Thermochimica Acta, 19 (1977) 319–325
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COMPARATIVE THERMAL ANALYSIS OF THERMALLY STABLE POLYMERS AND MODEL COMPOUNDS

II. AROMATIC DI- AND POLYKETONES

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(Received 17 August 1976)

ABSTRACT

Thermooxidative degradation in oxygen of aromatic diketones, cross-linked polyketones and model compounds has been investigated. It was found that 1,1′-di-(4″-phenoxybenzophenonyl ether exhibits the highest thermal stability among diketones. This is presumably due to the alternation of electron accepting and electron donating groups in the chain of this compound.

On the basis of data on the oxidation kinetics of cross-linked polyketones and model compounds, it was established that the thermal stability of the latter is much higher. This is due to the fact that the polymer contains unsaturated structures and residual acetyl groups because the curing process of diacetylaromatic compounds is incomplete.

It was shown that comparative thermal analysis (CTA) may be used to evaluate the extent of completeness of curing of di- and polyfunctional monomers.

CTA of thermally stable polymers and model compounds permits the determination of the minimum thermooxidative stability for an ideal polymer structure and, hence, the evaluation of the percentage of defects of structure in a real polymer[1].

This paper continues the consideration of thermooxidative degradation of thermally stable polymers, in particular, of polyketoarylenes—a new group of polymers obtained in recent years[2-6]

where:

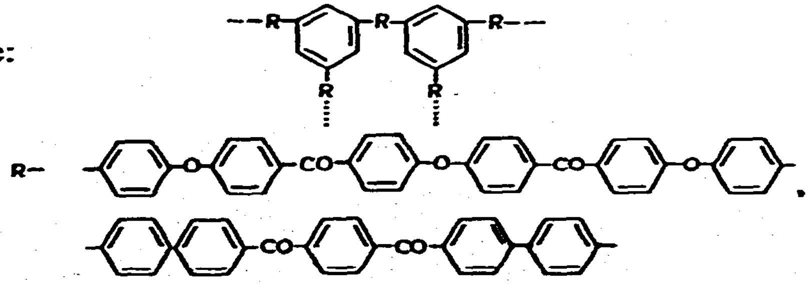
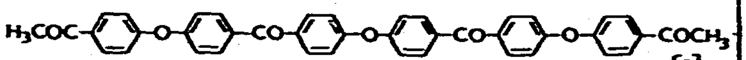
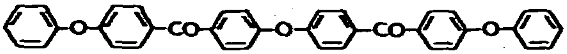
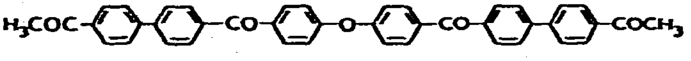
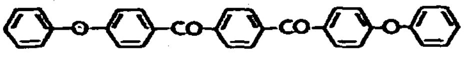
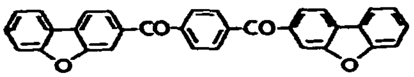
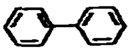
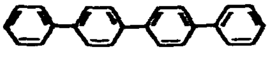
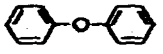
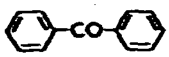
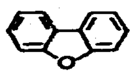
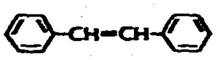
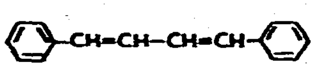
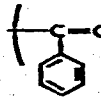


TABLE 1

THERMAL STABILITY OF DI- AND POLYKETONES AND MODEL COMPOUNDS IN OXYGEN

No.	*Compound*	*Temp. (°C) of mass loss (weight %) in sample oxidation to CO and CO_2*			
		0	*3*	*5*	*10*
1	Cross-linked polyketone obtained by polycyclotrimerization	250	340	365	—
	of compound (2) under vacuum	320[a]	460[a]	500[a]	515[a]
2	 [6]	260	346	395	—
3		385	431	438	—
4	Cross-linked polyketone obtained by polycyclotrimerization	285	374	394	—
	of the monomer	390[a]	470[a]	500[a]	540[a]
					
	in air				
5	 [6]	370	429	—	—
6	 [7]	375	411	428	—
7		345	425	—	—
8		340	397	403	—
9		340	402	410	—
10		343	403	414	—
11		385	424	431	—
12		345	398	408	—
13		310	359	374	—
14	 (*trans*)	240	259	274	—
15	 (*trans, trans*)	160	250	295	
16	 $n = \sim 10$	210	322	—	—

[a] Data of dynamic thermogravimetric analysis of samples in air at a heating rate of 4.5°C min^{-1}.

of individual aromatic diketones of a similar structure[6,7], and of simplest compounds modelling single fragments and units of di- and polyketones.

Table 1 shows results of thermooxidative degradation* of two cross-linked aromatic polyketones (obtained by polycyclotrimerization of corresponding diacetylaromatic ketophenylenes) and of compounds modelling the polymer chain, single blocks and units of the polymer.

A comparison of polymers to model compounds shows that the thermooxidative stability of the latter is much higher with the exception of models containing unsaturated groups (compounds (14) and (15)). For the interpretation of this peculiarity, it is advisable to consider first the thermal oxidation of the simplest fragments in the polymer chain.

Figure 1 shows the rate of CO and CO_2 formation vs. oxidation temperature for the simplest model compounds.

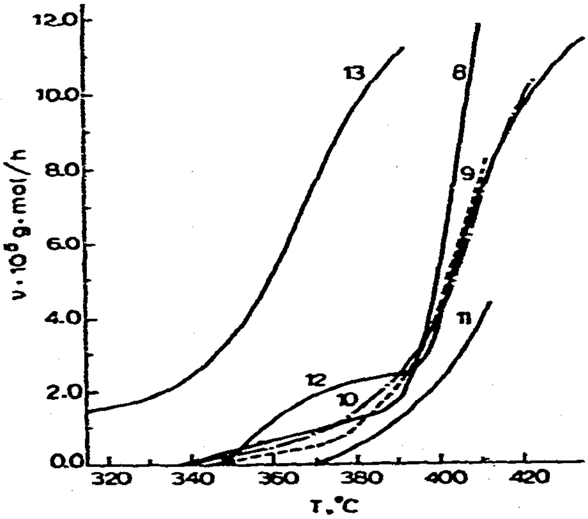


Fig. 1. Rate of formation of $CO+CO_2$ in oxidation of model compounds—benzene (8), diphenyl (9), quaterphenyl (10), diphenyloxide (11), benzophenone (12) and diphenyleneoxide (13) vs. temperature.

Table 1 and Fig. 1 show that among the low-molecular-weight models considered diphenyloxide and diphenylene oxide exhibit the highest and the lowest stability, respectively. Over the temperature range from 340 to 390 °C thermal stabilities of benzene, diphenyloxide, benzophenone and compounds of the diphenyl type are relatively close to each other. When the temperature is raised to 420 °C, benzene begins to differ from this group: its degradation becomes more pronounced. It should be noted that over the temperature range

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*The procedure for carrying out thermooxidative degradation of organic compounds in oxygen has been described previously[1].

from 390 to 420 °C degradation rates of benzophenone, diphenyl and quaterphenyl virtually coincide. This is probably due to oxidation of aromatic rings.

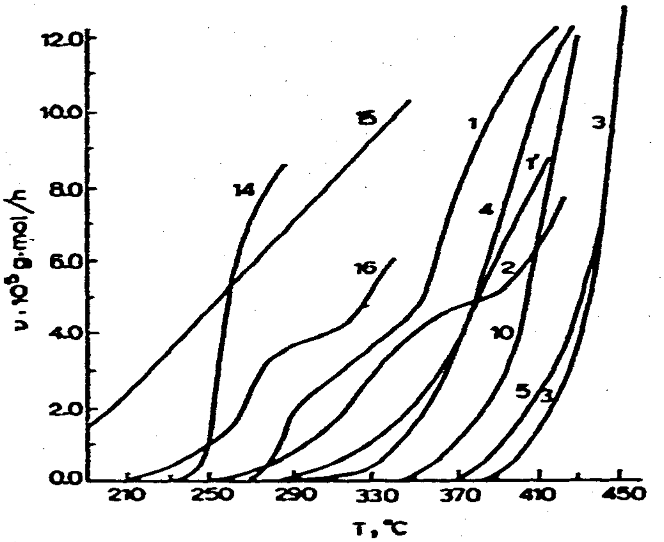


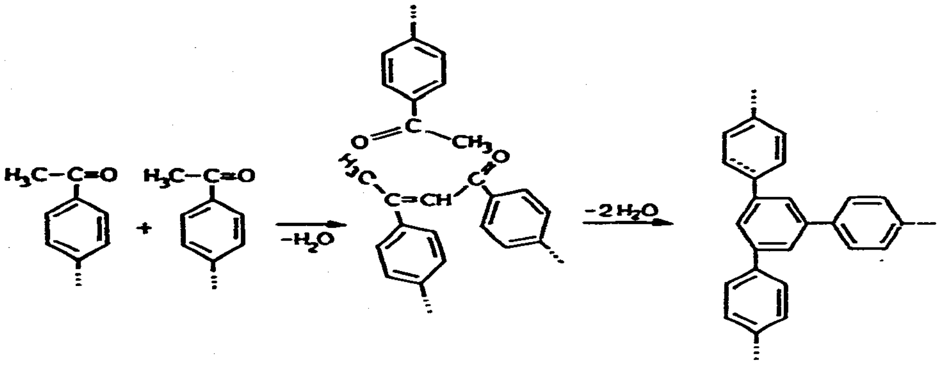
Fig. 2. Rate of formation of $CO+CO_2$ in oxidation of aromatic di- and polyketones and model compounds vs. temperature. Numbers of curves correspond to numbers of compounds in Table 1.

Table 1 and Fig. 2 show that compounds of higher molecular weight the molecules of which are a combination of simplest structures, are more stable to thermal oxidation. Thus, the stability of diphenyl (9) and benzophenone (12) is appreciably lower than that of di(biphenylylcarbonyl) benzene (5) and the stability of diphenyleneoxide (13) and benzophenone (12) is much lower than that of bis(dibenzonfurylcarbonyl) benzene (7). For this group of compounds this may be attributed to differences in the aggregate state, the concentration factor[1] and structural effects. Indeed, the most favourable conditions are observed for thermal oxidation of the simplest compounds (8), (9) and (11)-(14) (homogeneity of the process of oxidation in vapours). Under these conditions compounds (3) and (5)-(7) which are in the vapour-liquid state should oxidize slower. Moreover, twist angles between benzene rings are known to decrease on passing from the vapour state to liquid and solid states. This also leads to increasing thermal stability of compounds.

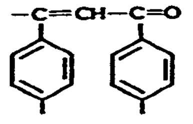
At the same time the increase in the thermal stability of compounds (3) and (7) as compared to corresponding low-molecular-weight compounds may also be induced by the alternation of electron-withdrawing and electron-donating groups which makes the bonds stronger. Experimental data show that compound (3) with a regular alternation of oxygen and carbonyl atoms between benzene rings exhibits the highest thermal stability among diketones.

It might be expected that on passing from models (3), (5) and (7) to polymers of a similar structure thermooxidative stability should increase. However, this is not observed. As Fig. 2 and Table 1 show, temperatures of 3–5 % mass loss of the cross-linked polyketone are by 70–90 °C lower than for the corresponding model diketone. Moreover, the stability of polyketone (1) is even lower than that of its monomer (2).

The reason for this seems to be stepwise character of polycyclotrimerization of diacetyl aromatic compounds which leads to the cross-linked polyketone:



If polycyclotrimerization could proceed to completion, alternation of ketophenylene or ketophenyleneoxide chains with star-like 1,3,5-triphenyl benzene groups should be expected; marked degradation of these groups begins at 390–400 °C. Nevertheless, in practice it is difficult to carry out the reaction to completion. As a result, when monomer (2) is cured under vacuum, defects of structure of the type



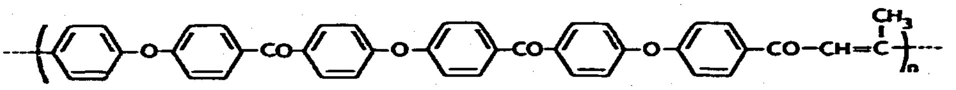
remain in the polymer. As wil be shown below, they drastically reduce the temperature of the start of thermooxidative degradation of polymer.

Thermal oxidation of stilbene (*tr*) (14), 1,4-diphenylbutadiene (*tr, tr*) (15) and polyphenylacetylene (16) begins already at 170–270 °C. In this series thermooxidative stability increases with increasing length of the conjugation chain. Figure 2 shows that monomer (2)—1,1′-di(4‴acetyl-4″-phenoxybenzophenonyl) ether is stable up to 260 °C and its acetyl groups undergo only slight oxidation even at 290 °C. On further temperature rise up to 340 °C its oxidation rate gradually increases.

It is of interest to note that within the range 340–390 °C the oxidation rate of this monomer increases slightly and only above this range a sharp increase is observed. In order to interpret this behaviour of monomer (2) it should be taken into account that at temperatures ranging from 280 to 390 °C apart from oxidation of acetyl groups a simultaneous process of polycondensation of ketones occurs. A comparison of oxidation curves (1) and (2) shows that polyketone obtained by curing under vacuum contains a considerable amount of intermediate readily oxidized unsaturated structures besides residual acetyl groups. When monomer (2) is heated in an atmosphere of oxygen, the oxidation of acetyl groups proceeds much slower than that of unsaturated structures. A comparison of curves (1) and (2) over the temperature range from 340 to 390 °C shows clearly that when ketone (2) is heated under oxygen for 1 hr (during its analysis), unsaturated structures are formed to a lesser extent than in prolonged curing under vacuum.

The suggestion that under conditions of thermal oxidation of monomer (2) only abstraction of oxidized acetyl groups occurs, does not seem probable since in this case considerable degradation of monomer (2) would begin at much higher temperatures (at 430–440 °C) rather than at 390–400 °C. Presumably, a pronounced thermal degradation of monomer (2) at 390–400 °C is caused by the degradation of 1,3,5-triphenylbenzene groups[*] formed during polycyclotrimerization.

Data on the kinetics of oxidation polymer (1) and unsaturated compounds (14), (15) and (2) allow an approximate evaluation of the percentage of defects of structure (unsaturation and residual acetyl groups) in a cross-linked polyketone. Figure 2 shows that at 290 °C $2.0 \cdot 10^{-5}$ g mol of $CO + CO_2$ is evolved from the polyketone sample. On the basis of thermal oxidation of models (14) and (15) at 290 °C it may be assumed that for a hypothetical unsaturated polymer:


(A)

under experimental conditions $\sim 4.6 \cdot 10^{-5}$ g mol of $CO + CO_2$ will be evolved. This corresponds to approximately 43 % of structures of type A in the sample of cross-linked polyketone (1). However, if a correction is made for oxidation of residual acetyl groups of the polymer, it is possible to determine the contents of structures of type A in polymer (1) with a higher precision. Figure 2 shows that at 290 °C $0.75 \cdot 10^{-5}$ g mol of CO and CO_2 is formed as a result of oxidation of acetyl groups of the monomer. Infrared spectra show that in the cured product (1) the number of acetyl groups do not exceed 30 %. This corresponds to the formation of $\sim 0.25 \cdot 10^{-5}$ g mol of CO and CO_2. Taking this into account, one might assume that in the oxidation of structures of type (A) only $1.75 \cdot 10^{-5}$ g mol of gas is formed at 290 °C. Hence, the content of these structures in the sample is approximately 38 %.

Cross-linked polyketones of higher thermal stability are formed when the curing process is carried out in air[4] or under vacuum with prolonged heating (Fig. 2)[1].

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[*] Compare with degradation curve (10) of quaterphenyl.

Nevertheless, in this case too, the thermal stability of polymer (4) is much lower than that of the corresponding model (5) (see Fig. 2).

Hence, results of this investigation show that CTA makes it possible to follow the process of curing of di- and polyfunctional monomers and thus to investigate possibilities of lowering the percentage of defects of structure in final polymer products. At the same time investigations of thermooxidation of model compounds (without defects of structure) are of great importance for the oriented synthesis of new thermally stable polymers.

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