H_{16}N_2O_6$ (MW = 428) in wt% calculated: C = 67.25, H = 3.73, N = 6.54; and found C = 68.05, H = 3.65, N = 6.35, IR (KBr pellet) in cm^{-1}: 1557, 1328 (NO_2), 1264 (C –O –C).

The step 2 of general procedure was followed using 4,4′ -di-[(4-nitrophenyloxy] biphenyl (c) 2 g (0.0045 mol), 10 ml of hydrazine monohydrate, 80 ml ethanol and 0.1 g of 5%



Scheme 4. 2,2′-Di-[4-(4-aminophenyloxy)phenyl]- propane (B).



Scheme 5. 4,4′-Di-(4-nitrophenyloxy) biphenyl (c).

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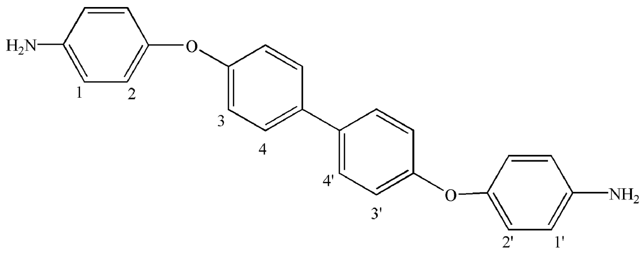

Scheme 6. 4,4′-Di-(4-aminophenyloxy) biphenyl (C).

palladium on carbon (Pd–C). The solid greenish white colored precipitates obtained were filtered and recrystallized from ethanol. Yield 76%, decomposing temperature >200 °C. Elemental analyses for $C_{24}H_{20}N_2O_2$ (MW = 368) in wt% calculated: C = 78.26 H = 5.43, N = 7.60; and found C = 78.15, H = 5.21, N = 7.23, IR (KBr pellet) in cm^{-1}: 3369, 3305 (NH_2 st), 1605 (NH_2 bend), 1313 (aromatic CN st) and 1235 (C –O –C st).^{1}H-NMR (DMSO-d_6) in δ (ppm) and J (Hz): 3.53 (4H, s, NH_2), 6.60 (4H, d, $J_1 = J_{1'} = 8.40$), 6.80 (4H, d, $J_2 = J_{2'} = 7.16$), 6.86 (4H, d, $J_3 = J_{3'} = 7.20$), 7.35 (2H, d, $J_4 = J_{4''} = 8.29$).

Polymer synthesis

Low-temperature solution polycondensation[23–27] was the general method used to prepare all aramids.

General procedure

In a two-necked flask (baked in vacuum to exclude moisture) equipped with a condenser and magnetic stirrer, 0.0016 mol of diamine was dissolved in 10 ml of hot THF (freshly dried and distilled) and treated with 10 ml of triethylamine. The temperature was lowered to 0 °C with an ice bath; 0.0016 mol of 1,1′-ferrocenedicarboxylic acid chloride dissolved in dry THF was then added drop-wise with vigorous stirring. The temperature was raised to room temperature slowly and the reaction mixture was stirred for an additional 4–5 h. The reaction mixture was filtered and the precipitates obtained were washed with methanol several times and then with THF and methanol to obtain the polymer, which was then vacuum dried for 24 h.

RESULTS AND DISCUSSION

Synthesis of ferrocene monomers

Ferrocene monomer (1,1′-ferrocenedicarboxylic acid chloride) was prepared in three steps starting from ferrocene using reported methods[20–22] (Fig. 1).

Synthesis of aromatic monomers (diamines)

The three new diamines (A, B and C) were synthesized in two steps according to a well-developed method,[28,29] as shown in Fig. 2. The first step was a Williamsons etherification of aromatic diols with *p*-nitrochlorobenzene in the presence of anhydrous K_2CO_3 in DMF. The diamines were readily obtained in high yields by the catalytic reduction of intermediate dinitro compounds (a–c) with hydrazine hydrate and Pd–C catalyst in refluxing ethanol. The structures of these monomers were confirmed by FTIR, ^{1}H-NMR and elemental analysis. The FTIR spectra of dinitro compounds exhibited the absorption bands representative of the nitro functionality which were identified in the 1538–1568 and 1328–1365 cm^{-1} regions (NO_2 symmetric and asymmetric stretches, see above). After reduction, the characteristic absorptions of dinitro groups disappeared and the amine group showed typical stretching bands in the region 3300–3380 cm^{-1}. The ^{1}H-NMR spectra confirm that the nitro compounds were converted to amine groups by the signal in the 3.39–3.59 ppm region corresponding to the primary aromatic amine protons. The elemental analyses of the monomers were close to calculated values and all NMR peaks could be assigned.

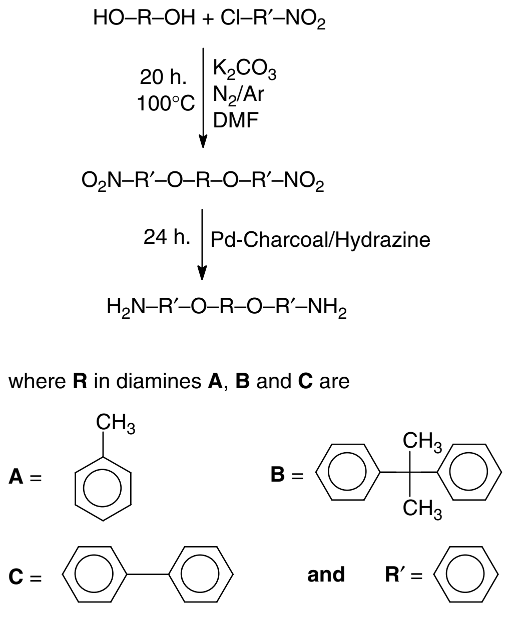

Figure 2. Synthesis of organic diamines.

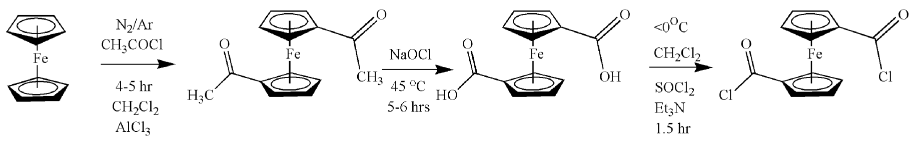

Figure 1. Synthesis of ferrocene monomers.

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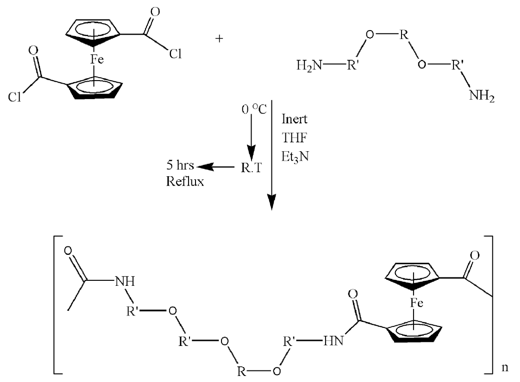

Figure 3. Synthesis of organometallic aromatic polyamides.

Polymer synthesis

The most widely used method for preparing aramids is low-temperature condensation of the diamine with the diacid chloride. This method was used to avoid detrimental side reactions associated with high-temperature organometallic condensation polymerizations.[23–27] The reaction of FcDA acid chloride with different aromatic diamines in THF as solvent with Et_3N as proton acceptor afforded aromatic polyamides (Fig. 3), which are labeled in Fig. 1.

Characterization

The stoichiometry and structure of the synthesized aramids were confirmed by their CHN and FTIR studies; the data are given in Tables 1 and 2, respectively. The percentages found for C, H and N are in good agreement with those calculated based on the structure of the repeat units. The IR spectra of all these aramids contain the bands characteristic of polyamides[30] together with those of ferrocenyl and phenylene groups that are present in the polymer backbone. All exhibit characteristic IR absorption bands of the amide groups appearing at 3410 (N –H stretching), 1638 (C =O stretching) and 1400 cm^{-1} (C =N bending) in aramid FP-A, 3247, 1600 and 1404 cm^{-1} in FP-B, and 3280, 1632, and 1410 cm^{-1} in FP-C, respectively, along with the characteristic bands of medium intensity due to Fe =Cp ring stretching, around 450–490 cm^{-1}.

Solubility

The solubility of the aramids was tested qualitatively in the solvents with poor to strong hydrogen bonding. It was found that only concentrated H_2SO_4 will solubilize all the polymers, forming dark brown colored solutions, probably due to strong hydrogen bonding. The presence of flexible units like –O–in the backbone helps to enhance the solubility of polymers,[31] but in all cases this group does not show any improvement in solubility except in concentrated H_2SO_4,27 from which the polymer can be reprecipitated with water and methanol. The polyamides have intermolecular hydrogen bonding and high polarity, which are mainly responsible for their limited solubility.[1,32–36] It is believed that concentrated H_2SO_4 also protonates the nitrogen of the amide bond to overcome hydrogen bonding forces, thus solubilizing the aramids.[1,37]

Table 2. FTIR analyses for the synthesized aramids (cm^{-1})

Band assignments	FP-A	FP-B	FP-C
C =O st	1638 s	1600 s	1632 s
N –H st	3410 m, b	3247 m, b	3280 m, b
C –N st	1400 s	1404 s	1410 s
C –O –C st	1209 s	1250 s	1230 s
Fe –Cp st	474 m	461 m	450 m

s = Sharp; m = medium; b = broad.

Thermal analysis

The thermal stability of the synthesized aramids was evaluated using DSC and TGA. Selected thermal properties are listed in Table 3. The chain stiffness of the polymer is characterized by its glass transition temperature (T_g) obtained from the DSC curves. All values are high and characteristic of the aromatic polyamides.

The T_g values for the polymers FP-B and FP-C containing rigid phenyl groups were higher when compared with that for FP-A. The reason might be the presence of rigid bulky groups and higher molecular weight of the polymers FP-B and FP-C as compared with polymers FP-A, a fact supported by the literature.[38]

The decomposition temperature (10% mass loss) was 450 °C for polymer FP-A, 470 °C for polymer FP-B and 450 °C for polymer FP-C. These values are low for polymers with flexible linkage and high for polymers containing stiff linkages, and are comparable with literature values for organic aramids.[39–41]

Table 1. CHN Analysis for synthesized aramids

			Calculated %			Found %		
Aramid	Yield[a]	Formula	C	H	N	C	H	N
FP-A	87%	$[C_{31}H_{24}N_2O_4Fe]_n$	68.38	4.41	5.14	68.19	4.28	5.05
FP-B	80%	$[C_{39}H_{32}N_2O_4Fe]_n$	72.22	4.93	4.32	72.03	4.85	4.23
FP-C	78%	$[C_{36}H_{26}N_2O_4Fe]_n$	71.28	4.29	4.62	70.95	4.42	4.32

[a] Elemental percentages are calculated based on the structure of the repeat unit. Yields are calculated based on the structure of the repeat units.

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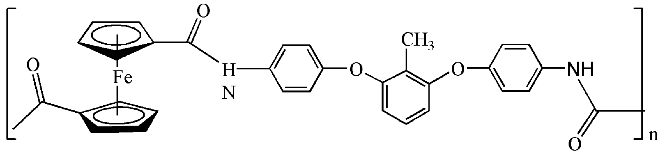
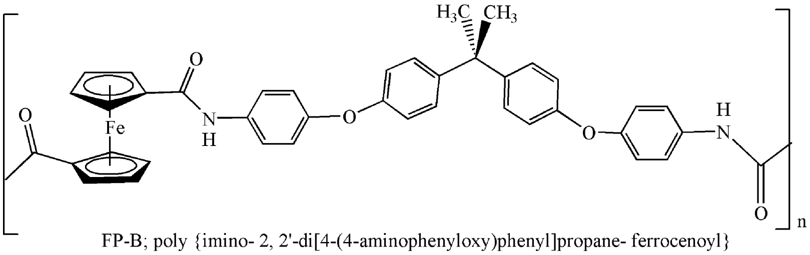
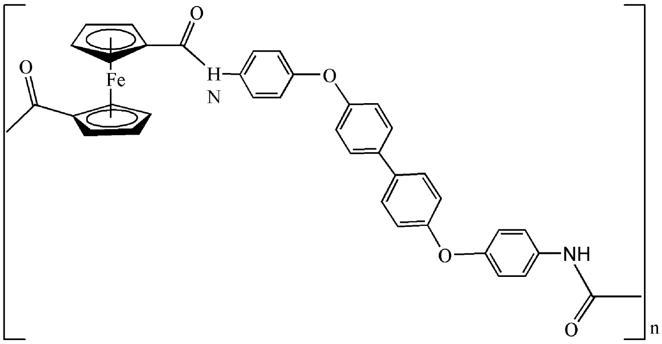


FP-A; poly {imino-2, 6-di [(4-aminophenyl) oxy] toluene-ferrocenoyl}



FP-B; poly {imino- 2, 2'-di[4-(4-aminophenyloxy)phenyl]propane- ferrocenoyl}



FP-C; poly (imino- 4, 4'-di [(4-aminophenyl) oxy] biphenyl-ferrocenoyl}

Figure 4. Ferrocene containing aramids prepared by solution polycondensation from corresponding diamines.

Table 3. Thermal properties of aramids

Aramids	T_g (°C)	T_{10} (°C)	T_f (°C)	E^* (kJ mol^{-1})	Weight loss(%)
Fp-A	365	449	661	84	14
FP-B	418	470	600	81	14
FP-C	386	450	600	89	23

All values were estimated from T_g curves except T_g, which was obtained as maxima at onset temperature from DSC curves. T_g = glass transition temperature; T_{10} = temperature at 10% weight loss;T_f = final temperature (at the end of curve); E^* = activation energy of pyrolysis (obtained by Horowitz & Metzger method.

The thermal degradation kinetic data for the polymers were calculated from TGA curves and the activation energies for pyrolysis were obtained from that data using the Horowitz and Metzger method.[42] The thermal degradation of polyamides in the absence of oxygen is believed to involve direct cleavage of the amino C –N bond. The activation energies calculated here fall into the range 80–90 kJmol^{-1}, which is slightly higher compared with the calculated values for organic aramids, i.e. 61–71 kJ mol^{-1},[43] which indicates that the ferrocene-containing aramids are thermally more stable as compared to the organic aramids.

Viscosity behavior

The synthesized polymers were found to be insoluble in almost all the solvents tested except concentrated H_2SO_4, which is widely used as a solvent in molecular weight determinations of aramids. The relative viscosities of the aramid solutions in concentrated H_2SO_4 were lower than unity. This may be attributed to the increase in shear rates of these polymers due to the decrease in their intramolecular cross-linking in concentrated H_2SO_4, thus decreasing the viscosities of the aramid solutions as mentioned in the literature.[44–46] Such a decrease in viscosity and increase in shear rate is known as *non-Newtonian behavior*[44–46] of the polymer molecules, which indicates high molecular weight of the polymer and the presence of long rod-like molecules that become oriented by the flow so that they slide past each other more freely. The probability of degradation of aramid molecules in concentrated H_2SO_4 was ruled out on the basis of the similarity of IR spectra of the reprecipitated products with the original ones. The viscometric data is given in Table 4.

CONCLUSION

Ferrocene-containing aromatic polyamides (aramids) were synthesized from 1,1′- ferrocenedicarboxylic acid chloride

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Table 4. Viscometric data of the polymers in concentrated H_2SO_4

Aramids	η_{rel}	η_{sp}	η_{red}	η_{inh}
Fp-A	0.93	−0.07	−0.27	−0.28
FP-B	0.97	−0.03	−0.13	−0.14
FP-C	0.90	−0.09	−0.37	−0.40

η_{rel}, relative viscosity ≈ time of flow for solution/time of flow for solvent; η_{sp}, specific viscosity = $\eta_{rel} - 1$; η_{red}, reduced viscosity = η_{sp}/c; η_{inh}, inherent viscosity = $(\ln \eta_{rel.})/c$.

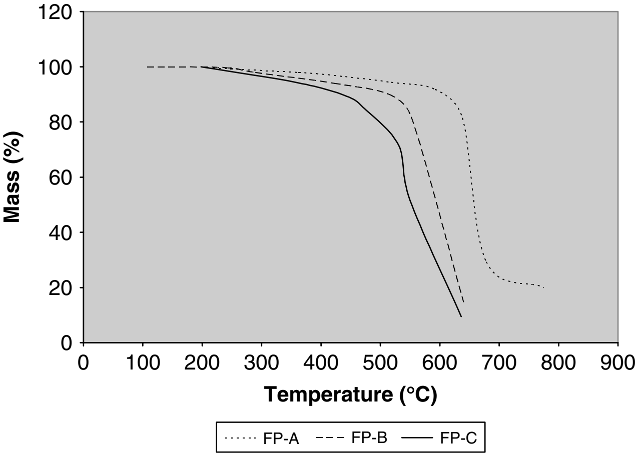

Figure 5. T_g curves of the synthesized aramids in nitrogen.

and newly synthesized aromatic diamines employing low-temperature solution phase polycondensation methods in continuation of our previous work.[39–41] It was expected that the resulting polymers would be soluble in some of the common organic solvents and have much higher T_g values as these have flexible ether linkages with sterically bulky groups. Unfortunately, however, they were also insoluble in the common organic solvents, yet they have improved thermal properties. The thermal analyses also provided clues to their polymeric nature. The high T_g values determined from DSC curves are characteristic of the aromatic polyamides. The molecular weights of these aramids could not be determined due to their insolubility in every common organic solvent, although their inherent viscosities were measured in concentrated H_2SO_4.

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