



Investigation of thermodynamic properties of liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal groups



Yanina S. Samosudova^a, Alexey V. Markin^{a,*}, Natalia N. Smirnova^a, Natalia I. Boiko^b, Valery P. Shibaev^b

^a Lobachevsky State University of Nizhni Novgorod, 23/5 Gagarin Av., 603950 Nizhni Novgorod, Russian Federation

^b Moscow State University, Leninskie Gory, 119991 Moscow, Russian Federation

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ABSTRACT

The temperature dependences of the heat capacity of liquid-crystalline carbosilane dendrimers of the first to the fourth generations with methoxyphenylbenzoate terminal groups have been measured by the method of adiabatic vacuum calorimetry over the range from $T = (6 \text{ to } 370) \text{ K}$ in the present investigation. The phase transformations have been detected and their thermodynamic characteristics have been estimated and analyzed in the above temperature range. The 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 potential Φ_m° , for the range from $T \rightarrow (0 \text{ to } 370) \text{ K}$ and the standard entropy of formation of dendrimers in different physical states at $T = 298.15 \text{ K}$ have been calculated based on the experimental values. The standard entropies of hypothetical synthesis of studied compounds were estimated. The linear dependences of changing the corresponding thermodynamic properties of the dendrimers on their molecular weight and the number of mesogenic groups on the outer layer have been obtained.

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1. Introduction

Dendrimers are represented monodisperse macromolecules with regular and highly branched three-dimensional architecture [1–5]. The construction of dendrimers can be realized by two basic ways: by a divergent approach, in which the molecule is growing from the core to the periphery, and a convergent approach, when the dendrimer molecule is built starting from the periphery fragments. The choice of the synthetic methods is determined by the available chemical reactions, requirements toward the dendrimer molecules and the other factors [6].

The basic features of dendrimers are hyper-branched topology; a low polydispersity, the absence of linking which are specific for long macromolecules and the large number of terminal groups. In addition, they are commonly characterized by low values of glass transition temperature, high solubility, and low viscosity in solutions [7–10]. The combination of dendrimers structural perfection and the possibilities of their groups' modification are specified their application as functional nanosized materials with unique electronic, optical, magnetic and chemical properties that are required for the elaboration of modern nanotechnology.

Liquid-crystalline (LQ) dendrimers take a special position among a wide variety of dendritic molecules due to their specific molecular structure combined flexible spherical dendritic architecture with rigid rod-like mesogenic groups capable of anisotropic LC mesophase formation. The induction and the control of the mesomorphic properties (phase type and stability) in dendrimers can be achieved by a dedicated molecular design which depends on the chemical nature and structure of both the functional groups and the dendritic matrix. Nowadays, different LC dendrimers on the base of polyorganosiloxane, carbosilane, polyimine and other dendritic structure were synthesized [11–16].

This research is continued the complex investigations of thermodynamics of liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal group. Earlier the thermodynamic properties of liquid-crystalline carbosilane dendrimers of the second and the fourth generations with methoxyphenylbenzoate terminal groups have been examined by us [17]. In this connection it seems interesting to find the dependences of changing the corresponding thermodynamic properties of the dendrimers on their structural parameters.

Thus, the goal of the present investigation is to study the thermodynamic properties of liquid-crystalline carbosilane dendrimers of the first to the fourth generations with methoxyphenylbenzoate terminal groups in the temperature range from (6 to 370) K by adiabatic vacuum calorimetry and to reveal the dependences of thermodynamic properties on dendrimers composition and structure.

* Corresponding author. Tel.: +7 831 462 35 59.

E-mail address: markin@calorimetry-center.ru (A.V. Markin).

2. Experimental

2.1. Samples

The synthesis and structure of liquid-crystalline carbosilane dendrimers of the first and the third generations with terminal methoxyphenyl benzoate groups are represented in figures 1 and 2. As regards the others dendrimers, these data were published in reference [17].

The samples of dendrimers under study have been synthesized in Moscow State University at the Laboratory of Polymers Chemical Transformations of High-molecular Compounds by the method described in detailed elsewhere [18]. Derived samples were cleaned by the methods of preparative gel permeation chromatography (a «KNAUER» device, column Waters 8 · 300 on ultrasilicagel with pore size (dimension) 100 nm, THF as an eluent, detector is the refractometer Waters R-410). The purity and individuality of studied dendrimers were approved by gel permeation chromatography (GPC) and NMR ^1H – spectroscopy (a Bruker WP-200 and WP-250 spectrometer in CCl_4 and CDCl_3 solutions).

NMR ^1H data for **G-1(Und-MPhB)₈**: (CCl_4 , 200 MHz): $\delta = 0.1$ (s, 12H), 0.2 (s, 96H), 0.8 (m, 64H), 1.5 (m, 124H), 1.9 (m, 16H), 2.8 (t, 16H), 7.1 (d, 16H), 7.3 (d, 32H), 7.4 (d, 16H), 8.4 (d, 16H).

G-2(Und-MPhB)₁₆: (CCl_4 , 200 MHz): $\delta = 0.1$ (s, 36H), 0.2 (s, 192H), 0.7 (m, 112H), 1.4 (m, 268H), 1.8 (m, 32H), 2.6 (m, 32H), 3.9 (t, 48H), 7.0 (d, 32H), 7.2 (d, 32H), 7.3 (d, 32H), 8.3 (d, 32H).

G-3(Und-MPhB)₃₂: (CDCl_3 , 250 MHz): $\delta = -0.08$ (s, 84H), 0.03 (s, 384H), 0.54 (m, 240H), 1.28 (m, 568H), 1.73 (m, 64H), 2.55

(m, 64H), $\delta = 3.79$ (t, 96H), 6.90 (d, 64H), 7.09 (d, 64H), 7.19 (d, 64H), 8.18 (d, 64H).

G-4(Und-MPhB)₆₄: (CDCl_3 , 250 MHz): $\delta = -0.08$ (s, 180H), 0.03 (s, 768H), 0.54 (m, 624H), 1.27 (m, 268H), 1.72 (m, 128H), 2.54 (m, 128H), $\delta = 3.78$ (t, 196H), 6.89 (d, 28H), 7.08 (d, 128H), 7.18 (d, 128H), 8.18 (d, 128H).

The polarizing microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarizing microscope. X-ray diffraction measurements were made using $\text{CuK}\alpha$ -radiation ($\lambda = 1.542 \text{ \AA}$) from 1.5 kW sealed tube. Monodispersity of compounds was confirmed by GPC analysis.

The information for all studied dendrimers is listed in table 1 as phase behavior and structure was published in detail in reference [19].

2.2. Apparatus

A precision automatic adiabatic vacuum calorimeter (BCT-3) with discrete heating was used to measure heat capacities over the temperature range from (6 to 370) K. The liquid helium and nitrogen were used as cooling reagents. The principle and structure of the adiabatic calorimeter are described in detail elsewhere [20,21]. The all measurements were performed with a computer-controlled measuring system comprising of an analogue-to-digital converter, a digital-to-analogue converter, and a switch. The calorimetric cell is a thin-walled cylindrical vessel made from titanium. The sensitivity of the thermometric circuit was

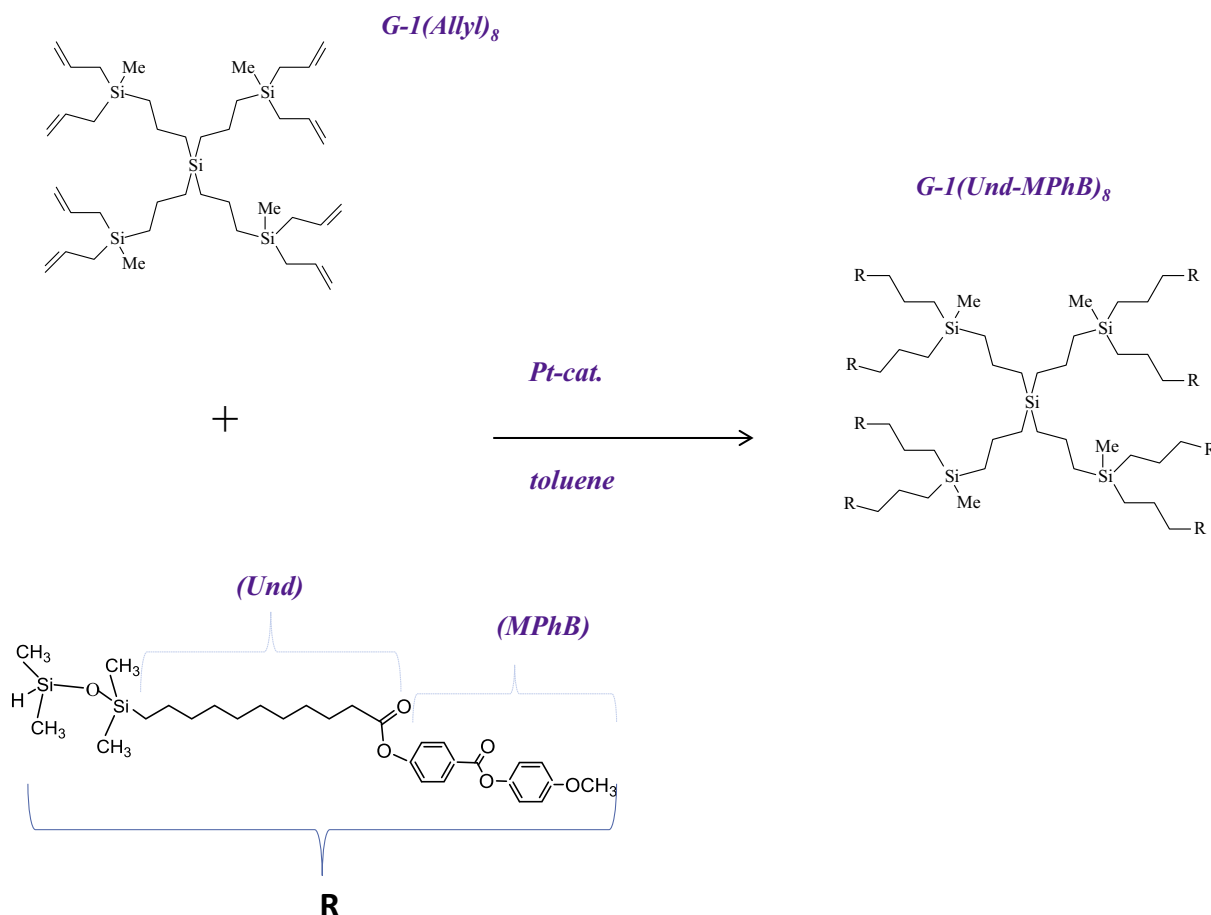


FIGURE 1. The scheme of synthesis and structure of liquid-crystalline carbosilane dendrimer of the first generation with terminal methoxyphenylbenzoate groups **G-1(Und-MPhB)₈**.

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