Thermochimica Acta, 134 (1988) 177–185
Elsevier Science Publishers B.V., Amsterdam

ON THE THERMAL STABILITY OF SOME NEW POLYAZINES AND POLYAZOMETHINES (II)

M. DUMITRIU, M. DARINGA, M. PASTRAVANU, CR. DUMITRIU and T. LIXANDRU
Department of Organic and Macromolecular Chemistry, Polytechnic Institute of Jassy, 23 August 11, Jassy, (Romania)

ABSTRACT

The thermal stability of new polymers from the class of polyphenanthrenequinone azines, polyanthraquinone azines, polyphenanthrenequinone azometines and polyanthraquinone azomethines was studied by means differential thermal analysis as well as thermogravimetry. It was established that polyazomethines show good thermal stability up 200°C, and are more stable than polyazine. The kinetical parameters for the thermodestruction reaction were determined by the Coats - Redfern method.

INTRODUCTION

Much attention is now being given to the conjugated polymers, especially because of their good thermal stability. For instance polymers containing nitrogen in the main chain and aromatic structures show particular stability /1-4/.

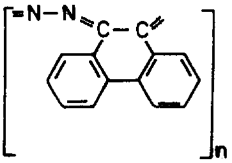
In the present paper a study is made of the behaviour under heating of some polycondensation, polyazine and polyazomethine whose syntheses and properties have previously been reported /5,6/.

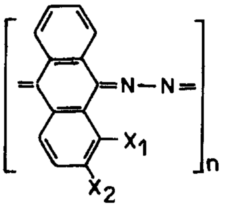
EXPERIMENTAL

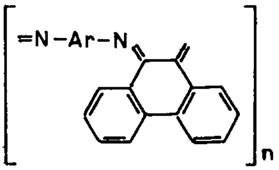
The polyphenanthrenequinone-azines (PPhQA) (1a), polyanthraquinone-azines(PAthQA) (1b), polyphenanthrenequinone-azomethines (PPhQAzm) (2a), and polyanthraquinone-azomethines(PAthQAzm) (2b) were prepared by the polycondensation of 9,10-phenanthrenequinone (PhQ), or 9,10-anthraquinone (AthQ) and 1-chloroanthraquinone (1-ClAthQ), 2-chloroanthraquinone (2-ClAthQ), with hydrazine hy-

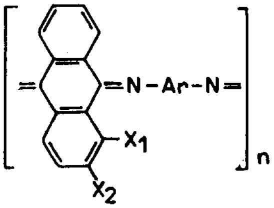
Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

drate, disulphinylhydrazine in various conditions /5/ or with m-phenylenediamine (mPhD), p-phenylenediamine (p-PhD), benzidine (Bz) in solvent DMF catalyst $ZnCl_2$, quinone/diamine mole ratio 1/1 or 1/2, respectively /6/.


1a


1b

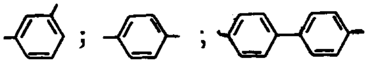

2a


2b

where: X_1, X_2 = H, H

X_1, X_2 = Cl, H

X_1, X_2 = H,Cl

Ar = 

The thermal curves were recorded on a Paulik - Paulik- Erdey (MOM, Budapest) apparatus. The runs were made with samples of 45 - 50 mg, heated in air at a rate of 10°/min, within the temperature range 20 - 900°C. The activation energies and the reaction orders for the destruction processes were calculated by the Coats - Redfern method /7/ with a Felix CE-32 computer. The thermal behaviour was characterised by taking into account the degradation temperature (Td) 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 stabilities of PPhQA, PAthQA, PPhQAzm and PAthQAzm were studied in comparison with those of the dicarbonylic and diaminic components employed in their synthesis.

In the case of dicarbonylic compounds (Table 1), the AthQ decomposition occurs in only one stage while, for its derivatives and for PhQ, two steps are to be noted. The temperature at which thermodestruction begins is 180°C and 190°C for AthQ and 1-ClAthQ, 2-ClAthQ, respectively, while, for PhO this temperature is only 170°C.

TABLE 1

Parameters of the thermal decomposition of dicarbonylic and diaminic compounds

Starting component	M.p.	Thermogravimetric data					
		Td*	Degradation steps	Temperature range	Weight losses	Ea	Reaction order
	(°C)	(°C)		(°C)	(%)	(Kcal/mol)	
AthQ	285	180	I	180 - 490	100	13.9	0.0
1-ClAthQ	162	190	I	190 - 350	90	14.0	0.0
			II	350 - 600	10	-	-
2-ClAthQ	210	190	I	190 - 380	96	13.1	0.0
			II	380 - 570	4	-	-
PhQ	206	170	I	170 - 490	95	13,7	0.0
			II	490 - 630	5	-	-
p-$C_6H_5(NH_2)_2$	130	120	I	120 - 240	45	22.9	1.7
			II	345 - 615	50	24.1	2.5
m-$C_6H_5(NH_2)_2$	65	120	I	120 - 280	71	13.6	0.0
			II	400 - 600	28	58.2	2.1
Bensidine	105	180	I	180 - 320	26	18.4	-
			II	365 - 675	74	22.0	-

* - The maximum temperature at which the samples do not show weight losses

All dicarbonylic compounds are characterized by the same values of the activation energy and of the reaction order - in the first stage of thermal decomposition.

For diaminic components two destruction stages are noticed. During the first stage the reactions take place in the liquid phase between 120 - 280°C, leading probably to stable structures resistant up to temperature higher than 350°C.

In the case of benzidine, a much higher thermal stability is to be observed, the starting temperature of the destruction process being - as compared with phenylenediamines - much higher, alongwith a much lower ratio of weight losses in the first stage. This stability may be correlated with the extended conjugated system, due to the two aromatic nuclei of benzidine. The characteristics of thermal decomposition of polyazines obtained from AthQ and its derivatives are listed in Table 2.

TABLE 2

Parameters of thermal decomposition of PAthQ and PPhQA

Quinone	Hydrazine derivative mol/ratio solvent/ catalyst	Thermogravimetric data					
		Td (°C)	Degradation steps	Temperature range (°C)	Weight losses (%)	Activation energy (Kcal/ mol)	Reaction order
AthQ	$H_2N-NH_2.H_2O$	180	I	180 - 330	18.3	33.3	2.5
	1/2		II	330 - 440	12.6	36.8	2.5
	$DMF/ZnCl_2$		III	440 - 830	69.0	43.8	2.5
1-ClAthQ	$H_2N-NH_2.H_2O$	185	I	185 - 490	35.7	9.7	0.0
	$DMF/ZnCl_2$		II	490 - 880	64.3	43.0	1.8
2-ClAthQ	$H_2N-NH_2.H_2O$	200	I	200 - 440	15.7	11.9	2.5
	$DMF/ZnCl_2$		II	440 - 820	78.3	29.6	2.5
AthQ	O=S=N-N=S=O	80	I	80 - 170	7.1	-	-
	1/1		II	210 - 500	38.2	9.7	0.0
	Pyridine		III	520 - 870	61.7	35.6	2.5
AthQ	O=S=N-N=S=O	80	I	80 - 180	27.3	27.6	1.9
	1/2		II	240 - 370	8.0	17.1	1.5
	Pyridine		III	370 - 490	8.0	50.0	2.0
			IV	490 - 840	55.2	36.6	2.5
PhQ	O=S=N-N=S=O	70	I	70 - 180	12.5	-	-
	1/2		II	180 - 375	29.0	34.3	1.9
	Pyridine		III	430 - 780	55.8	37.3	2.5
PhQ	$H_2N-NH_2.H_2O$	320	I	320 - 550	42.9	40.2	2.5
	1/1		II	550 - 885	57.1	42.3	2.5
	$DMF/ZnCl_2$						
PhQ	$H_2N-NH_2.H_2O$	290	I	290 - 540	51.7	-	-
	1/1		II	540 - 880	48.3	32.5	2.5
	Xylene						

The thermal stabilities of PAthQA are influenced by the reaction conditions (solvent, mole ratio) or by the diaminic component (Table 2).

Polyazines obtained with disulphinylhydrazine have a sensibly lower Td and weight losses of 7 - 27 % in a first stage of decomposition - which is characterized by activation energies having close values and the same reaction order - going on then in stages comparable - as temperature range and weight losses - with those of the polyazines obtained with hydrazine hydrate (Table 2). One can thus conclude that, in this first step, the terminal groups will be released as SO_2 and N_2. In such cases, the polycondensation degrees are not high, therefore, which has been actually demonstrated experimentally, through measurements of intrinsic viscosity /5/. The relatively large variables of the weight losses in the first stage in the case of polyazines obtained with disulphinyl hydrazine may be explained both through the differences of molecular weight - depending on the syntheses conditions - and the reaction agent employed, and also through the variation of the molar ratios of the two reactants (quinone and disulphinylhydrazine (Figure 1). The conclusion to be drawn is that polyazines obtained with quinones and disulphylhydrazine evidence a low thermal stability.

The stability of polyazines obtained with hydrazine hydrate from AthQ, 1-ClAthQ and 2-ClAthQ is slightly lower, as compared with those of PhQ (Table 2).

On comparing polyazines based on AthQ and its derivatives (Figure 2) one could observe that the introduction of the electron - withdrawing substituents induces a certain improvement of the thermal stability, which is to be observed from the Td values, i. e. 180, 185 and 200°C respectively as well as from the shifting of the decomposition stages towards higher temperatures (Table 2).

In the case of polyazines based on PhQ (Figure 3) high thermal stabilities are to be recorded. The starting temperatures of thermal destruction Td 290°C and 320°C - depending on the conditions in which the condensation reaction occurs (solvent, catalyst) indicate much higher values as against those of PAthQA.

In the case of PhQ having carbonylic groups in α , it is to be assumed that - on the condensation with hydrazine the formation of some "ansa" type cycles occurs, which are formed of 8-terms, having four nitrogen atoms and a conjugated system extended with aromatic rings. These condensed structures are stable, being thermally decomposed in two steps. In the first one, evidencing no exothermal effect condensed aromatic structure, very stable, are formed, which well burn (exothermal effect) in the second stage (550 - 885°C).

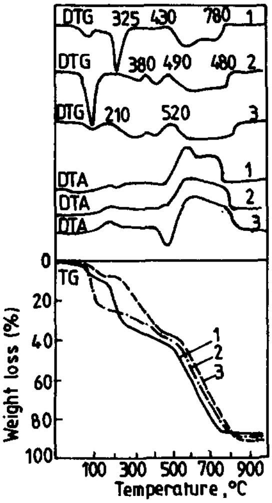


Fig. 1. DTA, DTG and TG curves of polyazines derived from disulphinylhydrazine with PhQ mole ratio 1/2 (1), AthQ mole ratio 1/2 (2) and AthQ mole ratio 1/1 (3).

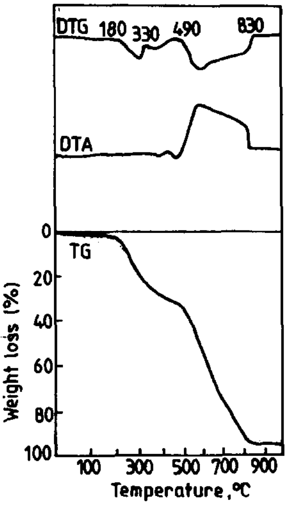


Fig. 2. DTA, DTG and TG of PAthQA.

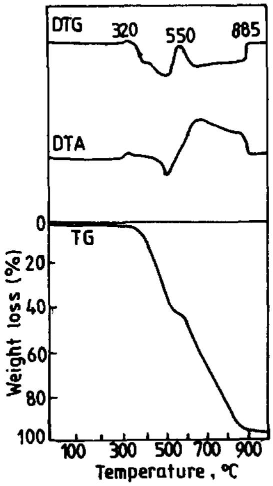


Fig. 3. DTA, DTG and TG curves of PPhQA obtained from PhQ and hydrazine hydrate (DMF/ZnCl$_2$).

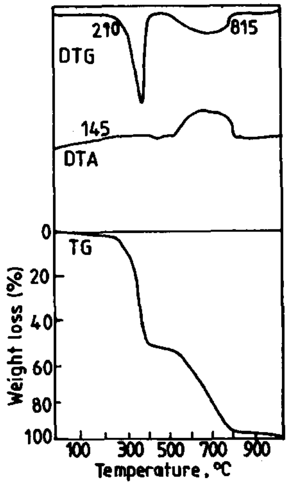


Fig. 4. DTA, DTG and TG of polyazomethine derived from 1-ClAthQ and p-phenylenediamine.

TABLE 3

Parameters of thermal decomposition of PAthAzm and PPhQAzm

Starting components		M.p.	Thermogravimetric data					
Quinone	$H_2N-Ar-NH_2$ Ar=	(°C)	Td (°C)	Degradation steps	Temperature range (°C)	Weight losses (%)	Activation energy (Kcal/mol)	Reaction order
AthQ	p-C_6H_4-	296	200	I	200 - 350	74.1	21.9	0.9
				II	350 - 375	5.5	-	-
				III	375 - 430	18.2	-	-
				IV	430 - 540	2.2	-	-
AthQ	m-C_6H_4-	290	190	I	190 - 395	94.9	18.5	1.7
				II	395 - 540	5.1	-	-
AthQ	-C_6H_4-C_6H_4-	280	200	I	200 - 375	44.4	20.1	0.7
				II	375 - 520	18.9	41.6	2.5
				III	520 - 695	30.0	66.1	2.5
1-ClAthQ	p-C_6H_4-	145	210	I	210 - 440	57.8	13.6	0.0
				II	480 - 815	42.2	30.2	2.5
1-ClAthQ	m-C_6H_4-	155	210	I	210 - 400	62.2	19.3	0.0
				II	460 - 790	36.7	29.1	2.5
1-ClAthQ	-C_6H_4-C_6H_4	140	210	I	210 - 400	71.1	15.9	0.3
				II	400 - 730	28.9	37.9	2.5
2-ClAthQ	p-C_6H_4-	155	200	I	200 - 435	74.4	16.5	0.8
				II	465 - 745	25.6	34.4	2.5
2-ClAthQ	m-C_6H_4-	150	180	I	180 - 390	68.5	8.8	0.0
				II	390 - 685	31.5	22.2	1.8
2-ClAthQ	-C_6H_4-C_6H_4	150	210	I	210 - 390	55.5	19.9	1.3
				II	485 - 860	44.5	28.3	2.5
PhQ*	p-C_6H_4-	250	200	I	200 - 370	21.4	18.5	1.8
				II	370 - 550	36.5	36.3	2.5
PhQ	p-C_6H_4-	250	200	I	180 - 800	90.0	5.0	0.0
PhQ	m-C_6H_4-	-	170	I	170 - 430	14.0	9.2	2.4
				II	430 - 920	86.0	22.5	2.5
PhQ	-C_6H_4-C_6H_4	-	230	I	230 - 500	17.4	18.7	2.5
				II	500 - 850	82.6	45.5	2.5

* - Polymer insoluble

The set of thermogrammes of polyazomethines obtained from PhQ (Table 3) evidence an increase in thermal stability, characterized by the increase of the Td value from 170 to 230°C, depending on the nature of the diaminic components in the series m-phenylenediamine < p-phenylenediamine < benzidine. At the same time, there is to be observed that insoluble fractions have a higher thermal stability.

Starting from AthQ and diaminic compounds, PAthQAzm can be obtained; an observation being made in this case, i. e. that structures containing para - substituents are more stable than those having position meta linkages.

Chlorine introduction in the AthQ nucleus generally induces a slight increase of the thermal stability and also a uniformisation of the stability of the polycondensation compounds with m-phenylenediamine, p-phenylenediamine and benzidine.

All compounds containing chlorine in their structure are decomposed in two steps, the former being characterised by a reaction order of 0 - 0.3, moderate activation energy (14 - 19 Kcal/mol), a high decomposition rate and the latter by a reaction order of 2.5, higher activation energies (30 - 40 Kcal/mol) and much lower decomposition rates (Figure 4).

The same observations are to be made for 2-ClAthQ polycondesated with diaminic compounds, the only difference laying in the fact that - again - in this series the increase of the thermal stability occurs, as function of the diaminic compounds in the m-phenylenediamine < p-phenylenediamine < benzidine (Td = 180°C, 200°C and 210°C respectively). In the series of polyazomethines and also in that of polyazines there is to be noted that the polycondensation products of PhQ have a slightly higher thermal stability than those of AthQ (Figure 5).

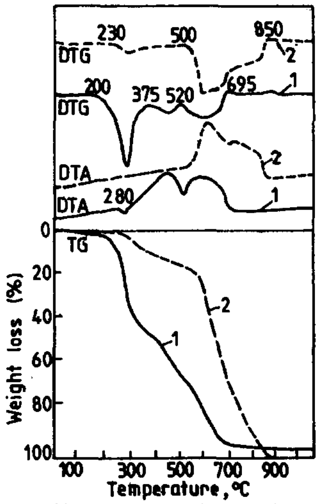


Fig. 5. DTA, DTG and TG curves of polyazomethines derived from benzidine and AthQ (1) and PhQ (2).

CONCLUSIONS

From the thermogravimetric analysis of PPhQA, PPhQAzm, PAthQA and PAthQAzm, the following conclusions may be drawn.

1. Polyazines obtained from quinones and disulphinylhydrazin have lower thermal stabilities than those based on hydrazine hydrate.

2. Among the compounds obtained through condensation with hydrazine hydrate - the PPhQA compounds are less sensitive showing a higher thermal stability. The difference in stability is significant as one would expect, due to the formation of the same condensated cyclic structure with a conjugated system of double bonds.

3. PPhQAzm, PAthQAzm, P-1-ClAthQAzm and P-2-ClAthQAzm show a good thermal stability comparable to that of other polyazomethines,

4. In the class of polyazomethines, an increase of the thermal stability can be observed, as depending on the diaminic compound in the series m-phenylenediamine < p-phenylenediamine < benzidine.

5. More thermal stable polyazomethines - as compared with polyazines - have been obtained from AthQ and their derivatives.

REFERENCES

1. S. M. Mezhikovskii, A. A. Gurov, N. I. Myagchilova, B. I. Liogonkii and A. A. Berlin, Vysokomol. Soedin. 15 (1973) 3.

2. K. Takao, N. Shigeo and M. Kentoro, Kobunshi Kagaku, 30 (1973) 491

3 M. Dumitriu, M. Dărîngă, M. Păstrăvanu and T. Lixandru, Rev. Roumaine Chim., 25 (1980) 981

4 L. Tătaru, M. Dărîngă, M. Vîtă, T. Lixandru and Cr. Simionescu, J. Therm. Analysis, 22 (1981) 259

5 M. Păstrăvanu, M. Dumitriu and T. Lixandru, Eur. Polym. J., 19 (1983) 633

6 M. Dumitriu, M. Păstrăvanu and T. Lixandru, Bul. Inst. Politeh. Iaşi XXXI (XXXV) (1985) 106

7 A. W. Coats and S. T. Redfern, Nature, 201 (1964) 68