Thermochimica Acta 617 (2015) 144–151

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Calorimetric and infrared studies of carbosilane dendrimers of the third generation with ethyleneoxide terminal groups

A.V. Markin[a,*], S.S. Sologubov[a], N.N. Smirnova[a], A.V. Knyazev[a], M. Mączka[b], M. Ptak[b], N.A. Novozhilova[c], E.A. Tatarinova[c], A.M. Muzafarov[c]

[a] *Lobachevsky State University of Nizhni Novgorod, 23/5 Gagarin Av., 603950 Nizhni Novgorod, Russia*
[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wroclaw, Poland*
[c] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70 Profsoyuznaya St., 117393 Moscow, Russia*

ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form 21 August 2015
Accepted 22 August 2015
Available online 24 August 2015

Keywords:
Carbosilane dendrimers
AC
DSC
Heat capacity
Glass transition
Thermodynamic functions
IR spectroscopy

ABSTRACT

In the present work, temperature dependences of heat capacities of carbosilane dendrimers of the third generation with ethyleneoxide terminal groups, denoted as $G3[(OCH_2CH_2)_1OCH_3]_{32}$ and $G3[(OCH_2CH_2)_3OCH_3]_{32}$, have been measured in the temperature ranges from $T = 6$ to 520 K by precision adiabatic calorimetry (AC) and differential scanning calorimetry (DSC). In the above temperature range the physical transformations, such as glass transition and anomalies, have been detected, and their standard thermodynamic characteristics have been determined and analyzed. Complementary temperature-dependent infrared (IR) studies of carbosilane dendrimer $G3[(OCH_2CH_2)_1OCH_3]_{32}$ have been performed in the range from $T = 4$ to 298 K in order to study the nature of the revealed transformations. The standard thermodynamic functions of dendrimers under study, namely, heat capacity $C_p^0(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$, and Gibbs energy $G^\circ(T) - H^\circ(0)$ have been calculated for the range from $T \to 0$ to 520 K. The standard thermodynamic properties of the investigated dendrimers have been discussed and compared with literature data for carbosilane dendrimers with different functional terminal groups.

1. Introduction

The synthesis, study and application of dendrimers are one of new and rapidly developing directions of polymer science. Dendrimers are complex monodisperse macromolecules with a regular and highly branched three-dimensional architecture and well-defined chemical structure [1,2]. Together with the hyperbranched polymers they represent a new class of polymeric materials, so-called macromolecular nanoobjects [3]. The synthesis of dendrimers is realized by repeating sequences of reaction steps. These sequences of reactions allow controlling the dendrimers composition, chemical structure, molecular weight and their outer layers nature.

Dendrimers combine the properties of macromolecules and individual particles; when compared to linear polymers, dendrimers have significantly increased solubility and very low viscosity in solutions [4]. The combination of structural perfection of dendrimers and possibilities of modification of their terminal functional groups enable to control the properties of dendrimers over wide ranges. Therefore, dendrimers have been widely and successfully applied to different up-to-date investigations [5–8].

The study of the standard thermodynamic properties of carbosilane dendrimers with different terminal groups in a wide temperature range by precision AC and DSC makes possible to determine and analyze their dependences on composition and structure [9–15]. The discovery of structural anomalies for carbosilane dendrimers of lower generations [9–11] and relaxation transitions for carbosilane dendrimers of higher generations [12–14] is an important result of the calorimetric studies.

This work continues previous studies of the thermodynamic properties of various carbosilane dendrimers with different terminal groups on the outer layer. The heat capacity and thermodynamic properties of dendrimer $G3[(OCH_2CH_2)_3OCH_3]_{32}$ were earlier studied in the range from $T = 6$ to 350 K [9].

The goals of the present work were to study calorimetrically the temperature dependences of heat capacities of carbosilane dendrimers of the third generation with ethyleneoxide terminal groups $G3[(OCH_2CH_2)_1OCH_3]_{32}$ in the temperature range from $T = 6$ to 520 K and $G3[(OCH_2CH_2)_3OCH_3]_{32}$ in the temperature range from $T = 350$ to 520 K; to reveal and determine the thermodynamic

---

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

http://dx.doi.org/10.1016/j.tca.2015.08.028
0040-6031/

characteristics of possible physical transformations upon heating and cooling, and to investigate these transformations by IR spectroscopy; to calculate the standard thermodynamic functions for the range from $T \to 0$ to 520 K, and the standard entropies of formation of dendrimers in the devitrified state at $T = 298.15$ K; to compare the standard thermodynamic properties of the investigated dendrimers with literature data for carbosilane dendrimers with different functional terminal groups.

2. Experimental

2.1. Samples

The notional scheme of the investigated carbosilane dendrimers is presented in Fig. 1a. The general designation of dendrimers is $Gn[X]_m$, where G is the dendrimer generation, n is the number of generation, X is the terminal groups on the outer layer of dendrimer macromolecules, and m is the number of terminal groups. For example, the structure of carbosilane dendrimer of the third generation with terminal butyl groups $G3[Bu]_{32}$ is illustrated in Fig. 1b.

The samples of carbosilane dendrimers with ethyleneoxide terminal groups $G3[(OCH_2CH_2)_1OCH_3]_{32}$ and $G3[(OCH_2CH_2)_3OCH_3]_{32}$ were synthesized at the Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences (Moscow). Under standard conditions the investigated dendrimers were colorless transparent viscous liquids. The composition and structure of the synthesized samples were confirmed by data of elemental analysis and ^{1}H NMR spectroscopy. The gel permeation chromatography (GPC) curves show that dendrimers under study are characterized by a narrow monomodal distribution. The purity of the tested dendrimers was confirmed by gas-liquid chromatography (GLC) results.

The true molecular masses of the synthesized dendritic macromolecules were determined by the static light scattering method. For $G3[(OCH_2CH_2)_1OCH_3]_{32}$: found $M_w = 10{,}900\ \mathrm{g\,mol^{-1}}$,

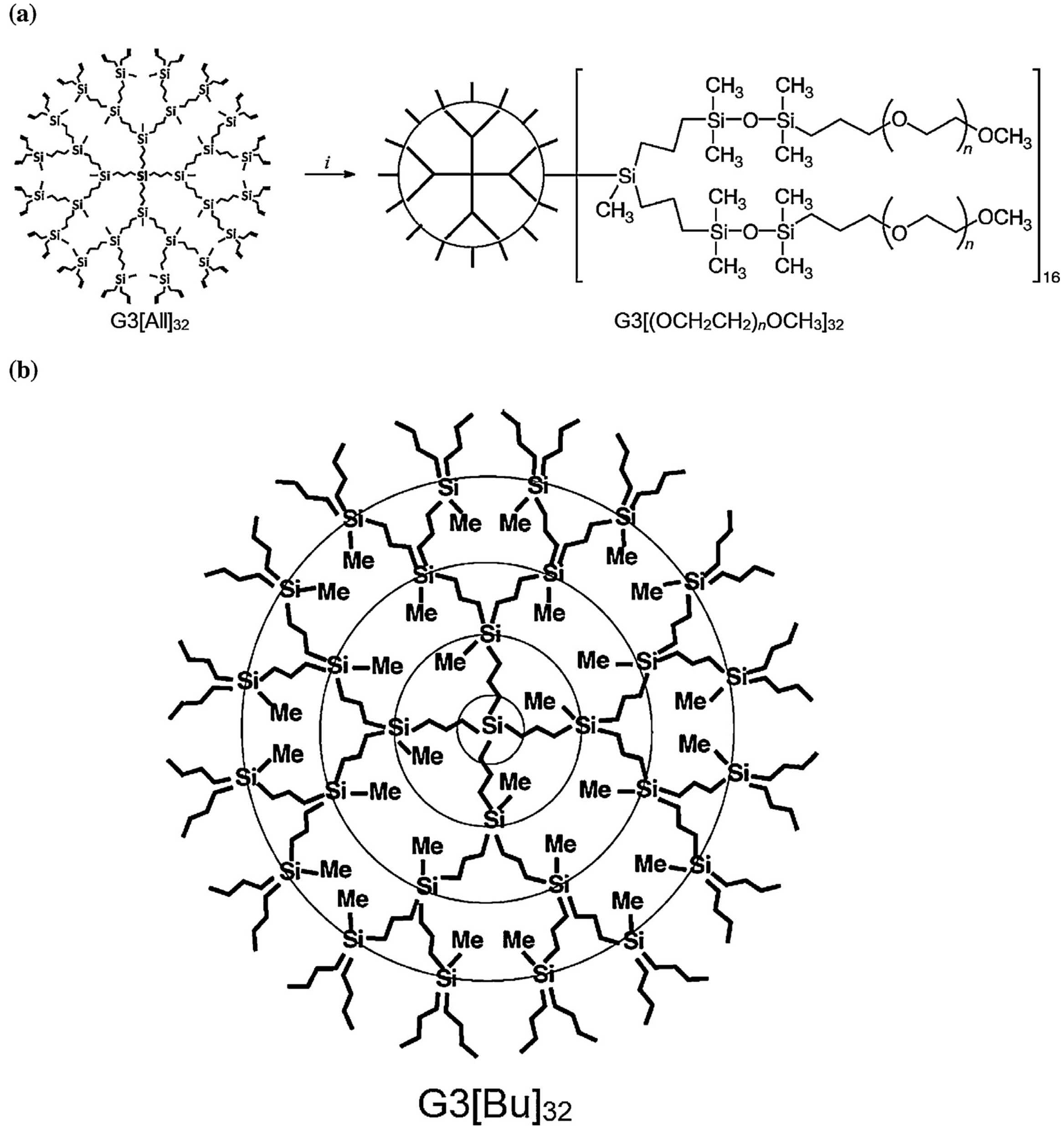

Fig. 1. (a) The scheme of carbosilane dendrimers of the third generation with ethyleneoxide terminal groups ($n = 1, 3$; i = the modifying agent containing ethyleneoxide units, Karstedt catalyst, toluene). (b) The structure of carbosilane dendrimer of the third generation with butyl terminal groups.