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ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев статью (Sologubov Semen S., Markin Alexey V., Sarmini Yuliya A., Smirnova Natalia N., Boldyrev Konstantin L., Tatarinova Elena A., Meshkov Ivan B., Muzafarov Aziz M., Thermodynamic investigation of G2 and G4 siloxane dendrimers with trimethylsilyl terminal groups) в журнал (Journal of Chemical Thermodynamics) подтверждает, что в материале ***не содержатся*** сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала ***не следует*** получать разрешение ***Минобрнауки России и/или Президиума РАН***

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Thermodynamic investigation of G2 and G4 siloxane dendrimers with trimethylsilyl terminal groups

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ABSTRACT

In this work, we report results of the calorimetric study of the second (G2[OSi(CH_3)$_3$]$_{12}$) and fourth (G4[OSi(CH_3)$_3$]$_{48}$) generation siloxane dendrimers with trimethylsilyl terminal groups. The heat capacities of dendrimers were precisely measured in the temperature range T = (5–520) K using a fully automated adiabatic calorimeter and a heat-flux differential scanning calorimeter. In the above temperature interval, the physical transformations of the studied compounds were detected, and its thermodynamic characteristics were determined. The fundamental thermodynamic functions (the enthalpy $[H°(T) - H°(0)]$, the entropy $[S°(T) - S°(0)]$, the Gibbs energy $[G°(T) - H°(0)]$) of dendrimers were calculated over the range from $T \to 0$ to 520 K using the experimentally determined heat capacities of the investigated compounds. The standard entropies of formation of dendrimers G2[OSi(CH_3)$_3$]$_{12}$ and G4[OSi(CH_3)$_3$]$_{48}$ were evaluated at T = 298.15 K. The obtained thermodynamic data of the investigated dendrimers were compared with those of the studied earlier siloxane dendrimers G1[OSi(CH_3)$_3$]$_6$ and G3[OSi(CH_3)$_3$]$_{24}$, which represent the structurally related homologous series of organosilicon dendrimers. As a result, the dependences between thermodynamic properties of the studied siloxane dendrimers and their molecular mass were established.

1. Introduction

Dendrimers are nanoscaled well-defined globular macromolecules with a low polydispersity (in comparison with traditional polymers) and a highly branched three-dimensional architecture constituted of three main structural elements: a core (a multifunctional atomic group, considered as the zeroth generation, *i.e.* G0), an inner sphere (tree-like branches emanating from the core, consisted of the repeating units, whose repetition is organized in a geometrical progression that results in a series of radially concentric layers called generations, *i.e.* G1, G2, G3, etc.), and an outer layer (many terminal functional groups, increased exponentially as a function of generation and located on the macromolecule surface, which play a key role in the properties of dendrimers) [1–3]. After the publication of the pioneering papers [4–7], which dealt with the development and the realization of this principally new molecular architecture, there has been a rapid and impressive progress in dendrimer science. As a result, the step-by-step controlled synthetic methods have been modified to produce representative series of dendrimers differing by their chemical nature and structure [8–10]. At present, the design of functional dendrimers is an area with unlimited possibilities for fundamental discoveries and practical applications.

In light of their unique molecular architecture, dendrimers have attracted increasing attention in the past few years. Due to the versatile physical and chemical properties of dendrimers, arising from the structural features, they are potential candidates for biomedical fields, nanoengineering, electronics, and catalysis [11–16].

Among the numerous dendritic macromolecules, carbosilane (Si–C) and siloxane (Si–O) dendrimers have emerged as one of the most important and promising classes of silicon-containing dendrimers [17,18]. The first oxygen-containing organosilicon dendrimers were synthesized by Rebrov et al. up to the fourth generation [19]. After that, series of siloxane dendrimers with longer branches was developed in the early 1990s [20–24]. These fully amorphous compounds, built from very flexible siloxane chains, have a lower glass transition temperature, a smaller hydrodynamic volume, and a lower viscosity than their linear analogues having the same chemical composition and molecular mass. Furthermore,

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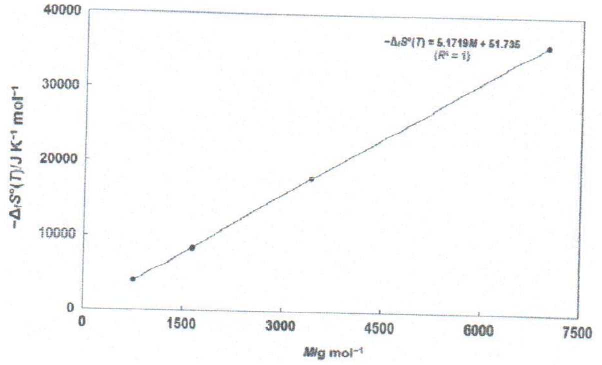

Fig. 10. The "entropy of formation *vs.* molecular mass" isothermal dependence at T = 298.15 K (●) for homologous series of siloxane dendrimers GX[OSi(CH$_3$)$_3$]$_z$.

transition were observed in the experimental temperature interval. The standard thermodynamic characteristics of these transformations were determined and compared with those for the studied earlier carbosilane dendrimers with different functional terminal groups on the surface layer. The standard thermodynamic functions of dendrimers G2[OSi(CH$_3$)$_3$]$_{12}$ and G4[OSi(CH$_3$)$_3$]$_{48}$ were calculated over the range from $T \to 0$ to 520 K using their experimentally determined heat capacities. The standard entropies of formation of the studied dendrimers were evaluated at T = 298.15 K. The obtained experimental results were used to establish the "thermodynamic property *vs.* molecular mass" dependences for the investigated homologous series of siloxane dendrimers GX[OSi(CH$_3$)$_3$]$_z$. The resulting isotherms can be used for validation of theoretical and empirical methods in order to predict thermodynamic properties of the unstudied dendrimers differing by their chemical nature and structure.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jct.2020.106318.

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