Физическая химия

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

P.D. Afonin[1], pavel_aphonin@live.ru
N.N. Smirnova[1], smirnova@ichem.unn.ru
A.V. Markin[1], markin@calorimetry-center.ru
G.P. Belov[2], gbelov@cat.icp.ac.ru
O.N. Golodkov[2], oleg@icp.ac.ru
O.N. Smirnova[1], smirnova@ichem.unn.ru
Yu.A. Rybakova[1], uliarybakova93@gmail.com

[1] *Lobachevsky State University of Nizhni Novgorod, Nizhny Novgorod, Russian Federation*
[2] *The Institute of Problems of Chemical Physics of the RAS, Chernogolovka, Moscow region, Russian Federation*

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 $T \to 0$ 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 CDCl$_3$ 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$_{3.29}$H$_{4.58}$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 PLgel 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.

30

Bulletin of the South Ural State University. Ser. Chemistry.
2016, vol. 8, no. 2, pp. 29–39

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.
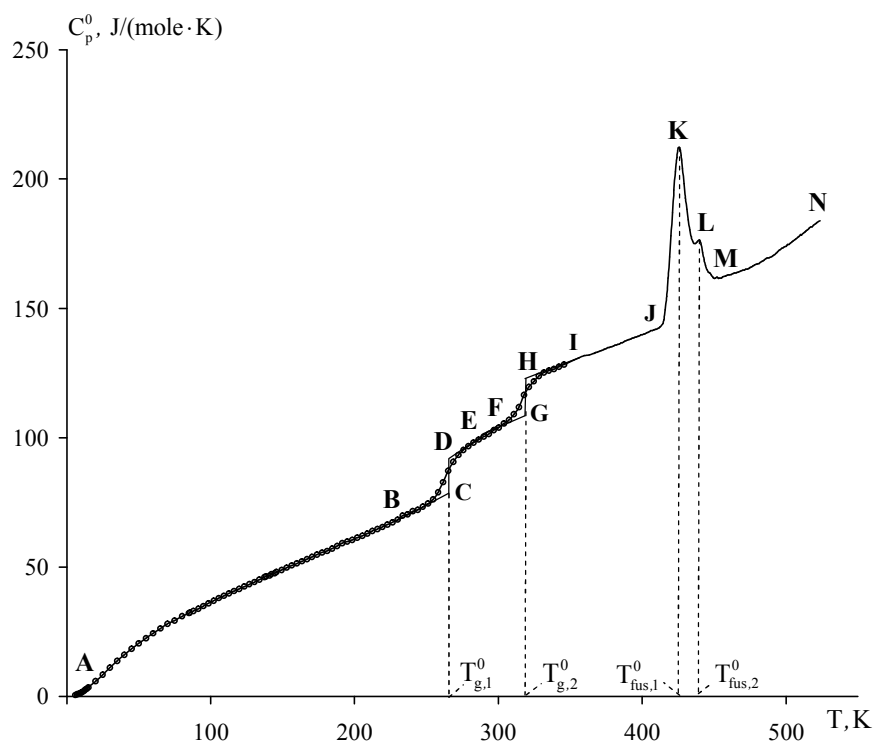

Fig. 1. Temperature dependence of the heat capacity of the terpolymer carbon monoxide–ethylene–butene-1:
AB is the heat capacity of the crystalline part of the copolymer and the amorphous part in the glassy state; BE and FI are the heat capacities of the copolymer within the devitrification range for 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 α-modification. When butene-1 is introduced as the third component, less dense β-modification is formed in the copolymer, and the units

of the third comonomer fit into the crystalline structure as defects [18]. When the defect (the third comonomer) concentration is greater than 5 %, α-modification disappears completely, while the following increase of butane fragments leads to significant decrease of the copolymer melting point and its enthalpy of fusion, as well as the crystallinity degree [18, 19].

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 ultra-low 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 lnC_v versus lnT. More specifically, if follows from the equation:

$$C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/Q_{max})^D, \qquad (1)$$

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 ξ-function, Θ_{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:

$$lnC_v = lnA + DlnT. \qquad (2)$$

The experimental C_p^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 Θ_{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 Θ_{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 $S^0(T) = f(T)$ 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]:

$$S_{conf}^0 = \int\limits_{T_2^0}^{T_g^0} \Delta C_p^0(T_g^0) d\ln T, \tag{3}$$

here T_2^0 is the Kauzmann temperature [27].

For polymers the ratio $T_g^0 / T_2^0 \approx 1.29$ [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 $S^0(0)$.

Table 1

Thermodynamic characteristics of the glass transition and glassy state for copolymers of carbon monoxide with ethylene and butene-1

Copolymer	Temperature range, K	$T_g^0 \pm 1$, K	$\Delta C_p^0(T_g^0) \pm 1$	$S_{conf}^0 \pm 1$	$S^0(0) \pm 1$
			J/(mole·K)		
COEB-2	247–282	263	14	6	6
	303–335	317	11		
COEB-1 [10]	244–278	264	8	5	5
	310–341	327	11		

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.

Table 2

Standard thermodynamic characteristics of fusion for copolymers of carbon monoxide with ethylene and butene-1

Copolymer	Temperature range, K	$T_{fus}^0 \pm 1$, K	ΔH_{fus}^0, J/mole	ΔS_{fus}^0, J/(mole·K)	α, %
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 β-phase of the alternating copolymer carbon monoxide–ethylene [3], equaling 7.79 kJ/mole. This fact has helped in evaluating the crystallinity degree (α) of the terpolymer sample from the formula [30]:

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

The value obtained according to this method is α = (20±4) %. The fusion entropy S_{fus}^0 has been calculated as the difference of integrals over the curve $C_p^0 = f(\ln T)$ 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:

$$C_p^0 = nD(\theta_D/T). \tag{5}$$

here n is the degrees of freedom, D is the symbol of Debye's function, Θ_D is the characteristic Debye temperature. At n = 2 and Θ_D = 134.4 the equation (5) describes the temperature dependence of heat capacity with an error ±1.8 %.

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 $C_p^0 = f(\ln T)$, Gibbs energy has been found with the use of enthalpy and entropy values:

$$G^0(T) - H^0(0) = \left[H^0(T) - H^0(0)] - T \cdot [S^0(T) - S^0(0) \right]. \tag{6}$$

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

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)

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	2	3	4	5
Partially crystalline state (the amorphous part is in glassy state)				
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

34

Bulletin of the South Ural State University. Ser. Chemistry.
2016, vol. 8, no. 2, pp. 29–39

Table 3 (end)

1	2	3	4	5
Partially crystalline state (the amorphous part of copolymer macrochains with the defects caused by noticeable content of butane units is in glassy state)				
263	90.96	11.14	85.60	11.38
298.15	103.6	14.56	97.79	14.60
300	104.3	14.75	98.43	14.78
317.4	110.6	16.62	104.5	16.55
Partially crystalline state (the amorphous part is in high-elasticity state)				
317.4	121.3	16.62	104.5	16.55
350	129.1	20.70	116.7	20.15
400	140	27.4	135	26
426	146	31.1	144	30
Liquid state				
426	156	32.7	147	30
450	161	36.5	156	34
500	174	44.8	174	42
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 $H^0(T) - H^0(0)$, $S^0(T)$, and $-[G^0(T) - H^0(0)]$ 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%.

References

1. Belov G.P., Novikova E.V. Polyketones as alternating copolymers of carbon monoxide. *Russian Chemical Reviews*, 2004, vol. 73, no. 3, pp. 267–291. DOI: 10.1070/RC2004v073n03ABEH000840.

2. Zehetmaier P.C., Vagin S.I., Rieger B. Functionalization of aliphatic polyketones. *MRS Bulletin*, 2013, vol. 38, pp. 239–243. DOI: 10.1557/mrs.2013.49.

3. Lebedev B.V., Zhogova K.B., Denisova Ya.V., Belov G.P., Golodkov O.N. Thermodynamics of alternating copolymer of ethylene and carbon monoxide in the 0–600 K region. *Russian Chemical Bulletin*, 1998, vol. 47, pp. 277–281. DOI: 10.1007/BF02498949.

4. Lebedev B.V., Tsevtkova A.V., Smirnova N.N., Belov G.P., Golodkov O.N., Kurskii Yu.A. Thermodynamics of alternating copolymer of propylene and CO in the 0–550 K region. *Russian Chemical Bulletin*, 1999, vol. 48, pp. 1507–1512. DOI: 10.1007/BF02496401.

5. Arapova A.V., Lebedev B.V., Smirnova N.N., Kulagina T.G., Belov G.P., Golodkov O.N. Thermodynamics of alternating copolymer of styrene and CO in the 0—600 K region. *Russian Chemical Bulletin*, 2001, vol. 50, pp. 2372–2376. DOI: 10.1023/A:1015031412516.

6. Bykova T.A., Smirnova N.N., Belov G.P., Novikova E.V. Thermodynamics of the alternating copolymer of endo-dicyclopentadiene and carbon monoxide in the 0–550 K range. *Polymer science. Series B*, 2004, vol. 46, pp. 374–378. DOI: 10.1007/s11172-005-0441-y.

7. Bykova T.A., Smirnova N.N., Kulagina T.G., Nikishchenkova L.V., Belov G.P., Novikova E.V. Thermodynamic properties of an alternating copolymer of bicyclo[2,2,1]hepta-2,5-diene and carbon monoxide in a region from T → 0 to 550 K. *Russian Chemical Bulletin*, 2005, vol. 54, pp. 1527–1531. DOI: 10.1007/s11172-005-0441-y.

8. Smirnova N.N., Nikishchenkova L.V., Bykova T.A., Kulagina T.G., Belov G.P., Novikova E.V. Calorimetric study of alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide in the range from T → 0 to 510 K. *Thermochim. Acta*, 2006, vol. 451, pp. 156–162. DOI: 10.1007/s11172-005-0441-y.

9. Smirnova N.N., Tsvetkova L.Y., Markin A.V., Aphonin P.D., Golodkov O.N., Belov G.P. Thermodynamics of an alternating carbon monoxide-ethylene-propylene copolymer in the region of T → 0 to 500 K. *Russian Journal of Physical Chemistry A*, 2015, vol. 89. no. 3. pp. 351–358. DOI: 10.1134/S0036024415030292.

10. Smirnova N.N., Golodkov O.N., Markin A.V. Tsevtkova L.Ya., Aphonin P.D., Smirnova O.N., Belov G.P., Zaharychev E.A. [Thermodynamics of alternating terpolymer of butene-1, ethylene and CO]. *Russian Chemical Bulletin*, 2016, no. 1, pp. 75–81. (in Russ.)

11. Belov G.P., Chepajkin E.G., Bezruchenko A.P., Smirnov V.I. [Alternating copolymerization of ethylene and carbon oxide in an acetic acid medium catalyzed by $PD(C_5H_7O_2)_2$-$P(C_6H_5)_3$-N-$CH_3C_6H_4SO_3H$]. *Polymer Science. Series A*, 1993, vol. 35, pp. 1585–1589. (in Russ.)

12. *GOST 9.049-91 Materialy polimernye i ikh komponenty. Metody laboratornykh ispytanij na stojkost' k vozdejstviyu plesnevykh gribov.* [State Standard 9.049-91. Polymeric materials and their components. Laboratory test methods for resistance to mold fungi]. Moscow, Standartiform Publ., 1992. 13 p. (in Russ.)

13. Malyshev V.M., Milner G.A., Sorkin E.L., Shibakinskiy V.F. [Automatic low-temperature calorimeter]. *Instruments and Experimental Techniques*, 1985, no. 6, pp. 195–197. (in Russ.)

14. Varushchenko R.M., Druzhinina A.I., Sorkin E.L. Low-temperature heat capacity of 1-bromoperfluorooctane. *The Journal of Chemical Thermodynamics*, 1997, vol. 29, pp. 623–637. DOI:10.1006/jcht.1996.0173.

15. Hohne G.W., Hemminger W.F., Flammersheim H.F. Differential Scanning Calorimetry. Verlag, Berlin–Heidelberg, 2003, 299 p.

16. Drebushchak V.A. Calibration coefficient of a heat-flow DSC; Part II. Optimal calibration procedure. *Journal of Thermal Analysis and Calorimetry*, 2005, vol. 79, pp. 213–218. DOI: 10.1007/s10973-004-0586-1.

17. Anokhin D.V., Neverov V.M., Chvalun S.N., Bessonova N.P., Godovsky Yu.K., Hollmann F., Meier U., Rieger B. Crystal structure of alternating propylene-carbon monoxide copolymers of different stereo-and regioregularities. *Polymer Science. Series A*, 2004, vol. 46, pp. 52–60.

18. Lommerts B.J., Klop E.A., Aerts J. Structure and melting of perfectly alternating ethylene-carbon monoxide copolymers. *Journal of Polymer Science Part B: Polymer Physics*, 1993, vol. 31, pp. 1319–1330. DOI: 10.1002/polb.1993.090311007.

19. Waddon A.J., Karttunen N.R. Poly(olefin ketone)s: Comparison of the Effects of CH_3 and CH_3CH_2 Side Groups on the Crystal Structure. *Macromolecules*, 2002, vol. 35, pp. 4003–4008. DOI: 10.1021/ma001589p.

20. Godovsky Yu.K., Konyukhova E.V., Chvalun S.N., Neverov V.M., Abu-Surrah A.S., Rieger B. Stretching calorimetry and X-ray characterization of deformational behavior of new high molecular weight propene-carbon monoxide alternating co- and terpolymers. *Macromolecular Chemistry and Physics*, 1999, vol. 200, pp. 2636–2644. DOI: 10.1002/(SICI)1521-3935(19991201)200:12<2636::AID-MACP2636>3.0.CO;2-#.

21. Lagaron J.M., Vickers M.E., Powell A.K., Davidson N.S. Crystalline structure in aliphatic polyketones. *Polymer*, 2000, vol. 41, pp. 3011–3017. DOI:10.1016/S0032-3861(99)00458-9.

22. Belov G.P. Catalytic copolymerization of olefins and carbon monoxide: a review. *Polymer science. Series B*, 1998, vol. 40, pp. 515–529.

23. Jakubov T.S. [About heat capacity of solids exhibiting fractal nature]. *Doklady akademii nauk SSSR,* 1990, vol. 310, no. 1, pp. 145–155. (in Russ.)

24. Lazarev V.B., Izotov A.D., Gavrichev K.S., Shebersheneva O.V. Fractal model of heat capacity for substances with diamond-like structures. *Thermochim. Acta*, 1995, vol. 269, pp. 109–116. DOI:10.1016/0040-6031(95)02529-4.

25. Alford S., Dole M. Specific Heat of Synthetic High Polymers. VI. A Study of the Glass Transition in Polyvinyl Chloride. *Journal of the American Chemical Society*, 1955, vol. 77, pp. 4774–4777. DOI: 10.1021/ja01623a024.

26. Bestul A.B., Chang S.S. Excess Entropy at Glass Transformation. *The Journal of Chemical Physics*, 1964, vol. 40, pp. 3731. DOI: 10.1063/1.1725086.

27. Kauzmann W. The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures, *Chemical Reviews*, 1948, vol. 43, pp. 219–256. DOI: 10.1021/cr60135a002.

36

**Bulletin of the South Ural State University. Ser. Chemistry.
2016, vol. 8, no. 2, pp. 29–39**

28. Bershtein V.A., Egorov V.M. *Differentsial'naya skaniruyushhaya kalorimetriya v fizicheskoj khimii polimerov* [Differential scanning calorimetry in the physical chemistry of polymers]. L: Himija pub., 1990. 256 p.

29. Smirnova N.N., Lebedev B.V., Belov G.P., Golodkov O.N., Kabo A.G. Thermodynamics of syndiotactic polystyrene in the range 0-600 K. *Polymer science. Series B*, 2001, vol. 43, no. 2, pp. 180–186.

30. Lebedev B.V., Smirnova N.N. *Termodinamika polimerov* [Thermodynamics polymers]. Textbook, Nizhni Novgorod, Pub. of UNN, 2006, 96 p.

31. Lebedev B.V. Application of precise calorimetry in study of polymers and polymerization processes. *Thermochimica Acta*, 1997, vol. 297, pp. 143–149. DOI: 10.1016/S0040-6031(97)00066-X.

КАЛОРИМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ ПОЛИКЕТОНА НА ОСНОВЕ МОНООКСИДА УГЛЕРОДА, ЭТИЛЕНА И БУТЕНА-1

П.Д. Афонин[1], Н.Н. Смирнова[1], А.В. Маркин[1], Г.П. Белов[2],
О.Н. Голодков[2], О.Н. Смирнова[1], Ю.А. Рыбакова[1]

[1] *Нижегородский государственный университет им. Н.И. Лобачевского,*
г. Нижний Новгород
[2] *Институт проблем химической физики Российской академии наук, г. Черноголовка*

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, $H^0(T)-H^0(0)$, $S^0(T)-S^0(0)$ и $G^0(T)-H^0(0)$, 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.

Литература

1. Белов, Г.П. Поликетоны – чередующиеся сополимеры монооксида углерода / Г.П. Белов, Е.В. Новикова // Успехи химии. – 2004. – Т. 73, № 3. – С. 292–319.

2. Zehetmaier, P.C. Functionalization of aliphatic polyketones / P.C. Zehetmaier, S.I. Vagin, B. Rieger // MRS Bulletin. – 2013. – V. 38. – P. 239–243. DOI: 10.1557/mrs.2013.49.

3. Термодинамика альтернантного сополимера этилена и монооксида углерода в области 0–600 K / Б.В. Лебедев, К.Б. Жогова, Я.В. Денисова и др. // Известия Академии наук. Серия Химическая. – 1998. – № 2. – С. 284–288.

4. Термодинамика чередующегося сополимера СО в области 0–550 K / Б.В. Лебедев, А.В. Цветкова, Н.Н. Смирнова и др. // Известия Академии наук. Серия Химическая. – 1999. – № 8. – С. 1527–1532.

5. Термодинамика чередующегося сополимера стирола и монооксида углерода в области 0–600 K / А.В. Арапова, Б.В. Лебедев, Н.Н. Смирнова и др. // Известия Академии наук. Серия Химическая. – 2001. – № 12. – С. 2264–2268.

6. Термодинамика чередующегося сополимера эндо-циклопентидиена и монооксида углерода в области 0–550 К / Т.А. Быкова, Н.Н. Смирнова, Г.П. Белов и др. // Высокомолекулярные соединения. Серия А. – 2004. – Т. 46, № 2. – С. 1–5.

7. Термодинамические свойства чередующегося сополимера бицикло[2,2,1]гепта-2,5-диена и монооксида углерода в области от Т → 0 до 550 К / Т.А. Быкова, Н.Н. Смирнова, Т.Г. Кулагина и др. // Известия Академии наук. Серия Химическая. – 2005. – Т. 54. – С. 1483–1487.

8. Calorimetric study of alternating copolymer of bicyclo[2,2,1]-hepta-2,5-diene and carbon monoxide in the range from T → 0 to 510 K / N.N. Smirnova, L.V. Nikishchenkova, T.A. Bykova, et al. // Thermochim. Acta. – 2006. – V. 451. – P. 156–162. DOI: 10.1007/s11172-005-0441-y.

9. Термодинамика чередующегося сополимера монооксид углерода-этилен-пропилен в области от Т → 0 до 500 К / Н.Н. Смирнова, Л.Я. Цветкова, А.В. Маркин и др. // Журнал физической химии. – 2015. – Т. 89, № 3. – С. 365–372. DOI: 10.7868/S0044453715030292.

10. Термодинамика чередующегося тройного сополимера бутена-1, этилена и монооксида углерода / Н.Н. Смирнова, О.Н. Голодков, А.В. Маркин и др. // Известия Академии наук. Серия Химическая. – 2016. – № 1. – С. 75–81.

11. Чередующаяся сополимеризация этилена и монооксида углерода в уксуснокислой среде, катализируемая PD($C_5H_7O_2$)$_2$-P(C_6H_5)$_3$-N-CH_3C_6 H_4SO_3H / Г.П. Белов, Е.Г. Чепайкин, А.П. Безрученко и др. // Высокомолекулярные соединения. Серия А. – 1993. – Т. 35. – С. 1585–1589.

12. ГОСТ 9.049-91 «Материалы полимерные и их компоненты. Методы лабораторных испытаний на стойкость к воздействию плесневых грибов». – М.: Изд-во стандартов, 1992. – 13 с.

13. Автоматический низкотемпературный калориметр / В.М. Малышев, Г.А. Мильнер, Е.Л. Сорокин и др. // Приборы и техника эксперимента. – 1985. – Т. 6. – С. 195–197.

14. Varushchenko, R.M. Low-temperature heat capacity of 1-bromoperfluorooctane / R.M. Varushchenko, A.I. Druzhinina, E.L. Sorkin // The Journal of Chemical Thermodynamics. – 1997. – V. 29. – P. 623–637. DOI:10.1006/jcht.1996.0173.

15. Hohne, G.W. Differential Scanning Calorimetry / G.W. Hohne, W.F. Hemminger, H.F. Flammersheim. – Berlin–Heidelberg: Verlag, 2003. – P. 299.

16. Drebushchak, V.A. Calibration coefficient of a heat-flow DSC; Part II. Optimal calibration procedure / V.A. Drebushchak // Journal of Thermal Analysis and Calorimetry. – 2005. – V. 79. – P. 213–218. DOI: 10.1007/s10973-004-0586-1.

17. Кристаллическая структура чередующихся сополимеров монооксид углерода-пропилен с различной стерео- и региорегулярностью / Д.В. Анохин, В.М. Неверов, С.Н. Чвалун и др. // Высокомолекулярные соединения. Серия А. – 2004. – Т. 46. – № 1. – С. 69–79.

18. Lommerts, B.J. Structure and melting of perfectly alternating ethylene-carbon monoxide copolymers / B.J. Lommerts, E.A. Klop, J. Aerts // Journal of Polymer Science Part B: Polymer Physics. – 1993. – V. 31. – P. 1319–1330. DOI: 10.1002/polb.1993.090311007.

19. Waddon, A.J. Poly(olefin ketone)s: Comparison of the Effects of CH_3 and CH_3CH_2 Side Groups on the Crystal Structure / A.J. Waddon, N.R. Karttunen // Macromolecules. – 2002. – V. 35. – P. 4003–4008. DOI: 10.1021/ma001589p.

20. Stretching calorimetry and X-ray characterization of deformational behavior of new high molecular weight propene-carbon monoxide alternating co- and terpolymers / Yu.K. Godovsky, E.V. Konyukhova, S.N. Chvalun et al. // Macromolecular Chemistry and Physics. – 1999. – V. 200. – P. 2636–2644. DOI: 10.1002/(SICI)1521-3935(19991201)200:12<2636::AID-MACP2636>3.0.CO;2-#.

21. Crystalline structure in aliphatic polyketones / J.M. Lagaron, M.E. Vickers, A.K. Powell et al. // Polymer. – 2000. – V. 41. – P. 3011–3017. DOI:10.1016/S0032-3861(99)00458-9.

22. Белов, Г.П. Каталитическая сополимеризация олефинов и монооксида углерода: обзор / Г.П. Белов // Высокомолекулярные соединения. Серия Б. – 1998. – Т. 40. – С. 89–103.

23. Якубов, Т.С. О теплоёмкости твёрдых тел, проявляющих фрактальный характер / Т.С. Якубов // Доклады Академии наук СССР. – 1990. – Т. 310. – №. 1. – С. 145–155.

24. Fractal model of heat capacity for substances with diamond-like structures / V.B. Lazarev, A.D. Izotov, K.S. Gavrichev et al. // Thermochim. Acta. – 1995. – V. 269. – P. 109–116. DOI:10.1016/0040-6031(95)02529-4.

25. Alford, S. Specific Heat of Synthetic High Polymers. VI. A Study of the Glass Transition in Polyvinyl Chloride / S. Alford, M. Dole // Journal of the American Chemical Society. – 1955. – V. 77. – P. 4774–4777. DOI: 10.1021/ja01623a024.

38

**Bulletin of the South Ural State University. Ser. Chemistry.
2016, vol. 8, no. 2, pp. 29–39**

26. Bestul, A.B. Excess Entropy at Glass Transformation / A.B. Bestul, S.S. Chang // The Journal of Chemical Physics. – 1964. – V. 40. – P. 3731. DOI: 10.1063/1.1725086.

27. Kauzmann, W. The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures / W. Kauzmann // Chemical Reviews. – 1948. – V. 43 – P. 219–256. DOI: 10.1021/cr60135a002.

28. Бернштейн, В.А. Дифференциальная сканирующая калориметрия в физической химии полимеров / В.А. Бернштейн, В.М. Егоров. – Л.: Химия, 1990. – 256 С.

29. Термодинамика синдиотактического полистирола в области 0–600 К / Н.Н. Смирнова, Б.В. Лебедев, Г.П. Белов и др. // Высокомолекулярные соединения. Серия Б. – 2001. – Т. 43. – № 2. – С. 315–321.

30. Лебедев, Б.В. Термодинамика полимеров: учеб. пособие / Б.В. Лебедев, Н.Н. Смирнова. – Нижний Новгород: Изд-во Нижегородского государственного университета, 2006. – 96 с.

31. Lebedev, B.V. Application of precise calorimetry in study of polymers and polymerization processes / B.V. Lebedev // Thermochimica Acta. – 1997. – V. 297. – P. 143–149. DOI: 10.1016/S0040-6031(97)00066-X.

Афонин Павел Дмитриевич – аспирант, химический факультет, Национальный исследовательский Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Нижний Новгород, пр. Гагарина, 23. E-mail: pavel_aphonin@live.ru

Смирнова Наталья Николаевна – доктор химических наук, профессор, заведующий лабораторией химической термодинамики, Национальный исследовательский Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Нижний Новгород, пр. Гагарина, 23. E-mail: smirnova@ichem.unn.ru

Маркин Алексей Владимирович – доктор химических наук, профессор, заведующий кафедрой физической химии, Национальный исследовательский Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Нижний Новгород, пр. Гагарина, 23. E-mail: markin@ calorimetry-center.ru

Белов Геннадий Петрович – доктор химических наук, профессор, заведующий лабораторией каталитических превращений олефинов, Институт проблем химической физики РАН. 142432, Московская обл., Ногинский р-н, г. Черноголовка, пр. Академика Семенова, 1. E-mail: gbelov@cat.icp.ac.ru

Голодков Олег Николаевич – старший научный сотрудник лаборатории каталитических превращений олефинов, Институт проблем химической физики РАН. 142432, Московская обл., Ногинский р-н, г. Черноголовка, пр. Академика Семенова, 1. E-mail: oleg@icp.ac.ru

Смирнова Ольга Николаевна – кандидат биологических наук, доцент, старший научный сотрудник отдела химико-биологических исследований, НИИ химии, Национальный исследовательский Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Нижний Новгород, пр. Гагарина, 23. E-mail: smirnova@ichem.unn.ru

Рыбакова Юлия Александровна – аспирант, химический факультет, Национальный исследовательский Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Нижний Новгород, пр. Гагарина, 23. E-mail: uliarybakova93@gmail.com