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Thermodynamics of alternating copolymer of propylene and CO in the 0—550 K region

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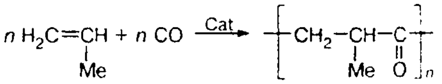
The temperature dependences of the heat capacity and the temperatures and enthalpies of physical transitions of the alternating copolymer of propylene and CO were studied in the 5—550 K region by adiabatic vacuum and dynamic calorimetry techniques. The heat of combustion of the copolymer was measured at 298.15 K in a calorimeter with a static bomb and an isothermal shield. The thermodynamic parameters of glass transition and fusing were estimated. The thermodynamic functions in the 0—450 K region and the 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 the alternating copolymerization of bulk propylene and CO were calculated in the 0—450 K region at standard pressure.

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

Alternating propylene copolymer with carbon monoxide (COP) is assigned to a new class of polymers — polyketones,[1,2] which are of great scientific and practical interest.[2,3]

Alternating COP is prepared by copolymerization of comonomers in the presence of palladium(II) complexes with chiral *cis*-bidentate ligands[4—7] or with nonsymmetrical phosphinephosphite.[8] The copolymerization reaction can be presented by the following scheme:



$$n\,H_2C{=}CH(Me) + n\,CO \xrightarrow{Cat} \left[-CH_2-CH(Me)-C(=O)-\right]_n \qquad (1)$$

MeOH, DCE, or toluene are most often used as solvents.[2] However, copolymerization can also occur in the gas phase.[9] Depending on the reaction conditions, copolymers with different microstructures of macromolecules can be formed: with different types of propylene and CO addition ("head-to-head," "head-to-tail") and different tacticities (isotactic, syndiotactic, and atactic).

The thermodynamic properties of the alternating ethylene and CO copolymer and the thermodynamic parameters of copolymerization in the 0—600 K region were studied.[10]

The purpose of this work is the calorimetric study of the thermodynamic properties of alternating COP in the 0—550 K region and calculation (from the data obtained) of the thermodynamic parameters of formation and physical transformations of COP using the corresponding thermodynamic parameters of CO and propylene.[11—13]

Experimental

The starting COP sample was prepared by the catalytic copolymerization of propylene with CO in the $Pd(CH_3COO)_2$—diphenylphosphinepropane—HBF_4 system (solvent, MeOH + CH_2Cl_2) at 298 K. Found (%): C, 68.52; H, 8.64. Calculated (%): C, 68.57; H, 8.57. The weight-average ($M_w = 3 \cdot 10^4$) and number-average ($M_n = 1.8 \cdot 10^4$) molecular weights of the copolymer were measured by the GPC method; polydispersity $M_w/M_n = 1.66$. ^1H and ^{13}C NMR spectra of a solution of the copolymer in $CDCl_3$ (concentration 0.1 g mL^{-1}) were recorded on a Gemini-300 instrument (Varian). The ^1H NMR spectrum (Fig. 1) contains signals in three regions, δ: 0.8—1.2 (CH_3); 2.2—2.5 (CH); 2.7—3.2 (CH_2). The ^{13}C NMR spectrum exhibits signals of C cores of different types, δ: 16.0—17.0 (CH_3); 38.5—41.0 (CH_2); 207.0—216.0 (C=O). Signals of the CO groups (Fig. 2) are additionally split into three regions, depending on the three possible positions of

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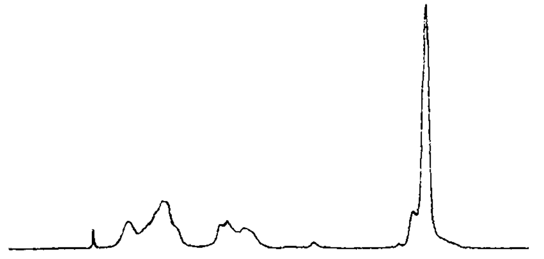

Fig. 1. ^{1}H NMR spectrum of propylene copolymer with carbon monoxide.

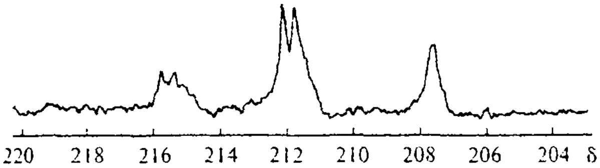

Fig. 2. ^{13}C NMR spectrum of propylene copolymer with carbon monoxide. Resonance region of CO groups, 3200 accumulations.

propylene with respect to the carbonyl group: "tail-to-tail," $CH(CH_3)CH_2COCH_2CH(CH_3)$, 208.0 ppm; "head-to-head," $CH_2CH(CH_3)COCH(CH_3)CH_2$, 214.5—216.0 ppm; and "head-to-tail," $CH_2CH(CH_3)COCH_2CH(CH_3)$, 211.0—212.5 ppm. Diethyl ketone, diisopropyl ketone, and ethyl isopropyl ketone can be model compounds for these fragments; signals of the CO groups in their ^{13}C NMR spectra appear[14] at 209.0, 215.4, and 213.4 ppm, respectively. Each random addition of the propylene molecule by the "head-to-head" type results in the appearance in the spectrum of the CO fragment with neighbors "head-to-head" and "tail-to-tail." Since the ratio of "head-to-head" and "tail-to-tail" fragments in the spectra recorded was 1 : 1, the addition can be considered random. The ratio of probabilities of "head-to-head" and "tail-to-tail" additions is 1.23. The signals of CO in the 211.0—212.5 and 214.5—216.0 ppm regions and the signals of C atoms in the CH_2 and CH groups are additionally split, probably due to different stereochemical sequences of chiral centers on the methylene C atom and due to the influence of the type of addition.

According to XRD data (X-ray diffraction patterns of samples were obtained on a DRON-UM1 diffractometer, Cu-Kα radiation), the copolymer is partially crystalline. The degree of crystallinity (α) estimated by us from the calorimetric data using the described procedure[15] was 60%.

To study the temperature dependence of the heat capacity and the temperatures and enthalpies of physical transformations in the 5—340 K region, we used a TAU-1 adiabatic vacuum calorimeter.[16] The error of measurements of the heat capacity of substances at helium temperatures was ±2% and decreased to ±0.4% for a temperature increase to 40 K and to 0.2% in the 40—340 K range.[17] To determine C°_p in the 300—550 K region, we used the ADKTTM thermoanalytical complex, a dynamic calorimeter working on the principle of a triple thermal bridge[18] (the measurement error for C°_p was 1—4%). Within the 300—340 K range, the heat capacity of substances was measured on adiabatic vacuum and dynamic calorimeters, and the conditions of measurements on the dynamic calorimeter were selected so that the C°_p values on both calorimeters coincided. Therefore, we assumed that the measurement error for C°_p on ADKTTM at $T > 340$ K was ±(0.5—1.5)%.

The combustion energy of partially crystallized COP was determined on a calorimeter with an isothermic shell and a V-08 static bomb, which was improved in the Research Institute of Chemistry at the Nizhnii Novgorod State University.[19] Verification of the calorimeter by combustion of standard succinic acid gave an enthalpy of combustion corresponding to the licensed value with an error of 0.017%.

The heat capacity (C°_p) of COP was measured on an adiabatic vacuum calorimeter in the 5—340 K region (weight of the sample, $0.4003 \cdot 10^{-3}$ kg) and on a dynamic calorimeter in the 300—550 K region (weight of the sample, $0.4677 \cdot 10^{-3}$ kg). In both calorimeters, the heat capacity of samples was 20—30% of the total heat capacity of the calorimetric ampules with the substance. In 15 series reflecting the order of measurements, we obtained 1387 experimental C°_p values. The mean-square deviations of the C°_p values from the corresponding averaging curves $C^\circ_p = f(T)$ did not exceed ±0.13% in the 5—90 K region, ±0.09% in the 90—240 K region, and ±0.02% in the 240—550 K region. Measurements of C°_p on the dynamic calorimeter were carried out in a regime of continuous heating. The rate of heating was $3.3 \cdot 10^{-2}$ K s^{-1}.

The COP sample with a weight of $(0.2677—0.3345) \cdot 10^{-3}$ kg was burnt in a mixture with benzoic acid 1 : 3 (the combustion energy (ΔU°_c) of benzoic acid is equal to -26454.4 J g^{-1}). Combustion energies were measured in four experiments.* The amount of evolving energy ΔU_c = 28765—30213 J. For calculation of the ΔU_c value, standard thermochemical corrections were applied. During preparation of experiments on combustion, all procedures with COP were carried out in air. The ratio of the weights of CO_2 found in the combustion products and calculated by the reaction equation of the oxidation of COP with dioxygen was 99.8—99.9%. Under conditions of combustion in a calorimetric bomb, we obtained the average value ΔU_c = -2193.1 ± 1.2 kJ mol^{-1}. Based on this value, we calculated the combustion energy of COP at the standard pressure ΔU°_c = -2191.9 ± 1.2 kJ mol^{-1}. The latter was used for calculation of the standard enthalpy of combustion of the copolymer ΔH°_c (α = 60%) = -2194.4 kJ mol^{-1}. The value obtained corresponds to the heat effect of the reaction

$$-\!\!\left[C_4H_6O\right]\!\!- \text{(p.cr)} + 5\,O_2\,\text{(g)} \longrightarrow 4\,CO_2\,\text{(g)} + 3\,H_2O\,\text{(l)}$$

at T = 298.15 K and standard pressure. The physical states of the reagents are indicated in parentheses: p.cr, partially crystalline state (degree of crystallinity α = 60%); l, liquid state; and g, gaseous state.

Results and Discussion

The heat capacity of the initial partially crystallized (α = 60%) COP increases smoothly with temperature increase within the 5—280 K region (Fig. 3, curve *AB*). Then it increases comparatively sharply, due, most likely, to the simultaneous beginning of processes of glass transition of the amorphous part of the polymer and

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* Experiments on measurements of the combustion energy of COP were carried out by E. G. Kiparisova.

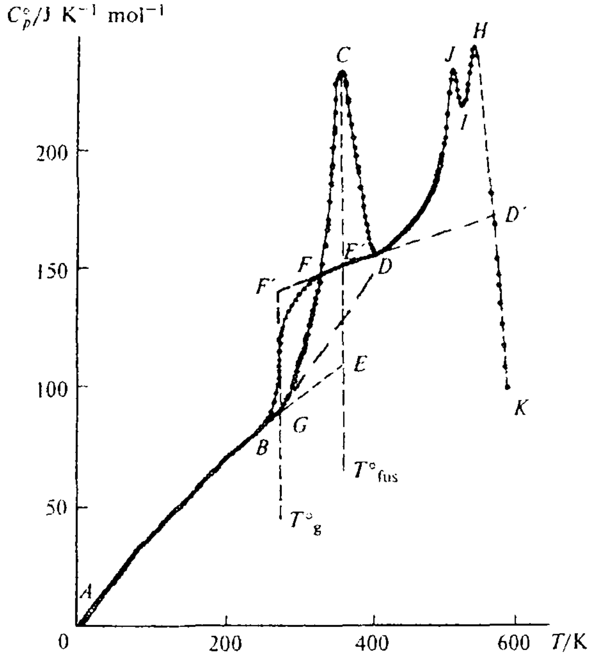

Fig. 3. Temperature dependence of the heat capacity of regular alternating COP: *ABG*, partially crystalline (α = 60%); *AB*, glassy; *ABGE*, crystalline (α = 100%) state; *BF*, heat capacity in the range of COP glass transition in the amorphous state (α = 0); *FD*, high-elasticity; *DD′*, liquid state; *GCD*, apparent heat capacity in the range of fusing of the crystalline part of COP; *DJIHD′K*, apparent heat capacity in the range of copolymer decomposition; *GF″*, increase in heat capacity in the glass transition range; T°_g, glass transition temperature; T°_{fus}, fusing temperature.

fusing of the crystalline part. Fusing proceeds within the 280—410 K region, and the apparent heat capacity corresponds to it (see Fig. 3, curve *GCD*). When the melt formed is cooled from ~415 K (the temperature that is ~5 K higher than the corresponding point *D*) to a temperature lower than the beginning of glass transition and fusing of the initial polymer sample, copolymer did not crystallize, but only vitrified, and its heat capacity is described by curve *ABFD*. Glass transition occurs within the 255—340 K interval, and the heat capacity is presented in curve *BF*. As for other polymers,[20] the heat capacities of the glassy and partially crystalline COP at $T < T^\circ_g$ coincide within the measurement error (~0.2%). The heat capacity of the copolymer in the high-elasticity state (curve *FD*) increases smoothly with temperature increase. The heat capacities of the liquid formed immediately after fusing of crystals of the initial copolymer sample and the liquid obtained by heating of the amorphous sample above point *D* increase relatively rapidly with temperature increase. This is not characteristic of polymers in the liquid state[21] but is related, most likely, to the beginning process of copolymer decomposition (in the absence of decomposition, the heat capacity would be described, probably, by straight line *DD′*). On further heating, decomposition develops intensely and occurs up to T = 550 K. The corresponding apparent temperature dependence of the heat capacity in the temperature region of copolymer decomposition (415—550 K) is described by curve *DJIH* (see Fig. 3).

The temperature dependence of C°_p for COP in the crystalline state (extrapolation, *ABGE* in Fig. 3) was obtained from the experimental functions $C^\circ_p = f(T)$ of the copolymer in the partially crystalline and glassy states. Substantiation of the extrapolation has previously been described.[22]

The parameters of the glass transition temperature and glassy (gl) state of COP (calculated per mole of repeated COP unit, M 70.091 g mol^{-1}) are presented below:

T°_g/K	$\Delta C^\circ_p(T^\circ_g)$ /J K^{-1} mol^{-1}	$H^\circ_{gl}(0) - H^\circ_{cr}(0)$ /kJ mol^{-1}	S°_{conf} /J K^{-1} mol^{-1}
280	46.4	4.9	12

The glass transition temperature (T°_g) was determined by the known method[23] from the inflection point of the plot of the temperature dependence of entropy $S^\circ = f(T)$ within the glass transition interval. The error of determination of T°_g by this method does not usually exceed 0.5—1.0 K. The increase in the heat capacity during glass transition (ΔC°_p) was found graphically by extrapolation of the standard run of the heat capacity of COP in the high-elasticity and glassy states to T°_g.

The configuration entropy (S°_{conf}) of the glassy polymer was calculated by the formula[24]

$$S^\circ_{conf} = \int_{T^\circ_2}^{T^\circ_g} \Delta C^\circ_p(T^\circ_g)\,\mathrm{d}\ln T, \qquad (2)$$

where T°_2 is the Kautzman temperature. For most of the polymers, $T^\circ_g/T^\circ_2 = 1.29 \pm 0.14$.[25] According to the published data,[26] the configuration entropy is close or equal to the residual (zero) entropy of the glassy polymer $S^\circ_{gl}(0)$. Based on this, we accepted $S^\circ_{conf} = S^\circ(0)$ and used it to estimate the absolute values of entropies of COP in the amorphous state, enthalpies of fusing of the copolymer in the crystalline state (α = 100%), and the difference of zero enthalpies of the copolymer in the glassy ($H^\circ_{gl}(0)$) and crystalline ($H^\circ_{cr}(0)$) states by the equation[20]

$$H^\circ_{gl}(0) - H^\circ_{cr}(0) = \int_0^{T^\circ_{fus}} \left[C^\circ_p(\mathrm{cr}) - C^\circ_p(\mathrm{a})\right]\mathrm{d}T + \Delta H^\circ_{fus}, \qquad (3)$$

where C°_p(cr) and C°_p(a) are the temperature dependences of the heat capacity of the copolymer in the crystalline (cr) and amorphous (a) states (see Fig. 3, curves *ABGE* and *ABGF′F″*, respectively), and ΔH°_{fus} is the enthalpy of fusing copolymer of 100% crystallinity.

Fusing of the COP sample is nonisothermic and occurs in the 290—410 K interval. The nonisothermic character of fusing is due to the polycrystallinity of the copolymer, an array of various metastable crystalline formations of ultramicroscopic and microscopic sizes with different chemical potentials and the presence of defects in the crystals.[20,26]

The temperature corresponding to the maximum value of the apparent heat capacity in the fusing interval C°_p = 231.8 J K^{-1} mol^{-1} (point *C* in Fig. 3) is taken as the fusing temperature of COP. The enthalpy of fusing of the sample $\Delta H^\circ_{fus}(\alpha)$ was calculated graphically as the surface area under the heat capacity curve *GCD* (see Fig. 3), subtracting the surface area under dotted line *GD*. The entropy of fusing $\Delta S^\circ_{fus}(\alpha)$ was calculated from the $\Delta H^\circ_{fus}(\alpha)$ and T°_{fus} values. The values obtained for the sample with the degree of crystallinity α (calculated per mole of repeated unit) are presented below.

α(%)	T°_{fus}/K	ΔH°_{fus}/kJ mol^{-1}	ΔS°_{fus}/J K^{-1} mol^{-1}
60	364	4.9	13.5
100	364	8.3	22.8

T°_{fus} of the studied COP sample (α = 60%) is taken as T°_{fus} of COP with 100% crystallinity. The entropy of fusing of the completely crystalline COP was calculated by the equation

$$\Delta S^\circ_{fus}\ (\alpha = 100\%) = S^\circ_{gl}(0) - \int_0^{T^\circ_{fus}} \left[C^\circ_p(\mathrm{cr}) - C^\circ_p(\mathrm{a})\right] \mathrm{d}\ln T. \quad (4)$$

The enthalpy of fusing of COP (α = 100%) was calculated from the entropy of fusing ΔS°_{fus} and T°_{fus} by the formula

$$\Delta H^\circ_{fus}\ (\alpha = 100\%) = T^\circ_{fus} \cdot \Delta S^\circ_{fus}\ (\alpha = 100\%). \quad (5)$$

The degree of crystallinity of the COP sample studied (α = 60%) was calculated from the formula

$$\alpha = \frac{\Delta H^\circ_{fus}(\alpha)}{\Delta H^\circ_{fus}(\alpha = 100\%)} \cdot 100\%. \quad (6)$$

To calculate the thermodynamic functions of COP (Table 1), the heat capacity within the 0—5 K temperature range was obtained by extrapolation of the experimental dependence $C^\circ_p = f(T)$ by the Debye function of heat capacity

$$C^\circ_p = nD(\theta_D/T), \quad (7)$$

where *D* is the Debye function of heat capacity, and *n* and θ_D are specially selected parameters. Equation (7) with the parameters *n* = 1 and θ_D = 62.17 K describes the experimental C°_p values in the 7—10 K temperature range with an error of ±0.6%. We accepted for the calculation of the functions that in the 0—5 K interval it reproduces the C°_p values with the same error. The enthalpy $H^\circ(T) - H^\circ(0)$ and entropy $S^\circ(T)$ were calculated by integration of the dependences of C°_p on *T* and ln*T*, respectively, and the Gibbs function was calculated from the values of the enthalpy and entropy from the formula

$$G^\circ(T) - H^\circ(0) = [H^\circ(T) - H^\circ(0)] - T \cdot S^\circ(T). \quad (8)$$

For the calculation of $S^\circ(T)$ of the amorphous polymer, we took into account its zero entropy $S^\circ(0)$.

Table 1. Heat capacity (C°_p/J K^{-1} mol^{-1}), enthalpy ($H^\circ(T) - H^\circ(0)$/kJ mol^{-1}), entropy ($S^\circ(T)$/J K^{-1} mol^{-1}), and Gibbs function ($G^\circ(T) - H^\circ(0)$/kJ mol^{-1}) of COP (calculated per mole of repeated monomeric unit of polymer)

T/K	$C^\circ_p(T)$	$H^\circ(T) - H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]$
		Crystalline state		
0	0	0	0	0
5	0.335	0.0004	0.1112	0.0001
10	2.05	0.0059	0.802	0.0021
15	4.27	0.0216	2.047	0.0090
20	6.82	0.0493	3.62	0.0231
25	9.51	0.0901	5.433	0.0456
30	12.14	0.1443	7.400	0.0777
40	16.00	0.2855	11.43	0.1720
50	18.93	0.4603	15.33	0.3060
60	22.70	0.6679	19.10	0.4781
70	26.46	0.9142	22.89	0.6881
80	30.04	1.197	26.66	0.9359
90	33.65	1.514	30.40	1.221
100	37.25	1.870	34.13	1.543
150	52.91	4.143	52.35	3.709
200	68.19	7.164	69.63	6.761
250	82.35	10.92	86.32	10.66
298.15	96.15	15.21	101.9	15.19
350	111.8	20.61	118.6	20.92
364	115.8	22.20	123.1	22.61
		Liquid state		
364	151.3	30.50	145.9	22.61
400	156.9	36.05	160.4	28.13
450	164.8	44.09	179.4	36.63
		Glassy state		
0	0	0	2.7	0
10	2.06	0.006	12.8	0.12210
20	6.827	0.0493	15.6	0.0263
30	12.15	0.1443	19.4	0.4377
40	16.00	0.2855	23.4	0.6520
50	18.94	0.4603	27.3	0.9060
60	22.70	0.6679	31.1	1.1982
70	26.46	0.9142	34.9	1.5282
80	30.02	1.197	38.7	1.899
90	33.65	1.515	42.4	2.301
100	37.25	1.870	46.1	2.744
150	52.91	4.144	64.4	5.510
200	68.20	7.165	81.6	9.16
250	82.35	10.92	98.32	13.66
280	90.85	13.49	108.02	16.76
		High-elasticity state		
280	137.2	13.49	108.02	16.76
298.15	140.3	16.00	116.73	18.80
350	149.0	23.51	139.92	25.46
364	151.3	25.61	145.90	27.46

Using the data of measuring the combustion energy of COP with 60% crystallinity (the amorphous part of the sample in the high-elasticity (h.e) state), the enthalpies of combustion and formation of the crystalline copolymer were calculated. Using the equations

$$\Delta H^\circ_c(\mathrm{cr}) = \Delta H^\circ_c(\alpha) + (1 - \alpha)\Delta H^\circ_{\mathrm{fus}}\ (298.15\ \mathrm{K}), \quad (9)$$

$$\Delta H^\circ_c(\mathrm{a}) = \Delta H^\circ_c(\alpha) - \alpha\Delta H^\circ_{\mathrm{fus}}\ (298.15\ \mathrm{K}) \quad (10)$$

(α is the degree of crystallinity expressed in fractions of unity), we calculated the enthalpies of combustion and formation (ΔH°_c, kJ mol^{-1} and ΔH°_f, kJ mol^{-1}, respectively), the Gibbs function of combustion (ΔG°_f, kJ mol^{-1}), the entropy of formation (ΔS°_f, J K^{-1} mol^{-1}), and the constant of formation (K°_f) for the polymer in the entirely crystalline and amorphous states. They are presented below (T = 298.15 K and p = 101.325 kPa, the error was ±1.0 in all cases):

State	ΔH°_c	ΔH°_f	ΔG°_f	ΔS°_f	$\ln K^\circ_f$
Crystalline	−2191.8	−239.7	−116.0	−415.0	47
High-elasticity	−2197.5	−234.0	−114.7	−400.3	46

The $\Delta H^\circ_{\mathrm{fus}}$ value (α = 100%) at 298.15 K was calculated from $\Delta H^\circ_{\mathrm{fus}}$ (α = 100%) at T°_{fus} and temperature dependences of the heat capacity in the crystalline and amorphous states by the formula

$$\Delta H^\circ_{\mathrm{fus}}\ (298.15\ \mathrm{K}) = \Delta H^\circ_{\mathrm{fus}}(T^\circ_{\mathrm{fus}}) + \int_{298.15}^{T^\circ_{\mathrm{fus}}}\left[C^\circ_p(\mathrm{cr}) - C^\circ_p(\mathrm{a})\right]\mathrm{d}T. \quad (11)$$

The entropies of formation of the polymer in the same physical states were calculated from the entropies of the polymer, carbon in the form of graphite, and gaseous hydrogen. The Gibbs function of formation ΔG°_f was calculated from the found ΔH°_f and ΔS°_f values. The values obtained correspond to the process

$$4\ \mathrm{C(gr)} + 3\ \mathrm{H_2(g)} + 0.5\ \mathrm{O_2(g)} \longrightarrow \mathrm{C_4H_6O},$$

where gr is graphite. The published[28] values of enthalpies of formation of H_2O(l), CO_2(g), C(gr), H_2(g), and O_2(g) at T = 298.15 K and p = 101.325 kPa were used for calculations (l is liquid).

The thermodynamic parameters of propylene copolymerization with CO are presented in Table 2. The enthalpy of copolymerization $\Delta H^\circ_{\mathrm{cop}}$ at 298.15 K and standard pressure was calculated from the enthalpies of formation of the copolymer (our work), propylene,[28] and carbon monoxide.[28] At other temperatures, $\Delta H^\circ_{\mathrm{cop}}(T)$ was calculated by the Kirchhoff law. The temperature dependences of the heat capacity and temperatures and enthalpies of physical transformations of propylene,[29] carbon monoxide,[12,30] and copolymer (see above) were taken from the corresponding works. The entropies of copolymerization $\Delta S^\circ_{\mathrm{cop}}(T)$ were calculated from the absolute values of the entropies of the reagents: the absolute values of the entropies of propylene and CO have previously been studied,[12,28,29] and those of the copolymer are presented above. The standard values of the Gibbs function for copolymerization $\Delta G^\circ_{\mathrm{cop}}(T)$ were calculated from the enthalpies and entropies of the reaction at the corresponding temperatures.

Table 2. Thermodynamic parameters of propylene copolymerization with CO in the bulk at T = 298.15 K and p = 101.325 kPa

T/K	Physical state of reagent			$-\Delta H^\circ_{\mathrm{cop}}$	$-\Delta G^\circ_{\mathrm{cop}}$	$-\Delta S^\circ_{\mathrm{cop}}$ /J K^{-1} mol^{-1}
	C_3H_6	CO	C_4H_6O	kJ mol^{-1}		
0	cr	cr	cr	108	108	0
	cr	cr	gl	103	103	12
100	l	g	cr	123	101	222
	l	g	gl	119	98	210
200	l	g	cr	130	76	268
	l	g	gl	125	74	256
298.15	g	g	cr	150	41	356
	g	g	h.e	144	39	341
300	g	g	cr	150	43	356
	g	g	h.e	144	42	341
400	g	g	l	139	8	327
450	g	g	l	136	−8	321

Note. The following designations were used: cr, crystalline; l, liquid; g, gaseous; gl, glassy; and h.e, high-elasticity state.

The enthalpies and entropies of the reaction are negative in the temperature region under study. It follows from this that the copolymerization process has an upper limiting temperature T°_{ceil}. It was determined graphically from the intersection point of the functions $\Delta H^\circ_{\mathrm{cop}} = f(T)$ and $T\cdot\Delta S^\circ_{\mathrm{cop}}(T) = f(T)$ as equal to 425 K. At $T < T^\circ_{\mathrm{ceil}}$ the standard Gibbs function is negative. This implies that the equilibrium of the process is shifted to the right (toward COP formation) and, by contrast, at $T > T^\circ_{\mathrm{ceil}}$ $\Delta G^\circ_{\mathrm{cop}}(T) > 0$ and, hence, the equilibrium of the process is shifted to the left. At $T > T^\circ_{\mathrm{ceil}}$ and standard pressure, the reaction does not occur because of thermodynamic reasons, and the copolymer is thermodynamically unstable under these conditions and can be dimerized more or less rapidly, under the corresponding kinetic conditions, to form the initial monomers, which occurs, in fact, with the copolymer under study. The fast increase in the apparent heat capacity in the DJ region of the dependence of C°_p on T (see Fig. 3) is explained, most likely, just by depolymerization.

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References

1. A. Sen, *Chemtech.*, 1986, 48.
2. G. P. Belov, *Vysokomol. Soedin., Ser. B*, 1998, **40**, 503 [*Russ. Polym. Sci.*, 1998, **40**, *B*, 89 (Engl. Transl.)].
3. N. S. Enikolopyan and P. E. Matkovskii, *Neorganicheskie gazoobraznye okisly kak somonomery* [*Inorganic Gaseous Oxides as Comonomers*], Nauka, Moscow, 1985, 85 pp. (in Russian).
4. Z. Jiang and A. Sen, *J. Am. Chem. Soc.*, 1995, **117**, 4455.
5. P. K. Wong, J. A. Van Doorn, E. Drent, O. Sudmeijer, and H. A. Stil, *Ind. Eng. Chem. Res.*, 1993, **32**, 936.
6. J. S. W. Chien, X. A. Zhao, and F. Y. Xu, *Polym. Bull.*, 1992, **28**, 315.
7. Eur. Pat. No. 0489473, 1993.
8. K. Nosaki, N. Sato, and H. Takay, *J. Am. Chem. Soc.*, 1995, **117**, 9911.
9. Eur. Pat. No. 0572087, 1993.
10. B. V. Lebedev, K. B. Zhogova, Ya. V. Denisova, G. P. Belov, and O. N. Golodkov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 284 [*Russ. Chem. Bull.*, 1998, **47**, 277 (Engl. Transl.)].
11. E. D. Coon and F. Daniels, *J. Phys. Chem.*, 1933, **37**, 1.
12. J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.*, 1932, **54**, 2610.
13. D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
14. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley Interscience, J. Wiley and Sons, New York, 1972.
15. B. V. Lebedev, *Usp. Khim.*, 1996, **65**, 1124 [*Russ. Chem. Rev.*, 1996, **65** (Engl. Transl.)].
16. V. M. Malyshev, G. A. Mil'ner, E. P. Sorkin, and V. F. Shibakin, *Pribory i tekhnika eksperimenta*, 1985, No. 6, 195 [*Instr. Exp. Techn.*, 1985, No. 6 (Engl. Transl.)].
17. V. I. Kosov, V. M. Malyshev, G. A. Mil'ner, E. P. Sorkin, and V. F. Shibakin, *Izmeritel'naya tekhnika*, 1985, No. 11, 56 [*Measur. Techn.*, 1985, No. 11 (Engl. Transl.)].
18. E. A. Gusev, A. A. Vecher, I. I. Kontarovich, and S. V. Dalidovich, *Termodinamika organicheskikh soedinenii. Mezhvuz. sb.* [*Thermodynamics of Organic Compounds. Interuniversity Collection of Works*], Izd-vo Gor'kovskogo Un-ta, Gor'kii, 1988, 72 (in Russian).
19. B. V. Lebedev and E. G. Kiparisova, *Zh. Fiz. Khim.*, 1996, **70**, 1351 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
20. B. V. Lebedev, *Termodinamika polimerov* [*Thermodynamics of Polymers*], Izd-vo Gor'kovskogo Un-ta, Gor'kii, 1989, 125 pp. (in Russian).
21. V. Bares and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, 1973, **11**, 861.
22. B. V. Lebedev and I. B. Rabinovich, *Vysokomol. Soedin., Ser. B*, 1976, **18**, 416 [*Polym. Sci. USSR*, 1976, **18**, *B* (Engl. Transl.)].
23. S. Alford and M. Dole, *J. Chem. Soc.*, 1955, **77**, 4774.
24. G. Adam and J. H. Gibbs, *J. Phys. Chem.*, 1965, **43**, 139.
25. B. Wunderlich and G. Baur, *Teploemkost' lineinykh polimerov* [*Heat Capacity of Linear Polymers*], Mir, Moscow, 1972 (Russ. Transl.).
26. B. V. Lebedev and I. B. Rabinovich, *Dokl. Akad. Nauk SSSR*, 1977, **237**, 691 [*Dokl. Chem.*, 1977 (Engl. Transl.)].
27. Leo Mandelkern, *Crystallization of Polymers*, McGraw—Hill, New York, 1964.
28. *Termicheskie konstanty veshchestv* [*Thermal Constants of Substances*], Ed. V. P. Glushko, VINITI, Moscow, 1965—1972, Nos. 1—6 (in Russian).
29. J. Chao and K. R. Hall, *Thermochim. Acta*, 1983, **64**, 285.
30. D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pizer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

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