

# Polyphenylenes with Phen-1,3,5-triyl Branching Moieties Based on *p*-Diacetylbenzene: Synthesis and Study of Porosity and Heat Resistance

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**Abstract**—Microporous three-dimensional polyphenylenes with phenetriyl branching moieties are synthesized by the trimerization polycyclocondensation of *p*-diacetylbenzene followed by additional heat treatment at 450°C. The structure of the polymers is studied by IR spectroscopy and the methods of thermal desorption of argon and low-temperature sorption of nitrogen. The volume of micropores amounts to more than 70% of the total pore volume. Calculations of the parameters of the microporous structure using the Dubinin–Radushkevich and Dubinin–Astakhov methods show that the average micropore size in the test sample is 1 nm. The surface of all pores, as calculated by various methods, is in the range from 470 to 980 m<sup>2</sup>/g. According to the TGA data, the polymer shows high heat resistance: when heated in an inert medium, its mass losses are as high as 20% in the range of 200–900°C.

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Materials with voids of molecular size have proven themselves in such technological processes as adsorption, heterogeneous catalysis, and gas storage, and they are widely used for the manufacture of membranes for various purposes [1–4]. Microporous materials are solids with a large and accessible surface area, which is usually 300–1300 m<sup>2</sup>/g [5], as measured by gas adsorption.

Previously, microporous materials were mainly crystalline inorganic substances or amorphous network structures. However, over the past decade there has been a significant progress in the study of microporous polymer-based network materials [5]. There is a need for materials with a controlled microporous structure and having various functional groups, which in some cases is necessary for chemisorption and the preparation of heterogeneous catalysts.

In this regard, polyphenylenes stand apart among other polymers, since almost any functional groups can be introduced into them either during the synthesis or by polymer-analogous transformations. At the same time, polyphenylenes themselves, unlike most polyheteroarylenes, have a high chemical resistance of the polymer skeleton not only in acidic but also in alkaline medium, which allows them to be used for a long time in aggressive media.

It should be noted that owing to the conformational flexibility of chains polymer molecules are usually “packed” under the influence of cohesive forces during the synthesis in such a way that the amount of free space in the material is minimized. Recently, the method providing the synthesis of polymers consisting of macromolecular spatial moieties characterized by high rigidity, which can no longer spontaneously “pack” in space [5], has been used to obtain materials of intrinsic microporosity. These polymers of intrinsic microporosity do not have rotational freedom along the chain, since their “structural skeleton” is fixed during synthesis, and the chains of macromolecules cannot change their conformation. As a result, a polymer of a high intrinsic microporosity is formed due to the continuous network of interconnected intramolecular voids.

Recently, several methods for the synthesis of microporous polyphenylenes have been published, and almost all of them involve catalysis by palladium complexes. For example, the homocondensation of 1,3,5-tribromobenzene according to the Yamamoto reaction [6] led to the production of polyphenylene with a specific surface area of 1255 m<sup>2</sup>/g. The copolycondensation of this monomer with bifunctional monomers *p*-dibromobenzene and 4,4'-dibromodiphenyl at a ratio of 1 : 1 sharply reduced the value of

**Table 1.** Synthesis conditions (6 mmol of *p*-diacetylbenzene) and the properties of polyphenylene-I and the specific surface area of polyphenylene-II

Sample	P-I					P-II
	Benzene, mL	CH(OEt) <sub>3</sub> , mmol	Synthesis time, h	Yield, %	$S_{sp}$ , m <sup>2</sup> /g	$S_{sp}$ , m <sup>2</sup> /g
1	9	14.4	2	110	0	0
2	9	14.4	24	106	0	11
3	16.5	14.4	2	107	0	79
4	33	21.6	2	103	30	131
5	66	21.6	2.5	101	43	759
6	132	21.6	3	101	253	634
7	180	21.6	4	92	86	558

this parameter to 292 and 475 m<sup>2</sup>/g, respectively. The polymer based on 2,2',7,7'-tetrabrom-9,9'-spirobi[9*H*-fluorene] had a specific surface area of 1275 m<sup>2</sup> g, and the copolymer with 1,3,5-tribromobenzene had a specific surface area of 580 m<sup>2</sup>/g [6]. Note that a three-dimensional polyphenylene sample obtained from tetra(4-bromophenyl)methane via the Yamamoto reaction [7] shows the largest surface area among all porous materials (the BET specific surface area is 5600 m<sup>2</sup>/g).

The trimerization homocondensation of 2,2',7,7'-tetraethynyl-9,9'-spirobi[9*H*-fluorene] and tetra(4-ethynylphenyl)methane yielded microporous polyphenylenes [8] with a specific surface area of 1043 and 762 m<sup>2</sup>/g, respectively.

The interaction of 2,2',7,7'-tetrabromo-9,9'-spirobi[9*H*-fluorene] with *p*-phenylene and *p*-diphenylene diboric acids via the Suzuki reaction afforded polymers [9] with a specific surface of 450 and 210 m<sup>2</sup>/g, respectively.

It should be noted that most of the above polyphenylenes contain *sp*<sup>3</sup>-hybridized carbon atoms, which significantly affects their heat resistance.

An alternative to the indicated methods for the synthesis of polyphenylenes is an extremely interesting and simple way based on the trimerization polycyclocondensation of acetylaromatic compounds [10, 11]. Such a reaction does not require ultrapure conditions and expensive catalysts.

This study addresses the synthesis of microporous polyphenylenes by the reaction of trimerization cyclocondensation of a diacetylaromatic compound, *p*-diacetylbenzene, and the investigation of their porosity and heat resistance.

## EXPERIMENTAL

In this work, we used *p*-diacetylbenzene (Aldrich) without further purification. Triethyl orthoformate was distilled in argon over potash, and the fraction

boiling at 143–145°C was taken. Benzene was distilled over sodium under argon, and the fraction boiling at 80°C was taken.

**Polyphenylenes-I (P-I).** Gaseous hydrogen chloride was passed for a certain time at room temperature through a solution of *p*-diacetylbenzene (0.98 g, 6 mmol) and the corresponding amounts of triethyl orthoformate and benzene (Table 1). The resulting gel was separated and washed with chloroform. The solvent and other components of the reaction solution were removed from the product via extraction with chloroform. The gel was dried at 80°C under reduced pressure.

**Polyphenylenes II (P-II).** P-I were heat treated at 450°C in an argon atmosphere for 3 h. The IR spectra of the samples were recorded on a Bruker Tensor-37 FTIR spectrometer.

The value of the internal specific surface  $S_{sp}$  was determined using the thermal desorption of argon on a Tsvet-211 instrument and calculated according to the BET theory using the Temkin formula for monolayer capacity:

$$V_m = V(1 - p/p_s)[1 + (p_s/p - 1)/C], \quad (1)$$

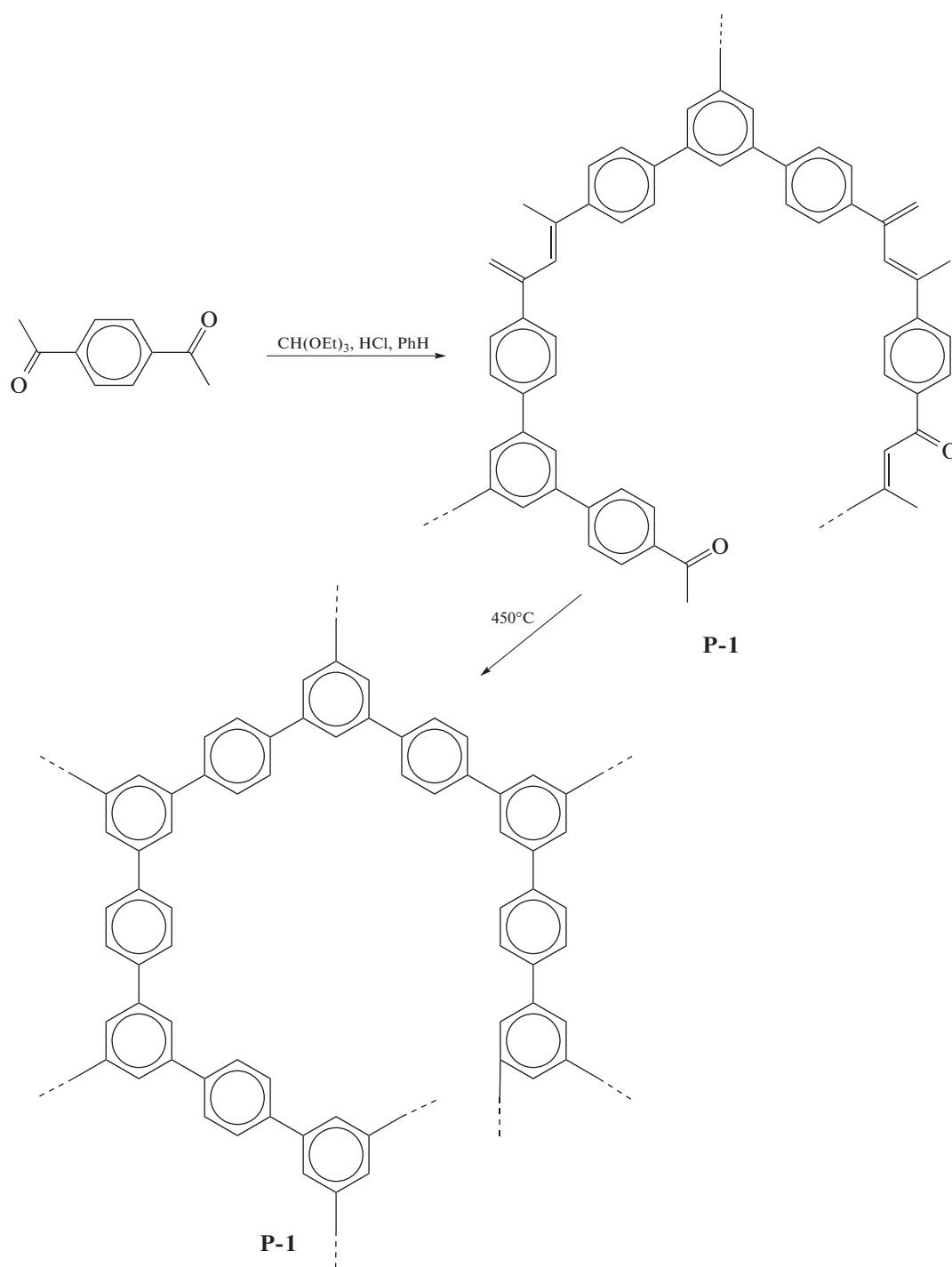
where  $V_m$  is the monolayer capacity, cm<sup>3</sup>/g;  $V$  is the value of adsorption corresponding to a given relative pressure  $p/p_s$ , cm<sup>3</sup>/g;  $p$  is the equilibrium pressure of argon, mmHg;  $p_s$  is the saturated argon vapor pressure at  $T = -196^\circ\text{C}$  and  $p_s = 240$  mmHg; and  $C$  is the BET constant, which depends on the adsorption energy and temperature (in calculations  $C$  is taken to be 60) [12].

The internal specific surface was assessed by the formula

$$S = 4.17V_m, \quad (2)$$

where 4.17 is the value of area occupied by 1 mL of argon poured by a monomolecular layer.

The porous structure of the synthesized polymers was studied on a NOVA 1200e specific surface and porosity analysis unit (Quantachrome Instruments, United States). Calculations were performed using the

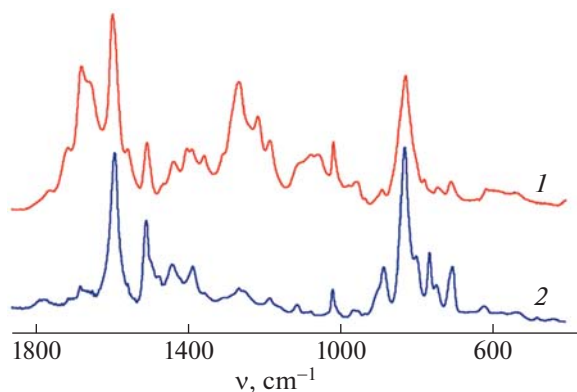


Scheme 1.

program NOVWin (version 11.04) with a built-in package of algorithms for calculating the basic parameters of porosity in terms of several theoretical methods based on the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda (**BJH**) theories and a large set of calculations options based on the density functional theory (**DFT**). Microporous structure analysis was carried out using Dubinin–Rudushkevich and Dubi-

nin–Astakhov methods, comparative *t*-method, the Møller–Plesset method, and Alpha-S method. Nitrogen was used as a sorbate gas, and the temperature of nitrogen sorption measurements was 77 K.

Polymer samples were preheated at 60°C in vacuum in the degassing station of the NOVA 1200e analyzer for 30–60 min. The sorbate volume was measured under the following conditions: a permissible



**Fig. 1.** IR spectra of (1) P-I and (2) P-II. Hereinafter in Figs. 2–7 see sample 5 from Table 1.

pressure deviation of 0.1 Torr and the minimum and maximum time for establishing equilibrium pressure needed to measure the value of adsorption of 60 and 240 s, respectively. To calculate the micropore volume according to the Alpha-S method, the standard carbon material isotherm was used (ACARB in the NowaWin program).

The used notations are as follows:  $S_{sp}$  is the total pore surface,  $W$  is the total pore volume,  $W_{micro}$  is the volume of micropores less than 2 nm in size;  $S_{fr}$  and  $W_{fr}$  are the total surface and volume of “size fractions” of pores with diameters in the range of  $D_{min} - D_{max}$  (on the pore size distribution curve); and  $D_{fr}$  is the diameter of pores (maximum on the pore size distribution curve).

The thermal properties of the synthesized polymers were studied by thermogravimetric and differential thermal analyses using a Q-1500 derivatograph (MOM, Hungary). The heating rate of the samples was 20°C/min, and in a stream of argon inert gas the heating rate was 180 mL/min. The experimental dependences of the change in the sample mass and thermal effects on the heating temperature were processed using the Origin 8.0 program.

## RESULTS AND DISCUSSION

Polyphenylenes-I were synthesized by the trimerization polycyclocondensation of *p*-diacetylbenzene at various concentrations of the monomer in the reaction solution (Table 1).

The resulting polymers were network products insoluble in organic solvents. It should be noted that the gelation process was visually observed in all cases 15–30 min after the start of synthesis. According to the thermal desorption of argon, when the reaction was carried out in highly concentrated solutions (Table 1, samples 1, 3), the value of the internal specific surface was low. This can apparently be explained by the presence of spatial hindrances related to the thickening of

polymer chains, thereby preventing the free rotation of fragmented polymer molecules needed to form phenyl, 1,3,5-triyl moieties. A significant increase in the reaction time (Table 1, sample 2) did not change the situation. To carry out the reaction in more dilute solutions, the concentration of the ketalizing agent (triethyl orthoformate) was slightly increased to 21.6 mmol, and the reaction time was slightly increased as the initial concentration of monomer in the reaction solutions decreased. However, the values of the specific surface area of the polymers (Table 1, samples 4–7) were still low.

The structure of the obtained polymers was analyzed by IR spectroscopy. For example, in the IR spectrum of P-I sample 5 (Fig. 1, curve 1), along with absorption bands at 827, 1266, 1596, and 1686  $\text{cm}^{-1}$  characteristic of the out-of-plane bending vibrations of C–H groups in the 1,4-disubstituted benzene ring, vibrations of arylalkyl ketones, plane stretching vibrations of phenylene moieties, and stretching vibrations of the C=O bond in the acetyl group, respectively, there are absorption bands at 1512 and 1660  $\text{cm}^{-1}$  related to the plane stretching vibrations of phenylene moieties and the stretching vibrations of the C=O group in the diphenylpropanone (dypnone) moiety (it is a dimeric intermediate in the trimerization process), respectively, as well as weak absorption bands at 700, 761, and 881  $\text{cm}^{-1}$  related to the out-of-plane bending vibrations of the C–H bond in the 1,3,5-trisubstituted benzene ring.

The yield of the polymers (Table 1) was calculated from the quantitative conversion of acetyl groups into phenylene structures. Owing to the fact that P-I polymers contained functional groups the yield of most of them exceeded 100%.

Since the synthesized polymer had acetyl groups and dypnone moieties in its structure, an approach based on the heat treatment of P-I in argon at 450°C was used to increase the degree of conversion of reactive groups and, accordingly, to increase the degree of cyclocondensation.

The initial analysis of the structure of heat-treated polymers (P-II) was carried out using the data on the thermal desorption of argon and IR studies. The specific surface of P-2 obtained from P-I, which were synthesized at a high concentration of the monomer in the reaction solution (Table 1, samples 1–4), was not high. At the same time, this parameter for samples 5–7 increased significantly compared to non-heat-treated samples and for the best P-II (sample 5) it was 759  $\text{m}^2/\text{g}$ . According to the IR spectrum (Fig. 1, curve 2), acetyl groups and dypnone moieties are practically absent in this sample, but the aromatic structure is preserved (absorption bands at 827, 1512, and 1596  $\text{cm}^{-1}$ ), and the intensity of the absorption bands at 700, 761, and 881  $\text{cm}^{-1}$  responsible for the vibrations of the 1,3,5-trisubstituted benzene ring increases significantly. This finding indicates a deeper cyclocon-

**Table 2.** Parameters of the porous structure of polyphenylene-II (from Table 1, sample 5)

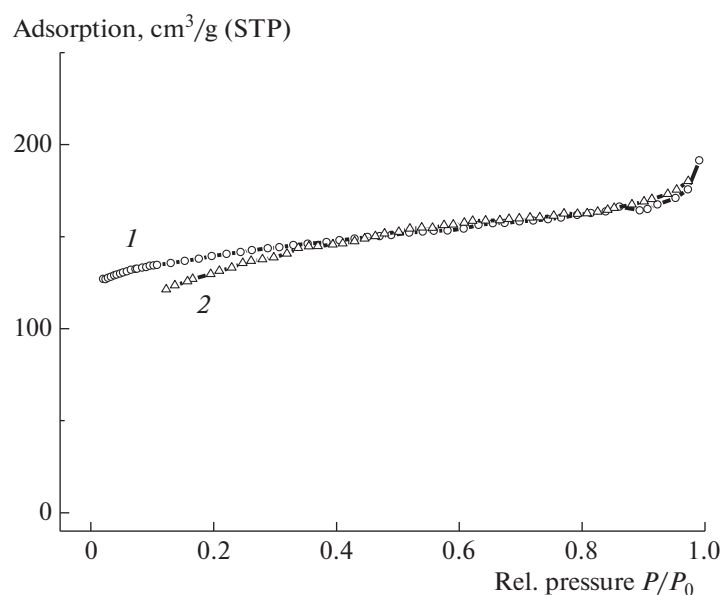
Method	$S_{sp}$ , m <sup>2</sup> /g	$W$ , cm <sup>3</sup> /g	$W_{micro}$ , cm <sup>3</sup> /g	$D_{fr}$ , nm	$D_{min} - D_{max}$ , nm	$S_{fr}/S_{sp}^*$ , %	$W_{fr}/W^*$ , %	$F_{err}^{**}$ , %
NLDFT (1)	780	0.274	0.200	4.0	3.3–4.4	1	5	0.55
				5.1	4.4–6.4	2	9	
NLDFT (2)	470	0.256	0.189	3.2	2.3–3.4	2	7	0.64
				3.9	3.4–5.6	3	7	
				4.9	3.1–7.5	4	17	
QSDFT (1)	977	0.266	0.188	4.9	3.1–7.5	4	17	0.62
QSDFT (2)	624	0.260	0.193	0.6	0.6–1.5	46	43	0.40
				3.0	1.5–5.0	4	15	
DR	601	–	0.213	1.0	–	–	–	$r = 0.98$
DA	–	–	0.226	1.0	0.5–4.0	–	–	
BJH	48	0.080	–	3.7	3.0–4.7	67	39	–
				5.1	4.7–6.1	13	11	
L	599	–	–	–	–	–	–	$r = 1.0$
Alpha-S	–	–	0.166	–	–	–	–	$r = 0.99$

\* Share of total surface  $S_{fr}$  or volume  $W_{fr}$  for the fraction of pores of medium size  $D_{fr}$ ; the rest of the total surface or pore volume is formed by pores with a diameter of less than  $D_{min}$  (for the BJH method, the diameters of pores are higher than  $D_{max}$ ).

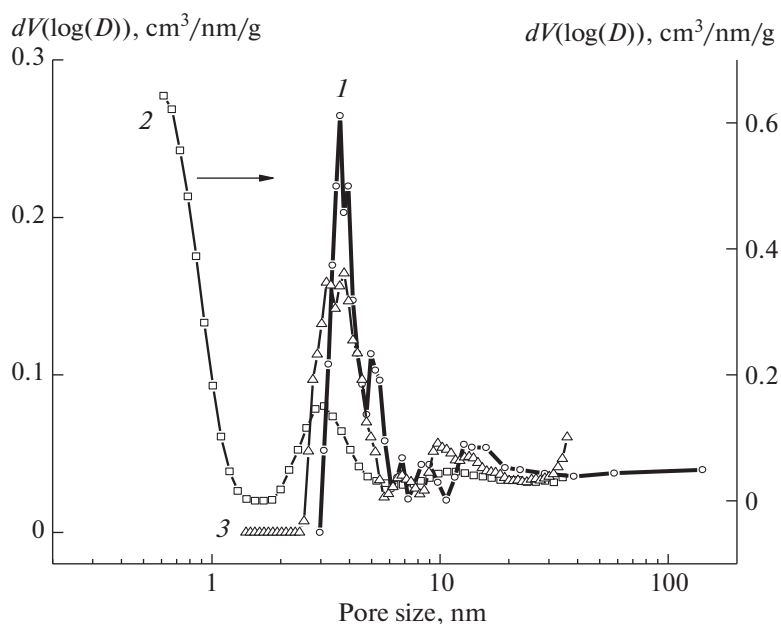
\*\* The maximum deviation of the experimental curve from the “model adsorption isotherm”  $r$  is the correlation coefficient.

densation process under the conditions of the proposed approach and, as a consequence, a more ordered structure of macromolecules. Thus, in the process of polycondensation, phen-1,3,5-triyl moieties are formed, which are branching centers, and, as a result, a three-dimensional polymer is formed having a continuous network of interconnected intramolecular voids due to the rigidity of all polymer units, as well as due to rod-shaped interjunction moieties and symmetrically branched junctions of the polymer network.

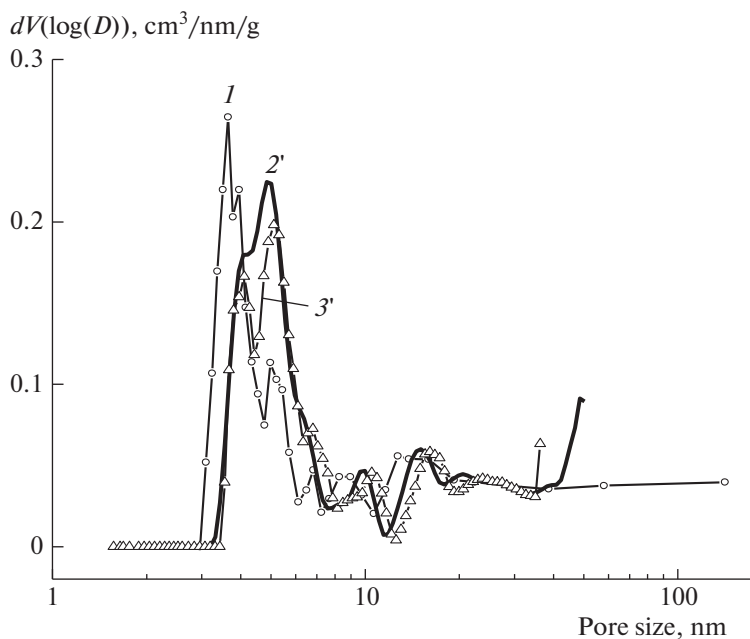
At present, the main experimental method for studying the porous structure of any inorganic or organic materials is the method of low-temperature sorption of gases [13]. The method allows one to assess the main parameters of the porous structure and analyze the pore size distribution using experimental data on gas sorption and various theoretical calculation methods. The basic experimental information for calculating the porosity parameters is the dependence of the volume of the absorbed gas, the sorbate, on its rel-



**Fig. 2.** Isotherms of nitrogen (1) sorption and (2) desorption at 77 K for P-II.



**Fig. 3.** Differential pore size distribution for P-II. Calculation methods: (1) BJH, (2) QSDFT, and (3) NLDFT (the slit pore model).



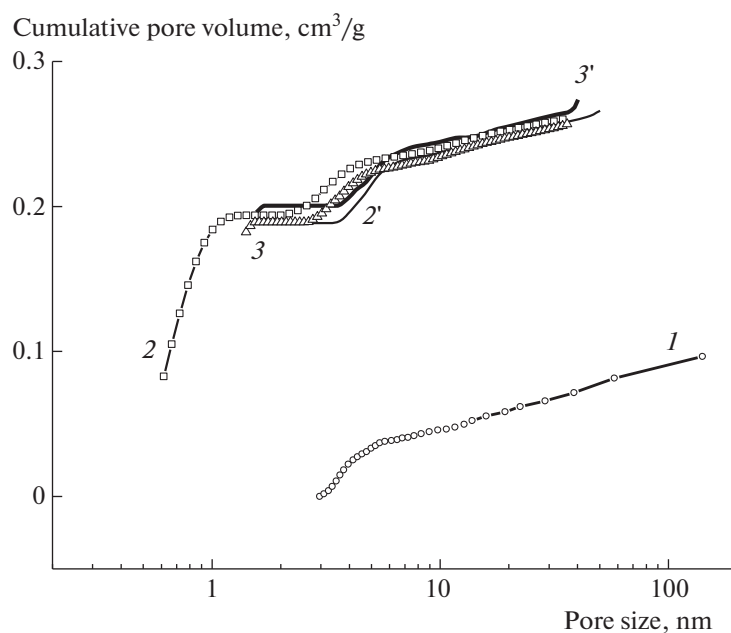
**Fig. 4.** Differential pore size distribution for P-II. Calculation methods: (1) BJH, (2') QSDFT, and (3') NLDFT (the cylindrical pore model).

ative pressure in a measuring cell at a low temperature (sorption isotherms).

Sample P-II having the largest specific surface according to the thermal desorption of argon (Table 1, sample 5) was used to study the porous structure of the obtained polyphenylenes. Nitrogen sorption isotherm of P-II (Fig. 2) belongs to the first type of isotherms characteristic of materials containing mainly micropores [14].

An analysis of nitrogen sorption isotherms of the studied materials using calculations according to the Langmuir theory (L), Dubinin–Radushkevich theory (DR), Dubinina–Astakhova theory (DA), and density functional theory [13] showed that the synthesized polymer has a marked internal specific surface area related to the developed micropore system.

To analyze the size distribution of mesopores for sample P-II according to the BJH method [15] the



**Fig. 5.** Integral pore size distribution for P-II. Calculation methods: (1) BJH, (2 and 2') QSDFT, and (3) and (3') NLDFT (2 and 3 are slit pores, and 2' and 3' are cylindrical pores).

calculations were performed for the desorption part of the isotherm in the relative pressure range of 0.35–0.97 (the pore size is from 3 to ~60 nm) using the cylindrical pore model. It was found that the volume of mesopores is small ( $\sim 0.08 \text{ cm}^3/\text{g}$ ) and 50% of this volume is made up of a 3–6 nm mesopore fraction (Table 2, Figs. 3, 4).

The methods of analyzing porous structure in terms of the density functional theory (DFT) make it possible to calculate pore sizes in the range from 0.3 to 100 nm. For example, the **NLDFT** method, which consists in modeling of the process of interaction of a sorbate and the surface of pore walls with an ordered structure, was used to describe the size distribution of pores in porous carbon and silicate materials [16, 17]. A similar method **QSDFT**, which was developed for modeling the process of gas adsorption on a “waffled” surface of walls with an amorphous structure in heterogeneous materials, was successfully used for various types of porous coals [18, 19].

In this work, software calculations of the characteristics of the porous structure of the studied material were performed using the NLDFT and QSDFT methods for two variants of modeling the porous structure of the studied polymer: in the first variant nitrogen sorption in cylindrical pores of a carbon material at 77 K was used; in the second one, nitrogen sorption in slit pores of the carbon material at 77 K. A similar approach for calculating the parameters of the porous structure of polymers was described in [20].

The differential pore size distribution curves and the cumulative pore volume distribution curves

obtained for P-II sample are shown in Figs. 3–5. The main parameters of the porous structure of sample P-II are listed in Table 2.

The volume of micropores with a size less than 2 nm, which was calculated by independent methods, ranged from 0.16 to  $0.22 \text{ cm}^3/\text{g}$  or 71–74% of the total volume of pores up to 50 nm in size, which was determined by various variants of the DFT method (Table 2). Moreover, for only one of the calculation options (QSDFT method, the slit pore model), a large fraction of micropores with a size of 0.6–1.5 nm was identified in the pore system (Figs. 3, 5; curves 2). The relative volume share of this fraction was 43% of the total pore volume (Table 2). The character of pore distribution according to other variants of the DFT method qualitatively coincides with the pore distribution calculated by the BJH method (Figs. 3, 4), which proves the presence of mesopores in the structure of P-II sample. In this case, the volume of the fraction of mesopores with an average size of 3–5 nm is a much smaller proportion of the total pore volume, from 5 to 17%, depending on the pore structure model used. The BJH method also demonstrated that there are few mesopores in the porous system, since their total surface does not exceed  $48 \text{ m}^2/\text{g}$ . The surface of all pores calculated by various independent methods ranged from 470 to  $980 \text{ m}^2/\text{g}$  (Table 2). This surface is mainly formed by a system of micropores smaller than 2 nm in size. The calculations of the parameters of the microporous structure according to the Dubinin–Radushkevich and Dubinin–Astakhov methods developed for carbon materials demonstrated that the average

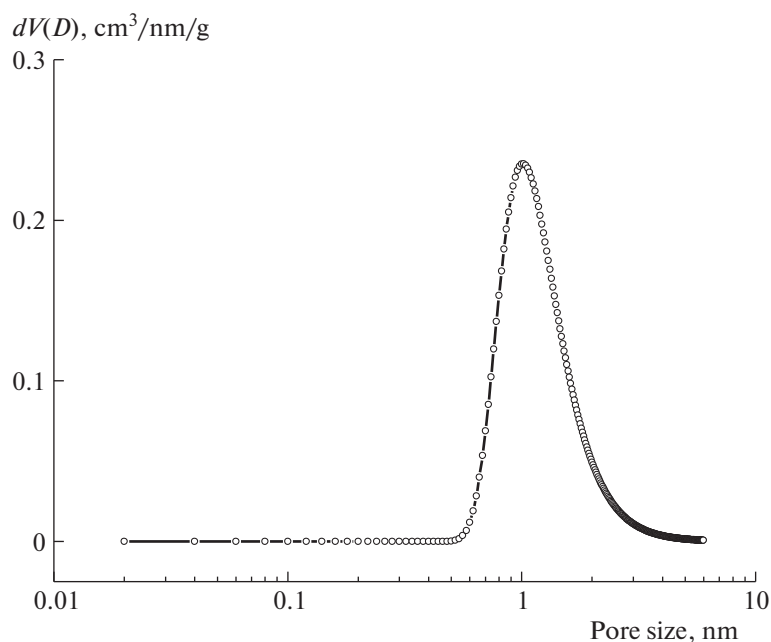


Fig. 6. Differential micropore size distribution curve by the Dubinin–Astakhov method.

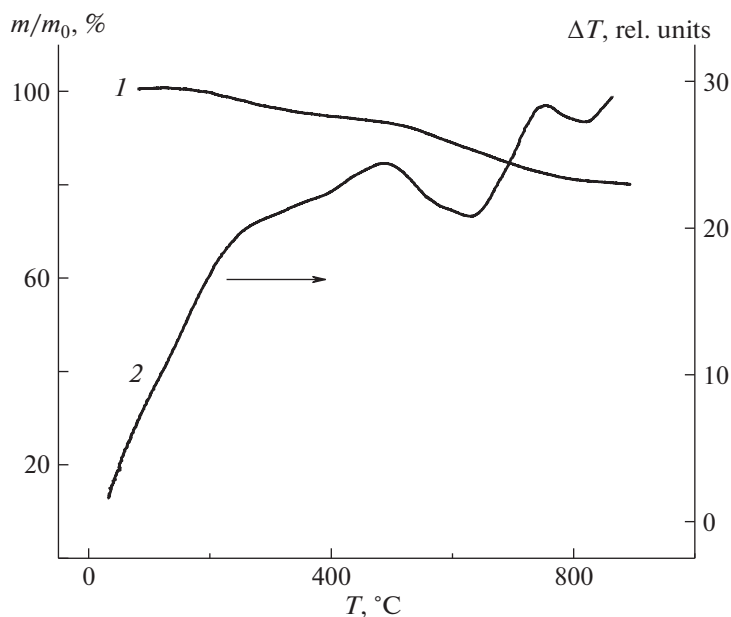


Fig. 7. (1) TGA and (2) DTA of polyphenylene-II in argon. The heating rate is 20°C/min.

micropore size in the studied sample is 1 nm (Table 2, Fig. 6).

When studying the thermal characteristics, P-II sample exhibited high heat resistance: when heated in an inert medium in the range of 200–900°C the mass loss was ~20%. Moreover, in the range of 600–700°C the thermogram showed a significant endo effect apparently associated with the structural rearrangement of the carbon material. An analysis of the porous structure of the carbon material after thermal analysis

revealed that the total pore volume at  $P/P_0 = 0.99$  (all pores up to 200 nm in size) remains virtually unchanged compared to the initial sample, 0.3 and 0.29 cm<sup>3</sup>/g, respectively. The specific surface of the carbon material determined by the “single-point” BET method ( $P/P_0 = 0.3$ ) was slightly higher than that of the initial sample, 558 and 445 m<sup>2</sup>/g, respectively, which is caused by a slight increase in the number of micropores as a result of partial “burnout” of the material of P-II sample.



Thus, in the present work, in an interesting and simple way, microporous heat-resistant polyphenylene was obtained, which by its properties seems to be a very promising microporous material capable of working under rather severe conditions, in particular, as a matrix of a heterogeneous catalyst.

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#### REFERENCES

1. G. Bengtson, S. Neumann, and V. Filiz, *Membranes* (Basel, Switz.) **7**, 28 (2017).
2. D. Ramimoghadam, E. MacA Gray, and C. J. Webb, *Int. J. Hydrogen Energy* **41**, 16944 (2016).
3. L. J. Abbott and C. M. Colina, *Macromolecules* **44**, 4511 (2011).
4. F. Schüth, K. S. W. Sing, and J. Weitkamp, *Handbook of Porous Solids* (Wiley, Weinheim, 2002).
5. N. B. McKeown and P. M. Budd, *Macromolecules* **43**, 5163 (2010).
6. J. Schmidt, M. Werner, and A. Thomas, *Macromolecules* **42**, 4426 (2009).
7. T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C. Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu, and G. S. Zhu, *Angew. Chem.* **48**, 9457 (2009).
8. S. W. Yuan, S. Kirklin, B. Dorney, D. J. Liu, and L. P. Yu, *Macromolecules* **42**, 1554 (2009).
9. J. Weber and A. Thomas, *J. Am. Chem. Soc.* **130**, 6334 (2008).
10. A. I. Kovalev, Yu. I. Lyakhovetskii, M. M. Teplyakov, A. L. Rusanov, P. V. Petrovskii, and S. O. Yakushin, *Russ. Chem. Bull.* **42**, 1529 (1993).
11. I. A. Khotina, O. E. Shmakova, D. Yu. Baranova, N. S. Burenkova, A. A. Gurskaja, P. M. Valetsky, and L. M. Bronstein, *Macromolecules* **36**, 8353 (2003).
12. N. E. Bukhnova and A. P. Karnaukhov, *Determining Specific Surface Area by Chromatographic Method of Heat-Induced Argon Desorption* (Nauka, Novosibirsk, 1965) [in Russian].
13. S. Lowell, J. E. Shields, M. A. Thomas, and M. Thommes, *Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density* (Springer, New York, 2004).
14. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press, London; New York, 1967).
15. E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.* **73**, 373 (1951).
16. J. Landers, G. Yu. Gor, and A. V. Neimark, *Colloids Surf., A* **437**, 3 (2013).
17. P. I. Ravikovitch, A. Vishnyakov, R. Russo, and A. V. Neimark, *Langmuir* **16**, 2311 (2000).
18. A. V. Neimark, Y. Lin, P. I. Ravikovitch, and M. Thommes, *Carbon* **47**, 1617 (2009).
19. G. Yu. Gor, M. Thommes, K. A. Cychosz, and A. V. Neimark, *Carbon* **50**, 1583 (2012).
20. A. V. Pastukhov, *Eur. Polym. J.* **124**, 109480 (2020).

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