APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 344–350

(www.interscience.wiley.com) DOI:10.1002/aoc.1061

Synthesis and characterization of some novel organometallic aromatic polyamides

Naseer Iqbal, Zareen Akhter*, M. Adnan Saeed and Muhammad Saif ullah Khan

Department of Chemistry, Quiad-i-Azam University, Islamabad-45320, Pakistan

Received 11 February 2006; Revised 13 February 2006; Accepted 22 February 2006

Some novel ferrocene containing aromatic polyamides were prepared by low-temperature solution phase polycondensation of 1,1′-ferrocenedicarboxylic acid chloride with some newly synthesized aromatic diamines in tetrahydrofuran, in the presence of triethylamine. The amorphous polymers were derived in good yields, and did not melt at >350 °C. The monomers and the resulting polymers were characterized by their physical properties, elemental analysis, ^{1}H-NMR, FTIR spectroscopy, differential scanning calorimetry and thermogravimetric analyses. The polymeric products were insoluble in common solvents tested. However, all were miscible in concentrated H_2SO_4, forming reddish brown solutions at ambient conditions. The glass transition temperatures (T_g) of these polymers were quite high, which is characteristic of aramids. They are stable up to 500 °C, with 10% mass loss observed in the range 400–650 °C. The activation energies of pyrolysis for each of the products were calculated by Horowitz and Metzger's method. Solution viscosities of the polymers were reduced in concentrated sulfuric acid, which is due to their non-Newtonian behavior.

KEYWORDS: ferrocene; aramids; organometallic aramids; polyamides

INTRODUCTION

Aromatic polyamides based on aromatic diamines[1] are the oldest high-temperature materials, offering a favorable balance of physical and chemical properties.[2]

Ferrocene, among organometallic compounds, is an excellent candidate for incorporation of metal into polymer backbones. Ferrocene-containing polymers and copolymers are commercially important owing to their redox, electrical, conducting/semi-conducting, optical, magnetic, catalytic, preceramic and elastomeric properties.[3–5] These properties arise due to their unusual conformational, mechanical and morphological characteristics and show their well-characterized redox behavior and superb photochemical and thermal stability.[3–7] The ferrocene polymers are also useful for electrosynthesis, electrocatalysis, ferromagnetic ceramics (iron silicon carbide ceramics), including super paramagnetic nano-structures, magnetic nano-wires with silicon carbide coatings and self-insulating semiconducting nanowires.[8,9] These have been reported in several different electronic devices like microelectrochemical diodes,[10] amperometric enzyme electrodes,[11] NADH and NADPH sensors and more lately also in nonlinear optical (NLO) materials.[12] Some ferrocene polymers have been used as polymerization initiators, for example, in the polymerization of some *p*-halogenated chloroformylated vinyl monomers.[12]

In the context of our previous research[13] low-temperature solution polycondensation techniques were followed to study the effect of different amines on aramid backbone. We have synthesized here aromatic diamines of comparatively rigid to flexible and sterically bulky natures to identify the effects of chain flexibility and bulkiness on the basic properties of the resulting organometallic aramids.

EXPERIMENTAL

Materials

All chemicals and reagents used were of highest purity or purified as described. Ferrocene, aluminum chloride, potassium carbonate, 2,6-dihydroxytoluene, bisphenol-A, 4,4′dihydroxybiphenyl and *p*-nitrobenzylchloride were purchased from Fluka, Switzerland and used as received. Hydrazine

---

*Correspondence to: Zareen Akhter, Department of Chemistry, Quaid-I-Azam University, Islamabad-45320, Pakistan.
E-mail: zareenakhter@yahoo.com
Contract/grant sponsor: Quaid-i-Azam University.

and thionyl chloride were obtained from Merck, Germany. Sodium hypochlorite was obtained from a commercial source and its strength was determined before use by titrating it against potassium iodide. Solvents were obtained from Merck, Germany (dichloromethane, chloroform, *n*-hexane, acetone, ethanol, diethyl ether and methanol); Fluka, Switzerland (ethyl acetate) and Riedel-deHaën, Germany (tetrahydrofuran, THF), freshly distilled and dried as required.

Measurements

Spectroscopy

The solid state Fourier Transform infrared spectra of the synthesized monomers and polymers (KBr pellets, 4000–400 cm^{-1}) were recorded on a Bio-Rad Excalibur FTIR model FTS 3000 MX.

^{1}H-NMR spectroscopy

All ^{1}H-NMR spectra were performed in DMSO-d_6 and recorded on a Bruker 250 MHz. Tetramethylsilane was used as an internal reference.

Elemental analyses

Elemental, C, H, N analyses of the synthesized products were carried out on Elementar Model Vario-EL, Germany.

Melting point determination

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.

Thermogravimetric analyses

Thermogravimetric (TG) measurements were conducted using a Perkin Elmer TGA 7 thermobalance at a heating rate of 20 °C/min in a nitrogen atmosphere with a hold for 1 min at 50 °C. DSC curves were recorded at a heating rate of 20 °C/min in nitrogen with α alumina as a standard, on a differential scanning calorimeter, Perkin Elmer models DSC 7 and DSC 404C.

Viscosimetric analyses

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

SYNTHETIC METHODOLOGY

Synthesis of ferrocene monomers

Ferrocene monomer (1,1′-ferrocenedicarboxylic acid (FcDAC)[14,15] was synthesized from ferrocene using thionyl chloride in dichloromethane with triethylamine as catalyst (Fig. 1).

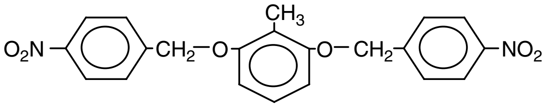
Syntheses of aromatic monomers (diamines)

The aromatic diamines were synthesized from different aromatic diols in two steps (Fig. 1). In the first step, the dinitro species were formed using the corresponding aromatic diols, anhydrous K_2CO_3 and *p*-nitrobenzylchloride in a 1 : 2 : 2 ratio. In the second step these dinitro products were reduced to the diamines using hydrazine monohydrate and 5% palladium on carbon (Pd–C).

2,6-di[(4-Aminophenyl) methyloxy] toluene (A)

2, 6-di [(4-nitrophenyl) methyloxy] toluene (a)

A mixture of 2,6-dihydroxytoluene 2 g (0.016 mol), anhydrous K_2CO_3 2.25 g (0.032 mol) and *p*-nitrobenzylchloride 5.5 g (0.032 mol) in 70 ml DMF was heated at 120 °C for 12 h under nitrogen atmosphere. The color of the solution changed from dark brown to dark red as the reaction proceeded. After cooling to room temperature, the reaction mixture was poured into 500 ml water to form a red colored precipitate which was filtered, washed thoroughly with water and recrystallized from ethanol. The purity was tested by TLC using hexane, ethylacetate and methanol in an 8 : 2 : 1 ratio; yield 81%, m.p. 154 °C. Elemental analysis for $C_{21}H_{18}N_2O_6$ (MW = 394) in wt%: calculated, C = 64.00, H = 4.56, N = 7.10; found, C = 64.61, H = 4.23, N = 6.95; IR (KBr pellet) in cm^{-1}, 1547, 1328 υ (N=O st), 1241 υ (C–O–C st), 750 ρ (C–H bend) and 3333 υ (C–H st).



2,6-di[(4-Aminophenyl) methyloxy] toluene (A)

A mixture of 2,6-di[(4-nitrophenyl)methyloxy]toluene (a) 2 g (0.005 mol), hydrazine monohydrate (10 ml), ethanol (80 ml) and 0.1 g of 5% palladium on carbon (Pd–C) was refluxed for 24 h and then filtered to remove the Pd–C. The filtrate was concentrated on a rotatory vacuum

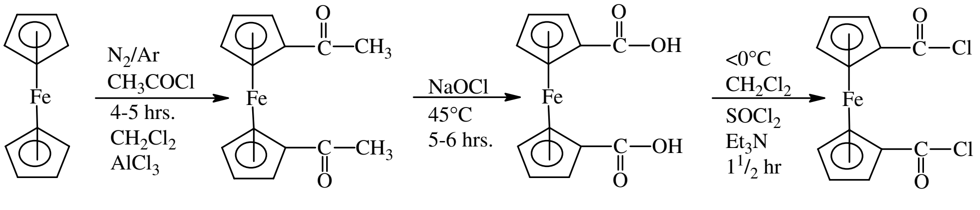
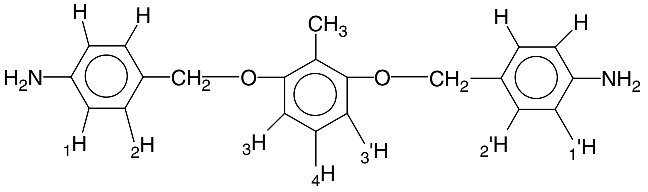


Figure 1. Synthesis of ferrocene monomers.

DOI: 10.1002/aoc

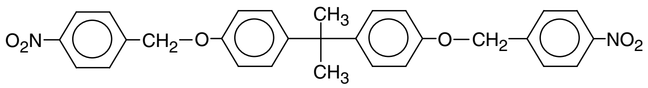
evaporator. The solid, dark-red colored precipitates were then recrystallized from ethanol, and purity was tested as above; yield 75%, m.p. 184 °C. Elemental analysis for $C_{21}H_{22}N_2O_2$ (MW = 334) in wt%: calculated, C = 75.45 H = 6.58, N = 8.34; found C = 71.45, H = 5.97, N = 7.62; IR (KBr pellet) in cm^{-1}, 3362, 3215 υ (N–H st), 1607 δ (N–H bend), 1283 υ (C–N st), 1241 υ (C–O–C st), 754 ρ (C–H bend) and 3362 υ (C–H st). ^{1}H-NMR (DMSO-d_6) in δ (ppm) and J(Hz): 3.66 (4H, s, NH_2), 2.07 (3H, s, CH_3), 5.03 (4H, s, CH_2), 6.49 (4H, d, $J_1 = J_{1'} = 8.79$), 6.56 (4H, d, $J_2 = J_{2'} = 7.14$), 6.69 (2H, dd, $J_3 = J_{3'} = 8.71$), 7.12 (1H, t, $J_4 = J_{3,3'} = 8.27$).



2,2′-di{4-[(4-aminophenyl) methyloxy] phenyl} propane (B)

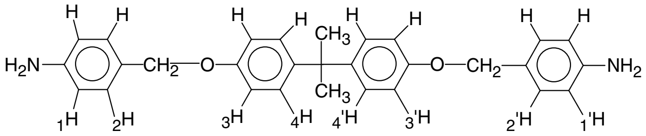
2,2′-di{4-[(4-nitrophenyl) methyloxy] phenyl} propane (b)

Bisphenol-A, 2 g (0.0087 mol) was mixed with 2.5 g (0.0165 mol) of anhydrous K_2CO_3 and 3 g (0.0165 mol) of *p*-nitrobenzylchloride in 70 ml DMF. The color of the solution changed from white to brown as the reaction proceeded. The light brown precipitates were washed thoroughly with water and collected by filtration. The crude product was recrystallized from ethanol; Yield 76%, m.p. 108 °C. Elemental analysis for $C_{29}H_{26}N_2O_6$ (MW = 498) in wt%: calculated, C = 70.00, H = 5.22, N = 5.62; found, C = 69.12, H = 5.08, N = 5.18; IR (KBr pellet) in cm^{-1}, 1527, 1338 υ (N=O st), 1234 υ (C–O–C st), 749 ρ (C–H bend) and 3065 υ (C–H st).



2,2′-di{4-[(4-aminophenyl) methyloxy] phenyl} propane (B)

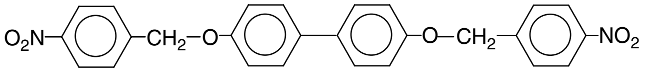
The second step of the general procedure was followed using 2 g (0.004 mol) of 2,2″-di{4-[(4-nitrophenyl) methyloxy] phenyl} propane(b), and 10 ml hydrazine monohydrate, 80 ml ethanol and then 0.1 g 5% palladium on carbon (Pd–C) were added. The reaction mixture was refluxed for 24 h and then filtered to remove the Pd–C. Solid brown precipitates were obtained. The compound B was synthesized and recrystallized according to the same procedure as compound A; yield 70%, m.p. 99 °C. Elemental analysis for $C_{29}H_{30}N_2O_2$ (MW = 438) in wt%: calculated, C = 79.09, H = 7.27, N = 6.36; found, C = 75.48, H = 6.62, N = 5.86; IR (KBr pellet) in cm^{-1}, 3360, 3343 υ (N–H st), 1603 δ (N–H bend), 1350 υ (C–N st), 1238 υ (C–O–C st), 831 ρ (C–H bend) and 2965, 3065 υ (C–H st). ^{1}H-NMR (DMSO-d_6) in δ (ppm) and J (Hz): 3.70 (4H, s, NH_2), 1.72 (6H, s, CH_3), 5.35 (4H, s, CH_2), 6.62 (4H, dd, $J_1 = J_{1'} = 8.47$), 6.90 (4H, dd, $J_{2,3} = J_{2',3'} = 8.12$), 7.01 (4H, d, $J_4 = J_{4'} = 8.45$).



4,4′-di[(4-aminophenyl) oxymethyl] biphenyl (C)

4,4′-di[(4-nitrophenyl) oxymethyl] biphenyl (c)

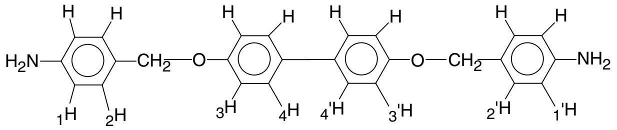
The general procedure was followed using 2 g (0.011 mol) 4,4′-dihydroxybiphenyl, 3.25 g (0.022 mol) anhydrous K_2CO_3 and 3.60 g (0.022 mol) *p*-nitrobenzylchloride in 70 ml DMF. The color of the solution changed from white to off-white as the reaction proceeded. The pale white precipitates obtained were thoroughly washed with water and collected by filtration. The crude product was recrystallized from ethanol; yield 86%, decomposition temperature >200 °C. Elemental analysis for $C_{26}H_{20}N_2O_6$ (MW = 456) in wt%: calculated, C = 68.42, H = 4.38, N = 6.14; found, C = 68.25, H = 3.94, N = 6.40; IR (KBr pellet) in cm^{-1}, 1567, 1347 υ (N=O st), 1254 υ (C–O–C st), 809 ρ (C–H bend) and 3035 υ (C–H st).



4,4′-di[(4-aminophenyl) oxymethyl] biphenyl (C)

The second step of the general procedure was followed using 4, 4′-di [(4-nitrophenyl) oxymethyl] biphenyl (c) 2 g (0.0043 mol), 10 ml hydrazine monohydrate, 80 ml ethanol and 0.1 g 5% Pd–C. Reaction mixture was refluxed for 24 h and Pd–C was removed by filtration. Solid pale white colored precipitates were then recrystallized from ethanol; yield 85%, decomposing temperature >230 °C. Elemental analysis for $C_{26}H_{24}N_2O_2$ (MW = 396) in wt%: calculated, C = 78.78, H = 6.06, N = 7.07; found C = 76.48, H = 5.98, N = 7.12; IR (KBr pellet) in cm^{-1}, 3323, 3284 υ (N–H st), 1609 δ (N–H bend), 1298 υ (C–N st), 1248 υ (C–O–C st), 818 ρ (C–H bend)and 3035 υ (C–H st). ^{1}H -NMR (DMSO-d_6) in δ (ppm) and J (Hz): 3.61 (4H, s, NH_2), 2.07 (4H, s, CH_2), 6.53 (4H, d, $J_1 = J_{1'} = 8.22$), 6.78 (4H, d, $J_2 = J_{2'} = 7.10$), 7.16 (4H, d, $J_3 = J_{3'} = 8.32$), 7.30 (2H, d, $J_4 = J_{4'} = 8.41$).

DOI: 10.1002/aoc



SYNTHESIS OF ORGANOMETALLIC AROMATIC POLYAMIDES

Organometallic aromatic polyamides (aramids) were prepared by low temperature condensation[16–20] of the diamines with ferrocene diacid chloride (Fig. 3).

General procedure

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

RESULTS AND DISCUSSION

Monomer synthesis

Synthesis of ferrocene monomers

Ferrocene monomer (1,1′-ferrocenedicarboxylic acid chloride) was prepared in three steps starting from ferrocene using reported methods[14,15] (Fig. 1).

Synthesis of aromatic monomers (diamines)

The three new diamines (A, B and C) were synthesized in two steps (Fig. 2) according to a well-developed method.[21,22] The first step was a Williamson etherification of aromatic diols with *p*-nitrobenzylchloride 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, b and c) with hydrazine hydrate and a Pd–C catalyst in refluxing ethanol.

The structures of these monomers were confirmed by FTIR, NMR and elemental analyses. The FTIR spectra of the dinitro compounds (a, b and c) exhibit absorption bands representative of the nitro functionality at 1538–1568 and 1328–1365 cm^{-1} corresponding to NO_2 symmetric and asymmetric stretches. After reduction, the characteristic dinitro group absorptions disappeared and those of the product amines showed typical N–H stretching bands in the region 3300–3380 cm^{-1}. The ^{1}H-NMR spectra confirm that the nitro compounds were converted to amine group by the signal in the 3.50–3.70 ppm region corresponding to primary aromatic amine protons. The elemental analysis values for the monomers were close to the calculated values and all NMR peaks could be assigned exactly.

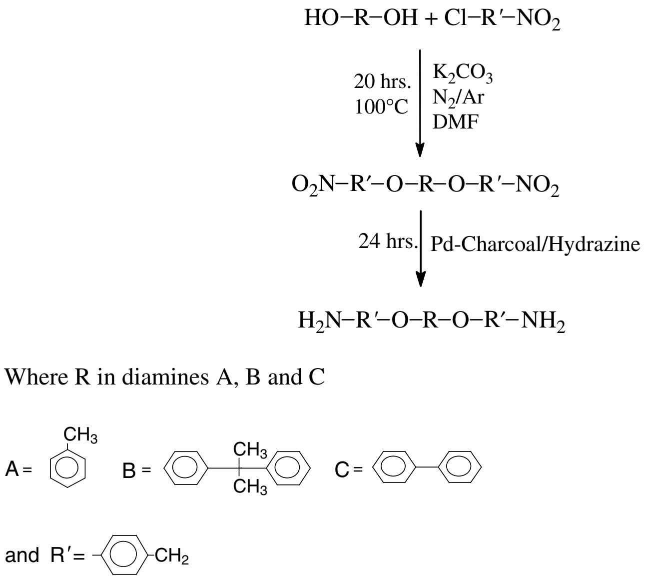


Figure 2. Synthesis of organic diamines.

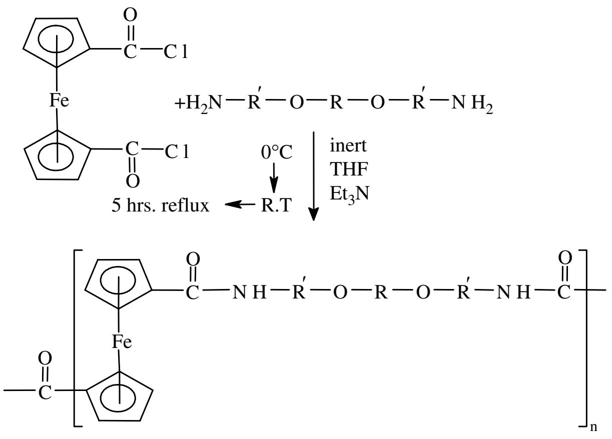


Figure 3. Synthesis of organometallic aromatic polyamides.

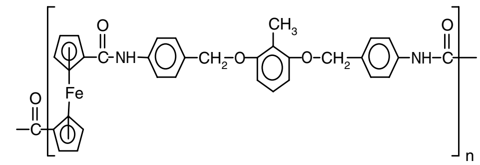
Polymer synthesis

The low temperature condensation technique[16–20] was followed for polymer synthesis. The reaction of FcDA acid chloride with different aromatic diamines in THF with Et_3N as proton acceptor afforded aromatic polyamides (Fig. 3). The polymers, obtained in good yields (77–84%), were amorphous with $T_m > 350\,°C$.

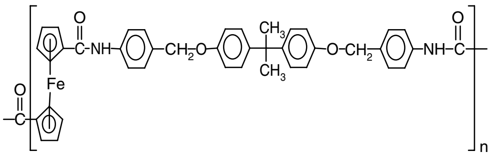
Characterization

The stoichiometry and structure (Fig. 4) of the synthesized aramids were established by their elemental analyses (carbon,

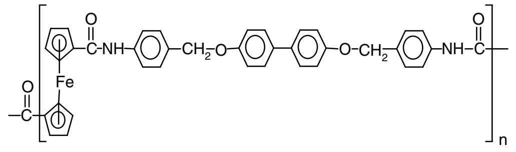
DOI: 10.1002/aoc



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



FP-B; poly {imino- 2,2′-di{4-[(4- aminophenyl) methyloxy]phenyl}propane- ferrocenoyl}



FP-C; poly {imino- 4, 4′-di[(4-aminophenyl)- oxymethyl] biphenyl-ferrocenoyl)

Figure 4. Ferrocene-containing aramids prepared by solution polycondensation from corresponding diamines A, B and C.

Table 1. CHN analysis for synthesized aramids

Aramid	Formula	Calculated (%)			Found (%)		
		C	H	N	C	H	N
FP-A	$[C_{33}H_{28}N_2O_4Fe]_n$	69.23	4.89	4.89	68.78	4.72	4.67
FP-B	$[C_{41}H_{36}N_2O_4Fe]_n$	72.78	5.32	4.14	71.19	5.13	4.05
FP-C	$[C_{38}H_{30}N_2O_4Fe]_n$	71.92	4.73	4.41	70.35	4.25	4.27

Elemental percentages are calculated based on the structure of the repeat unit.

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

Band assignments	FP-2 (a)	FP-4 (a)	FP-6 (a)
υ (C=O st)	1649 s	1635 s	1631 s
υ (N–H st)	3360 m,b	3302m,b	3339 m,b
υ (C–N st)	1318 s	1375 s	1400 s
υ (C–O–C st)	1180 s	1248 s	1217 s
υ (Fe–Cp st)	487 m	470 m	449 m

s = sharp, m = medium, b = broad.

hydrogen and nitrogen) and FTIR studies, the results for which 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 somewhat higher amounts of carbon calculated and found may be accounted for by the ferrocenyl acid end groups, which are not included in the calculations. The IR spectra of all these aramids contain the bands characteristic of polyamides[23] together with those of ferrocenyl and benzyl groups that are present in the polymer backbone. These all exhibit characteristic IR absorption bands of the amide groups appearing at 3360 (N–H stretching), 1649 (C=O stretching) and 1318 cm^{-1} (C–N bending) in aramid FP-A, 3302, 1635 and 1375 cm^{-1} in FP-B, and 3339, 1631 and 1400 cm^{-1} in FP-C, along with the characteristic bands of medium intensity due to Fe–Cp ring stretching, around 450–490 cm^{-1}.

Solubility behavior

The solubility of the aramids was tested qualitatively in the solvents from poor to strong hydrogen bonding. They are soluble in concentrated H_2SO_4 forming dark brown solutions due to strong hydrogen bonding.[24] The polyamides have intermolecular hydrogen bonding and high polarity, which are mainly responsible for their limited solubility.[1,25–29] The polymers FP-A, FP-B and FP-C are partially soluble in some organic solvents like DMAc and DMSO at room temperature, while solubility is enhanced on heating. This may be due to the presence of bulky groups, which provide a wider separation of polymer chains and weakening of intermolecular hydrogen bonding and polarity.[24]

Concentrated H_2SO_4 is a generally used solvent for most of the polyamides[30] from which the polymer can be precipitated with water or methanol. It is believed that concentrated H_2SO_4 protonates the nitrogen of the amide bond to overcome the hydrogen bonding forces, thus solubilizing the aramids.[1,30]

Thermal analysis

The thermal stability of the synthesized aramids was determined by DSC and TG experiments carried out in nitrogen. Some of the thermal properties of these aramids are listed in Table 3 and the TG curves are presented in Fig. 5. The chain stiffness of a polymer is characterized by its glass transition temperature (T_g) obtained from the DSC curves. These high values (410–490 °C) are characteristic of the aromatic polyamides.

The T_g for polymer FP-B containing flexible benzyl groups is higher than that for polymers FP-A and C. The reason might be the presence of more bulky groups and higher molecular weight calculated for repeat units of the polymer, a fact supported by the literature.[31]

The decomposition temperature (T_d 10% mass loss) is 440 °C for polymer FP-C, 525 °C for polymer FP-B and 615 °C for polymer FP-A. These values are low for polymers with flexible linkages and high for polymers containing stiff linkages and are also comparable with the literature values of organic aramids.[32–34]

The thermal degradation kinetics for the polymers was calculated from TG curves and the activation energies of pyrolysis obtained using the Horowitz and Metzger method.[35] 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 in the range 75–90 kJ mol^{-1}, which is slightly higher than the values calculated for organic aramids, i.e. 61–71 kJ mol^{-1},[36] suggesting that the ferrocene containing aramids is thermally more stable compared with the organic aramids.

Table 3. Thermal properties of aramids

Aramids	T_g (°C)	T_{10} (°C)	T_f (°C)	E^* (kJ mol^{-1})	Weight loss (%)
FP-A	430	615	775	77	10
FP-B	494	525	594	75	33
FP-C	410	440	600	86	6

All were estimated from T_g curves except T_g, which were obtained form 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 using Horowitz and Metzger method).

Viscosity behavior

The synthesized polymers were insoluble in all solvents as noted above, except for concentrated H_2SO_4, which was used as a solvent in the molecular weight determination of the aramids. Unfortunately, the relative viscosities of the aramid solutions were lower than unity, as shown in Table 4. This is due to the non-Newtonian behavior[37] of the polymer molecules, which indicates 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

Table 4. Viscometric data of the polymers in concentrated H_2SO_4

Aramids	η_{rel}	η_{sp}	η_{red}	η_{inh}
FP-A	0.960	−0.040	−0.160	−0.163
FP-B	0.957	−0.043	−0.172	−0.175
FP-C	0.876	−0.123	−0.492	−0.523

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 = $(\ln \eta_{rel.})/c$.

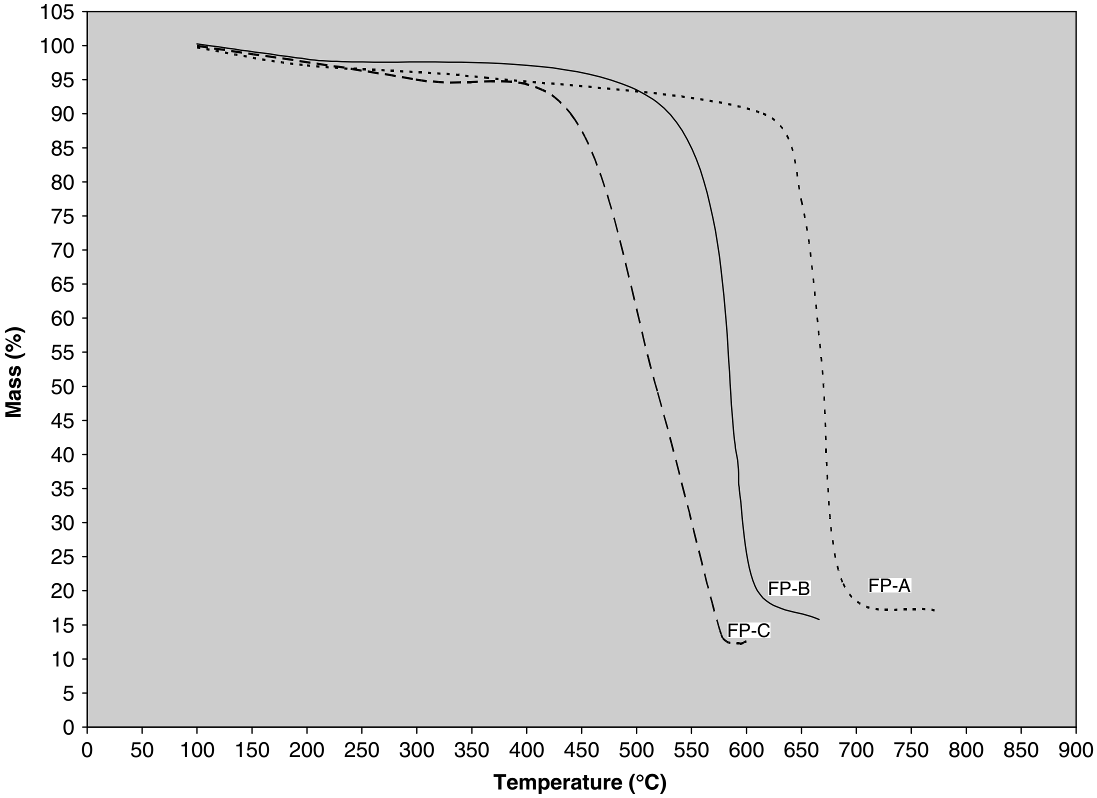


Figure 5. T_g curves of the synthesized aramids.

DOI: 10.1002/aoc

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.

CONCLUSIONS

A low-temperature solution phase polycondensation method was employed for synthesis of ferrocene containing aromatic polyamides (Aramids) from the monomers 1,1′-ferrocenedicarboxylic acid chloride and newly synthesized aromatic diamines. The resulting polymers were characterized by physical properties, elemental analysis and FTIR-spectral analysis. The thermal analysis also provided clues for 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, but their inherent viscosities were measured in concentrated H_2SO_4.

Acknowledgement

The authors are grateful to Quaid-i-Azam University for partially funding this project.

REFERENCES

1. Seymour RB, Carraher CE Jr. *Polymer Chemistry, an Introduction*. Marcel Dekker: New York, 1981; 217.
2. Cassidy PE. *Thermally Stable Polymers*. Marcel Dekker: New York, 1980; 71.
3. Peckham J, Gomez-Elipe P and Manners I. Metallocene based polymers. In *Metallocenes; Synthesis, Reactivity and Applications*, Vol. 2, Togni A, Halterman RL (eds). Wiley-VCH: New York, 1998; 723.
4. Fery-Forgues S and Delavaux-Nicot B. *J. Photochem. Photobiol. A: Chem.* 2000; **132**: 137.
5. Nguyen P, Gómez-Elipe P and Manners I. *Chem. Rev.* 1999; **99**: 1515.
6. Alonoso B, Cuadrado I, Morán M and Losada J. *J. Chem. Soc. Chem. Commun.* 1994; 2575.
7. Casado CM, Cuadrado I, Morán M, Alonso B, Garcia B, González B and Losada J. *Coord. Chem. Rev.* 1999; **185–186**: 53.
8. Kittlesen GP, White HS and Wrighton HS. *J. Am. Chem. Soc.* 1985; **107**: 7373.
9. Bu HZ, English AM and Mikkelsen SR. *J. Phys. Chem. B* 1997; **101**: 9593.
10. Foulds NC and Lowe CR. *Anal. Chem.* 1986; **60**: 2473.
11. Hale PD, Boguslavsky LI, Inagaki T, Karan HI, Lee HS and Skothein TA. *Anal. Chem.* 1991; **63**: 677.
12. Casado CM, Morán M, Losada J and Cuadrado I. *Inorg. Chem.* 1995; **34**: 1668.
13. Akhter Zareen, Bashir Mubasher A and Saif ullah Khan M. *Appl. Organometal. Chem.* 2005; **19**: 848.
14. Rosenblum M and Woodward RB. *J. Am. Chem. Soc.* 1958; **80**: 543.
15. Knobloch F, Rauscher W. *J. Polym. Sci. Part A* 1961; **10**: 651.
16. Morgan PW. *Condensation Polymers by Interfacial and Solution Methods*. Interscience: New York, 1965; 5.
17. Negi YS, Suzuki YI, Kawamura I, Kakimoto MA and Imai Y. *J. Polym. Sci. Polym. Chem.* 1996; **34**: 1663.
18. Varma IK, Kumar R and Bhattacharyya AB. *J. Appl. Polym. Sci.* 1990; **40**: 531.
19. Yamashita M, Kakimoto MA and Imai Y. *J. Polym. Sci. Polym. Chem.* 1993; **31**: 1513.
20. Carter KR, Furuta PT and Gong V. *Macromolecules* 1998; **31**: 208.
21. Yang CP, Chen WT. *Macromolecules* 1993; **26**: 4865.
22. Tamai S, Yamaguchi A, Ohta M. *Polymer* 1996; **37**: 3683.
23. Sweeny W, Zimmerman J. Polyamides. In *Encyclopedia of Polymer Science and Technology*, Vol. 10. Wiley: New York, 1968; 539.
24. Liaw DJ, Liaw BY, Su KL. *J. Polym. Sci., Part A: Polym. Chem.* 1999; **37**: 1997.
25. Yang CP, Oishi Y, Kakimoto MA and Imai Y. *J. Polym. Sci. Polym. Chem.* 1989; **27**: 3895.
26. Stern SA. *J. Membr. Sci.* 1994; **94**: 1.
27. Aguilar-Vega M and Paul DR. *J. Polym. Sci. Polym. Phys. Edn* 1993; **31**: 1599.
28. Pixton MR and Paul DR. *Polymer* 1995; **36**: 2745.
29. Grulke EA. Solubility parameter values. In *Polymer Handbook*, 4th edn, Brandrup J, Immergut EH, Grulke EA (eds). Wiley: New York, 1999; 677.
30. Liou GS, Hsiao SH, Ishida M, Kakimoto M and Imai Y. *J. Polym. Sci. Part A: Polym. Chem.* 2002; **40**: 2810.
31. Andrews RJ and Grulke EA. Glass transition temperatures of polymers. In *Polymer Handbook*, 4th edn, Bandrup J, Immergut EH, Grulke EA (eds). Wiley: New York, 1999; 197.
32. Oishi Y, Shoichi N, Kakimoto M, Imai Y. *J. Polym. Sci., Part A: Polym. Chem.* 1993; **31**: 1115.
33. Oishi Y, Shoichi N, Kakimoto M, Imai Y. *J. Polym. Sci., Part A: Polym. Chem.* 1992; **30**: 2220.
34. Jeong H, Kakimoto M, Imai Y. *J. Polym. Sci., Part A: Polym. Chem.* 1991; **29**: 771.
35. Horowitz HH and Metzger G. *Anal. Chem.* 1963; **35**: 1464.
36. David C. *Comprehensive Chemical Kinetics, Degradation of Polymers*, Benford CH, Tipper CFH (eds). Elsevier: New York, 1975; 14, 109.
37. Atkins PW. *Physical Chemistry*, 2nd edn. WH Freeman: San Fransisco, CA, 1982; 827.

DOI: 10.1002/aoc