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Thermodynamics of alternating copolymer of styrene and CO in the 0—600 K region

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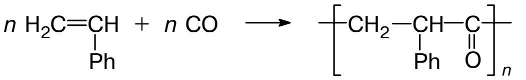
The temperature dependence of heat capacity and the temperatures and enthalpies of physical transitions of the alternating copolymer of styrene and CO were studied in the 5—600 K region by the adiabatic vacuum and dynamic calorimetric techniques. The heat of combustion of the copolymer was measured at 298.15 K in a calorimeter with a static bomb and an isothermal shield. The thermodynamic parameters of glass transition and fusion were determined. The thermodynamic functions in the 0—550 K region and thermodynamic characteristics of the formation of the copolymer from simple substances at T = 298.15 K and p = 101.325 kPa were calculated. The thermodynamic parameters of alternating copolymerization in the bulk of styrene and CO were calculated in the 0—350 K region at a standard pressure.

Key words: styrene—carbon monoxide copolymer, thermodynamic functions, heat capacity, enthalpy, entropy, Gibbs function.

Alternating copolymers of styrene and carbon monoxide (SCO) are representatives of a new class of polymers, *viz.*, polyketones, which are of great scientific and practical interest.[1,2] They are prepared by the copolymerization of styrene and CO in the presence of palladium(II) complexes with the bidentate N—N or P—N ligands.[1,3] The reaction in the general form can be presented by the following scheme (Scheme 1).

Scheme 1



$$n\,H_2C{=}\underset{\displaystyle Ph}{CH} + n\,CO \longrightarrow \left[-CH_2-\underset{\displaystyle Ph}{CH}-\underset{\displaystyle O}{\overset{}{C}}-\right]_n$$

Copolymerization is performed in both protic (for example, in alcohol) and aprotic solvents, however, the reaction can occur in the gas phase.[4] Depending on conditions, copolymers with different microstructures of macromolecules can be formed: with different types of connection between styrene and CO ("head-to-head," "head-to-tail," "tail-to-tail") and different tacticities (atactic, isotactic, or syndiotactic copolymers).

We have previously[5,6] published the results of calorimetric studies of the thermodynamic properties of alternating copolymers of CO with ethylene and propylene and the thermodynamic characteristics of these reactions in the 0—500 K region.

This work is aimed at calorimetric studying the thermodynamic properties of alternating SCO in the 5—600 K region, namely, the heat capacity as function of temperature and the temperatures and enthalpies of physical transitions; determination of the combustion energy of the copolymer; calculation (from the obtained data) of the thermodynamic characteristics of physical transitions and thermodynamic functions in the 0—550 K region and the standard thermodynamic parameters of formation of the copolymer from simple substances at 298.15 K and standard pressure; calculation of the thermodynamic parameters of the reaction in Scheme 1 in the 0—350 K region using the thermodynamic parameters of CO and styrene published earlier.[7—9]

Experimental

The sample of SCO was obtained by a known procedure[10] using the Pd-containing catalytic system. Found (%): C, 81.94. Calculated (%): C, 81.79. The viscosity of the copolymer [η] = 0.5 dL g^{-1} was determined at 299 K in *m*-cresol. ^{13}C NMR spectra obtained on a Gemini-300 instrument (Varian) showed that the sample is syndiotactic. The copolymer with this microstructure is insoluble in standard solvents but is soluble in *m*-cresol. According to X-ray diffraction data (DRON-UM1), the SCO sample is partially crystalline. Based on our calorimetric measurements, the degree of its crystallinity is α = 43%.

A TAU-1 adiabatic vacuum calorimeter was used for studying the temperature dependence of the heat capacity of the copolymer and the temperatures and enthalpies of its physical transitions in the 5—340 K region.[11,12] In this instrument, the error of measurements of heat capacities of substances at helium temperatures is ±2%, ±0.4% at 40 K, and 0.2% within 40—340 K.[13] To study the heat capacity of SCO in the

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300—600 K region, we used an ADKTTM thermoanalytical complex, that is a dynamic calorimeter operating by the principle of triple thermal bridge[14] (with the measurement error of $C_p°$ 1—4%). In the 300—340 K interval, the heat capacity of substances was measured using adiabatic vacuum and dynamic calorimeters. The operating conditions of the dynamic calorimeter were chosen in such a way that the $C_p°$ values in both calorimeters were the same. The error of measurement of $C_p°$ in ADKTTM at $T > 340$ K was accepted to be equal to ±(0.5—1.5)%.

The combustion energy of the SCO sample was measured in a V-08 calorimeter with an isothermic shield and static bomb. The calorimeter was modified by the Research Institute of Chemistry of the Nizhnii Novgorod State University.[15] The verification of the calorimeter by combustion of the standard succinic acid gave the enthalpy of combustion corresponding to the passport value with an error of 0.017%.

The heat capacity $C_p°$ of the copolymer was measured in the adiabatic vacuum calorimeter in the 5—340 K region (specimen 0.3255 g) and in the dynamic calorimeter in the 300—600 K region (specimen 0.4078 g). In both calorimeters the heat capacity of the specimens was 15—35% of the overall heat capacity of the corresponding calorimetric ampules filled with the substance. In 15 series of measurements we obtained ~1500 experimental $C_p°$ values. Experimental $C_p°$ values were averaged using a computer. The root-mean-square deviations of the $C_p°$ values from the corresponding averaging curves $C_p° = f(T)$ were at most ±0.12% within 5—90 K, ±0.08% in the 90—340 K region, and ~±0.2% within 340—600 K. Measurements of $C_p°$ in a dynamic calorimeter were carried out in the continuous heating mode with a heating rate of 0.02 K s^{-1}.

The SCO sample was burnt in a mixture with standard benzoic acid in a ratio of 1 : 3 (the standard combustion energy $\Delta U_c°$ of benzoic acid is −26454.4 J g^{-1}). The combustion energy was determined in seven experiments. The weights of the SCO specimens to be burnt were 0.1461—0.1929 g. The quantity of energy ΔU_c evolved under the conditions of calorimetric bomb was 19209—21260 J. Standard thermochemical corrections were introduced in the calculation of the standard combustion energy $\Delta U_c°$. When preparing the combustion experiments, all procedures with SCO were carried out in air. The ratios of the weights of CO_2 found in the combustion products and those calculated from the reaction equation of SCO oxidation with dioxygen were 99.8—99.9%. The average value is $\Delta U_c = -4563.9 \pm 3.8$ kJ mol^{-1}. Based on this value, the combustion energy of SCO was calculated at a standard pressure: $\Delta U_c° = -4560.6 \pm 3.8$ kJ mol^{-1}. The latter, in turn, was used for the calculation of the standard enthalpy of combustion of the copolymer $\Delta H_c°(\alpha = 43\%) = -4564.3$ kJ mol^{-1}. It corresponds to the thermal effect of the reaction

$$\text{-}\!\!\left[C_9H_8O\right]\!\!\text{-}\ (\text{p.cr}) + 10.5\ O_2\ (\text{g}) \longrightarrow$$
$$\longrightarrow 9\ CO_2\ (\text{g}) + 4\ H_2O\ (\text{l})$$

at 298.15 K and a standard pressure (physical states of reactants are indicated in parentheses: p.cr is partially crystalline, g is gaseous, and l is liquid).

Results and Discussion

Heat capacity. The temperature dependence of heat capacity ($C_p°$) of SCO is presented in Fig. 1. Only each of three measured $C_p°$ values are presented in Fig. 1 because of great number of experimental $C_p°$ values obtained in a dynamic calorimeter (at $T > 340$ K). It is seen that the heat capacity of the initial partially crystalline SCO sample increases gradually in the 5—360 K region (curve *AB*). Further, in the 360—430 K interval (curve *BG*), the increase in $C_p°$ becomes somewhat faster, most likely, due to the devitrification of the amorphous part of the polymer. This effect is observed in a wide temperature interval (~70 K), which is probably related to the influence of the crystalline phase.[16] In the 430—500 K interval, $C_p°$ again increases smoothly with temperature (curve *GD*). At 500 K the heat capacity increases sharply, which is related to the beginning of fusion of the crystalline constituent of the sample. Fusion occurs in the 500—550 K region, and the apparent heat capacity *DEF* corresponds to fusion. The heat capacity of the melt before the beginning of thermal decomposition of the polymer is described by curve *FR* (in the 550—570 K interval). When the polymer is heated above ~570 K the heat capacity increases sharply (curve *RM*) due to copolymer decomposition. On cooling the melt from ~555 K to $T < T_{gl}°$ ($T \approx 300$ K), the copolymer did not crystallize but supercooled and vitrified. The devitrification of such an amorphous SCO sample occurred in the 360—390 K interval, and the corresponding plot of $C_p°$ *vs.* T is described by curve *BL*. The heat capacity of the SCO supercooled melt (highly elastic) is described by curve *LP*, and that of the liquid sample is reflected by curve *PR*.

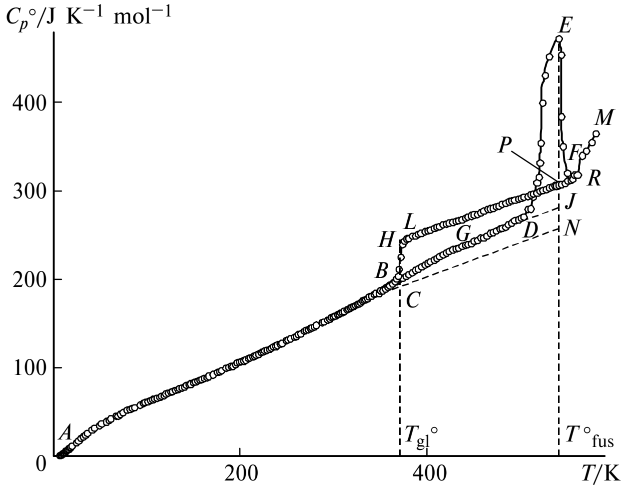

Fig. 1. Temperature dependence of heat capacity of SCO: *ABGD* is the partially crystalline sample (*AB* is the amorphous fraction of the copolymer in the glassy state, *GD* is the amorphous fraction of the copolymer in the highly elastic state, *BG* in the devitrification interval of the amorphous fraction of the partially crystalline copolymer), *DEF* is the apparent heat capacity in the fusion region of the crystalline part of the copolymer, *FR* is melt, *RM* is the apparent heat capacity in the copolymer decomposition region; *ACN* is the crystalline sample, *AC* is the glassy sample; *HP* is the copolymer in the highly elastic state, *PR* is melt, *BL* is the devitrification interval; $T_{gl}°$ is the vitrification temperature, $T°_{fus}$ is the fusion temperature.

Parameters of vitrification and glassy state. Below we present the parameters of vitrification and the glassy (gl) state of SCO obtained from our calorimetric data.

T_{gl}° /K	$\Delta C_p^\circ(T_{\mathrm{gl}}^\circ)$	S°_{conf}	$H_{\mathrm{gl}}^\circ(0) - H_{\mathrm{cr}}^\circ(0)$ /kJ mol^{-1}
	J K^{-1} mol^{-1}		
373	45.0	12	7.4

The temperature interval of vitrification $\Delta T_{\mathrm{gl}}^\circ$ was determined from the plot (see Fig. 1, curve *BL*): the temperature corresponding to point *B* belongs to the beginning of devitrification, and point *L* indicates the end.

The vitrification temperature T_{gl}° was determined from the inflection point in the temperature plot of entropy $S^\circ(T) = f(T)$ in the vitrification interval.[17] The error of determination of T_{gl}° by this method is usually at most 0.5—1.0 K. The increase in the heat capacity during devitrification $\Delta C_p^\circ(T_{\mathrm{gl}}^\circ)$ was found graphically (*CH* segment in Fig. 1).

The configurational entropy S°_{conf} of the glassy copolymer was calculated from the formula[18]

$$S^\circ_{\mathrm{conf}} = \int_{T_2^\circ}^{T_{\mathrm{gl}}^\circ} \Delta C_p^\circ(T_{\mathrm{gl}}^\circ)\,\mathrm{d}\ln T\,, \qquad (1)$$

where T_2° is the Kauzmann temperature.[19] It is usual for polymers that $T_{\mathrm{gl}}^\circ/T_2^\circ = 1.29\pm0.14$.[18] In the calculation of S°_{conf} we assumed that this ratio is also fulfilled in the case of SCO. It was established[18,20] that S°_{conf} makes the main contribution to the zero entropy $S_{\mathrm{gl}}^\circ(0)$ of the polymer in the glassy state, and often $S^\circ_{\mathrm{conf}} \approx S_{\mathrm{gl}}^\circ(0)$. Based on this, we also accepted $S^\circ_{\mathrm{conf}} = S_{\mathrm{gl}}^\circ(0)$ with the purpose for using it further for the estimation of absolute values of entropy of SCO in the amorphous state. The difference of zero enthalpies of the copolymer in the glassy and crystalline states ($H_{\mathrm{gl}}^\circ(0)$ and $H_{\mathrm{cr}}^\circ(0)$, respectively) was calculated by the equation (see, *e.g.*, Ref. 21)

$$H^\circ_{\mathrm{gl}}(0) - H^\circ_{\mathrm{cr}}(0) = \int_0^{T^\circ_{\mathrm{fus}}} \left[C_p^\circ(\mathrm{cr}) - C_p^\circ(\mathrm{a})\right]\mathrm{d}T + \Delta H^\circ_{\mathrm{fus}}\,, \qquad (2)$$

where $C_p^\circ(\mathrm{cr})$ and $C_p^\circ(\mathrm{a})$ are the temperature functions of the heat capacity of the copolymer in the crystalline (cr) and amorphous (a) states, and $\Delta H^\circ_{\mathrm{fus}}$ is the enthalpy of fusion of the copolymer with 100% crystallinity.

It was accepted in the calculation of $H_{\mathrm{gl}}^\circ(0) - H_{\mathrm{cr}}^\circ(0)$ of SCO that curve *ACN* (see Fig. 1) corresponds to C_p° of the copolymer with 100% crystallinity, and curve *ABLP* corresponds to C_p° of the copolymer in the amorphous state. This approach is based on the fact that in the temperature region from 80 K to T_{gl}° the heat capacities of the polymer in the glassy, partially crystalline, and crystalline states coincide within the error of measurements of C_p° (~0.2%).[21,22] At $T < 80$ K the heat capacity C_p° of the polymer in the amorphous state is usually by several percents higher than that for the same polymer in the crystalline state.[23] Therefore, the real plot of C_p° *vs.* T for crystalline SCO at $T < 80$ K lies somewhat lower than the corresponding region of curve *AC*, whereas that for the amorphous sample lies a little higher. This approximation must not contribute a considerable error to the calculation of the $H_{\mathrm{gl}}^\circ(0) - H_{\mathrm{cr}}^\circ(0)$ value, although we should keep in mind that the obtained value is somewhat overestimated.

Thermodynamic parameters of fusion. Fusion of SCO occurs in the 500—550 K interval. The temperature corresponding to the maximum value of the apparent heat capacity in the fusion interval $C_p^\circ = 473$ J K^{-1} mol^{-1} (point *E*, see Fig. 1) is accepted to be the fusion temperature T°_{fus} of SCO. The enthalpy of fusion of the studied sample $\Delta H^\circ_{\mathrm{fus}}(\alpha)$ was calculated graphically as a surface area confined by line *DEFPJD*. The entropy of fusion $\Delta S^\circ_{\mathrm{fus}}(\alpha)$ was calculated from the $\Delta H^\circ_{\mathrm{fus}}(\alpha)$ and T°_{fus} values.

The entropy of fusion of completely crystalline SCO was calculated by the equation

$$\Delta S^\circ_{\mathrm{fus}}(\alpha = 100\%) = S^\circ_{\mathrm{gl}}(0) - \int_0^{T^\circ_{\mathrm{fus}}} \left[C_p^\circ(\mathrm{cr}) - C_p^\circ(\mathrm{a})\right]\mathrm{d}\ln T\,. \qquad (3)$$

(Designations of the quantities in the equation are presented above.)

For the temperature functions $C_p^\circ(\mathrm{cr})$ and $C_p^\circ(\mathrm{a})$, we accepted the same assumptions as those for the calculation of $H_{\mathrm{gl}}^\circ(0) - H_{\mathrm{cr}}^\circ(0)$.

The enthalpy of fusion of SCO ($\alpha = 100\%$) was calculated from the entropy of fusion $\Delta S^\circ_{\mathrm{fus}}(\alpha = 100\%)$ and T°_{fus} using the formula

$$\Delta H^\circ_{\mathrm{fus}}(\alpha = 100\%) = T^\circ_{\mathrm{fus}} \cdot \Delta S^\circ_{\mathrm{fus}}(\alpha = 100\%). \qquad (4)$$

The degree of crystallinity of the studied SCO sample ($\alpha = 43\%$) was calculated from the formula[24]

$$\alpha = \frac{\Delta H^\circ_{\mathrm{fus}}(\alpha)}{\Delta H^\circ_{\mathrm{fus}}(\alpha = 100\%)} \cdot 100\,. \qquad (5)$$

The calculated thermodynamic parameters of fusion for the SCO sample with crystallinity α and for the completely crystalline sample at $T^\circ_{\mathrm{fus}} = 538$ K are presented below.

α (%)	$\Delta H^\circ_{\mathrm{fus}}$ /kJ mol^{-1}	$\Delta S^\circ_{\mathrm{fus}}$ /J K^{-1} mol^{-1}
43	5.5	10.2
100	12.8	24.0

Thermodynamic functions. For the calculation of the thermodynamic functions of SCO (Table 1), the heat capacity in the 0—5 K temperature range was obtained by the extrapolation of the experimental dependence $C_p^\circ = f(T)$ using the Debye function of heat capacity

$$C_p^\circ = nD(\theta_{\mathrm{D}}/T), \qquad (6)$$

where D is the Debye function of heat capacity, and n and θ_{D} are specially selected parameters. At $n = 2$ and

Table 1. Thermodynamic functions of SCO (calculated per mole of the monomeric unit of the copolymer)

T/K	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
		Crystalline state		
0	0	0	0	0
5	0.4712	0.157	0.0006	0.0002
10	3.118	1.179	0.0088	0.0030
15	7.418	3.227	0.0347	0.0136
20	11.91	5.965	0.0829	0.0364
25	16.42	9.103	0.1535	0.0740
30	20.83	12.49	0.2467	0.1279
40	28.86	19.61	0.4963	0.2881
50	35.71	26.82	0.8206	0.5204
60	41.57	33.86	1.207	0.8240
70	47.03	40.68	1.651	1.197
80	52.18	47.30	2.147	1.637
90	57.04	53.73	2.693	2.142
100	61.66	59.98	3.287	2.710
150	83.52	89.13	6.919	6.451
200	106.6	116.3	11.66	11.59
250	131.6	142.7	17.61	18.07
298.15	157.1	168.0	24.56	25.55
350	186	196	33.5	35.0
400	213	222	43.4	45.4
450	240	249	54.8	57.2
500	267	276	67.5	70.3
538	293	296	78.0	81.1
		Liquid state		
538	306	320	90.8	81.1
550	311	326	94.0	85.0
555	313	329	96.1	86.7
		Glassy state		
0	0	12	0	0
10	3.118	12.8	0.0068	0.1208
15	7.418	14.8	0.0325	0.1895
20	11.91	17.5	0.0811	0.2698
25	16.42	20.7	0.1513	0.3656
30	20.83	24.1	0.2449	0.4770
40	28.86	31.2	0.4944	0.7529
50	35.71	38.4	0.8191	1.100
60	41.57	45.4	1.207	1.518
70	47.03	52.2	1.650	2.007
80	52.18	58.9	2.146	2.563
90	57.04	65.3	2.693	3.184
100	61.66	71.6	3.286	3.868
150	83.52	100.7	6.918	8.187
200	106.6	127.8	11.66	13.91
250	131.6	154.3	17.61	20.96
273.15	143.7	166.5	20.80	24.67
298.15	157.2	179.6	24.56	29.00
300	158.2	180.6	24.85	29.33
350	187	207	33.5	39.0
373	200	219	37.9	43.9
		Highly elastic state		
373	245	219	37.9	43.9
400	255	237	44.7	50.1
450	273	268	57.9	62.7
500	292	298	72.0	76.9
538	306	320	83.4	88.6

θ_D = 70.02 K Eq. (6) describes the experimental $C_p°$ values in the 5—10 K temperature interval with an error of ±0.6%. It was accepted in the calculations that in the 0—5 K interval Eq. (6) reproduces the $C_p°$ values with the same error. The enthalpy $H°(T) - H°(0)$ and entropy $S°(T)$ were calculated by the integration of the functions of $C_p°$ *vs.* T and $\ln T$, respectively, and the Gibbs function was calculated from the enthalpy and entropy values using the formula

$$G°(T) - H°(0) = [H°(T) - H°(0)] - TS°(T). \qquad (7)$$

In the calculation of $S°(T)$ of the amorphous copolymer, its zero entropy $S°(0)$ was taken into account and was accepted equal to its $S°_{\text{conf}}$. The equations for the calculation of the functions have been published in Ref. 21.

Thermodynamic parameters of SCO formation. The combustion energy of the SCO sample with 43% crystallinity (with the amorphous constituent in the glassy state) was used for the calculation of enthalpies of combustion of the copolymer in the crystalline (cr) and amorphous (a) states using the equations

$$\Delta H°_c\ (\text{cr}) = \Delta H°_c\ (\alpha) + (1 - \alpha)\Delta H°_{\text{fus}}(298.15\ \text{K}), \qquad (8)$$

$$\Delta H°_c\ (\text{a}) = \Delta H°_c\ (\alpha) - \alpha\Delta H°_{\text{fus}}(298.15\ \text{K}), \qquad (9)$$

where α is the degree of crystallinity, and $\Delta H°_{\text{fus}}(298.15\ \text{K})$ is the enthalpy of fusion of the copolymer at 298.15 K. The $\Delta H°_{\text{fus}}(298.15\ \text{K})$ value was calculated from $\Delta H°_{\text{fus}}(\alpha = 100\%)$ at $T°_{\text{fus}}$ and temperature plots of the heat capacity of the copolymer in the crystalline and amorphous states using the formula[15]

$$\Delta H°_{\text{fus}}(298.15\ \text{K}) = \\ = \Delta H^{\circ}_{\text{fus}}(T^{\circ}_{\text{fus}}) + \int_{298.15}^{T^{\circ}_{\text{fus}}} \left[C^{\circ}_{\text{p}}(\text{cr}) - C^{\circ}_{\text{p}}(\text{a})\right] \mathrm{d}T. \qquad (10)$$

The enthalpies of formation $\Delta H_f°(\text{cr})$ and $\Delta H_f°(\text{a})$ were calculated similarly. The entropy of formation of the copolymer in the same physical states was calculated using the values of entropies of the copolymer, carbon in the graphite form, and gaseous H_2.[8] The Gibbs function of formation $\Delta G_f°$ was calculated from $\Delta H_f°$ and $\Delta S_f°$. The obtained values correspond to the process

$$9\ \text{C (gr)} + 4\ \text{H}_2\ \text{(g)} + 0.5\ \text{O}_2\ \text{(g)} \longrightarrow$$

$$\longrightarrow \left[\text{C}_9\text{H}_8\text{O}\right] \text{(cr or a)},$$

where gr is graphite. The enthalpies of formation of liquid H_2O (l) and gaseous CO_2 (g) necessary for calculations and the entropies of formation of graphite C (gr), H_2 (g), and O_2 (g) at T = 298.15 K and p = 101.325 kPa were taken from Ref. 8. The values of all mentioned standard quantities are presented below.

Parameter	Crystal	Highly elastic state
$-\Delta H_c°$/kJ mol^{-1}	4560.0±2.0	4567.5±2.0
$-\Delta H_f°$/kJ mol^{-1}	124.9±2.0	117.4±2.0
$\Delta G_f°$/kJ mol^{-1}	26.6±2.0	30.7±2.0
$-\Delta S_f°$/J K^{-1} mol^{-1}	508.3±2.0	496.7±2.0
$-\ln K_f°$	10.7	12.4

Thermodynamic parameters of copolymerization of styrene and CO. The enthalpy of copolymerization $\Delta H°_{cop}$ at 298.15 K and a standard pressure was calculated from the enthalpies of formation of the reactants, *viz.*, copolymer (see above), styrene,[8] and CO.[8] At other temperatures $\Delta H°_{cop}(T)$ was calculated using the Kirchhoff formula (Table 2). The temperature plots of the heat capacity, temperatures and enthalpies of physical transitions of styrene and CO were determined earlier,[7,9] and those for the copolymer, in this work. The entropies of copolymerization $\Delta S°_{cop}(T)$ (see Table 2) were calculated from the absolute values of entropy of the reactants: the absolute entropies of styrene and CO were published earlier,[7,9] and for those of the copolymer see above. The standard values of the Gibbs function of copolymerization $\Delta G°_{cop}(T)$ (see Table 2) were calculated from the enthalpy and entropy of the reaction at the corresponding temperatures.

The enthalpy and entropy of the reaction in the studied temperature region are negative except $\Delta S°_{cop}(0)$. It follows from this that the copolymerization process has the ceiling temperature $T°_{ceil}$. It was determined graphically from the interception point of the plots $\Delta H°_{cop}(T) = f(T)$ and $T\Delta S°_{cop}(T) = f(T)$, and it turned out to be 450 K. It was established[25] that $T°_{ceil}$ is maximal for processes in the bulk. In this case, the $T°_{ceil}$ value found for SCO indicates that the copolymer is thermodynamically stable at $T < T°_{ceil}$ and at $T > T°_{ceil}$ it can additionally be depolymerized to the initial reactants under the corresponding kinetic conditions.

Table 2. Thermodynamic parameters* of the copolymerization of CO—styrene in bulk at p = 101.325 kPa

T /K	Physical state of reactants**			$-\Delta H°_{cop}$	$-\Delta G°_{cop}$	$-\Delta S°_{cop}$
	C_8H_8	CO	$-[-C_9H_8O-]_n-$			
0	cr	cr	cr	86	86	0
	cr	cr	gl	79	79	−12
100	cr	g	cr	97	81	158
	cr	g	gl	90	75	146
200	cr	g	cr	101	63	190
	cr	g	gl	93	57	178
298.15	l	g	cr	118	40	261
	l	g	gl	111	37	249
350	l	g	cr	121	27	269
	l	g	gl	113	23	257

* Standard values of Gibbs function ($\Delta G°_{cop}$/kJ mol^{-1}), enthalpy ($\Delta H°_{cop}$/kJ mol^{-1}), and entropy ($\Delta S°_{cop}$/J K^{-1} mol^{-1}).
** The following designations were used: cr is crystalline, gl is glassy, l is liquid, g is gaseous phases.

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