Thermodynamic properties of pyridine-containing polyphenylene dendrimers of the first—fourth generations

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The temperature dependence of the heat capacity $C_p° = f(T)$ of hard pyridine-containing polyphenylene dendrimers of the first, third, and fourth generations was studied for the first time in an adiabatic calorimeter at 6—300 K. Using the experimental data obtained, the standard thermodynamic functions, *viz.*, heat capacity, enthalpy, entropy, and Gibbs energy in the range from $T \to 0$ to 300 K, were calculated for these dendrimers and the value of standard entropy of formation of the studied compounds at $T = 298.15$ K was estimated. The low-temperature heat capacity of the dendrimers was analyzed on the basis of the Tarasov and Debye theories of heat capacity of solids and by the multifractal method. The characteristic temperatures and fractal dimensionality D were determined, and some conclusions about the type of structure topology were drawn. The isotherms of the dependence of thermodynamic functions of the dendrimers on the molecular weight were obtained.

Key words: pyridine-containing polyphenylene dendrimers, calorimetry, fractal dimensionality, thermodynamic functions.

One of the most promising and rapidly developed directions of modern chemistry is the study of dendrimers representing spatially hyperbranched macromolecules with highly ordered controlled and regular structures.[1—7] Dendrimers are obtained by multiple repetition of a chosen sequence of reactions, which makes it possible to control the architecture of the framework, the number of functional groups on the surface of macromolecules, their shape and size, and the molecular weight.[8—10] Various classes of dendrimers have been synthesized to the present time: carbochain, carbosilane, phenylethynyl, phosphine, phosphonium, phenylene, and others.[11—14] Owing to the unique structure and a complex of specific properties, dendrimers find wide use; in particular, they can be used as standards in mass spectrometry, electronic and atomic spectroscopy, and ultrafiltration and for encapsulation and immobilization of guest low-molecular-weight compounds, including physiologically active substances, *etc.*

In this work hard pyridine-containing polyphenylene dendrimers[15,16] are considered. They are characterized by high chemical and thermal stability, which allows one to use them in aggressive media and at elevated temperatures. Due to their hard structure, these compounds can be used for the synthesis of new hybrid nanostructured systems (dendrimer—metal) with catalytic properties and for the development of nanosized optical and electronic devices.[15,17,18]

The purpose of the present work is the calorimetric study of the temperature dependence of the heat capacity $C_p° = f(T)$ of hard pyridine-containing polyphenylene dendrimers of the first (G1-8Py), third (G3-42Py), and fourth (G4-90Py) generations at 6—300 K; calculation of the standard thermodynamic functions $C_p°(T)$, $[H°(T) - H°(0)]$, $S°(T)$, and $[G°(T) - H°(0)]$ from the obtained experimental data in the range from $T \to 0$ to 300 K; determination of the standard entropy of formation of the studied compounds at 298.15 K; evaluation of the type of structure topology by the data of low-temperature (20—50 K) heat capacity; and obtaining of isotherms ($T = 200$ and 298.15 K) of the dependences of the heat capacity, enthalpy, and entropy on the molecular weight for the dendrimers of this series from the first to fourth generations.

Experimental

Samples of dendrimers G1-8Py, G3-42Py, and G4-90Py were synthesized at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, using the procedure described earlier.[15,16] The structures of the studied

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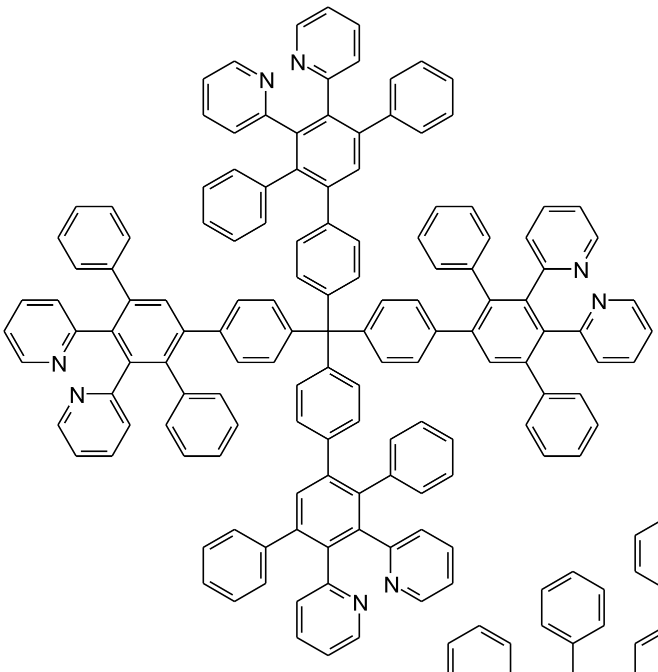
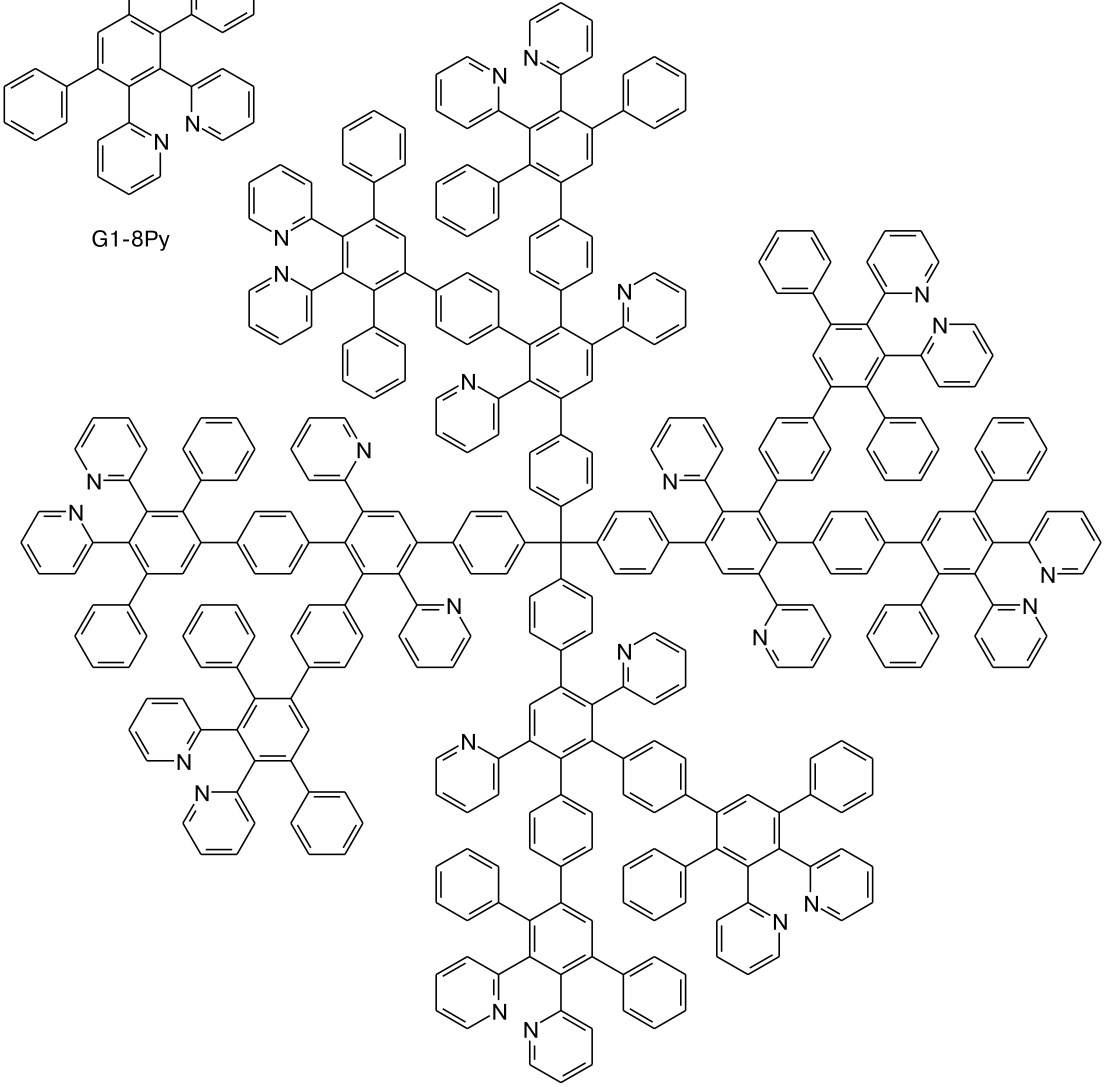


G1-8Py

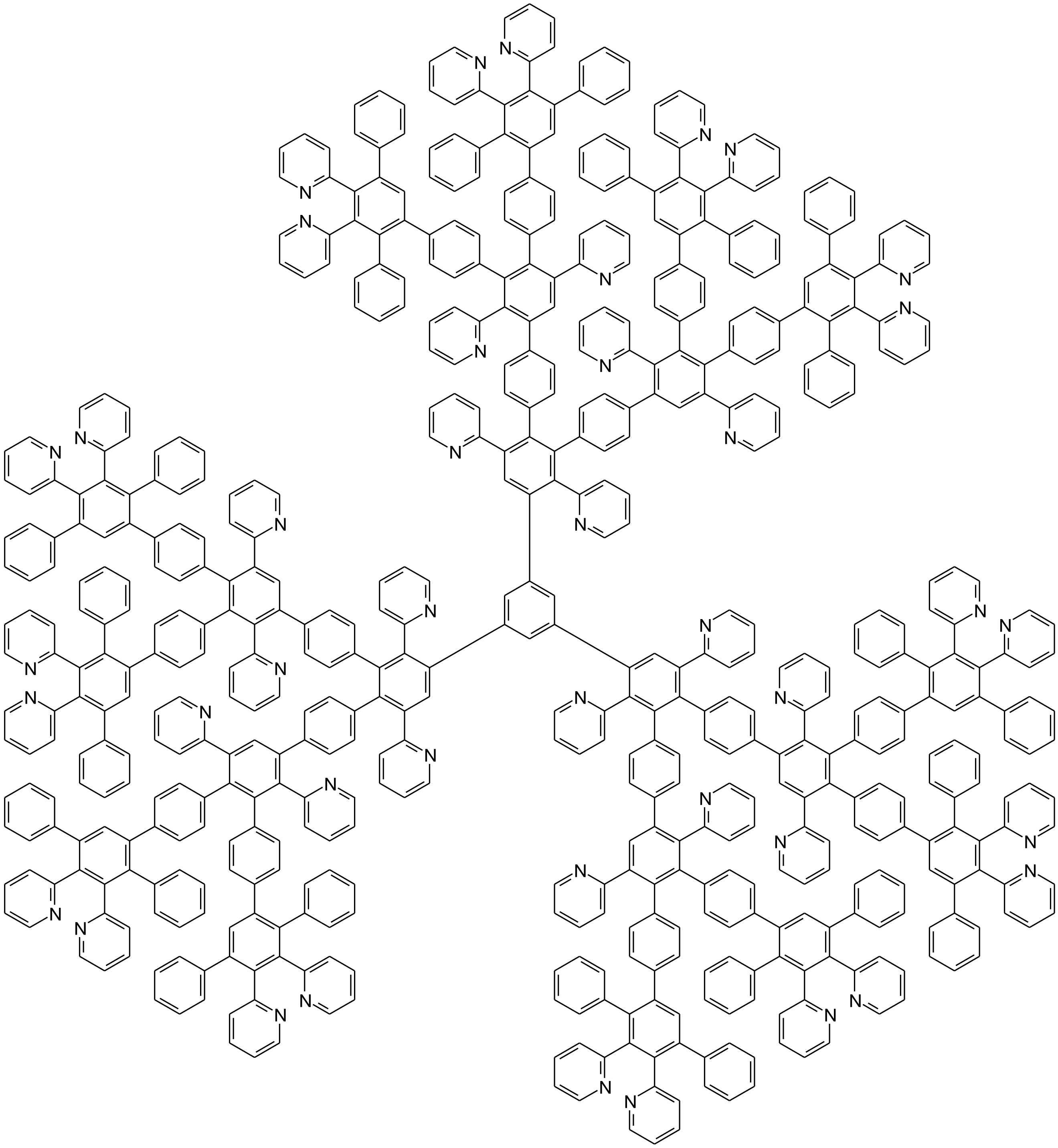


G2-24Py

samples were confirmed by the data of NMR spectroscopy, MALDI-TOF mass spectrometer, and elemental analysis data.[15] The structures of dendrimers G1-8Py, G2-24Py, G3-42Py, and G4-90Py are presented above and below.

According to the thermogravimetric analysis data, the studied samples of dendrimers exhibit high thermal stability, and their destruction (10% weight loss) begins at ~848 K in a nitrogen atmosphere and at ~753 K in air.[15]

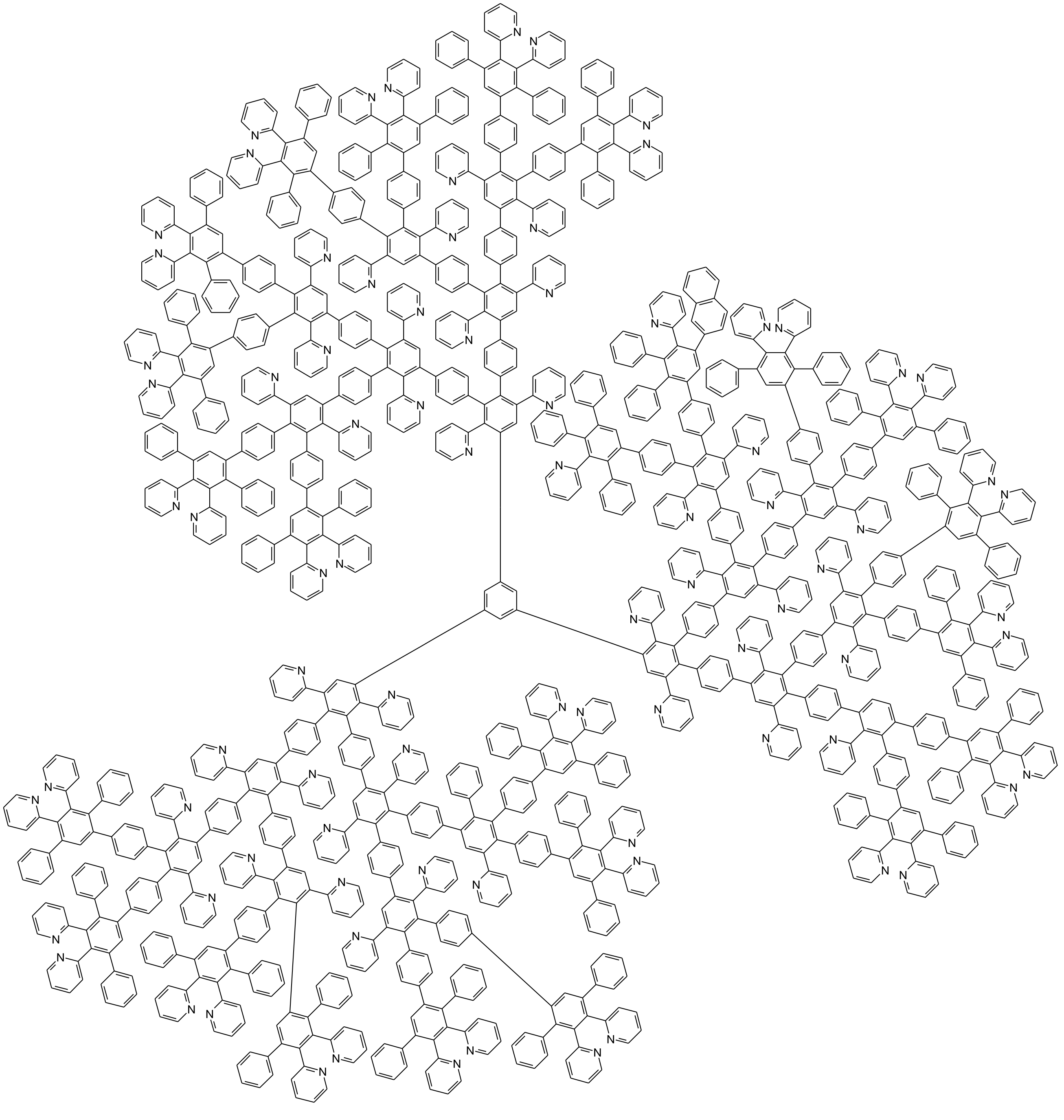
A BKT-3 completely automated adiabatic vacuum calorimeter designed and produced at the Termis joint-stock closed company (Mendeleevo, Mosocow Region) was used for the study of the temperature dependence of heat capacity $C_p° = f(T)$ of the samples at 6—300 K. Liquid helium and nitrogen were used as cooling agent. Ampules with substances were filled with dry helium (as a heat-exchange gas) to a pressure of 4 kPa at room temperature. The structure of the calorimeter and the procedure are analogous to those described earlier.[19,20] Reliability of operation of the calorimeter was checked by measuring $C_p°$ of standard samples of ultrapure copper, standard corundum, and benzoic acid (K-3 trade mark), and by determining characteristics of melting of *n*-heptane. It was established as a result that the equipment and measurement procedure made it possible to ob-



G3-42Py

tain $C_p°$ of substances with an inaccuracy of ±2% at $T < 15$ K, ±0.5% in the range 15—40 K, and ±0.2% in the range 40—300 K, and the temperatures of phase transitions can be measured with an inaccuracy of ±0.01 K according to the ITS-90.

The heat capacity of the dendrimers was studied in the range 6—300 K. Weights of the samples placed in BKT-3 calorimetric ampules were ~0.1500 g. In two series reflecting the sequence of experiment for G1-8Py, G3-42Py, and G4-90Py we obtained 175, 149, and 165 experimental values of $C_p°$, respectively. The heat capacity of the sample ranged from 25 to 35% of the total heat capacity of the calorimetric ampule with the substance. The experimental points of $C_p°$ were smoothened as power and semilogarithmic polynomials, and the corresponding coefficients were selected by special computer programs. The relative deviation of experimental values of $C_p°$ from the smoothened curve $C_p° = f(T)$ in the temperature ranges 6—20, 20—50, and 50—300 K was ±1.3, ±0.4, and ±0.25%, respectively.



G4-90Py

Results and Discussion

Heat capacity. The experimental values of C_p° and smoothing curves of $C_p^\circ = f(T)$ for the denrimers are presented in Fig. 1. Under the experimental conditions, the studied substances were cooled from room temperature to the temperature of measurements (~6 K) with a rate of $0.02\ \mathrm{K\ s^{-1}}$. On subsequent heating, the heat capacity of the dendrimers increased smoothly with temperature and had no anomalies. No devitrification and crystallization of the dendrimer samples occurred under the conditions of calorimetric experiment. It is most likely that defreezing of segmental mobility of particular regions of the macromolecules begins at a temperature higher than 300 K because of the hard structure of the dendrimers.

It was of interest to evaluate the topological structure of the dendrimers on the basis of the Tarasov and Debye theories of heat capacity of solids and the multifractal model of processing C_p°.

According to the Tarasov theory,[21—23] the skeletal heat capacity of chain polymers is described by the two-parameter function of heat capacity

$$C_{1,3} = D_1(\theta_1/T) - \theta_3/\theta_1[D_1(\theta_3/T) - D_3(\theta_1/T)], \qquad (1)$$

where D_1 and D_3 are the symbols of the Tarasov and Debye functions of heat capacity; θ_1 and θ_3 are the corresponding characteristic temperatures; and θ_3/θ_1 is the interchain interaction parameter varying from zero to unity. The specific type of functions D_1 and D_3 is given, *e.g.*, in Refs 21—23.

Assuming that at $T < 100$ K the contribution of atomic vibrations to the heat capacity of the polymers considered is small, it can be accepted that in this temperature range $C_p^\circ = C_{1,3}$. Taking into account this assumption on the experimental values of heat capacity of the dendrimers studied, we selected for them the values of θ_1 and θ_3 (Table 1). To calculate θ_1 and θ_3 of the second generation dendrimer, the values of C_p°, which we obtained for this dendrimer earlier,[24] were used.

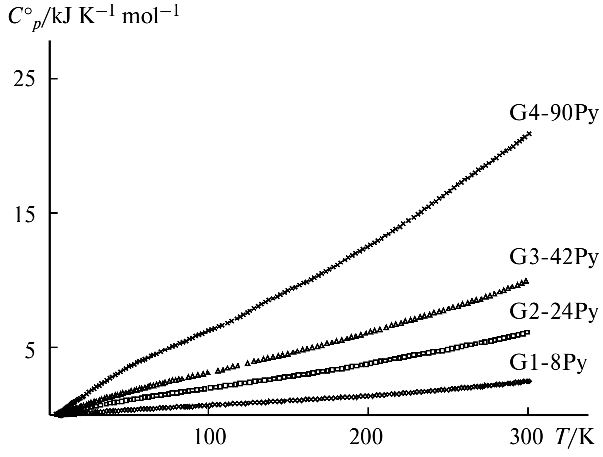


Fig. 1. Temperature plots of the heat capacity of dendrimers G1-8Py—G4-90Py.

Table 1. Fractal dimensionalities (D) and characteristic temperatures (θ_{max}) of the pyridine-containing polyphenylene dendrimers*

Dendrimer	D	$\theta_{max}(\theta_3)$	θ_1	θ_1/θ_3
		K		
G1-8Py	1.3	68.28	227.6	0.3
G2-24Py	1.3	81.29	406.5	0.2
G3-42Py	1.4	61.67	308.4	0.2
G4-90Py	1.3	81.73	408.7	0.2

* Temperature range 20—50 K.

Values of θ_1 and θ_3 were selected using the Chernoplekov tables.[25] Note that with the selected values of θ_1 and θ_3 Eq. (1) reproduces the experimental values of heat capacity in the range 20—50 K for all considered compounds with the inaccuracy within ±2.5%.

The values obtained by us (see Table 1) show that the character of interchain interaction is approximately the same for all dendrimers considered.

The results agree with the data of multifractal processing of the low-temperature (20—50 K) heat capacity. The main parameter of the Debye multifractal model of the theory of heat capacity of solids[26] is fractal dimensionality D (see Refs 26 and 27), *viz.*, exponent at the temperature. Fractal dimensionality can possess the values from 1 to 4, which allow one to judge about the type of topology of structure of solids.[27] For the chain, layer, and spatial structures, $D = 1$, 2, and 3, respectively. Fractal dimensionality can be estimated from the experimental data on heat capacity from the slope of the corresponding rectilinear regions of the plot of $\ln C_v$ *vs* $\ln T$, accepting that at $T < 50$ K $C_p^\circ = C_v$. This follows from the equation

$$C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/\theta_{max})^D, \qquad (2)$$

where N is the number of particles in the molecule, k is Boltzmann´s constant, $\gamma(D + 1)$ is the Gamma-function, $\xi(D + 1)$ is the Riemann ξ-function, θ_{max} is the characteristic temperature, and D is fractal dimensionality.

The values of D obtained by us (see Table 1) indicate the chain-layer topology of the structure of the studied dendrimers.

As the temperature decreases ($T \le 20$ K), the heat capacity of all samples is well described by the Debye cubic limiting law.

Standard thermodynamic functions. For the calculation of the standard thermodynamic functions (Tables 2—4), the temperature dependence of the heat capacity was extrapolated from 6 to 0 K by the Debye function of heat capacity of solids. The enthalpy and entropy were determined by numerical integration of the curves $C_p^\circ = f(T)$

Table 2. Standard thermodynamic functions of the polyphenylene pyridine-containing dendrimer of the first generation (M = 1850 g mol^{-1})

T/K	$C_p°(T)$	$S°(T)$	$\Delta H°$*	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	5.66	1.89	0.0071	0.00236
10	38.20	14.20	0.1050	0.03690
15	85.00	38.40	0.4120	0.16400
20	128.10	68.70	0.9442	0.43080
25	170.30	101.60	1.6890	0.85130
50	379.6	285.8	8.631	5.66
100	726.9	657	36.39	29.31
200	1419	1370	143.2	130.8
298.15	2478	2120	330.9	301.1
300	2505	2135	335.5	305

* $H°(T) - H°(0)$.

and $C_p° = \ln f(T)$, respectively, over the temperature. The Gibbs function was calculated by the Gibbs—Helmholtz equation. The calculation procedure was described in detail before.[28] It was assumed that the errors of calculated values of the functions were ±2, ±0.5, and ±0.2% at $T < 15$ K and in the temperature ranges of 15—40 and of 40—300 K, respectively.

The standard entropy of formation at T = 298.15 K was calculated according to Eqs (3)—(5) using the values of absolute entropies for the dendrimers (see Tables 2—4) and simple substances: carbon, hydrogen, and nitrogen.[29] For G1-8Py, G3-42Py, and G4-90Py $\Delta_f S°$ is −5444±18, −23 388±78, and −157 889±166 kJ K^{-1} mol^{-1}, respectively.

$$137\,C\,(gr) + 46\,H_2\,(g) + 4\,N_2\,(g) \longrightarrow C_{137}H_{92}N_8\,(gl) \tag{3}$$

Table 3. Standard thermodynamic functions of the polyphenylene pyridine-containing dendrimer of the third generation (M = 8110 g mol^{-1})

T/K	$C_p°(T)$	$S°(T)$	$\Delta H°$*	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	37.4	12.6	0.047	0.0157
10	183.0	70.2	0.474	0.1710
15	400.0	211.0	2.200	0.9700
20	588.2	351.8	4.664	2.3710
25	788.1	504.1	8.098	4.5050
50	1706	1355	40.1	27.65
100	3153	2989	162.1	136.8
200	6102	6043	619.4	589.1
298.15	9900	9137	1392	1332
300	9992	9199	1410	1349

* $H°(T) - H°(0)$.

Table 4. Standard thermodynamic functions of the polyphenylene pyridine-containing dendrimer of the fourth generation (M = 17289 g mol^{-1})

T/K	$C_p°(T)$	$S°(T)$	$\Delta H°$*	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	44.6	14.9	0.056	0.0186
10	324.0	115.0	0.858	0.2930
15	792.0	333.0	3.630	1.3700
20	1214.0	621.6	8.688	3.7440
25	1615.0	934.6	15.730	7.6260
50	3501	2653	80.41	52.22
100	6210	5939	325.1	268.8
200	12482	12067	1245	1168
298.15	20555	18516	2857	2663
300	20718	18643	2895	2698

* $H°(T) - H°(0)$.

$$594\,C\,(gr) + 192\,H_2\,(g) + 21\,N_2\,(g) \longrightarrow C_{594}H_{384}N_{42}\,(gl) \tag{4}$$

$$1266\,C\,(gr) + 408\,H_2\,(g) + 45\,N_2\,(g) \longrightarrow C_{1266}H_{816}N_{90}\,(gl) \tag{5}$$

(physical states of the reactants are given in parentheses: gr is graphite, g is gas, and gl is glassy).

Figure 2 presents the isotherms of the dependences of heat capacity $C_p°$ on the molecular weight of the pyridine-containing polyphenylene dendrimers of the first—fourth generations at 200 and 298.15 K. At these temperatures the dendrimers exist in the same physical states. As can be seen from Fig. 2, the experimental points agree well with the averaging straight lines. The reliability of approximation is $R^2 = 1$. The maximum arithmetical mean error of deviation of the experimental points from the correspond-

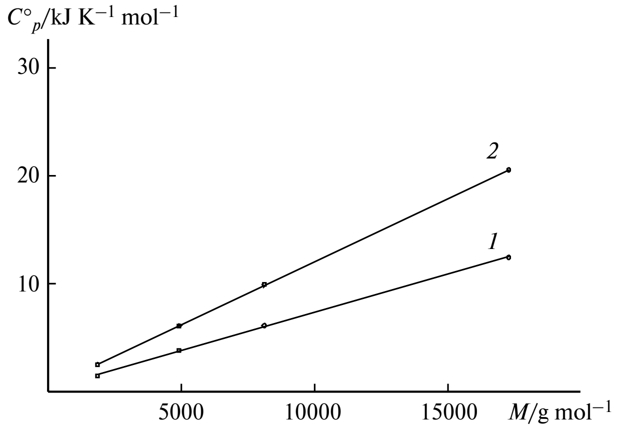


Fig. 2. Isotherms of the heat capacity *vs* molecular weight M of the pyridine-containing polyphenylene dendrimers of the first—fourth generations at 200 (*1*) and 298.15 K (*2*).

ing straight lines for the dendrimers of the first—fourth generations is ~2.5%. For the dendrimer of the first generation, the value of deviation increases to 14%. This, most likely, is related to the fact that the dendrimer of the first generation has a low molecular weight and can be considered as a low-molecular-weight compound. The equations of isotherms of the dependences of the thermodynamic functions of the studied dendrimers on their molecular weight M are given below.

$$C_p°(200) = 0.7089M + 232.97 \tag{6}$$

$$C_p°(298.15) = 1.1707M + 337.42 \tag{7}$$

$$H°(200) - H°(0) = 0.0707M + 31.04 \tag{8}$$

$$H°(298.15) - H°(0) = 0.1627M + 54.188 \tag{9}$$

$$S°(200) = 0.6844M + 332.76 \tag{10}$$

$$S°(298.15) = 1.0525M + 426.64 \tag{11}$$

In Eqs (6)—(11) heat capacity is presented in kJ K^{-1} mol^{-1}, enthalpy is given in kJ mol^{-1}, and entropy is presented in J K^{-1} mol^{-1}.

Assuming that the obtained dependences are valid for the dendrimers of higher generations (G > 4), the numerical values of their thermodynamic functions can be estimated from the corresponding equations.

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References

1. Y. Kim, S. C. Zimmerman, *Current Opinion Chem. Biol.*, 1998, **2**, 733.
2. A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
3. G. V. Korolev, M. L. Bubnova, *Polym. Sci.*, 2007, **49**, 32.
4. I. P. Beletskaya, A. V. Chuchurkin, *Usp. Khim.*, 2000, **69**, 699 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2000, **69**, 639].
5. C. C. Lee, J. A. Mackay, J. M. Frechet, F. C. Szoka, *Nature Biotech.*, 2005, **23**, 1517.
6. K. Esumi, *Top. Curr. Chem.*, 2003, **227**, 31.
7. D. Mery, D. Astruc, *Coord. Chem. Rev.*, 2006, **250**, 1965.
8. U. M. Wiesler, T. Weil, K. Muellen, *Nanosized Polyphenylene Dendrimers, Dendrimers III. Design, Dimension, Function. Topics in Current Chemistry*, Springer-Verlag, Berlin—Heidelberg, 2001, **212**.
9. T. M. Miller, T. X. Neenan, *Chem. Mater.*, 1990, **2**, 346.
10. J. S. Moore, *Acc. Chem. Res.*, 1997, **30**, 402.
11. D. A. Tomalia, A. M. Naylor, W. A. Goddart, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138.
12. A. M. Muzafarov, E. A. Rebrov, *Vysokomol. Soedin.*, 2000, **42**, 2015 [*Polym. Sci.* (*Engl. Transl.*), 2000, **42**, 55].
13. S. M. Grayson, M. J. Frechet, *Chem. Rev.*, 2001, **101**, 3819.
14. K. Inoue, *Prog. Polym. Sci.*, 2000, **25**, 453.
15. Z. B. Shifrina, M. S. Rajadurai, N. V. Firsova, L. M. Bronstein, X. Huang, A. L. Rusanov, K. Muellen, *Macromolecules*, 2005, **38**, 9920.
16. Z. B. Shifrina, M. S. Averina, N. V. Firsova, A. L. Rusanov, K. Muellen, *Dokl. Akad. Nauk*, 2005, **400**, 774 [*Dokl. Chem.* (*Engl. Transl.*), 2005, **400**, 34].
17. N. V. Kuchkina, L. M. Bronshtein, A. L. Rusanov, Z. B. Shifrina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 844 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 862].
18. Z. B. Shifrina, N. V. Kuchkina, A. L. Rusanov, V. A. Izumrudov, *Dokl. Akad. Nauk*, 2007, **416**, 66 [*Dokl. Chem.* (*Engl. Transl.*), 2007, **416**, 213].
19. V. M. Malyshev, G. A. Mil´ner, E. L. Sorkin, V. F. Shibakin, *Pribory i tekhnika eksperimenta* [*Instruments and Experimental Equipment*], 1985, **6**, 28 (in Russian).
20. R. M. Varushchenko, A. I. Druzhinina, E. L. Sorkin, *J. Chem. Thermodyn.*, 1997, **29**, 623.
21. V. V. Tarasov, *Zh. Fiz. Khim.*, 1953, **27**, 1430 [*J. Phys. Chem. USSR* (*Engl. Transl.*), 1953, **27**].
22. V. V. Tarasov, *Zh. Fiz. Khim.*, 1950, **24**, 111 [*J. Phys. Chem. USSR* (*Engl. Transl.*), 1950, **24**].
23. V. V. Tarasov, G. A. Yunitskii, *Zh. Fiz. Khim.*, 1965, **39**, 2076 [*J. Phys. Chem. USSR* (*Engl. Transl.*), 1965, **39**].
24. N. N. Smirnova, A. V. Markin, Yu. A. Zakharova, N. V. Kuchkina, A. L. Rusanov, Z. B. Shifrina, *Zh. Fiz. Khim.*, 2010, **84**, 628 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2010, **84**].
25. P. A. Chernoplekov, *Zh. Fiz. Khim.*, 1953, **27**, 878 [*J. Phys. Chem. USSR* (*Engl. Transl.*), 1953, **27**].
26. T. S. Yakubov, *Dokl. Akad. Nauk SSSR*, 1990, **310**, 145 [*Dokl. Chem.* (*Engl. Transl.*), 1990].
27. V. B. Lazarev, A. D. Izotov, K. S. Gavrichev, O. V. Shebersheneva, *Thermochim. Acta,* 1995, **269**, 109.
28. B. V. Lebedev, *Thermochim. Acta*, 1997, **297**, 143.
29. *Codata Key Values for Thermodynamics*, Eds J. D. Cox, D. D. Wagman, V. A. Medvedev, Hemisphere Publishing Corp., New York, 1984.

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