

# Thermodynamic properties of superbranched pyridine-containing polyphenylene in the range from $T \rightarrow 0$ TO 350 K

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*For the first time, the thermodynamic properties of amorphous superbranched pyridine-containing polyphenylene have been studied by the methods of precision adiabatic calorimetry in the region of 6-350 K. In the low-temperature region (10-20 K), the polymer exhibits an anomalous change in the heat capacity, reminiscent of the shape of the G-type transition. According to the experimental data obtained by methods of classical thermodynamics, the standard thermodynamic functions of the polymer for the region from  $T = 0$  to 350 K and the standard entropy of its formation at  $T = 298.15$  K are calculated.*

**Keywords:** superbranched pyridine-containing polyphenylene, adiabatic calorimetry, heat capacity, thermodynamic functions.

## 1. Introduction

At present, interest in the study of superbranched polymers has increased. Such an increase in the attention of the world scientific community to polymers of superbranched structure, apart from scientific and fundamental interest, is related to their practical importance when used in a wide variety of industries [1]. The latter is due to the unique physicochemical properties of this class of compounds, which, being irregular analogues of dendrimers, combine a number of their dignities with the simplicity of obtaining "classical" polymers [2]. The unique properties of superbranched polymers are associated, first of all, with their molecular architecture, characterized by an internal globular structure and a large number of outer terminal functional groups. Superbranched polymers act as thermally stable matrices that simultaneously stabilize nanoparticles and also control their dimensions [3]. They also act as unique controlling agents for the formation of nanoparticles of an atypical structure. They can be used to transport anionic molecules in the blood, such as nucleic acid molecules, including ODN and RNAi molecules, and other anionic drugs with which they can interact, thereby protecting them from interacting with proteins in the plasma and /or enhancing the degree their penetration into the target cells [4]. Superbranched polymers can be used to bind anionic molecules to surfaces, and can also be administered as active components to prevent or treat diseases caused by viruses such as HIV or hepatitis C, or prions whose life cycle they are capable of breaking [3, 4].

Despite the increase in publications dealing mainly with the synthesis of these polymers [3, 5], the study of their thermodynamic properties was practically not carried out, apart from studying the thermodynamic properties of superbranched polyphenylene-germans [6, 7].

This paper is devoted to the study of the thermodynamic properties of the superbranched pyridine-containing polyphenylene in the region of 6-350 K.

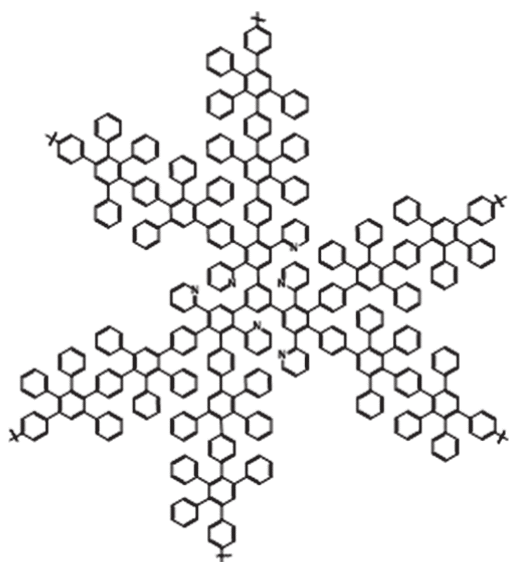
The aim of this work is the calorimetric study of superbranched pyridine-containing polyphenylene (SPCP): heat capacity over a wide range of temperatures, the appearance of possible physical transformations and the determination of their characteristics; Calculation of standard thermodynamic functions on the isolated conventional mole in the region from  $T \rightarrow 0$  to 350 K, as well as the standard mole entropy of its formation at  $T = 298.15$  K.

## 2. Experiment

### 2.1. Characteristics of the studied sample

The SPCP sample was synthesized and characterized from the point of view of its structure and composition in the A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences. A schematic representation of the polymer studied is shown in Fig. 1.

The gross formula of the nominal repeating monomeric link of the polymer  $[C_{30}H_{19}]_n$  (when isolating the nominal link for the quantitative calculation of the values of the thermodynamic functions, the presence of N atoms in the macromolecule was



**Fig. 1.** Schematic representation of a link of superbranched pyridine-containing polyphenylene

neglected). Molar mass  $M = 379.18$  g/mol, calculated from the table of atomic weights IUPAC [8]. The studied polymer was amorphous by calorimetric data, which was also confirmed by X-ray diffraction (XRD-6000 diffractometer of Shimadzu).

## 2.2. Instrumentation and measurement technique

The heat capacity of the SPCP in the 6–350 K region was measured using the well-known technique [9] using the automated adiabatic vacuum calorimeter BKT-3, designed and manufactured at Termis (Mendeleevo, Moscow Region) [10]. All measurements are automated and controlled by a computer-measuring system, including a personal computer, analog-digital and digital-to-analog converters, as well as a voltage switch. Calorimetric ampoule is a thin-walled cylindrical titanium vessel with a volume of  $1.5 \times 10^{-6}$  m<sup>3</sup>.

The reliability of the calorimeter's operation was verified by measuring the heat capacity of standard substances—benzoic acid of mark K-2 and synthetic sapphire prepared at the VNIIM D.I. Mendeleev Institute for Metrology (St. Petersburg). The results of calibration of the calorimeter showed that the error in measuring the heat capacity did not exceed  $\pm 2\%$  to 15 K,  $\pm 0.5\%$  in the range 15–40 K and  $\pm 0.2\%$  in the region of 40–350 K. The error in determining the melting point  $\pm 0.01$  K, melting enthalpy  $\pm 0.2\%$ , glass transition temperature  $\pm 1$  K.

Before measurement, the BKT-3 ampoule with the polymer was filled at room temperature with dry helium of special purity serving as a heat exchange gas to a pressure of 8 kPa. Liquid helium and nitrogen were used as refrigerants. The average heating rate of the ampoule with the polymer in the experiment was 0.2 K / min.

The thermogravimetric (TG) analysis was carried out using of thermomicrobalances “Netzsch Gerätebau TG 209 F1” in an argon atmosphere, in the region of 300–850 K. Thermomicroveses TG 209 F1 allows fixing the mass change to  $\pm 0.1$   $\mu$ g. The average heating rate of the crucible with the substance was 5 K / min. The method of conducting the TG-analysis is standard, according to Netzsch Software Proteus. It is established that the temperature of the beginning of decomposition of the investigated polymer is 570 K.

In the calorimetric ampoule BKT-3 0.1632 g of sample was placed. The heat capacity of the polymer was 25–30% of the total heat capacity of the calorimetric ampoule with matter. Smoothing of the experimental values was carried out using of semi-rhythmical polynomials of the general form  $\ln C_p^o = \ln(a + bT + cT^2 + dT^3 + eT^4 + fT^5 + gT^6)$  with the special programs. In the range of 6–15 K, the smoothing was performed by  $T^3$ -the Debye law. Deviations of the experimental values of the specific heat from the smoothed curve amounted to 1.6% in the region till 15 K, 0.25% in the interval 15–300 K and 0.45% in the interval 300–350 K.

In two series, showing the sequence of the experiment, 114 experimental values of  $C_p^o$  were obtained (table 1).

## 3. Results and discussion

### 3.1. Heat capacity

The experimental values of the heat capacity and the smoothed curve of the SPCP are shown in Fig. 2. The initially loaded sample was cooled from room temperature to the measurement start temperature of 6 K and, during its heating, the heat capacity was measured, which gradually increased with increasing temperature to 350 K (section AB, figure 2), except for the region from 10 to 20 K, where an abnormal change in the specific heat, graphically resembling devitrification, was manifested.

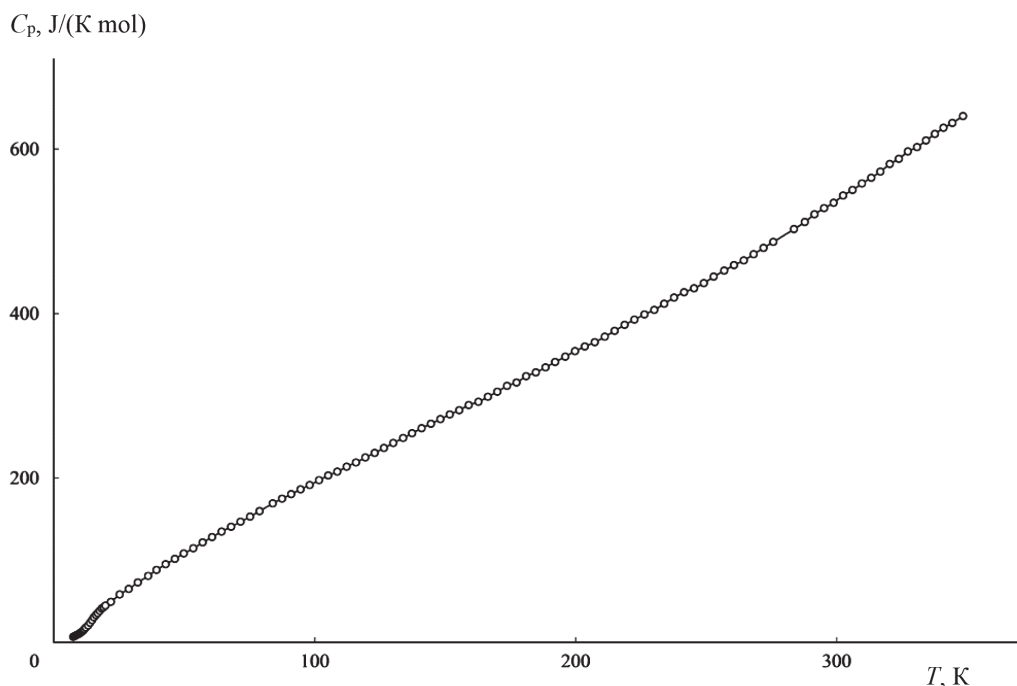
### 3.2. Multifractal processing of low-temperature heat capacity

Using the experimental data on the low-temperature heat capacity for the SPCP, the value of the fractal dimension  $D$  was estimated [11, 12]. Fractal dimension  $D$  is the exponent at the temperature in the basic equation of the fractal model for process-

Table 1

The experimental values of the heat capacity in J / (K×mol) of superbranched pyridine-containing polyphenylene per allotted conventional (условно выделенный) mole [ $-C_{30}H_{19}-$ ],  $M = 379.18$  g / mol

$T / K$	$C_p^o$	$T / K$	$C_p^o$	$T / K$	$C_p^o$
<i>Series 1</i>		28.74	54.23	130.13	202.2
7.50	5.59	32.21	60.78	133.92	207.4
7.76	5.96	36.16	67.40	137.35	212.1
8.15	6.53	39.37	73.54	140.95	217.2
8.20	6.62	42.88	79.29	144.56	221.6
8.52	7.09	46.42	84.62	148.18	226.4
8.90	7.63	49.86	90.23	151.80	231.2
9.26	8.14	53.46	95.42	155.43	235.5
9.29	8.19	57.06	101.3	159.07	240.6
9.65	8.64	60.68	106.7	162.72	244.1
9.68	8.68	64.31	112.3	166.37	249.1
10.04	9.27	67.95	117.3	170.04	254.2
10.08	9.40	71.59	122.4	173.70	260.1
10.45	10.1	75.24	127.5	177.38	263.4
10.86	11.0	78.89	133.2	181.06	269.9
11.28	12.0	<i>Series 2</i>		184.75	273.9
11.72	13.3	78.90	133.1	188.45	278.8
12.32	15.0	83.95	141.0	192.17	284.3
13.13	17.1	87.49	145.7	196.04	289.7
13.91	19.7	91.03	150.4	199.78	295.4
14.67	22.5	94.57	155.2	203.53	300.0
15.41	25.43	98.10	159.7	207.36	304.5
16.15	27.84	101.64	164.6	211.16	310.1
16.87	29.69	105.17	169.2	214.97	315.9
17.59	31.98	108.72	173.1	218.77	322.1
18.38	34.35	112.27	178.2	222.57	327.3
19.09	35.50	115.83	182.5	226.37	332.6
19.78	37.17	119.40	187.5	230.17	337.2
21.90	41.10	122.97	192.1	233.97	343.4
25.30	48.51	126.54	197.2	237.77	349.6
241.57	355.1	283.66	419.2	320.37	485.2
245.36	359.2	287.86	426.3	323.88	490.6
249.16	364.3	291.56	434.0	327.37	498.0
252.94	371.1	295.24	440.4	330.83	502.3
256.94	377.0	298.89	445.8	334.27	509.1
260.72	382.7	302.52	453.3	337.69	515.8
264.49	387.4	306.13	458.9	341.03	521.9
268.26	393.7	309.72	465.5	344.38	526.9
272.01	400.2	313.29	471.1	348.50	533.8
275.76	406.2	316.84	477.5		



**Fig. 2.** Temperature dependence of heat capacity of superbranched pyridine- containing polyphenylene

ing the low-temperature heat capacity. The values of  $D$  allow us to make some conclusions about the type of topology of the structure of solids, and they can be obtained from the graph  $\ln C_v$  on  $\ln T$ . In particular, this follows from equation (1):

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

$k$  – the Boltzmann constant,  $N$  – the number of atoms in the molecule,  $\gamma(D+1)$  – the Gamma function,  $\xi(D+1)$  – Riemann  $\xi$ -function,  $\theta_{\max}$  – is the characteristic temperature.

For a particular solid body  $D(D+1)kN\gamma(D+1)\xi(D+1)(1/\theta_{\max})^D = A$  – is a constant. Then equation (2) can be written as:

$$\ln C_v = \ln A + D \ln T. \quad (2)$$

The experimental values  $C_p^o$  without a noticeable error for  $T < 50$  K can be taken equal to  $C_v$ . Then, using the corresponding experimental data on the heat capacity for the 25–50 K interval (in this temperature range where there are no physical transformations for the SPCP), and Eq. (2), it is possible to obtain the value of  $D$ . It turned out that for the SPCP the fractal dimension is 1.1, and the characteristic temperature  $\theta_{\max} = 272.2$  K. These values are determined with an error of  $\pm 0.3\%$ . According to this model,  $D = 1$  corresponds to the bodies of the chain structure,  $D = 2$  – of the layered structure and  $D = 3$  – of the spatial structure. The value

$D = 1.1$  obtained by us indicates a chain topology of the structure.

### 3.3. Standard thermodynamic characteristics of anomalous change of heat capacity in the helium temperature range

In the range from 10 to 20 K, an anomalous change in the specific heat, resembling in shape the G-type transition, is observed. The temperatures of the beginning and the end of the anomalous dependence of the heat capacity were taken as the temperatures of the beginning ( $T_{c,i}^o$ ) and the end of the transition ( $T_{c,e}^o$ ): at  $T_{c,i}^o$ , the dependence of  $C_p^o = f(T)$  begin to deviate from the normal course (section BC) of the dependence of  $C_p^o = f(T)$  in the temperature interval by 3–7 K below  $T_{c,i}^o$ ; at  $T_{c,e}^o$ , the dependence  $C_p^o$  from  $T$  again becomes normal (SD segment). The increase in the heat capacity for the transition of the G type of the sample ( $\Delta C_p^o(T_c^o) = 18$  J/(K $\times$ mol) – segment BE) was found graphically by extrapolating of the averaging curves of the  $C_p^o = f(T)$  dependence at the ranfe before the transition and after this transition to transition temperature  $T_c^o = 15$  K, which was determined with error  $\pm 1$  K from the inflection point of the graphs  $S^o(T) - S^o(0) = f(T)$  in this interval [13]. The configurational entropy  $S_{\text{conf}}^i = (10 \pm 2)$  J/(K mol) was calculated by the equation proposed in Ref. [14]:

Table 2

Standard thermodynamic functions of superbranched pyridine-containing polyphenylene  
per allotted conventional (условно выделенный) mole  $[-C_{30}H_{19}-]$ ,  $M = 379.18$  g/mol

$T, K$	$C_p^{\circ}(T),$ J/(K mol)	$H^{\circ}(T) - H^{\circ}(0),$ kJ/mol	$S^{\circ}(T) - S^{\circ}(0),$ J/(K mol)	$-[G^{\circ}(T) - H^{\circ}(0)],$ kJ/mol
5	2.15	0.00275	0.743	0.000939
10	9.38	0.0309	4.35	0.0126
15	23.60	0.1090	10.49	0.0484
20	37.41	0.2656	19.41	0.1225
25	47.58	0.4785	28.87	0.2432
30	56.78	0.7397	38.37	0.4113
40	74.25	1.396	57.11	0.8890
50	90.51	2.221	75.46	1.552
60	105.6	3.202	93.30	2.396
70	120.3	4.331	110.7	3.417
80	134.9	5.606	127.7	4.609
90	149.0	7.026	144.4	5.969
100	162.4	8.584	160.8	7.496
110	175.1	10.27	176.9	9.184
120	188.2	12.09	192.7	11.03
130	202.1	14.04	208.3	13.04
140	215.6	16.13	223.8	15.20
150	228.6	18.35	239.1	17.51
160	241.4	20.70	254.2	19.98
170	254.4	23.18	269.3	22.60
180	267.6	25.79	284.2	25.36
190	281.2	28.53	299.0	28.28
200	295.1	31.41	313.8	31.34
210	309.2	34.43	328.5	34.55
220	323.3	37.60	343.2	37.91
230	337.5	40.90	357.9	41.42
240	351.9	44.35	372.6	45.07
250	366.4	47.94	387.2	48.87
260	381.4	51.68	401.9	52.82
270	397.0	55.57	416.6	56.91
280	413.3	59.62	431.3	61.15
290	430.3	63.84	446.1	65.54
298.15	444.7	67.40	458.2	69.22
300	448.0	68.23	461.0	70.07
310	466.0	72.80	476.0	74.76
320	484.0	77.55	491.1	79.59
330	501.8	82.48	506.2	84.58
340	519.3	87.58	521.5	89.72
350	536.8	92.86	536.8	95.01

$$S_{\text{conf}}^{\circ} = \Delta C_p^{\circ}(T_c^{\circ}) \ln T_c^{\circ} / T_2^{\circ}, \quad (3)$$

$T_2^{\circ}$  –Kautzman temperature [15]. To estimate the configuration entropy of the PFC we assumed that  $T_c^{\circ} / T_2^{\circ} = 1.29 \pm 0.14$  [13].

It should be noted that the polyphenylene germanes also have a low-temperature transformation in this temperature range [6, 7]. The nature of these transformations is not clear, since their interpretation requires additional studies in an area close to 0 K.

### 3.4. Standard thermodynamic functions

The thermodynamic functions calculated for the SPCP are presented in Table. 2. To calculate the thermodynamic functions, the temperature dependence of the heat capacity was extrapolated to 0 K from the temperature of the beginning of the measurements by the Debye function

$$C_p^{\circ} = nD(\theta_D/T), \quad (4)$$

$D$  – Debye heat capacity function,  $n$  and  $\theta_D$  – specially selected parameters.

For  $n = 3$  and  $\theta_D = 43$  K equation (4) reproduces  $C_p^{\circ}$  values in the interval 6-9 K with an error of  $\pm 1.7$ . The enthalpy  $H^{\circ}(T) - H^{\circ}(0)$  and the entropy  $S^{\circ}(T) - S^{\circ}(0)$  of heating were calculated by integrating the dependences  $C_p^{\circ}$  on  $T$  and  $\ln T$  respectively, and the Gibbs energy from enthalpy and entropy values:

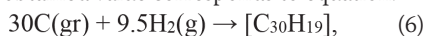
$$G^{\circ}(T) - H^{\circ}(0) = [H^{\circ}(T) - H^{\circ}(0)] - T[S^{\circ}(T) - S^{\circ}(0)]. \quad (5)$$

Details of the calculation of functions are described in detail in [16].

From the values of the entropy of the SPCP (Table 2) and the absolute entropy of the corresponding simple substances, C (gr), H<sub>2</sub> (g), O<sub>2</sub> (g), N<sub>2</sub> (g) [17] at  $T = 298.15$  K, we calculated the standard entropy of the formation of the SPCP for the allotted conventional mole

$$\Delta_f S^{\circ}(C_{30}H_{19}, 298.15) = -951 \pm 6 \text{ J/(K}\cdot\text{mol)}.$$

The obtained value corresponds to equation:



gr is graphite, g is gas, the nominal repetitive link of the polymer is indicated in square brackets

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