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Synthesis, characterization and properties of novel polyamides containing ferrocene unit and flexible spacers

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Synthesis and characterization of ferrocene-containing main-chain polyamides are reported in this article. A new, interesting type of organometallic monomer (FDADO) based on ferrocene was prepared by interfacial condensation of 1,1′-dichlorocarbonyl ferrocene with 2 mol 1,8-diamino-3,6-dioxaoctane (DADO). A series of ferrocene-based polyamides was prepared via polycondensation of the ferrocenyl diamine (FDADO) with different diacid chlorides using two different methods. The monomer and polymers were characterized by elemental analysis, infrared and NMR spectroscopy. The thermal stability and behavior of the synthesized polymers were evaluated by thermal gravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and differential scanning calorimetry (DSC). The crystallinity of polymers was examined by X-ray diffraction analysis. Inherent viscosity, solubility and flame-retardancy of the polymers were also studied. The obtained polymers showed good heat-resistance and flame-retardancy, and improved solubility vs generally reported polyamides in some common organic solvents.

KEYWORDS: ferrocene; diamine; polyamide; polycondensation; heat-resistant; flame-retardant; spacer

INTRODUCTION

In recent years organometallic polymers have attracted much attention since polymers containing metals might be expected to possess properties different from those of conventional organic polymers.[1,2] In contrast to organic polymer science, the corresponding macromolecular chemistry of inorganic elements is at an earlier stage of development. This is particularly the case for transition metal-based polymers which would be expected to possess a broad range of interesting characteristics.[3] In addition, the incorporation of transition elements into polymers provides further possibilities for supramolecular chemistry and for the properties of the resulting superstructures.[4] The potential for the precise introduction of metal-containing components into structures with controlled hierarchical order is particularly intriguing and, if achieved, would make an important contribution to one of the major areas of synthetic challenge in the twenty-first century.[5]

The discovery of ferrocene and its structural characterization initiated an explosive rebirth of organometallic chemistry. Today, 55 years after this event, new uses are still being found for this remarkable organometallic moiety.[6] Ferrocene-containing polymers possess outstanding properties, including air-, heat- and photochemical stability. These interesting features have made them suitable for a wide spectrum of applications, including heat-resistant lubricants and heat-resistant elastomers.[7,8]

It is known that aromatic polyamides are a class of high temperature-resistant polymers with good chemical resistance, thermal stability, low flammability and very good mechanical properties. Owing to these properties they are of major commercial and industrial importance. The demand for aromatic polyamides and other high-performance polymeric materials is growing steadily due to their superior performance characteristics, which are increasingly expected from engineering polymers in the aero-space, electronics, automobile and other industries.[9–11] However, one of the drawbacks to the employment of these polymers is the difficulty in processing due to their insoluble nature in organic solvents in addition to their high melting and/or glass transition

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temperatures. These characteristics result from the sequence of aromatic units, the inherent rigidity of the amide linkage and chain stiffness and intermolecular dipole–dipole and hydrogen bonding between amide groups.[12] Therefore, some significant synthetic efforts in the area of high temperature-resistant polymers have been focused on improving their processability and solubility through the design and synthesis of new monomers.

Here we describe the synthesis of a new diamine with special structural features including ferrocene units, preformed amide groups and flexible spacers to obtain certain polyamides with specific properties. For this purpose the diamine was prepared via conversion of ferrocene to 1,1′-ferrocenedicarboxylic acid and subsequently to 1,1′-dichlorocarbonyl ferrocene, and finally reaction of this compound with 1,8-diamino-3,6-dioxaoctane. Related polyamides were prepared through polycondensation reactions of this diamine with four different diacid chlorides via two different methods. The obtained polyamides were fully characterized and their physical properties were studied.

EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. *N*-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Dichloromethane was refluxed over CaH_2 and distilled immediately before use. Pyridine, petroleum ether and oxalyl chloride was freshly distilled before use. Trimethylchlorosilane (TMSCl) was twice distilled under nitrogen. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were purified by sublimation. LiCl was dried for 10 h at 110 °C.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany). Spectra of solid samples were performed using KBr pellets. Vibrational transition frequencies were reported as wavenumber (cm^{-1}).

The H-NMR spectra of the polymer powders were recorded in dimethyl sulfoxide (DMSO-d_6) solution using a Bruker Avance DPX 250-MHz instrument (GmbH, Germany) in the region $\delta = 0-15$ ppm. Tetramethylsilane (TMS) was used as an internal reference. Proton resonances were designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m).

A CHN-O-Rapid Heraeus elemental analyzer was used to perform elemental analyses (Wellesley, MA, USA) for powder specimens. The weight percentages of carbon, hydrogen and nitrogen were found in each sample.

Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 (London, UK) over a temperature range of 25–250 °C at a heating rate of 10 °C/min. The value of heat flow vs temperature was recorded for each sample. Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) trace were recorded in the region of 25–600 °C on a Polymer Lab TGA-1500 (London, UK) at a heating rate of 10 °C/min. The mass loss vs temperature and the first derivative of TGA vs temperature were recorded for TGA and DTG, respectively.

The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of 25–250 °C at 1 Hz and a heating rate of 5 °C/min (Surrey, UK). The values of tanδ and the storage modulus vs temperature were recorded for each sample.

Inherent viscosities were measured by a standard procedure using an Ubbelohde routine viscometer in a concentration of 0.5 g/dl in DMF at 30 °C.

Wide angle X-ray diffraction was performed at room temperature on an X-ray Jeol Jdx-8030 diffractometer (London, UK) using Ni-filtered Cu Kα radiation (40 kV, 25 mA) with scanning rate of 3°/min.

The weight-average molecular weight (M_w) was determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 ml/min, and DMF was used as solvent.

Monomer synthesis

1,1′-Ferrocenedicarboxylic acid was prepared according to the reported procedure using trichloroacetyl chloride in the presence of $AlCl_3$ and CS_2 via Friedel-Crafts reaction.[13]

1,1′-Dichlorocarbonyl ferrocene was prepared based on the following method. A mixture of 3.25 g (0.012 mol) of 1,1′-ferrocenedicarboxylic acid, 50 ml of dry CH_2Cl_2, 5 ml of freshly distilled oxalyl chloride and two drops of pyridine was poured and stirred in a round-bottomed flask at room temperature under N_2 in the dark for 14 h and then refluxed at 40 °C for 6 h. The mixture was distilled to dryness under reduced pressure. The residue was extracted repeatedly at 80 °C with dry petroleum ether (b.p. 100–140 °C). Then the solvent was evaporated under reduced pressure and the product was dried under vacuum at 40 °C. The weight of the product was about 2.80 g (9.0 mmol) (yield 76%).

FDADO diamine was prepared according to the following procedure: 1.22 g (3.93 mmol) of 1,1′-dichlorocarbonyl ferrocene was dissolved in 12 ml of dry CH_2Cl_2. To this vigorously stirred mixture, a solution of sodium hydroxide (1.07 g) in 17.5 ml water and 2.37 g (15.7 mmol) of DADO was added in one lot. After 10 min the monomer was filtered and washed thoroughly with dichloromethane and dried in a vacuum oven at 40 °C. The weight of the product was about 1.64 g (0.31 mmol; yield 78%).

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Polymer synthesis

Method A

A 100 ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 5.0 mmol (2.67 g) of FDADO and 35 ml of dry NMP. The mixture was stirred at 0 °C for 0.5 h. Then about 2.5 ml (35.7 mmol) of propylene oxide was added, and after a few minutes 5.0 mmol of diacid chloride (1.02 g of TPC or IPC, or 0.92 g of AC, and or 1.20 of SC) was added and the mixture was stirred at 0 °C for 0.5 h. The temperature was raised to room temperature and the solution was stirred for 6 h. Polyamide was precipitated by pouring the flask content into water. Then it was filtered and purified using a DMF–H_2O solvent–non solvent system. After filtration, it was washed with hot water successively and dried overnight under vacuum at 80 °C.

Method B

A 100 ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and a calcium chloride drying tube was charged with 0.51 g of LiCl and 20 ml of dry NMP. The mixture was stirred at room temperature then 5.0 mmol (2.67 g) of FDADO was added and the mixture was stirred until all solids were dissolved. The solution was cooled to −5 °C and 3.0 mmol (0.45 g) of TMSCl was slowly added. The temperature was raised to room temperature and the solution was stirred for 15 min to assure the formation of silylated diamine. The solution was once again cooled to −5 °C and 5.0 mmol of diacid chloride (1.02 g of TPC or IPC, or 0.92 g of AC, and or 1.20 of SC) in 6 ml of NMP was added. The reaction mixture was stirred for 0.5 h at that temperature, and then warmed to room temperature and stirred for 24 h. The polymer was precipitated by pouring the flask contents into 200 ml of water. It was filtered, and purified with DMF–H_2O (as solvent–non-solvent) system by dissolving the polymer in 5 ml of DMF and reprecipitating in 200 ml of H_2O. Then it was washed with 30 ml of hot water several times, and finally it was dried overnight under vacuum at 80 °C.

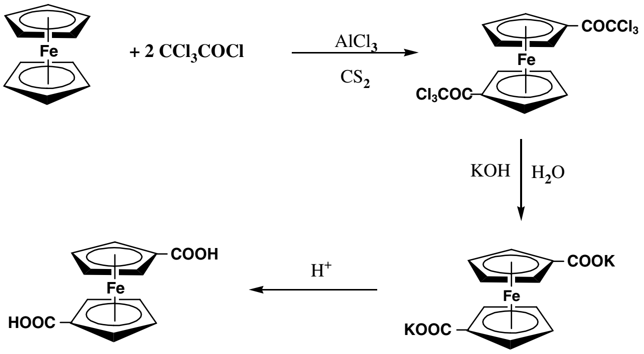
RESULTS AND DISCUSSION

While the first half of the twentieth century saw many advances in organic and inorganic polymer chemistry, it was not until the 1950s that organometallic polymers were identified as a new class of polymeric materials. The incorporation of transition metals into organic monomers and polymers has been thoroughly examined over the past five decades in light of the promising electrical, magnetic, optical and catalytic properties that these organometallic materials possess. Ferrocene was one of the first organometallic compounds to be synthesized that retains its structure up to 500 °C. This high thermal stability has made ferrocene suitable for fire retardant applications, although it is too expensive. Ferrocene-containing polymers possess very useful properties including high thermal stability, radiation resistance and electrical conduction properties.[3,14–18] Incorporation of the ferrocene ring system into polymer chains provides an opportunity to introduce a rigid fragment structurally unlike any other previously used.

Literature survey reveals that aromatic polyamides as heat-resistant polymers are an important class of high-performance polymers. One of the disadvantages to the employment of these polymers is the difficulty in processing due to their high melting and/or glass transition temperatures. Many attempts and researches have focused on improving their processability and solubility through the design and synthesis of new monomers. Diamines are important monomers in the synthesis of polyamides. To extend the utility of these high performance polymers, the main aim has focused on the preparation of diamines, which produce soluble and processable polyamides without sacrificing too much heat-resistance. To enhance their processability, structural modifications of polyamides are continuously under study. One of the main strategies of this field is incorporation of flexible or kinked linkages, such as ether groups, into the polymer backbone.[19,20] Although most soluble polymers have been prepared by combinations of structural modifications, it does appear that a flexible or kinked linkage is a necessary prerequisite for solubility.

Based on our continuing interest in the preparation of novel polyamides,[21–27] the aim of this study was preparation, characterization and properties investigation of new types of organometallic polyamides that show high thermal stability and also suitable solubility to extend their applications.

Accordingly, in this study, a novel monomeric diamine with a ferrocenyl structure and flexible ether units was prepared. Reaction of ferrocene with trichloroacetyl chloride in the presence of $AlCl_3$ and CS_2 (Friedel-Crafts reaction) gave the corresponding 1,1′-ditrichloroacetyl ferrocene (Scheme 1). The hydrolysis of this compound in basic media gave the potassium salt of 1,1′-ferrocene dicarboxylic acid, which on acidification gave the related diacid.[13] For activation of the diacid toward nucleophilic reaction, this diacid was converted to the 1,1′-dichlorocarbonyl ferrocene with oxalyl chloride in dry CH_2Cl_2 (Scheme 2). The structures of these compounds were confirmed by spectral analyses. In the FT-IR



Scheme 1. Preparation of 1,1′-ferrocenedicarboxylic acid.

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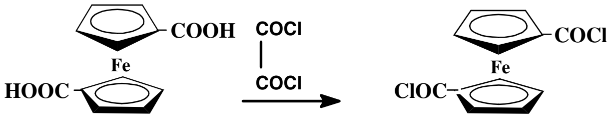
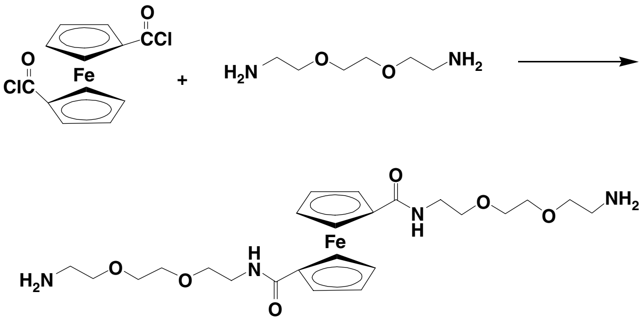
spectrum of 1,1′-dichlorocarbonyl ferrocene the characteristic carbonyl band of 1,1′-ferrocenedicarboxylic acid at 1683 cm^{-1} disappeared and a band at 1758 cm^{-1} appeared.

The FDADO monomeric diamine was prepared via reaction of two moles of 1,8-diamino-3,6-dioxaoctane with one mole of 1,1′-dichlorocarbonyl ferrocene (Scheme 3). A novel diamine (FDADO) with special structural features including ferrocene bulky group, preformed amide groups and flexible ether and methylene units was prepared. The data obtained from the characterization of FDADO from FT-IR and H-NMR spectra and also elemental analysis are collected in Table 1 and the FT-IR spectrum is shown in Fig. 1.

After confirmation of the structure of monomeric diamine with common techniques, its polycondensation reactions with four different acid chlorides including terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), adipoyl chloride (AC) and sebacoyl chloride (SC) led to the preparation of novel ferrocene-based polyamides (Scheme 4 and Table 2). For preparation of the polymers two methods were applied.



Scheme 2. Preparation of 1,1′-dichlorocarbonyl ferrocene.



Scheme 3. Preparation of ferrocene diamine (FDADO).

In method A, polymerization reaction was carried out in the presence of propylene oxide (PO). In this reaction, PO served as an acid scavenger. However, according to the results from inherent viscosity of the polyamides ($\eta_{\mathrm{Inh}} < 0.30$ dl/g measured at 0.5 g/dl in DMF at 30 °C), only oligomers formed.

According to the literature, one efficient method for activating diamines to obtain higher molecular weight polyamides is by silylation of the diamine.[28–31] There has been increasing interest in the activation of the diamine component by *in-situ* addition of trimethylchlorosilane (TMSCl) to the diamine solutions.[32,33] Formation of a complex between TMSCl and acid chloride facilitate the nucleophilic attack of amine toward the carbonyl group in which exclusion of TMSCl is the driving force of the reaction. Also, due to high tendency of TMSCl in reaction with water, it can react with probable traces of water present in the reaction media and prevent destruction of the moisture-sensitive acid chlorides. Therefore, in method B for the preparation of poly(amide ether amide)s, activation of the diamine by *in-situ* silylation was applied.

Conventional methods including FT-IR, H-NMR and elemental analysis techniques were used to characterize the structures of the polyamides and the results were collected in Table 2 and a representative FT-IR spectrum is shown in Fig. 2. For evaluation of molecular weights, the inherent viscosity of the polyamides was measured at a concentration of 0.5 g/dl in DMF at 30 °C that was in the range 0.41–0.49 dl/g. Also, the weight average molecular weights (M_{w}) of the polymers that were determined by GPC are collected in Table 3.

The crystallinity of polymers was examined by X-ray powder diffractometry in the region of $2\theta = 5–70°$ at room temperature. As shown in Fig. 3, the X-ray diffractography of FDADO-TPC showed few sharp peaks with a broad background, indicating that the polymers were almost amorphous. The amorphous nature of polyamides is also reflected in their excellent solubility. The introduction of bulky ferrocenyl group decreases chain-to-chain interactions interrupting the close packing of polymer chains. This leads to enhanced solubility and decreases crystallinity in agreement

Table 1. Characterization data for ferrocenyl diamine (FDADO)

	Elemental analysis			
	Calculated	Found		
Substrate	C H N	C H N	IR (KBr, cm^{-1})	NMR[a] (DMSO-d$_6$, δ)
FDADO	53.94/7.17/10.48	54.16/7.01/10.82	3200–3350 (N–H), 3089 (C–H Arom.) 2925 (C–H Aliphatic), 1655(CO–NH) 1587 (N–H bending), 1440–1575 (C=C), 1160 (C–O)	1.27s (4H, An), 2.79t (4H, CH$_2$) 3.13t (4H, CH$_2$), 3.54t (8H, CH$_2$) 3.62t (4H, CH$_2$), 3.65t (4H, CH$_2$) 4.31s (4H, Cp), 4.76s (4H, Cp) 8.09s (2H, Ad)

[a] 5,6,9 ring, qualified polymerse as am Cp, cyclopentadiene; An, amine; Ad, amide.

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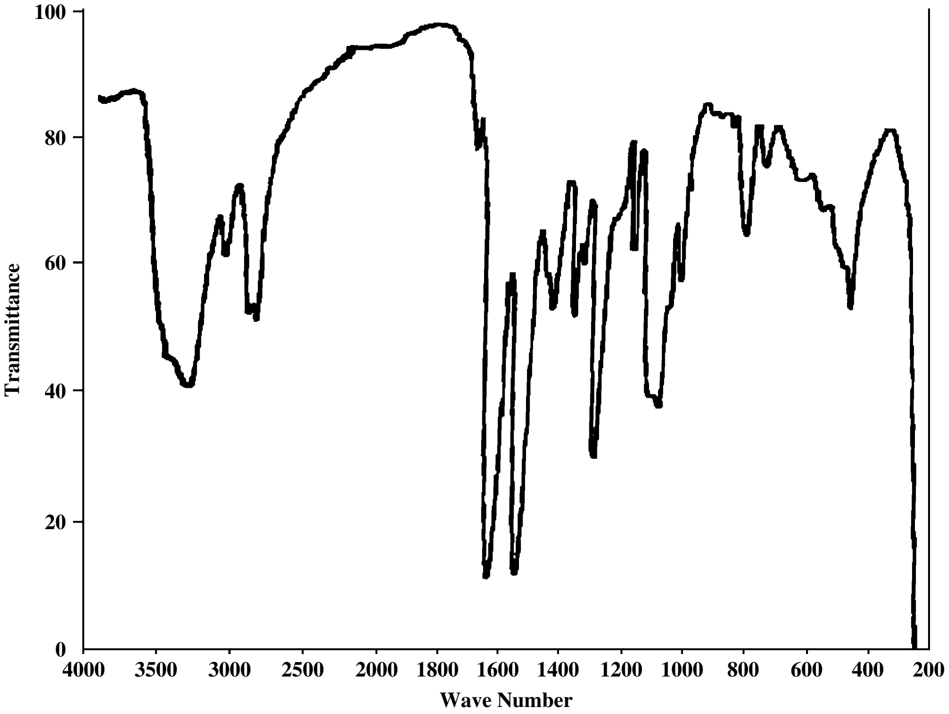
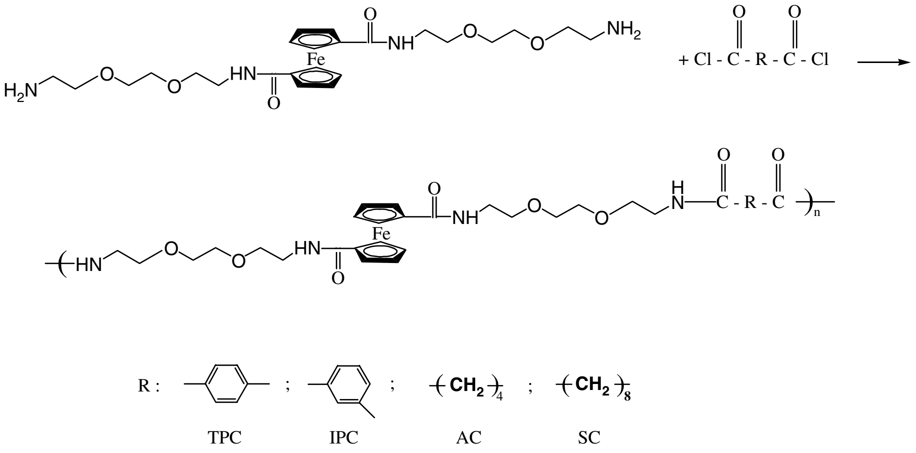


Figure 1. FTIR spectrum of FDADO monomer.



Scheme 4. Preparation of polyamides.

with the general rule that the solubility increases with decreasing crystallinity.

The polymers were soluble in dipolar aprotic solvents such as NMP, DMF, DMSO, DMAc and also in *m*-cresol. They were also partially soluble in pyridine and tetrahydrofuran (THF). The improved solubility is attributed mainly to the presence of flexible spacers units, including ether linkages and methylene groups, and also ferrocene bulky group. FDADO-SC polymer showed the highest solubility among the prepared polymers because of high flexibility of the structure and FDADO-TPC showed the lowest solubility due to the rigidity and symmetry of the structure. FDADO-IPC polymer was more soluble than FDADO-TPC polymer. This was due to the relative disruption of the symmetry and subsequent penetration of solvent molecules to these structures.

The glass transition temperatures (T_g) of the polymers according to DSC (the midpoint of the change in slope of baseline) and DMTA (decrease in storage modulus with increasing tanδ) analyses were about 99–149 °C. These polymers showed lower T_g than conventional polyamides due to the presence of flexible spacers, which means better processability in comparison to the other common

Table 2. Polymer characterization

			Elemental analysis	
			Calculated	Found
Polymer	IR (KBr, cm^{-1})	NMR (DMSO-d_6, δ)	C H N,	C H N
FDADO-TPC	3342–3448, 3079 2918, 1636 (broad), 1532, 1431, 1091	2.90 (4H), 3.21 (4H), 3.50 (8H), 3.54 (4H), 3.60 (4H), 4.30 (4H) 4.73 (4H), 8.12 (4H) 8.18–8.21 (4H)	57.84/6.07/8.43,	57.41/6.39/8.12
FDADO-IPC	3335–3439, 3085 2920, 1634 (broad), 1533, 1433, 1093	2.88 (4H), 3.19 (4H) 3.47 (8H), 3.51 (4H) 3.57 (4H), 4.20 (4H) 4.74 (4H), 7.63 (1H) 7.94 (2H), 8.14–8.16 (4H), 8.46 (1H)	57.84/6.07/8.43,	57.40/5.90/8.69
FDADO-AC	3330–3428, 3082 2975, 1626 (broad), 1531, 1439, 1094	1.58 (4H), 2.36 (4H) 2.81 (4H), 3.15 (4H) 3.42 (4H), 3.45 (8H) 3.54 (4H), 4.27 (4H) 4.70 (4H), 8.01 (2H) 8.12 (2H)	55.90/6.88/8.69,	56.13/6.39/8.88
FDADO-SC	3331–3430, 3070 2977, 1623 (broad), 1534, 1420, 1095	1.27 (8H), 1.60 (4H) 2.35 (4H), 2.72 (4H) 2.87 (4H), 3.35 (8H) 3.44 (4H), 3.51 (4H) 4.27 (4H), 4.71 (4H) 7.86 (2H), 8.10 (2H)	58.28/7.48/8.00,	58.01/7.11/8.30

Figure 2. FTIR spectrum of FDADO-TPC polymer.

polyamides. Thermal stabilities were evaluated by TGA obtained at heating rates of 10 °C/min. The temperatures corresponding to 0 and 10% mass losses, and the maximum decomposition temperatures (T_{max}) derived from the first derivative of TGA versus temperature, and also char yield at 600 °C, are listed in Table 4. The temperature for 10% mass loss, T_{10}, is an important criterion for the evaluation of the thermal stability from TGA data. Comparison of data in Table 4 showed that FDADO-TPC polyamide was more stable than FDADO-IPC polyamide, which was related to

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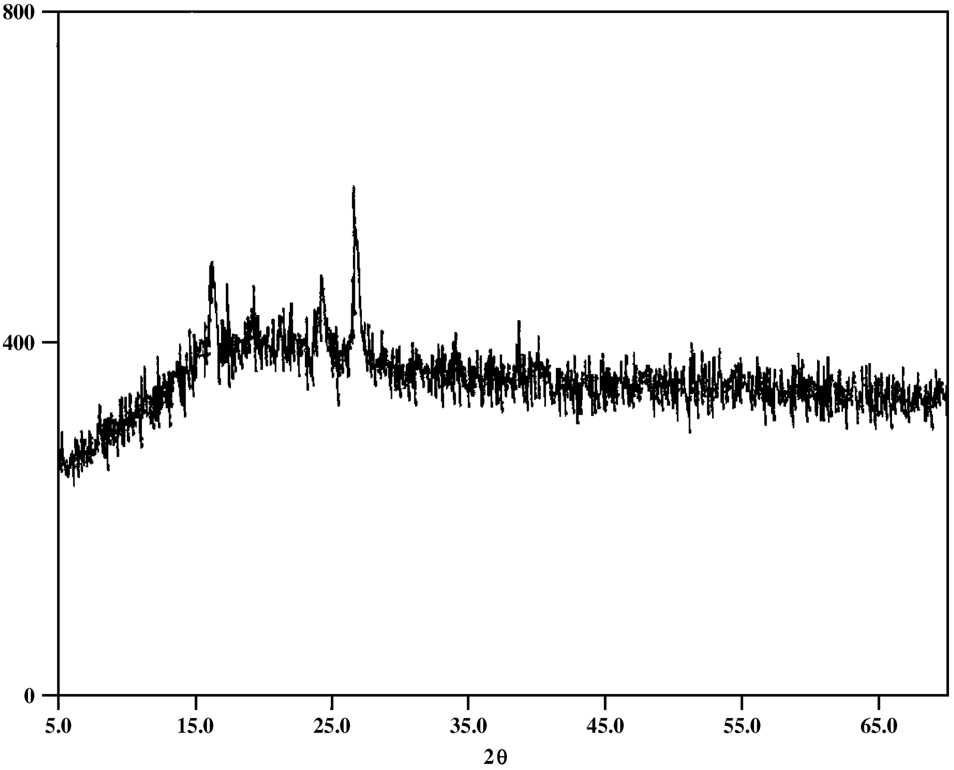

Figure 3. Wide angle X-ray diffraction of FDADO-TPC polymer.

Table 3. Yield, inherent viscosity, and molecular weights of the polymers

Polymer	Yield (%)[a]	η_{Inh} (dl/g)[b]	M_w[c]
FDADO-TPC	95	0.49	23 900
FDADO-IPC	92	0.47	22 500
FDADO-AC	90	0.41	20 000
FDADO-SC	91	0.43	23 100

[a] Based on the weights of monomer, theoretical and found values of polymer (repeat unit).

[b] Measured at a concentration of 0.5 g/dl in DMF at 30 °C.

[c] According to GPC measurement using polystyrene standards, in g/mol.

Table 4. Thermal analysis data

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	$T_{\max}$ (°C)	Char yield at 600 °C (%)
FDADO-TPC	149	206	321	409	40
FDADO-IPC	140	195	314	402	36
FDADO-AC	108	169	274	328	28
FDADO- SC	99	158	269	319	26

T_g, glass transition temperature; T_0, initial decomposition temperature; T_{10}, temperature for 10% weight loss; $T_{\max}$, maximum decomposition temperature. Char yield, weight of polymer remained.

para linkages in polymer FDADO-TPC as compared with *meta* linkages in polymer FDADO-IPC. More symmetric FDADO-TPC polymer led to more close packing of the units and therefore more chain-to-chain interactions. Also, the symmetry of the structure has a great effect on the increasing of molecular weight. By increasing the molecular weight of a polymer, the chain to chain interaction increases because more interactions occur in the repeat units. On the other hand, FDADO-SC was less thermally stable than the other polymers because of weak methylene linkages in the structure. It is noteworthy that the presence of ferrocenyl group in these polymers increases their thermal stability due to the inorganic nature of its structure.

The flame-retardancy of these ferrocene-based poly(ether amide amide)s was measured according to the ASTM standard.[34] The average oxygen index (OI) of these polyamides was about 25.5–27.0 vol% whereas, according to the literature, the average OI for common polyamides without ferrocene unit is about 21–22 vol%.

CONCLUSION

A series of novel ferrocene-based polyamides with flexible spacers was synthesized from a new ferrocene-diamine with different diacid chlorides through polycondensation reactions using TMSCl as an activating reagent of diamine. The polymers showed heat- and flame-resistance and improved solubility. The main factors for preparing novel polyamides with improved solubility without remarkable satisfaction of thermal stability were: introduction of ether and methylene linkages, disruption of symmetry, and presence of ferrocene group and preformed amide units.

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