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Thermodynamic properties of the block copolymer based on hyperbranched perfluorinated poly(phenylenegermane) and atactic polystyrene in the range from $T \rightarrow 0$ to 518 K

O.G. Zakharova, N.N. Smirnova, A.V. Markin[*], Yu.D. Semchikov

Nizhny Novgorod State University, Gagarin Prospekt 23/2, 603950 Nizhny Novgorod, Russia

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Abstract

In the present work, temperature dependence of heat capacity of the block copolymer based on hyperbranched perfluorinated poly(phenylenegermane) and atactic polystyrene has been measured first in the range from 6 to 350 K and between 320 and 534 K, respectively, by precision adiabatic vacuum and dynamic calorimetry. In the above temperature ranges, the devitrification of constituent blocks was detected and its thermodynamic characteristics have been determined and analyzed. 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 $S^\circ(T) - S^\circ(0)$ and Gibbs function $G^\circ(T) - H^\circ(0)$, for the range from $T \rightarrow 0$ to 518 K. The standard thermodynamic properties of the said substance were compared with corresponding data for the initial homopolymers as well as for the block copolymer on basis of hyperbranched perfluorinated poly(phenylenegermane) and atactic poly(methylmeth)acrylate studied earlier.

Keywords: Block copolymers; Hyperbranched polymers; Adiabatic vacuum calorimetry; Heat capacity; Thermodynamic functions; Devitrification of constituent blocks

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1. Introduction

Hyperbranched polymers, which were first synthesized a little more than one decade ago, are now one of the fastest-developing areas of chemistry [1–4]. The progress in this field has given origin to a novel, unusual macromolecular architecture and to some properties of polymers (good solubility, low viscosity and high sorption). Physico-chemical properties of the hyperbranched polymers have not been sufficiently studied [5–7]. These are a particular class of high-molecular compounds containing non-regular branches that may be used as mosaic-type building blocks for hybrid macromolecules [8,9]. Depending on the chemical nature of the blocks and their length, one can prepare polymers whose structure and properties differ from the properties of the initial components. Now they are potentially applied in medicine, technique and optoelectronics.

Earlier [10] some physico-chemical, in particular, thermodynamic properties of the block copolymer on the basis of hyperbranched perfluorinated poly(phenylenegermane) and atactic poly(meth)acrylate were studied by us. The present work continues the complex research of standard thermodynamic properties of block copolymers on the basis of hyperbranched perfluorinated poly(phenylenegermane) and vinyl polymers.

The goal of the work is to calorimetrically determine the temperature dependence of the heat capacity $C_p^\circ = f(T)$ of the block copolymer based on hyperbranched perfluorinated poly(phenylenegermane) and atactic polystyrene from 6 to 534 K, to detect the possible physical transformations on its heating and cooling and to estimate their thermodynamic characteristics, to calculate the standard thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$ and $G^\circ(T) - H^\circ(0)$ in the range from $T \rightarrow 0$ to 518 K, to carry out the physico-chemical interpretation of the obtained results in the aggregate with the data for the initial homopolymers.

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[*] Corresponding author. Tel.: +7 831 465 64 50; fax: +7 831 434 50 56.
E-mail address: markin@calorimetry-center.ru (A.V. Markin).

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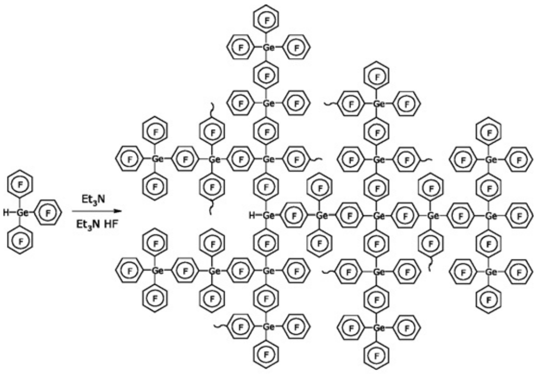
2. Experimental

2.1. Sample

The structure of the hyperbranched perfluorinated poly(phenylenegermane) (PPG) is shown as an example below.



PPG

Block copolymer based on the PPG and atactic polystyrene (a-PSt) was prepared in two steps. At the first stage of synthesis, a (C_6F_5)Ge-group was introduced into a polystyrene macromolecule via the chain-transfer reaction. Upon subsequent activated copolycondensation with tris(pentafluorophenyl)germane, the first generation of dendritic hyperbranched poly(phenylenegermane) is formed at the end of the polystyrene macromolecule [11].

The relative content of linear and hyperbranched fragments in the block copolymer was estimated by IR-spectroscopy ("Bruker ISF-110") and on the basis of mass analysis of the polymer sample upon their extraction in a Soxhlet apparatus using specially selected solvents. It was demonstrated that a hybrid macromolecule contains on average 89 wt% polystyrene and 11 wt% perfluorogermane units. The molecular mass of block copolymer was estimated by size exclusion chromatography (SEC) ("Shimadzu" Prominence LC20, THF). The values of the number-average molecular weight and weight-average molecular weight as well as the polydispersity are $M_n = 26{,}300$, $M_w = 98{,}900$ and $p = 3.8$, respectively.

The detailed description of the synthesis technique of block copolymer and some characteristics of its structure are given in Ref. [11].

The block copolymer has 2.04 mol% PPG and 97.96 mol% a-PSt; its molecular mass was estimated as 113.2 g/mol. The gross-formulae of the repeating monomer unit for the copolymer is $[(C_8H_8)_{0.9796}\{(C_6F_5)_2GeC_6F_4\}_{0.0204}]$. All the following calculations were made per indicated mole [12]. The sample under investigation was denoted conventionally as $(PPG)_{0.0204}$(a-PSt)$_{0.9796}$.

2.2. Apparatus and measurement procedure

To measure the heat capacity C_p° of the tested substance in the range from 6 to 350 K, a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The calorimeter design and the operation procedure were described earlier [13,14]. The calorimeter was tested by measuring the heat capacity of special-purity copper (OSCH) and reference samples of synthetic corundum and K-2 benzoic acid. The analysis of the results showed that an uncertainty of measurements of the heat capacity of the substance at helium temperatures was within ±2%, with rising temperature up to 40 K it decreased to ±0.5% and was equal to ±0.2% at $T > 40$ K. Temperatures of physical transformations can be determined with an error of ±0.02 K.

To measure the heat capacity of the sample between 320 and 534 K, an automatic thermoanalytical complex (ADKTTM) – a dynamic calorimeter operating by the principle of triple thermal bridge – was used [15,16]. The device design and the measurement procedure of the heat capacity, temperatures and enthalpies of physical transformations were demonstrated in detail in the same papers. The reliability of the calorimeter operation was checked by measuring the heat capacity of the standard sample of synthetic corundum as well as the thermodynamic characteristics of fusion of indium, tin and lead. As a result, it was found that the calorimeter and the measurement technique allow one to obtain the heat capacity values of the substances in solid and liquid states with a maximum error of ±1.5% and the physical transformation temperatures within ca. ±0.5 K. Since the heat capacity of the examined compound was also measured between 320 and 350 K in the adiabatic vacuum calorimeter with an error of ±0.2% and the conditions of measurements in the dynamic device were chosen so that in the above temperature interval the C_p° values measured with the use of both calorimeters coincided, it was assumed that at $T > 350$ K the heat capacity was determined with an error of 0.5–1.5%. The data on the heat capacity of the object under study were obtained in the range from 320 to 534 K at the average rate of heating of the calorimeter and the substance of 0.0333 K/s.

3. Results and discussion

3.1. Heat capacity

The C_p° measurements were carried out between 6 and 534 K. The masses of the sample loaded in the calorimetric ampoules of the BKT-3.0 and ADKTTM devices were 0.4415 and 0.3243 g, respectively. In the BKT-3.0 calorimeter 140 experimental C_p° values were obtained in two series of experiments. The heat capacity of the sample varied from 20 to 60% of the total heat capacity of (calorimetric ampoule + substance) over the range between 6 and 534 K. The averaging of the experimental C_p° points in the region where any transformations were absent was made as degree and semilogarithmic polynomials, the corresponding coefficients were chosen by means of computer programs.

The experimental values of the molar heat capacity of $(PPG)_{0.0204}$(a-PSt)$_{0.9796}$ over the range from 6 to 534 K and the averaging $C_p^\circ = f(T)$ plot are presented in Fig. 1. The heat capacity C_p° of this compound increases gradually with rising temperature and does not show any peculiarities up to 330 K.

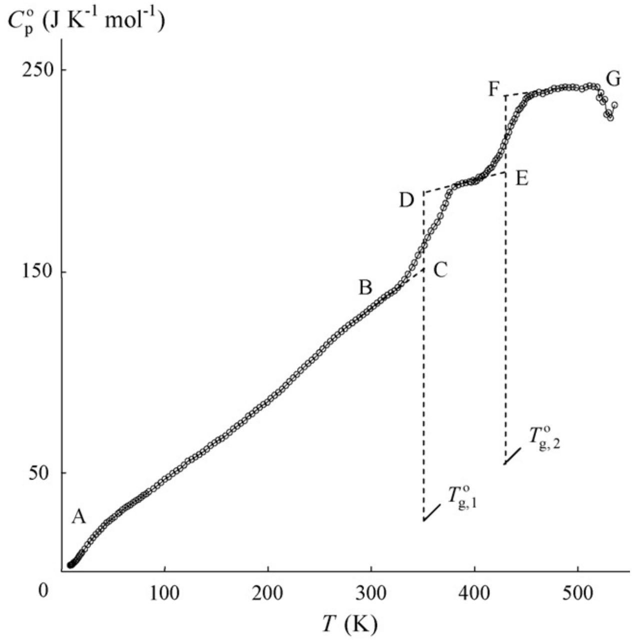


Fig. 1. Temperature dependence of heat capacity of block copolymer $(PPG)_{0.0204}(a\text{-}PSt)_{0.9796}$: ABC—the glassy state of PPG and a-PSt blocks; FG—the high elasticity state of PPG and a-PSt blocks; CD and EF—the increase in heat capacity on devitrification of a-PSt and PPG, respectively; DE—the high elasticity state of a-PSt block and glassy state of PPG block.

The tested substance under the conditions of our apparatus was cooled from room temperature to the temperature of the measurement onset (∼6 K) at the rate of 0.01 K/s. On subsequent heating the block copolymer underwent devitrification over the ranges from 330 to 385 K and from 400 to 460 K. A sharp decrease in heat capacity beginning from ∼518 K is apparently related to the onset of thermal degradation of the block copolymer under examination, as evidenced by changes in the sample when the calorimetric experiment was completed. It should be noted that the $C_p^\circ = f(T)$ curve and the observed physical transformations were reproduced upon repeated heating and cooling of the block copolymer to ∼518 K (Fig. 1, section ABG on the curve). Thus, the constituents of the blocks existed in the glassy and high-elasticity states in the temperature range considered.

Within the 40–300 K interval, the heat capacity is a linear function of the temperature ($C_p^\circ \sim T^1$); at 6–20 K, the heat capacity is described rather well by Debye heat capacity function for solids; that is, $C_p^\circ \sim T^3$. In accordance with Ref. [17], a change in the C_p° of the block copolymer with temperature over the 6−300 K range is quite regular.

3.2. *Thermodynamic characteristics of devitrification and glassy state*

The thermodynamic characteristics of devitrification of block copolymer constituent and glassy state and, for comparison, of PPG [18], a-PSt [17] and $(PPG)_{0.0435}(PMMA)_{0.9565}$ [10] are listed in Table 1. The temperature devitrification intervals were determined graphically on $C_p^\circ = f(T)$ curve (Fig. 1). The glass transition temperature of blocks was determined by Alford and Dole method [19]—from the inflection of the plot of the temperature dependence of entropy of heating. An increase in the heat capacity on devitrification (Fig. 1, CD and EF) was determined graphically, too. The configuration entropies of blocks [S_{conf}°(PPG) and S_{conf}°(a-PSt)] were calculated by the following equation [20]:

$$S_{\text{conf}}^\circ = \Delta C_p^\circ(T_g^\circ)\ \ln \frac{T_g^\circ}{T_2^\circ} \qquad (1)$$

where T_2° is Kauzmann temperature [21], the ratio T_g°/T_2° is equal to 1.29 ± 0.14 [20,22]. It is suggested that the ratio is also valid in this case.

The zero entropy of block copolymer was estimated as the sum of configuration entropies contributions

$$S^\circ(0) = S_{\text{conf}}^\circ(\text{PPG}) + S_{\text{conf}}^\circ(\text{a-PSt}) \qquad (2)$$

The entropy of mixing is not considered in Eq. (2) because for most polymer systems its value is small in comparison with configuration entropy [23].

3.3. *Standard thermodynamic functions*

To calculate the standard thermodynamic functions (Table 2) of the block copolymer based on hyperbranched perfluorinated poly(phenylenegermane) and atactic polystyrene its C_p° values were extrapolated from the temperature of the measurement onset to 0 K by Debye's function of heat capacity

$$C_p^\circ = nD\left(\frac{\theta_D}{T}\right) \qquad (3)$$

where D is the symbol of Debye's function, $n = 1$ and $\theta_D = 45.31$ K are specially selected parameters. Eq. (3) with

Table 1
The standard thermodynamic characteristics of devitrification and glassy state for the $(PPG)_{0.0204}(a\text{-}PSt)_{0.9796}$ and $(PPG)_{0.0435}(a\text{-}PMMA)_{0.9565}$ block copolymers and corresponding homopolymers

Sample	$T_{g,1}^\circ \pm 1$ (K)	$T_{g,2}^\circ \pm 1$ (K)	$\Delta C_p^\circ(T_{g,1}^\circ)$	$\Delta C_p^\circ(T_{g,2}^\circ)$	$S_{\text{conf},1}^\circ$	$S_{\text{conf},2}^\circ$
			J K^{-1} mol^{-1}			
$(PPG)_{0.0204}(a\text{-}PSt)_{0.9796}$	356	432	29.3	29.6	7	8
$(PPG)_{0.0435}$ $(a\text{-}PMMA)_{0.9565}$ [10]	352	390	34.8	31.7	9	8
a-PSt [17]	373	–	31	–	8	–
a-PMMA [25]	375	–	35.0	–	9[a]	–
PPG [18]	–	436	–	64	–	16

[a] The value was estimated by us in Ref. [10].

Table 2
The thermodynamic functions of the $(PPG)_{0.0204}(a\text{-}PSt)_{0.9796}$; $M = 113.195$ g/mol, $p^0 = 0.1$ MPa

T (K)	$C_p^\circ(T)$ (J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(0)$ (kJ mol^{-1})	$S^\circ(T) - S^\circ(0)$ (J K^{-1} mol^{-1})	$-[G^\circ(T) - G^\circ(0)]$ (kJ mol^{-1})
Glassy state of the PPG and a-PSt blocks				
5	0.828	0.0011	0.286	0.000361
10	3.55	0.0124	1.74	0.00496
20	9.25	0.0722	5.659	0.04094
40	21.60	0.3893	16.16	0.2573
50	27.20	0.6342	21.61	0.4461
60	31.54	0.9288	26.97	0.6891
80	38.63	1.632	37.03	1.331
100	46.10	2.477	46.43	2.166
120	54.17	3.480	55.55	3.186
140	62.19	4.644	64.50	4.387
150	66.05	5.285	68.93	5.054
200	86.13	9.070	90.56	9.043
220	96.04	10.90	99.26	10.94
240	105.9	12.92	108.0	13.01
250	110.7	14.00	112.5	14.12
298.15	132.6	19.89	133.9	20.05
300	133.2	20.13	134.8	20.30
320	142.3	22.89	143.6	23.08
350	157.2	27.36	157.0	27.59
356	160.5	28.31	159.7	28.54
High elasticity state of a-PSt block and glassy state of PPG block				
356	189.8	28.31	159.7	28.54
380	194.6	32.92	172.2	32.52
400	198.9	36.86	182.3	36.07
420	204.0	40.88	192.1	39.82
432	206.9	43.31	197.8	42.12
High elasticity state of the PPG and a-PSt blocks				
432	236.5	43.31	197.8	42.12
440	237.6	45.25	202.3	43.76
450	238.9	47.64	207.6	45.81
480	243.1	54.87	223.2	52.27
500	245.1	59.75	233.2	56.84
518	246.1	64.17	241.9	61.11

the above parameters describes the experimental C_p° values of the compound between 6 and 11 K with an error of ±1.8%. When calculating the functions it was assumed that Eq. (3) reproduces the C_p° values of block copolymer at $T < 6$ K with the same error. The calculations of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T) - S^\circ(0)$ were made by the numerical integration of $C_p^\circ = f(T)$ and $C_p^\circ = f(\ln T)$ curves, respectively and the Gibbs function $G^\circ(T) - H^\circ(0)$ was estimated from the enthalpies and entropies at the corresponding temperatures [24]. It was suggested that the error of the function values is ±1% at $T < 40$ K, ±0.5% between 40 and 80 K, ±0.2% in the range from 80 to 350 K and ±1.5% between 350 and 518 K.

3.4. Comparison of standard thermodynamic properties of the hybrid block copolymers $(PPG)_{0.0204}(a\text{-}PSt)_{0.9796}$ and $(PPG)_{0.0435}(a\text{-}PMMA)_{0.9565}$ and respective homopolymers (PPG, a-PMMA and a-PSt)

It was of interest to compare some physico-chemical properties of the tested block copolymer and corresponding homopolymers (PPG and a-PSt) as well as the hybrid block copolymer $(PPG)_{0.0435}(a\text{-}PMMA)_{0.9565}$ [10] that we have studied earlier.

It can be seen from the analysis of heat capacity temperature dependence for compared block copolymers, the transition of the G type in the 14–22 K range and the exothermic transformation in the 200–240 K range which are seen for the initial PPG [12,18] are absent on $C_p^\circ = f(T)$ curves. The first transformation was attributed to the excitation of the oscillatory motion of pentafluorophenyl and tetrafluorophenyl radicals linked to the germanium atom in PPG molecules [12]. One of the reasons why transition is absent in block copolymers is, apparently, the mutual influence of their components. Another reason for the observed results divergence may be an insufficient molar amount of PPG in the block copolymer, taking into account the thermodynamic characteristics of the low-temperature anomalies [12].

The interaction between the two blocks of copolymers is confirmed by the finding that, up to devitrification temperature, the difference in the heat capacities of the tested samples and corresponding additive mixtures of PPG, a-PSt and a-PMMA homopolymers is much larger than the experimental error in determination of C_p°. Evidently, this may be explained by the fact that linear a-PSt and a-PMMA units situated inside the hyperbranched macromolecule hinder the oscillations of C_6F_4 and C_6F_5 groups also situated there.

In Table 1, the numerical values of devitrification temperatures T_g° and the increase in the heat capacity $\Delta C_p^\circ(T_g^\circ)$ at devitrification are shown for the block copolymers under study and their corresponding homopolymers. The values of temperatures 432 and 390 K indicate the devitrification of PPG block whereas 356 and 352 K correspond to the devitrification of a-Pst and a-PMMA blocks, respectively. It should be noted that values T_g° and $\Delta C_p^\circ(T_g^\circ)$ for the block copolymers and the initial homopolymers-analogues are slightly different. This is caused by the structural changes and mutual influence of some sites of block macromolecules. Thus, the devitrification of a-PSt and PPG blocks occurs 17 and 4 K earlier than that of the initial a-PSt [17] and PPG [12,18], respectively. The observed differences denotes a more friable nature of the block copolymer under investigations in comparison with initial a-PSt and PPG. This is also proved by a rather small value θ_D $(n = 1) = 45.31$ K of the characteristic Debye's temperature.

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