

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

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Abstract

In the present work, temperature dependence of heat capacity of the block copolymer based on hyperbranched perfluorinated poly(phenylene-germane) 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(phenylene-germane) and atactic poly(methylmeth)acrylate studied earlier.

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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(phenylene-germane) 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(phenylene-germane) and vinyl polymers.

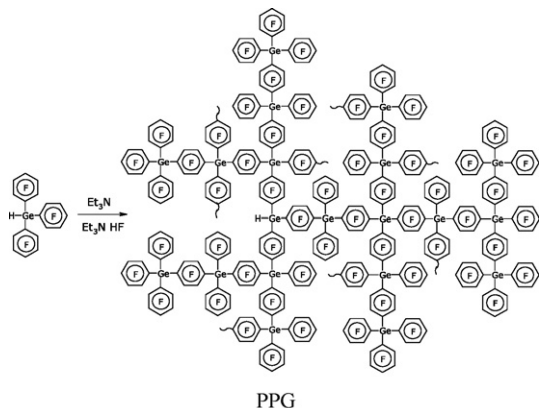
The goal of the work is to calorimetrically determine the temperature dependence of the heat capacity $C_p^\circ = f(T)$ of the block copolymer based on hyperbranched perfluorinated poly(phenylene-germane) and atactic polystyrene from 6 to 534 K, to detect the possible physical transformations on its 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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2. Experimental

2.1. Sample

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



Block copolymer based on the PPG and atactic polystyrene (a-PSt) was prepared in two steps. At the first stage of synthesis, a $(C_6F_5)_2Ge$ -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 $[(C_8H_8)_{0.9796}\{(C_6F_5)_2GeC_6F_4\}_{0.0204}]_n$. 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 $\pm 2\%$, with rising temperature up to 40 K it decreased to $\pm 0.5\%$ and was equal to $\pm 0.2\%$ 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 $\pm 1.5\%$ 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 $\pm 0.2\%$ 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.

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