

## THERMAL TRANSFORMATIONS OF OLIGOARYLENES

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Thermal transformations of oligoarylenes, relating to polymers with conjugate systems, have been investigated in air and in vacuo, depending on the molecular weight and degree of branching of the original material. The extreme character of the thermostability in air versus the  $\bar{M}_n$  value of oligoarylene, and the possibility of increasing the thermal oxidative stability by enhancing the degree of branching have been explained by different intensities of intermolecular processes of dehydropolycondensation in the period before the starting of substantial weight losses. The influence of the solidification (or carbonization) conditions of the oligoarylenes on the structures and thermooxidative stabilities of the resulting samples was studied.

Oligoarylenes deserve attention with a view to creating polymer systems which display high thermal stability [1]. In the present work thermal transformations of oligoarylenes (based on condensed aromatic compounds) were investigated in air and in vacuo, at 20–800°, depending on  $\bar{M}_n$  and the degree of branching in the starting material. The effects of the solidification (or carbonization) conditions (heating rate and final temperature) on the thermooxidative stability and structure of the resulting products were also investigated. These investigations were carried out for oligoarylenes of various  $\bar{M}_n$  values and degrees of branching.

### Experimental

Experiments were carried out with oligoarylenes based on anthracene (*pA*) and naphthalene (*pN*), as well as copolycondensation products of naphthalene and benzene (*pNB*) prepared in the presence of Friedel–Crafts catalyst and an oxidizing agent such as copper chloride [2, 3] and nitrobenzene [4]. The fractionated *pA* samples were characterized by the  $\bar{M}_n$  value (by measuring the condensation heat effects), IR spectra (UR-20 spectrometer), electronic spectra (SF-14 spectrometer), softening point (from thermomechanical curves), and concentration of paramagnetic centers (*PMC*) (EPR-2 radiospectrometer). In the case of *pNB* (consisting generally of 1,4-naphthalene units with phenyl branches [5]) the degree of branching ( $K_{br}$ ) was estimated from the IR spectra using the formula:

$$K_{\text{branch}} = - \frac{C_b}{C_{\text{npha}}} = \frac{\log(I_{\text{ph}}/I_{\text{max}}) 700}{\log(I_{\text{ph}}/I_{\text{max}}) 480} - 0.26 \quad (6)$$

7.3

where  $C_b$  is the proportion of phenyl rings in *pNB*  
 $C_{\text{npha}}$  is the proportion of naphthalene rings (naphthylene and naphthyl rings, assuming  $C_b + C_{\text{npha}} = 1$ )  
 $I_{\text{ph}}$  is the absorption phone intensity, and  
 $I_{\text{max}}$  is the maximum intensity.

The thermomechanical curves were recorded on the instrument described in [7] under a specific load of 0.8 kg/sq · cm and a rate of temperature increase of 1.5 deg/min.

Thermal stability was estimated by thermogravimetry on an automatic thermobalance, ATB-2 in air and BTB-1 in vacuo, under dynamic and isothermal conditions. Under the dynamic conditions the rate of temperature increase was 3°/min apart from the cases where the heating rate is specially mentioned.

The X-ray diffraction spectra were taken on a URS-60 instrument with a  $\text{CuK}_\alpha$  source in an RKD chamber, and the roentgenograms were then subjected to photometry by means of an MF-4 microphotometer.

### Results and discussion

The characteristics of the fractionates oligoanthracenes are listed in Table 1. Their TG data demonstrate a continuous increase in the thermal stability measured in vacuo, while an extremum was observed in air (Fig. 1) [6, 8] with increasing mean molecular weight. A decrease of thermal stability in air after attaining a certain molecular weight has also been observed for some other oligoarylene fractions [8].

Table 1  
 Characteristics of various oligoanthracene fractions

Fraction No. Characteristics	1	2	3	4	5
$\bar{M}_n$	550	780	1080	1620	2230
PMC concentra- tion, spin/g	$1.5 \cdot 10^{17}$	$1.6 \cdot 10^{17}$	$8.7 \cdot 10^{17}$	$3.1 \cdot 10^{18}$	$6.7 \cdot 10^{18}$
Soft. pt. °C	165	210	270	320	380

The observed effects of  $\bar{M}_n$  on thermal and thermooxidative stabilities have been confirmed for oligomers of various molecular weights prepared by a special change of synthetic conditions [9]. The respective data for *pNB* are shown in Fig. 2. As can be seen from Fig. 2, when the  $\bar{M}_n$  values are sufficiently low, the higher

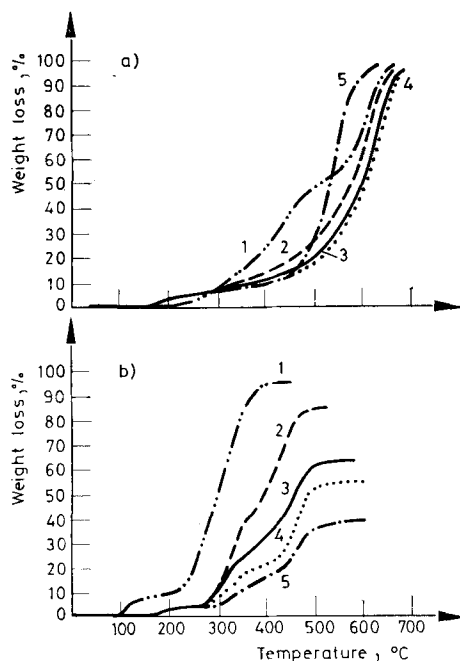


Fig. 1. TG curves: in air (a), in vacuo (b); oligoanthracene fractions with  $\bar{M}_n = 550$  (1), 780 (2), 1080 (3), 1620 (4), 2230 (5)

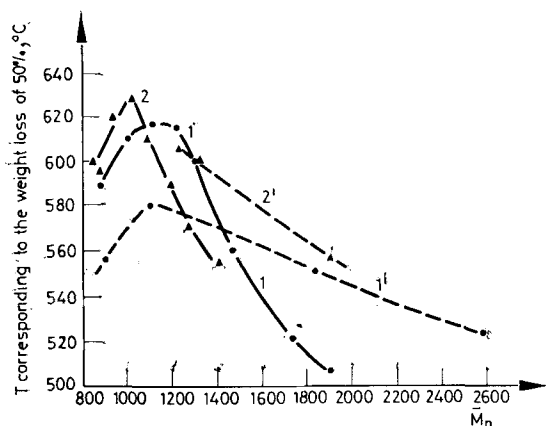


Fig. 2. The effect of  $\bar{M}_n$  and the degree of branching ( $K_{br}$ ) on the thermooxidative stability of pNB (TG data in air): 1 — samples prepared in the presence of  $\text{CuCl}_2$ ,  $C_{\text{benz}}/C_{\text{npha}} = 0 \div 0.08$ , 1' — the same, but  $C_{\text{benz}}/C_{\text{npha}} = 0.50 \div 0.70$ , 2 — samples prepared in the presence of nitrobenzene,  $C_{\text{benz}}/C_{\text{npha}} = 0.40 \div 0.53$ , 2' — the same, but  $C_{\text{benz}}/C_{\text{npha}} = 1.0 \div 1.8$

degree of branching decreases the thermal stability in air, while in the high molecular weight oligoarylenes the thermooxidative stability may increase substantially with the degree of branching. Investigation of a large number of oligoarylenes having different  $\bar{M}_n$  values and degrees of branching led to the conclusion that a certain optimum (as regards thermooxidative stability) degree of branching corresponds to each  $\bar{M}_n$ ; above this value the thermal stability in air decreases. This value increases with the  $\bar{M}_n$  of the oligoarylene.

The abnormal thermooxidative stability versus  $\bar{M}_n$  and the degree of branching in the starting oligomer observed from the first have been explained essentially by the different rates of the intermolecular polycondensation processes [10] before the initial intensive weight losses ( $\sim$  to 350–400°). For oligoarylenes having different  $\bar{M}_n$  values and degrees of branching a comparative estimation of the intensities of such processes was performed on the basis of the shift of the softening point, the change in the TG curves in vacuo, elemental composition and structural characteristics,  $\bar{M}_n$  and accumulation of the insoluble fractions, and finally from the change in PMC concentration in the course of sample heating to 350° in air. As an example, Table 2 shows the accumulation of insoluble fractions and the  $\bar{M}_n$  of the soluble part versus the molecular weight and the degree of branching of *pNB* samples [6]. These data and the results obtained by the procedures mentioned above show that in the course of the "induction period" greater changes in molecular weight and structure are observed for higher  $\bar{M}_n$  values and lower degrees of branching in the starting oligoarylene.

Table 2

The effects of  $\bar{M}_n$  and the degree of branching in the starting *pNB* on the change of molecular weight and the yield of insoluble fractions\* after heating prior to an intensive weight loss

Oxidizing agent used in the synthesis	No.	Characteristics of starting products		Insoluble part after heating,* %	$\bar{M}_n$ of soluble part after heating
		$\bar{M}_n$	degr. of branch.		
CuCl <sub>2</sub>	1	870	0.05	2.5	1120
	2	1050	0.06	4.0	900
	3	930	0.41	1.4	1230
	4	1050	0.40	3.0	1200
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	5	1290	0.42	31.0	800
	6	1350	0.20	77.0	440
	7	1330	1.00	3.0	1000

\* The solubility was determined in cold chloroform.

In terms of these results the abnormal change of the thermooxidative stability with  $\bar{M}_n$  and the degree of branching could be explained. In fact the thermal stability of a polymer is discussed as stability with respect to the purely thermal

processes and to the oxidation at high temperatures on the other hand. With the increase of the  $\bar{M}_n$  of the polymer its thermal stability increases, whereas that to thermooxidation decreases owing to an intensive polycondensational structuration.

At a certain value of  $\bar{M}_n$  the second factor is predominant, and thus thermal stability vs. molecular weight in air show an extremum. Increase of the thermooxidative stability with the degree of branching at sufficiently high  $\bar{M}_n$  may be explained by the fact that branching inhibits the intermolecular polycondensation processes prior to intensive weight loss.

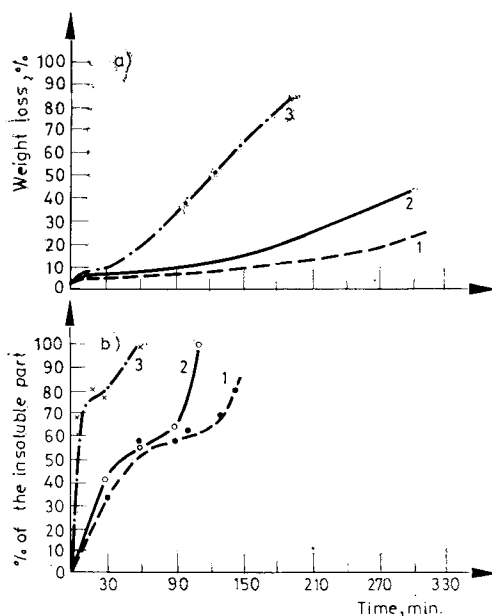


Fig. 3. The kinetic curves of weight losses (a) and insoluble fraction accumulation (b) for pNB with  $\bar{M}_n = 1240$  at 421 (1), 435 (2) and 473 °C (3)

The specificities observed in thermal oxidative stability versus  $\bar{M}_n$  and the degree of branching in the starting product may be essentially of a general character in the conjugate polymers, since they are connected with a stability towards structuration on heating common for this class of products. Indeed the order of stability for the polymers with conjugate systems has been found to reverse in vacuo and oxygen [11]. The effect of the degree of branching on the thermal stabilities of polyarylvinylenes has been observed in [12].

The data of Fig. 3 may serve as evidence that the insoluble fractions formed in the initial steps of heating the polymer affect its thermal stability decisively. According to these data, an inflection in the kinetic curves of insoluble fraction accumula-

tion corresponds to completion of the induction period in isothermal curves taken at several temperatures. The insoluble fractions contain cross-linked, more or less strained parts where free radical formation and nucleation of the chain oxidation processes on further temperature increase are possible.

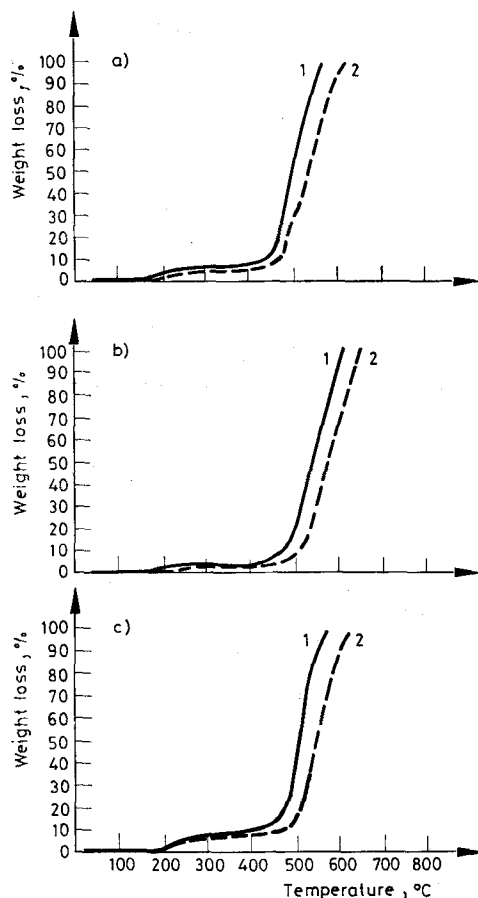


Fig. 4. TG curves (in air) of the solidification products of pN (a), pNB — 0.07 (b) and pNB — 1.01 (c) prepared by heating in vacuo to 550°C at a rate of 10 (1) and 0.6°C/min (2)

In this respect it seemed interesting to investigate the effect of the solidification (or carbonization) conditions on the structures and thermooxidative stabilities of the solidified products.

The soluble oligoarylenes were solidified (or carbonized) by heating in vacuo ( $10^{-4}$  mm Hg) to 425, 550 and 770°. The heating rate varied from 0.6 to 10°/min. The products were extracted with chloroform, removing the soluble part, dried

and subjected to thermogravimetric analysis in air. The data of Figs 4 and 5 show that for all of the oligoarylenes investigated, characterized by different degrees of branching, an increase of heating rate from 0.6 to 10°/min at 550 and 770° considerably decreased the thermooxidative stabilities of the solidified samples (TG data).

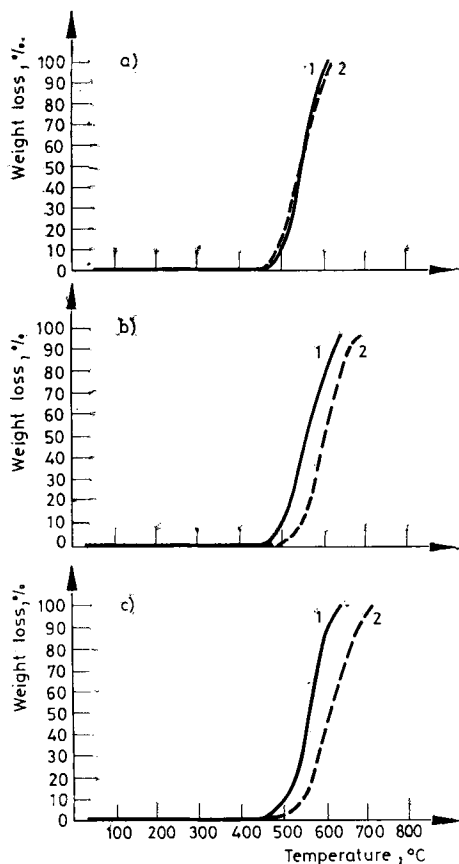


Fig. 5. TG curves (in air) of the solidification products of pN (a), pNB — 0.07 (b) and pNB — 1.01 (c) prepared by heating in vacuo to 770 °C at a rate of 10 (1) and 0.6 °C/min (2)

We have naturally suggested that the increase in thermooxidative stability with decreasing heating rate is a result of a highly-ordered carbonizate structure produced under slower heating. The X-ray diffraction patterns of the carbonizates reveal two broad reflections (11–12.5 and 20–22°) owing to a diffraction on the packets, which are composed of planar aromatic fragments-layers, and the layers

themselves. Moreover, the spectra show essentially diffused scattering at a small angle due to the presence of defects in a carbon net, thus indicating the fluctuation of interatomic distances in the carbon nets. The results of analysis of X-ray diffraction patterns of pNB samples having different degrees of branching, and of pN samples with different molecular weights, lead to the conclusion that always the heating rate of 0.6°/min at 550° and 770° afforded essentially perfect carbon nets and a narrow fractional composition of the packets composed of the nets. As an example, Fig. 6 and Table 3 give the data for two pNB samples solidified at 770° and heating

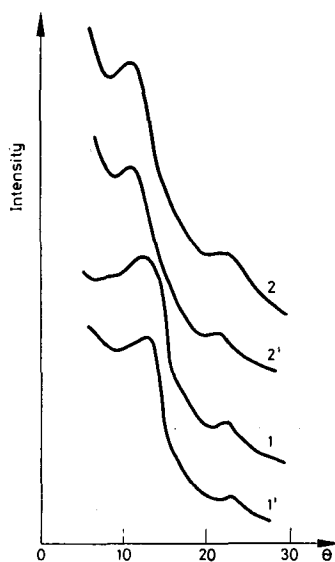


Fig. 6. Microphotometric data of roentgenograms of the solidification products of pNB — 0.07 (1 and 1') and pNB — 1.01 (2 and 2') prepared by heating in vacuo to 770°C at a rate of 10 (1 and 2) and 0.6°C/min (1' and 2')

Table 3

The structural characteristics of carbonizates obtained from pNB at different heating rates to 770°

No.	pNB characteristics		Heating rate, °C/min	Structural characteristics of carbonizates		
	$\bar{M}_n$	$K_{\text{branch}}$		$L_c$ , Å	$N_c$	$a_s$ , Å
1	1220	0.07	10	15	4.2	3.56
1'	1220	0.07	0.6	28	7.9	3.56
2	1220	1.01	10	15	3.8	4.04
2'	2	1.01	0.6	23	5.8	4.04



rates of 10 and  $0.6^{\circ}/\text{min}$ . It can be seen that the decrease in heating rate led to more perfect nets with thicker packets ( $L_c$ ) and a greater number of nets in a packet ( $N_c$ ).

It can be seen from the results of Figs 4a, 4b and 4c and 5a, 5b and 5c, that thermooxidative stability versus the heating rate is determined by the lability of the oligomeric chains at various temperatures, which depends partially on the degree of branching in the starting oligoarylene. Indeed, from a comparison of Figs 4 and 5 it follows that in *pNB* with sufficiently labile chains an increase in temperature to  $770^{\circ}$  enhances the effect of the heating rate. However, in *pN* with maximum  $\bar{M}_n$  (1440) and a minimum degree of branching (maximum structuration rate on heating) this dependence is different in principle. From a comparison of Figs 4a and 5a it is evident that in *pN* the thermooxidative stability increased when the heating rate was changed from 10 to  $0.6^{\circ}/\text{min}$  at  $550^{\circ}$ , whereas no difference was observed at  $770^{\circ}$ . These data are in complete agreement with the X-ray analysis: the carbonizate obtained from *pN* at  $550^{\circ}$  and a heating rate of  $0.6^{\circ}/\text{min}$  has a more perfect structure and in particular a greater packet thickness  $L_c$  than that obtained at  $10^{\circ}/\text{min}$ . On the other hand, the X-ray structures of the samples prepared from *pN* at  $770^{\circ}$  and heating rates of 0.6 and  $10^{\circ}/\text{min}$  differ fairly negligibly.

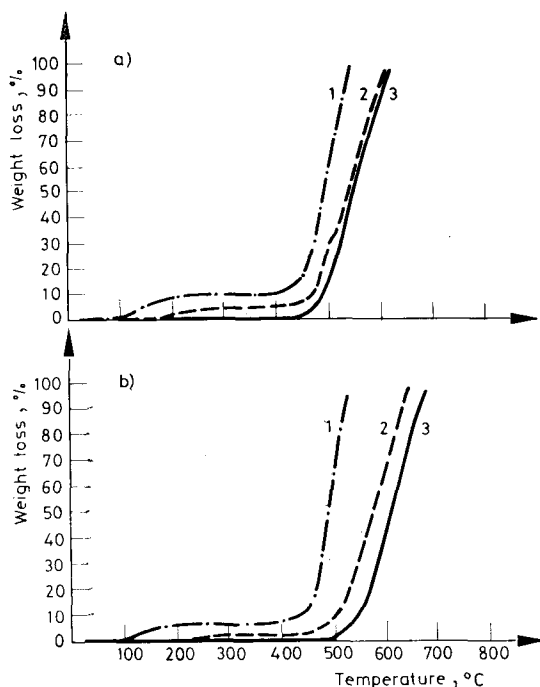


Fig. 7. The effect of the final heating temperature in vacuo at  $0.6^{\circ}\text{C}/\text{min}$  on the thermooxidative stability of the solidification products of *pN* (a) and *pNB* — 0.07 (b): 1 —  $425^{\circ}$ , 2 —  $550^{\circ}$ , 3 —  $770^{\circ}$

The thermooxidative stabilities of the solidification products increase appreciably when the temperature of thermal treatment of the oligoarylenes is changed from 425 to 770° (Fig. 7). This may be due to the higher C/H ratio and to the more ordered carbonizate structure. In fact, it was shown that for *pNB* with  $M_n = 1220$  and  $K_{\text{branch}} = 0.07$  an increase in the final solidification temperature from 550 and

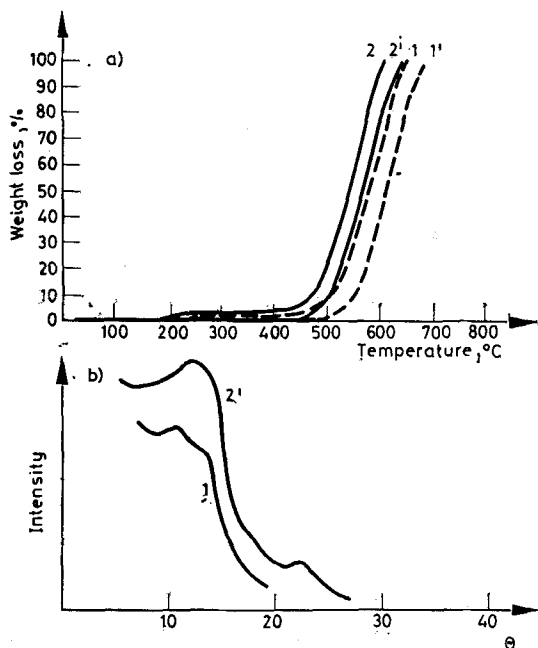


Fig. 8. The TG curves (in air) of *pNB* - 0.07 solidification products obtained in vacuo at a heating rate of 0.6°C/min (1 - 550°, 1' - 770°C) and 10°C/min (2 - 550°, 2' - 770°C) (a) and the results of microphotometry of the roentgenograms of products 1 and 2' (b)

770° at a heating rate of 0.6°/min increased the C/H ratio from 25.5 to 57.8 (according to elemental analysis). Simultaneously, X-ray spectra exhibited an essentially lower absorption phone as a result of structural homogeneity. Apparently, when the final solidification temperature is increased the polymer is more deeply carbonized in the bulk, and thus more perfect carbon layer packets are produced.

It is interesting to note that the effect of the heating rate on the structural homogeneity and thermooxidative stability of the carbonizates may overlap the temperature effect. Thus, carbonizate obtained from *pNB* with  $\bar{M}_n = 1220$  and  $K_{\text{branch}} = 0.07$  at 550° and a rate of 0.6°/min has a higher thermooxidative stability than the solidification product of the same *pNB*, obtained by heating to 770° at 10°/min (curves 1 and 2', Fig. 8). The C/H ratio of the first product is substantially lower than that of the second (25.5 instead of 44.2). Thus, the C/H value itself (from elemental analysis) does not determine the thermooxidative stability

of the carbonizate. The higher thermal stability of the first sample may be explained by the presence of 4–5 times thicker packets, constituting nearly half the bulk, along with thin packets present in both carbonizates (cf. Fig. 8).

These data demonstrate that the degree of structural homogeneity of the nets produced by solidification of oligoarylenes plays a substantial (if not decisive) role in their thermal oxidative stability. Earlier, a similar effect was observed for resole solidification products [13]. Recently, polyamides have been found to display greater thermooxidative stability with increasing macromolecular packing homogeneity [14]. Thus, it is very important to develop methods of directed structure formulation. The TG curves shown in Figs 4 and 5 demonstrate that among the oligoarylenes studied, and within the solidification temperatures and heating rates investigated, the carbonizate obtained from the most branched  $pNB(K_{\text{branch}} = 1.01)$  by heating up to  $770^\circ$  at a rate of  $0.6^\circ/\text{min}$  had the highest thermooxidative stability.

All these results lead to the conclusion that to prepare carbonizates with maximum thermooxidative stability it is advisable to employ as the starting materials oligoarylenes which retain chain lability within the widest temperature range. Thus, at the higher temperature and lower heating rate one may observe intermolecular reconstruction processes enhancing the thermooxidative stabilities of the carbonizates.

The results obtained in the present work exhibit rather wide possibilities for a directed change of structure and thermooxidative stability in the insoluble cross-linked products obtained from oligoarylenes. This is done by the choice of a suitable type of original oligoarylene and also by varying the solidification conditions, primarily the heating rate and the final temperature of heat treatment. An optimum correlation of these factors permits preparation of the solidification products of oligoarylenes with maximum thermooxidative stability.

To conclude, we note that the data obtained yield the following methodical consequences as well:

1. In comparative estimations of the thermooxidative stabilities of different polyconjugate systems using TG, one should take into account the  $\bar{M}_n$  values and the degrees of branching of the starting materials, which affect such estimations considerably.

2. The experimental conditions, and in particular the heating rate in dynamic TG, exhibit a noticeable effect on estimations of the thermooxidative stabilities of the soluble and fusible products having a tendency towards structuration on heating. This factor should also be considered in the comparison of data on various polymers investigated by different authors.

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RÉSUMÉ — On a étudié dans l'air et sous vide la transformation thermique de quelques oligoarylènes consistant en polymères conjugués, en fonction du poids moléculaire et du degré de ramification du produit original. Les limites de la stabilité thermique dans l'air en fonction de la valeur de  $\bar{M}_n$  de l'oligoarylène et la possibilité d'augmenter la stabilité thermique vis-à-vis de l'oxydation par accroissement du degré de réticulation ont été établies et expliquées par les intensités différentes des processus intermoléculaires de déshydropolycondensation pendant la période qui précède le début de la perte de poids. L'influence des conditions de solidification (ou de carbonisation) des oligoarylènes sur la structure et la stabilité thermique vis-à-vis de l'oxydation des substances formées est discutée.

ZUSAMMENFASSUNG — Die thermische Umwandlung von Oligoarylenen zu Polymeren mit konjugierten Systemen wurde in Luft und im Vakuum als Funktion des Molekulargewichts und des Verzweigungsgrads des Ausgangsproduktes untersucht. Der extreme Charakter der Thermostabilität in Luft als Funktion des  $\bar{M}_n$ -Wertes des Oligoarylens und eine Möglichkeit die thermische Oxidationsstabilität durch Erhöhung des Verzweigungsgrades zu erhöhen wurden durch die verschiedenen Intensitäten der intermolekularen Dehydropolykondensationsvorgänge der Periode vor Beginn der wesentlichen Gewichtsverluste erklärt. Die Einflüsse der Verfestigungs- (Karbonisierungs-) Bedingungen der Oligoarylene auf die Struktur und die Oxidationsstabilität der gebildeten Produkte wurden untersucht.

Резюме — Для представителей полисопряженных систем — олигоариленов на основе конденсированных ароматических соединений — исследованы термические превращения на воздухе и в вакууме в зависимости от величины  $\bar{M}_n$  и степени разветвленности структуры исходного продукта.

Установлено, что экстремальный характер зависимости термоокислительной стабильности от  $\bar{M}_n$ , равно как и возможность ее повышения при увеличении степени разветвленности структуры, связаны с различной интенсивностью протекания межмолекулярных поликонденсационных процессов в период до начала интенсивных потерь веса.

Для олигоариленов различной природы исследовано влияние условий отверждения на структуру и термоокислительную стабильность отвержденных образцов.