CALORIMETRIC STUDY OF POLYKETONE FORMED FROM CARBON MONOXIDE, ETHYLENE AND BUTENE-1

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The temperature dependence of the heat capacity for partially crystalline polyketone derived from carbon monoxide with ethylene and butene-1 (the butane units content is 14.6 mol %) was studied over the range 6–520 K by the methods of precision adiabatic vacuum calorimetry and differential scanning calorimetry. Thermodynamic characteristics of the glass transition and glassy state and melting characteristics were determined. The standard thermodynamic functions, namely, \( C_p^0 \), \( H^0(T) - H^0(0) \), \( S^0(T) - S^0(0) \) and \( G^0(T) - H^0(0) \), were calculated for the temperature range from \( T \rightarrow 0 \) to 400 K, based on the experimental data. Thermal stability temperature for polyketone (520 K) has been specified by the thermogravimetry method.

Keywords: ternary alternating copolymer, heat capacity, thermodynamic parameters of melting, thermodynamic functions.

Poly(olefin)ketones constitute one of the classes of polymer materials. One of the basic methods to obtain them is the copolymerization reaction of carbon monoxide with various olefins. The first poly(olefin)ketone was synthesized in 1939 by radical polymerization at high temperature and pressure [1]. Systematic data on synthesis, structure, and properties of these compounds began appearing in the literature in the mid-1980s [1]. These polymers have good chemical stability toward solvents, acids and alkalis, impermeability to hydrocarbons, high rigidity and shock resistance, therefore they have wide range of possible applications [2]. The use of carbon monoxide as a comonomer for polymerization with various olefins is attractive not only because of ready availability of the components, but also due to the fact that it is possible to obtain polymers with completely different properties by changing the sequence of the CO groups introduction into the polymer chain [2, 3].

In the earlier papers we have investigated the thermodynamic properties of alternating copolymers (1 : 1) of carbon monoxide with ethylene (COE), propylene (COP), some cyclodienes [3–8], as well as the samples of terpolymers of carbon monoxide, ethylene and propylene (mole fraction of the propylene blocks is up to 30 %) [9] and of carbon monoxide, ethylene and butene-1 (COEB-1) (mole fraction of the butane units is 10.7 %) [10]. This study is the extension of the research on terpolymers.

The aim of the paper is the calorimetric study of the terpolymer of carbon monoxide, ethylene and propylene with the content of the butane units 14.6 mol % (COEB-2): the temperature dependence of the heat capacity \( C_p^0 = f(T) \) over the range 6–520 K; identification of possible phase and physical transitions in the studied compound, their physical and chemical interpretation; calculation of standard thermodynamic functions of the copolymer (enthalpy, entropy and Gibbs energy of heating) within above temperature range.
Experimental

Characterization of the studied sample. The sample of the terpolymer carbon monoxide–ethylene–butane-1 was synthesized in the Institute of Problems of Chemical Physics of the RAS in Chernogolovka by the research group of Professor G.P. Belov. The synthesis technique is described in detail in [11].

The investigation of the copolymer sample by the $^1$H and $^{13}$C NMR method was carried out on Bruker 400 MHz spectrometer. The spectra were recorded at room temperature, using CDCl$_3$ as the solvent and CDC$_3$ as the internal standard (signals 7.26 ppm for $^1$H NMR and 77.16 ppm for $^{13}$C NMR). It was shown that the macromolecule contained lengthy fragments (–ethane–CO–ethane–CO–)$_n$, as well as shorter fragments (–butane–CO–)$_m$. The mole fraction of the butane units equaled 14.6 % of the total amount of monomer units. The empirical formula was C$_{12}$H$_{458}$O, the molar mass of the monomer unit M = 60.1605 g/mol.

Molecular mass characteristics were determined by the gel permeation chromatography method at 313 K on Waters GPCV-2000 liquid chromatograph (hexafluoroisopropanol as the eluent, the rate of eluent delivery equaled 1 mL/min), with an additional light scattering detector DAWN HELEOS II (Wyatt), the PL-gel 5 mm MIXED-C column: M$_n$ = 8000, M$_w$ = 11200, M$_p$ = 7100, heterogeneity index was 1.4.

The thermal stability of the copolymer sample was studied on TG-209 F1 thermomicrobalance manufactured by Netzsch Gerätebau (Germany). It was shown that in an argon follow the sample was stable up to temperature 520 K.

Biodegradability of the copolymer was studied according to the standard method [12]. The samples were placed into Petri dishes and infested by water suspension of fungi spores (active destructors of polymer materials): Aspergillus niger van Thighem, Aspergillus terreus Thom, Penicillium chrysogenum-Thom, Alternaria alternata (Fr.) Keissler, Trichoderma viride Pers. Ex S.F. Gray. The concentration of spores for each fungus species equaled 1–2 mln/cm$^3$. The samples in dishes were placed into a climate camera, temperature-controlled for 28 days at temperature 302 ± 2 °C and humidity exceeding 90%. Resistance to fungi was evaluated according to intensity of fungi development. It was found that the copolymer was decomposed by some fungus species, such as Trichoderma viride and Penicillium chrysogenum (the degree of fungi growth was evaluated as grade 5 in the 6-grade scale [12]). It testified that those fungi could use the studied copolymer as nourishment (carbon and energy) source, consequently, could actively utilize it.

Growth of other fungus species (Aspergillus niger, Aspergillus terreus, Alternaria alternata) was not detected on the studied samples.

Equipment and measurement procedure. The heat capacity was studied over the range from 6 to 350 K with the use of BKT-3 adiabatic vacuum calorimeter, manufactured by CJSC "Thermis" [13] according to the technique described in paper [14]. The calorimetric ampoule was a thin-walled cylindrical vessel with the 1.5·10$^{-6}$ m$^3$ volume. Temperature was measured by iron-rhodium resistance thermometer, calibrated according to ITS-90. The temperature difference between the ampoule and the adiabatic shell was controlled by the copper-iron-chrome-aluminum thermocouple. The calibration test results showed that the measurement error for heat capacity did not exceed ± 2 % up to 15 K, ± 0.5 % in the range 15–40 K and ± 0.2 % in the range 40–350 K. In order to delete adsorbed moisture from the copolymer sample, the ampoule with the substance was degassed until mass constancy was reached. After that the ampoule was filled by gaseous helium of high-purity grade to improve the thermal conductivity of the system. The average cooling rate of the calorimetric system was equal to 0.12 K/min.

The heat capacity over the range 350–520 K was studied with the use of DSC 204 F1 Phoenix differential scanning calorimeter, manufactured by Netzsch Gerätebau (Selb, Germany). The calorimeter design and the experiment procedure were similar to those described earlier [15, 16]. Calibration of the calorimeter was performed by measurement of thermodynamic characteristics of indium, tin, and bismuth melting. It was found that the equipment and measurement technique permitted determination of the phase transition temperatures to a tolerance ± 0.5 K, and ± 1 % for transition enthalpies. The heat capacity was studied by the "ratio method" [16]. Corundum was used as the material standard. The measurement error of the abovementioned method did not exceed ± 2 %. The average heating rate of the ampoule with the substance in argon was equal to 5 K/min.
The copolymer samples 0.3794 g and 0.0120 g were placed into calorimetric ampoules of BKT-3 and DSC, respectively. Smoothing of experimental dependencies was carried out with the use of formal power polynomials and semilogarithmic regression by special computer programs so that the standard deviation of the points from the smoothed curve \(C_p^0 = f(T)\) did not exceed the heat capacity measurement error.

**Results and Discussion**

**Heat capacity.** Figure 1 shows the obtained experimental data and the smoothed curve \(C_p^0 = f(T)\) per one mole of conditionally repeated unit COEB-2. The heat capacity of the copolymer sample studied in the adiabatic vacuum calorimeter has reached from 25 to 40 % of the heat capacity of calorimetric system as a whole.

![Graph showing temperature dependence of heat capacity](image)

**Fig. 1. Temperature dependence of the heat capacity of the terpolymer carbon monoxide–ethylene–butene-1:**

AB is the heat capacity of the crystalline part of the copolymer and the amorphous part in the glassy state; BE and FI are the heat capacities of the copolymer within the devitrification range for the fragments of macrochains with relatively larger and relatively smaller number of butane defects, respectively; IJ is the heat capacity of the mixture of the crystalline part of the copolymer and the amorphous part in the high-elasticity state; JKLM is the apparent heat capacity within the fusion range; MN is the heat capacity of the liquid

Before beginning of the measurements the ampoule with the COEB-2 sample was cooled to 6 K. When temperature rises up to 247 K (section AB), the heat capacity smoothly increases without any anomalies. In the range 247–282 K (section BE) the heat capacity increases at somewhat greater rate, which is caused by transition from the glassy state into the high-elasticity state of the macrochain fragments of one kind. In the range 303–335 K (section FI) the heat capacity increases in the similar way, which is related to devitrification of the macrochain fragments of another kind. Within the range 398–470 K (section JKLM) the heat capacity sharply increases, which is due to fusion of the crystalline part of the sample. Higher than 520 K thermal destruction of the copolymer sample is observed.

In studies [17–22] it has been shown that the structure, as well as mechanical and thermophysical properties of a copolymer, is influenced by the production method. In work [17] it has been found that the alternating copolymer of carbon monoxide and ethylene exists in \(\alpha\)-modification. When butene-1 is introduced as the third component, less dense \(\beta\)-modification is formed in the copolymer, and the units
The presence of double fusion peaks on the DSC curves the authors of the study [19] associate with two kinds of macrochain crystals with high and low content of butane defects. Therefore, the presence of two fusion peaks on the obtained heat capacity curve can be related to melting of two different kinds of crystals: the fairly lengthy fragments (blocks) of macrochains with relatively high content of butane defects and the blocks with lower content of the defects.

By analogy with fusion, it is possible to explain the presence of two devitrification processes, related to the transition from the glassy state into the high-elasticity state for two blocks of the copolymer amorphous parts with different defect structure.

It is of interest that the heat capacity values for COEB-2 are greater than those for COEB-1 by 2–3 % in the range where both copolymers are in partially crystalline state, at that the amorphous part exists in the glassy state.

**Multifractal treatment of low-temperature heat capacity.** Using the experimental data of ultralow temperature heat capacity for COEB-2, we have evaluated the fractal dimensionality D [23, 24]. The fractal dimensionality D is the temperature exponent in the basic equation of the fractal model of low-temperature heat capacity. The D values allow certain conclusions about the topology type of structures for solids; they can be obtained from the plot of \(\ln C_v\) versus \(\ln T\). More specifically, if follows from the equation:

\[
C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/\Theta_{max})^D,
\]

(1)

here \(k\) is Boltzmann’s constant, \(N\) is the number of atoms in a molecule, \(\gamma(D + 1)\) is the gamma function, \(\xi(D + 1)\) is Riemann’s \(\xi\)-function, \(\Theta_{max}\) is the characteristic temperature.

For a specific solid body \(D(D + 1)kN\gamma(D + 1)\xi(D + 1)(1/\Theta_{max})^D = A\) is a constant. Then the equation can be rewritten as:

\[
\ln C_v = \ln A + D\ln T.
\]

(2)

The experimental \(C_v^0\) values can be taken as \(C_v\) without significant error for \(T < 50\) K. Then it is possible to calculate the D value, with the use of the corresponding experimental heat capacity data for the range 20–50 K and equation (2). It turns out that for COEB-2 the fractal dimensionality equals 1.9 and the characteristic temperature \(\Theta_{max} = 191.6\) K, while for COEB-1 they equal 1.7 and 204.6 K, respectively. These values are determined with the errors ± 0.6 and 0.5 %. According to this model, \(D = 1\) is associated with the chain structure, \(D = 2\) is for lamellar structure, and \(D = 3\) is for spatial structure. The obtained D value points at lamellar chain topology of the copolymer structure. Reasoning from the \(\Theta_{max}\) values, it is possible to state that COEB-2 has somewhat looser structure than COEB-1, which corresponds to the determined crystallinity degree of the studied copolymers.

**Parameters of the glass transition and glassy state.** Table 1 shows the parameters of the glass transition and glassy state for the sample of terpolymer carbon monoxide–ethylene–butene-1, calculated with an obtained calorimetric data. The glass transition intervals have been determined graphically (Fig. 1), as the temperature difference of the beginning and the end of glass transition (points B and E, F and I, respectively), the glass transition temperatures have been determined graphically from the inflection point of the plot \(S^0(T) = \dot{\theta}(T)\) within the glass transition interval [25]. The measurement error for the glass transition temperature does not exceed ± 1 K in this method. Increase of the heat capacity at the devitrification temperature have also been determined graphically (sections CD and GH, respectively). Configuration entropy has been calculated from the formula suggested in [26]:
where $T_2^0$ is the Kauzmann temperature [27].

For polymers the ratio $T_2^0 / T_2^0 \approx 1.29$ [26]. At calculation the zero entropy is taken to be equal to the configuration entropy $S_{conf}^0$. This is allowed to evaluate the absolute values of entropy for amorphous polymers according to the third law of thermodynamics with allowance made for zero entropy $S(0)$.

Table 1 lists the glass transition temperature and thermodynamic characteristics of devitrification for COEB-1 [10]. Devitrification of COEB-1 also proceeds in two stages, as with COEB-2. However, if the temperatures of the first devitrification, related to the blocks containing the fairly lengthy fragments of macrochains with relatively high content of butane fragments, are close to each other, in fact, the devitrification temperature for the blocks with lower content of butane units noticeably decreases. The changes in heat capacity at devitrification temperature also differ, which is associated with not only different values of their heat capacities, but even to a greater extent with different crystallinity degrees of the studied copolymers.

**Thermodynamic parameters of melting.** Melting of the crystalline part of the sample proceeds in two stages: in the range 414–438 K and in the range 438–454 K. Table 2 presents the parameters of COEB-2 melting, determined by differential scanning calorimetry. The melting point, according to technique [28], was taken as the temperature corresponding to the maximal value of apparent heat capacity in the melting interval. Since we were unable to separate the melting intervals, the enthalpy of fusion, corresponding to the sum of enthalpies of fusion of both crystalline forms, was calculated as the difference between the line integral over the general curve of the apparent heat capacity in the melting interval and the line integral over the normal curve $C_p^0 = f(T)$ (determined by the data of three measurements 1480, 1659, 1541 J/mole) [29].

Based upon the suggestion in [21] concerning two kinds of polyketone crystals, related to different degrees of imperfection, the existence of two fusion peaks on our heat capacity curve can be interpreted as melting of two different kinds of crystals.

| Copolymer | Temperature range, K | $T_{fus}^0 \pm 1$, K | $\Delta H_{fus}^0$, J/mole | $\Delta S_{fus}^0$, J/(mole·K) | $\alpha$, % |
|-----------|---------------------|---------------------|------------------------|------------------------|---------|
| COEB-2    | 414–438             | 426                 | 1560 ± 66              | 3.6 ± 0.2              | 20 ± 4  |
|           | 438–454             | 441                 |                        |                       |         |
| COEB-1 [10] | 420–452           | 448                 | 4300 ± 150             | 10 ± 0.4              | 50 ± 10 |
|           | 452–486             | 468                 |                        |                       |         |
In the literature there are data about fusion enthalpy of completely crystalline $\beta$-phase of the alternating copolymer carbon monoxide–ethylene [3], equaling 7.79 kJ/mole. This fact has helped in evaluating the crystallinity degree ($\alpha$) of the terpolymer sample from the formula:

$$\alpha = \frac{H_{fus}^0(\alpha) \cdot 100}{H_{fus}^0(\alpha = 100)} \quad (4)$$

The value obtained according to this method is $\alpha = (20\pm4)$ %. The fusion entropy $S_{fus}^0$ has been calculated as the difference of integrals over the curve $C_p^0 = f(lnT)$ of the apparent heat capacity and the normal curve in the melting interval.

Table 2 also contains the thermodynamic parameters of fusion for COEB-1 [10]. The copolymer COEB-1 melts in two stages, just as the studied copolymer. However, in spite of modest difference in composition of the copolymers, their thermodynamic parameters of fusion differ significantly. Thus, the melting points for both crystalline forms are noticeably lower for COEB-2 compared to COEB-1, just as enthalpies and entropies of fusion. The reason is most likely due to the fact that samples with higher content of butane fragments have lower crystallinity degree and less perfect crystals because of greater defects, which leads to the obtained variations in the parameters of fusion.

**Standard thermodynamic functions.** In order to calculate thermodynamic functions, the temperature dependence of heat capacity has been extrapolated from the temperature of the measurement beginning to 0 over Debye's heat capacity function:

$$C_p^0 = nD(\Theta_D/T). \quad (5)$$

here $n$ is the degrees of freedom, $D$ is the symbol of Debye's function, $\Theta_D$ is the characteristic Debye temperature. At $n = 2$ and $\Theta_D = 134.4$ the equation (5) describes the temperature dependence of heat capacity with an error $\pm1.8\%$.

The calculated thermodynamic functions are presented in Table 3. Enthalpy has been calculated by integration of the dependence $C_p^0 = f(T)$, entropy has been obtained by integration of the dependence $C_p^0 = f(lnT)$, Gibbs energy has been found with the use of enthalpy and entropy values:

$$G^0(T) - H^0(0) = [H^0(T) - H^0(0)] - T \cdot [S^0(T) - S^0(0)]. \quad (6)$$

The calculation of functions is described in detail in ref. [31].

| T, K | $C_p^0$, J/(mole·K) | $H^0(T) - H^0(0)$, kJ/mole | $S^0(T) - S^0(0)$, J/(mole·K) | $-[G^0(T) - H^0(0)]$, kJ/mole |
|------|----------------|-----------------|----------------|-----------------|
| 1    | 2866           | 0.0004          | 0.123          | 0.0002          |
| 5    | 0.2866         | 0.0004          | 0.123          | 0.0002          |
| 10   | 1.44           | 0.0047          | 0.677          | 0.0020          |
| 15   | 3.51           | 0.0169          | 1.628          | 0.0075          |
| 20   | 5.883          | 0.0403          | 2.968          | 0.0190          |
| 25   | 8.416          | 0.0763          | 4.528          | 0.0369          |
| 50   | 20.50          | 0.4456          | 14.31          | 0.2700          |
| 100  | 36.37          | 1.903           | 33.88          | 1.486           |
| 150  | 49.10          | 4.046           | 51.09          | 3.618           |
| 200  | 60.90          | 6.797           | 66.84          | 6.571           |
| 250  | 73.66          | 10.16           | 81.79          | 10.29           |
| 263  | 76.64          | 11.14           | 85.60          | 11.38           |

**Table 3**

Standard thermodynamic functions for the copolymer
of carbon monoxide with ethylene and butane-1 (COEB-2) (M = 60.1605 g/mol, p = 0.1 MPa)
Table 3 (end)

|   | 1   | 2   | 3   | 4   | 5   |
|---|-----|-----|-----|-----|-----|
|   |     |     |     |     |     |
| 1 |     |     |     |     |     |
| 2 |     |     |     |     |     |
| 3 |     |     |     |     |     |
| 4 |     |     |     |     |     |
| 5 |     |     |     |     |     |

Partially crystalline state (the amorphous part of copolymer macrorhains with the defects caused by noticeable content of butane units is in glassy state)

|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| 1 | 263 | 90.96 | 11.14 | 85.60 | 11.38 |
| 2 | 298.15 | 103.6 | 14.56 | 97.79 | 14.60 |
| 3 | 300 | 104.3 | 14.75 | 98.43 | 14.78 |
| 4 | 317.4 | 110.6 | 16.62 | 104.5 | 16.55 |

Partially crystalline state (the amorphous part is in high-elasticity state)

|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| 1 | 317.4 | 121.3 | 16.62 | 104.5 | 16.55 |
| 2 | 350 | 129.1 | 20.70 | 116.7 | 20.15 |
| 3 | 400 | 140 | 27.4 | 135 | 26 |
| 4 | 426 | 146 | 31.1 | 144 | 30 |

Liquid state

|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| 1 | 426 | 156 | 32.7 | 147 | 30 |
| 2 | 450 | 161 | 36.5 | 156 | 34 |
| 3 | 500 | 174 | 44.8 | 174 | 42 |
| 4 | 520 | 183 | 48.4 | 181 | 45 |

Conclusion

The sample of the terpolymer carbon monoxide–ethylene-butene-1 with mole fraction of butane units 14.6% has been studied calorimetrically. Physical transformations (devitrification of the amorphous part of the sample and fusion of its crystalline part) have been identified on the heat capacity curve, the thermodynamic characteristics have been determined, standard thermodynamic functions \( H(T) - H(0) \), \( S(T) \), and \( [G(T) - H(0)] \) have been calculated in the studied temperature range. It has been shown that the copolymer sample is stable up to \( T = 520 \) K. The thermodynamic characteristics of the investigated copolymer have been compared to the copolymer with the mole fraction of butane units 10.7%.

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Калориметрическое изучение поликетона на основе монооксида углерода, этилена и бутена-1

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Методами прецизионной адиабатической и дифференциальной сканирующей калориметрии в интервале 6–520 K изучена температурная зависимость теплоемкости частично кристаллического поликетона, полученного на основе монооксида углерода с этиленом и бутеном-1 с содержанием бутановых звеньев 14,6 мол. %, определены его характеристики стеклования и стеклообразного состояния и термодинамические параметры плавления. По полученным экспериментальным данным рассчитаны стандартные термодинамические функции $C_p^0$, $\Delta H^0(T) - \Delta H^0(0)$, $S^0(T) - S^0(0)$ и $G^0(T) - G^0(0)$, для области от $T \rightarrow 0$ до 520 K. Методом термогравиметрии определена температура его термической устойчивости, проведены исследования по определению биоразлагаемости поликетона.

Ключевые слова: тройной чередующийся сополимер, теплоемкость, термодинамические параметры плавления, термодинамические функции, биоразлагаемость.

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