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Thermodynamic properties of liquid-crystalline carbosilane dendrimers of the second and the fourth generation with methoxyphenylbenzoate terminal groups

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ABSTRACT

In the present work temperature dependences of heat capacity of liquid-crystalline carbosilane dendrimers with terminal methoxyphenylbenzoate groups of the second and the fourth generations have been determined in the range from 6 to 370 K by the precision adiabatic vacuum calorimetry. In the above temperature range the phase transformations have been detected and their thermodynamic characteristics have been determined and analyzed. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity $C_p^o(T)$, enthalpy $H^o(T) - H^o(0)$, entropy $S^o(T) - S^o(0)$ and Gibbs energy $G^o(T) - H^o(0)$, for the range from $T \to 0$ to 370 K. The standard entropies of formation of dendrimers in liquid-crystalline state at $T = 298.15$ K and the standard entropies of hypothetic synthesis at the same temperature were estimated. It was shown that thermodynamic properties dendrimers under study do not depend on generation number and are defined by nature of terminal groups.

1. Introduction

Dendrimers are specially class of high-molecular compounds whose molecules are highly ordered spatially hyperbranched topologically completely acyclic compositions with structure of continuously branching tree [1,2]. Liquid-crystalline (LC) dendrimers, which molecules combine structural units (commonly referred to as mesogenic groups) capable to impart the liquid-crystalline properties with amorphous dendritic architecture have attracted progressively growing attention of researchers engaged in the chemistry and physics of liquid crystals, physical chemistry of polymers, and supramolecular chemistry [3–8]. This interest is related to the search for new materials for nanotechnology and electronics which need molecules – particles with a size of several nanometers – that are capable of ordering and changing their properties under application of external fields.

Carbosilane liquid-crystalline dendrimers hold a particular position among a wide scope of studied dendrimers. This is connected with their kinetic and thermodynamic stability and vast possibilities to change their dendritic architecture via specific reactions typical of silicon [3–8].

The structure and phase state of different generation LC carbosilane dendrimers with various types of terminal groups are examined in detail at the present time [9–12]. However the data on thermodynamic properties of liquid-crystalline dendrimers are absent.

In this connection the aim of this study is calorimetric investigation on the temperature dependence of heat capacity of LC carbosilane dendrimers of the second and the fourth generations with terminal methoxyphenylbenzoate groups G-2 $(Und\text{-}MPhB)_{16}$ and G-4$(Und\text{-}MPhB)_{64}$ in the range 6–370 K, detection of possible phase transformations and determination of their thermodynamic characteristics, calculation thermodynamic functions $C_p^o(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$ and $G^\circ(T) - H^\circ(0)$ over the temperature range from $T \to 0$ to 370 K and standard entropies of formation of dendrimers in liquid-crystalline state at $T = 298.15$ K and the revealing of dependences of dendrimers thermodynamic functions on their composition.

2. Experimental

2.1. Sample

The scheme of synthesis and structure of liquid-crystalline carbosilane dendrimers of the second and the fourth generations with terminal methoxythenyl benzoate groups are shown on Fig. 1.

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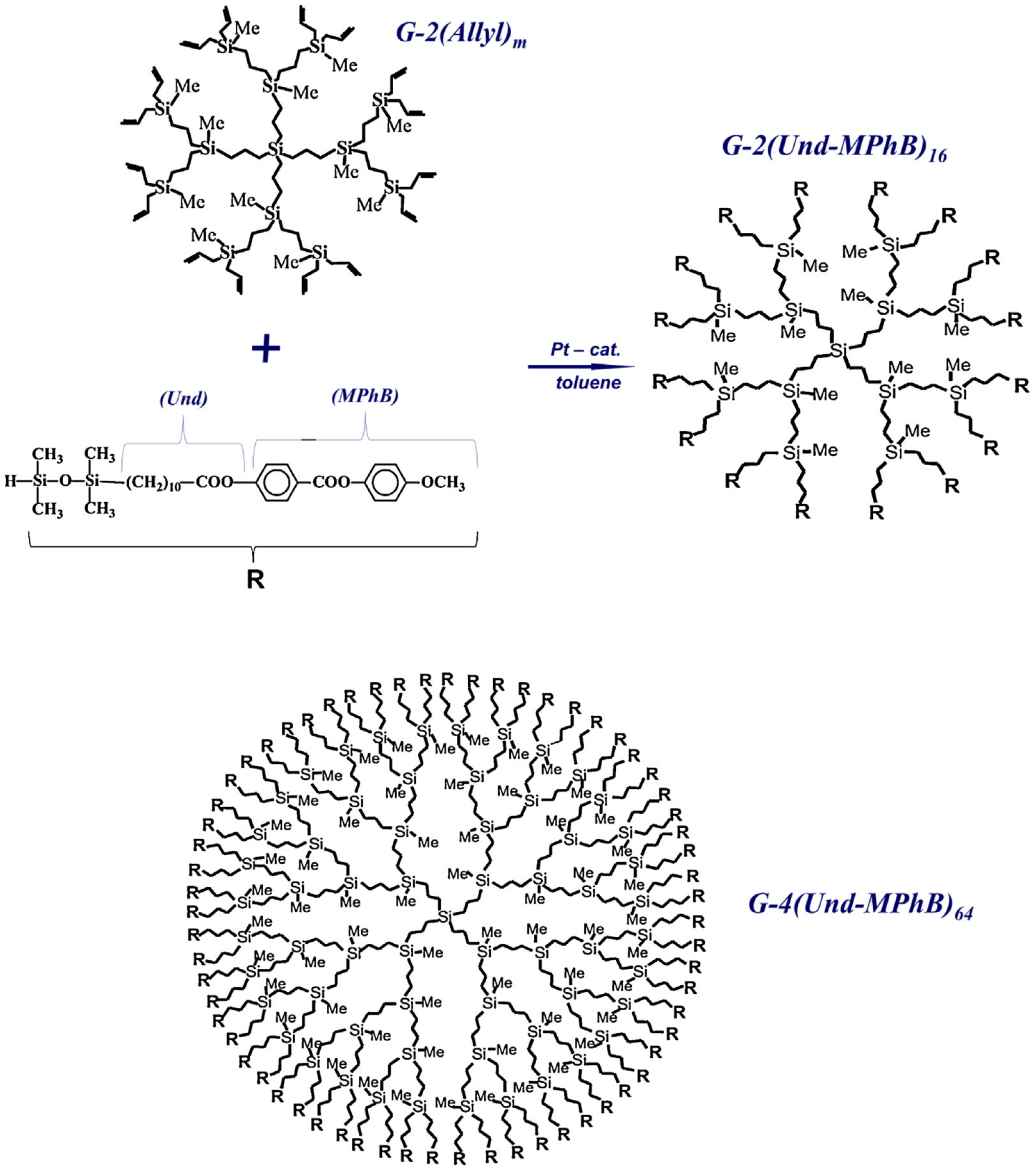

Fig. 1. The scheme of synthesis and structure of liquid-crystalline carbosilane dendrimers of second and fourth generations with terminal methoxyphenylbenzoate groups.

The samples of dendrimers under study were synthesized in Moscow State University at the Laboratory of Polymers Chemical Transformations of High-molecular Compounds by the method described in detailed elsewhere [13].

Obtained dendrimer samples were cleaned by the methods of preparative gel permeation chromatography (a «KNAUER» device, column Waters 8 × 300 on ultrasilicagel with pore size (dimension) 10^3 Å, THF as an eluent, detector is the refractometer Waters R-410). Purity and individuality of studied dendrimers were approved by GPC analysis and NMR ^{1}H-spectroscopy (a Bruker WP-200 and WP-250 spectrometer in CCl_4 and $CDCl_3$ solutions).

NMR ^{1}H data for **G-2(Und-MPhB)$_{16}$**: (CCl_4, 200 MHz): δ = 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). NMR ^{1}H data for **G-4(Und-MPhB)$_{64}$**: ($CDCl_3$, 250 MHz): δ = −0.08 (s, 180H), 0.03 (s, 768H), 0.54 (m, 624H), 1.27 (m, 268H), 1.72 (m, 128H), 2.54 (m, 128H), δ = 3.78 (t, 196H), 6.89 (d, 28H), 7.08 (d, 128H), 7.18 (d, 128H), 8.18 (d, 128H).

Table 1
Samples information.

Sample	Source	State	Mole fraction purity	Purification and analysis methods
G-2(Und-MPhB)$_{16}$	Present work	Liquid-crystalline	0.99	GPC[a] NMR ^{1}H-spectroscopy, X-ray diffraction analysis
G-4(Und-MPhB)$_{64}$	Present work	Liquid-crystalline	0.99	GPC[a] NMR ^{1}H-spectroscopy, X-ray diffraction analysis

[a] Gel permeation chromatography.