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THERMAL STABILITY OF SOME POLYFERROCENYLENIMINOIMIDES AND POLYFERROCENYLENAZOMETHINES

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The thermal stability of new ferrocene polymers from the class of polyferrocenyleniminoimides and polyferrocenylenazomethines was studied by means of differential thermal analysis as well as thermogravimetry.

It was established that polyferrocenylenazomethines show good thermal stability up to 200° and are more stable than polyferrocenyleniminoimides.

The presence of ethereal, sulphidic and disulphidic bridges in the diaminic component of the polymers decreases their thermal stability.

Much attention is now being to the ferrocene polymers, especially because of their good thermal stability. For instance, the ferrocene polymers containing nitrogen in the main chain show particular stability in an inert medium up to 600–700° [1, 2], the polyazomethines up to 450–500° [3], the polypyrazoles up to 400° [4], the polyazines up to 300–400° [5–8], the polyhydrazides up to 220° [9], the polyurethanes up to 200–250° [10–12] and the polyamides up to 110–470° [12–14].

In the present paper a study is made of the behaviour under heating of some polycondensation polyferrocenyleniminoimides and polyferrocenylenazomethines whose syntheses and properties have previously been reported [15, 16].

Experimental

The polyferrocenyleniminoimides (PFcImImd) and polyferrocenylenazomethines (PFcAzm) were prepared by the polycondensation of 1,1'-diacetylferrocene (DiAcFc) and 1,1'-bis-[β-(2-furyl)-acryloyl] ferrocene (DiAcFcF) with biuret ($ZnCl_2$ as catalyst) [15], benzidine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulphide, 4,4'-diamino-2,2'-dinitrodiphenyl sulphide ($ZnCl_2$ or p-toluenesulphonic acid as catalyst) [16] and N,N'-disulphynyl-bis(4-amino-2-nitrophenyl) disulphide (pyridine as catalyst), respectively.

The complex-structured polymers contain units of the *a, b, c, d* types [15, 16].

The thermal curves were recorded on a Paulik–Paulik–Erdey (MOM, Budapest) apparatus. The runs were made with samples of 35 mg, heated in air at a rate of 10°/min, within the temperature range 20–900°.

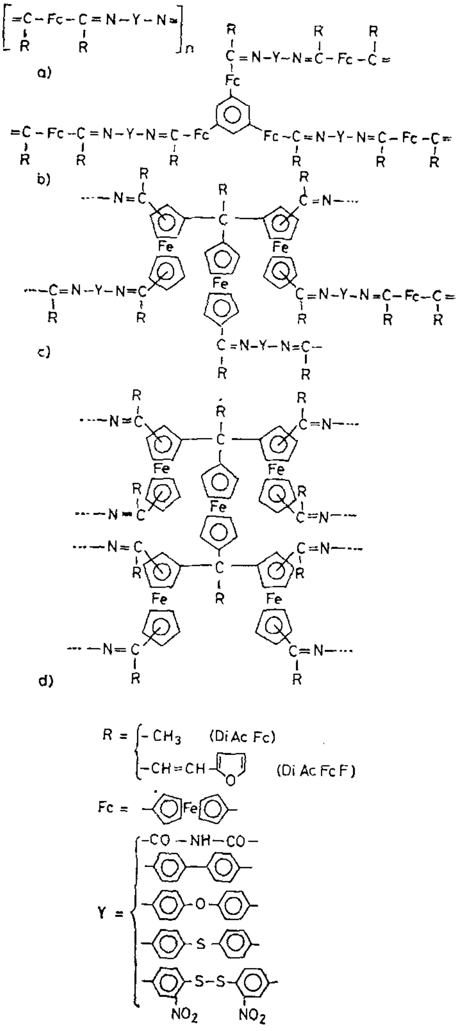


Fig. 1. Unit types of the complex-structured polymers

The activation energies and the reaction orders for the destruction processes were calculated by the Coats–Redfern method [17] with a Felix CE-32 computer. The thermal behaviour was characterized by taking into account the degradation temperature (T_d), referred to as the temperature where weight loss begins, the temperature ranges of the destruction stages, as well as the weight loss percentage for every stage. The thermal effects were estimated qualitatively from the DTA curves.

Results and discussion

The thermal stabilites of PcFlmImd and PFcAzm were studied in comparison to those of the dicarbonylic and diaminic components employed in their synthesis.

1,1'-Diacetylferrocene is degraded in two stages. The thermal degradation proceeds at a higher rate during the first stage (155–260°) than during the second stage (260–450°). By taking the weight loss percentage into account, the first stage may be considered to correspond to the scission of acetyl groups (25% weight loss compared with 31.85% as calculated) (Table 1), and the second one to destruction of the ferrocene nucleus (50.7% weight loss compared with 47.4% as calculated).

The decomposition of 1,1'-bis [β-(2-furyl)-acryloyl]-ferrocene proceeds in a single stage, the product being more stable than 1,1'-diacetylferrocene. This increased thermal stability might be due to the stabilization of the $C_1 - C_{carbonyl}$ and $C'_1 - C_{carbonyl}$ bonds, owing to the expansion of the electron conjugation. The DTA curve shows an exothermal process without weight loss at 160°; this value corresponds to the melting point of the product. It might be assumed that an exothermal transfusion takes place simultaneously with the substance melting, this prevailing over the endothermal melting.

Biuret begins to change with weight loss at 120°. The three stages of the thermal decomposition correspond to the literature data on the thermal conversion of biuret into cyanuric and cyanic acids.

Table 1

Parameters of thermal decomposition of dicarbonylic and diaminic components

No.	Starting component	M.p., °C	Decomposition range	Weight losses, %	Energy of activation, kJ/mole
1.	1,1'-Diacetylferrocene	122	155–260	25.00	67
			260–450	50.70	107
2.	1,1'-Bis[β-(2-furyl)-acryloyl] ferrocene	160	230–660	84.00	31
3.	Biuret	120	120–220	30.00	84
			220–265	23.75	256
			290–445	46.25	237
4.	Benzidine	105	180–320	25.70	77
			365–675	74.28	92
5.	4,4'-Diamine-2,2'-dinitrodiphenyl-disulphide	222	200–260	21.40	258
			275–395	20.00	134
			395–625	58.60	71
6.	N,N'-Disulphinyl-bis(4-amino-2-nitrophenyl)disulphide		120–210	7.14	89
			210–275	17.85	216
			275–350	17.14	260
			350–660	60.00	82

The thermal degradation of 4,4′-diamino-2,2′-dinitrodiphenyl disulphide takes place in three stages. The first occurs explosively (reaction order zero) with nitro group elimination. The product is stable up to 200°; the weight losses begin below the melting point.

The data in Table 1 show that the thermal degradation of N,N′-disulphynyl-bis-(4-amino-2-nitrophenyl) disulphide begins at 120° and proceeds in four stages. The first stage migth be attributable to SO_2 elimination from two product molecules, the weight losses indicated by the TG curve (7.14%) being in agreement with the calculated percentage (7.4%). The following two stages correspond to nitro groups elimination, their activation energies of 216 and 260 kJ/mol, respectively, being close to that calculated for the elimination from 4,4′-diamino-2,2′-dinitrodiphenyl disulphide (258 kJ/mol).

The characteristics of the thermal decomposition of PFclmImd are listed in Table 2.

The thermal stabilities of PFclmImd are not influenced either by the reaction conditions (solvent, temperature) or by the dicarbonylic component, the degradation temperatures (T_d) being of about the same value for PFclmImd derived from DiAcFc (185–195°) and from DiAcFcF (185–200°) (Table 2).

Table 2

Parameters of thermal decomposition of PFclmImd

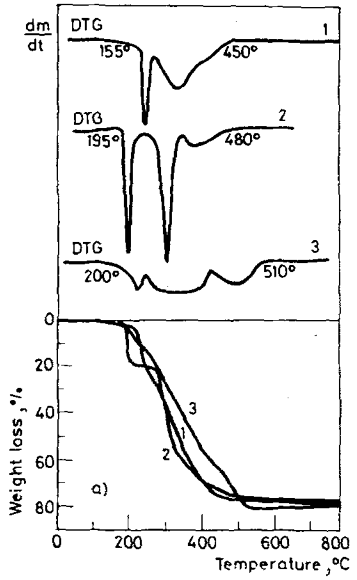
Diaminic component	Dicarbonylic component	No.	Polycondensation conditions*		Range	Weight losses, %	Energy of activation, kJ/mole
			Temperature, °C	Solvent			
Biuret	DiAcFc	1_{ins}	120	Dioxan	185–230	24.60	
					230–390	56.50	
		2_{ins}	120	DMSO	195–260	20.16	
					260–345	47.58	145
					345–480	17.74	124
		3_{sol}	90	DMSO	185–250	17.90	
					250–340	60.93	140
					340–445	12.50	102
	DiAcFcF	4_{sol}	120	Dioxan	190–270	25.90	140
					270–400	61.73	96
		5_{sol}	90	DMSO	185–265	20.31	102
					265–480	76.56	129
		6_{ins}	90	DMSO	200–290	10.30	110
					290–435	50.62	98

* Catalyst $ZnCl_2$. Duration 20 hours

Instead, the molecular structure of the polymer, is rather important, the compounds soluble in the reaction medium being degraded at a lower temperature than the insoluble ones. This rather small temperature difference appears in every soluble-insoluble determination (Table 2).

The PFcImImd are about 60–80° more stable than biuret. The T_d values are 30–40° higher than those corresponding to DiAcFc (Fig. 2a) and 30–50° lower than the degradation temperature of DiAcFcF (Fig. 2b). It may be concluded that during the first degradation stage of PFcImImd the decomposition processes take place in the dicarbonylic component, similarly to those of the second stage of biuret degradation. The rather close temperature ranges of the first stage of PFcImImd decomposition and of the second stage of biuret decomposition, the small weight losses in this interval, and the corresponding reaction orders, support this conclusion.

The thermal stabilities of PFcAzm were found not to depend on the dicarbonylic component. Hence, it may be concluded that the first decomposition stage of samples 1–6 and the first two decomposition stages of samples 7–19 (Table 3) are characterized by scission of the diaminic component. With samples 7–19 an explosive decomposition of the nitro groups takes place in the first stage.



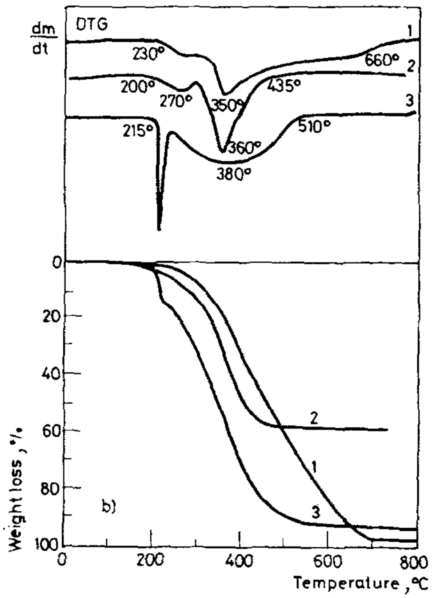


Fig. 2a. DTG and TG curves of polyferrocenyleniminoimides and polyferrocenylenazomethines derived from 1,1'-diacetylferrocene 1 — DiAcFc; 2 — PFcImImd (sample 2; Table 2); 3 — PFcAzm (sample 17; Table 3)

Fig. 2b. DTG and TG curves of polyferrocenyleniminoimides and polyferrocenylenazomethines derived from DiAcFcF. 1 — DiAcFcF; 2 — PFcImImd (sample 6; Table 2); 3 — PFcAzm (sample 19; Table 3)

Table 3

Parameters of thermal decomposition of PFcAzm

Diaminic component	Dicarbonylic component	No.	Polycondensation conditions				Decomposition range	Weight losses, %	Energy of activation, kJ/mole
			Temp., °C	Duration, h	Solvent	Catalyst			
Benzidine	DiAcFc	1_{ins}	120	20	Dioxan	$ZnCl_2$	220–285 285–365 365–470	13.2 23.5 45.6	112 136 187
		2_{ins}	150	21	Melt	$ZnCl_2$	200–245 245–450 450–580	6.6 50.7 15.5	 95 194
	DiAcFcF	3_{ins}	150	21	Melt	$ZnCl_2$	225–310 320–430 430–520	11.7 40.3 25.6	128 97 169
4,4′-Diaminodiphenylether	DiAcFc	4_{ins}	120	10	Dioxan	$ZnCl_2$	280–335 335–660	6.4 70.0	259 103
	DiAcFcF	5_{ins}	120	10	Dioxan	$ZnCl_2$	205–260 260–520	11.4 74.3	246 80
4,4′-Diaminodiphenyl-tioether	DiAcFc	6_{ins}	120	10	Dioxan	$ZnCl_2$	200–320 320–630	10.4 51.9	52 99
4,4′-Diamino-2,2′-dinitro-diphenyldisulphide		7_{sol}	120	10	Dioxan	$ZnCl_2$	200–310 310–470 470–640	14.3 50.8 17.5	82 102 204
		8_{ins}	120	10	Dioxan	$ZnCl_2$	210–275 275–370 370–420 420–540	17.7 41.5 15.4 16.0	111 123

4,4′-Diamino-2,2′-dinitrodiphenyldisulphide	DiAcFc	9_{ins}	120	10	Dioxan	AcPTS	225—685	94.00	38
		10^{*}_{ins}	*120	10	Dioxan	$ZnCl_2$	195—205	34.7	
							275—300	14.4	369
							300—500	23.6	135
		11_{ins}	120	20	Dioxan	$ZnCl_2$	210—275	7.8	
							275—365	22.8	128
							365—500	60.0	141
		12_{ins}	120	35	Dioxan	$ZnCl_2$	210—260	15.6	35
							260—385	25.6	152
							385—505	50.0	128
		13_{ins}	150	23	Melt	$ZnCl_2$	210—350	17.8	77
							350—510	68.1	142
	DiAcFcF	14_{ins}	120	20	Dioxan	$ZnCl_2$	220—270	26.6	134
							270—350	25.8	138
							350—505	42.9	85
		15_{ins}	200	35	Dioxan	$ZnCl_2$	200—270	14.3	89
							270—355	26.9	181
							355—500	53.9	180
		16_{ins}	200	20	Melt	$ZnCl_2$	250—375	29.8	95
							375—550	47.7	224
N,N′-Disulphynyl-bis(4-amino-2-nitrophenyl)disulphide	DiAcFc	17_{ins}	80	10	Benzene	Py	200—255	7.6	
							255—400	50.6	53
							400—510	22.7	164
		18_{ins}	80	20	Benzene	Py	200—240	15.5	
							240—400	50.0	64
							400—495	25.1	
	DiAcFcF	19_{ins}	80	10	Benzene	Py	215—260	14.5	
							260—510	76.9	76

sol = fraction soluble in the reaction medium; ins = insoluble product; AcPTS = p-toluenesulphonic acid; * = dicarbonylic to diaminic component mole ratio 1/2

The data in Table 3 show that the temperature ranges of the destruction stages which follow after those attributed to the diaminic component are situated at values equal or higher for PFcAzm with DiAcFcF than for those with DiAcFc.

The polycondensation duration does not influence the thermal stability of PFcAzm.

For samples 17 and 18 the data in Table 3 show that the doubling of the reaction time results in a residue decrease of about 9 %, while the total weight loss in the first two stages affecting the disulphinylic component increases by the same value. Since the residue results exclusively from the diketonic component, it follows that the polymer obtained with a longer reaction duration has a lower content of dicarbonylic component; hence the macromolecule has diaminic residues at both ends.

As regards the polycondensation catalyst, since it does not influence the polymer structures [16] it does not cause an essential difference in their thermal behaviour.

The PFcAzm synthesized in the presence of $ZnCl_2$ (either in solution or in melt) or pyridine exhibit two or three decomposition stages, the weight loss in the first being small in most cases, about 10–15 %. Only one polymer (sample 9), synthesized in the presence of p-toluenesulphonic acid, decomposes in a single stage. However, it would be possible for several superposed stages to exist.

The T_d values of PFcAzm and the dicarbonylic components are in a ratio similar to that mentioned for PFcImImd (Tables 2 and 3).

As with other polyazomethines [18, 19], the –O–, –S–, and –S–S– bridges between the aromatic rings in the diaminic component decrease the T_d

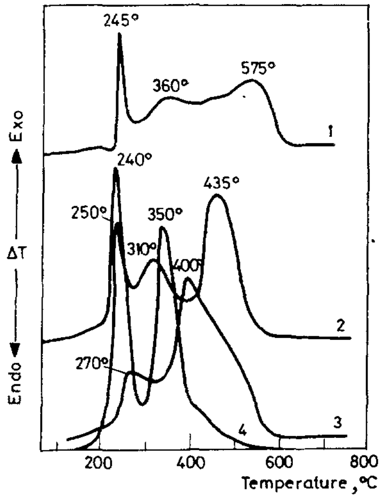


Fig. 3. DTA curves of some PFcImImd and PFcAzm. 1 — 4,4′-diamino-2,2′-dinitrodiphenyldisulphide; 2 — PFcAzm with 4,4′-diamino-2,2′-dinitrodiphenyldisulphide (sample 11; Table 3); 3 — PFcAzm with benzidine (sample 3; Table 3); 4 — PFcImImd (sample 2; Table 2)

values (Table 3) due to the lower conjugation. This means that the C–O and C–S bonds are split first as they are weaker than the $>C=N-$ bond.

PFcAzm are thermally more stable than PFcImImd. The thermal stabilities of the PFcAzm synthesized by us [16] which display appreciable weight losses at

As can be seen from the DTA curves in Fig. 3, the thermal decompositions of PFcImImd and PFcAzm are exothermic processes.

300–400° (air), are comparable to those of the compounds synthesized by Neuse *et al.* [3] by the polycondensation of 1,1'-diformyl – ferrocene with p-phenylenediamine (rapid weight loss at 450–500°, in argon) and of other Schiff polybases [18].

Conclusions

From the thermogravimetric analysis of PFcImImd and PFcAzm the following conclusions may be drawn

1. PFcAzm are more stable than PFcImImd.
2. PFcImImd and PFcAzm obtained from DiAcFc are more resistant than DiAcFc to the increase of temperature, while the polymers belonging to both classes derived from DiAcFcF show weight losses at lower temperatures than for the dicarbonylic component.
3. The ethereal, sulphidic or disulphidic bridges in the diaminic component structure decrease the thermal stability of the polymer.
4. PFcAzm shows a good thermal stability, comparable to that of other polyazomethines.

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Zusammenfassung — Die Thermostabilität neuer Ferrocenpolymerer der Klasse von Polyferrocenyleniminoimiden und Polyferrocenylenazomethinen wurde durch Differentialthermoanalyse und Thermogravimetrie untersucht.

Es wurde festgestellt, dass die Polyferrocenylenazomethine bis zu 200 °C eine gute Thermostabilität aufweisen und stabiler sind als die Polyferrocenyleniminoimide.

Die Gegenwart von Äther-, Sulfid- und Disulfidbrücken in der Diaminkomponente der Polymeren setzt ihre Thermostabilität herab.

Резюме — С помощью дифференциального термического анализа и термогравиметрии изучена термическая устойчивость новых ферроценовых полимеров класса полиферроцениленииминоимидов и полиферроцениленазометинов. Установлено, что полиферроцениленазометины обладают хорошей термической устойчивостью до 200 °C и более устойчивы, чем полиферроцениленииминоимиды. Наличие в диаминовой компоненте полимера кислородных, сульфидных и дисульфидных мостиков, уменьшает термоустойчивость полимеров.