Revealing inner structure of the polycarbosilane dendrimers from small-angle neutron scattering data

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Abstract. Polycarbosilane dendrimers of the ninth generation are studied experimentally with small-angle neutron scattering (SANS) method. It is shown that monodispersity, that is, consistency of shape and form between different molecules, is one of the main features of the polycarbosilane dendrimers of the ninth generation. The samples are studied by SANS facility YuMO, Dubna, Russia [1]. The obtained experimental data are analyzed by means of contrast variation method.

1. Introduction

The evolution of synthesis from linear polymers to dendritic structure was realized from 1920s till 1980s [2,3]. Now the forth class of macromolecular architecture can be attained by chemical synthesis as well as linear, cross-linked and branched architectures. Generally speaking, dendrimer is nothing but highly branched three-dimensional structure with a high degree functionality. They were synthesized in the middle of ‘80s and studied by many methods [1,4–6]. However, some problems of the dendrimer structure are still unresolved; for instance, it is not clear whether internal hollows exist inside the dendrimers and whether a solvent can penetrate into the hollows [7]. Solution of these problems is important for practical using of dendrimer macromolecules as the functional carriers of universal purpose.

In the present paper, our previous investigations [8-13] are developed in order to resolve these problems. We experimentally investigate the structure of polycarbosilane dendrimers of the 9th generation G9Bu with 4-functional core and butyl end groups [2]. Synthesis of such a kind of dendrimers is well controlled, and presence of the non-functional end groups provides long-term stability of the chemical structure, which is essential for investigating properties with various physical methods and long-term storing.
2. Materials and methods
SANS experiments were performed with the two-detector system [14,15] at the YuMO instrument. The measured samples were solved in mixture of benzene C\textsubscript{6}H\textsubscript{6} and deuterated benzene C\textsubscript{6}D\textsubscript{6} with the following mass ratio C\textsubscript{6}H\textsubscript{6}/C\textsubscript{6}D\textsubscript{6}: 0/1, 0.75/0.25, 0.5/0.5, 0.25/0.75, 1/0. Concentration of the dendrimers in the solvent was 20 mg/cm\textsuperscript{3}. The solutions were placed into Hellma standard cells with thickness of 1 mm in the direction of neutron beam. The samples were kept at 20±0.03 °C in a special thermal box connected to a Lauda computer-controlled thermostat. The range of transferred momentum was 0.007 – 0.35 Å\textsuperscript{-1}. The experimental data were treated with SAS package [16], which allows us to sum up the data for the same sample, calculate the instrumental resolution function for given experimental conditions, correct the data for the dead times of neutron detectors and subtract the substrate background from the detector data, normalize the obtained spectrum to spectrum of standard vanadium scatter, and subtract the background sample data [17].

3. Results and discussion
SANS data for the dendrimers in mixtures of C\textsubscript{6}H\textsubscript{6}/C\textsubscript{6}D\textsubscript{6} are shown in figure 1. Behaviour of the curves does not change with the contrast, which is indirect evidence of homogeneity of scattering density inside the investigated dendrimer.

The presence of two maximums in the scattering curve confirms the assumption about monodispersity of the dendrimers (see figure 2).

Guinier approximation for experimental curves of figure 1 is shown in figure 3. The mean radius of gyration $R_g$ is equal to 38.1 ±0.2 Å.

The squared radius of gyration via the reverse contrast is shown in figure 4.

Figure 1. SANS data for dendrimers in mixtures of C\textsubscript{6}H\textsubscript{6}/C\textsubscript{6}D\textsubscript{6} from bottom to top: 0/100, 75/25, 50/50, 25/75, 100/0, wt/wt%.

Figure 2. SANS data for dendrimers in mixtures of C\textsubscript{6}H\textsubscript{6}/C\textsubscript{6}D\textsubscript{6} after the smoothing procedure.

Figure 3. Guinier approximation of SANS data of figure 1.

Figure 4. Squared radius of gyration via the reverse contrast.
The value $R_g^2$ is independent of the contrast within experimental error (see figure 4). For a deeper analysis, one can use the fitting formula $R_g^2 = R^2 + \frac{\alpha}{(\rho_{m.p.} - \rho_s)} - \frac{\beta}{(\rho_{m.p.} - \rho_s)}$, where the coefficients $\alpha$ and $\beta$ show the distribution of scattering length density inside the molecule of dendrimer [18]. In our case, these parameters are close to zero. This implies the homogeneous distribution of scattering length density inside the dendrimers.

In figure 5, the intensity in zero angle is shown as a function of scattering length density. As one can see, the fitting parabola attaches zero value within experimental error of the intensity. This means [8-12] that the dendrimers are monodisperse with respect to the scattering length density.

Concluding, presented data can be considered as an experimental evidence of, first, homogeneous distribution of the scattering length density inside the dendrimers, and, second, identical dendrimers’ inner structure.

This work was supported by Russian Foundation for Basic Research.

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