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Heat capacity and thermodynamic functions of fullerene-containing derivatives of atactic poly(methyl methacrylate)

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Abstract

In the present work by precision adiabatic vacuum and dynamic scanning calorimetry the heat capacity of covalent-bonded fullerenes C_{60} and C_{70} containing derivatives of atactic poly(methyl methacrylate) has been measured over the range from 6 to 350 K and from 330 to 460 K, respectively. Low-temperature heat capacity has been analyzed on the basis of Debye and Tarasov theories of the heat capacity of solids and the multifractal generalization and, as a result, some conclusions on the heterodynamics of their structures have been drawn. Temperature interval and thermodynamic characteristics of devitrification as well as their thermal stability regions have been determined. The experimental data were used to calculate standard thermodynamic functions, namely, the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$ and Gibbs function $G^\circ(T) - H^\circ(0)$, for the range from $T \to 0$ to 430 K. The thermodynamic characteristics of fullerene-containing derivatives of atactic poly(methyl methacrylate) and a polymer-analog not including C_{60} and C_{70} have been compared.

Keywords: Fullerene-containing atactic poly(methyl methacrylate); Adiabatic vacuum calorimetry; Heat capacity; Thermodynamic functions; Devitrification characteristics

1. Introduction

An intensive growth of researches concerning fullerenes C_{60} and C_{70} and their various functional derivatives is demonstrated in numerous reviews [1–9] and explained, first of all, with an unique structure of fullerenes and wide potential spheres of their application in practice. Fullerene-containing polymers that are formed by the polymerization of neighbouring C_{60} [10] and C_{70} molecules and different modifications of fairly well studied vinyl [11–13], cyclic [14] and organosilicon polymers [7] represent a new fairly promising class of high-molecular compounds. First of all, they evoke interest because of their ability to combine properties of an initial polymer and exceptional characteristics of the fullerene itself. It was found that the fullerene-containing polymers are able not only to preserve a lot of useful properties of the polymer but to noticeably enhance them that allows the expansion of areas of their practical application.

Up to the present, the synthesis methods of fullerene-containing polymers in macroscopic quantities were designed that shows prospects of studying their individual physicochemical features. So, the hydrodynamic and electrooptic properties of the covalent-bonded fullerenes C_{60} and C_{70} containing the atactic poly(methyl methacrylate) derivatives, PMMA-C_{60} and PMMA-C_{70}, were examined [15] The thermodynamic properties of PMMA-C_{60} and PMMA-C_{70} have not been studied yet. In this connection, the goal of the given work is to calorimetrically determine the temperature dependence of isobaric heat capacity for PMMA-C_{60} and PMMA-C_{70} between 6 and 460 K, to detect possible physical transformations on heating and cooling the samples, to determine and interpret in terms of physical chemistry their thermodynamic characteristics, to calculate from the data obtained the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ over the range from $T \to 0$ to 430 K

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and to compare the thermodynamic properties of PMMA-C_{60} and PMMA-C_{70} with appropriate data for the analog not containing fullerenes C_{60} and C_{70}, i.e. the atactic poly(methyl methacrylate) studied earlier [16].

2. Experimental

2.1. Sample

The examined samples of PMMA-C_{60} and PMMA-C_{70} were synthesized at the Organometallic Chemistry Institute of Russian Academy of Sciences by the method of block polymerization of MMA analogous to those described elsewhere [15], the fullerenes being introduced into the monomer as a dichlorobenzene solution at the starting stage prior to the addition of an initiator. The polymer macromolecules were molecules of fullerene C_{60} and C_{70} covalent-bonded with PMMA chains. Spectral properties of polymer films were characterized by UV- and NMR-spectroscopy (a Perkin-Elmer Lambda 25 UV–vis and a Bruker Avance DPX-200 (200 Mhz) spectrometers) at 25 °C [17]. The concentration of C_{60} and C_{70} in the samples of PMMA-C_{60} and PMMA-C_{70} was found to be 0.043 and 0.0053 mass%, respectively, i.e. on the average one molecule of C_{60} or C_{70} per 1.67×10^4 (1.58×10^5) monomeric units of the macromolecules. According to our calorimetric data, the samples of PMMA-C_{60} and PMMA-C_{70} were amorphous. The intrinsic viscosity $[\eta]$ of the tested samples was 2.0 and 2.87 dl/g, respectively (as determined in benzene at 299 K).

Gross-formulae of monomeric units of the polymers (PMMA-C_{60} and PMMA-C_{70}) are $C_{5.003}H_8O_2$ and $C_{5.0004}H_8O_2$ with $M = 100.154$ and 100.122 g/mol, respectively. All consequent calculations were made for them. The elemental analysis data for the synthesized samples of PMMA-C_{60} and PMMA-C_{70} correspond to formula calculations.

2.2. Apparatus and measurement procedure

To study the temperature dependence of the heat capacity, temperatures of physical transitions of PMMA-C_{60} and PMMA-C_{70} samples in the range from 6 to 350 K a VST-3 thermophysical automatic device designed and manufactured in "Termis" (Mendeleevo, Moscow Region) was employed. The calorimeter design and the operation procedure were described earlier [18,19]. The reliability of the calorimeter operation was checked by measuring C_p° of standard samples of special-purity copper, corundum and K-2 benzoic acid. It was ascertained that the apparatus and the measurement technique enable to determine the heat capacity C_p° of substances with an uncertainty of not more than ± 1.5% nearby 10 K, ± 0.5% between 15 and 40 K and ± 0.2% in the range from 40 to 350 K and to measure the physical transition temperatures within to about ± 0.01 K.

To examine the relation $C_p^\circ = f(T)$ and temperatures of physical transformations in the range from 300 to 450 K a thermoanalytical device operating by the principle of triple thermal bridge, an ADCTHB differential scanning calorimeter, was used [20,21]. The reliability of the calorimeter operation was tested by measuring the heat capacity of standard samples of synthetic corundum and special-purity copper and temperatures and enthalpies of melting of indium, tin and lead. It was found that the apparatus allows the measurements of C_p° of substances with an uncertainty of ± 1.5% in the whole temperature interval, the temperatures of physical transitions within to ca. ± 0.5 K. However, since the heat capacity of the examined substances in the range from 300 to 350 K was measured also in the adiabatic vacuum calorimeter with an error of ±0.2% and the measurement conditions in the dynamic calorimeter were chosen so that in the above temperature range the C_p° values obtained in two calorimeters coincided, it was assumed that at $T > 350$ K the heat capacity was determined within to ±0.5–1.5%.

3. Results and discussion

3.1. Heat capacity

The heat capacity of PMMA-C_{60} was measured in the range from 6.9 to 456 K and for PMMA-C_{70} between 7.3 and 406 K. The masses of the examined samples located in a calorimetric ampoule were 0.3845 and 0.4337 g for PMMA-C_{60} and PMMA-C_{70}, respectively. In the adiabatic vacuum calorimeter in four series of measurements 228 experimental C_p° points were obtained for PMMA-C_{60} and 197 experimental values of C_p° for PMMA-C_{70} (Fig. 1). The heat capacity over the range 330–460 K was measured at an average heating rate of the calorimeter with the substance 0.0133 K/s. In the whole temperature interval the heat capacity of the fullerene-containing polymer PMMA-C_{60} was from 20 to 40% of the total heat capacity of the calorimetric ampoule and the substance and for PMMA-C_{70} from 20 to 60%. A computer-assisted averaging of the experimental C_p° values was made by means of degree and semilogarithmic polynomials. The root mean square deviation of them from the averaging $C_p^\circ = f(T)$ curve was ±0.5% in the range 6–80 K, ±0.04% from 80 to 340 K and ±0.6% between 330 and 460 K.

The experimental C_p° values and the averaging $C_p^\circ = f(T)$ plots are illustrated in Fig. 1 for PMMA-C_{60} (curve 1) and PMMA-C_{70} (curve 2) and for comparison, the temperature dependence of C_p° for the atactic poly(methyl methacrylate) (curve 3) is shown too [16]. It is seen that in the studied temperature range the devitrification of the samples of PMMA-C_{60}, PMMA-C_{70} and the polymer-analog not containing fullerenes C_{60} and C_{70} occurs in the interval from 360 to 400 K (section BE, Fig. 1).

The heat capacity of the PMMA-C_{60} and PMMA-C_{70} samples in a glassy state as well as of the atactic PMMA shows no peculiarities: it smoothly increases with rising tem-

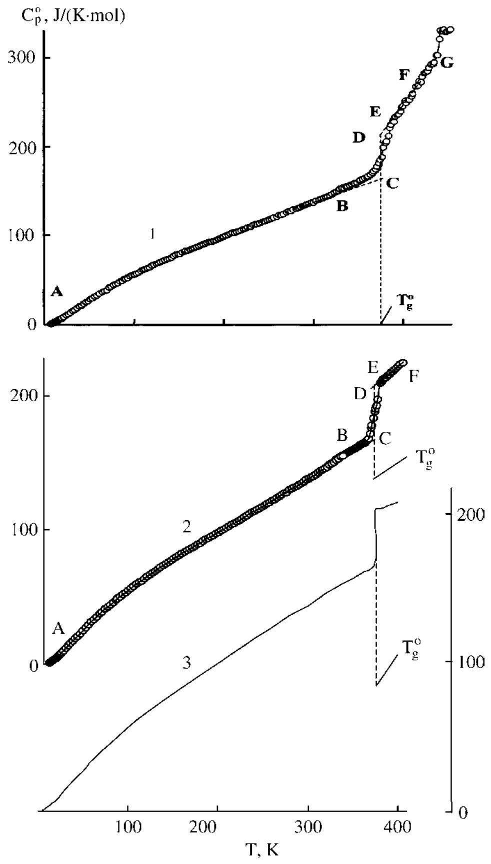

Fig. 1. Temperature dependence of heat capacity of samples of: (1) PMMA-C_{60}; (2) PMMA-C_{70}; and (3) the polymer-analog PMMA [16]; ABC: in the glassy state, DEF: in the high-elasticity state, CD: the increase in the heat capacity on devitrification, point G corresponds to the onset of thermal decomposition of PMMA-C_{60}.

perature. Besides, as for many linear polymers at $T > 80$ K their heat capacity obeys T^1-law. Such character of the dependence remains till about 330 K and further the relationship $C_p^\circ = f(T)$ deviates from a linear one and a relatively rapid increase in the heat capacity takes place that is, probably, due to approaching of C_p° the devitrification region. In the glassy state the differences in the heat capacity values of PMMA-C_{60} and PMMA-C_{70} are about ∼9% between 6 and 15 K, 2–3% from 15 to 50 K and those do not exceed the measurement uncertainty in the range from 50 to 370 K. It should be noted that the numerical magnitudes of C_p° for PMMA-C_{60} are almost always lower than those of PMMA-C_{70}. The differences in the C_p° values of the atactic PMMA and the tested PMMA-C_{60} and PMMA-C_{70} are noticeable only at $T < 50$ K. Nevertheless, the heat capacity values of them change, as temperature rises, in a similar manner. At $T > 50$ K the differences in C_p° of the objects compared are small and average ±1%. The deviations are quite explicable and result from a small content of fullerenes C_{60} and C_{70} in PMMA-C_{60} and PMMA-C_{70} and the conservation of their linear structure. The heat capacity of PMMA-C_{60} in a high-elasticity state rather sharply grows with rising temperature (section EFG, curve 1, Fig. 1), undergoing a visible jump at $T \sim 437$ K, and afterwards the C_p° values increase still more rapidly. The observed behavior of the temperature dependence of the heat capacity of PMMA-C_{60} in the high-elasticity state is similar to that of the polymer-analog PMMA, according to the calorimetric data for the latter [16]. This jump ($T \sim 437$ K) on the $C_p^\circ = f(T)$ plot is attributed to a temperature of the onset of the polymer thermal decomposition. It is worth of note that after completing the calorimetric experiment and unloading the samples of PMMA-C_{60} and PMMA-C_{70} from the ampoule they were not transparent, dark-yellow colored unlike the starting samples and their masses differed by 6 and 8%, respectively, from the masses prior to the beginning of measurements. This corroborates, certainly, the onset of their thermal decomposition under conditions of the calorimetric apparatus. A plot of the temperature-dependent heat capacity of PMMA-C_{70} is shown in the temperature range where it is thermostable being in the glassy and high-elasticity states (curve 2, Fig. 1). However, the temperature of its thermal decomposition onset (433 K) was calorimetrically determined by us. It is seen that the character of the change in C_p° of PMMA-C_{70} in the high-elasticity state with rising temperature slightly differs from that of PMMA and PMMA-C_{60}, i.e. the C_p° values of PMMA-C_{70} increase more gradually. The latter is likely to be explained by the influence of C_{70} available in the polymer composition.

A similar character of the change of the low-temperature ($T < 60$ K) heat capacity, as temperature rises, is common for the samples of the fullerene-containing derivatives of poly(methyl methacrylate) and the polymer-analog. Meanwhile, the thermal decomposition of PMMA-C_{60} sets in at a temperature by 4 K higher than of PMMA. The difference observed is surely small but noticeably greater than an experimental uncertainty of the determination of the transition temperatures. On the other side, the destruction range could, perhaps, shift towards a higher temperature range with growing the content of fullerene C_{60} in the polymer composition. It is natural to suppose that the effect of fullerene C_{70} on the temperature of the thermal decomposition onset will be similarly governed by its content in poly(methyl methacrylate). On this assumption, the close values of the temperatures of the decomposition onset of PMMA and PMMA-C_{70} are fairly explicable as in the latter there is at an average only one molecule of fullerene C_{70} per 160×10^3 monomeric units of a macromolecule. To assert with confidence in the given case about the extent of the influence of the fullerenes on the polymer properties is not quite correct, in our opinion, because the content of C_{60} in the PMMA-C_{60} sample is higher by nearly 1 order than of C_{70} in PMMA-C_{70}. To detect qualitative and quantitative dependences of the temperatures of the thermal decomposition onset and the devitrification of the fullerene-containing derivatives of poly(methyl methacrylate) it is expedient to continue their calorimetric study, using samples with a larger content of C_{60} and C_{70} in the polymer composition.

It was of interest to evaluate for the objects compared the values of the most signifant parameter of the multifractal

Table 1
Data of multifractal calculations of low-temperature heat capacity for the PMMA, PMMA-C_{60} and PMMA-C_{70}

Compound	Temperature interval (K)	D	θ_{max} (K)	δ (%)
PMMA-C_{60}	8–15	3.0	128.4	2.8
	20–50	1.5	237.5	0.9
PMMA-C_{70}	7–15	3.0	125.9	3.7
	20–50	1.6	224.8	1.4
PMMA	7–15	3.0	124.3	2.2
	20–50	1.5	237.8	1.3

variant of Debye's theory of heat capacity of solids [22,23], the fractal dimension D, that makes it possible to come to some conclusions about the heterodynamics character of the solids. The value of D, the exponent of a power at T in Eq. (1), can be estimated from the experimental C_p° values in the temperature range where $C_p^\circ \sim C_v$, plotting the corresponding curve on the $\ln C_v$ versus $\ln T$ coordinates [22,23]:

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)\left(\frac{T}{\theta_{max}}\right)^D, \tag{1}$$

where N is the number of atoms in a repeating monomeric unit, k: Boltzmann costant, $\gamma(D+1)$: γ-function, $\xi(D+1)$: Riemannian ξ-function, θ_{max}: the characteristic temperature, D: the fractal dimension which can vary from 1 to 4 right until fractional values [24,25]. Denoting in Eq. (1) a factor before $(T/\theta_{max})^D$ with A and taking logs, Eq. (2) was derived:

$$\ln C_v = \ln A + D \ln T. \tag{2}$$

Quite regularly assuming that at $T < 50$ K $C_p^\circ = C_v$ and graphically solving Eq. (2), the values of D and θ_{max} (Table 1) were determined. It should be noted that for the range 7–15 K the θ_{max} values were calculated for the degree of freedom $n = 3$ and between 20 and 50 K for $n = 6$. It was found that for the compared objects $D = 3$ over the range 7–15 K, i.e. their heat capacity in the above interval follows Debye's T^3 law. The value $D = 3$ in a hyperlow-temperature interval is, probably, due to a relatively close nature of intramolecular and intermolecular interaction for this range and this leads to that solids, regardless of the heterodynamic topology of a layer, become similar to bodies of spatial structure. With rising temperature from 20 to 40 K the fractal dimension decreases (Table 1) and takes an average between 1 and 2 and, perhaps, such magnitude remains at higher temperatures as well. This value of D points to a chain-plane structure of polymers [24,25]. On the other side, the fractal dimension different from $D = 1$ that is characteristic of linear polymers, to which the atactic poly(methyl methacrylate) belongs, seems to be caused by an appreciable interaction of the polymer chain fragments. These segments, certainly, possess another character of the structure heterodynamics that affects the D value [24,25].

According to Tarasov [24,26], a skeleton heat capacity of chain polymers is described by two-parameter function of heat capacity:

$$C_{1,3} = D_1\left(\frac{\theta_1}{T}\right) - \frac{\theta_3}{\theta_1}\left[D_1\left(\frac{\theta_3}{T}\right) - D_3\left(\frac{\theta_1}{T}\right)\right], \tag{3}$$

where D_1 and D_3 are symbols of Tarasov and Debye function of heat capacity, respectively; θ_1 and θ_3 are the corresponding characteristic temperatures; θ_3/θ_1 is the interchain interaction parameter varying from zero to unit. The mathematical expression of D_1 and D_3 functions was given earlier [24–26].

Proceeding from the supposition that at $T < 50$ K the contribution of atom oscillations to the heat capacity of the polymers under consideration is insignificant it can be assumed that in the above temperature range $C_p^\circ = C_{1,3}$ (C_v). Taking this into account, the values of θ_1 and θ_3 were chosen for the samples from their experimental C_p° values. For PMMA-C_{60} $\theta_1 = 128.4$ K and $\theta_3 = 118.8$ K between 22 and 32 K and in the case of PMMA-C_{70} $\theta_1 = 124.9$ K and $\theta_3 = 112.4$ K over the range from 20 to 30 K. For the polymer-analog without fullerenes, using its C_p° values [16], $\theta_1 = 124.3$ K and $\theta_3 = 118.9$ K were selected for the range from 18 to 30 K. With such values of θ_1 and θ_3 Eq. (3) reproduces the experimental values of the heat capacity with an uncertainty of ±0.97, ±2 and ±0.6% for PMMA-C_{60}, PMMA-C_{70} and PMMA, respectively, in the above temperature intervals.

The selection of the characteristic temperatures θ_1 and θ_3 was made by means of Chernoplekov's tables [27].

The parameter of interchain interaction θ_3/θ_1 proved to be 0.8 for PMMA-C_{60} and the polymer-analog PMMA, and in the case of PMMA-C_{70} $\theta_3/\theta_1 = 0.9$. This means [27] that energies of the interchain and intrachain interactions of the objects are relatively close. The difference in the θ_3/θ_1 values of these three polymers is likely to be within an error of its determination with regard of relatively similar C_p° values of the polymers, as was noted above.

3.2. Thermodynamic characteristics of devitrification and glassy state

As seen in Fig. 1, the devitrification of the fullerene-containing derivatives of poly(methyl methacrylate) and the atactic poly(methyl methacrylate) takes place practically in the same temperature range. The thermodynamic characteristics of devitrification are listed in Table 4. However, the glass transition temperatures (Table 2) of the objects, estimated from the relation $S^\circ = f(T)$, slightly differ [28]. The reasons of the distinctions are the same as with the temperatures of their

Table 2
Standard thermodynamic characteristics of devitrification and glassy state for PMMA-C_{60}, PMMA-C_{70} and atactic PMMA

Compound	Temperature interval (K)	$T_g^\circ \pm 1$ (K)	J/(K mol)		
			$\Delta C_p^\circ(T_g^\circ)$	S°_{conf}	$S^\circ(0)$
PMMA-C_{60}	360–400	379	39.2	10	10
PMMA-C_{70}	360–400	374	40.1	10	10
PMMA-a [16]	360–400	375	35.0	9	9

Table 3
Thermodynamic functions of studied PMMA-C_{60} and PMMA-C_{70} samples per mole of repeating unit ($M = 100.154$ and 100.122 g/mol, respectively); $p = 0.1$ MPa

T (K)	$C_p^\circ(T)$ (J/(K mol))		$H^\circ(T)-H^\circ(0)$ (kJ/mol)		$S^\circ(T)$ (J/(K mol))		$-[G^\circ(T)-H^\circ(0)]$ (kJ/mol)	
	PMMA-C_{60}	PMMA-C_{70}	PMMA-C_{60}	PMMA-C_{70}	PMMA-C_{60}	PMMA-C_{70}	PMMA-C_{60}	PMMA-C_{70}
Glassy state								
0	0	0	0	0	10	10	0	0
5	0.352	0.420	0.000400	0.000500	10	10	0.0501	0.0502
10	2.18	2.40	0.00620	0.00710	10.8	11.0	0.102	0.103
15	4.886	4.698	0.02360	0.02460	12.2	12.4	0.1597	0.1608
20	7.941	7.981	0.05560	0.0560	14.0	14.1	0.2251	0.2269
30	14.65	15.03	0.1682	0.1710	18.5	18.7	0.3871	0.3903
40	21.34	21.52	0.3485	0.3524	23.7	23.9	0.5976	0.6031
50	27.65	28.67	0.5937	0.6040	29.1	29.5	0.8612	0.8696
60	33.92	34.85	0.9014	0.9223	34.7	35.3	1.180	1.193
70	40.35	40.61	1.273	1.300	40.4	41.1	1.555	1.575
80	46.50	46.51	1.708	1.735	46.2	46.9	1.988	2.014
90	51.86	51.94	2.200	2.229	52.0	52.7	2.479	2.512
100	56.87	56.99	2.744	2.774	57.7	58.4	3.028	3.068
110	61.86	61.82	3.338	3.368	63.4	64.1	3.634	3.680
120	66.66	66.54	3.981	4.010	68.9	69.7	4.295	4.349
130	71.28	71.11	4.671	4.698	74.5	75.2	5.013	5.073
140	75.69	75.50	5.406	5.432	79.9	80.6	5.785	5.852
150	79.90	79.70	6.184	6.208	85.3	85.9	6.611	6.685
160	83.94	83.74	7.003	7.025	90.6	91.2	7.490	7.571
170	87.86	87.66	7.862	7.882	95.8	96.4	8.422	8.509
180	91.69	91.51	8.760	8.778	101	102	9.406	9.499
190	95.47	95.32	9.696	9.712	106	107	10.44	10.54
200	99.24	99.13	10.67	10.68	111	112	11.53	11.63
210	103.0	103.0	11.68	11.69	116	117	12.66	12.77
220	106.8	106.8	12.73	12.74	121	121	13.84	13.96
230	110.6	110.7	13.82	13.83	126	126	15.08	15.20
240	114.4	114.6	14.94	14.96	130	131	16.36	16.48
250	118.3	118.5	16.11	16.12	135	136	17.68	17.82
260	122.0	122.4	17.31	17.33	140	140	19.06	19.20
270	125.9	126.3	18.55	18.57	145	145	20.48	20.63
280	129.7	130.3	19.83	19.85	149	150	21.95	22.10
290	133.5	134.3	21.14	21.18	154	154	23.46	23.62
298.15	136.7	137.6	22.24	22.29	158	158	24.73	24.90
300	137.4	138.4	22.50	22.54	158	159	25.03	25.19
310	141.5	142.6	23.91	23.95	163	164	26.63	26.81
320	146.3	147.0	25.35	25.39	168	168	28.29	28.47
330	151.1	152.1	26.83	26.89	172	173	29.98	30.17
340	155.6	156.8	28.37	28.43	177	178	31.73	31.93
350	159.6	160.7	29.94	30.02	181	182	33.52	33.72
360	165.4	163.9	31.57	31.64	186	187	35.36	35.57
370	171.1	167.3	33.25	33.30	191	191	37.24	37.46
374	173.5	168.6	33.94	33.97	192	193	38.00	38.23
379	176.3	–	34.82	–	195	–	38.97	–
High elasticity state								
374	–	208.8	–	33.97	–	193	–	38.23
379	215.5	210.2	34.82	35.02	195	196	38.97	39.20
380	217	210.6	35.03	35.23	195	196	39.17	39.39
390	231	215	37.3	37.4	201	202	41.1	41.4
400	245	219	39.6	39.5	207	207	43.2	43.4
410	257	–	42.2	–	213	–	45.3	–
420	275	–	44.8	–	220	–	47.5	–
430	289	–	47.6	–	226	–	49.7	–

thermal decomposition onset and are attributed to a positive effect of the fullerenes available in the macromolecule composition on the physicochemical properties. The increase in the heat capacity on the devitrification $\Delta C_p^\circ(T_g^\circ)$ was found graphically (Fig. 1). The $\Delta C_p^\circ(T_g^\circ)$ values, as seen, are close because the polymers exist in an amorphous state and those were taken by us to evaluate the configurational entropy S°_{conf} of glass by Gibbs–Adam expression [29]:

$$S^\circ_{\mathrm{conf}} = \Delta C_p^\circ(T_g^\circ)\ \ln 1.29 \tag{4}$$

Table 4
Thermodynamic functions of studied PMMA-C_{60}, PMMA-C_{70} and PMMA [16] samples per mole of repeating unit (M = 100.154, 100.122 and 100.117 g/mol, respectively) at T = 298.15 K p = 0.1 MPa

Substance	$C_p^\circ(T) \pm 0.5$ J/(K mol)	$H^\circ(T) - H^\circ(0) \pm 0.18$ kJ/mol	$S^\circ(T) \pm 1.0$ J/(K mol)	$-[G^\circ(T) - H^\circ(0)]$, ± 0.20 kJ/mol
PMMA-C_{60}	136.7	22.24	158	24.73
PMMA-C_{70}	137.6	22.29	158	24.90
PMMA-a	135.7	22.09	157	24.70

where (1.29 + 0.14) is the ratio of T_g° and Kautzman hypothetical temperature T_2 [30].

According to the conclusions in [23,24], the S°_{conf} values were put equal to the zero entropy $S^\circ(0)$ of glassy polymers (Table 2) without a significant uncertainty. The values of the latter were used in the consequent calculation of the absolute entropy of the objects studied.

3.3. *Thermodynamic functions*

In Table 3 are summarized the standard thermodynamic functions of the samples of PMMA-C_{60} and PMMA-C_{70} in the glassy and high-elasticity states in the range from $T \to 0$ to 430 and 400 K, respectively. To estimate the functions the heat capacity of the compounds was extrapolated from 6 to 0 K by Debye's function of heat capacity of solids:

$$C_p^\circ = nD\left(\frac{\theta_D}{T}\right) \tag{5}$$

here D is the symbol of Debye's function of heat capacity; $n = 1$ and $\theta_D = 61.2$ and 57.6 K are specially chosen parameters for the polymers PMMA-C_{60} and PMMA-C_{70}, respectively. Eq. (5) describes the experimental C_p° values between 6 and 12 K within to ±1.5%; while calculating it was assumed that from 0 to 6 K Eq. (5) reproduces C_p° with the same uncertainty.

The calculation of the enthalpy $H^\circ(T) - H^\circ(0)$, the absolute entropy $S^\circ(T)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ was made by methods of the classical equilibrium thermodynamics, as demonstrated in [31]

Wunderlich et al. [16] generalized the works on the calorimetric study of thermodynamic properties of various samples of atactic poly(methyl methacrylate) and performed their critical analysis. So, in work [16] are given the recommended and the most precise up to the present values of C_p°, the characteristics of devitrification and the standard thermodynamic functions of the atactic PMMA sample with the maximum content of the main substance. The standard thermodynamic functions at 298.15 K and their relative deviations are given in Table 4 for the samples of PMMA-C_{60}, PMMA-C_{70} and the polymer-analog [16]. It is clear that the numerical differences in the corresponding thermodynamic functions of the objects being compared are small, they are not likely to exceed uncertainties of their estimation. In reality, it is not surprising and quite normal because C_{60} and C_{70} content in the samples is too low for prominent effects on the C_p° values in the regions where no physical transitions occur.

The standard entropy of formation $\Delta_f S^\circ = -597.9 \pm 1.8$ J/(K mol) of the tested polymers at 298.15 K was calculated by Eqs. (6) and (7) with using the values of their absolute entropy (Table 3) and the absolute entropy of simple substances (carbon [32], hydrogen and oxygen [33]:

$$5.003\mathrm{C_{gr}} + 4\mathrm{H_2} + \mathrm{O_2} \to \mathrm{C_{5.003}H_8O_2}, \tag{6}$$

$$5.0004\mathrm{C_{gr}} + 4\mathrm{H_2} + \mathrm{O_2} \to \mathrm{C_{5.0004}H_8O_2}. \tag{7}$$

The standard entropy of the synthesis reactions (8) and (9) of the polymers from poly(methyl methacrylate) [16] and fullerenes C_{60} and C_{70} [4] at 298.15 K was evaluated by the first corollary of Hess law. As a result, it was found that $\Delta_r S^\circ(\text{PMMA-C}_{60}) = -426.1$ J/(K mol) and $\Delta_r S^\circ(\text{PMMA-C}_{70}) = -452.3$ J/(K mol).

$$\mathrm{PMMA} + \mathrm{C_{60(fcc)}} \to \mathrm{PMMA\text{-}C_{60}}, \tag{8}$$

$$\mathrm{PMMA} + \mathrm{C_{70(cr)}} \to \mathrm{PMMA\text{-}C_{70}}. \tag{9}$$

In brackets are given the physical states of the reagents: fcc, a face-centered cubic phase; cr, crystalline.

4. Conclusion

A comparative physicochemical analysis of the standard thermodynamic properties of the fullerene-containing derivatives of atactic poly(methyl methacrylate) studied by us and the polymer-analog itself allowed the following inferences. The above concentrations of fullerenes C_{60} and C_{70} in the polymer composition do not change the heat capacity behavior with temperature and the character of their structure heterodynamics; the numerical values of C_p° of the compared objects are virtually close. However, a small but significant effect of fullerene C_{60} in the polymer composition on its temperatures of devitrification and thermal decomposition was detected. On the other side, since the researches were focused on the polymers with a low concentration of fullerenes C_{60} and C_{70} and the content of C_{60} in the sample of PMMA-C_{60} is almost by one order higher than C_{70} in PMMA-C_{70}, the question about the intensity of the affect of fullerenes C_{60} and C_{70} on the physicochemical properties of the polymer derivatives is left open for the present and calls for a subsequent complex approach to its solution.

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