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Thermodynamics of polyacenaphthylene between 0 and 340 K

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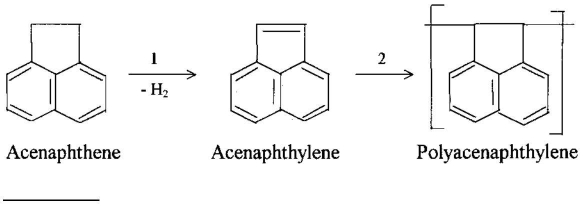
Abstract

The heat capacity C_p^0 of glassy polyacenaphthylene has been determined using an adiabatic vacuum calorimeter between 6 and 338 K within about 0.2%. From the experimental data the thermodynamic functions $C_p^0(T)$, $H^0(T)-H^0(0)$, $S^0(T)-S^0(0)$, $G^0(T)-H^0(0)$ have been calculated over the range from 0 to 340 K. From literature data on the enthalpy of formation $\Delta_f H^0$ and the absolute entropy $S^0(T)$ of the polymer obtained in the present work, the thermochemical characteristics for reaction of formation (entropy $\Delta_f S^0$, Gibbs energy $\Delta_f G^0$ and logarithm of thermodynamic equilibrium constant lg K_f^0) of polyacenaphthylene in a glassy state from simple substances at T=298.15 K and standard pressure have been estimated. The results and the proper data for acenaphthylene have been used to calculate the thermodynamic quantities associated with polymerization of acenaphthylene $\Delta_{pol}H^0(T)$, $\Delta_{pol}S^0(T)$, $\Delta_{pol}G^0(T)$ into polyacenaphthylene from 0 to 340 K and of dehydrogenation of acenaphthene $\Delta_{dehydr}H^0(T)$, $\Delta_{dehydr}S^0(T)$, $\Delta_{dehydr}G^0(T)$ to acenaphthylene in the range from 0 to 350 K. The ceiling temperature T_{ceil}^0 of the polymerization process of acenaphthylene has been estimated.

Keywords: Polyacenaphthylene; Thermodynamic functions; Enthalpy; Entropy; Gibbs energy

1. Introduction

Polyacenaphthylene (PA) and special copolymers of acenaphthylene with various monomers are widely used in practice since they show a wide variety of important technical properties [1–3]. The polymer is prepared by the polymerization of acenaphthylene which in turn is formed by dehydrogenation of acenaphthene. Both processes can be represented by the following scheme:



The thermodynamic parameters of acenaphthene dehydrogenation with the formation of acenaphthylene (process 1) and acenaphthylene polymerization (process 2) dependent on physical states of reagents and temperature are not yet known. Recently Cheda and Westrum [4] reported the thermodynamic characteristics of hydrogenation process of acenaphthylene to acenaphthene at T=298.15 K and p=101.325 kPa (acenaphthene and acenaphthylene are crystalline and hydrogen is gaseous). The calculations of the characteristics were made on the base of precise measurements performed in [4,5]. The results of direct calorimetric determinations for polymerization enthalpy of acenaphthene to polyacenaphthylene are given elsewhere [6–10]. Joshi and Zwolinski [11] measured the combustion energy of the polymer and calculated its enthalpies of combustion and formation at T=298.15 K and standard pressure. Any

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other data on the thermodynamic parameters of processes 1 and 2 as well as the thermodynamic properties of polyacenaphthylene have not been published. The goal of the present work is to study the temperature dependence of heat capacity C_p^0 of polyacenaphthylene in the range from 6 to 340 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 the polymer from 0 to 340 K. The results enable us to estimate the thermochemical parameters of formation $\Delta_f S^0$, $\Delta_f G^0$ and $\lg K_f^0$ of polyacenaphthylene from the constituent simple substances in their standard states at T=298.15 K and p=101.325 kPa and to evaluate the thermodynamic characteristics for the bulk polymerization reaction $\Delta_{pol}H^0(T)$, $\Delta_{pol}S^0(T)$, and $\Delta_{pol}G^0(T)$ of acenaphthylene to polyacenaphthylene over the range from 0 to 340 K and of acenaphthene dehydrogenation $\Delta_{dehydr}H^0(T)$, $\Delta_{dehydr}S^0(T)$, $\Delta_{dehydr}G^0(T)$ with the formation of acenaphthylene between 0 and 350 K at standard pressure.

2. Experimental

2.1. Sample

To prepare the polymer sample, the commercial acenaphthylene of Aldrich which is a mixture of 85 mass% acenaphthylene and 15 mass% acenaphthene was used. It was dissolved in toluene and a solution with 24 mass% content of acenaphthylene was formed. Benzoyl peroxide in the amount of 0.3 mass% of the monomer weight was added in the solution and the polymerization was conducted at 358 K till 60% conversion of the monomer to the polymer as determined gravimetrically. Polyacenaphthylene was subjected to fivefold reprecipitation with methanol from its 3–4% solutions in benzene. The polymer was dried under vacuum at 303 K till a constant mass. The molecular weight of polyacenaphthylene was determined by viscosimetry method in an Ubbelohde viscosimeter (the constants in Mark-Coon-Hovink equation were K=9.66·10^4, α=0.87, tetrahydrofuran, T=293 K [2]). The intrinsic viscosity was found to be $[\eta]$=12.3 cm^3 g^{-1} and it corresponds to the weight-average molecular weight M_w=5.2·10^4. Elementary analysis indicated (in mass%): C 94.61, H 4.54 (theoretically C 94.70, H 5.30). From X-ray structure analysis data (a Dron-3 device) the polymer sample was completely amorphous.

2.2. Apparatus and methods

To measure the heat capacity in the range from 5 to 340 K, an automatic thermophysical device TAU-1 – an adiabatic vacuum calorimeter designed and manufactured at the Research Institute of Physicotechnical and Radiotechnical Measurements of the State Standards of Russian Federation (Moscow) – was employed. The calorimeter design and the operation procedure were described earlier [12,13]. All measurements were automated and monitored by a computer-measuring system consisting of a computer, an analog-to-digital and a digital-to-analog converter and a switch. The calorimetric ampoule is made of a thin-walled cylindrical vessel from stainless steel of 1.5·10^{-6} m^3 in internal volume. Its weight is 2.06· 10^{-3} kg. Temperature was measured with an iron–rhodium resistance thermometer (resistance $R_0 \cong 100\ \Omega$). The difference in temperatures between the ampoule and an adiabatic shield was controlled by a four-junction copper–iron–chromel thermocouple. The sensitivity of a thermometric circuit was 10^{-3} K, of the analog-to-digital converter 0.1 μV. The speed of the computer-measuring system was 10 measurements per second. The calorimeter was calibrated electrically. The heat capacity C_{cal} of an empty calorimetric ampoule changed from 0.0045 J K^{-1} at 5 K to 1.465 J K^{-1} at 340 K. The root mean square deviation of the experimental data of C_{cal} from the smoothed curve C_{cal}=(T) did not exceed 0.16%. The reliability of the calorimeter operation was tested by measuring the heat capacity of special-purity copper (OSCH-11-4), standard synthetic sapphire and K-2 benzoic acid prepared at the D.I. Mendeleyev Research Institute of Metrology (St. Petersburg) in the range from 5 to 340 K. The analysis of the results showed that the uncertainty of measurement of the heat capacity for the substances at helium temperatures was about 2%, with increasing temperature up to 40 K it decreased to 0.4% and it was approximately 0.2% above 40 K. As cooling agents, liquid helium and nitrogen were used and as a heat-exchange gas, special-purity helium was taken.

Table 1
Experimental data on heat capacity at constant pressure of polyacenaphthylene (per mole of repeating monomer unit in polymer; M_m=152.195 g mol^{-1})

T (K)	C_p^0 (J K^{-1} mol^{-1})
Series 1	
6.78	2.045
7.13	2.233
7.61	2.543
8.26	3.001
9.08	3.560
10.04	4.310
11.09	5.085
12.32	6.158
13.69	7.227
15.13	8.457
17.18	9.992
18.48	11.07
19.95	12.30
21.58	13.59
23.31	14.96
25.13	16.32
27.05	17.65
29.14	18.81
33.85	21.85
35.67	23.04
37.34	24.06
38.87	24.87
40.30	25.71
Series 2	
41.51	26.56
45.05	28.51
46.08	28.99
47.73	30.03
49.46	30.99
51.41	32.12
53.63	33.45
56.02	34.69
58.46	36.09
60.84	37.32
63.23	38.68
65.88	39.82
68.62	41.09
71.22	42.12
73.91	43.63
76.90	45.09
79.95	46.12
83.41	47.77
86.41	49.03
92.19	51.57
94.94	52.62
Series 3	
96.23	52.82
98.19	53.50
102.37	55.10
104.68	56.21
107.10	56.98
109.55	58.33
112.08	59.51
114.74	60.78
117.48	61.93
120.30	63.47
123.20	65.05
Series 4	
125.87	66.47
128.50	67.93
131.21	69.08
134.03	70.66
Series 5	
143.37	75.33
148.61	78.60
Series 6	
137.15	72.37
139.43	73.61
141.95	74.69
144.60	76.17
147.26	77.88
150.01	79.14
152.81	81.00
155.62	82.31
158.46	83.98
161.26	85.53
164.04	87.54
Series 7	
149.65	78.93
151.91	80.41
162.82	86.86
Series 8	
162.98	87.02
165.74	88.38
168.47	90.20
171.19	91.78
173.89	93.43
176.57	95.30
179.23	96.99
Series 9	
213.34	121.8
215.49	123.6
220.93	127.4
224.03	129.3
226.90	131.4
229.87	133.1

Table 1 (*continued*)

T (K)	C_p^0 (J K^{-1} mol^{-1})
232.84	134.9
Series 10	
226.86	131.3
230.60	134.0
232.37	134.7
Series 11	
236.73	137.4
239.33	139.2
242.13	141.2
244.98	142.7
250.68	146.6
253.54	148.5
256.41	150.0
Series 12	
249.74	146.1
254.94	149.5
259.78	152.1
Series 13	
262.18	154.0
267.00	157.0
269.90	158.7
275.88	161.8
278.69	163.1
281.62	164.6
284.60	166.3
287.67	168.4
290.73	170.4
Series 14	
291.29	170.5
293.86	172.0
299.92	174.6
305.01	178.1
307.20	179.4
Series 15	
306.19	179.5
309.19	182.2
312.43	183.5
315.77	185.8
319.23	187.2
322.73	190.3
329.77	197.3
338.31	205.7
Series 16	
180.66	98.33
184.90	101.1
187.11	102.6
189.75	104.7
192.43	106.7
195.10	108.8
197.79	111.0
200.51	112.9
203.21	115.1
205.91	116.5
208.58	118.3
211.25	120.2
Series 17	
315.26	185.2
318.36	187.6
323.14	189.6
326.56	194.2
333.55	200.6
336.75	204.4

2.3. Experimental measurement data

The heat capacity C_p^0 of polyacenaphthylene was measured in the range from 6 to 338 K. The mass of the polymer sample located in the calorimetric ampoule was 2.8870 g. Its heat capacity was 12–35% of the total heat capacity of the calorimetric ampoule and the substance. 142 experimental points of C_p^0 were obtained in 17 series, the numbers of which denote the sequence of the heat capacity measurements (Table 1). The averaging of the experimental points of C_p^0 was made on a computer. The root mean square deviation of the C_p^0 points from the corresponding smoothed curve C_p^0=(T) was 0.36% in the range from 5 to 90 K and 0.13% between 90 and 338 K.

3. Results and discussion

3.1. Heat capacity

Fig. 1 shows the temperature dependence of heat capacity $C_p^0 = (T)$ of polyacenaphthylene. Its distinction is the absence of a linear relation C_p^0 vs. T common for chain polymers over the range from (50–60) K to a glass transition temperature T_g^0 [14]. The above relationship is observed only in the intervals (40–80) and (240–338) K (sections BC and DE, curve C_p^0 vs. T, Fig. 1). In the range from 80 to 240 K

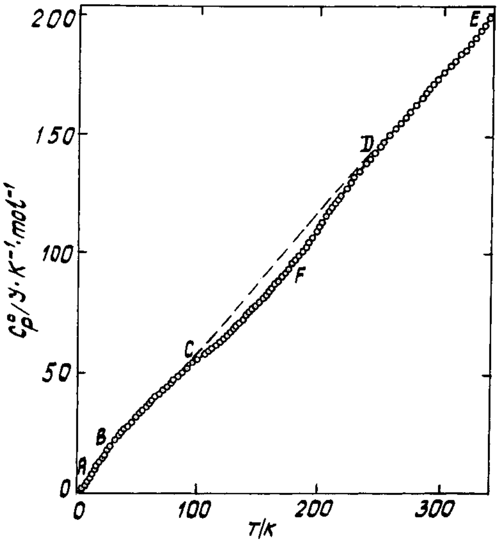

Fig. 1. Heat capacity of glassy polyacenaphthylene: CFD – the region of anomalous relation C_p^0 vs. T, CD – the normal trend of temperature dependence of heat capacity (a dashed line).

(section CD) a gradual negative deviation of C_p^0 from a normal trend of the heat capacity of the polymer (the relation C_p^0 vs. T illustrated with a dashed curve in Fig. 1) takes place. The maximum deviation of the C_p^0 values measured from the normal expected values is about 10 J K^{-1} mol^{-1} at T=160 K, viz. at a temperature which lies in the middle of the C_p^0 anomaly region. The above deviation is approximately 11% of the normal value of the polymer heat capacity at this temperature. The anomaly of the heat capacity was reproduced every time on measuring C_p^0 of the sample heated up to T>240 K and then cooled down to T<240 K. The thermodynamic parameters of the anomaly were estimated to be $\Delta H^0=-1.1$ kJ mol^{-1}, $\Delta S^0=-7.3$ J K^{-1} mol^{-1}. The enthalpy was evaluated as the difference in integrals over the curve $C_p^0 = (T)$ on sections CD of real (a solid line) and expected (a dashed line) heat capacities of polyacenaphthylene; the entropy was determined similarly, but the integration over the heat capacity curves in the same temperature interval was made over d ln T. The nature of the anomalous heat capacity is not clear.

In the range from 40 to 60 K the heat capacity of the polymer is well described by Tarasov's two-parameter function of heat capacity [15] for interacting polymer chains:

$$C_{1,3} = D_1(\Theta_1/T) - (\Theta_3/\Theta_1)[D_1(\Theta_3/T) - D_3(\Theta_3/T)], \qquad (1)$$

where $C_{1,3}$ is the heat capacity of interacting chain structures, D_1 the symbol of Tarasov's function of heat capacity, D_3 the Debye function of heat capacity, Θ_1 and Θ_3 are the characteristic Tarasov and Debye temperatures, respectively. The ratio Θ_3/Θ_1 is the characteristic of the interchain interaction and changes between 0 and unity. $\Theta_3/\Theta_1=0$ corresponds to hypothetical chain polymers which have no interchain interaction and $\Theta_3/\Theta_1=1$ to the polymers whose energies of interchain and intrachain interaction are similar. For polyacenaphthylene $\Theta_1=305.44$ K, $\Theta_3=91.63$ K and the ratio Θ_3/Θ_1 is equal to 0.3 that indicates a substantial interchain interaction. According to Tarasov, at low temperatures ($T\rightarrow0$) Eq. (1) changes into the following equation:

$$C_{1,3(T\rightarrow0)} = (\Theta_3/\Theta_1)12/5\pi^4 R(T/\Theta_3)^3, \qquad (2)$$

where Θ_1 and Θ_3 are the same as in Eq. (1), R is the universal gas constant and $\pi=3.14$.

By Tarasov's estimates a cubic dependence of the heat capacity of interacting chains has to be observed over the temperature interval from $0.1\Theta_3$ to $T=0$. Taking into account the numerical magnitude of Θ_3, the relation C_p^0 vs. T^3 is to take place between 0 and 9 K for polyacenaphthylene. In reality, from the experimental C_p^0 data of polyacenaphthylene Eq. (3) reproducing the experimental points of C_p^0 in the range from 7 to 13 K within ±1% was chosen by us:

$$C_p^0 = nD(\Theta_D/T), \qquad (3)$$

where D represents the Debye function, n=2 and $\Theta_D=60.92$ K are adjustable parameters. This means that in the above temperature interval the relation C_p^0 vs. T^3 is observed that is in good agreement with theoretical conclusions of Tarasov. It should be noted that the calculation of C_p^0 by Eq. (2) gives low values. Eq. (1) is often used for the estimation of skeleton contributions to the heat capacity of chain polymers [15]. With the chosen parameters Θ_1 and Θ_3, it may be taken for the evaluation of the contribution from the skeleton macromolecule oscillations to the heat capacity of polyacenaphthylene.

Table 2
Thermodynamic functions of polyacenaphthylene in glassy state (per mole of repeating monomer unit; M_{m}=152.195 g mol^{-1})

T (K)	C_p^0 (J K^{-1} mol^{-1})	$H^0(T)-H^0(0)$ (kJ mol^{-1})	$S^0(T)-S^0(0)$ (J K^{-1} mol^{-1})	$-[G^0(T)-H^0(0)]$ (kJ mol^{-1})
5	0.7120	0.0009	0.243	0.0003
10	4.280	0.0125	1.70	0.0045
15	8.330	0.0443	4.22	0.0190
20	12.32	0.0956	7.15	0.047
25	16.19	0.1671	10.3	0.091
30	19.50	0.2565	13.6	0.151
35	22.59	0.3619	16.8	0.227
40	25.57	0.4823	20.0	0.319
45	28.49	0.6174	23.2	0.427
50	31.32	0.7669	26.4	0.551
60	36.88	1.108	32.6	0.845
70	41.77	1.502	38.6	1.20
80	46.25	1.942	44.5	1.62
90	50.51	2.426	50.2	2.09
100	54.35	2.951	55.7	2.62
110	58.51	3.514	61.1	3.20
120	63.31	4.123	66.4	3.84
130	68.63	4.783	71.7	4.53
140	73.72	5.495	76.9	5.27
150	79.31	6.260	82.2	6.07
160	84.95	7.081	87.5	6.92
170	91.11	7.961	92.8	7.82
180	97.69	8.904	98.2	8.77
190	104.8	9.916	104	9.78
200	112.6	11.00	109	10.9
210	119.5	12.16	115	12.0
220	126.6	13.39	121	13.2
230	133.3	14.69	126	14.4
240	139.6	16.06	132	15.7
250	146.1	17.49	138	17.0
260	152.5	18.98	144	18.4
270	158.7	20.54	150	19.9
280	164.0	22.15	156	21.4
290	169.5	23.82	162	23.0
298.15	174.2	25.52	166	24.0
300	175.4	25.54	167	24.7
310	181.4	27.32	173	26.4
320	188.5	29.17	179	28.1
330	197.0	31.10	185	29.95
340	206.6	33.12	191	31.8

3.2. Thermodynamic functions

To calculate the thermodynamic functions (Table 2) – enthalpy $H^0(T)-H^0(0)$, entropy $S^0(T)-S^0(0)$ and Gibbs energy $G^0(T)-H^0(0)$ – the heat capacity of polyacenaphthylene was extrapolated from 6 to 0 K by means of Eq. (3). On calculating the functions, we assumed that the equation reproduces the heat capacity in the interval 0–6 K with the same accuracy as that in the range from 7 to 13 K (within about ±1%). The calculations were made by using known expressions:

$$H^0(T) - H^0(0) = \int_0^T C_p^0(T)\,\mathrm{d}T, \qquad (4)$$

Table 3
Enthalpy of combustion $\Delta_c H^0$ and enthalpy $\Delta_f H^0$, entropy $\Delta_f S^0$ and Gibbs energy of formation $\Delta_f G^0$ of polyacenaphthylene in glassy state at T=298.15 K and p=101.325 kPa

$-\Delta_c H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})	$-\Delta_f S^0$ (J K^{-1} mol^{-1})	$\Delta_f G^0$ (kJ mol^{-1})	$\lg K_f^0$
5978.9±1.6 [10]	113.5±1.6 [10]	408±1.5	235±2	−41.2

$$S^0(T) - S^0(0) = \int_0^T C_p^0(T)\,\mathrm{d}\ln T, \qquad (5)$$

$$G^0(T) - H^0(0) = [H^0(T) - H^0(0)] - T[S^0(T) - S^0(0)], \qquad (6)$$

where C_p^0 is the heat capacity for polyacenaphthylene.

3.3. Thermochemical parameters of formation

In [11] the enthalpies of combustion $\Delta_{comb}H^0$ and formation $\Delta_f H^0$ were reported for polyacenaphthylene in the glassy state at T=298.15 K and standard pressure. By using the absolute magnitude of the entropy of the polymer S^0 (298.15 K)=183 J K^{-1} mol^{-1} obtained in the given work and $\Delta_f H^0$ from [11], we calculated the entropy $\Delta_f S^0$ and the Gibbs function $\Delta_f G^0$ of formation of polyacenaphthylene from simple substances in their standard state (Table 3). The values of the quantities given are related to the process

$$n[12\mathrm{C}\ (\mathrm{gr}) + 4\mathrm{H}_2\ (\mathrm{g})] \rightarrow (\mathrm{C}_{12}\mathrm{H}_8)_n\ (\mathrm{gl})$$

In brackets the physical states of the reagents are given: gr is carbon in the form of graphite, g is gaseous and gl is glassy. The entropies of graphite and gaseous hydrogen are taken from the work of Glushko [16]. While estimating the absolute entropy of glassy polyacenaphthylene, we used the value of S^0 (298.15 K)$-S^0(0)$ (Table 2) and the zero (residual) entropy of the glassy polymer $S_{gl}^0(0) \cong 17$ J K^{-1} mol^{-1} calculated from the inference in [14].

3.4. Thermodynamic parameters of reactions resulting in polyacenaphthylene (processes 1 and 2)

Dehydrogenation of acenaphthene. The thermodynamic characteristics of process 1 are listed in Table 4. The enthalpy of dehydrogenation reaction at 298.15 K and standard pressure was calculated from the enthalpies of formation of the reagents. The enthalpies of formation of acenaphthene and acenaphthylene were taken from the work of Boyd et al. [5]. At other temperatures the $\Delta_{dehydr}H^0$ value was estimated by the formula of Kirchhoff [17]. The entropy of reaction $\Delta_{dehydr}S^0$ was determined from the absolute values of entropies of acenaphthene and acenaphthylene cited in [4] and of hydrogen [18] at the corresponding temperatures. The change in the standard Gibbs energy of reaction $\Delta_{dehydr}G^0$ was calculated from the enthalpies and entropies of dehydrogenation by using the equation

$$\Delta_{dehydr}G^0 = \Delta_{dehydr}H^0 - T\Delta_{dehydr}S^0. \qquad (7)$$

It was found that the standard Gibbs energy of reaction is positive in the whole temperature interval studied. This implies that only a small fraction of acenaphthylene is present in the equilibrium reaction mixture, judging by the numerical value of the stan-

Table 4
Thermodynamic parameters of dehydrogenation of acenaphthene with formation of acenaphthylene; p=101.325 kPa

T (K)	Physical state of reagents[a]	$\Delta_{dehydr}H^0$ (kJ mol^{-1})	$\Delta_{dehydr}S^0$ (J K^{-1} mol^{-1})	$\Delta_{dehydr}G^0$ (kJ mol^{-1})
0	cr; crIII, g	107	30	107
100	cr; crIII, g	110	104	100
200	cr; crI, g	114	138	89
298.15	cr; crI, g	117	148	73
350	cr; crI, g	118	151	65

[a] cr, crI, crIII – crystalline; g – gaseous.

Table 5
Thermodynamic parameters of polymerization of acenaphthylene in bulk at p=101.325 kPa

T (K)	Physical state of reagents[a]	$-\Delta_{pol}H^0$ (kJ mol^{-1})	$-\Delta_{pol}S^0$ (J K^{-1} mol^{-1})	$-\Delta_{pol}G^0$ (kJ mol^{-1})
0	crIII; gl	69	−17	69
100	crIII; gl	70	−4	70
200	crI; gl	73	20	69
298.15	crI; gl	74 [10]	23	67
350	crI; gl	74	24	66

[a] crIII, crI – crystalline; gl – glassy.

dard Gibbs energy of reaction. To shift the equilibrium to the right a substantial decrease of the $\Delta_{dehydr}G^0$ value is necessary. It is seen that the temperature rise leads, on the one hand, to the decrease of $\Delta_{dehydr}H^0$ and, on the other hand, to the increase of $\Delta_{dehydr}S^0$. Both these factors, in turn, bring about the reduction of $\Delta_{dehydr}G^0$ that is used in practice. Acenaphthylene is formed by catalytic vapor-phase dehydrogenation of acenaphthene at $T \geq 500$ K [1]. In this case, however, a spontaneous transformation to polymer products is possible to occur if a proper action on the acenaphthylene stabilization is not taken. The process can happen to take place in acenaphthylene sample during heating of the dynamic calorimeter up to T>400 K when we made attempts to measure its heat capacity in the range of higher temperatures.

Polymerization of acenaphthylene. In Table 5 are given the thermodynamic parameters of polymerization reaction of acenaphthylene in bulk. The enthalpy of polymerization $\Delta_{pol}H^0$ at T=298.15 K was calculated from the enthalpies of formation of acenaphthylene and polyacenaphthylene [5,11]. For other temperatures we estimated it by use of the Kirchhoff's formula. The polymerization entropy $\Delta_{pol}S^0$ was calculated from the entropies of the polymer (Table 2) and the monomer [4]. On calculating $\Delta_{pol}S^0(T)$, the value of the zero entropy of polyacenaphthylene was taken into account. The Gibbs energy of polymerization $\Delta_{pol}G^0(T)$ was estimated from the enthalpy and entropy of reaction. Since the $\Delta_{pol}H^0(T)$ and $\Delta_{pol}S^0(T)$ values with rising temperature are still negative, the process should have a ceiling limiting temperature. Its estimation by the Dainton's method [19] gives $T^0_{ceil} > 1000$ K which is certainly higher than temperatures of the onset of thermal decomposition. Judging by the sign and the absolute value of the standard Gibbs energy of polymerization, the process is almost completely shifted towards the formation of polyacenaphthylene.

First the enthalpy of polymerization of acenaphthylene was measured calorimetrically by Dainton et al. [6] in *o*-dichlorobenzene: two values $\Delta_{pol}H^0$(s;s)=-98.2 ± 1.5 kJ mol^{-1} and $\Delta_{pol}H^0$(s;s)=-100 ± 1.5 kJ mol^{-1} at 300 K were given in [6] and one value $\Delta_{pol}H^0$(s;s)=-100.4 kJ mol^{-1} at 350 K was reported in [7]. It is obvious that the results coincide well within experimental errors. It is seen that the difference in temperatures at which the polymerization process was performed (by 50 K) did not virtually influence the value of $\Delta_{pol}H^0(T)$. In [9,10] the values of enthalpy of polymerization of acenaphthylene were measured at 348 K in an isothermal calorimeter of Mathews type (in benzene solution), $\Delta_{pol}H^0$(s;s)=-73.7 ± 1.7 kJ mol^{-1}, and in *o*-dichlorobenzene $\Delta_{pol}H^0$(s;s)=-70.7 ± 1.7 kJ mol^{-1}. Besides, in the same works the polymerization enthalpy $\Delta_{pol}H^0$(s;s)=-99.6 ± 1.7 kJ mol^{-1} (300 K, *o*-dichlorobenzene) and $\Delta_{pol}H^0$(cr;gl)=-82.0 ± 1.7 kJ mol^{-1} (300 K, the monomer in the crystalline state (cr) and the polymer in the glassy state (gl)) were reported. It is clear that the usage of various solvents at 348 K leads only to small differences in the polymerization enthalpies of acenaphthylene and the $\Delta_{pol}H^0$(s;s) value is slightly larger if the reaction is carried out in benzene. However, a substantial influence of temperature for the polymerization process was manifested. So, the enthalpies of polymerization in benzene at 348 and 300 K differ by about 19 kJ mol^{-1}, the $\Delta_{pol}H^0$(s;s) value being higher if the polymerization of acenaphthylene proceeds at 300 K.

A significant difference in the enthalpies of polymerization performed under the same physical conditions (*o*-dichlorobenzene, 350 K [7]) and 348 K [9,10]) attracts attention. The enthalpy values differ by approximately 30 kJ mol^{-1}, the difference being larger in [7]. The comparison of the $\Delta_{\rm pol}H^0$(s;s) values (*o*-dichlorobenzene as a solvent) and $\Delta_{\rm pol}H^0$ (cr;gl) [9,10] shows the effect of the solvent and physical states of the reagents on the polymerization enthalpy. Some time ago the authors [8] measured calorimetrically the enthalpy of polymerization of acenaphthylene in methylene chloride at three different temperatures and obtained $\Delta_{\rm pol}H^0$(s;s)=$-$87.8$\pm$2 kJ mol^{-1} at 273 K, $-$84.2$\pm$2 kJ mol^{-1} at 291 K and $-$83.6$\pm$2 kJ mol^{-1} at 308 K (the monomer and the polymer are in solution). It is clear that the difference between the values of $\Delta_{\rm pol}H^0$(s;s) in [8] and those published in [7,9,10] is due to the solvent effect and different temperatures of experiments. It is worth to note that the enthalpy of bulk polymerization of acenaphthylene at 298.15 K $\Delta_{\rm pol}H^0$ (crI;gl)= $-$74 kJ mol^{-1} (the monomer in the form of crystals crI, the polymer is glassy) (Table 5), as calculated from the combustion enthalpies of the monomer and polymer [11], is much lower than that obtained for the polymerization in solutions [6–10] (the monomer and the polymer formed are in an appropriate solution). The maximum difference between $\Delta_{\rm pol}H^0$(s;s) as reported in [6] and $\Delta_{\rm pol}H^0$ (crI;gl) in [11] at $T\cong300$ K is 26 kJ mol^{-1}. This is firstly connected with different physical states of reagents and the solvent influence. The enthalpy of dissolution of acenaphthylene crystals crI is likely to make a significant contribution to this difference. The enthalpy seems to be close to a hypothetical enthalpy of melting of crystals crI at T=300 K (the measured values $T^0_{\rm fus}=362.60$ K, $\Delta_{\rm fus}H^0$=6.94 kJ mol^{-1}) were cited elsewhere [20]. This conforms to the rule according to which a phase transition in a monomer makes the polymerization enthalpy lower by the value of the enthalpy of this transition and in a polymer, just the other way, makes greater [14].

An unusually high magnitude of the polymerization enthalpy of acenaphthylene which, in principle, can be considered as a 1,2-disubstituted vinyl monomer is drawn attention. Because of steric interactions of substituents, the polymerization enthalpy should be much lower – almost similar, for example, to that of α-methylstyrene ($-$35 kJ mol^{-1}, i.e. smaller by a factor of about 2.5–3 [21]). Mortimer [22] interpreted this experimental fact and noted that a high enthalpy of polymerization of acenaphthylene ($-$100 kJ mol^{-1}) [7] is due to the release of a fairly large energy of deformation of a five-membered ring in the course of polymerization [23].

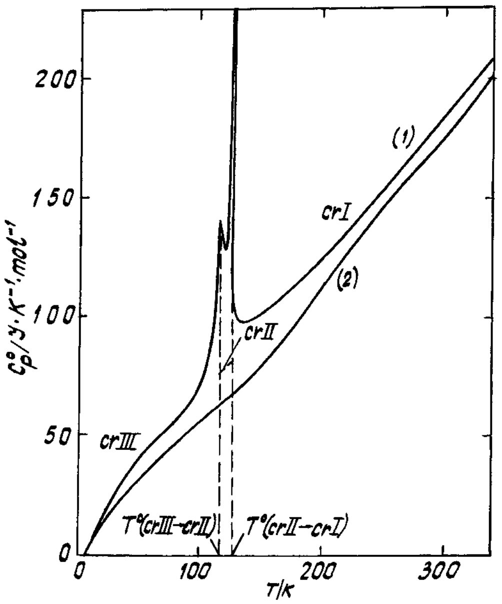

Fig. 2. Mutual location of temperature dependences of heat capacity for crystalline acenaphthylene (curve 1, [4]) and glassy polyacenaphthylene (curve 2, the present work): crIII, crII and crI – crystalline forms of the monomer, T^0 (crIII→crII) and T^0 (crII→crI) – temperatures of transitions crIII→crII, crII→crI.

In conclusion, it is to be noted that the dependence of thermodynamic parameters of polymerization reaction on temperature and the physical states of reagents is determined by the difference in the heat capacities of the polymer and the monomer along with the existence of phase transitions in them. Fig. 2 illustrates a mutual location of the heat capacity curves of acenaphthylene and polyacenaphthylene. It is seen that the heat capacity values of the monomer are everywhere larger than those of the polymer. Moreover, acenaphthylene crystal has two phase transitions. The thermodynamic quantities associated with the transitions were studied in detail earlier [4]. According to the equations

$$\Delta_{\rm pol}H^0(T)=\Delta_{\rm pol}H^0\ (298.15)+\int_{298\,\rm K}^{T}\Delta C_p^0(T)\,{\rm d}T+\sum\Delta_{\rm trs}H^0, \quad (8)$$

$$\Delta_{\text{pol}}S^0(T) = \Delta_{\text{pol}}S^0\ (298.15) + \int_{298\,\text{K}}^{T} \Delta C_p^0(T)\,\text{d}\ln T + \sum \Delta_{\text{trs}}S^0, \tag{9}$$

the enthalpy and entropy have to decrease with rising temperature since the temperature dependence of the difference in the heat capacity for the polymer and monomer in the temperature interval (0–340) K is $\Delta C_p^0(T) < 0$ and the phase transformations occur only in the monomer. At the same time, as $\Delta_{\text{pol}}H^0(T)$ and $\Delta_{\text{pol}}S^0(T)$ are negative (except the polymerization entropy at a temperature below 200 K) $\Delta_{\text{pol}}G^0(T)$ has to decrease with rising temperature and the polymerization process has ultimately the ceiling limiting temperature T^0_{ceil}.

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