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Synthesis, characterization and thermal degradation kinetics of ferrocene-containing aramids

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Low-temperature solution-phase polycondensation of 1,1′-ferrocenedicarboxylic acid chloride with different aromatic diamines was carried out in tetrahydrofuran in the presence of triethylamine to afford ferrocene-containing aramids. The products were characterized by their solubilities, inherent viscosities, elemental analysis, FTIR spectroscopy, differential scanning calorimetry and thermogravimetry. All of them were insoluble in common solvents tested, except aramid-IV (derived from 1,8-naphthalene diamine), which was slightly soluble in *N,N′*-dimethylacetamide, *N,N′*-dimethylformamide, dimethylsulfoxide and formic acid. However, all were miscible with concentrated H_2SO_4, forming red-coloured solutions. These all show a reduction in their solution viscosities at ambient conditions in concentrated H_2SO_4 which may be attributed to their non-Newtonian behaviour. The glass transition temperature for each aramid was quite high, and stable up to 390 °C. The integral procedural decomposition temperatures for the products were calculated using Doyle's method and were found to be intermediate to that of Nylon 66 (419 °C) and Teflon (555 °C), and the activation energy for decomposition of each product was calculated by the Horowitz and Metzger method. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ferrocene; aramids; organometallic aramids; polyamides

INTRODUCTION

Carbon-based organic aromatic polyamides (aramids) are well known for their high-temperature stability, which makes them high-performance polymers.[1–3] On the other hand, polymers containing metals are useful to access materials with unusual and attractive properties, like electrical, magnetic, preceramic, catalytic, and nonlinear optical (NLO) effects as a result of electron delocalization.[4–10] Incorporation of metal into aramids, therefore, creates the possibility to produce materials with useful electrical and/or catalytic properties, combined with thermal stability.[11–14]

Ferrocene, owing to its favourable electrochemical properties and air, moisture, and thermal stability, is a promising candidate for incorporating metal into polymeric structures.[15–19] In fact, polymers with ferrocene units incorporated into or onto the main chain are useful for several applications, e.g. in the fabrication of amperometric enzyme electrodes,[20] as precursors to ferromagnetic ceramics,[21,22] or in electro-catalysis.[23] Polymer-attached ferrocene compounds are also used for medical applications, e.g. in cancer treatment.[24]

Our interest was to study the effect of incorporation of ferrocene as an aromatic diacid chloride into aramid backbones using low-temperature solution polycondensation techniques. One such example reported in literature involves the interfacial condensation of 1,1′-ferrocenedicarboxylic acid chloride with *p*-phenylene diamine.[25] However, the product was insoluble in all organic solvents and, thus, other physical properties were not discussed. We have used aromatic diamines ranging from rigid to flexible and of a sterically bulky nature in order to gauge the effects of chain flexibility and bulkiness on the basic properties of the as-produced organometallic aramids. Solubilities in common organic solvents with varying degrees of hydrogen bonding, thermal stability and thermal degradation kinetics were studied, along with elemental and Fourier transform IR (FTIR) spectroscopic characterization. Solubility behaviour in concentrated sulfuric acid was also studied, in which the products were found to form red-coloured solutions.

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EXPERIMENTAL

Materials

All the chemicals and reagents used were of the highest purity or purified as described. Ferrocene, aluminium chloride, 1,4-diaminophenylene, 4,4′-diaminophenyl ether, and triethylamine were obtained from Fluka (Switzerland) and used as received. 4,4′-Diaminobiphenyl was purchased from Schuchardt München (Germany) and was vacuum dried before use. 1,8-Naphthalene diamine was obtained from Aldrich (UK). Tetrahydrofuran (THF) was purchased from Riedeldehaën (Germany) and used after distillation from sodium–benzophenone under nitrogen.

Methods

1,1′-Ferrocene dicarboxylic acid chloride[25,26] was prepared from ferrocene in three steps, as shown in Fig. 1. Condensation reactions were carried out in oven-dried flasks under inert atmosphere using vacuum-line techniques and dry helium. The purity of intermediate products was monitored by thin-layer chromatography (TLC) using pre-coated kieselgel 60-HF_{250} TLC plates. The trifluoroacetylation of each product was carried out by the addition of a weighed amount of the respective aramid in an excess of trifluoroacetic anhydride.

Analytical techniques and instrumentation

Elemental analyses were carried out on an Elementar Model Vario-EL, Germany. Melting points were determined on a Mel-Temp. (Mitamura Riken Kogyo, Inc.) using open capillary tubes. Solid-state FTIR spectra in KBr pellets were recorded on a Perkin Elmer 1600 series FTIR spectrophotometer. Thermogravimetric (TG) measurements were conducted using a Perkin Elmer TGA 7 thermobalance at a heating rate of 20 °C min^{-1} in nitrogen with a hold for 1 min at 50 °C. Differential scanning calorimetry (DSC) curves were recorded at a heating rate of 20 °C min^{-1} in nitrogen with sapphire as standard, on a differential scanning calorimeter (Perkin Elmer models DSC 7 and DSC 404C). Viscosimetric studies in concentrated H_2SO_4 were carried out using a U-tube (Ostwald) viscometer with a 1 mm capillary tube, at 25.0 ± 0.1 °C.

Polymer synthesis

In a two-necked oven-dried flask, the corresponding diamine (1.88 mmol) was dissolved in 15 ml of freshly distilled, hot THF and mixed with 10 ml of triethylamine. The temperature was lowered to 0 °C using an ice bath, and 0.600 g (1.92 mmol) of 1,1′-ferrocenedicarbonyl chloride dissolved in 10 ml dry THF was added dropwise with vigorous stirring. The temperature was slowly raised to ambient and the mixture was stirred for an additional 3 h. The precipitated product was collected by filtration, washed with THF (3 × 5 ml) and several times with methanol. The resulting coloured product was dried in vacuum for 24 h. The syntheses of the various aramids are summarized in Fig. 2.

RESULTS AND DISCUSSION

Monomer synthesis

Ferrocene monomer (1,1′-ferrocenedicarboxylic acid chloride) was prepared using reported methods[24,25] starting from ferrocene using thionyl chloride as chlorinating agent in dichloromethane with triethylamine as catalyst (Fig. 1).

Aramid synthesis

Low-temperature solution polycondensation[27–31] was the general method (Fig. 2) used for the preparation of all the aramids to avoid side reactions associated with the high-temperature organometallic condensation polymerizations.[32,33] The yields, colour and heating behaviour of the products are given in Table 1.

Characterization

The stoichiometry and structure (Fig. 3) of the aramids were confirmed by elemental analyses (carbon, hydrogen, nitrogen)

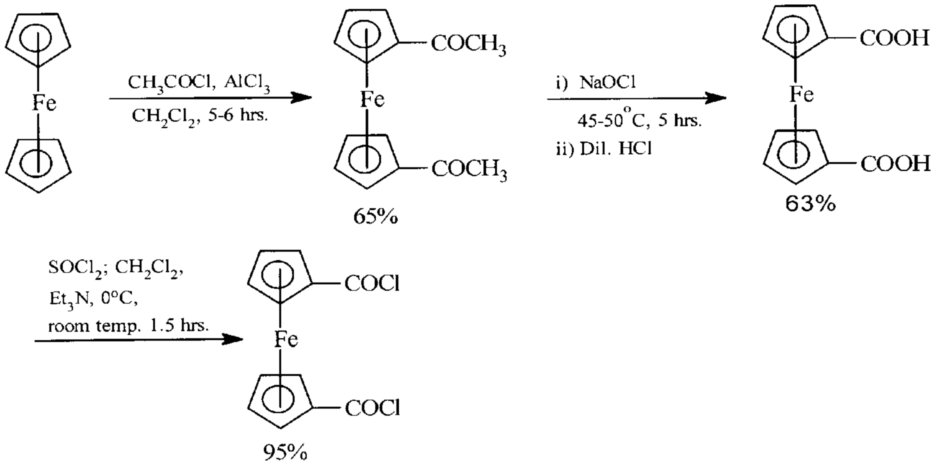


Figure 1. Synthesis of monomer 1,1′-ferrocenedicarboxylic acid chloride from ferrocene.

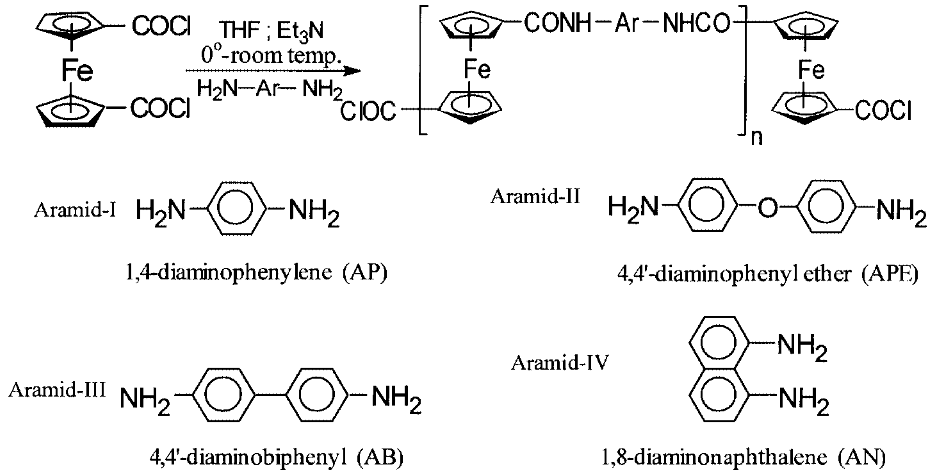


Figure 2. Synthesis of ferrocene-containing aramids prepared by solution polycondensation.

Table 1. Some physical properties and elemental analysis of the aramids synthesized[a]

Aramid	Colour	Yield (%)	Repeat unit	Elemental analysis[b] (%) Found (calc.) C	H	N
Aramid-I	Orange–yellow	87	$C_{18}H_{12}N_2O_2Fe$	59.35 (62.43)	3.69 (4.04)	7.43 (8.09)
Aramid-II	Mustard	91	$C_{24}H_{18}N_2O_3Fe$	63.73 (65.75)	3.27 (4.11)	6.23 (6.39)
Aramid-III	Brown	80	$C_{24}H_{18}N_2O_2Fe$	66.09 (68.24)	4.20 (4.26)	6.79 (6.63)
Aramid-IV	Dark brown	77	$C_{22}H_{16}N_2O_2Fe$	63.58 (66.66)	3.84 (4.04)	6.45 (7.07)

[a] All aramids did not melt till 400 °C.

[b] Yields and elemental percentages are calculated based on the structure of the repeat units.

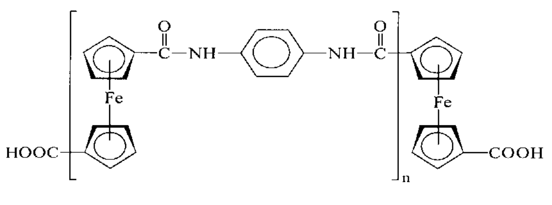
Table 2. FTIR (KBr) spectral data for the aramids[a]

	Band assignments (cm^{-1}) Aramid-I	Aramid-II	Aramid-III	Aramid-IV
N–H stretch	3364 m, b	3428 m, b	3385 m, b	3373 m, b
C=O stretch	1651 s	1635 s	1661 s	1648 s
N–H bend	1515 s	1500 s	1500 s	1533 s
C–H stretch (Ar)	2990 w	3010 w	3098 w	2888 w
p-C_6H_4	830 m	810 m	823 m	(814, 759)[b] m
C–O stretch	—	1210 s	—	—
O–H bend	1312 m	1306 m	1308 m	1286 m
Fe–Cp stretch	491 m	488 m	490 m	500 m

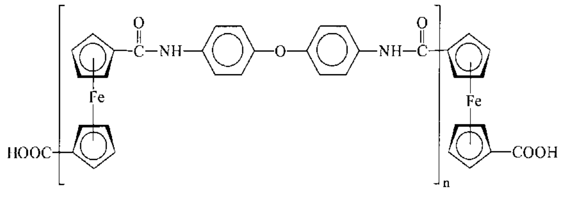
[a] s: sharp; m: medium; w: weak; b: broad.

[b] This aramid contains naphthyl instead of phenyl groups.

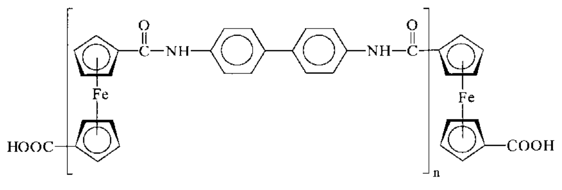
and FTIR spectroscopy, the results for which are given in Tables 1 and 2 respectively. The percentages found for hydrogen and nitrogen are in good agreement with those calculated based on the structure of the repeat units. The somewhat higher amounts of carbon calculated and found may be accounted for by the ferrocenyl acid end groups, which are not included in the calculations. They all exhibit characteristic IR absorption bands of the amide groups appearing at 3364 (N–H stretching), 1651 (C=O stretching) and 1515 cm^{-1} (N–H bending) in aramid-I, at 3428, 1635, and 1500 cm^{-1} in aramid-II, at 3385, 1661, and 1500 cm^{-1} in aramid-III, and at 3373, 1648, and 1533 cm^{-1} in aramid-IV, along with the characteristic bands of medium intensity due to Fe–Cp ring stretching at around 490 cm^{-1}.



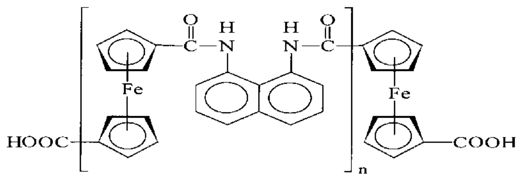
Aramid-I = poly(imino-1,4-phenyleneiminoferrocenoyl) from 1,4-diaminophenylene (AP)



Aramid-II = poly(imino-4,4′-phenylene-ether-iminoferrocenoyl) from 4,4′-diaminophenyl ether (APE)



Aramid-III = poly(imino-4,4′-biphenyleneiminoferrocenoyl) from 4,4′-diaminobiphenyl (ABP)



Aramid-IV = poly(imino-1,8-naphthyleneiminoferrocenoyl) from 1,8-diaminonaphthalene (AN)

Figure 3. Ferrocene-containing aramids prepared by solution polycondensation from corresponding diamines.

Solubility

The solubility of the aramids was tested qualitatively, and all of them were insoluble in the solvents tested, except in concentrated H_2SO_4. The intermolecular hydrogen bonding and the high polarity of these polyamides are responsible for their limited solubility.[1,34–38] Aramid-IV (derived from 1,8-naphthalene diamine) is slightly soluble in some of the solvents. This may be due to the bulky nature of this group, which provides a wider separation of polymer chains and weakening of intermolecular hydrogen bonding and polarity. Aramid-II and -IV (which contain ether linkages) were trifluoroacylated more readily using trifluoroacetic anhydride to solubilize in THF, compared with the other two, which contain somewhat rigid aromatic groups and require refluxing conditions in accord with the fact that the presence of flexible units in the backbones enhances the solubility of polymers.[39]

These aramids form red solutions in concentrated H_2SO_4 and could be precipitated with methanol, water, etc. It is believed that concentrated H_2SO_4 also protonates the nitrogen of the amide bond to overcome the hydrogen bonding forces, thus solubilizing the aramids.[1,40]

Viscosity behaviour

As all the aramids were soluble in concentrated H_2SO_4 to form red-coloured solutions, it was decided to check their viscosity behaviour in this solvent, which ultimately might be proved helpful in the determination of their viscosity average molecular weight. Unfortunately, the relative viscosities of the aramid solutions were lower than unity, as shown in Table 3. The probability of degradation of aramid molecules in concentrated H_2SO_4 was ruled out on the basis of the similarity of the IR spectra of the reprecipitated products with those of the original ones. This unusual behaviour may also be attributed to the non-Newtonian behaviour[41] of the polymer molecules, which suggests the presence of rod-like molecules that become oriented by the flow so that they slide pass each other more freely.

Thermal properties

DSC and TG experiments were carried out in nitrogen to evaluate the thermal properties of the aramids synthesized. The thermal behavior data are given in Table 4 and the TG curves are presented in Figure 4. The chain stiffness is characterized by its glass transition temperature T_g, obtained from the DSC curves. All values are high and are characteristic of the aromatic polyamides.[42–44] The data show that the T_g of aramid-II is lower than the others, probably due to the presence of the flexible ether linkage in its backbone.[45]

T_i is the initial temperature or procedural decompositional temperature (PDT), a temperature at which cumulative mass change reaches a magnitude that the thermobalance can detect. It is highest for aramid-II, which has ether linkages. These values are high, indicating that ferrocene-containing aramids are thermally quite stable, like other organic

Table 3. Viscosimetric data of the polymers in concentrated H_2SO_4

Aramid	η_{rel}[a]	η_{sp}[b]	η_{red}[c]	η_{inh}[d]
Aramid-I	0.986	−0.014	−0.140	−0.014
Aramid-II	0.982	−0.018	−0.180	−0.018
Aramid-III	0.985	−0.015	−0.150	−0.015
Aramid-IV	0.965	−0.035	−0.350	−0.035

[a] Relative viscosity $\eta_{rel} \cong$ time of flow for solution/time of flow for solvent.
[b] Specific viscosity $\eta_{sp} = \eta_{rel} - 1$.
[c] Reduced viscosity $\eta_{red} = \eta_{sp}/c$.
[d] Inherent viscosity $\eta_{inh} = \ln(\eta_{red}/c)$.
(where C is the concentration of the solution)

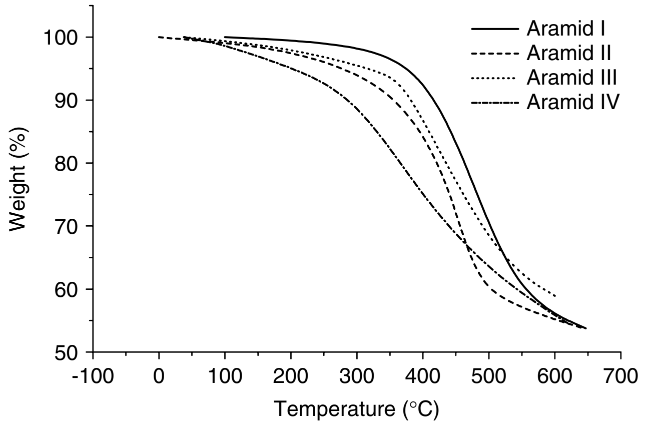


Figure 4. TG curves of the aramids synthesized.

Table 4. Thermal properties of aramids[a]

Aramid	T_g (°C)	T_i (°C)	T_f (°C)	T_s (°C)	T_{10} (°C)	E* (kJ mol^{-1})	Wt loss (%)
Aramid-I	390	310	740	470	420	85	48
Aramid-II	360	390	750	430	410	94	48
Aramid-III	380	290	600	450	410	85	41
Aramid-IV	370	290	620	370	300	88	45

[a] All were estimated from TG curves except T_g, which was obtained from DSC curves. T_{10}: temperature at 10% weight loss; T_{exotherm}: temperature at which the exotherm appeared in DSC curve; T_s: temperature at maximum weight loss; T_f: final temperature (at the end of curve); E^*: activation energy of pyrolysis (obtained by Horowitz and Metzger method).

aromatics polyamides, due to the presence of intermolecular hydrogen bonding, high polarity and chain stiffness.[46–48]

The decomposition temperature (10% weight loss) values are low for polymers with flexible linkages and high for polymers containing stiff linkages; and they are also comparable to the literature values of organic aramids.[49,50]

The activation energy for decomposition of the products was calculated using the Horowitz and Metzger method[51] from the TG traces. 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 85–95 kJ mol^{-1}, which is slightly higher than the calculated values for organic aramids, i.e. 61–71 kJ mol^{-1},[52] which indicates that the ferrocene-containing aramids are thermally more stable than the organic aramids.

Integral PDTs (IPDTs) were also calculated from TG traces using Doyle's method.[53] This is the temperature that is independent of the small variations in heating rates, so these are highly reproducible.[54] The IPDT values obtained for these aramids are quite high, in the range of 460–500 °C (Table 5). These values can be used for the comparative study of the synthesized polymers with reported values. It has been found that the synthesized aramids with rigid ferrocene moieties in the polymer backbones are more stable thermally than Nylon 66 (IPDT value 419 °C) and polystyrene (IPDT value 395 °C) and less stable than Teflon (IPDT value 555 °C).[54] These values are also lower for polymers with flexible linkages and higher for polymers containing stiff linkages, in accord with the results obtained from other methods.

Table 5. Calculations of IPDT[a]

Aramid	A^*	T_{A^*} (°C)	K^*	A^*K^*	IPDT (°C)
Aramid-I	0.77	701	0.69	0.54	496
Aramid-II	0.75	685	0.68	0.51	473
Aramid-III	0.75	684	0.70	0.53	486
Aramid-IV	0.74	669	0.67	0.50	460

[a] Calculated from TG traces. A^*: total curve area; T_{A^*}: end-of-volatilization temperature; K^*: ratio of the curve area to the rectangular area bounded by the characteristic end-of-volatilization temperature and the residual mass at end of test temperature of 900 °C.

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