



Thermodynamic properties of poly(phenylene-pyridyl) dendrons of the second and the third generations



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ABSTRACT

The temperature dependence of the heat capacity of poly(phenylene-pyridyl) dendrons of the second and the third generations have been measured by the method of adiabatic vacuum and differential scanning calorimetry over the range from 6 K to (500–520) K in the present research. Phase transformations have been detected and their thermodynamic characteristics have been estimated and analysed in the above temperature range. The standard thermodynamic functions, namely, the heat capacity $C_p^0(T)$, enthalpy $H^0(T) - H^0(0)$, entropy $S^0(T) - S^0(0)$ and potential Φ_m^0 , for the range from $T \rightarrow 0$ K to (500–520) K and the standard entropy of formation of the dendrons in different physical states at $T = 298.15$ K have been calculated based on the experimental results. The thermodynamic characteristics of the samples under study and investigated earlier, poly(phenylene-pyridyl) dendrons decorated with dodecyl groups of the same generations have been compared and discussed.

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1. Introduction

Dendrimers and corresponding to them dendrons are unique monodisperse macromolecules with regular and highly branched three-dimensional architecture [1–6]. Dendrons are represented structural units of dendrimers and may be used for their construction based on convergent approach. According to this method firstly, there is the growth of branched monomers (dendrons), which are attached to the dendrimer core at the last synthesis step. In return, dendrons have been derived via consequence repetition of reaction steps.

At the present time, a wide variety of different classes of dendrimers have been synthesized, on basic amines, carbosilanes, siloxanes, esters, ethers, and various organometallic and amino acid-based structures [3]. As a result of well-defined regular architecture and broad possibilities for modification of their surface groups, dendrimers may be employed as functional nanosized materials with unique electronic, optical, magnetic and chemical properties that are required for the elaboration of modern nanotechnology.

In contrast to dendrimers containing conformationally flexible single bonds (as in carbosilane, carbosilanesiloxane dendrimers),

polyphenylene dendrimers are stiff, and conformational changes can only occur via rotation around the inter-ring C–C bonds [7]. Furthermore, poly(phenylene-pyridyl) dendrimers and dendrons possess high chemical and thermal stability similar to linear polyphenylenes, but with greatly increased solubility due to the prevention of intermolecular packing, which is typical for linear poly-p-phenylenes [8].

In addition, the rigid structure of poly(phenylene-pyridyl) dendrimers opens possibility of their application for the construction of novel hybrid nanostructure systems (dendrimer – metal) with catalytic properties. Thus, poly(phenylene-pyridyl) dendrimers were found to serve as a powerful template for metal nanoparticle formation, resulting in excellent nanoparticle stability [9,10].

The scheme of structures of poly(phenylene-pyridyl) dendrons of the second and the third generations are shown on Fig. 1 [4]. On Fig. 1, D2 and D3 are designated the number of generation. It is very significant to indicate the generation number, because dendrimers and dendrons are formed by series of reiterative or generational reactions, they are typically identified by the number of generations to which they have been reacted.

If the calorimetric investigation of dendrimers with various composition and architecture had continued for a several decades, then thermodynamic properties of individual dendrons would have been sufficiently studied. Only in papers [11,12] by the methods of precision adiabatic vacuum and differential scanning

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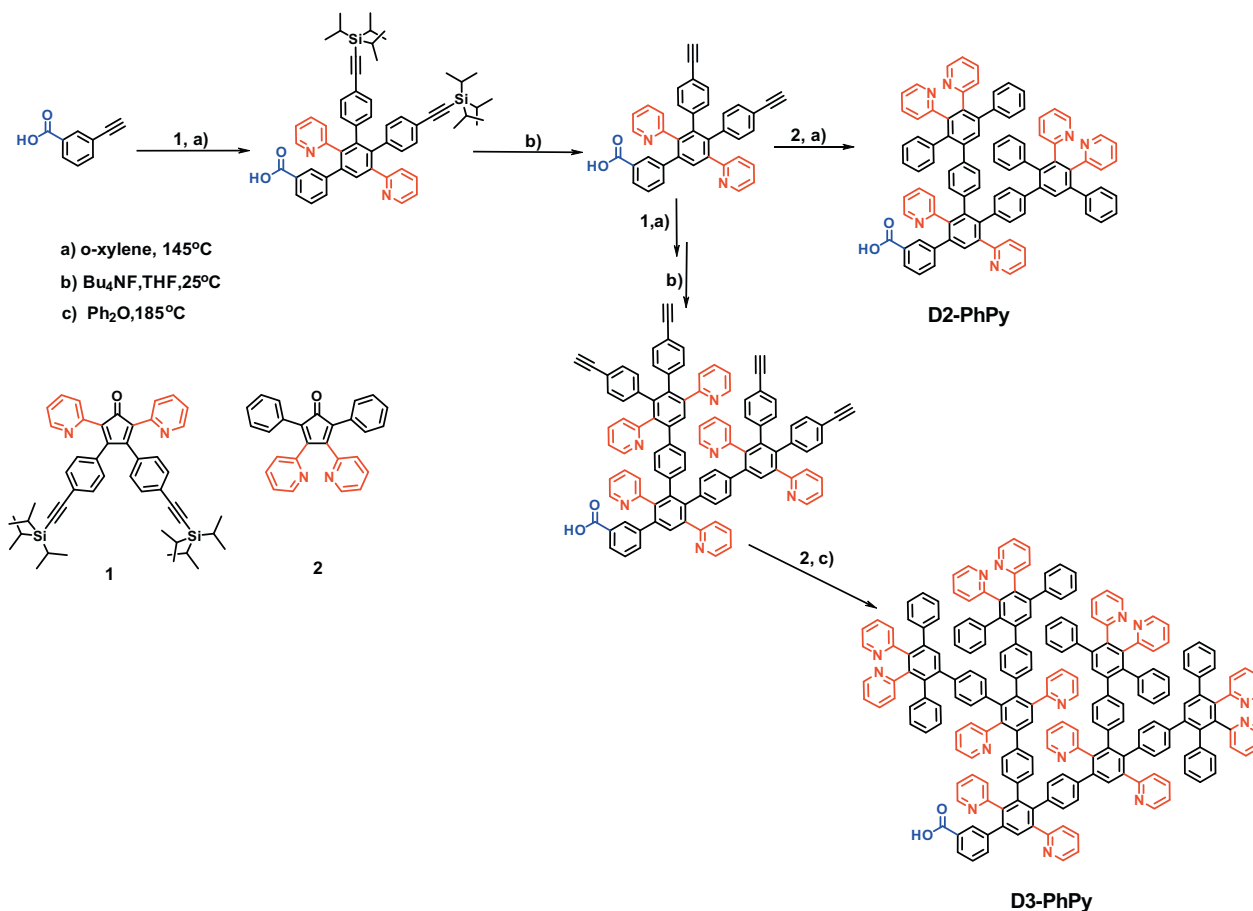


Fig. 1. The scheme of synthesis and structures of poly(phenylene-pyridyl) dendrons.

calorimetry have the heat capacities been studied for poly(phenylene-pyridyl) dendrons decorated with dodecyl groups of the second D2-C₁₂H₂₅ (α_1 , α_2) and the third D3-C₁₂H₂₅ generations. Thermodynamic properties of the dendrons are evidently required for the determination of synthesis regularities for dendrimers.

Thus, the goal of the present investigation is to study the thermodynamic properties of poly(phenylene-pyridyl) dendrons of the second and the third generations over the temperature range from 6 K to (500–520) K by the methods of adiabatic vacuum and differential scanning calorimetry and to reveal the dependences of thermodynamic properties on the composition and structure of dendrimers.

2. Experimental

2.1. Samples

The samples of D2-PhPy (α) and D3-PhPy (gross-formulae C₉₁H₆₀N₆O₂ and C₂₀₃H₁₃₂N₁₄O₂ correspondingly) were synthesized in A.N. Nesmeyanov Institute of Organoelement compounds, Russian Academy of Science of (Moscow) by the method described in detailed elsewhere [13]. The molar masses of these units were calculated from the International Union of Pure and Applied Chemistry (IUPAC) table of atomic weights [14].

The purity and monodispersity of the dendrons have been confirmed by the methods of MALDI-TOF mass spectrometry (a Bruker Biflex III MALDI-TOF instrument) and NMR ¹H-spectroscopy (a Bruker Avance 600 spectrometer). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 510P FT-IR spectrometer. The

investigations by the method of transmission electron microscopy (TEM) were acquired at an accelerating voltage of 80 kV on a JEOL JEM1010 transmission electron microscope. X-ray diffraction measurements have been obtained using a Scintag theta-theta powder diffractometer with a CuK_α source (0.154 nm).

NMR ¹H data for **D2-PhPy** (α): (600 MHz, CDCl₃): 13.0 (s, 1H, COOH), 8.61 (d, 1H, PyH), 8.28 (d, 5H, PyH), 7.8 (s, 1H, ArH), 7.78 (s, 1H, ArH), 7.73 (s, 1H, ArH), 7.66 (s, 1H, ArH), 7.4–6.65 (m, 49H).

D3-PhPy: (600 MHz, CDCl₃): 13.0 (s, 1H, COOH), 8.62 (d, 3H, PyH), 8.22 (d, 11H, PyH), 7.93 (s, 1H, Ar), 7.78 (s, 1H), 7.59–7.47 (m, 6H, Ar), 7.40–6.47 (m, 118H, Ar).

The information for the dendrons under study is listed in Table 1.

2.2. Apparatus

A precision automatic adiabatic vacuum calorimeter (Block Calorimetric Thermophysical, BCT-3) with discrete heating was used to measure the heat capacities over the temperature range from 6 K to 350 K. Liquid helium and liquid nitrogen were used as cooling reagents. The calorimeter design and the operation procedure are described in detail elsewhere [15,16]. 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 0.001 K, and the sensitivity of the analogue-to-digital converter was 0.1 μV . The energy introduced into the sample cell and the equilibrium temperature of the cell

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