

## Thermodynamic properties of an alternating copolymer of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide in a region from $T \rightarrow 0$ to 550 K

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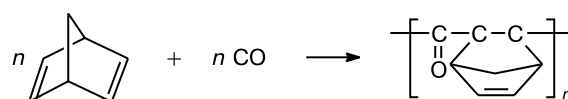
The temperature dependence of the heat capacity of an alternating copolymer of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide in the temperature range 6–550 K (with an error of 0.2–0.5% at 6–350 K and 0.5–1.5% at 330–550 K) was studied by the adiabatic vacuum and dynamic calorimetry. Physical transformations of the copolymer in the studied temperature region were identified, and their thermodynamic characteristics were determined. The combustion energy of the copolymer at 298.15 K was measured in a calorimeter with a static bomb and isothermal jacket. The thermodynamic functions for a region of 0–550 K, enthalpy of combustion, and thermodynamic parameters of copolymer formation from simple substances at  $T = 298.15$  K and  $p = 101.325$  kPa were calculated from the obtained experimental data. The new results and earlier published data were used for the calculation of the thermodynamic characteristics of the alternate copolymerization of bicyclo[2.2.1]hepta-2,5-diene and CO under standard pressure for a region of 0–350 K for the bulk reaction.

**Key words:** copolymer of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide, heat capacity, enthalpy, entropy, Gibbs function, calorimetry, thermodynamics.

The thermodynamic properties of alternating copolymers of carbon monoxide with ethylene, propylene, styrene, and *endo*-dicyclopentadiene and the thermodynamic characteristics of the reactions of formation of these copolymers in a range of 0–500 K have previously been studied<sup>1–4</sup> by calorimetric methods. These copolymers are representatives of a new class of polymers, *viz.*, polyketones,<sup>5,6</sup> which are of significant scientific and practical interest.<sup>6,7</sup> They are obtained by the copolymerization of  $\alpha$ -olefins, styrene and its derivatives, dienes, and some other monomers with carbon monoxide in the presence of palladium(II), nickel(II), and ruthenium(II) complexes predominantly with bidentate N–N or P–N ligands.<sup>8,9</sup> In this work, we extend calorimetric investigations of polyketones to the thermodynamic properties of the alternating copolymer of bicyclo[2.2.1]hepta-2,5-diene with carbon monoxide and the thermodynamic characteristics of its synthesis (Scheme 1) in a region of 0–550 K under standard pressure.

The purpose of this work is to study the temperature dependence of the heat capacity ( $C_p^\circ$ ) of the alternating copolymer of bicyclo[2.2.1]hepta-2,5-diene with carbon

Scheme 1



monoxide in the 6–550 K range by calorimetry, examine physical transformations on heating of the copolymer in this temperature interval, and determine their thermodynamic characteristics. It was also of interest to determine the combustion energy of the copolymer and use our experimental data and data from literature to calculate the thermodynamic functions ( $C_p^\circ = f(T)$ ,  $H^\circ(T) - H^\circ(0)$ ,  $S^\circ(T) - S^\circ(0)$ , and  $G^\circ(T) - H^\circ(0)$ ) for the 0–550 K region, the standard enthalpy of combustion ( $\Delta_c H^\circ$ ), and the standard enthalpy ( $\Delta_f H^\circ$ ), entropy ( $\Delta_f S^\circ$ ), and Gibbs function ( $\Delta_f G^\circ$ ) of copolymer formation from simple substances at  $T = 298.15$  K. It was also desirable to calculate the thermodynamic characteristics of the alternate copolymerization of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide for the 0–350 K region.

## Experimental

A sample of the studied copolymer was prepared by the alternate cooligomerization of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide in the presence of arylpalladium(II) complexes using a known procedure.<sup>10</sup> Cooligomerization conditions:  $[\text{Pd}(\text{AcO})_2] = 5 \cdot 10^{-4} \text{ mol L}^{-1}$ , ligand : Pd = 1.5,  $\text{CH}_2\text{Cl}_2$  (60 mL), bicycloheptadiene (20 mL), MeOH (100 mL),  $p_{\text{CO}} = 4 \text{ MPa}$ ,  $T = 320 \text{ K}$ , duration 6 h. The copolymer is soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , MeOH, and THF. Found (%): C, 79.78; H, 7.80. Calculated (%): C, 79.97; H, 6.71.  $M_w = 1.9 \cdot 10^3$  (GPC data). The  $^{13}\text{C}$  NMR spectra obtained on a Gemini-300 instrument (Varian) showed that the sample under study is syndiotactic and has a keto-*exo-cis*-structure. According to the calorimetric data, the copolymer is a partially crystalline material. Commercial reagents (Aldrich) were used.

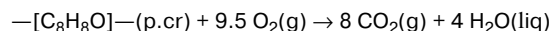
A BKT-3 adiabatic vacuum calorimeter designed and produced at the AOZT "Termis" (Mendeleev, Moscow Region, Russia) was used to study the temperature dependence of the heat capacity of the copolymer along with temperatures and enthalpies of its physical transformations in the 6–350 K region. A structure of the calorimeter and procedure of its operation are similar to those described earlier.<sup>11,12</sup> As found from the results of calibration and verification of the calorimeter, the error of measurement of heat capacities of substances at helium temperature is  $\pm 2\%$  and decreases to  $\pm 0.4\%$  with the temperature increase to 40 K and to 0.2% in the 40–350 K range. An ADKTTM dynamic calorimeter—thermoanalytical complex operating according to the triple thermal bridge principle<sup>13</sup> was used to study the heat capacity of the copolymer in a region of 330–550 K (in this calorimeter, the measurement error of  $C_p^\circ$  ranges from 1 to 4%). In the 330–370 K interval, the heat capacities of substances were measured in adiabatic vacuum and dynamic calorimeters. For the dynamic calorimeter, the measurement conditions were matched to provide coincidence of the  $C_p^\circ$  values in both calorimeters. Therefore, the error of  $C_p^\circ$  measurement in ADKTTM at  $T > 330 \text{ K}$  is  $\pm(0.5\text{--}1.5)\%$ .

The combustion energy of the partially crystalline copolymer was measured in a V-08 calorimeter with an isothermal jacket and static bomb improved at the Research Institute of Chemistry of the Nizhny Novgorod State University. The calorimeter structure, main improvements, and results of calibrations and verifications have been described previously.<sup>14</sup> The combustion enthalpy value corresponding to the nameplate value with an accuracy of 0.017% was obtained by the verification of the calorimeter using combustion of standard succinic acid.

The heat capacity of the studied copolymer was measured in an adiabatic vacuum calorimeter in the 6–370 K region (sample weight 0.2690 g) and in a dynamic calorimeter in the 330–550 K region (sample weight 0.1635 g). In both calorimeters, the heat capacity of samples was 14–35% of the total heat capacity of the corresponding calorimetric ampoules filled with the substance. Five series of experiments in the adiabatic vacuum calorimeter gave 147 experimental values of  $C_p^\circ$ . The  $C_p^\circ$  values were averaged graphically and on a computer using power and semilogarithmic polynomials to ensure that their root-mean-square deviation from the smoothed curve  $C_p^\circ = f(T)$  did not exceed the error of heat capacity measurements. The root-mean-square deviations of  $C_p^\circ$  from the corresponding averaging curves  $C_p^\circ = f(T)$  did not exceed  $\pm 0.12\%$  in a region of 6–90 K,

$\pm 0.08\%$  at 90–340 K, and approximately  $\pm 0.2\%$  at 340–550 K. Measurements of  $C_p^\circ$  in the dynamic calorimeter were carried out in a continuous heating regime with a rate of  $0.017 \text{ K s}^{-1}$ .

On determination the combustion energy of a copolymer sample, paraffin with the combustion energy  $\Delta_c U^\circ = -46744 \pm 9 \text{ J g}^{-1}$  derived from preliminary experiments was used as an auxiliary substance. When experiments on combustion were prepared, all procedures with the copolymers were carried out in air. The combustion energy was determined in six entries. The weights of combusted copolymer samples were 0.0810–0.1262 g. The total amount of energy  $\Delta_c U$ , evolved in experiments conducted under the calorimetric bomb conditions, was 16246–19484 J. Standard thermochemical corrections to the combustion of paraffin and a cotton thread used for the ignition of a weighed sample and the formation of an  $\text{HNO}_3$  solution were used in the calculation of the standard combustion energy  $\Delta_c U^\circ$ . The mass ratios of the  $\text{CO}_2$  found in the combustion products to those calculated by the equation of copolymer oxidation with oxygen were 99.40–100.6%. The average combustion energy of the copolymer ( $\Delta_c U = -4252.1 \pm 2.1 \text{ kJ mol}^{-1}$ ) was used for the calculation of the combustion energy under standard pressure ( $\Delta_c U^\circ = -4249.7 \pm 2.1 \text{ kJ mol}^{-1}$ ), and the standard enthalpy of combustion of the partially crystalline copolymer ( $\Delta_c H^\circ = -4253.4 \pm 2.1 \text{ kJ mol}^{-1}$ ) was determined from the last value. The enthalpy of combustion corresponds to the thermal effect of the reaction



at  $T = 298.15 \text{ K}$  and standard pressure (physical states of reactants: p.cr is partially crystalline, liq is liquid, and g is gaseous).

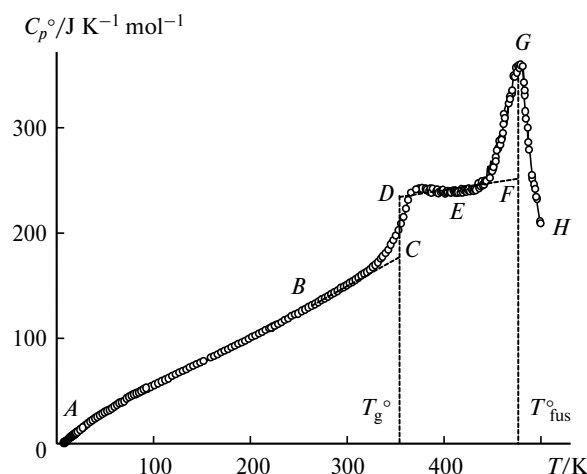
## Results and Discussion

**Heat capacity.** The temperature dependence of the heat capacity of the copolymer, *viz.*, experimental points and averaging curves  $C_p^\circ = f(T)$ , is presented in Fig. 1. It is seen that the heat capacity of the starting copolymer increases smoothly with the temperature increase in a region of 6–300 K (region *ABC*), and at  $T > 60 \text{ K}$   $C_p^\circ \approx T^1$ , as for many other linear polymers. At  $T > 300 \text{ K}$ , the plot of  $C_p^\circ$  vs.  $T$  deviates from linearity and the heat capacity increases rather rapidly, which is related to the onset of copolymer devitrification. This process occurs in an interval of 300–400 K; the glassy formation temperature ( $T_g^\circ$ ) found from the break in the  $S^\circ(T)$  plot<sup>15</sup> is equal to  $367 \pm 1 \text{ K}$ . The increase in the heat capacity for devitrification ( $\Delta C_p^\circ = 136 \text{ J K}^{-1} \text{ mol}^{-1}$ ) was obtained from the plot (see Fig. 1, region *CD*). It was found from a known equation<sup>16</sup>

$$S_{\text{conf}}^\circ = \Delta C_p^\circ(T_g^\circ) \ln 1.29 \quad (1)$$

that the configurational entropy ( $S_{\text{conf}}^\circ$ ) of the partially crystalline copolymer is  $15 \text{ J K}^{-1} \text{ mol}^{-1}$ .

At  $T > 400 \text{ K}$ , the heat capacity increases sharply due to the fusion onset but does not go to completion because



**Fig. 1.** Temperature plot of the heat capacity ( $C_p^\circ$ ) of the alternating copolymer of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide:  $ABC$  is the heat capacity of the amorphous part in the glassy state;  $DEF$  is the heat capacity of the amorphous part in the highly elastic state;  $BE$  is the heat capacity in the devitrification interval;  $CD$  is the increase in the heat capacity of the amorphous part during copolymer devitrification; and  $EGH$  is the apparent heat capacity in the interval of fusion of the crystalline part.

of the beginning of decomposition of a copolymer sample. The fusion temperature was accepted to be  $T_{\text{fus}}^\circ = 477.4$  K, which corresponds to the maximum value of the apparent heat capacity ( $C_p^\circ = 503.8$  J K<sup>-1</sup> mol<sup>-1</sup>) in the fusion interval.

We estimated the fractal dimensionality value  $D$ , which is the most important parameter of the multifractal variant of the Debye theory<sup>17,18</sup> of heat capacity, from the experimental data on the heat capacity of the copolymer. As a result,  $D = 1.4$  was obtained in the 20–50 K range, and the maximum characteristic temperature is  $\theta_{\text{max}} = 215.7$  K. The estimation of  $D$  was based on the assumption that for  $T < 50$ –60 K  $C_p^\circ \approx C_V^\circ$ . Under this condition, the equation presented previously<sup>17</sup>

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

where  $N$  is the number of atoms in a molecule,  $k$  is the Boltzmann constant,  $\gamma(D+1)$  is the  $\gamma$ -function,  $\xi(D+1)$  is the Riemann  $\xi$ -function, and  $\theta_{\text{max}}$  is the characteristic temperature, can be written as

$$C_V = AT^D, \quad (3)$$

in which  $A = [3D(D+1)kN\gamma(D+1)\xi(D+1)]/\theta_{\text{max}}^D$ . Then, the  $D$  values for linear regions can easily be read from the slope of the  $\ln C_p^\circ - \ln T$  plot. The  $D$  value is considered<sup>19</sup> to indicate the heterodynamic nature of solids:  $D = 1$  corresponds to bodies with the chain structure,  $D = 2$  is attributed to layer structures, and  $D = 3$  can be ascribed to space structures. Fractional  $D$  values indicate

**Table 1.** Thermodynamic functions of the partially crystalline copolymer of bicyclo[2.2.1]hepta-2,5-diene with carbon monoxide ( $p = 101.325$  kPa)

$T/\text{K}$	$C_p^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$-[G^\circ(T) - H^\circ(0)]$
	$\text{J K}^{-1} \text{mol}^{-1}$		$\text{kJ mol}^{-1}$	
Amorphous part in glassy state				
0	0	15	0	0
5	0.359	15.1	0.0004	0.075
10	2.490	15.9	0.0068	0.152
15	6.740	17.7	0.0300	0.236
20	10.30	20.2	0.0724	0.331
25	13.94	22.8	0.1330	0.438
30	17.70	25.7	0.2121	0.559
40	24.50	31.8	0.4241	0.847
50	30.15	37.9	0.6981	1.19
100	55.39	66.9	2.867	8.82
150	77.41	93.5	6.185	7.84
200	99.97	119	10.61	13.2
250	124.0	144	16.20	19.7
298.15	149.1	168	22.79	27.2
350	176.0	194	31.21	36.6
367	185.0	202	34.27	40.0
Amorphous part in highly elastic state				
367	243.0	202	34.27	40.0
400	241.2	223	42.26	47.0

mixed heterodynamic structures. For the copolymer under study, the numerical value of  $D$  in the considered temperature interval indicates that this structure is layer-chain.

**Thermodynamic functions.** To calculate the thermodynamic functions of the copolymer (Table 1), the heat capacity in the 0–7 K temperature range was obtained by the extrapolation of the experimental plot  $C_p^\circ = f(T)$  using the Debye heat capacity

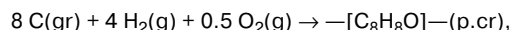
$$C_p^\circ = nD(\theta_D/T), \quad (4)$$

where  $D$  is the Debye heat capacity function, and  $n$  and  $\theta_D$  are specially selected parameters. For  $n = 2$  and  $\theta_D = 76.72$  K, Eq. (4) describes experimental  $C_p^\circ$  values in an interval of 7–11 K with an error of  $\pm 1.5\%$ . It was accepted in the calculation of the functions that at  $T < 7$  K the  $C_p^\circ$  values are reproduced with the same error. The enthalpy  $H^\circ(T) - H^\circ(0)$  and entropy  $S^\circ(T) - S^\circ(0)$  were calculated by integrating the dependences of  $C_p^\circ$  on  $T$  and  $\ln T$ , respectively; and the Gibbs function  $G^\circ(T) - H^\circ(0)$  was calculated from the enthalpy and entropy values. For subsequent calculations, we estimated the zero entropy  $S^\circ(0)$  of the partially crystalline copolymer accepted it equal to the configurational entropy of its glassy part ( $S_{\text{conf}}^\circ = 15$  J K<sup>-1</sup> mol<sup>-1</sup>). The numerical  $S_{\text{conf}}^\circ$  value is close to the zero entropy of the polymer  $S^\circ(0)$ ,<sup>20,21</sup> which can be used to estimate the absolute entropy values of vitrifying substances.<sup>20</sup>

**Thermodynamic parameters of formation.** The combustion energy of the partially crystalline copolymer (amorphous part of the sample in the glassy state) was used to calculate its enthalpy of combustion ( $\Delta_c H^\circ$ ) from which the enthalpy of formation ( $\Delta_f H^\circ$ ) at  $T = 298.15$  K and  $p = 101.325$  kPa was calculated. The entropy of formation of the copolymer in the same physical state was calculated from the absolute values of the entropies of the copolymer, carbon in the graphite form, and gaseous hydrogen and oxygen; the zero entropy of the partially crystalline copolymer was taken into account in calculations of  $\Delta_f S^\circ$ . The Gibbs function of formation ( $\Delta_f G^\circ$ ) was determined from  $\Delta_f H^\circ$  and  $\Delta_f S^\circ$ .

Parameter	$\Delta_c H^\circ$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\Delta_f S^\circ$
		kJ mol <sup>-1</sup>		/J K <sup>-1</sup> mol <sup>-1</sup>
Value	-4253.4±2.1	-37.9±2.1	111.9±2.8	-502.5±2.2

The resulting values correspond to the hypothetical reaction



where gr stands for graphite. The values of enthalpies of formation of liquid water and gaseous carbon dioxide and entropies of formation of carbon in the graphite form and gaseous  $\text{H}_2$  and  $\text{O}_2$  at  $T = 298.15$  K and  $p = 101.325$  kPa, which are necessary for calculations, were taken from literature.<sup>22</sup>

**Thermodynamic characteristics of copolymerization of bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide.** The enthalpy of copolymerization ( $\Delta_{\text{cop}} H^\circ$ ) at 298.15 K under standard pressure was calculated from the enthalpies of formation of the reactants: copolymer (see above), carbon monoxide,<sup>23</sup> and bicyclo[2.2.1]hepta-2,5-diene.<sup>24</sup> For other temperatures,  $\Delta_{\text{cop}} H^\circ(T)$  (Table 2) was calculated using the Kirchhoff formula. The temperature dependences of the heat capacity and temperature and enthalpy of physical transformations for carbon monoxide and bicyclo[2.2.1]hepta-2,5-diene have been determined ear-

lier,<sup>23,25</sup> and those for the copolymer are results of this work. The entropies of copolymerization  $\Delta_{\text{cop}} S^\circ(T)$  were calculated from the absolute entropies of the reactants: the absolute entropies of bicycloheptadiene and CO have been published earlier<sup>23,25</sup> and those of the copolymer are given above. As in the case of  $\Delta_f S^\circ$ , the zero entropy of the copolymer  $S^\circ(0)$  was taken into account. The standard Gibbs functions of copolymerization  $\Delta_{\text{cop}} G^\circ(T)$  were calculated from the reaction enthalpy and entropy at the corresponding temperatures (see Table 2).

The enthalpies and entropies of the reaction in the studied temperature interval are negative, except  $\Delta_{\text{cop}} S^\circ(0)$ . Therefore, the copolymerization process has a ceiling limiting temperature ( $T_{\text{ceil}}^\circ$ ). The latter was determined from the intersection point of the plots  $\Delta_{\text{cop}} H^\circ(T) = f(T)$  and  $T\Delta_{\text{cop}} S^\circ(T) = f(T)$  according to a known method<sup>26</sup>: 630 K. At  $T < T_{\text{ceil}}^\circ$ , the values of the standard Gibbs functions of copolymerization are negative. This means that the equilibrium of the process is shifted to the right, *i.e.*, toward copolymer formation. To the contrary, for  $T > T_{\text{ceil}}^\circ$   $\Delta_{\text{cop}} G^\circ(T) > 0$  and, hence, the equilibrium is shifted to the left. Thus, at  $T > T_{\text{ceil}}^\circ$  and standard pressure the reaction does not occur for thermodynamic reasons, and the copolymer is thermodynamically unstable under these conditions and can depolymerize to form the starting substances under the corresponding kinetic conditions.

The authors are grateful to A. V. Markin for measuring the heat capacity of the copolymer at 330–550 K.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 01-03-33248, 02-03-32162, and 05-03-32363) and the Ministry of Industry, Science, and Technologies of the Russian Federation (Decision of January 15, 1996).

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**Table 2.** Thermodynamic characteristics of copolymerization of bicyclo[2.2.1]hepta-2,5-diene with carbon monoxide in the bulk ( $p = 101.325$  kPa)

$T/\text{K}$	Physical states of reactants*	$-\Delta_{\text{cop}} H^\circ$	$-\Delta_{\text{cop}} G^\circ$	$\Delta_{\text{cop}} S^\circ$
		kJ mol <sup>-1</sup>		/J K <sup>-1</sup> mol <sup>-1</sup>
0	cr, cr; p.cr	123	123	-15
100	cr, g; p.cr	126	111	153
200	cr, g; p.cr	128	95	166
298.15	liq, g; p.cr	141	74	226
350	liq, g; p.cr	142	63	230

\* cr is crystalline, p.cr is partially crystalline, liq is liquid, and g is gaseous.

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Received February 13, 2004