

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/284280158>

Thermochemical structural transformations of polyoxadiazoles

Article in Russian Journal of Applied Chemistry · August 2015

DOI: 10.1134/S1070427215080121

CITATION

1

READS

28

8 authors, including:



Irina Dobrovolskaya

Russian Academy of Sciences

58 PUBLICATIONS 178 CITATIONS

[SEE PROFILE](#)



Vlad Lysenko

National Academy of Sciences of Ukraine

22 PUBLICATIONS 25 CITATIONS

[SEE PROFILE](#)



Dmitry Kosyakov

Northern Arctic Federal University

86 PUBLICATIONS 184 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Russian Science Foundation [View project](#)



High-resolution mass spectrometry for structural analysis of lignins [View project](#)

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Thermochemical Structural Transformations of Polyoxadiazoles

Yu. N. Sazanov^a, I. P. Dobrovol'skaya^a, V. A. Lysenko^b, P. Yu. Sal'nikova^b, D. S. Kosyakov^c,
S. A. Pokryshkin^c, G. N. Fedorova^a, and E. M. Kulikova^a

^a Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi pr. 31, St. Petersburg, 199004 Russia

^b St. Petersburg State University of Technology and Design, Sadovaya ul. 54, St. Petersburg, 190068 Russia

^c Lomonosov Northern (Arctic) Federal University, nab. Severnoi Dviny 17, Arkhangelsk, 163002 Russia

e-mail: sazanov@hq.macro.ru; valys@mail.ru; dkosyakov@narfu.ru

Received August 31, 2015

Abstract—Changes in the physical and chemical structure of polyoxadiazole upon high-temperature heat treatment of Arselon fiber in inert and oxidizing atmosphere were studied. The role of the morphological rearrangement of the polymer in the turbostratic nucleation of carbon structures was determined. The mechanism of the thermochemical degradation and intramolecular cyclization of intermediate and final polyheterocyclic compounds formed in the process was elucidated.

DOI: 10.1134/S1070427215080121

Polyoxadiazoles (PODs) are important polymeric compounds used in highly heat-resistant materials and articles based on them. As noted in a review [1], POD-based fibers are characterized by high levels of heat resistance and strength. They withstand long operation at 230–250°C, and the temperature of their thermal degradation is in the range 460–480°C. Upon prolonged (300 h) heating at 300°C, the strength of POD fibers and materials is preserved to more than 50%. A valuable property of these fibers is small change in their size at elevated temperatures. For example, in the range 430–500°C, the deformation of POD fiber fabrics does not exceed 2–4%, which is important when using protecting clothes of Arselon fabric (Arselon is the trade name of POD yarns). Arselon fibrous materials are used for the production of specialty fabrics for filtering hot gases and aggressive media, of interior materials for aviation and automobile transport and for rooms with increased fire danger, and of friction materials without asbestos composites.

Under definite conditions, POD fibers can undergo carbonization with a high yield of the coke residue,

acting as carbon material precursors [2]. Addition of fireproofing compounds and nanoadditives allows sufficient fire resistance to be imparted to these materials [3, 4].

Among the POD advantages, as already noted [5], are simplicity of preparing the precursor of carbon materials without pretreatment in the form of preoxidation and extension, as done in the case of polyacrylonitrile and hydrated cellulose.

It is known [2] that carbonization of polymers starts with the rearrangement of their structure as a result of thermal degradation of weak bonds, accompanied by the release of volatile products and formation of various polycyclic compounds. This process determines the kinetics of nucleation of primary turbostratic carbon structures. For heat-resistant polymers, this phenomenon has been studied in sufficient detail for polyimides and polyacrylonitrile as examples.

As for polyoxadiazole, the characteristics of its heat resistance were determined by thermal gravimetric analysis for samples of Oksalon and Arselon fibers in oxidizing and inert atmosphere [6–8]. The results ob-

tained show that these materials start to degrade in the temperature interval 410–440°C with approximately 35–40% weight loss. However, the qualitative composition of volatile thermal degradation products and the structures of the intermediate compounds initiating the nucleation of the carbon structure were not considered in these papers. Attempts to determine the pathways of the formation of carbon structures in the course of thermal degradation of POD were made in early studies [5, 9, 10] using X-ray and microscopic analysis. In these studies, the particular role of the supramolecular organization of the formed polyoxadiazole fibers in ensuring high strength and elastic characteristics and high (up to 42%) yield of the carbon fiber was emphasized. It was also shown that the geometric characteristics of the internal structure of POD carbonization products depend on the ratio of the amorphous and crystalline domains in the initial fiber and of their mutual arrangement. However, the mechanism of the rearrangement of the initial structure of POD fiber under the conditions of thermal and thermal oxidative degradation in the temperature range in which these processes occur actively is still poorly understood.

This study was aimed at determining the mechanism of these processes, leading to the formation of the

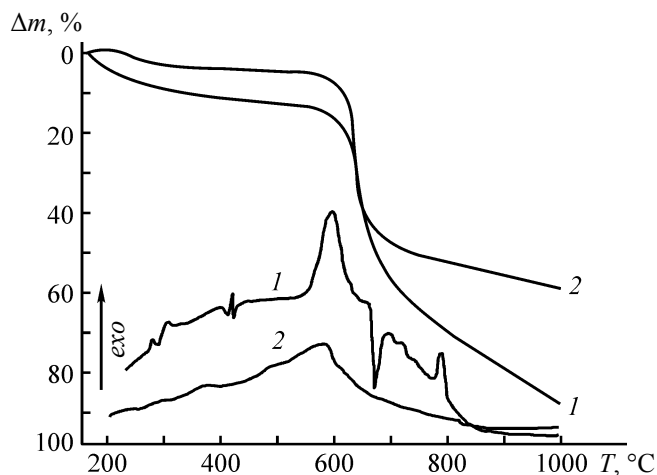
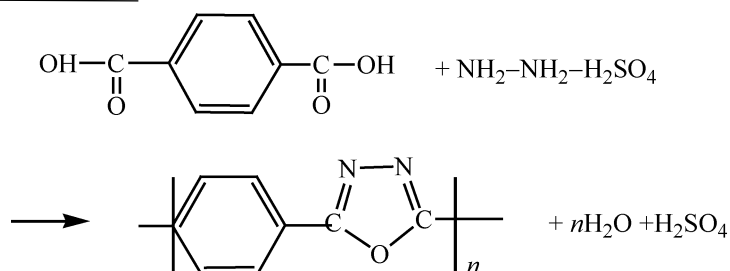


Fig. 1. TG and DTA curves of Arselon fiber in (1) oxidizing and (2) inert atmosphere. (Δm) Weight loss and (T) temperature.

primary nuclei of the carbon structure as the basis for the formation of carbon materials.

EXPERIMENTAL

POD fibers (Arselon) were prepared from poly-*p*-phenylene-1,3,4-oxadiazole, which was synthesized by polycondensation of terephthalic acid with hydrazine sulfate:



The polymer synthesis was performed in a reactor at 90–130°C. The released water was bound with oleum. The polycondensation occurred with a slight (no more than 5%) excess of hydrazine sulfate. To reach the required molecular mass, the reaction mixture viscosity was continuously monitored. The reaction was terminated by adding a small amount of sulfuric acid. After this operation, the solution at 70–90°C was stirred for 6 h and cooled to 60°C, after which it was fed to the yarn forming. The subsequent treatment was performed by the standard procedure.

To determine the thermal characteristics of POD fiber and the kinetics of its degradation in oxidizing and inert medium and in a vacuum, we used a C-1500 derivatograph and the previously described [11] TVA system. Conditions of measurements with the derivatograph: sample weight 50 mg, heating rate 10 deg min⁻¹, DTA scale 1/5, air (static) or argon (50 mL min⁻¹) atmosphere. TVA conditions: sample weight 20 mg, heating rate 7 deg min⁻¹, pressure 10⁻² mmHg.

To determine the qualitative composition of volatile thermal degradation products, we performed pyroly-

sis with an EGA/PY-3030D pyrolyzer (Frontiêr Lab) equipped with a cryogenic trap. The pyrolysis products were analyzed by gas chromatography–mass spectrometry with a GCMS-QP2010Plus device (Shimadzu, Japan). The sample (0.2 ± 0.03 mg) was subjected to stepwise heating with the discharge of pyrolysis products released in fixed temperature intervals. After the accumulation in the trap, the pyrolysis products were heated, and the chromatogram was recorded.

X-ray diffraction measurements were performed with DRON-1,5 and KRM-1 installations (Russia) with CuK_α radiation.

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTA curves of POD samples, recorded in the course of heating in oxidizing and inert atmosphere. As can be seen, in the initial step of heating (up to 100°C) in the oxidizing atmosphere, the POD sample loses approximately 8–10% of its weight owing to the removal of the adsorbed moisture. This is confirmed by the results of the GC–MS analysis, showing that water amounts to 98% of the volatile products. In an argon atmosphere, the amount of the released water is 2–4% on heating to 157°C .

On further heating to 400°C , the total weight loss of the sample in the oxidizing atmosphere is 15%. Apart from the water released on heating to 100°C , the remaining 5% are constituted by some aliphatic aldehydes, ketones, and alcohols such as 2-hexanone, butanal, butanol, hexanol, and other homologs. No nitrogen-containing derivatives were detected in volatile products. In an inert atmosphere, the weight loss due to POD degradation on heating to 400°C is approximately 5%, of which about 30% is constituted by CO_2 , and the remainder, by various aliphatic homologs of monoaldehydes. Thus, it can be stated that heating to 400°C does not lead to appreciable degradation of the POD backbone and oxadiazole rings.

The thermal and thermal oxidative degradation of POD develops in the temperature interval 400 – 500°C . It is characterized by a sharp increase in the weight loss rate both in oxidizing (about 40%) and inert (about 45%) atmosphere.

Among the released volatile products of thermal oxidative degradation, the major components, along with CO_2 (approximately 23%), are various nitrogen-

containing compounds, mainly benzonitrile (19%) and benzodinitrile (47%). In the inert atmosphere, the relative amount of CO_2 was lower (19%), that of benzonitrile was appreciably lower (5%), and that of benzodinitrile was higher (56%). Despite significant difference in the relative amount of volatile degradation products, the main features of the POD molecule degradation are similar: degradation of the polymer chain with the release of low-molecular-mass fragments such as 2,5-bis(*p*-cyanophenyl)-1,3,4-oxadiazole, breakdown of the oxadiazole ring, and secondary reactions of recombination of the resulting fragments.

Further transformation of POD occurs at temperatures higher than 540°C , and its mechanism depends on the surrounding atmosphere. In thermal oxidation, the weight loss rate is significantly higher than in an inert atmosphere (Fig. 1), amounting on the average to 1°deg^{-1} up to 1000°C . In the inert atmosphere, the degradation rate sharply decelerates (by a factor of almost 10), with the formation of the carbonized residue at 1000°C in 50% yield. One more distinctive feature of the POD degradation in this temperature interval is the appearance of an endothermic effect at 577°C and of an exothermic effect at 689°C in the DTA curve recorded in the oxidizing atmosphere. Such peaks are not observed in the argon atmosphere. In their shape and in the fact that the deviations in the synchronous TG curve are small (Fig. 1), such peaks resemble the thermal effects of melting and crystallization, observed previously in the course of polyacrylonitrile degradation in the oxidizing atmosphere in the similar temperature interval [12]. Such phenomena are similar to the previously noted [5] phase transformations of the crystalline and amorphous domains, noted previously [5] and detected by changes in the density of POD samples in the course of their pyrolysis in the temperature interval 475 – 600°C . The increase in the density, observed at the end of this period, is attributable to melting of the intermediate crystalline phase, manifested as an endothermic peak with a maximum at 577°C . As the temperature is increased further, the molten intermediate undergoes new thermochemical transformations with the formation of a crystalline compound (maximum at 689°C).

It can be noted that the temperature range of the observed phenomena corresponds to the initial period of the nucleation of the turbostratic carbon structure, and the observed thermal effects reflect a complex process of random degradation and rearrangement of POD

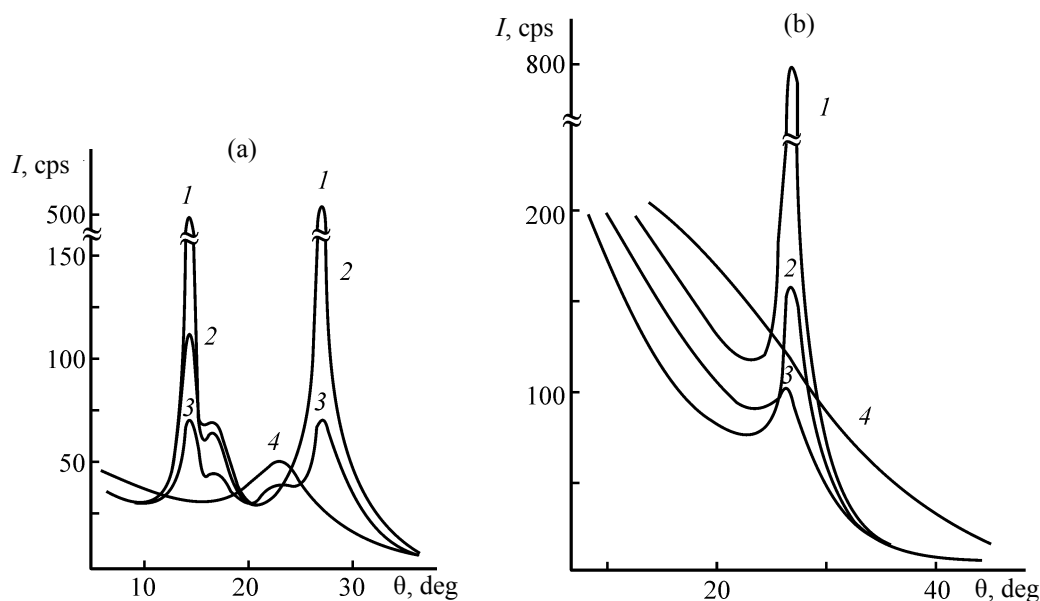


Fig. 2. X-ray diffraction patterns of the (1) initial POD fiber and POD fiber subjected to pyrolysis at (2) 450, (3) 500, and (4) 525°C. (I) Intensity and (θ) Bragg angle; the same for Fig. 3. Pattern recorded in (a) equatorial and (b) meridional directions.

macromolecules. As noted in [9], the geometry of the nuclei of the carbon structure depends on nonuniform cleavage of POD molecules between amorphous and crystalline regions. The formation of the nuclei in the form of layers parallel to the surface of the POD sample occurs in the course of the degradation. Their structure probably repeats the structure of separate fragments of the POD chain, such as 2,5-bis(*p*-cyanophenyl)-1,3,4-oxadiazole and malononitrile-2-indeno[1,2-pyridin-5-ylidene], detected in pyrolysis products of the POD samples examined in this study. Along with the above-indicated compounds, the qualitative composition of the products of thermal degradation above 500°C is characterized by high content of nitrogen-containing

fragments of the polymer chain, the majority of which are various aromatic mono- and dinitriles. In addition, the presence of CO₂ deserves attention. Its amount depends on the pyrolysis temperature and on the composition of the surrounding atmosphere (Table 1).

The CO₂ percentage in the pyrolysis products was calculated from the TGA data, according to which in the oxidizing atmosphere the weight loss is about 10% in the temperature interval 100–400°C, about 40% in the interval 400–500°C, and up to 38% in the interval 500–800°C. In the inert atmosphere, the weight loss is 5.45 and 2–3%, respectively.

Analysis of the oxygen-containing products of POD pyrolysis revealed the presence of phenyl isocyanate

Table 1. Release of CO₂ in the course of POD pyrolysis

Pyrolysis conditions ^a	CO ₂ content, %, in indicated temperature interval of pyrolysis, °C		
	100–400	400–500	500–800
Oxidizing atmosphere, rapid heating	–	22.9	7.2
Oxidizing atmosphere, slow heating	–	36.7	–
Inert atmosphere, rapid heating	27.2	18.3	68.5
Inert atmosphere, slow heating	80.6	29.0	76.6

^a Rapid heating was performed according to the following program: (1) initial temperature 100°C, (2) heating at a rate of 60 deg min^{–1} to 400°C, (3) heating at a rate of 10 deg min^{–1} to 500°C, and (4) heating at a rate of 60 deg min^{–1} to 800°C; slow heating was performed similarly, except that heating to 500°C was performed at a rate of 1 deg min^{–1}.

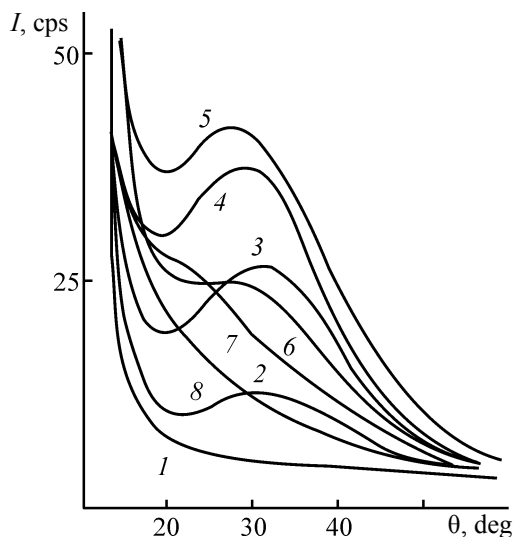
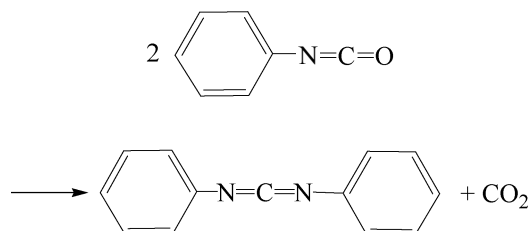


Fig. 3. Small-angle X-ray diffraction patterns of the (1) initial POD fiber and POD fiber subjected to pyrolysis at (2) 450, (3) 475, (4) 500, (5) 525, (6) 550, (7) 575, and (8) 600°C.

molecules. Above 450°C, they transform into carbodiimide with the release of CO₂:



The release of CO₂ in the course of POD pyrolysis and decomposition of the POD macromolecule into separate fragments indicated above confirms the previously made [5] conclusions on the nucleation

of the carbon structure on the matrix of the oriented polymer in the course of its shrinkage. Such internal rearrangement yields a longitudinally ordered structure, which leads to the enhancement of deformation and strength characteristics upon heat treatment of POD fibers at 455°C. Table 2 shows how the strain modulus E and relative modulus E/E_0 depend on the temperature of the heat treatment of the POD fibers.

Thus, at elevated temperatures of heat treatment at the boundary of the POD heat resistance the arising carbon structures of layer-by-layer packing undergo orientation based on the orientation extension of the initial polymer. This statement was confirmed in subsequent studies [9, 10], in which it was noted by the examples of the POD fiber and film that the shrinkage of the interlayer space below 0.345 nm for carbon layers based on POD starts with increasing layer size. In the process, the 3D orientation in films is successfully realized after the interlayer space becomes smaller than 0.340 nm. For fibers, this effect is observed as twisting of the circular cross section of the fiber into triangular shape with deceleration of the contraction of the interlayer space. Such phenomenon confirms the hypothesis that the turbostratic carbon structure arises before complete breakdown of POD crystals [5]. As the pyrolysis temperature is increased over 500°C, the carbon structure nuclei fill the whole sample volume, which is reflected in the X-ray diffraction pattern.

According to the data of large-angle X-ray diffraction analysis, intense degradation of the polymer is preceded by amorphization of the crystal structure. Figure 2 shows that the large-angle diffraction pattern remains unchanged up to 450°C. This fact indicates that the crystal structure of the fiber remains unchanged. At higher temperatures, its amorphization starts. It is manifested in a decrease in the intensity of POD reflections until they fully disappear at 520°C.

Small-angle X-ray diffraction studies showed that a meridional small-angle reflection absent in the pattern of the initial fiber appeared at 470°C, when the crystal structure underwent partial amorphization (Fig. 3). The intensity of this reflection in the maximum, I_{max} , first increases with temperature and then decreases (Fig. 4).

Experiments show that the pyrolysis of polyoxadiazole starts at 450°C, which is consistent with the data of [13]. Formation and accumulation of aromatic structural units of carbon starts from this moment. Fusion of six-membered carbon rings results in formation of carbon planes. Their formation is manifested in large-angle

Table 2. Modulus of POD fiber at different temperatures of heat treatment

Heat treatment temperature, °C	E , GPa	E/E_0
Initial sample	6.1	—
420	5.0	0.82
430	4.7	0.77
455	8.3	1.35
460	6.1	0.99
465	5.1	0.83

X-ray diffraction patterns (Fig. 4). They show that the POD fibers subjected to pyrolysis at temperatures higher than 550°C contain carbon (002) planes. Specifically the formation of carbon structures is responsible for an increase in the fiber density, strength, and elastic modulus at 550°C and higher temperatures.

Thus, two processes occur simultaneously in the course of pyrolysis of POD fibers: degradation of the initial structure and formation of a new carbon structure exhibiting higher density $[(1.6\text{--}2.0) \times 10^3 \text{ kg m}^{-3}]$ compared to that of polyoxadiazole ($1.45 \times 10^3 \text{ kg m}^{-3}$). This fact suggests that the density heterogeneity arising in the course of pyrolysis of polyoxadiazole fibers is due to the formation of domains with a denser carbon structure.

It should be noted that the turbostratic carbon structure arises before complete breakdown of polyoxadiazole crystallites. This fact also counts in favor of the assumption that the carbon structure nucleation starts in intercrystallite amorphous regions of polyoxadiazole.

At the carbonization temperature higher than 520°C, the whole volume becomes involved in the rearrangement, which leads to a decrease in the density heterogeneity and is manifested in the DTA curves as an endothermic effect of the intermediate crystal formation.

Thus, according to the suggested scheme, the POD pyrolysis is characterized by an increase in the density heterogeneity, followed by the structure homogenization. A specific feature of pyrolyzed POD fiber is the presence of domains with turbostratic carbon structure, which are weakly ordered but are considerably denser than the amorphized POD domains.

The qualitative composition of products of thermal and thermal oxidative degradation of POD samples above 500°C remains similar to that of products formed in the previous steps and is characterized by the release of a series of nitrogen-containing compounds, mainly mono- and dinitriles, and of traces of aromatic and heterocyclic compounds. Their amount is restricted by reactions of intra- and intermolecular cyclization responsible for the growth of carbon layers, especially noticeable when carbonization is performed in an inert atmosphere, in which it is manifested as a sharp decrease in the sample weight loss rate (Fig. 1).

The thermochemical reactions of the rearrangement of the POD structure in the course of pyrolysis in a vacuum occur in several steps (Fig. 5). Up to 400°C, the

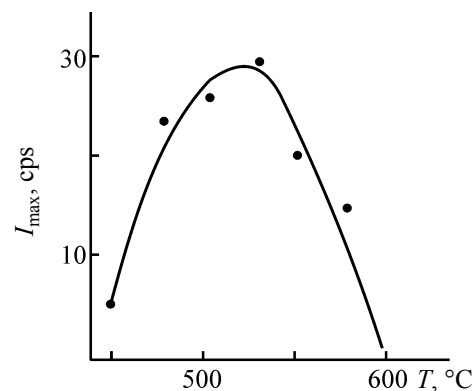


Fig. 4. Variation of I_{\max} in the course of pyrolysis of POD fibers. (T) Temperature.

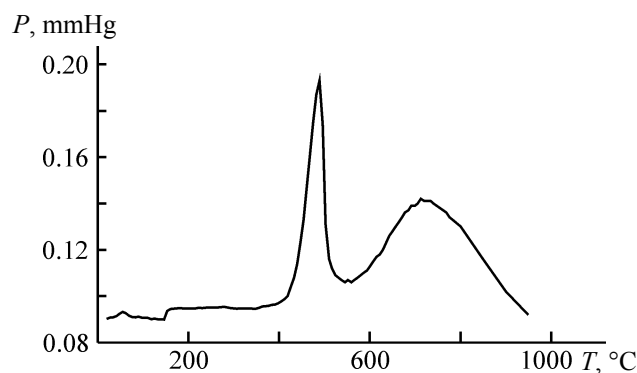


Fig. 5. TVA curve of POD pyrolysis in a vacuum. (P) Pressure and (T) temperature.

weight loss amounts to 5–7% and is due to evaporation of the adsorbed water and process impurities. In the range 400–500°C, there is a sharp peak corresponding to the release of volatile degradation products consisting of approximately 20 different compounds. The total weight loss is 52%. In the range 550–800°C, the peak of the release of volatile products reflects a superposition of several processes. Because the total weight loss in this step of thermal degradation is only 4% of the initial sample weight, it can be concluded that the carbonization involves the release of hydrogen and residual amounts of aromatic mono- and dinitriles.

CONCLUSIONS

(1) The morphological and thermochemical transformations of the polyoxadiazole structure at elevated temperatures are tightly associated with each other.

(2) The initiation of the carbon structure nucleation is associated with the orientation parameters of the initial polymer, which allows the polymer matrix to be used as a stereospecific precursor of turbostratic carbon.

(3) The successive steps of transformation of separate fragments of polyoxadiazole macromolecule via formation of intermediate nitriles, isocyanates, carbodiimides, and complex polycyclic nitrogen-containing structures were determined.

(4) The decisive role of nitrogen atoms in formation of the layered carbon structure via a series of morphological transformations in the temperature interval 100–1000°C was demonstrated.

ACKNOWLEDGMENTS

The study was performed using the equipment of the Arktika Center for Shared Use of Scientific Equipment of the Lomonosov Northern (Arctic) Federal University and was supported by the Ministry of Education and Science of the Russian Federation (agreement no. 14.594.21.0004, unique identifier RFMEFI59414X0004).

REFERENCES

1. Perepelkin, K.E., Makarova, R.A., Dresvyanina, E.N., and Trusov, D.Yu., *Khim. Volokna*, 2008, no. 5, pp. 8–14.
2. Sazanov, Yu.N. and Gribanov, A.V., *Karbonizatsiya polimerov* (Carbonization of Polymers), St. Petersburg: NOT, 2013.
3. Lysenko, A.A., Lysenko, V.A., Astashkina, O.V., and Gladunova, O.I., *Khim. Volokna*, 2010, no. 5, pp. 10–17.
4. Gladunova, O.I., Lysenko, V.A., Astashkina, O.V., et al., *Russ. Khim. Zh. (Zh. Ross. Khim. O-va. im. D.I. Mendeleeva)*, 2011, vol. 55, no. 3, pp. 35–38.
5. Dobrovol'skaya, I.P., Chereiskii, Z.Yu., and Stark, I.M., *Vysokomol. Soedin., Ser. A*, 1981, vol. 23, no. 6, pp. 1261–1265.
6. Perepelkin, K.E., Malan'ina, O.B., Pakshver, E.A., and Makarova, R.D., *Khim. Volokna*, 2004, no. 5, pp. 45–48.
7. Perepelkin, K.E., Malan'ina, O.B., Basok, M.O., et al., *Khim. Volokna*, 2005, no. 3, pp. 36–38.
8. Perepelkin, K.E., Pakshver, E.A., Andreeva, I.V., et al., *Khim. Volokna*, 2005, no. 5, pp. 27–31.
9. Shoya, M., Shinotani, K., and Takaku, A., *J. Mater. Sci.*, 1999, vol. 34, pp. 6015–6025.
10. Murakami, M., Yasujima, H., Yumoto, Y., et al., *Solid State Commun.*, 1983, vol. 45, pp. 1085–1088.
11. Sazanov, Yu.N. and Sysoev, V.A., *Eur. Polym. J.*, 1974, vol. 10, pp. 867–869.
12. Gubanova, G.N., Grigor'ev, A.I., Sazanov, Yu.N., et al., *Russ. J. Appl. Chem.*, 2008, vol. 81, pp. 971–975.
13. Kudryavtsev, G.I., Varshavskii, V.Ya., Shchetinin, A.M., and Kazakov, M.E., *Armiryuyushchie khimicheskie volokna dlya kompozitsionnykh materialov* (Reinforcing Chemical Fibers for Composite Materials), Moscow: Khimiya, 1992.