# Thermodynamics of alternating copolymer of ethylene and carbon monoxide in the 0—600 K region

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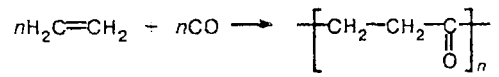
The temperature dependence of the heat capacity of the alternating copolymer (ACP) of carbon monoxide with ethylene was studied, and temperatures and enthalpies of its phase transformations were measured by adiabatic vacuum, dynamic, and isothermal calorimetry in the temperature range from 8 to 600 K. The energy of burning of ACP was measured at 298.15 K in a calorimeter with the static bomb and isothermal shell. The thermodynamic parameters of transformation of the α-form of ACP crystals into the β-form and fusion of the β-form were determined. The thermodynamic functions for the 0—507 K range and thermodynamic characteristics at $T$ = 298.15 K and $p$ = 101.325 kPa were calculated. The thermodynamic parameters of the alternating copolymerization of ethylene and CO at 0—507 K and standard pressure were calculated for the bulk reaction.

**Key words**: copolymer of ethylene and carbon monoxide, heat capacity, thermodynamic functions; copolymerization, enthalpy, entropy, Gibbs function.

The alternating copolymer of ethylene with CO is a representative of a new class of polymers, polyketones.[1—3] It can be obtained by catalytic copolymerization of the following monomers[1—5]



The interest in polyketones arises from the following facts.[6] First of all, they represent a new, almost unstudied class of polymers. The existence of the >CO= group in the macromolecules opens up new possibilities for modification of these polyketones, which is important from the viewpoint of ecological demands. Since data on the physicochemical properties of polyketones are limited, their identification and interpretation of results of syntheses are difficult.[3] Data on the thermodynamic properties of polyketones are scarce. The thermograms for the crystallization and fusion regions have been obtained, and the fusion temperature and enthalpy have been estimated only for the alternating copolymer (ACP) of ethylene with CO.[3,7] To determine these values, the dependence of the fusion temperature of ACP on the presence of admixtures[8] described by the Flory—Huggins equation[9] has been studied.

In this work, the temperature dependence of the heat capacity $C_p^\circ$ of ACP in the region of 8—600 K was studied, and the temperatures and enthalpies of its phase transformations and the energy of burning at $T$ = 298.15 K were measured by calorimetric methods. Based on the experimental data obtained, we calculated the thermodynamic characteristics of these transformations and thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$, $G^\circ(T) - H^\circ(0)$, and standard thermochemical parameters of the formation of ACP from simple substances and the copolymerization of ethylene with CO at 0—507 K.

## Experimental

NMR spectra were recorded on a Bruker CXP-200 instrument. IR spectra were recorded on UR-20 and Specord M-80 instruments. Calorimetric measurements were carried out on a DSM-2M instrument.

ACP samples were synthesized in the Institute of Chemical Physics of the Russian Academy of Sciences by the procedure described previously.[3] Found (%): C, 64.17; H, 7.17. Calculated (%): C, 64.01; H, 7.19. The intrinsic viscosity [η] = 0.88 and 3.0 dL g$^{-1}$ was calculated from measurements of the viscosity of solutions of ACP in *m*-cresol (Ubbelohde viscosimeter).[4] The structure of ACP was confirmed by the data of IR and NMR spectroscopy.[4] According to the data of calorimetric measurements, no devitrification of the amorphous portion of the copolymer is observed in the thermograms of the ACP samples, which is characteristic of polymers with a crystallinity close to 100% (the published[10] X-ray patterns of ACP are also evidence for almost 100% crystallinity of this

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copolymer). The ACP was assumed to be completely crystalline in all calculations and estimations.

A TAU-1 adiabatic vacuum calorimeter was used to study the temperature dependences of the heat capacity and the temperatures and enthalpies of the phase transformations in the 8—340 K temperature region.[11] It was established from the calorimeter calibrations that the measurement accuracy of the heat capacity of the substances at helium temperatures is ±2% and decreases to ±0.4% and to ±0.2% as the temperature increases to 40 K.[12] To determine $C_p^\circ$ in the 250—600 K region, an ADKTTM thermoanalytical complex was used, which is a dynamic calorimeter working as a triple thermal bridge[13] (accuracy of $C_p^\circ$ measurements ranges from 1 to 4%). However, since in the 250—340 K region the heat capacity of the compounds was measured on adiabatic vacuum and dynamic calorimeters, and in the dynamic calorimeter the measurement conditions were chosen in such a way that the $C_p^\circ$ values coincided on both calorimeters, we assumed that the accuracy of measurements of $C_p^\circ$ on ADKTTM at $T > 340$ K was ±(0.5—1.5)%.

The energy of burning of ACP was determined using a calorimeter with an isothermal shell and a static bomb (V-08 trade mark), which was modified in the Research Institute of Chemistry, Nizhnii Novgorod State University. The construction of the calorimeter, the working procedure, and results of calibrations and verifications have been previously published.[14] Verification of the calorimeter by burning of standard succinic acid gave a value of its burning enthalpy corresponding to the standard value with an accuracy of 0.017%.

The heat capacity $C_p^\circ$ of ACP was measured in the adiabatic vacuum calorimeter (weight of the sample 389.0 g) in the 8—340 K region and in the dynamic calorimeter (weight of the sample 420.5 g) in the 300—600 K region. The heat capacity of the samples in both calorimeters was 20—50% of the total heat capacity of the calorimetric tubes filled with the compound. In eight series, reflecting the sequence of measurements, 126 experimental values of $C_p^\circ$ were obtained. Mean square deviations of the $C_p^\circ$ points from the corresponding averaging curves $C_p^\circ = f(T)$ in the 8—100 K range were not greater than 0.5%, and in the 100—340 K range, not greater than 0.2%.

Measurements of $C_p^\circ$ on the dynamic calorimeter were carried out in the regime of continuous heating from 300 to 600 K. The experiments were performed with three heating rates (K s$^{-1}$): $2.5 \cdot 10^{-2}$, $3.3 \cdot 10^{-2}$, and $4.2 \cdot 10^{-2}$. The $C_p^\circ = f(T)$ dependences obtained are presented in Fig. 1. The temperature corresponding to the maximum magnitude of the apparent heat capacity in the fusion range (points *A*, *B*, and *C*) was determined at each of the three heating rates. The fusion temperatures of ACP for the corresponding heating rates $T^\circ_{fus,v}$ were determined by this method, and the fusion temperature corresponding to zero heating rate was determined from these data by extrapolation of the $T^\circ_{fus,v}$ line[15] from $v^{1/2}$ to $v^{1/2} = 0$ (here $v$/K s$^{-1}$ is the heating rate).

ACP was burnt in a mixture with benzoic acid in a 1 : 3 ratio ($\Delta_b U^\circ$ of benzoic acid = −26454.4 J g$^{-1}$). Burning energies were measured in five experiments.* The weights of the ACP samples burnt in the experiments were 0.2677—0.3345 g. The amount of the energy ($\Delta_b U$) evolved under the conditions of the calorimetric bomb was 27159—31526 J. Standard thermochemical corrections were introduced in the calculation of the $\Delta_b U^\circ$ value. All procedures with ACP concerning preparation of burning experiments were carried out in air. The ratio of the $CO_2$ weights found in the burning products to those

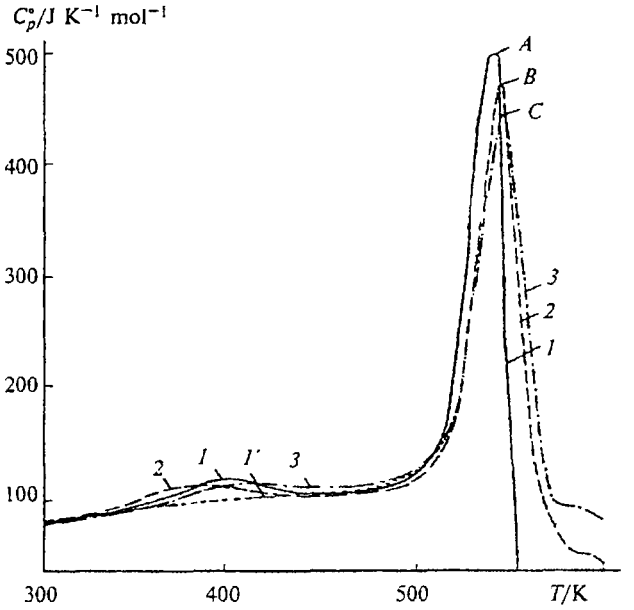


**Fig. 1.** Temperature dependences of the heat capacity of ACP ($C_p^\circ$) measured for different heating rates of the calorimeter (K s$^{-1}$): $2.5 \cdot 10^{-2}$ (*1*), $3.3 \cdot 10^{-2}$ (*2*), and $4.2 \cdot 10^{-2}$ (*3*) were obtained for the starting copolymer sample; $2.5 \cdot 10^{-2}$ (*1′*) was obtained for the sample heated to 480 K and then cooled to 300 K. *A*, *B*, and *C* are the points with the maximum values of the apparent heat capacity.

calculated from the equation of the reaction of the ACP oxidation by oxygen was 96.1—96.3%. Taking into account the results of elemental analysis of the ACP samples studied and the fact that the ACP burning was complete (no solid burning products remained in the calorimetric bomb), we assumed that the difference between the $CO_2$ amount found and 100% is due to the fact that the polymer sorbs a small amount of moisture from air. Therefore, the burning energies determined in experiments were recalculated to the 100% content of $CO_2$ in the burning products. As a result, $\Delta_b U^\circ = -1597.1 \pm 1.2$ kJ mol$^{-1}$ was obtained. This value was used for calculating the burning energy of ACP at the standard pressure ($\Delta_s U^\circ = -1596.3 \pm 1.2$ kJ mol$^{-1}$). The value of $\Delta_s U^\circ$ thus determined corresponds to the thermal effect of the reaction at $T = 298.15$ K and standard pressure

$$[-C_3H_4O-](c) + 3.5\ O_2(g) \rightarrow 3\ CO_2(g) + 2\ H_2O(liq),$$

where c, g, and liq refer to the crystalline, gaseous, and liquid substances, respectively.

## Results and Discussion

***Heat capacity.*** When the starting ACP is heated in the 8—330 K range during measurements of the heat capacities, its heat capacities $C_p^\circ$ increase smoothly as the temperature increases (Fig. 2, curve *AB*). In the 330—460 K temperature range, the dependence of $C_p^\circ$ on $T$ appears in the form of a relatively smeared "hump" (curve *BCD*), which is related to the transformation of

* Experiments on measurement of the energies of burning of ACP were carried out by E. G. Kiparisova.

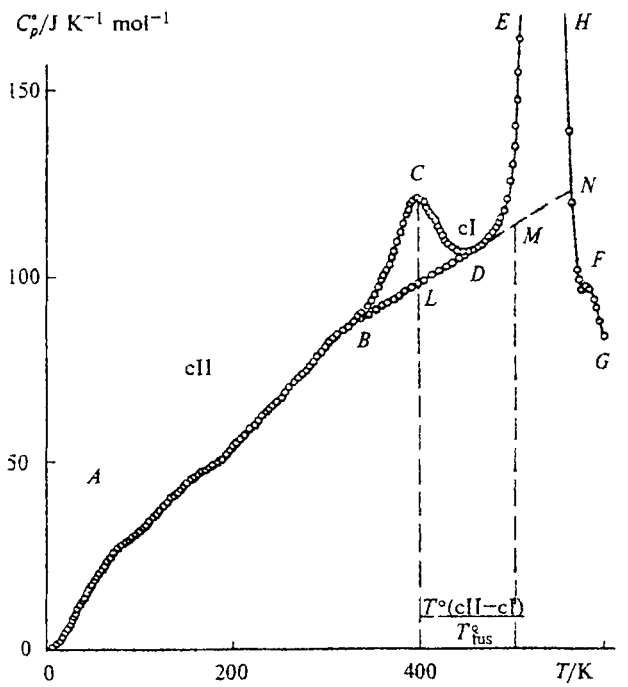


**Fig. 2.** Temperature dependence of the heat capacity of ACP: curve *ABCD*, crystals cII; curve *ABLDM*, crystals cI; curve *DEHN*, apparent heat capacity in the interval of fusion of crystals cI, and curve *NFG*, apparent heat capacity related to the beginning of the thermal destruction of the copolymer.

crystals in the α-form (cII)* into the β-form crystals (cI).[16] The further heating of ACP results in a sharp increase in the heat capacity (see Fig. 2, curve *DE*) caused by the beginning of fusion of crystals cI. As soon as fusion ceases, the thermal decomposition of ACP begins, accompanied by the exothermic effect and a related sharp decrease in the apparent heat capacity of the copolymer (see Fig. 2, curve *NFG*). Further heating results in a decrease in the weigh of the polymer sample. When heating of the calorimeter with the substance is stopped at a temperature between the temperatures of the end of the cII → cI transformation and the beginning of fusion of the crystals (for example, in point *D*) followed by cooling of the calorimeter to $T < T^\circ(\text{cII} \rightarrow \text{cI})$, $C_p^\circ$ is described by curve *BLD*. The "hump" observed on the $C_p^\circ = f(T)$ dependence (curve *BCD*) is not reproduced, and the heat capacities of crystals cII and cI at $T < T^\circ(\text{cII} \rightarrow \text{cI})$ coincide within measurement accuracy.

***Thermodynamic parameters of the cII → cI transformation and fusion.*** According to the published data,[10,16] the cII and cI forms have similar (orthorhombic) crystal lattices differing only in the following parameters: for the cII form, $a = 6.91$ Å, $b = 5.12$ Å, and $c = 7.60$ Å; for cI, $a = 7.97$ Å, $b = 4.16$ Å, and $c = 7.47$ Å. The densities of the copolymer also differ: $\rho = 1387$ (cII) and 1297 (cI) kg m$^{-3}$. The conformations of the ACP macromolecules in crystals cII and cI are identical. However, the spatial arrangement of the carbonyl groups in crystals cI is more disordered than in crystals cII where it is strongly ordered. It is also shown[16] that the difference in the spatial arrangement of the carbonyl groups results in a change in the dipole-dipole interaction in the copolymer, which reflects its density in states cII and cI and a change in parameters *a*, *b*, and *c* of the orthorhombic lattice. The cII → cI transformation is isothermal and observed within the 330—460 K temperature range. A maximum of the apparent heat capacity in the transition interval (120 J K$^{-1}$ mol$^{-1}$) corresponds to the temperature of 400 K, which is accepted to be the temperature of the cII → cI transition and is designated hereinafter as $T^\circ(\text{cII} \rightarrow \text{cI})$. The enthalpy of the transition $\Delta_{\text{cII}\rightarrow\text{cI}}H^\circ = 1260$ J mol$^{-1}$ within the 330—460 K temperature range was determined from the plot as a difference between the enthalpies of heating of the polymer calculated by integration along curves *BCD* and *BLD* (see Fig. 2). The entropy of the transition $\Delta_{\text{cII}\rightarrow\text{cI}}S^\circ = 3.15$ J K$^{-1}$ mol$^{-1}$ was determined from the enthalpy and temperature of the transition using the formula

$$\Delta_{\text{cII}\rightarrow\text{cI}}S^\circ = \Delta_{\text{cII}\rightarrow\text{cI}}H^\circ/T^\circ(\text{cII} \rightarrow \text{cI}). \quad (1)$$

Thus, based on X-ray diffraction[10,15] and calorimetric data (this work), we can attribute the cII → cI transformation to transitions of the "order ⇌ disorder" type. However, it should be taken into account that, unlike many transitions of this type,[16] the transition considered is irreversible. The number of statistical disordering ($N_I = 1.5$) was calculated from the formula[17]

$$\Delta_{\text{cII}\rightarrow\text{cI}}S^\circ = R\ln(N_I/N_{II}), \quad (2)$$

where *R* is the universal gas constant, and $N_{II}$ is the number of statistical disordering of the CO groups in the cII form. According to the previously published data,[15] $N_{II} = 1$. Thus, the CO groups in the cI state are partially disordered. For complete disordering, $N_I = 2$ with the corresponding value $\Delta_{\text{cII}\rightarrow\text{cI}}S^\circ = 5.76$ J K$^{-1}$ mol$^{-1}$.[17]

The cII copolymer is formed when ethylene and CO are copolymerized in the presence of palladium phosphine complexes,[1] whereas the copolymerization in the presence of radical initiators at high pressure affords the cI form.[8] In this work, we showed that the cII → cI transition is irreversible.

Crystals cI are fused in a wide temperature range (500—570 K). The reasons for this phenomenon for polymers have been described in detail.[18] The temperature $T^\circ_{\text{fus}}$, enthalpy $\Delta_{\text{fus}}H^\circ$, and entropy $\Delta_{\text{fus}}S^\circ$ of ACP fusion measured in this work and published in Ref. 8 are presented in Table 1. These values have been previously obtained from the depression of the melting point, which is dependent on low-molecular additives introduced in the equilibrium melt; in addition, the hypothetical melting point of the perfect defect-free ACP crystals has been determined. Of course, it is higher than

* Designations cII and cI were introduced in accordance with those accepted in the thermodynamics of organic compounds.[17]

**Table 1.** Thermodynamic parameters of the ACP fusion (calculated per mole of the repeating polymer unit; $M$ = 56.032 g mol$^{-1}$)

| $T^\circ_{fus}$ /K | $\Delta_{fus}H^\circ$ /kJ mol$^{-1}$ | $\Delta_{fus}S^\circ$ /J K$^{-1}$ mol$^{-1}$ | Reference |
|---|---|---|---|
| 507 | 7.79 | 15.4 | * |
| 517 | 7.49 | 14.5 | 8 |
| 519 | 6.72 | 12.9 | 4 |

* This work.

the melting point of the real ACP sample determined in this work. The thermodynamic parameters of fusion obtained from the data of dynamic calorimetry agree well with the results of Ref. 8 but differ somewhat from the values obtained by the other authors.[4] The higher $T^\circ_{fus}$ value (see Ref. 4) is associated with the fact that it is related to the heating rate of $2.7 \cdot 10^{-1}$ K s$^{-1}$. The reasons for somewhat reduced values of $\Delta_{fus}H^\circ$ and $\Delta_{fus}S^\circ$ are not clear.

***Thermodynamic functions.*** To calculate the thermodynamic functions (Table 2) within the 0—8 K temperature range, the $C_p^\circ$ values were obtained by extrapolation to the Debye heat capacity

$$C_p^\circ = nD(\theta_D/T), \qquad (3)$$

where D is the function of the Debye heat capacity, and $n$ and $\theta_D$ are specially selected parameters. For $n$ = 1 and $\theta_D$ = 91.80 K, Eq. (3) describes the experimental $C_p^\circ$ values within the 8—12 K temperature range with an error of ±0.8%. For calculation of the functions, we accepted that in the 0—8 K temperature range it reproduces the $C_p^\circ$ with the same error.

The $H^\circ(T) - H^\circ(0)$ enthalpy and $S^\circ(T) - S^\circ(0)$ entropy were calculated by integration of the dependences of $C_p^\circ$ on $T$ and ln$T$, respectively, and the Gibbs function was calculated from the enthalpy and entropy values.

***Thermochemical parameters of formation of ACP.*** The energy of ACP burning at $T$ = 298.15 K and standard pressure $\Delta_s U^\circ$ was used to calculate the enthalpy of burning ($\Delta_b H^\circ$ = −1597.4±1.2 kJ mol$^{-1}$). Using the obtained $\Delta_b H^\circ$ value, we calculated the enthalpy of formation of ACP ($\Delta_f H^\circ$ = −154.8±1.2 kJ mol$^{-1}$). In the calculation of the entropy of formation ($\Delta_f S^\circ$ = −296.6±0.5 J K$^{-1}$ mol$^{-1}$), the condition $S^\circ(298.15\ K) - S^\circ(0) = S^\circ(298.15\ K)$ is assumed, since it has been previously shown[19] that the zero entropy values $S^\circ(0)$ of polymers in the crystalline state are negligible. The Gibbs function of formation $\Delta_f G^\circ$ = −66.4±1.3 kJ mol$^{-1}$ was calculated from the determined values of $\Delta_f H^\circ$ and $\Delta_f S^\circ$. The values obtained correspond to the process

$$3\ C(gr) + 2\ H_2(g) + 0.5\ O_2(g) \rightarrow C_3H_4O(cII\ or\ cI),$$

where gr is graphite. The enthalpies of formation of $H_2O$(liq), $CO_2$(g) and entropies of formation of C(gr), $H_2$(g), and $O_2$(g) at $T$ = 298.15 K and $p$ = 101.325 kPa, which are necessary for calculations, are taken from the published work.[20]

***Thermodynamic parameters of copolymerization of ethylene with CO.*** The thermodynamic parameters of this reaction are presented in Table 3. The enthalpy of copolymerization $\Delta_{cop}H^\circ(T)$ at 298.15 K and standard pressure was calculated from the enthalpies of formation of the copolymer (obtained in this work), ethylene,[20] and carbon monoxide.[20] At other temperatures, $\Delta_{cop}H^\circ(T)$ was obtained by Kirchhoff's formula. The temperature dependences of the heat capacity and the values of temperatures and enthalpies of the physical transformations of ethylene,[21,22] carbon monoxide,[23,24] and copolymer (see Table 2) were taken from the corresponding works. The entropies $\Delta_{cop}S^\circ(T)$ were calculated from the absolute values of the entropy of the reagents; the absolute entropies of ethylene and CO were taken from the previously published works,[21—24] and those for the copolymer are presented in Table 2; the $S^\circ(0)$ value of the polymer was neglected. The standard values of the Gibbs function for the copolymerization $\Delta_{cop}G^\circ(T)$ were calculated from the enthalpy and entropy of the reaction at the corresponding temperatures.

The ethalpies and entropies of the reaction in the temperature range studied are negative: the copolymerization has the upper limiting temperature $T^\circ_{lim}$. It was determined from the plot by intersection of the $\Delta_{cop}H^\circ(T) = f(T)$ and $T \cdot \Delta_{cop}S^\circ(T) = f(T)$ dependences, and it is equal to 292 K. At $T < T^\circ_{lim}$, the values of the standard

**Table 2.** Thermodynamic functions of ACP (calculated per mole of the repeating monomeric unit of the polymer)

| $T$ /K | $C_p^\circ(T)$ | $S^\circ(T)-S^\circ(0)$ | $H^\circ(T)-H^\circ(0)$ | $-[G^\circ(T)-H^\circ(0)]$ |
|---|---|---|---|---|
| | J K$^{-1}$ mol$^{-1}$ | | kJ mol$^{-1}$ | |
| | | Crystals cII | | |
| 5 | 0.1047 | 0.03559 | 0.00014 | 0.00004 |
| 10 | 0.7994 | 0.2763 | 0.00208 | 0.00069 |
| 15 | 2.228 | 0.8511 | 0.00942 | 0.00335 |
| 20 | 4.140 | 1.741 | 0.02512 | 0.00970 |
| 30 | 8.598 | 4.249 | 0.08850 | 0.03898 |
| 40 | 13.50 | 7.418 | 0.1998 | 0.09693 |
| 50 | 18.00 | 10.91 | 0.3577 | 0.1884 |
| 100 | 32.07 | 28.47 | 1.664 | 1.182 |
| 150 | 44.10 | 43.73 | 3.567 | 2.992 |
| 200 | 54.65 | 57.83 | 6.030 | 5.536 |
| 250 | 66.80 | 71.29 | 9.057 | 8.765 |
| 298.15 | 79.53 | 84.14 | 12.44 | 12.35 |
| 330 | 87.50 | 92.62 | 15.24 | 15.32 |
| | | Mixture of crystals cII and cI | | |
| 350 | 93.82 | 97.93 | 17.05 | 17.23 |
| 400 | 120.0 | 112.3 | 22.44 | 22.48 |
| 450 | 105.9 | 125.5 | 28.03 | 28.43 |
| | | Crystals cI | | |
| 460 | 106.3 | 127.8 | 29.09 | 29.70 |
| 500 | 112.0 | 136.9 | 33.45 | 34.99 |
| 507 | 113.0 | 138.7 | 34.31 | 35.98 |

**Table 3.** Thermodynamic parameters of the copolymerization of ethylene with $T = 298.15$ K and standard pressure

| $T$/K | Reagent* | | | $-\Delta_{cop}H°$ | $-\Delta_{cop}G°$ | $-\Delta_{cop}S°$ |
|---|---|---|---|---|---|---|
| | $C_3H_4O$ | $C_2H_4$ | | kJ mol$^{-1}$ | | /J K$^{-1}$ mol$^{-1}$ |
| 0 | cII | c | cII | 63.4 | 63.4 | 0 |
| 100 | cII | c | g | 75.4 | 57.4 | 180 |
| 200 | cII | g | g | 96.6 | 31.6 | 325 |
| 298.15 | cII | g | g | 96.6 | −0.71 | 327 |
| 400 | cII+cI | g | g | 97.7 | −33.2 | 320 |
| 500 | cI | g | g | 92.5 | −65.0 | 315 |

* Physical states of the reagents: c, crystalline and g, gaseous.

Gibbs function are negative. This means that the equilibrium of the process is shifted to the right, toward the formation of ACP, and, by contrast, at $T > T°_{lim}$ $\Delta_{cop}G°(T) > 0$ and, hence, the equilibrium is shifted to the left. Thus, at the standard pressure the reaction does not occur because of thermodynamic reasons; under these conditions, the copolymer is thermodynamically unstable and can be depolymerized under the corresponding kinetic conditions to form the starting monomers. These conclusions agree with the fact[3] that the catalytic copolymerization of ethylene with CO is carried out under elevated pressures (0.5—1.5 MPa) at $T =$ 360 K. At the standard pressure, the spontaneous conversion of ethylene and CO to ACP is also possible, but at reduced temperatures, *i.e.*, in the temperature region where $\Delta_{cop}G°(T) < 0$. However, in this cases, the reaction rate is most likely very low.

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