

THERMODYNAMICS OF PHENYLATED POLYPHENYLENE BETWEEN 0 AND 340 K

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(Received January 21, 2003; in revised form July 22, 2003)

Abstract

In an adiabatic vacuum calorimeter, the temperature dependence of the heat capacity C_p^0 of phenylated polyphenylene and initial comonomer 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene was studied between 6 and 340 K with an uncertainty of about 0.2%. In a calorimeter with a static bomb and an isothermal shield their energies of combustion ΔU_{comb} were measured. From the experimental data, the thermodynamic functions $C_p^0(T)$, $H^0(T)-H^0(0)$, $S^0(T)-S^0(0)$, $G^0(T)-H^0(0)$ were calculated from 0 to 340 K, and standard enthalpies of combustion ΔH_{comb}^0 and thermodynamic parameters of formation—enthalpies ΔH_f^0 , entropies ΔS_f^0 , Gibbs functions ΔG_f^0 —of the substances studied were estimated at $T=298.15$ K at standard pressure. The results were used to calculate the thermodynamic characteristics (ΔH_f^0 , ΔS_f^0 , ΔG_f^0) of phenylated polyphenylene synthesis in the range from 0 to 340 K.

Keywords: 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene, fractal dimension, heat capacity, phenylated polyphenylene, standard enthalpies of combustion, thermodynamic functions, thermodynamic parameters of formation

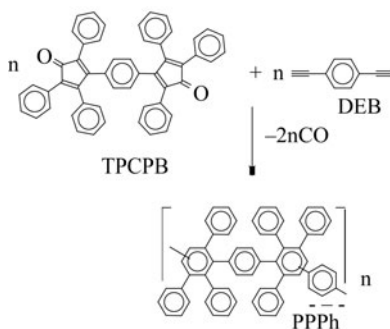
Introduction

Polyphenylenes (PPh) are polymers with alternating benzene ring along a chain. The peculiarities of the structure of these compounds are responsible for their unique properties [1], in particular, for high thermal resistance. The data of the calorimetric studies of poly-*p*-phenylene and poly-*m*-phenylene as well as the thermodynamic parameters of their synthesis by the catalytic dehydrogenation of benzene and the copolymerization of phenylacetylene with *p*-diethynylbenzene, respectively, in the range from 60 to 700 K were published earlier [2, 3].

The present work is concerned the calorimetric study of the thermodynamic properties of phenylated polyphenylene (PPPh) prepared by Diels-Alder cycloaddition of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (TPCPB) with *p*-diethynylbenzene (DEB) accompanied with the carbon monoxide elimination [4] and

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those of TPCPB not calorimetrically studied yet. The aim of this work was to measure the heat capacity C_p^0 between 6 and 340 K and the energies of combustion ΔU_{comb} of the above compounds at $T=298.15$ K, to calculate the thermodynamic functions $C_p^0(T)$, $H^0(T)-H^0(0)$, $S^0(T)-S^0(0)$, $G^0(T)-H^0(0)$ of PPPh and TPCPB from 0 to 340 K, the enthalpies of combustion ΔH_{comb}^0 and the standard thermodynamic characteristics of formation (ΔH_f^0 , ΔS_f^0 , ΔG_f^0) of the above compounds from the constituents at $T=298.15$ K, and from the data obtained in the present work and the corresponding literature data for DEB [3] and carbon monoxide [5, 6] to estimate the thermodynamic parameters of the synthesis reaction of PPPh {enthalpy $\Delta H^0(T)$, entropy $\Delta S^0(T)$, Gibbs function $\Delta G^0(T)$ } over the interval from 0 to 340 K. The reaction of PPPh synthesis is represented by the following scheme:



It should be noted that PPPh formed exhibits a remarkable specific feature, namely, a high solubility in common solvents such as toluene, methylene chloride, chloroform and others [4]. The reaction proceeds without thermodynamic hindrances in a high yield of PPPh and, nevertheless, it is interesting to obtain the thermodynamic characteristics for this reaction.

Experimental

Samples

1,4-Bis(triphenylcyclopentadienone-3-yl)benzene was prepared by the procedure published elsewhere [7] and phenylated polyphenylene was synthesized by the procedure described in detail previously [4]. The characterization of both objects was performed by ^1H and ^{13}C NMR spectroscopy (a Bruker AMX 500 instrument), mass spectrometry (a VG Trio 2000 (EI, 70 eV) device) and size-exclusion chromatography (SEC). It was found that $M_w=17.4\cdot 10^3$ g mol $^{-1}$, $M_w/M_n=2.0$. The elemental analysis results showed the coincidence of the CO_2 amount found in the combustion products with that calculated by the chemical formula of the compound within ± 0.2 mass% for TPCPB and ± 0.7 mass% for PPPh. Obviously, the polymer is amorphous [4].

Apparatus and methods

To measure the heat capacity, temperatures and enthalpies of physical transitions of TPCPB and PPPh, an adiabatic vacuum calorimeter designed and manufactured at the Research Institute of Physicotechnical and Radiotechnical Measurements (Moscow) was employed. The design and the operation procedure of the calorimeter are similar to those described elsewhere [8]. It is to be noted that all measurements were automated and monitored by a data acquisition system consisting of a computer, an analog-to-digital and a digital-to-analog converter, and a switch. The calorimetric ampoule is a thin-walled cylindrical vessel made from titanium with a volume of $1.5 \cdot 10^{-6} \text{ m}^3$. Its mass is $1.48 \cdot 10^{-3} \text{ kg}$. Its heat capacity gradually changed from $0.001632 \text{ J K}^{-1}$ at 5 K to 1.324 J K^{-1} at 350 K. The temperature was measured with an iron-rhodium resistance thermometer ($R=100 \Omega$) calibrated according to ITS-90 [9]. The difference in temperatures between the ampoule and the adiabatic shield was controlled by a four-junction copper-iron-chrome thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3} \text{ K}$ and that of the analog-to-digital converter $0.1 \mu\text{V}$. The speed of the data acquisition system was 10 measurements per second. The calorimeter was calibrated electrically. The reliability of the calorimeter operation was tested by measuring the heat capacity of standard substances such as special purity copper, synthetic sapphire and K-1 benzoic acid prepared at D.I. Mendeleev Research Institute of Metrology (St. Petersburg) and standard measures. As the calibration and test results showed, the experimental error of the heat capacity C_p^0 measurements for the substances at helium temperatures was about 2%; with rising temperature up to 40 K, it decreased down to 0.4% and was equal to 0.2% in the range from 40 to 350 K. Liquid helium and nitrogen were used as cooling agents, and special purity helium as a heat-exchange gas.

The combustion enthalpies of both compounds were measured in a V-08 calorimeter with an isothermal shield and a static bomb improved at the Chemistry Institute of the Nizhny Novgorod State University [10]. The calorimeter design, the calibration and test results were published earlier [11, 12]. The energetic equivalent of the calorimeter $W=75873 \text{ J } \Omega^{-1}$ was determined from the results of 10 experiments on the combustion of K-1 benzoic acid prepared at the Research Institute of Metrology of the State Standard of RF. The reliability of the calorimeter operation was tested by the combustion of standard succinic acid prepared also at the above Institute. Our measured value of the combustion enthalpy of standard succinic acid $\Delta H_{\text{comb}}^0 = -1492.1 \pm 0.3 \text{ kJ mol}^{-1}$ coincided with the value in the certificate $\Delta H_{\text{comb}}^0 = -1492.4 \pm 0.2 \text{ kJ mol}^{-1}$ within 0.017%.

Results and discussion

Heat capacity

The heat capacity of TPCPB was measured over the range from 6 to 340 K and of PPPh between 6.5 and 340 K. The sample masses located in the calorimetric ampoule were 4.119 and 2.179 g, respectively. For TPCPB 172 experimental C_p^0 values were obtained in two series of measurements and for PPPh 153 values of the heat capacity

were measured in two series. The heat capacity of TPCPB sample was from 25 to 50% and that of the sample of PPPh was from 25 to 30% of the total heat capacity of the calorimeter and the substance. In both cases, the above values decreased as temperature rose. The averaging of the experimental C_p^0 values was made by means of a computer. In the case of TPCPB, the root-mean-square deviation of the C_p^0 values from the corresponding smoothed curves $C_p^0=f(T)$ was $\pm 0.10\%$ between 6 and 100 K and $\pm 0.03\%$ in the range from 100 to 340 K; the deviation of the C_p^0 values of PPPh was equal to $\pm 0.07\%$ between 6 and 90 K and $\pm 0.03\%$ from 90 to 340 K.

The experimental C_p^0 values and the averaged curves $C_p^0=f(T)$ for TPCPB and PPPh are shown in Figs 1 and 2. It can be seen that the temperature dependences of the heat capacity for both compounds have no any peculiarities: the C_p^0 values gradually increase with rising temperature.

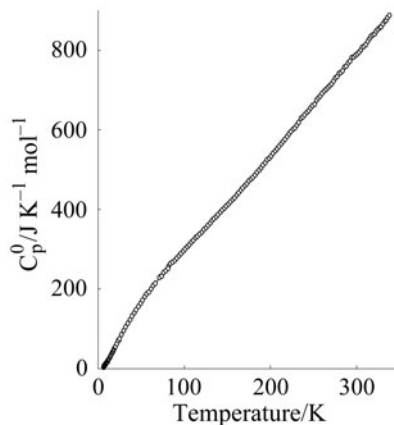


Fig. 1 Heat capacity of crystalline 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene

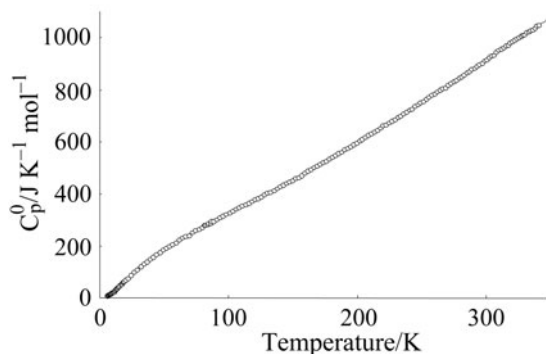


Fig. 2 Heat capacity of phenylated polyphenylene

For PPPh under study the estimation of the fractal dimension D [13], the most important value in the fractal variant of the Debye theory of the heat capacity for solid bodies [13, 14], seemed to be of interest. The D value allows the judgement about the

character of the solid body heterodynamics. The value of D can be obtained from the plot $\ln C_v$ vs. $\ln T$ that follows from the expression [13]:

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

where k is the Boltzmann constant, N is the number of atoms in a molecule or a repeating monomer unit of a polymer, $\gamma(D+1)$ is the γ -function, $\xi(D+1)$ is the ξ -function of Rimann and θ_{\max} is the maximum characteristic temperature. For a concrete solid body $3D(D+1)kN\gamma(D+1)\xi(D+1)=A$ is the constant and Eq. (2) can be described as follows:

$$\ln C_v = \ln A + D \ln(T/\theta_{\max}) \quad (3)$$

It can be assumed without a noticeable uncertainty that at $T < 50$ K for PPPh, like other monomeric and polymeric compounds [15], $C_p^0 = C_v$ and then, using the experimental data on the heat capacity, we obtain $D=1.8$ over the range from 8 to 15 K and $D=1.4$ between 25 and 50 K. It is known [16] that for chain solid bodies $D=1$, for layer ones $D=2$ and for bodies of a spatial structure $D=3$. Since for PPPh $D=1.4$ in the interval from 25 to 50 K and perhaps, at $T > 50$ K it may be concluded that PPPh is a layer-chain polymer. The increase in the D value up to 1.8 with lowering temperature from 25 to 8 K is quite natural due to the enhancement of the intermolecular interaction as temperature drops. At the lowest temperatures for solid bodies of any structure $D=3$ that corresponds to the Debye T^3 -law.

Thermodynamic functions

To calculate the thermodynamic functions the C_p^0 values of the substances under investigation were extrapolated from 7 to 0 K for TPCPB and from 5 to 0 K for PPPh using the Debye function for the heat capacity:

$$C_p^0 = nD(\Theta_D/T) \quad (4)$$

where D denotes the Debye function of the heat capacity, Θ and Θ_D are adjustable parameters. For TPCPB $n=7$, $\Theta_D=60.30$ K and for PPPh $n=5$ and $\Theta_D=39.41$ K. Equation (4) describes the experimental C_p^0 values for TPCPB in the range from 7 to 11 K with an uncertainty of $\pm 0.9\%$ and in the case of PPPh within about 0.5% between 5 and 8 K. It was assumed that at $T < 7$ K and $T < 5$ K, respectively, Eq. (4) reproduces the C_p^0 values of both compounds with an uncertainty not exceeding the error of the experimental C_p^0 values, i.e. within 2%.

The thermodynamic functions were calculated from the data of the relation $C_p^0 = f(T)$ (Tables 1 and 2) according to the procedure demonstrated earlier [17]. By our estimation, the uncertainty of the thermodynamic function values is from 2 to 0.5% at $T < 30$ K, 0.5–0.2% between 30 and 80 K and 0.2% in the range 80 to 340 K.

Table 1 Thermodynamic functions of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene ($M=690.84 \text{ g mol}^{-1}$)

T/K	$C_p^0/\text{J K}^{-1}\text{mol}^{-1}$	$H^0(T)-H^0(0)/\text{kJ mol}^{-1}$	$S^0(T)/\text{J K}^{-1}\text{mol}^{-1}$	$-[G^0(T)-H^0(0)]/\text{kJ mol}^{-1}$
5	2.568	0.0032	0.8604	0.00108
10	15.31	0.0446	6.088	0.01625
15	33.79	0.1662	15.69	0.06908
20	55.28	0.3891	28.28	0.1765
25	76.31	0.7184	42.95	0.3553
30	96.76	1.152	58.71	0.6098
35	115.9	1.684	75.07	0.9440
40	133.7	2.308	91.72	1.361
45	150.4	3.018	108.4	1.861
50	166.2	3.810	125.1	2.445
60	196.2	5.623	158.1	3.862
70	224.9	7.73	190.5	5.605
80	250.8	10.11	222.3	7.670
90	274.8	12.74	253.2	10.05
100	297.9	15.61	283.4	12.73
110	320.6	18.70	312.9	15.71
120	343.1	22.02	341.7	18.99
130	365.4	25.56	370.1	22.55
140	388.0	29.33	398.0	26.39
150	410.8	33.32	425.5	30.50
160	434.1	37.55	452.8	34.90
170	457.8	42.01	479.8	39.56
180	482.1	46.70	506.6	44.49
190	506.9	51.65	533.4	49.69
200	532.2	56.84	560.0	55.16
210	558.0	62.30	586.6	60.89
220	584.2	68.01	613.2	66.89
230	610.5	73.98	639.7	73.15
240	636.9	80.22	666.3	79.69
250	663.2	86.72	692.8	86.48
260	689.3	93.48	719.3	93.54
270	714.9	100.50	745.8	100.9
280	740.1	107.80	772.3	108.5
290	764.9	115.30	798.7	116.3

Table 1 Continued

$T/$ K	$C_p^0/$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^0(T)-H^0(0)/$ kJ mol^{-1}	$S^0(T)/$ $\text{J K}^{-1} \text{mol}^{-1}$	$-[G^0(T)-H^0(0)]/$ kJ mol^{-1}
298.15	784.9	121.6	820.1	122.9
300	789.4	123.1	825.0	124.4
310	813.9	131.1	851.3	132.8
320	838.7	139.4	877.5	141.5
330	864.4	147.9	903.7	150.4
340	891.8	156.6	929.9	159.5

Table 2 Thermodynamic functions of phenylated polyphenylene ($M=760.976 \text{ g mol}^{-1}$)

$T/$ K	$C_p^0/$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^0(T)-H^0(0)/$ kJ mol^{-1}	$S^0(T)-S^0(0)/$ $\text{J K}^{-1} \text{mol}^{-1}$	$-[G^0(T)-H^0(0)]/$ kJ mol^{-1}
5	6.0	0.0080	2.14	0.00274
10	23.8	0.0794	11.34	0.03398
15	46.3	0.2512	24.97	0.1234
20	70.1	0.5428	41.58	0.2888
25	92.63	0.9499	59.66	0.5415
30	114.3	1.468	78.49	0.8869
35	134.9	2.091	97.67	1.327
40	154.0	2.814	116.9	1.864
45	171.6	3.629	136.1	2.497
50	187.9	4.528	155.0	3.225
60	218.7	6.562	192.1	4.961
70	248.3	8.898	228.0	7.062
80	276.2	11.52	263.0	9.518
90	300.8	14.41	297.0	12.32
100	327.5	17.55	330.1	15.46
110	353.2	20.96	362.5	18.92
120	378.3	24.61	394.3	22.70
130	403.6	28.52	425.6	26.80
140	429.6	32.69	456.4	31.21
150	456.5	37.12	487.0	35.93
160	484.2	41.82	517.3	40.95
170	512.7	46.81	547.5	46.28
180	541.8	52.07	577.6	51.90
190	571.2	57.64	607.7	57.83
200	601.0	63.50	637.8	64.06

Table 2 Continued

$T/$ K	$C_p^0/$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^0(T)-H^0(0)/$ kJ mol^{-1}	$S^0(T)-S^0(0)/$ $\text{J K}^{-1} \text{mol}^{-1}$	$-[G^0(T)-H^0(0)]/$ kJ mol^{-1}
210	631.0	69.66	667.8	70.58
220	661.2	76.12	697.9	77.41
230	691.7	82.89	727.9	84.54
240	722.5	89.96	758.0	91.97
250	753.8	97.34	788.1	99.7
260	785.6	105.0	818.3	107.7
270	817.9	113.1	848.6	116.1
280	850.8	121.4	878.9	124.7
290	884.2	130.1	909.4	133.6
298.15	911.5	137.4	934.2	141.2
300	917.8	139.1	939.9	142.9
310	951.4	148.4	970.5	152.4
320	984.5	158.1	1001.0	162.3
330	1016.0	168.1	1032.0	172.5
340	1046.0	178.4	1063.0	182.9

Thermodynamic characteristics

The experimental data on the determination of the combustion energies of TPCPB and PPPh are given in Tables 3 and 4. The following symbols were used in these Tables: $m(\text{TPCPB})$, $m(\text{PPPh})$, $m(\text{par})$, $m(\text{pe})$ and $m(\text{cot.thr.})$ are the masses of the samples studied, auxiliary substances such as paraffin (par), polyethylene (pe) and a cotton thread (cot.thr.), respectively; W is the energetic equivalent of the calorimeter; $\Delta R + \Delta(\Delta R)$ is the change in the resistance of the platinum thermometer corrected for the heat exchange; ΔU_{comb} is the total energy amount released on burning of the substances in experiments carried out in a calorimetric bomb; $\Delta U_{\text{comb}}(\text{TPCPB})$, $\Delta U_{\text{comb}}(\text{PPPh})$, $\Delta U_{\text{comb}}(\text{par})$, $\Delta U_{\text{comb}}(\text{pe})$, $\Delta U_{\text{comb}}(\text{cot.thr.})$, $\Delta U_{\text{f}}(\text{HNO}_3)$ are the energy amounts liberated in experiments under the same physical conditions on the combustion of the samples studied, paraffin, polyethylene and the cotton thread (used to fire the substance) and the energy of formation of nitric acid solution, respectively; $m(\text{CO}_2)_{\text{exp}}/m(\text{CO}_2)_{\text{calc}} \times 100\%$ is the ratio of the amounts of CO_2 found in the combustion products of the monomer and the polymer to the amounts of CO_2 calculated from their chemical formulae; $\Delta U_{\text{comb}}(\text{TPCPB})$ and $\Delta U_{\text{comb}}(\text{PPPh})$ are the molar energies of combustion carried out in a calorimetric bomb. In all experiments, complete combustion of the main and auxiliary substances occurred. In the calculation of the $\Delta U_{\text{comb}}(\text{TPCPB})$ and $\Delta U_{\text{comb}}(\text{PPPh})$ values, the common thermochemical corrections for the combustion of paraffin, polyethylene, the cotton thread and for the formation of HNO_3 solution were made. The val-

Table 3 Experimental data on the energy of combustion of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene ($C_{52}H_{34}O_2$, ($M=690.84 \text{ g mol}^{-1}$))

Values ^a	Exp. No. 1	Exp. No. 2	Exp. No. 3	Exp. No. 4	Exp. No. 5	Exp. No. 6
$m(\text{TPCPB})/\text{g}$	0.1235	0.0973	0.0959	0.0896	0.1221	0.1322
$m(\text{par.})/\text{g}$	0.3981	0.3689	0.3153	0.3135	0.3938	0.3866
$m(\text{cot.thr.})/\text{g}$	0.0028	0.0023	0.0028	0.0023	0.0020	0.0023
$W/J \Omega^{-1}$	75873	75873	75873	75873	75873	75873
$\Delta R + \Delta(\Delta R)/\Omega$	0.307566	0.276396	0.241265	0.238356	0.303903	0.304466
$-\Delta U_{\text{comb}}/J$	23323.3	20971.0	18410.4	18084.9	23058.0	23100.7
$-\Delta U_{\text{comb}}(\text{par.})/J$	18608.3	17243.5	14740.6	14654.0	18405.4	18070.7
$-\Delta U_{\text{comb}}(\text{cot.thr.})/J$	46.86	38.49	46.86	38.49	33.47	38.49
$-\Delta U_f(\text{HNO}_3)/J$	20.08	21.76	10.46	18.41	22.59	17.99
$M(\text{CO}_2)_{\text{exp}}/m(\text{CO}_2)_{\text{calc}} \times 100\%$	99.87	—	99.93	99.89	99.89	100.2
$-\Delta U_{\text{comb}}(\text{TPCPB})/J \text{ g}^{-1b}$	37636.1	37677.7	37669.1	37656.0	37645.7	37622.5

^aThe symbols are given in the text^b $-\Delta U_{\text{comb}}(\text{TPCPB}) = 37651.1 \pm 48.4 \text{ J g}^{-1} = 30088.8 \pm 9.6 \text{ kJ mol}^{-1}$; $-\Delta U_{\text{comb}}^0 = 25992.7 \pm 9.6 \text{ kJ mol}^{-1}$

Table 4 Experimental data on the energy of combustion of phenylated polyphenylene ($C_{60}H_{40}$, $M=760.976 \text{ g mol}^{-1}$)

Values ^a	Exp. No. 1	Exp. No. 2	Exp. No. 3	Exp. No. 4	Exp. No. 5	Exp. No. 6
$m(\text{PPPh})/\text{g}$	0.0907	0.1122	0.0851	0.1306	0.1379	0.1462
$m(\text{pe})/\text{g}$	0.2257	0.2423	0.3102	0.2848	0.2222	0.2477
$m(\text{cot.thr.})/\text{g}$	0.0023	0.0020	0.0027	0.0022	0.0021	0.0021
$W/J \Omega^{-1}$	75873	75873	75873	75873	75873	75873
$\Delta R + \Delta(\Delta R)/\Omega$	0.185474	0.206481	0.234462	0.242265	0.207603	0.227626
$-\Delta U_{\text{comb}}/\text{J}$	14072.5	15666.1	17789.1	18381.1	15751.5	17270.7
$-\Delta U_{\text{comb}}(\text{pe})/\text{J}$	10477.1	11247.8	14400.1	13221.0	10314.8	11498.5
$-\Delta U_{\text{comb}}(\text{cot.thr.})/\text{J}$	38.49	33.47	46.02	36.82	35.15	35.15
$-\Delta U_f(\text{HNO}_3)/\text{J}$	16.32	18.83	18.83	21.34	13.81	22.59
$M(\text{CO}_2)_{\text{exp}}/m(\text{CO}_2)_{\text{calc}} \times 100\%$	100.1	—	99.73	100.3	100.7	99.29
$-\Delta U_{\text{comb}}(\text{PPPh})/\text{J g}^{-1\text{b}}$	39035.0	38925.4	39067.7	39070.6	39073.5	39085.7

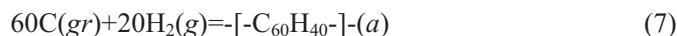
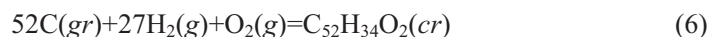
^aThe symbols are given in the text^b $-\Delta U_{\text{comb}}(\text{PPPh}) = 39043.0 \pm 48.9 \text{ J g}^{-1} = 29710.8 \pm 37.2 \text{ kJ mol}^{-1}$

ues of ΔU_{comb} and the combustion energy at standard pressure ΔU_{comb}^0 are given with a double root-mean-square error estimated by means of Eq. (5):

$$\delta=2(\Sigma\chi^2/n(n-1))^{1/2} \quad (5)$$

where χ is the deviation of each value from the average and n is the number of experiments. The ΔU_{comb}^0 value was calculated on the basis of the average magnitudes of the combustion energies ΔU_{comb} of TPCPB and PPPh.

The enthalpies of combustion, enthalpies, entropies and Gibbs functions of formation of TPCPB and PPPh are listed in Table 5. The value of ΔH_{comb}^0 was evaluated from the combustion energy at standard pressure ΔU_{comb}^0 as described in [11]. While calculating the enthalpy of formation ΔH_f^0 , the standard enthalpies of formation of liquid water and gaseous carbon dioxide cited in work [18] were used. The entropy of formation was estimated from the values of the entropies of TPCPB and PPPh (Tables 1 and 2) and literature data [18] on the entropies of gaseous hydrogen and oxygen as well as crystalline carbon in the form of graphite. The values of zero entropies $S^0(0)$ for amorphous PPPh were neglected. The Gibbs function of formation was calculated from the values of ΔH_f^0 and ΔS_f^0 . All the values given in Table 5 conform to reactions (6) and (7):



The physical states of the reagents are given in brackets (*cr* – crystalline, *g* – gaseous, *a* – amorphous, *gr* – graphite).

Table 5 Enthalpies of combustion and thermodynamic parameters of formation of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (TPCPB) and phenylated polyphenylene(PPPh); $T=298.15$ K, $p=101.325$ kPa

Compound	$-\Delta H_{\text{comb}}^0/\text{kJ mol}^{-1}$	$\Delta H_f^0/\text{kJ mol}^{-1}$	$-\Delta S_f^0/\text{J K}^{-1} \text{mol}^{-1}$	$-\Delta G_f^0/\text{kJ mol}^{-1}$	$\lg K_f^0$
TPCPB	26011.1±9.6	689.5±9.6	1902.3±1.8	1256±9.8	507
PPPh	29747.8±37.2	387.7±37.2	2020.6±2.0	989±37	399

Thermodynamic characteristics of synthesis reaction of phenylated polyphenylene

The enthalpy ΔH_r^0 , entropy ΔS_r^0 and the standard Gibbs function ΔG_r^0 of PPPh synthesis are given in Table 6. The reaction scheme is illustrated above. The enthalpy of reaction at $T=298.15$ K ($\Delta H_r^0=-985.6$ kJ mol⁻¹) was calculated from the enthalpies of formation of reagents TPCPB and PPPh obtained in the present work, *p*-diethynylbenzene and carbon oxide taken from [3, 18], respectively. At other temperatures ΔH_r^0 was calculated using Kirchhoff's expression. The temperature dependences of heat capacities, enthalpies of physical transformations of the reagents are taken for DEB from [3], carbon oxide from works [5, 6], (they are shown in Figs 3 and 4) and for TPCPB and PPPh they are listed in Tables 1 and 2 of the present paper. The en-

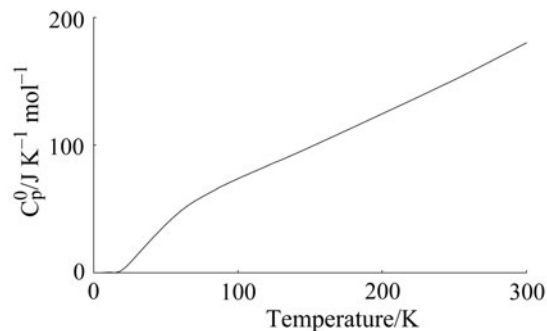


Fig. 3 Heat capacity of crystalline *p*-diethynylbenzene [3]

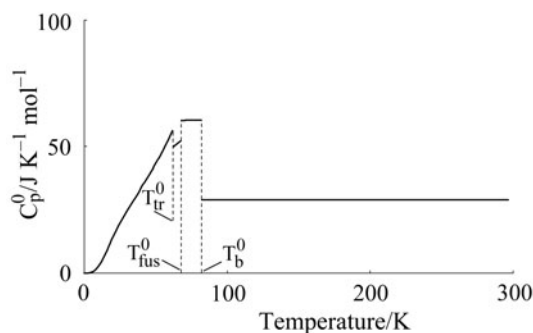


Fig. 4 Heat capacity of carbon monoxide [5, 6]

entropy of reaction ΔS_r^0 was evaluated on the basis of absolute values of the entropies for the reagents. The absolute entropies of DEB and carbon oxide were taken from works [3, 5, 6] and for TPCPB and PPPh those are given in Tables 1 and 2. The $S^0(0)$ value of the polymer in an amorphous state as in the calculation of its ΔS_r^0 was ignored. The standard Gibbs functions ΔG_r^0 were estimated from the ΔH_r^0 and ΔS_r^0 values at the corresponding temperatures. It is seen that the values of the standard Gibbs function of reaction are everywhere negative and judging by its absolute magnitudes, one may arrive at a virtually total shift of the equilibrium towards the formation of the reaction products. The entropy of reaction is always positive that is, certainly, caused by the liberation of two moles of carbon monoxide. The entropy of their formation substantially exceeds the decrease of entropy which accompanies the formation of PPPh from TPCPB and DEB. The enthalpy of reaction is negative, and it is obvious that it accounts for the main part of the Gibbs function. The contribution of the entropy factor to the value of ΔG_r^0 is relatively small. Since $\Delta H_r^0 < 0$ and $\Delta S_r^0 > 0$ it is clear that with rising temperature of the reaction the ΔG_r^0 value decreases too. This implies that the process of PPPh synthesis has neither upper nor lower limiting temperature and that PPPh formed is thermodynamically stable relative to depolycondensation [17]. Thus, in the present work a complex thermodynamic analysis of the new promising polymer PPPh, the initial comonomer TPCPB and the synthesis reaction of the above polymer was made for the first time from the precision calorimetry data in

the range 0 to 340 K at standard pressure. The results obtained can be used in the design of the technology of PPPh synthesis and its optimization, the choice of physico-chemical conditions of its practical application and in a wide variety of thermodynamic calculations of reactions involving PPPh.

Table 6 Thermodynamic characteristics of synthesis reaction of phenylated polyphenylene
 $C_{52}H_{34}O_2 + C_{10}H_6 \rightarrow C_{60}H_{40} + 2CO$; $p=101.325$ kPa

T/K	Physical states of reagents	$-\Delta H_r^0/kJ\ mol^{-1}$	$\Delta S_r^0/J\ K^{-1}\ mol^{-1}$	$-\Delta G_r^0/kJ\ mol^{-1}$
0	<i>cr, cr; p.cr.; crII</i>	1006	0	1006
100	<i>cr, cr; p.cr; crII</i>	986	309	1017
200	<i>cr, cr; p.cr, g</i>	986	314	1048
298.15	<i>cr, cr; p.cr, g</i>	985	315	1079
340	<i>cr, cr; p.cr, g</i>	971	319	1079

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The authors thank the Russian Foundation of Basic Researches for the financial support of the work (grants No 99-03-33352, No 01-03-06285 and No 00-03-40136).

The authors wish to thank T. A. Bykova for the participation in the measurements of the heat capacity of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene.

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