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Calorimetric study of alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide in the range from $T \to 0$ to 510 K

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Abstract

By adiabatic vacuum and dynamic calorimetry, the temperature dependence of heat capacity for alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide has been determined over the 6–510 K range with an uncertainty of 0.2–0.5% between 6 and 350 K and 0.5–1.5% from 330 to 510 K. In the above temperature ranges, the physical transformations of the copolymer have been detected and their thermodynamic characteristics have been estimated. In a calorimeter with a static bomb and an isothermal shield, the energy of combustion of the copolymer has been measured at 298.15 K. Based on the experimental data, the thermodynamic functions of the copolymer, namely, the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ have been determined for the range from $T \to 0$ to 400 K. The enthalpy of combustion $\Delta_c H^\circ$ and the thermodynamic parameters $\Delta_f H^\circ$, $\Delta_f S^\circ$, $\Delta_f G^\circ$ and $\ln K_f^\circ$ of reaction of formation of the copolymer from simple substances at $T = 298.15$ K and $p = 0.1$ MPa have been calculated. The data cited in the present work and literature data were used to calculate the thermodynamic characteristics of the alternating copolymerization in bulk of bicyclo[2,2,1]-hepta-2,5-diene and CO in the 0–340 K range at standard pressure as well as to compare them with the thermodynamic characteristics of the synthesis of isomeric polyketone.
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1. Introduction

The present work is devoted to the study of the alternating copolymer of carbon monoxide and bicyclo[2,2,1]-hepta-2,5-diene (norbornadiene). It is a part of the calorimetric examination of thermodynamic properties of polyketones and processes of their preparation by copolymerization of carbon monoxide with various monomers. Earlier [1–5], by methods of adiabatic vacuum and dynamic calorimetry, the thermodynamic properties of alternating copolymers of carbon monoxide with ethylene, propylene, styrene, *endo*-dicyclopentadiene and norbornadiene (keto-exo-cis structure) were investigated and besides, the thermodynamic characteristics of reactions of their synthesis between $T \to 0$ and 500 K were determined. A wide variety of polyketones are prepared by copolymerization of α-olefins, styrene and its derivatives, dienes and some other monomers with carbon monoxide in the presence of complexes of palladium(II), nickel(II) and ruthenium(II) chiefly with bidentate N–N or P–N ligands [6,7]. In addition, copolymers with different molecular-mass distribution and a number of valuable properties (thermoplasticity, impact strength, chemical resistance, high thermal stability, ability to be easily photo- and biodestructed with the formation of nontoxic products) are produced.

At present, published works concerning the examination of thermodynamic properties of polyketones are found extremely seldom in literature. Nevertheless, it is obvious that the determination of calorimetric data for these copolymers in a wide temperature interval and the calculation of their thermodynamic functions and thermodynamic characteristics of physical transformations and reactions of their preparation from starting comonomers are urgent tasks. Polyketones as representatives of a relatively new polymer class are not enough investigated.

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They are interesting in terms of theory and the study of their physicochemical properties is essential. Besides, the estimation of the thermodynamic characteristics of the synthesis processes of polyketones over a wide temperature range allows the expansion of the areas of their possible application.

The goal of the present work is to calorimetrically study the thermodynamic properties (the temperature dependence of the heat capacity, temperatures and enthalpies of physical transformations) of the alternating copolymer of carbon monoxide with norbornadiene of keto-ketal-exo-cis structure (CON) between 6 and 510 K, to determine its energy of combustion $\Delta_c H^\circ$ and to calculate from the data the thermodynamic characteristics of physical transformations and the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$ and $G^\circ(T) - H^\circ(0)$ over the range from $T \to 0$ to 400 K. Moreover, in the given paper, the standard characteristics of formation of the copolymer from simple substances at 298.15 K and standard pressure and the thermodynamic characteristics of copolymerization reaction $\Delta_{cop}H^\circ$, $\Delta_{cop}S^\circ$ and $\Delta_{cop}G^\circ$ of carbon monoxide with norbornadiene from $T \to 0$ to 340 K have been estimated.

2. Experimental

2.1. Sample

The sample to be tested of CON was prepared by alternating cooligomerization of bicyclo[2,2,1]-hepta-2,5-diene (norbornadiene, NBD) and carbon monoxide under the action of Pd(II) complexes according to the procedure [8]. The cooligomerization conditions are as follows: $Pd(CH_3COO)_2 = 7 \times 10^{-4}$ mol/l, ligand/Pd = 1.5, 58 ml CH_2Cl_2, 10 ml NBD; 2 ml methanol, pressure of CO is 4 MPa, temperature 308 K; time 6 h. The copolymer is soluble in chloroform, CH_2Cl_2, methanol and THF. According to GPC, the copolymer has $M_w = 2250$. ^{13}C NMR spectra recorded on a "Gemini-300" device of Varian firm showed that the sample is syndiotactic with keto-ketal-exo-cis structure. As follows from the experimental data of the given work, CON is partially crystalline.

2.2. Apparatus and measurement procedure

For studying the temperature dependence of the heat capacity of CON, temperatures and enthalpies of its physical transformations in the range 6–350 K, a BKT-3 adiabatic vacuum calorimeter designed and manufactured at joint company "Termis" (Mendeleevo, Moscow region) was employed. All measurements of the heat capacity on the device were conducted automatically and controlled with a computer-measurement system consisting of a computer and a unit of analogous control. The substance was placed in a calorimetric ampoule—a thin-walled cylindrical titanium vessel (an internal volume 1 cm^3, mass *ca.* 1.6 g), screwing up with a bronze cap with an indium seal. Temperature was measured with an iron–rhodium resistance thermometer ($R \approx 100\,\Omega$). The design and the operation principle of the calorimeter are similar to those described earlier [9,10]. The reliability of the measurement procedure was tested by measuring the heat capacity of special purity copper, standard synthetic corundum and K-2 benzoic acid prepared at metrological institutions of the State Standard of the Russian Federation. From the calibration and testing results of the calorimeter it was found that the measurement uncertainty of the heat capacity of the substances is ±2% at helium temperatures, it decreases till ±0.4% as temperature rises up to 40 K and is equal to 0.2% between 40 and 350 K.

The measurement of the heat capacity of CON over the range 330–510 K was performed on an ADKTTM thermoanalytical complex—a high-precision dynamic calorimeter operating by the principle of triple thermal bridge. The calorimeter design and the heat capacity measurement procedure are described in detail, for example, in refs. [11,12]. The reliability of the calorimeter operation was checked by measuring the heat capacity of the standard sample of synthetic corundum and thermodynamic characteristics of fusion of indium, tin and lead. While testing it was found that the calorimeter and measurement technique allow to obtain data on the heat capacity of substances in solid and liquid states with the uncertainty of ±1.5% and temperatures of physical transformations with an error of about ±0.3 K. The heat capacity of the examined compound was also measured between 330 and 350 K in the adiabatic vacuum calorimeter with an uncertainty of ±0.2% and the conditions of measurements in the dynamic device were chosen so that in the above temperature interval the C_p° values, measured with employing both calorimeters, coincided. Therefore, it was assumed that at $T > 350$ K the heat capacity was determined with an uncertainty of 0.5–2.0%.

The energy of combustion for the partially crystalline CON was measured in a V-08 calorimeter with an isothermal shield and a static bomb improved at the Research Institute of Chemistry of Nizhny Novgorod University. The calorimeter design, its improvements and measurement technique are demonstrated elsewhere. On testing the calorimeter by burning the standard succinic acid the value of its combustion enthalpy that coincides with a certificate value within to 0.017% was obtained. The absence of CO was controlled by means of indicator tubes (the analysis sensitivity was 6×10^{-6} g). No soot and CO were found in any experiment.

The heat capacity of CON was measured in the adiabatic vacuum calorimeter between 6 and 350 K (the sample mass was 0.1304 g) and in the dynamic one from 327 to 509 K (the sample mass 0.1635 g). In both calorimeters, the heat capacity of the samples was not more than 25–50% of the summary heat capacity of the calorimetric ampoules with the substance. The C_p° measurements in the dynamic calorimeter were made in conditions of continuous heating at a rate of 0.017 K/s. Two hundred and forty-eight experimental values were obtained in four series of measurements. The averaging of C_p° points was made by means of degree and semi-logarithmic polynomials so that the mean-square deviation of points from the $C_p^\circ = f(T)$ curve was not larger than the measurement uncertainty.

To determine the energy of combustion of the CON sample, the paraffin with the combustion energy $\Delta_c U^\circ = -46744 \pm 9$ J/g, as determined in preliminary runs, was used in the role of an auxiliary substance. The experimental data on the combustion energy for the copolymer are listed in

Table 1
Experimental data on the energy of combustion of copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide ($M = 120.1509$ g/mol)

Value	Experiment				
	1	2	3	4	5
m_{sam}[a] (g)	0.0388	0.0328	0.0488	0.0377	0.0486
m_{par}[a] (g)	0.4630	0.4024	0.4191	0.5484	0.4189
m_{thread}[a] (g)	0.0027	0.0022	0.0025	0.0026	0.0024
W[b] (J/g)	75,927	75,927	75,927	75,927	75,927
$\Delta R + \Delta(\Delta R)$[c] ($\Omega$)	0.303968	0.263463	0.281683	0.355974	0.281232
$-\Delta_c U_{\sum}$[d] (J)	23079.4	20001.9	21387.4	27028.4	21353.1
$-\Delta_c U_{\text{par}}$[e] (J)	21642.2	18809.5	19604.1	25634.1	19580.7
$-\Delta_c U_{\text{thread}}$[e] (J)	45.19	36.81	41.84	43.51	40.17
$-\Delta_c U_{\text{HNO}_3}$[f] (J)	28.87	8.79	24.68	24.68	25.10
($m^{e}CO_2/m^{c}CO_2$)[g] × 100%	99.65	99.55	–	99.72	99.70
$-\Delta_c U$[h] (J/g)	35132.6	35025.9	35169.6	35165.7	35126.4

$-\Delta_c\bar{U} = (35125.9 \pm 53.1)$ J/g $= (4220.4 \pm 6.3)$ kJ/mol, the mean energy of combustion of copolymer; $-\Delta_c U^0 = (4217.9 \pm 6.3)$ kJ/mol, the energy of combustion of copolymer at standard pressure.

[a] m_{sam}, m_{par}, m_{thread}, masses of the tested sample, paraffin and a cotton thread, respectively.

[b] W, the energy equivalent of the calorimeter.

[c] $\Delta R + \Delta(\Delta R)$, the change in resistance of platinum-resistance thermometer with correction for heat exchange.

[d] $\Delta_c U_{\sum}$, the total energy released during the experiment.

[e] $\Delta_c U_{\text{par}}$, $\Delta_c U_{\text{thread}}$, amounts of energy released on burning paraffin and cotton thread, respectively.

[f] $\Delta_f U_{\text{HNO}_3}$, the energy of formation of nitric acid.

[g] ($m^{e}CO_2/m^{c}CO_2$) × 100%, the ratio of masses of CO_2 in the combustion products of the copolymer and calculated by its chemical formula.

[h] $\Delta_c U$, the energy released on burning of the copolymer.

Table 1. Ratios of CO_2 masses in the combustion products and calculated by means of the equation of oxidation reaction of CON with oxygen were 99.7–99.8%. The average $\Delta_c\bar{U} = -4220.4 \pm 6.3$ kJ/mol was adjusted to standard conditions and amounted to -4217.9 ± 6.3 kJ/mol. On its basis, the standard enthalpy of combustion of the copolymer $\Delta_c H^\circ = -4221.6 \pm 6.3$ kJ/mol corresponding to the thermal effect of the reaction:

$$-[C_8H_8O]-(\text{p.cr}) + 9.5O_2\,(\text{g}) \rightarrow 8CO_2\,(\text{g}) + 4H_2O\,(\text{l})$$

was estimated at $T = 298.15$ K and standard pressure (in parentheses the physical states of the reagents are given: p.cr, partially crystalline; g, gaseous; l, liquid).

3. Results and discussion

3.1. Heat capacity

The temperature dependence of the heat capacity for CON – the experimental C_p° values measured in the adiabatic vacuum and dynamic calorimeters – and the smoothed $C_p^\circ = f(T)$ curves are illustrated in Fig. 1. It was ascertained that in the temperature interval under study CON exists in a partially crystalline state. It is seen that the heat capacity of the initial sample of CON gradually increases with rising temperature in the 6–280 K range (ABC curve) and, besides, at $T > 60$ K as for many other chain polymers $C_p^\circ \sim T^1$. Two jumps of the heat capacity are observed on the plot C_p° *versus* T. The first occurring between 300 and 385 K is related to the devitrification of an amorphous part of the sample (BE curve). The second in the range 400–500 K is caused by the fusion of the copolymer crystalline part that, however, does not cease because of the incipient decomposition. The availability of the decomposition is confirmed by an exothermal effect manifesting itself on the curve in a sharp decrease of the apparent heat capacity and the reduction of the sample mass.

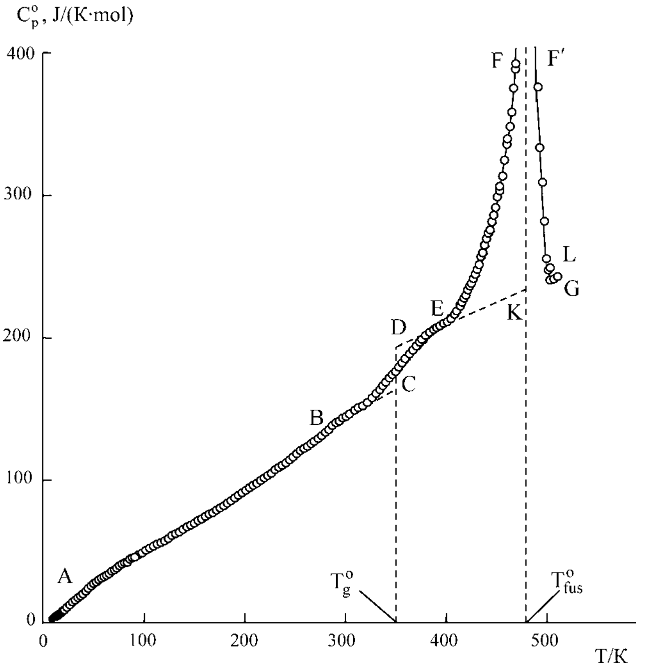


Fig. 1. Temperature dependence of heat capacity of partially crystalline (α) copolymer of carbon monoxide and norbornadiene: ABC, amorphous part in glassy state; DEK, amorphous part in high-elasticity state; BE, heat capacity in the interval of devitrification; CD, increase in heat capacity on devitrification of amorphous part of copolymer; EFF′L, apparent heat capacity in the melting interval of crystalline part and the beginning of thermal decomposition of the copolymer.

Table 2
Thermodynamic characteristics of glass transition and glassy state[a] of CON (M = 120.1509 g/mol); p = 0.1 MPa

$T^\circ_{g,i}$–$T^\circ_{g,f}$ (K)	T°_g (K)	$\Delta C^\circ_p(T^\circ_g)$, α (J/(K mol))	S°_{conf} (α) (J/(K mol))
300–385	350 ± 1	18.6	4.7

[a] $T^\circ_{g,i}$, $T^\circ_{g,f}$, the beginning and ending temperatures of glass transition; T°_g, the glass transition temperature; $\Delta C^\circ_p(T^\circ_g)$, α, the increase of heat capacity during glass transition; S°_{conf} (α), the configurational entropy.

The thermodynamic characteristics of glass transition of the copolymer are given in Table 2. The glass transition temperature T°_g was determined by the method described in [13] from the inflection point of the temperature dependence plot $S^\circ(T) = f(T)$ in a vitrification interval. The vitrification interval and an increase in the heat capacity on devitrifying $\Delta C^\circ_p(T^\circ_g)$ were obtained graphically (Fig. 1, DC section). The configurational entropy, S°_{conf}, of the partially crystalline CON was estimated by Adam–Gibbs expression [14]:

$$S^\circ_{conf} = \int_{T^\circ_2}^{T^\circ_g} \Delta C^\circ_p(T^\circ_g)\, \mathrm{d}\ln T, \tag{1}$$

where T°_2 is Kauzmann temperature [15]. For polymers, it is usual that $T^\circ_g/T^\circ_2 = 1.29 \pm 0.14$. On calculating S°_{conf}, it was suggested that such ratio is seen in the case of CON too. The temperature corresponding to the maximum value of the apparent heat capacity $C^\circ_p = 623.8\,\mathrm{J/(K\,mol)}$ in the melting interval was regarded as the temperature of fusion ($T^\circ_{fus} = 481.9 \pm 0.3\,\mathrm{K}$) that does not come to end because of the incipient decomposition of the sample.

From the experimental data on the heat capacity of CON its fractal dimension D, as the most important parameter of Debye's theory of heat capacity and its multifractal generalization [16,17], was evaluated. As a result, for the range 20–50 K, D = 1.4 and the maximum characteristic temperature θ_{max} = 232.4 K were obtained. While calculating the D value, it was assumed that $C^\circ_p \approx C^\circ_v$ at T < 50–60 K. Under such condition, the equation [16]:

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)\left(\frac{T}{\theta_{max}}\right)^D, \tag{2}$$

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

$$C_v = AT^D, \tag{3}$$

in which $A = [3D(D+1)kN\gamma(D+1)\xi(D+1)]/\theta^D_{max}$. From the $\ln C^\circ_v$–$\ln T$ plot, the D value can be easily determined for rectilinear sections as an angle coefficient of the corresponding straight lines. According to [18], the D parameter points to the heterodynamics of solids: D = 1 corresponds to bodies having a chain structure, D = 2 to a layer structure and D = 3 to a spatial one. Fractal values of D testify to mixed heterodynamic structures. With CON the fractal numerical magnitude of D in the considered temperature range points to a layer–chain structure of the copolymer.

Table 3
Thermodynamic functions of partly crystalline copolymer (α) of carbon monoxide and norbornadiene (CON) (M = 120.1509 g/mol); p = 0.1 MPa

T (K)	C°_p (T) (J/(K mol))	$S^\circ(T)$ (J/(K mol))	$H^\circ(T) - H^\circ(0)$ (kJ/mol)	$-[G^\circ(T) - H^\circ(0)]$ (kJ/mol)
Amorphous part in glassy state				
0	0	4.7	0	0
5	0.4388	4.8	0.0005	0.024
10	2.9600	5.81	0.0082	0.050
15	5.5400	7.51	0.0296	0.083
20	8.6600	9.51	0.0648	0.125
25	12.05	11.8	0.1163	0.179
30	14.88	14.3	0.1852	0.244
35	17.86	16.8	0.2671	0.322
40	20.89	19.4	0.3638	0.412
50	27.41	24.8	0.6058	0.633
100	49.81	50.9	2.5570	2.54
110	53.98	55.9	3.0769	3.07
120	57.25	60.7	3.6329	3.65
130	61.63	65.5	4.2264	4.28
140	65.97	70.1	4.8642	4.96
150	70.02	74.9	5.545	5.69
200	92.43	97.9	9.579	10.0
250	117.8	121	14.81	15.5
298.15	143.9	144	21.10	21.9
300	144.8	145	21.36	22.1
350	177.7	169	29.22	30.0
Amorphous part in high-elasticity state				
350	196.3	169	29.22	30.0
350	196.3	169	29.26	30.0
400	198.1	196	39.12	39.1

Table 4
Enthalpy of combustion and thermodynamic characteristics of formation of carbon monoxide and norbornadiene copolymer; $T = 298.15$ K, $p = 0.1$ MPa

Substance	Physical state	$-\Delta_c H^\circ$ (kJ/mol)	$-\Delta_f H^\circ$ (kJ/mol)	$-\Delta_f S^\circ$ (J/(K mol))	$\Delta_f G^\circ$ (kJ/mol)
CON	p.cr	4221.6 ± 6.3	70 ± 1	531.1 ± 1.1	88.5 ± 1.3

3.2. Thermodynamic functions

The thermodynamic functions of the partially crystalline copolymer are listed in Table 3. To calculate the thermodynamic functions the heat capacity values were obtained for the range from the measurement onset to 0 K by extrapolating the temperature dependence of the heat capacity for CON by Debye's heat capacity function with using expression (4):

$$C_p^\circ = n\mathrm{D}\left(\frac{\theta_D}{T}\right), \tag{4}$$

where D denotes Debye's function of heat capacity, n and θ_D are specially selected parameters. With $n = 2$ and $\theta_D = 71.71$, Eq. (4) describes the experimental C_p° values in the range from 7 to 11 K with the uncertainty of ±1.8%. It was assumed that at $T < 7$ K, Eq. (4) reproduces the heat capacity values for CON with the same uncertainty. As to the thermodynamic functions of the CON sample, those were estimated from the experimental data on the heat capacity between $T \to 0$ and 400 K. The calculation of the enthalpy $H^\circ(T) - H^\circ(0)$ and the entropy $S^\circ(T) - S^\circ(0)$ of the copolymer was made by the numerical integration of the relations $C_p^\circ = f(T)$ and $C_p^\circ = f(\ln T)$, respectively. The change of the Gibbs function $G^\circ(T) - H^\circ(0)$ was evaluated from the enthalpy and entropy values at appropriate temperatures, as demonstrated earlier [19]. For subsequent calculations, the zero entropy $S^\circ(0)$ of the partially crystalline copolymer was estimated by adopting it equal to the value of configurational entropy of its glassy part $S^\circ_{\mathrm{conf}} = 4.7$ J/(K mol). As the data [20] show, the numerical S°_{conf} value is usually close or equal to the value of the residual (zero) entropy $S^\circ(0)$ of a polymer and this fact was taken into account on estimating the absolute value of the entropy for the tested copolymer.

3.3. Standard enthalpy of combustion and thermodynamic parameters of copolymer formation

The values of the enthalpy of combustion and the enthalpy, entropy and Gibbs function of formation of the alternating copolymer of CO and norbornadiene at $T = 298.15$ K and standard pressure (Table 4) correspond to the equation:

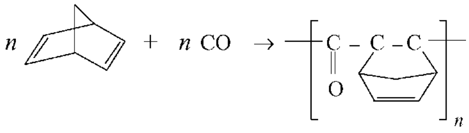
$$8\mathrm{C\,(gr)} + 4\mathrm{H_2\,(g)} + 0.5\mathrm{O_2\,(g)} \rightarrow -[\mathrm{C_8H_8O}]-\mathrm{(p.cr)}.$$

In parentheses are given the physical states of reagents: p.cr, partially crystalline; g, gaseous; gr, graphite.

The energy of combustion of partially crystalline CON (the amorphous part of the sample in the glassy state) was used to calculate its enthalpy of combustion $\Delta_c H^\circ$ and based on the latter the enthalpy of formation $\Delta_f H^\circ$ of the copolymer at $T = 298.15$ K and $p = 0.1$ MPa was estimated. On evaluating $\Delta_f H^\circ$ the standard enthalpies of formation of liquid water and gaseous carbon dioxide [21] were taken. The entropy of formation was calculated from the data on the entropy of CON with regard of the zero entropy of the partially crystalline copolymer (Table 3), entropies of gaseous hydrogen and oxygen as well as the crystalline carbon in the form of graphite [21]. The Gibbs function of formation $\Delta_f G^\circ$ was calculated from the $\Delta_f H^\circ$ and $\Delta_f S^\circ$ values under standard conditions.

3.4. Thermodynamic parameters of copolymerization of norbornadiene and CO

The copolymerization process of carbon monoxide with norbornadiene can be represented by the following scheme:



Scheme 1.

The values of the enthalpy, entropy and Gibbs function of copolymerization of carbon monoxide with norbornadiene in bulk with the formation of regularly alternating copolymer are given in Table 5. The enthalpy of copolymerization $\Delta_{\mathrm{cop}} H^\circ$ at $T = 298.15$ K and standard pressure was estimated from enthalpies of formation of the reagents such as CO [22],

Table 5
Thermodynamic characteristics of copolymerization process of carbon monoxide and norbornadiene in bulk resulting in formation of partly crystalline copolymer (α); $p = 0.1$ MPa

T (K)	Physical state of reagents[a]			$-\Delta_{\mathrm{pol}} H^\circ$ (kJ/mol)	$-\Delta_{\mathrm{pol}} S^\circ$ (J/(K mol))	$-\Delta_{\mathrm{pol}} G^\circ$ (kJ/mol)
	C_7H_8	CO	C_8H_8O			
0	cr	cr	p.cr	155	–5	155
100	cr	g	p.cr	155	169	138
200	cr	g	p.cr	160	187	123
298.15	l	g	p.cr	175	250	100
300	l	g	p.cr	175	250	100
340	l	g	p.cr	175	254	89

[a] cr, crystalline; l, liquid; g, gas; p.cr, partly crystalline state.

norbornadiene [23] and the copolymer (Table 4) and at other temperatures by Kirchhoff's formula. Temperature dependences of the heat capacity, temperatures and enthalpies of physical transformations of norbornadiene and CO were determined earlier [22,24] and for the copolymer in the present work. Entropies of copolymerization $\Delta_{cop}S^\circ(T)$ (Table 5) were evaluated from the absolute values of the entropy for CO and norbornadiene [22,24] and the copolymer (Table 3), and as in the case of $\Delta_f S^\circ$, the zero entropy $S^\circ(0)$ of the copolymer being taken into consideration. The values of the standard Gibbs function of copolymerization $\Delta_{cop}G^\circ(T)$ (Table 5) were determined by Gibbs–Helmholtz equation from the values of the enthalpies and entropies of the copolymerization process at the corresponding temperatures.

In the examined temperature range, the standard Gibbs function of copolymerization is negative and, therefore, the process equilibrium is shifted towards the formation of the copolymer and, judging by the Gibbs function value, an equilibrium reaction mixture mainly contains the copolymer.

The enthalpies and entropies of reaction in the temperature range under study are negative: the copolymerization process of norbornadiene and CO has the ceiling limiting temperature T°_{ceil}. It was determined graphically from the crossover point of the relations $\Delta_{cop}H^\circ(T) = f(T)$ and $T\Delta_{cop}S^\circ(T) = f(T)$ by the method described in [25] and, thus, T°_{ceil} was found to be 508 K. It was established [26] that T°_{ceil} has the maximum for processes proceeding in bulk. In this case, the T°_{ceil} value for CON testifies to the fact that at $T < T^\circ_{ceil}$ the copolymer is thermodynamically stable. If $T > T^\circ_{ceil}$, the copolymer depolymerization till the initial reagents is possible under appropriate kinetic conditions.

4. Thermodynamic properties of copolymers of norbornadiene and carbon monoxide of various structure

Earlier [5] the copolymer of norbornadiene and carbon monoxide of keto-exo-cis structure (CON1) was studied between 6 and 550 K. The C°_p values of CON lie below the heat capacity values of CON1 in the range $10\,K < T < 330\,K$ (Fig. 2). The difference in C°_p of the copolymers is 9–13% in the range $10\,K < T < 60\,K$. It amounts to *ca.* 11% in the interval $60\,K < T < 220\,K$ and at higher temperatures (220–330 K), where a smooth practically linear variation of the heat capacity of both copolymers occurs, the difference becomes lower (5–7%). Thus, the above C°_p differences cannot be attributed to an experimental uncertainty of the heat capacity measurement. The melting temperatures T°_{fus} and thermodynamic characteristics of fusion of the copolymers coincide within the measurement uncertainty while the fusion process does not complete because of the inceptive thermal destruction of the samples in the 495–510 K range.

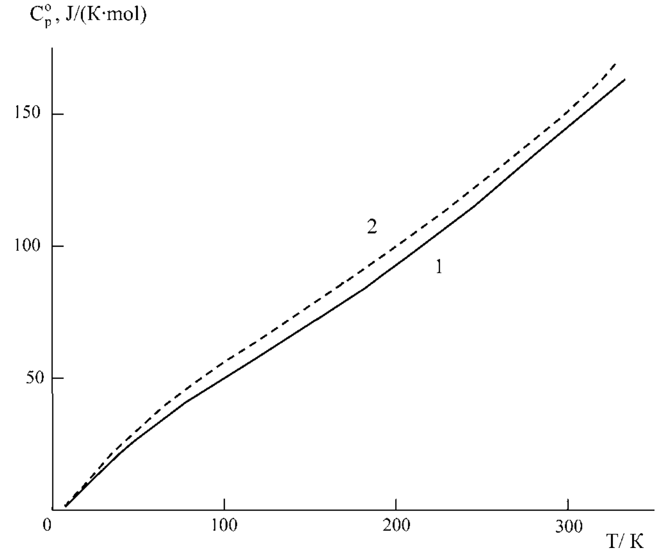


Fig. 2. Temperature dependences of heat capacity of partially crystalline copolymers of carbon monoxide and norbornadiene with different structures: 1, heat capacity of keto-ketal-exo-cis-form; 2, heat capacity of keto-exo-cis form.

The character of the change in the apparent heat capacity of the copolymers in the devitrification ranges is practically similar: the transformation occurs between 320 and 420 K, the value of the heat capacity jump on the devitrification differing by about 118 J/(K mol) that seems to be associated with the different degree of the crystallinity of the samples.

The calculated glass transition temperatures T°_g of CON and CON1 copolymers were 350 ± 1 and 367 ± 1 K, respectively, and consequently, those differ by ~20 K. This fact can be explained by various structures of the samples. The larger C°_p values of CON1 as compared to CON point to a more rigid structure of the latter that is related to the excitation of vibrational degrees of freedom at higher temperatures.

It was of interest to compare a relative thermodynamic stability of CON and CON1 by comparing their standard Gibbs functions of formation from the corresponding comonomers per the same mole of a repeating unit. The characteristics of the copolymerization of CO with norbornadiene at $T = 298.15$ K and $p = 101.325$ kPa are summarized in Table 6. The results show the differences in the $\Delta_f G^\circ$ values of the polyketones (for CON and

Table 6
Thermodynamic characteristics of formation of copolymers with keto-exo-cis and keto-ketal-exo-cis structure from corresponding monomers (CO and norbornadiene); $T = 298.15$ K, $p = 0.1$ MPa

Copolymer	Physical state of reagents[a]			$-\Delta_{pol}H^\circ$ (kJ/mol)	$-\Delta_{pol}S^\circ$ (J/(K mol))	$-\Delta_{pol}G^\circ$ (kJ/mol)
	C_7H_8	CO	C_8H_8O			
CON1	l	g	p.cr	141	226	74
CON				175	250	100

[a] l, liquid; g, gaseous; p.cr, partially crystalline.

CON1 100 and 74 ± 5 kJ/mol, respectively) that in turn points to a greater stability of CON, *i.e.* the copolymer with keto-ketal-exo-cis structure.

The copolymerization of CO with norbornadiene is thermodynamically permitted in the whole temperature range: $\Delta_{\mathrm{cop}}G^\circ < 0$. It is also seen that the thermodynamic parameters of the copolymerization process of CO and norbornadiene with the formation of copolymers with a different structure noticeably distinguish. For example, at 298.15 K for the copolymerization according to Scheme 1 the values of $\Delta_{\mathrm{cop}}H^\circ$ and $\Delta_{\mathrm{cop}}S^\circ$ when the copolymer of keto-ketal-exo-cis structure is formed are smaller by 34 and 24 J/(K mol), respectively. At the same time, the $\Delta_{\mathrm{cop}}G^\circ$ value is lower by 26 kJ/mol than that in the case of the copolymer with keto-exo-cis structure. The estimation of the ceiling limiting temperatures of the copolymerization by the procedure demonstrated in [25] gives the values 630 and 787 K for the synthesis of copolymers of keto-exo-cis and keto-ketal-exo-cis structure, respectively (liquid norbornadiene, gaseous CO, partially crystalline polymer).

Thus, in the present work, on the base of the thermodynamic properties determined by methods of adiabatic and isothermal calorimetry for the regularly alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide (keto-ketal-exo-cis structures) and the literature data on the regularly alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide of keto-exo-cis structure, the effect of the copolymer structure on its thermodynamic properties has been shown.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.09.018.

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