The Investigation of Thermostability of Poly(Sulfophenylene Quinones)*

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It has been established that the process of destruction of the investigated polymers occurs in stages. One of the stages is the process of destruction of sulfo groups whose rate does not depend on the presence of oxygen in the system. Calculations have been made of the kinetic parameters of the separate stages of destruction of poly(arylene quinones). The destruction is accompanied by crosslinking reactions which transform the initial linear structure of the polymers into a branched and cross-linked structure.

The paper presents the results of studying thermal and oxidative thermal destruction of poly(sulfophenylene quinones) (PSPQ) in oxidized (*I*) and reduced (*II*) forms
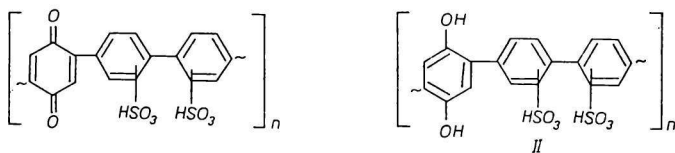
A comparison is given with the data for poly(arylene quinone) (PAQ) of the following structure
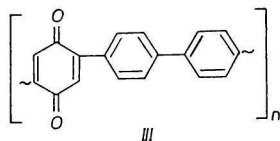
Experimental

The methods of synthesis and characterization of the objects are described in [1]. Before being tested the samples were dried in vacuum (10^{-2} mmHg) at $110-120°C$ for $8-10$ hours. The samples were tested on a derivatograph ("MOM", Hungary) of the system designed by F. Paulik, I. Paulik, and L. Erdey under the conditions of nonisothermal heating. The rate of temperature rise was 3 ± 0.1 deg min^{-1}. The batch of the sample was 100 mg. The inert material for differential thermal analysis (DTA) consisted

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of Al$_2$O$_3$ (100 mg) calcined up to 1200°C. To carry out the thermal destruction in an inert atmosphere argon deprived of moisture and oxygen was made to pass above the sample 1 hour before heating in order to remove traces of air from the reaction volume. For special experiments the samples were evacuated in quartz ampoules for 3 1/2 hours at 320°C.

The infrared spectra were measured at room temperature with an UR-10 spectrometer (Zeiss, Jena).

The kinetic parameters of destruction were calculated according to thermogravimetric (TGA) data by the method [2] based on determining the rate of weight losses at the thermogravimetric curve inflection point $(-\mathrm{d}w/\mathrm{d}T)_{\max}$. The use of derivatography makes this method of calculation particularly convenient since, first of all, automatic differentiation (DTG) makes possible to determine with great precision both the temperature and the value of the rate at the maximum point; secondly, a comparison between the DTG and DTA curves, obtained in one experiment, permits to identify satisfactorily the separate stages of destruction.

Calculation of the kinetic parameters was made separately for each stage. In this connection the weight of the sample which was involved (or might have been involved) in the transformation at the given stage of destruction in the specified temperature range was assumed, for the sake of calculation, to equal 100%. In those cases when the peaks on the DTG curve under the selected conditions of heating could not be completely separated, the residual weight (W_f) was determined by successive extrapolation of the TGA curve [5].

Results and Discussion

Analysis of the derivatographic data given in Figs. 1—4 shows that the losses in weight when the polymers under investigation are heated, take place in several stages. For polymers containing HSO$_3$ groups, the first stage (60—190°C) is connected with desorption of moisture. This is attested by practically similar character of the decomposition of polymers *I* and *II* in the air and in argon at 60—190°C (Figs. 1 and 2); also by the endothermic peak on the DTA curve characterizing this stage (Figs. 3 and 4) and the invariability of the proper structure of the polymer when heated to 200°C (Table 1 and Fig. 6). The amount of moisture sorbed may be as large as 25—27%, depending on the pre-history of the sample (Fig. 5). As can be seen from Table 2, the removal of moisture from the polymer proceeds as a reaction of the first order with an activation energy of 10—11 kcal mole^{-1}. The relatively high value of E_{act} for processes of this type [3], shows that in this case there is not only and not so much the physical adsorption of water molecules as
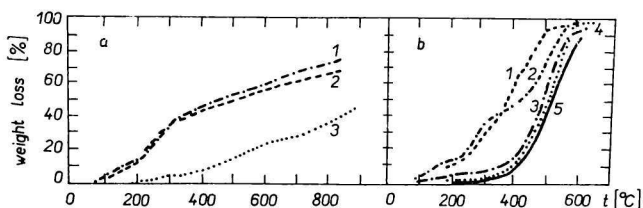

Fig. 1. TGA curves of destruction in argon (*a*) and in the air (*b*) of initial PSPQ-*I* (*1*), PSPQ-*II* (*2*), PAQ-*III* (*3*) and after thermal treatment in vacuum, PSPQ-*II* (*5*) and PAQ-*III* (*4*).

a stronger interaction, possibly chemisorption, the HSO_3 groups being the active centres of chemisorption. The following experimental facts may serve in this concrete case as arguments corroborating the last assertion, in addition to the widely known facts regarding the reactivity of sulfo groups in relation to water:

a) The PAQ-*III* polymer, which differs from PSPQ-*I* only in that that it contains no HSO_3 groups, practically loses no weight within the range of $60-190°C$ (Fig. 1).

b) Reduction in the content of HSO_3 groups in the polymer leads to a decrease in the amount of the sorbed moisture (see Table 1 and Fig. 6).

c) Removal of sulfo groups from PSPQ-*II*, precludes the "leap" of losses in weight within the range of $60-190°C$ (Fig. 1).

The second stage of decomposition, the process of desulfonation begins under our conditions of heating at a temperature of $200-210°C$. It terminates at $400°C$ in an inert atmosphere. Desulfonation is complicated in the air by oxidation of the polymer, which starts at $320-350°C$ (Fig. 2).

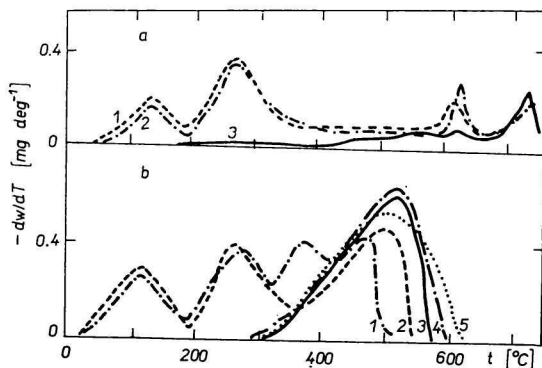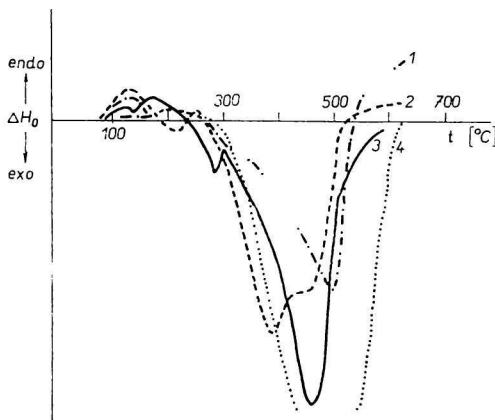*Fig. 2.* DTG curves of destruction.
See Fig. 1 for denotations.

Fig. 3. DTA curves in the air of initial PSPQ-*II* (*1*), PSPQ-*I* (*2*), PAQ-*III* (*3*) and after thermal treatment in vacuum, PAQ-*III* (*4*).
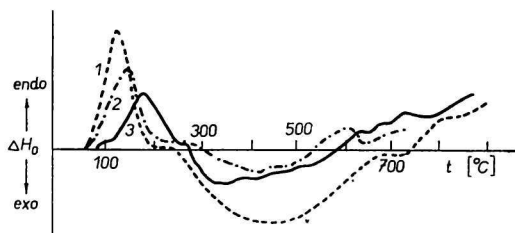
Fig. 4. DTA curves in argon.
See Fig. 3 for denotations.

The following supports the fact that the S-shaped curve within the range of $200-400°C$ is connected with the splitting off the HSO_3 groups:

a) a considerable reduction in the relative sulfur content in the PSPQ residue after heating up to $325-390°C$ (Table 1);

b) a reduction in the infrared spectrum of the polymeric residue (after heating) of the intensity of the bands in the region of $1000-1200$ cm^{-1}, assigned to the sulfo groups (Fig. 6).

The kinetic parameters given in Table 2 indicate that for PSPQ-*II* the process of desulfonation occurs as a reaction of the first order with E_{act} $16-17$ kcal mole^{-1}.

A fractional order of reaction and a higher value of the effective activation energy was obtained for polymer *I* during thermal oxidation within the temperature range corresponding to the process of splitting off the HSO_3 groups. This is related to the fact that the reactions of desulfonation of PSPQ-*I* are complicated by oxidation of the polymer

Table 1

Elementary composition of poly(sulfophenylene quinone) *II*

Polymer	Elementary composition		
	% C	% H	% S
calculated for structure *II*	49.3	2.6	17.5
initial	50.1	3.8	17.2
after 200°C in the air	50.1	3.1	17.1
after 325°C in the air	63.2	3.2	6.2
after 390°C in the air	68.4	3.2	3.5
after thermal treatment in vacuum	69.6	3.2	2.3

itself, which for PSPQ-*I* begin earlier and proceed in a more complex way than for other investigated poly(arylene quinones). Superimposition of these two processes determines the result so obtained. The fact that in an argon atmosphere, when oxidizing processes are precluded, the kinetic characteristics of reactions of desulfonation within the range of $200-400°C$ practically coincide with similar parameters for the same range during thermal oxidation of PSPQ-*II*, leads to the assumption that the process of desulfonation of PSPQ-*I* and *II* occurs identically, and that these differences, within the bounds of the

chosen method, are connected with the superimposition of different types of reaction and with the insufficient accuracy of their identification.

The above processes are accompanied by crosslinking reactions which transform the structure of the polymer from a linear to a branched and cross-linked structure. Crosslinking is connected not only with the processes of saturation of valency in the place of the break of the HSO₃ groups but it also occurs independently in other mechanisms.
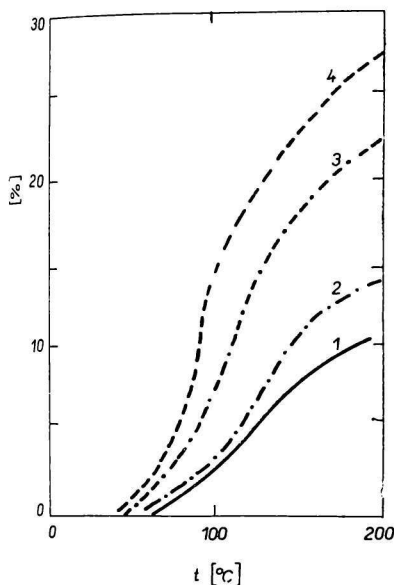

Fig. 5. Initial parts of TGA curves of PSPQ-*II*:

1. immediately after evacuation, time of contact with air 20 minutes;
2. kept in a dessicator for 24 hours, time of contact with air 20 minutes;
3. the same sample as on curve *1*, but after heating up to 200°C and subsequent contact with air for 48 hours;
4. after contact with air for six weeks.

The experimental information which made possible to draw such conclusions, comes to the following:

a) The DTA curves of polymers *I* and *II* within the temperature range 250—300°C change the tendency and pass from the endothermic to the exothermic region (Figs. 3 and 4).

b) Thermal treatment of PAQ-*III* for 3 1/2 hours at 320°C in vacuum results in the disappearance of the exothermic peak at 290°C, typical of the initial polymer (Fig. 3).

c) Following thermal treatment, PAQ-*III* loses its solubility. (This polymer contains no HSO₃ groups.)

d) Results of thermomechanical tests [4].

The stage of oxidation of the examined polymers occurs at an appreciable speed at 330—570°C. The processes of oxidation of poly(arylene quinone) are complicated, which, above all, is attested by the fractional order of the reaction (Table 2). The effective activation energy is a comparatively low value. The kinetic parameters of thermal oxidation do not practically depend on preliminary heat treatment in vacuum, although the latter leads to a greater exothermic oxidation effect (Fig. 3) and a wider range within which the process is completed (Figs. 1 and 2). The oxidative thermal destruction of PSPQ-*I* proceeds in a more complex way than in the case of other poly(arylene quinones) studied. It is shifted to the low temperature range and has two clearly pronounced stages.

Table 2

Kinetic parameters of thermal and oxidative thermal destruction of poly(arylene quinone

Polymer	Conditions of destruction	Temperature range [°C]	n	E_{act} [kcal mole⁻¹
PSPQ-*I*	air	60—200	1.0	9.5—10.5[*]
PSPQ-*I*	air	200—300	1.6	30—40[*]
PSPQ-*I*	air	300—400	1.8	35—55[*]
PSPQ-*I*	air	440—520	0.5	25—32[*]
PSPQ-*I*	argon	50—190	1.0	10.5
PSPQ-*I*	argon	200—320	1.1	17.5
PSPQ-*I*	argon	350—630	1.1	27.5
PSPQ-*II*	air	60—200	1.0	10—12.5[**]
PSPQ-*II*	air	200—300	1.0	15.5—17[**]
PSPQ-*II*	air	330—550	1.0	18—20[**]
PSPQ-*II* after thermal treatment	air	330—640	0.5	17.5
PSPQ-*II*	argon	60—200	1.0	12.0
PSPQ-*II*	argon	200—350	1.0	17.0
PAQ-*III*	air	330—575	0.5	15.5
PAQ-*III* after thermal treatment	air	330—600	0.5	15.0
PAQ-*III*	argon	350—650	1.0	25.0
PAQ-*III*	argon	700—840	2.8	50.0

*Extreme values of five parallel experiments.

** Extreme values of seven parallel experiments.

The effective kinetic parameters of decomposition of PSPQ-*I* are given in Table 2.

At temperatures in excess of 400°C, thermal destruction in an atmosphere of argo proceeds practically in the same way in all the investigated polymers. The basic difference discussed above were revealed when heating at lower temperatures.
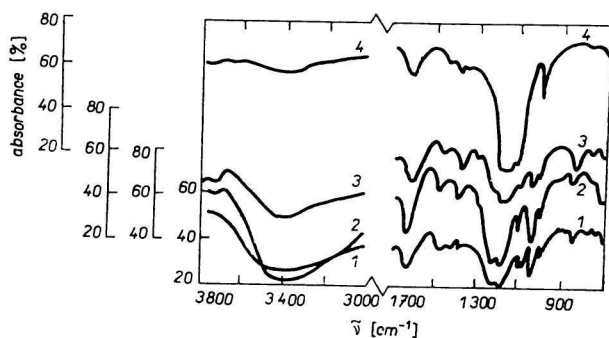

Fig. 6. Infrared spectra of PSPQ-*II*:
1. initial; *2.* after heating up to 200°C in the air; *3.* after heating up to 325°C in the air
4. after thermal treatment in vacuum.

PAQ-*III* has at least four stages of destruction. The losses in weight up to $300-350°C$ (5—6%) are apparently linked with the removal of low molecular volatile fragments. Within the range of 350 to $600-650°C$, where the polymer loses $20-21\%$ of its weight, the reaction is of the first order with $E_{act} = 25-26$ kcal mole^{-1}. At a temperature of $700-850°C$, PAQ-*III* loses 7% more in weight. The effective activation energy at this stage increases up to $49-50$ kcal mole^{-1}. The reaction is of a fractional order. In the next stage the rate of weight losses continues to grow.

The processes of thermal destruction are likewise accompanied by crosslinking. In addition to the factors mentioned above, the occurrence of processes leading to cross-linking is attested by the results of DTA: the exothermic plateau within the range of $300-350°C$ upon the heating of the polymers in argon (see Fig. 4). It is also worth noting that during thermal destruction in argon the differences in the decomposition of PSPQ-*I* and *II* which are clearly manifested during heating in an oxygen atmosphere, practically disappear. This suggests that during thermal destruction the difference in the stability of PSPQ-*I* and *II* is related not to the stability proper to the quinone and hydroquinone nuclei, but to their influence on the thermal oxidation of the products and the processes of crosslinking.

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