

THERMAL STABILITY OF FERROCENE DERIVATIVES AND FERROCENE-CONTAINING POLYAMIDES

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Abstract

Thermogravimetric data and the kinetic interpretation of the curves of mass loss for ferrocene, ferrocenecarboxylic and ferrocenedicarboxylic acids and a series of ferrocene-containing polyamides are presented. The results indicate that the degradation process occurred with more than one stage of thermal degradation. The apparent activation energy values and the FTIR spectra of the degradation products suggest that the degradation mechanism occurred by either scission of weak links or by random scission of the chain. Apparently, the *N*-vicinal methylene group was the primary site of attack of oxygen on the polymer chain.

Keywords: ferrocene derivatives, polyamides, thermal degradation

Introduction

Ferrocene derivatives have been extensively used as precursors in chemical reactions, mainly in the synthesis of compounds suitable for use as selective neutral receptors for cations and anions [1, 2], in micro-organism activity [3], enzymatic electrodes [4] and amperometric biosensors [5]. Ferrocenyl-containing acyl thiourea derivatives prepared from ferrocenoyl chloride, for example, were studied in terms of their electrochemical behaviour [6], intramolecular hydrogen bonding [7] and coordination compound [8] formation. Reports on ferrocene-containing polymers, such as polyesters and polyamides [9, 10], have described in general, studies on preparation and solubility. Considering that only a few reports related to thermal analysis and thermal stability of ferrocene derivatives and ferrocene-containing polyamides have appeared [11–13], the purpose of this work was to analyze the thermal stability of ferrocenecarboxylic and 1,1'-ferrocenedicarboxylic acid and four ferrocene-containing polyamides, mainly in relation to the apparent activation energy and the mechanism of the reaction of thermal degradation.

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Experimental

Materials

All the solvents used in this work were purified before use. Ferrocene (Fc), ethylenediamine, 1,6-hexanediamine, 1,12-dodecanediamine and triethylenetetramine were received from Aldrich and were used without further purification. Ferrocene derivatives such as ferrocenecarboxylic acid [FcCOOH] and 1,1'-ferrocenedicarboxylic acid [Fc(COOH)₂] were prepared as described in the literature [14] and were compared with samples obtained from Aldrich. The ferrocene-containing polyamides were prepared by the reaction of 1,1'-ferrocenedicarboxylic acid with the above-mentioned diamines in 1,4-dioxane. By this method, we prepared four polyamides designated as PFDA-2, PFDA-6, PFDA-12 and PFTA-6 as products of the polycondensation of Fc[COOH]₂ and ethylenediamine, 1,6-hexanediamine, 1,12-dodecanediamine and triethylenetetramine, respectively. The following procedure was typical. The diamines ($1.79 \cdot 10^{-3}$ mol) were added to 1,1'-ferrocenedicarboxylic (0.3 g; $1.1 \cdot 10^{-3}$ mol) dissolved in 30 mL of 1,4-dioxane. The mixture was refluxed for 24 h in nitrogen atmosphere. The solid product was isolated by filtration and washed exhaustively with n-hexane, and after the solvent evaporation was dried in a vacuum oven. The characterization was made considering FTIR, elemental analysis, melting temperature and ¹H-NMR. PFDA-2: *m.p.* 194°C (determined by DSC); FTIR (bands in cm⁻¹) 3290 (N–H stretching), 3082, 2951 and 2845 (C–H stretching), 1626 (amide I), 1523 (amide II), 1460 (CH₂ deformation) and 831 (C–H out-of-plane deformation, ferrocene). Elemental analysis (%) (experimental; calculated): C (52.1; 53.1), H (4.9; 5.0) and N (8.8; 8.9). ¹H-NMR (CF₃COOD): δ 5.05 (H–CpCHCCO); δ 4.71 (H–CpCCO) and δ 3.87 (N(CH₂CH₂)). PFDA-12: *m.p.* 203°C (determined by DSC); FTIR (bands in cm⁻¹) 3290 (N–H stretching), 3088, 2921 and 2851 (C–H stretching), 1632 (amide I), 1563 (amide II), 1472 (CH₂ deformation) and 824 (C–H out-of-plane deformation, ferrocene). Elemental analysis (%) (experimental; calculated): C (65.0; 64.5), H (6.8; 7.7) and N (5.4; 6.3). ¹H-NMR (CF₃COOD): δ 6.75 (HN–CO); δ 5.09 (H–CpCHCCO); δ 4.76 (H–CpCCO), δ 3.31 (CH₂CH₂(CH₂)₈); δ 1.87 (CH₂CH₂(CH₂)₈) and δ 1.41 (CH₂CH₂(CH₂)₈). PFDA-6: *m.p.* 196°C (determined by DSC); FTIR (bands in cm⁻¹) 3345 (N–H stretching), 3081, 2935 and 2858 (C–H stretching), 1618 (amide I), 1543 (amide II), 1458 (CH₂ deformation) and 811 (C–H out-of-plane deformation, ferrocene). Elemental analysis (%) (experimental; calculated): C (58.6; 58.0), H (6.1; 6.4) and N (7.4; 7.5). ¹H-NMR (CF₃COOD) as in PFDA-12. PFTA-6: *m.p.* 200°C (determined by DSC); FTIR (bands in cm⁻¹) 3345 (N–H stretching), 3081, 2935 and 2858 (C–H stretching), 1618 (amide I), 1543 (amide II), 1458 (CH₂ deformation) and 811 (C–H out-of-plane deformation, ferrocene). Elemental analysis (%) (experimental; calculated): C (54.6; 53.7), H (6.6; 6.5) and N (12.2; 13.9). ¹H-NMR (CF₃COOD): δ 5.19 (1H, H–CpCHCCO); δ 4.82 (1H, H–CpCCO) and δ 4.13 (3H, (CH₂)₃). The percentage of Fe in the PFTA-6 was determined by atomic absorption, and the observed value of 15.1% was very close to the calculated value (14.6%). Determination of the molecular mass was difficult due to the insolubility of the polyamides in suitable solvents for techniques such as gel-permeation chromatography

and osmometry. Our attempt to determine the molecular mass of the prepared polyamides using osmometry was frustrated due to the above-mentioned problem and also because the obtained values were not reproducible. From the literature, it is known that ferrocene-containing polyamides with similar structures to those studied in this work have molecular masses lower than 5000 g mol^{-1} [10].

Methods

TG measurements were carried out on a Shimadzu 50 thermogravimetric analyzer. For Fc, FcCOOH and Fc(COOH)₂, non-isothermal experiments were performed in the temperature range 25 to 600°C at heating rates of 5, 10 and 20°C min⁻¹ on each sample. The thermogravimetric data were analyzed using the Ozawa [15] and Freeman–Carroll [16] methods. For the Ozawa method, the parameters were determined using the associated TGA-50 software, and the apparent activation energy was derived from the slope of the heating-rate dependence upon the reciprocal absolute temperature, at defined mass loss. In the Freeman–Carroll method, the degradation rate (r) is considered to be dependent on temperature and composition. In terms of temperature, the degradation rate is related to the Arrhenius equation. However, the composition dependence, assuming a kinetic of order n , is defined by Eq. (1), where x is the ratio

$$F(x)=(1-x)^n \quad (1)$$

between the volatilized and the initial mass. Both contributions to the degradation rate can be described by Eq. (2), where A represents the pre-exponential factor, E the apparent activation energy, R the universal constant of gases and T

$$r=K(T)F(x)=Ae^{-E/RT}(1-x)^n \quad (2)$$

the absolute temperature. Considering W as the remaining mass fraction in a TG curve that represents the thermal degradation at a constant heating rate, and assuming the reaction order to be equal to unity, we obtain the final Eq. (3). The slope of the plot of $\ln(r/W)$ vs. $-1/RT$ determines the apparent activation energy (E) and the linear coefficient corresponds to the pre-exponential factor (A).

$$\ln(r/W)=E(-1/RT)+\ln A \quad (3)$$

The kinetic parameters for the four polyamides were determined by the Freeman–Carroll method from TG degradation curves at a heating rate of 10°C min⁻¹.

For the degradation process, the samples were put into an adapted oven in which the required temperature was maintained with an accuracy of $\pm 5^\circ\text{C}$, in presence of air. After one hour of thermal degradation, the samples were cooled to room temperature for the FTIR analysis.

The infrared spectra of ferrocene derivatives, polyamides, and of the thermally-degraded samples, were performed on a Perkin Elmer spectrometer (Model 16PC), with a resolution of 4 cm^{-1} , in the range of $4000\text{--}400 \text{ cm}^{-1}$. The KBr technique was applied to all the analyzed samples.

Results and discussion

Thermal degradation

Figure 1 represents the relationship of the residual mass fraction (1A) and corresponding derivative (1B) to temperature (range of 25 to 800°C) for Fc, FcCOOH and Fc(COOH)₂ at a heating rate of 10°C min⁻¹. For ferrocene, the TG curve corresponds to the sublimation process which took place in a temperature range of 100 to 200°C. The ferrocene sublimation process occurred at 175°C (just one stage) leading to almost 100% mass loss. For FcCOOH and Fc(COOH)₂, more than one stage of thermal degradation was observed. The FcCOOH showed two degradation stages with maximum temperatures of 250 and 410°C, respectively, but the residual weight mass at 600°C increased to ca 12%. For the Fc(COOH)₂, three degradation stages at 298, 448 and 680°C were observed. However, the residual weight mass increased to ca 30% at 600°C, increasing the stability in relation to the monoacid. The last decomposition stage (680°C) for the Fc(COOH)₂ was not considered for the kinetic studies.

For the kinetic studies, we considered only the two major processes of degradation as indicated for the maximum temperatures in Table 1. The apparent activation energies of Fc (for sublimation), FcCOOH and Fc(COOH)₂, determined using the Ozawa method [15], vs. the mass loss fraction (α), are shown in Fig. 2. For the ferrocene sublimation, the values remain practically the same (average value of 56.4 kJ mol⁻¹) in the mass-fraction range of 0.1 to 0.9. However, for FcCOOH, two well-defined ranges were observed. Up to a mass loss fraction of 0.65, the E values are almost constant. Above 0.65, E increases markedly, rising to approximately 240 kJ mol⁻¹ when $\alpha=0.85$. A more complex behavior

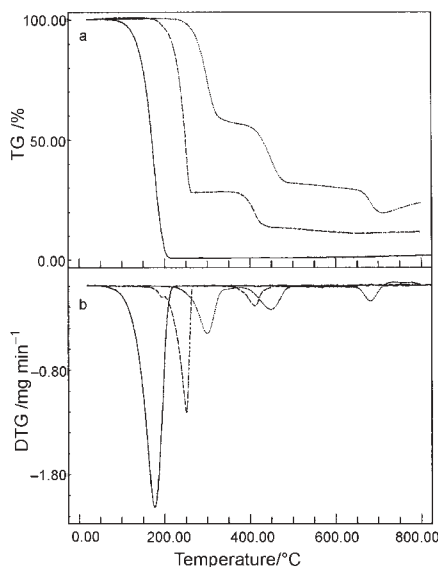


Fig. 1 Thermogravimetric curves (a) and derivative curves (b) for: — Fc, --- FcCOOH and Fc(COOH)₂. All the curves were performed at a heating rate of 10°C min⁻¹

ious, on the other hand, was observed for $\text{Fc}(\text{COOH})_2$ in which the variation of E was more accentuated. The apparent activation energy for the degradation process of the three compounds mentioned above was determined also by the Freeman–Carroll method. The values obtained showed more clearly changes in the degradation mechanism for these systems. For ferrocene, at the sublimation stage, was observed three values for E rather than a single one determined by the Ozawa method. Similar behaviour was observed for FcCOOH and $\text{Fc}(\text{COOH})_2$, noting that the E values for the first degradation stage, determined by the Ozawa method, were approximately equal to the average of the corresponding three values determined by the Freeman–Carroll method. This behaviour is not evident at the corresponding second degradation stages, where the values determined by the Freeman–Carroll method are higher than those obtained by the Ozawa method. The variation of E with conversion is probably related to changes in the degradation mechanism. Both assumptions must be related to the occurrence of more than one stage of degradation in the studied compounds.

Table 1 Kinetic and thermogravimetric parameters for the thermal decomposition of ferrocene derivatives

Systems	$T_{\text{max}}^{\text{a}}/$ $^{\circ}\text{C}$	Ozawa		Freeman–Carroll			Residual ^c / %
		$E^{\text{b}}/\text{kJ mol}^{-1}$	$\log A$	$E^{\text{c}}/\text{kJ mol}^{-1}$	$\log A$	r^{d}	
Fc	175	56.4	6.1	66.7	5.2	0.9999	–
				71.2	3.1	0.9999	
				86.5	5.0	0.9998	
FcCOOH	250	110.0	10.6	121.4	7.3	0.9998	12
				86.1	3.2	0.9993	
				112.5	6.0	0.9993	
Fc(COOH) ₂	298	158.3	13.9	283.8	16.6	0.9996	30
				217.9	11.2	0.9993	
				130.1	6.2	0.9997	
Fc(COOH) ₂	448	151.6	13.2	165.2	9.9	0.9999	30
				117.3	5.0	0.9996	
				214.5	10.0	0.9997	

^aDetermined considering the TG derivative

^bDetermined as the average of the values plotted in Fig. 2

^cRepresents the activation energy values for the different decomposition stages

^dRepresents the correlation coefficient for the $\ln(r/W)$ vs. $-1/(RT)$ plot as in Eq. (3)

^eValues determined at 600°C at a heating rate of 10°C min⁻¹

The TG curves and the respective derivatives for the polyamides are shown in Fig. 3. In all the analyzed curves, the presence of more than one degradation stage is clear. The residual mass loss values were comparable to those observed for $\text{Fc}(\text{COOH})_2$, suggesting a similar stability. The E values determined by the Freeman–Carroll method, considering only the two major processes of degradation, are shown in Table 2. The good correlation coefficients obtained for all the $\ln(r/W)$ vs. $-1/(RT)$ plots are indicative that

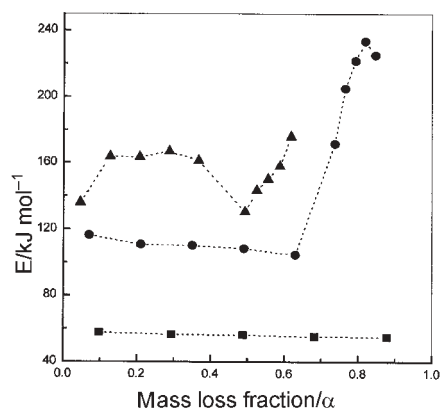


Fig. 2 Plots of the apparent activation energy vs. mass loss fraction for
 ■ – Fc, ● – FcCOOH and ▲ – Fc(COOH)₂

the Freeman–Carroll method was adequate for the E determination in all the studied systems. The complexity of the degradation process is evident by the multiple energy values, even for a single temperature. For example, the PFDA-2 at the degradation stage with a maximum temperature of 240°C showed two E values, indicating probably a change in the degradation mechanism with conversion. The change in the reaction mechanism is a reflection of the existence of multiple competing steps in the polymer degradation. Similar behaviour was observed for all the polyamides, even at different degradation temperatures. Another interesting aspect is related to the range of E values that do not exceed

Table 2 Kinetic and thermogravimetric parameters for the thermal decomposition of the polyamides^a

Systems	$T_{\max}/^{\circ}\text{C}$	Freeman–Carroll method			Residual/%
		$E/\text{kJ mol}^{-1}$	$\log A$	r	
PFDA-2	240	63.8	1.2	0.9995	31
		103.4	4.7	0.9996	
	347	95.3	2.1	0.9992	
PFDA-6	223	98.8	4.5	0.9963	25
		152.7	10.7	0.9992	
	321	94.9	2.3	0.9994	
PFDA-12	218	141.3	8.9	0.9992	40
		187.4	7.3	0.9995	
	465	120.7	2.5	0.9992	
PFTA-6	215	66.0	1.1	0.9996	35
		102.1	5.4	0.9997	
	270	57.5	–	0.9993	
		69.5	–	0.9996	

^aThe same considerations such as in Table 1

200 kJ mol⁻¹. In general, E values lower than 100 kJ mol⁻¹ occurred at lower degradation temperatures and are attributable to scission of weak links in the polymers. On the other hand, high E values are associated with random scission throughout the polymer. Polypropylene, for example, showed two E values (98.3 and 327.9 kJ mol⁻¹) that correspond exactly to the above-mentioned behaviour [17]. Apparently, the E values shown in Table 2 reflect also the difference in the size of the polymer chains. For example, for the first degradation stage of PFDA-2, PFDA-6 and PFDA-12, the E values are 63.8, 98.8 and 141.3 kJ mol⁻¹, respectively. The same tendency was observed in the second stage for the mentioned polyamides. In the polyamide structure, the numbers 2, 6 and 12 represent the number of methylene groups of ethylenediamine, 1,6-hexanediamine and 1,12-dodecanediamine, respectively, in the polycondensation reaction. In the polyamide with branch chains such as PFTA-6, the E values do not show a specific tendency. Aliphatic polyamides, in general, showed a very broad scattering of the measured apparent activation energy. In polyamide-6,6, for example, values in the range of 40–225 kJ mol⁻¹ were reported [18]. For polyamide-6,10, on the other hand, the values vary in the range of 155–225 kJ mol⁻¹ [18]. Apparently, the E values determined for PFDA-2, PFDA-6 and PFTA-6 suggest that the thermal degradation occurred by either scission of weak links or by random scission of the chain. For PFDA-12, on the other hand, the E values suggest only random scission of the chain.

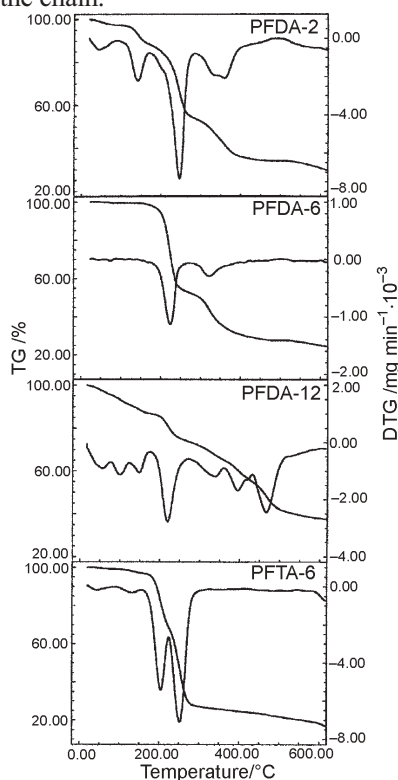


Fig. 3 Thermogravimetric and derivative curves for the polyamides at a heating rate of 10°C min⁻¹

FTIR spectroscopy

The degradation mechanism was evaluated through FTIR spectra at different temperatures during thermal treatment. At room temperature, the main FTIR bands exhibited by ferrocene are associated with C–H stretching at 3094 cm^{-1} , C=C at 1630 cm^{-1} , C–C at 1410 and 1106 cm^{-1} and C–H deformation at 992 and 810 cm^{-1} . With the temperature increased up to 210°C , only decreases in bands intensity were observed, suggesting that the Fc structure was still stable. Only at 350°C did most of the bands disappear, indicating that the ferrocene decreased in stability. In the FTIR spectra of $\text{Fc}(\text{COOH})_2$ at 25°C shown in Fig. 4, the main bands are related with the C–H stretching at 3114 cm^{-1} , O–H stretching in the $3600\text{--}2500\text{ cm}^{-1}$ region (combination bands), C=O at 1677 cm^{-1} , C–C at 1103 and 1403 cm^{-1} , and CH deformation at 992 and 846 cm^{-1} . For the FcCOOH , the FTIR spectra was not included because the same bands were observed and the same analysis was performed. After treatment up to 150°C , the spectra seem very similar to those of the undegraded $\text{Fc}(\text{COOH})_2$ or FcCOOH , and decreases in intensity of some bands only are observed. At 210°C , almost all bands disappeared, including the C=O stretching that at this temperature forms evolved CO_2 . A shoulder observed at 1708 cm^{-1} is probably related with isolated acid groups as a product of the chain scission which has still not formed evolved CO_2 . At 350°C , a band related with unsaturated structures (1626 cm^{-1}) was observed, suggesting, in agreement with the E values, that the thermal degradation occurred also by a mechanism of chain scission.

Figure 5 shows the FTIR spectra for PFDA-12 at different degradation temperatures. Because the behaviour is essentially the same for all the studied polyamides, we discuss only the FTIR spectra for PFDA-12. The main bands for the unheated

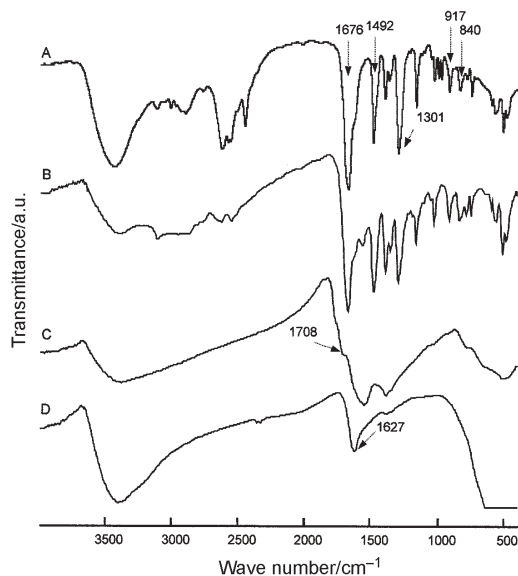


Fig. 4 FTIR spectra of $\text{Fc}(\text{COOH})_2$ during thermal degradation at: A – room temperature, B – 150°C , C – 210°C and D – 350°C

PFDA-12 are indicated in Fig. 5. As usual, the observed band at ca 3415 cm^{-1} corresponds to a free N–H, as has been reported for other systems [19, 20]. The band corresponding to bonded N–H (3290 cm^{-1}) was not clearly observed, probably due to a low spectra resolution. The observed bands at 2920 and 2850 cm^{-1} correspond to the CH_2 stretching, whereas the two bands at 1632 and 1563 cm^{-1} are related to the carbonyl stretching in $\text{C(O)}\text{--NH}$ and N–H deformation, respectively. Bending vibrations of CH_2 in $\text{CH}_2\text{--N}$ and $\text{CH}_2\text{--CO}$ are observed at 1465 and 1390 cm^{-1} , respectively. Bending vibrations of the CONH group are observed at 1027 and 915 cm^{-1} , whereas the C–H out-of-plane deformation corresponding to ferrocene appears at 824 cm^{-1} . After heating up to 150°C , some band shifts were observed, although the intensity remained practically the same. A very weak band (as a shoulder) observed for the degradation in the presence of air at ca 1700 cm^{-1} (1715 cm^{-1} at 210°C) indicated probably the presence of imide structure that appears when the N-vicinal methylene group is the primary site of attack of oxygen on the polymer chain. Imide structure formation was reported as a degradation mechanism for aliphatic polyamides after heating up to 170°C [21, 22]. At 210°C , most of the above-described bands disappeared because a chain scission is able to occur either at NH--CH_2 or at $\text{C(O)}\text{--NH}$ bonds. The observed shoulder at ca 1715 cm^{-1} and the disappearing band at 1465 cm^{-1} (N-vicinal methylene group) confirm the imide structures as PFDA-12 degradation products. At 350°C , the bands related with CH_2 (2920 and 2850 cm^{-1}) and the bending vibration of the --CONH-- group (1027 cm^{-1}) are completely missed. The infrared spectra indicated that the PFDA-12 thermal degradation occurred even before 200°C , confirming

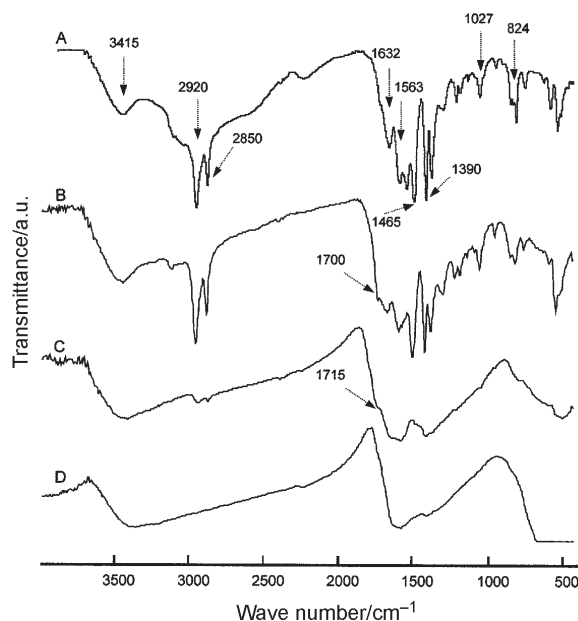


Fig. 5 FTIR spectra of PFDA-12 during thermal degradation at different temperatures such as in Fig.4

the behaviour observed by the thermal degradation curves shown in Fig. 2. Similar behaviour was observed for all the other polyamides studied in this work.

Conclusions

The thermal degradation of ferrocene derivatives and ferrocene-containing polyamides was discussed. The apparent activation energy values determined using the Ozawa and Freeman–Carroll methods indicated that more than one stage of thermal degradation occurred in all the studied systems. A more complex behaviour was observed for $\text{Fc}(\text{COOH})_2$ and the studied polyamides in relation to the degradation mechanism. Imide structure was apparently observed as intermediate product of the polyamides degradation considering that probably the *N*-vicinal methylene group was the primary site of attack of oxygen on the polymer chain. For the studied systems, the apparent activation energy and the FTIR spectra also suggest that the degradation mechanism occurred either by weak links or by random scission of the chain.

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References

- 1 P. D. Beer, A. R. Graydon, A. O. M. Johnson and D. K. Smith, *Inorg. Chem.*, 36 (1997) 2112.
- 2 P. D. Beer, *J. Organ. Chem.*, 490 (1995) 143.
- 3 F. D. Popp and E. M. Bradley, *Medical Chem.*, 13 (1970) 1020.
- 4 T. Tatsuma and N. Oyama, *Polym. Adv. Tech.*, 8 (1996) 534.
- 5 S. F. Hou, H. Q. Fang and H. Y. Chen, *Anal. Lett.*, 30 (1997) 1631.
- 6 Y. F. Yuan, L. Y. Zhang, J. P. Cheng and J. T. Wang, *Transition Met. Chem.*, 22 (1997) 281.
- 7 Y. F. Yuan, S. M. Ye, L. Y. Zhang, J. T. Wang and H. G. Wang, *Polyhedron*, 16 (1997) 2271.
- 8 Y. F. Yuan, S. M. Ye, L. Y. Zhang and J. T. Wang, *Transition Met. Chem.*, 22 (1997) 561.
- 9 C. U. Pittman, *J. Phys. Chem.*, 100 (1996) 8448.
- 10 C. U. Pittman, *J. Polym. Sci. Part A-1*, 6 (1968) 1687.
- 11 R. G. Gamper, P. T. Funke and A. A. Volpe, *J. Polym. Sci. Part A-1*, 9 (1971) 2137.
- 12 L. A. Godinez, S. Patel, C. M. Criss and A. E. Kaifer, *J. Phys. Chem.*, 99 (1995) 17449.
- 13 V. T. Yilmaz, A. Karadag and H. Icbudak, *Thermochim. Acta*, 261 (1995) 107.
- 14 R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, 76 (1954) 4025.
- 15 a T. Ozawa, *Bull. Chem. Soc. Japan*, 38 (1965) 1965.
b T. Ozawa, *J. Thermal Anal.*, 7 (1975) 601.
- 16 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 17 J. H. Chan and S. T. Balke, *Polym. Degrad. Stab.*, 57 (1997) 135.
- 18 K. Y. Tsang, H. Diaz, N. Graciani and J. W. Kelly, *J. Am. Chem. Soc.*, 116 (1994) 3988.
- 19 S. H. Gellman, G. P. Dado, G.-B. Liang and B. R. Adams, *J. Am. Chem. Soc.*, 113 (1991) 1164.
- 20 S. V. Levchik, E. D. Weil and M. Lewin, *Polym. Int.*, 48 (1999) 532.
- 21 M. Svoboda, B. Schneider and J. Stork, *Collect. Czech. Chem. Commun.*, 56 (1991) 1461.
- 22 V. L. Sergei, E. D. Weil and M. Lewin, *Polym. Int.*, 48 (1999) 532.