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SANS study of poly(benzyl ether) dendrimers

G. Evmenenko[a,*], B.J. Bauer[b], N. Mischenko[a], B. Forier[a], W. Dehaen[a], R. Kleppinger[a], E.J. Amis[b], H. Reynaers[a]

[a]*Laboratory of Macromolecular Structural Chemistry, Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*

[b]*National Institute of Standards and Technology, Gaithersburg, Maryland 200899, USA*

Abstract

The analysis of SANS data for a series of the poly(benzyl ether) dendrimers of different molecular architecture in deuterated tetrahydrofuran and toluene allowed to obtain information about some regularities of the relation between the topology of the dendrimer molecule and its structural parameters. The dimension of the present dendrimers of the poly(benzyl ether) type points to a scaling law of the type $R_g \sim M^{1/3}$ in line with literature information obtained for other chemically different dendrimers.

Keywords: Diffuse scattering; Macromolecular systems

Dendrimers are synthetic polymeric macromolecules with a highly branched, three-dimensional architecture emanating from a central point of functionality f [1]. The placement of functional groups at the polymer chain ends or in well-defined segments can determine the ultimate properties of the macromolecules and provide highly controlled polymer systems [2]. In this paper a SANS study is presented of the relationship between topological properties and structural parameters of different dendrimers based on benzyl ether monomers including the effects of chemical structure, shell groups and solvent.

The dendrimer systems were synthesized via a convergent approach using preformed building blocks (wedges or dendrons) [3]: 101b ($C_{184}H_{272}O_{16}$), 150a ($C_{448}H_{384}O_{56}$) and 150b ($C_{896}H_{768}O_{120}$) – second and third generations of this dendrimer, 124 ($C_{200}H_{176}O_{48}$), 134 ($C_{432}H_{400}O_{104}$). Dendrimer solutions with a concentration of 1 wt% were prepared by mixing appropriate amounts of the compounds into HPLC-grade deuterated tetrahydrofuran (THF) or toluene. The neutron scattering length densities ρ_{sol} of deuterated solvents used were 6.36×10^{10} cm^{-2} (THF) and 5.66×10^{10} cm^{-2} (toluene).

The small-angle neutron scattering measurements (SANS) were carried out using the 8 m SANS facility at the National Institute of Standards and Technology. The incident wavelength was 8 Å with $\Delta\lambda/\lambda = 25\%$. The radially averaged scattering patterns were corrected for absorption, solvent scattering and instrumental background and converted into an elastic scattering cross-section (absolute intensity scale) $d\Sigma/d\Omega(q)$ using water as a secondary standard.

The scattering intensity at zero angle (at $q = 0$), $d\Sigma/d\Omega(0)$, and the radius of gyration R_g were obtained by linear fitting of the experimental curves in the representation $\ln(d\Sigma/d\Omega(q))$ versus q^2 in the Guinier regime ($qR_g < 1$). The q-range of fitting was $0.01\ \text{Å}^{-1} < q < 0.14\ \text{Å}^{-1}$. The characteristics of all dendrimer solutions under study and the appropriate fit parameters are given in Table 1. In this table the scattering length densities of dendrimers ρ_{dendr}, the mean scattering length densities of scattering heterogeneities of dendrimer solutions $\langle\rho\rangle = |33.3/R_g \cdot \{d\Sigma/d\Omega(0)/\phi R_g\}^{1/2} - \rho_{sol}|$ and the fraction of solvent in dendrimer molecule $\phi_{sol} = (\langle\rho\rangle - \rho_{dendr})/(\rho_{sol} - \rho_{dendr})$ are presented. The scattering length densities ρ_{dendr} were calculated from chemical composition of dendimer molecule.

* Corresponding author. Tel.: +32-1632-7472; fax: +32-1632-7990.

E-mail address: guennady.evmenenko@chem.kuleuven.ac.be (G. Evmenenko)

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Table 1
The characteristics of the poly(benzyl ether) dendrimers

Sample code	M	Solvent	C (wt%)	ρ_{dendr}, 10^{10} (cm^{-2})	$d\Sigma/d\Omega(0)$ (cm^{-1})	R_g (Å)	$\langle\rho\rangle$ 10^{10} (cm^{-2})	ϕ_{sol} (% v/v)
101b	2736	THF	1	0.66	0.215	13.0	3.07	42.3
		Toluene	1		0.189	13.4	2.71	41.0
150a	6656	Toluene	1	1.69	0.156	12.7	2.75	26.7
		THF	1		0.221	12.7	2.90	25.9
150b	13440	Toluene	1	1.69	0.301	16.0	2.81	28.2
		THF	1		0.414	15.9	2.98	27.6
124	3344	THF	1	1.71	0.0945	11.8	3.83	45.5
134	6888	THF	1	1.73	0.222	16.4	4.00	49.0

As one can see from Table 1 the dendrimers with more close and dense architecture (such as 150-samples) have a more compact conformation with more dense packing of polymer chain and significantly lesser content of solvent penetrating into the dendrimer in comparison with dendrimers with more open structure (101b, 124- and 134-samples). The change of solvent from non-polar toluene to polar THF with practically the same solubility parameters involves a contraction of the end linear chains to the central core of the 101b-dendrimer and does not change the structural parameters of the more compact 150-samples.

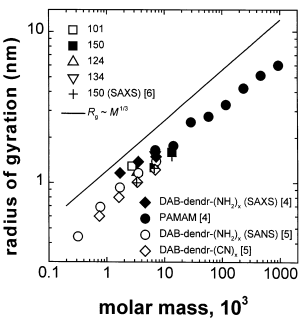

Fig. 1. The dependence of radius of gyration obtained by SANS and SAXS for the different dendrimers on their molar mass, in log–log representation [4–6]. The solid line represents the scaling behaviour $R_g \sim M^{1/3}$.

The SANS data show clearly the relationship between the topology of the dendritic molecules and its expression in the parameters of their supermolecular structure. The poly(benzyl ether) dendrimers have an homogeneous density profile. The size of these dendritic molecules increases as $M^{1/3}$ (Fig. 1), which is indicative of a compact (space-filling) structure. A comparison of known structural data for the different dendritic systems (see Fig. 1) allows to conclude that this scaling law and the similar structural organization is valid in a wide range of chemically different dendrimers.

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