Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 1, 229–234

THERMODYNAMIC PROPERTIES OF POLY[*bis*(TRIFLUOROETHOXY)PHOSPHAZENE] IN THE RANGE FROM $T\to 0$ TO 620 K

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By adiabatic vacuum and dynamic calorimetry, heat capacity for poly[*bis*(trifluoroethoxy)phosphazene] has been determined over the 6–620 K range. Physical transformations of the polymer on its heating and cooling have been detected and characterized. Smoothed heat capacity $C_p^0(T)$ and standard thermodynamic functions ($H^0(T)-H^0(0)$, $S^0(T)$ and $G^0(T)-H^0(0)$) of poly[*bis*(trifluoroethoxy)phosphazene] have been evaluated for the temperature range from $T\to 0$ to 560 K. The standard entropy of formation $\Delta_f S^0$ at T=298.15 K has been also determined. Fractal dimensions D in the heat capacity function of the multifractal variant of Debye's theory of heat capacity of solids characterizing the heterodynamics of the tested polymer have been determined.

Keywords: *calorimetry, heat capacity, poly[bis(trifluoroethoxy)phosphazene], thermodynamic functions*

Introduction

Poly[*bis*(trifluoroethoxy)phosphazene] (PTFP) is a flexible-chain polymer possessing a number of promising properties important for practical applications [1–6]. It is a representative of polyorganophosphazenes – a relatively new class of organoelement polymers that have been intensively studied during the last two or three decades. In particular, as the data of DSC, thermomechanical analysis, NMR and radiography showed, PTFP has two-phase transitions [7–10]: the first transition interpreted as the transition of the polymer crystals to the mesomorphic state (the mesophase) (crystal⇆mesophase) and the second one attributed to the transition of the mesophase to isotropic liquid (mesophase⇆isotropic liquid). These two transformations are separated with a wide temperature range about 150–180 K [5–9].

At present, the precise calorimetric data on the temperature dependence of the heat capacity of PTFP in the wide temperature interval are unavailable and the thermodynamic functions values are not published although those are needed to make precise thermodynamic calculations of processes with its participation.

The goal of the present work is to measure heat capacity for poly[*bis*(trifluoroethoxy)phosphazene] between 6 and 620 K, to detect the physical transformations of the polymer on its heating and cooling and to determine their thermodynamic characteristics as well as to calculate standard thermodynamic functions $C_p^0(T)$, $H^0(T)-H^0(0)$, $S^0(T)$ and $G^0(T)-H^0(0)$ over the temperature range of from $T\to 0$ to 560 K and the standard entropy of formation $\Delta_f S^0$ of the compound under study from simple substances at 298.15 K.

Experimental

Sample

The initial poly[*bis*(trifluoroethoxy)phosphazene] (PTFP-1) was prepared by the interaction of polydichlorophosphazene with sodium fluoroalcoholate in THF solution at 296 K by the procedure described earlier [11]. Its characteristics are as follows: the characteristic viscosity $[\eta]$=3.59 dL g^{-1} (was determined in THF at 298 K); viscosity-average molecular mass M_η=19.96·10^6; the content of Cl was <0.01 mass%. For measuring the heat capacity, PTFP-1 was heated up to the temperature (~370 K) corresponding to the mesomorphic state and then was cooled down to T~180 K. Afterwards, its heat capacity was measured again (the sample cooled from the mesophase is denoted as PTFP-2). The crystallinity degree (α) of PTFP-1 and PTFP-2 was found to be 34 and 61%, respectively. The technique of the crystallinity degree determination is considered in detail in the discussion of the results.

The calculations were made per mole of repeating monomeric unit with gross-formulae $-(C_4H_4O_2NPF_6)-$.

Apparatus and methods procedure

Heat capacity of PTFP was measured over the range 6–370 K in a BKT-3.0 fully automatic adiabatic vacuum calorimeter with liquid helium and nitrogen used

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1388–6150/$20.00

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as cooling agents. The calorimeter design and measurement procedure are similar to those reported elsewhere [12]. The reliability of its operation was tested by measuring the heat capacity of special purity copper, standard synthetic corundum and K-2 benzoic acid prepared at the Metrology Institute of the State Standard of RF. The error in C_p^0 values is within ±2% from 6 to 10 K, ±0.5% between 10 and 40 K and to ca. 0.2% for T>40 K.

Heat capacity of PTFP between 300 and 620 K was measured using an automatic thermoanalytical system operating on the principle of triple thermal bridge [13, 14], a dynamic calorimeter designed to study thermodynamic properties of substances in the above temperature range. The calorimeter design and the measurement procedure of the heat capacity, temperatures and enthalpies of physical transformations are similar to those described in [14]. Experimental error of C_p^0 varies from ±1 to ±2.5%. However, as the heat capacity measurements in two calorimeters overlap in the range from 300 to 370 K, it was assumed that the experimental error of C_p^0 at T>300 K was ±0.5–1.5%. The reliability of the calorimeter operation was checked by measuring the heat capacity of a standard sample of synthetic corundum and also the thermodynamic characteristics of fusion of indium, tin and lead. Our C_p^0 values for corundum differ from the recommended data by less than ±2.0%. The errors in melting points for indium, tin and lead are 0.2, 0.6 and 0.3 K, respectively. It was found that the calorimeter and the measurement procedures allow us to determine the heat capacity of substances in solid and liquid states with the maximum error of ±2.0%, the temperatures of transitions with ±0.5 K and the enthalpies of transitions ±1%.

Heat capacity was measured between 6 and 370 K for PTFP-1 and 180–620 K for PTFP-2. Sample mass of the PTFP inside the adiabatic calorimeter was 0.3783 g. The pressure of the heat-exchange gas (high-purity helium) in the calorimeter was 40 kPa at room temperature. Total 278 points for PTFP-1 and PTFP-2 were measured in the adiabatic vacuum calorimeter. The heat capacity of PTFP between 300 and 620 K was measured in the dynamic calorimeter at the average heating rate of 1.5 K min^{-1}. In dynamic calorimetry, sample mass of PTFP-2 was 0.5067 g. In the whole temperature range under study the heat capacity of PTFP was not more than 20–60% of the total heat capacity of the overall heat capacity of the calorimetric ampoule with the substance. The experimental C_p^0 values were smoothed by the fitting to semi-logarithmic polynomials. The mean-square deviation of the C_p^0 points from the smooth curve did not exceed ±0.11% in the range 6–40 K, ±0.08% between 40 and 90 K and ±0.05% from 90 to 370 K (in the range 300–620 K the measurements were made continuously).

Results and discussion

Heat capacity

The heat capacity for PTFP-1 and PTFP-2 are shown in Fig. 1. In the range 180–235 K for PTFP-1 and between 185 and 230 K for PTFP-2, the glass transition of an amorphous part of the samples is seen on the $C_p^0=f(T)$ curves (Fig. 2). The glass transition temperatures of PTFP-1 (206±1) K and PTFP-2 (207±1) K were estimated by the Alford and Dole method [15]. An increase in the heat capacity $\Delta C_p^0(T_g^0)$ on the glass transition of PTFP-2 (23 J K^{-1} mol^{-1}) is lower than that of PTFP-1 (39 J K^{-1} mol^{-1}), pointing to a greater crystallinity degree of PTFP-2 as compared to PTFP-1.

The heat capacity of PTFP-1 in the range 180–235 K is higher than of PTFP-2 and this situation holds up to the temperatures of the beginning of the crystal⇆mesophase transition. At the temperature lower than that the glass transition onset, the heat capacity values of PTFP-1 and PTFP-2 are the same within the error of measurements [16].

The transition crystal⇆mesophase of PTFP-1 appears in the range 290– 355 K and between 305 and 360 K for PTFP-2. It is worth to note that the relationship $C_p^0=f(T)$ was plotted for PTFP-1 (Fig. 1, section ABDFPN) cooled from about 295 K to the starting measurement temperature (6 K) at the rate of 0.01–0.02 K s^{-1} and for the PTFP-2 previously annealed at T~370 K for one hour and further cooled at the above rate down to the starting temperature of measurements (180 K) (section BEHLM, the lower curve).

The fusion of the mesophase is seen in Fig. 1 (section QRS) between 503 and 535 K. A relatively sharp increase of C_p^0 at T>560 K (section VW, Fig. 1) is the

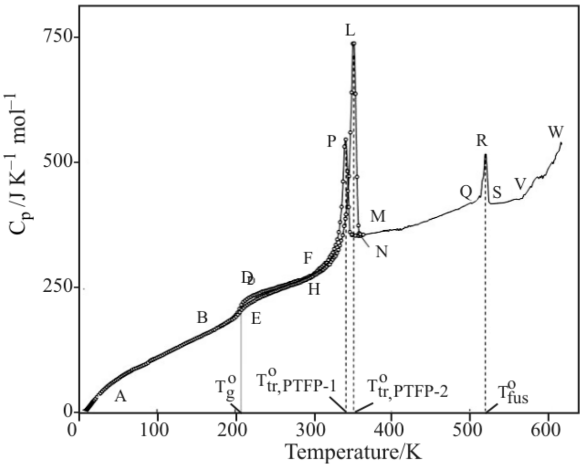

Fig. 1 Heat capacity of poly[*bis*(trifluoroethoxy)phosphazene]: ABDF – 34% crystallinity, ABEH – 61% crystallinity, AB and AE – amorphous part in glassy state, DF and EH – amorphous part in high-elasticity state, MQ – heat capacity of the polymer (61% mesophase state and 39% high-elasticity state), SV – heat capacity of isotropic melt

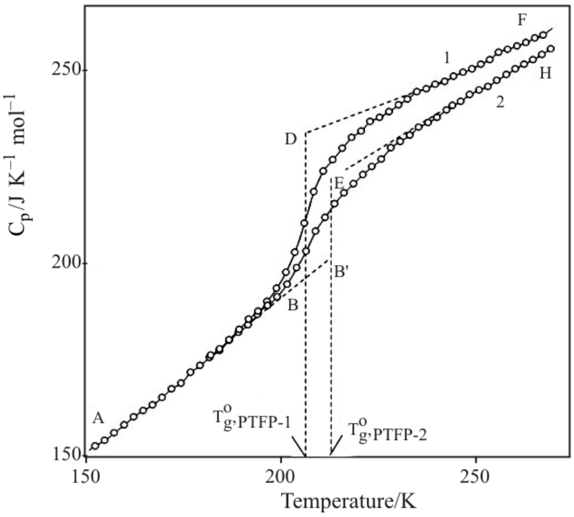

Fig. 2 Heat capacity of 1 – PTFP-1 and 2 – PTFP-2 in the interval of glass transition: AB and AB', amorphous part in glassy state, DF and EH, amorphous part in high-elasticity state, BD and B'E, the increase in the heat capacity in the glass transition interval

Table 1 Fractal dimensions and characteristic temperatures for PTFP-1

Temperature range/K	D	θ_{max}/K	δ^a/%
6–12	3	59.64	1.90
20–40	1.3	180.1	0.20
40–60	1	245.6	0.38

[a] δ is an uncertainty with which Eq. (1) reproduces the experimental C_p^0 values with the determined values of D and θ_{max}.

onset of the polymer thermal decomposition. This was confirmed by the reduction of the mass of the sample after the experiment by 7% and by the fact that on repeated measurements after the cooling from 620 down to 450 K the heat capacity was not reproduced. Similar behavior of PTFP on heating and cooling was observed earlier in DTA [7, 8] and DSC [9, 10] experiments.

The values of the fractal dimension D (Table 1) – the most significant parameter of the fractal version of Debye's theory of heat capacity of solids [17, 18] – were determined from the experimental data on the heat capacity of PTFP-1. The values of D were estimated using the technique described in our works [19, 20] with the use of Eq. (1):

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

where N is the number of atoms in a molecular unit, k the Boltzmann constant, $\gamma(D+1)$ the γ-function, $\xi(D+1)$ the Riemann ξ-function and θ_{max} is the characteristic temperature. According to [21], $D=1$ corresponds to the solids with chain structure, $D=2$ to those with a layered structure and $D=3$ [22] to those with a spatial structure. For the tested polymer $D=1$ at $T>30$ K corresponds to the chain structure that is retained at higher temperatures. The increase in the D values from 1 between 20 and 60 K to 3 over the range 6–12 K is associated with the reduction of the polymer volume and the increase of the interchain interaction as well as a gradual transition of the polymer to the state when the energies of intrachain and interchain interaction become equal. At the same time, the temperature dependence of the heat capacity is described with the law $C_p^0=AT^3$ that is characteristic of Debye's crystals [22].

Thermodynamic characteristics of phase transitions 'crystal⇆mesophase' and 'mesophase⇆isotropic liquid'

Figure 3 shows $C_p^0=f(T)$ for PTFP-1 and PTFP-2 near the crystal⇆mesophase transition. The temperatures (P and L, Fig. 3) corresponding to the maximum apparent heat capacity $C^0_{p,max}$ are regarded as the temperatures of transition $T^0_{tr,PP\text{-}1}$ of PTFP-1 and $T^0_{tr,PP\text{-}2}$ of PTFP-2. The enthalpies of crystal⇆mesophase transition of partially crystalline PTFP-1 ($\Delta_{tr}H^0(\alpha_1)$) and PTFP-2 ($\Delta_{tr}H^0(\alpha_2)$) were determined as a difference of enthalpies of heating calculated by numerical integration with respect to the temperature of the experimental $C_p^0=f(T)$ curves (sections APH and BLM, Fig. 3) and the corresponding 'normal' curves (sections ADFH and BEHM, Fig. 3). The entropies of crystal⇆mesophase transition were estimated from the enthalpies and temperatures of transition of partly crystalline PTFP-1 and PTFP-2 (Table 2).

Determination of crystallinity degree of PTFP-1 and PTFP-2

The crystallinity degrees of PTFP-1 and PTFP-2 are denoted α_1 and α_2, respectively. From the experimental data on the increase in the heat capacity on glass transition of PTFP-1 $\Delta C_p^0(\alpha_1)$ and PTFP-2 $\Delta C_p^0(\alpha_2)$ and enthalpies of their transition ($\Delta_{tr}H^0(\alpha_1)$, $\Delta_{tr}H^0(\alpha_2)$) to the mesophase state and, taking into account that for completely amorphous PTFP $\Delta C_p^0(\alpha=0)$ and completely crystalline polymer $\Delta_{tr}H^0(\alpha=100\%)$, the following equations can be written:

$$\alpha_1=1-\Delta C_p^0(\alpha_1)/\Delta C_p^0(\alpha=0) \tag{2a}$$

$$\alpha_1=\Delta_{tr}H^0(\alpha_1)/\Delta_{tr}H^0(\alpha=100\%) \tag{2b}$$

for PTFP-1 and

$$\alpha_2=1-\Delta C_p^0(\alpha_2)/\Delta C_p^0(\alpha=0) \tag{3a}$$

$$\alpha_2=\Delta_{tr}H^0(\alpha_2)/\Delta_{tr}H^0(\alpha=100\%) \tag{3b}$$

for PTFP-2.

Taking the right-hand parts of 2a and 3a equal to 2b and 3b, respectively, we obtained a set of two

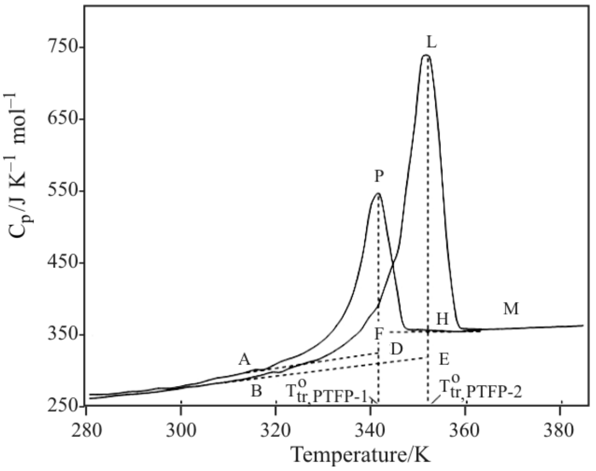

Fig. 3 Heat capacity of poly[*bis*(trifluoroethoxy)phosphazene] in the range of crystal⇆mesophase transition: AD – polymer consisting of 34% crystals and 66% in high-elasticity state, FH – polymer consisting of 34% mesophase and 66% in high-elasticity state, BE – polymer consisting of 61% crystals and 39% in high-elasticity state, HM – polymer consisting of 61% mesophase and 39% in high-elasticity state

Table 2 Thermodynamic characteristics[a] of phase transition crystal⇆mesophase of the polymer, M=243.05 g mol^{-1}, p°=0.1 MPa

Sample	T^0_{tr}/K	$C^0_{p,max}$/ J K^{-1} mol^{-1}	$\Delta_{tr}H^0$/ kJ mol^{-1}	$\Delta_{tr}S^0$/ J K^{-1} mol^{-1}
PTFP-1	341.7	547.1	2.89	8.46
PTFP-2	352.2	738.0	5.19	14.7

[a] T^0_{tr}, the transition temperature; $C^0_{p,max}$, the maximum apparent heat capacity in the crystal⇆mesophase transition interval, $\Delta_{tr}H^0$, the enthalpy of transition, $\Delta_{tr}S^0$, the entropy of transition.

equations in two unknowns $\Delta C^0_p(\alpha=0)$ and $\Delta_{tr}H^0(\alpha=100\%)$. Solving it for these two values, we obtained $\Delta C^0_p(\alpha=0)=59.1$ J K^{-1} mol^{-1} and $\Delta_{tr}H^0(\alpha=100\%)=8.5$ kJ mol^{-1}. Then, from Eqs (2) and (3) it was found that for PTFP-1 α_1=34% and for PTFP-2 α_2=61%.

Such an approach to the calculation of the crystallinity degree was described earlier, for example, in works [16, 23–26].

On cooling the annealed (at 370 K) sample and repeat measurement of the increase of C^0_p the enthalpy of crystal⇆mesophase transition and the shift of T^0_{tr} occur simultaneously. As was demonstrated earlier [9], the relation between these parameters is close to linear. Such dependence allows one to infer that the increase of α in the cooled sample that is indicated also by the decrease in $\Delta C^0_p(T^0_g)$ is mainly related to the growing crystallite sizes and correspondingly the expansion on annealing of mesomorphic regions from which the crystals are formed. The data reported in [9] point also to the availability of correlation between sizes of mesomorphic and crystalline regions.

The transition mesophase⇆isotropic liquid (fusion) occurred in the range 503–535 K. The temperature corresponding to the maximum apparent heat capacity $C^0_{p,max}$=517.7 J K^{-1} mol^{-1} in the above interval was considered as the melting temperature T^0_{fus}=520 K (point R, Fig. 1). The enthalpy of fusion $\Delta_{fus}H^0(\alpha=61\%)=0.793$ kJ mol^{-1} was estimated in a similar way as in the case of $\Delta_{tr}H^0$ value. The entropy of fusion $\Delta_{fus}S^0(\alpha=61\%)=1.53$ J K^{-1} mol^{-1} was calculated from the values of T^0_{fus} and $\Delta_{fus}H^0$. In the case of fusion of 100% mesophase the corresponding values of enthalpy and entropy are 1.30 kJ mol^{-1} and 2.50 J K^{-1} mol^{-1}. In conclusion it should be noted that the difference in T^0_{tr} and T^0_{fus} of PTFP equal to 168 K and $\Delta_{tr}H^0(\alpha=100\%)/\Delta_{fus}H^0(\alpha=100\%)=6.5$.

Our $\Delta_{tr}H^0$ and $\Delta_{fus}H^0$ values agree well with those obtained in DTA [7, 8] and DSC [9, 10] experiments, with the account of the difference in the crystallinity degrees of the PTFP samples under study and the conditions of measurements.

Thermodynamic functions

To calculate the standard thermodynamic functions of PTFP (Table 3), the relation C^0_p *vs.* T was extrapolated from 6 to 0 K by Debye's heat capacity function:

$$C^0_p=nD(\theta_D/T) \qquad (4)$$

where D denotes Debye's heat capacity function, n=4 and θ_D=59.6 K are specially selected parameters. Equation (4) describes heat capacity over the range 6–12 K with the error of ±1.9%. When calculating the functions, it was assumed that at T<6 K Eq. (4) reproduces the heat capacity of the polymer with the same error.

The enthalpy $H^0(T)-H^0(0)$ and entropy $S^0(T)$ were calculated by the numerical integration of the relations $C^0_p=f(T)$ and $C^0_p=f(\ln T)$, respectively. The Gibbs function $G^0(T)-H^0(0)$ was estimated from the enthalpy $H^0(T)-H^0(0)$ and entropy $S^0(T)$ values. A detailed procedure of the estimation is described in [16].

Taking the entropy value of PTFP-1 at T=298.15 K from Table 3 and the values of absolute entropies of carbon in the form of graphite, gaseous hydrogen, oxygen, nitrogen and fluorine as well as phosphorus from [27], the standard molar entropies of formation of the polymer in the crystalline and high-elasticity state at T=298.15 K were calculated: $\Delta_f S^0(\text{cr})=-920.9\pm1.5$ J K^{-1} mol^{-1} and $\Delta_f S^0(\text{h.e.})=-901\pm2$ J K^{-1} mol^{-1}. They correspond to the process:

$$4\text{C(gr)}+2\text{H}_2(g)+\text{O}_2(g)+0.5\text{N}_2(g)+\text{P(cubic, white)}+3\text{F}_2(g)\rightarrow-(\text{C}_4\text{H}_4\text{O}_2\text{NPF}_6)-$$

Table 3 Thermodynamic functions of poly[*bis*(trifluoroethoxy)phosphazene], M=243.05 g mol^{-1}, p°= 0.1 MPa

T/K	C_p^0/J K^{-1} mol^{-1}	$H^0(T)–H^0(0)$/ kJ mol^{-1}	$S^0(T)$/J K^{-1} mol^{-1}	$–[G^0(T)–H^0(0)]$/kJ mol^{-1}
		glassy state		
0	0	0	2	0
5	1.522	0.0019	2.51	0.0106
10	8.867	0.0269	5.70	0.0301
15	18.90	0.0967	11.2	0.713
20	28.88	0.2169	18.1	0.144
25	37.79	0.3837	25.5	0.253
50	70.79	1.780	62.9	1.36
100	113.0	6.423	126	6.14
150	151.3	13.0	179	13.8
200	187.8	21.5	227	23.9
207	192.9	22.8	234	25.6
		high-elasticity state		
207	252.0	22.8	234	25.6
250	275.5	34.2	284	36.8
298.15	300.7	48.1	334	51.6
300	301.6	48.6	336	52.2
350	328.0	64.4	385	70.3
400	354.0	81.4	430	90.6
450	380.2	99.8	473	113
500	406.4	119	515	138
520	413.8	128	531	148
		crystal I		
5	1.522	0.0019	0.5103	0.00064
10	8.867	0.0269	3.700	0.01007
15	18.90	0.0967	9.198	0.04128
20	28.88	0.2169	16.05	0.1042
25	37.79	0.3837	23.47	0.2031
50	70.79	1.783	60.96	1.265
100	113.0	6.423	123.6	5.942
150	151.3	13.04	176.7	13.48
200	187.8	21.51	225.3	23.54
250	224.5	31.82	271.12	35.96
298.15	259.7	43.48	313.7	50.04
300	261.1	43.96	315.3	50.63
350	297.7	57.93	358.3	67.47
352	299.2	58.52	360.0	68.19
		crystal II		
352	328.9	67.02	384.1	68.19
400	354.0	83.41	427.7	87.68
500	406.4	121.4	512.3	134.7
510	411.6	125.5	520.4	139.9
520	413.8	129.6	528.5	145.2

to be continued

Table 3 continued

T/K	C_p^0/J K^{-1} mol^{-1}	$H^0(T)$–$H^0(0)$/ kJ mol^{-1}	$S^0(T)$/J K^{-1} mol^{-1}	–[$G^0(T)$–$H^0(0)$]/kJ mol^{-1}
		liquid (isotropic melt)		
520	413.8	130.9	531.0	145.2
550	424.0	143.5	554.5	161.4
570	430.6	152.1	569.7	172.7

Conclusions

- The heat capacity for poly[*bis*(trifluoroethoxy)phosphazene] has been measured in the range from 6 to 620 K.
- The glass-transition, transitions ‘crystal⇆mesophase’ and ‘mesophase⇆isotropic liquid’ of the examined polymer on its heating and cooling in the above temperature interval have been detected and their thermodynamic characteristics were determined and interpreted.
- Based on our calorimetric data, the crystallinity degrees of poly[*bis*(trifluoroethoxy)phosphazene] samples were estimated.
- From experimental data the standard thermodynamic functions of poly[*bis*(trifluoroethoxy)phosphazene], namely, the heat capacity $C_p^0(T)$, enthalpy $H^0(T)$–$H^0(0)$, entropy $S^0(T)$ and Gibbs function $G^0(T)$–$H^0(0)$ have been calculated for the range 0 to 560 K for different physical states.

Acknowledgements

The work was performed with the financial support of Innovational Educational Program of NNSU in the framework of the National project ‘Education’.

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Received: January 25, 2008
Accepted: June 9, 2008
OnlineFirst: October 20, 2008

DOI: 10.1007/s10973-008-9038-7