Appl. Phys. A 74 [Suppl.], S396–S398 (2002) / Digital Object Identifier (DOI) 10.1007/s003390201515

Applied Physics A
Materials
Science & Processing

Structural properties of star-like dendrimers in solution

S. Rathgeber[1,*], **A.P. Gast**[2], **J.L. Hedrick**[3]

[1] Forschungszentrum Jülich GmbH, IFF Weiche Materie, 52425 Jülich, Germany
[2] Stanford University, Stanford, CA 94305-5025, USA
[3] IBM Almaden Research Center, San Jose, CA 95120-6099, USA

Received: 13 July 2001/Accepted: 13 November 2001 –

Abstract. We measured the form factor of star-like poly-ϵ-caprolactone dendrimers under good solvent conditions with small-angle neutron scattering (SANS). The parameters varied in the experiment were the dendrimer generation $g = 1, 2, 3$ and the number of segments between the branching units $n = 5, 10, 15, 20$. The results are discussed in the frame work of the Beaucage model from which we cannot only derive the radius of gyration R_g of the dendrimers but also their fractal dimensions. Decreasing the number of spacer units between the branching points results in a strong stretching of the dendrons. The fractal dimension increases monotonically with increasing generation and spacer number between the limit expected for a low-functionality star $P \approx 5/3$ (loose, polymeric structure) and that expected for a high-functionality star $P \approx 3$ (compact shape).

PACS: 61.12.Ex, 61.25.Hq

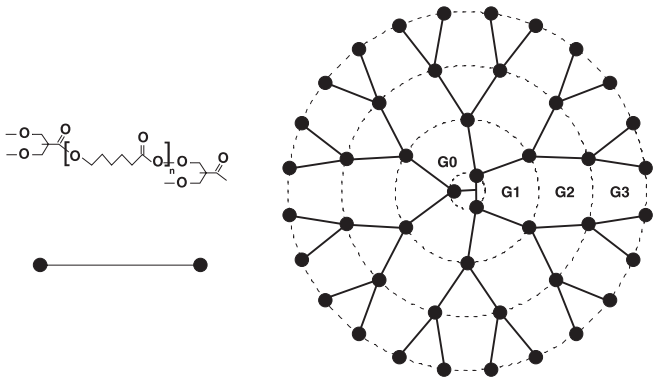

Fig. 1. Sketch of a star-like dendrimer ($g = 3$) with six dendrons emanating from a central core ($g = 0$)

Dendrimers are regular branched, treelike macromolecules which are synthesized from a multi-functional core (see Fig. 1). The addition of multi-functional monomers results in controlled branching and multiplication of the number of monomers from one generation to the next. In the case of star-like dendrimers there are several repeat units between the branching points. Like high-functionality stars, high-generation dendrimers are known to have a rather well defined globular, compact shape [1]. On the other hand dendrimers are polymeric entities. The strong increase of the monomer number per generation accompanied with sterical crowding within the dendrimer should have a strong impact on the conformation of the dendrons. In this paper we would like to focus (1) on the fractal dimension as a measure of the "compactness" of the dendrimers and (2) on the radius of gyration or equivalent on the segment length as a measure for the stiffness of the dendrons. The results are compared to analogous low- and high-functionality stars.

*Corresponding author. (Fax: +49-2461/612280, E-mail: s.rathgeber@fz-juelich.de)

1 Theory

Beaucage [2, 3] parameterizes the form factor of an arbitrary particle with fractal dimension P and radius of gyration R_g into the sum of a Guinier term describing the low-q scattering regime and a Porod term reflecting the typical power-law decay at high scattering vectors q

$$P(q) = \exp[-(qR_g)^2/3] + B\, q^{\star -P} \tag{1}$$

with B being the amplitude of the Porod term relative to the contribution of the Guinier term and

$$q^\star = q \left[\mathrm{erf}(q\, R_g/\sqrt{6})\right]^{-3}, \tag{2}$$

where erf is the error function. Due to the finite size of the particle its fractality should not be visible on length scales of the radius of gyration. Replacing q by a reduced scattering vector $q^\star$ in eq. (1) ensures a diminution of the power-law contribution to the total scattering for small q-values. From a comparison of eq. (1) with the high-q asymptotic form factor of an arbitrary mass fractal derived by Benoit [4] the amplitude of the Porod term can be determined to

$$B = P\, R_g^{-P}\, \Gamma(P/2), \tag{3}$$

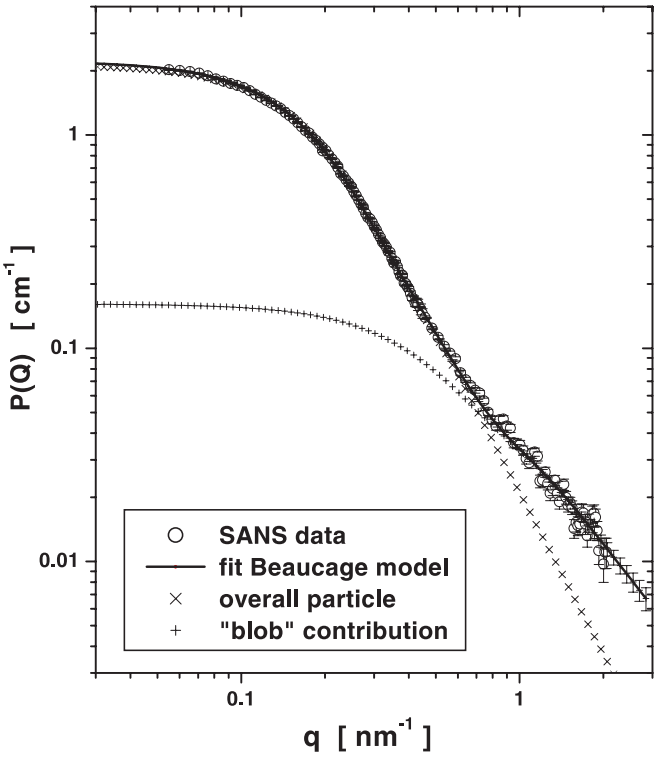

Fig. 2. SANS spectrum obtained for the dendrimer ($g = 3, n = 20$). The result of a fit using the Beaucage model including the separate contributions of the large-scale and small-scale structure are shown

where Γ denotes the gamma function. As can be seen from Fig. 2 the SANS spectra from the star-like dendrimers show two distinguishable scattering regimes. The scattering at lower q values stems from the overall shape of the dendrimer with the fractal dimension P. At higher q values the loose, polymeric structure of the dendrimer becomes visible adding a second sub-structure with a different fractality P_S to our model. In analogy to the model introduced by Daoud and Cotton [5] for star polymers on length scales smaller than the correlation length ξ the dendrons have to be described as self avoiding walks and excluded volume interactions have to be taken into account. Hence the fractal dimension of the subunit called "blob" (spherical volume of radius ξ) should be given by the inverse of the Flory–Huggins parameter ν which is equal to 3/5 for good solvent conditions. By simply taking the sum of both scattering contributions, (1) can be extended to

$$P(q) = \exp\left(\frac{-q^2 R_g^2}{3}\right) + B\,\exp\left(\frac{-q^2\,\xi^2}{3}\right) q^{\star -P} + A_S\left[\exp\left(\frac{-q^2\,\xi^2}{3}\right) + B_S\, q_S^{\star -5/3}\right] \quad (4)$$

where $q_S^\star$ and B_S are defined by replacing R_g with the "blob" radius ξ and P with P_S=5/3 in (2) and (3). A_S gives the weight of the "blob" scattering relative to the contribution stemming from the overall shape of the dendrimer. On length scales of the dimension of the subunit the scattering should not be sensitive to the fractality of the overall particle. The exponential cutoff function ensures a diminution of the intermediate power-law decay on length scales of the order of ξ.

2 Experiment

The SANS measurements were performed on the NG3 30 m SANS instrument at the NIST Center for Neutron Research of the National Institute of Standards and Technology, Gaithersburg, MD, USA. The instrument was operated at an incident neutron wavelength of 0.6 nm with a wavelength spread of 15% covering a q-range of $0.055\,\mathrm{nm}^{-1} \le q \le 2\,\mathrm{nm}^{-1}$. All experiments were performed at a temperature of 20 °C with a stability of ±0.1 °C. The data were corrected for detector efficiency, incoherent background and empty cell scattering via standard procedures and are converted to absolute intensity scale using a calibrated secondary standard. The convolution of the spectra with the experimental q resolution is taken into account in the fitting routine.

The star-like dendrimers have 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) branching units of functionality $m = 2$. The 1,1,1-tris(4-hydroxyphenyl)ethan core is hexa hydroxy functionalized ($f = 6$) by bis-MPA. The linear units, with varying number of repeat units ($n = 5, 10, 15, 20$) between the branching points, are built from ϵ-caprolactone monomers. The synthesis of the dendrimers is discussed more detailed in [6]. Measurements were performed in solutions of deuterated toluene at concentrations between 0.25% and 1%. The small influence of the structure factor for $q \le 0.1\,\mathrm{nm}^{-1}$ has been corrected by Zimm extrapolation to zero concentration.

3 Results and discussion

Practical fitting involves the radius of gyration R_g, the dimension P of the overall dendrimer and the "blob" radius ξ as free parameters. The fractal dimension of the subunit is kept fixed to the value of 5/3 as expected for good solvent conditions. Leaving all parameters free in the fit yielded only in a slight change of ξ around an average value of about $\bar{\xi} = 2.5 \pm 0.1$ nm for the different dendrimers. Therefore also the "blob" radius was kept fixed in the fitting procedure to its average value $\bar{\xi}$. In Fig. 3 the fit results for the radius of gyration R_g^{fit} are plotted as a function of the generation g and of the number of spacers between the branching units n. Assuming a Gaussian distribution for the distances between the freely jointed segments La Ferla [7] derived an analytical expression for the radius of gyration R_g^G of a dendrimer with an arbitrary number of spacer units n between the branching points:

$$R_g^{G\,2}\,(N_t/l)^2 = \frac{n^3\,f\,[c^2\,(f\,g\,m - f\,g - f - m) + c\,(2\,f + f\,g - f\,g\,m - g + g\,m^2) - f + m]}{(m-1)^3} - \frac{f\,n\,(n-1)\,(c-1)\,[3\,f\,n\,(c-1) + 2\,(n+1)\,(m-1)]}{6\,(m-1)^2} \quad (5)$$

with $c = m^g$ and N_t the total number of segments in the dendrimer:

$$N_t = \frac{n\,f\,(m^g - 1)}{(m-1)} + 1 \quad (6)$$

Here l denotes the segment length and $m = 2$ and $f = 6$ are the functionalities of the branching units and the core. From the measured form factor of a poly-ϵ-caprolactone homopoly-

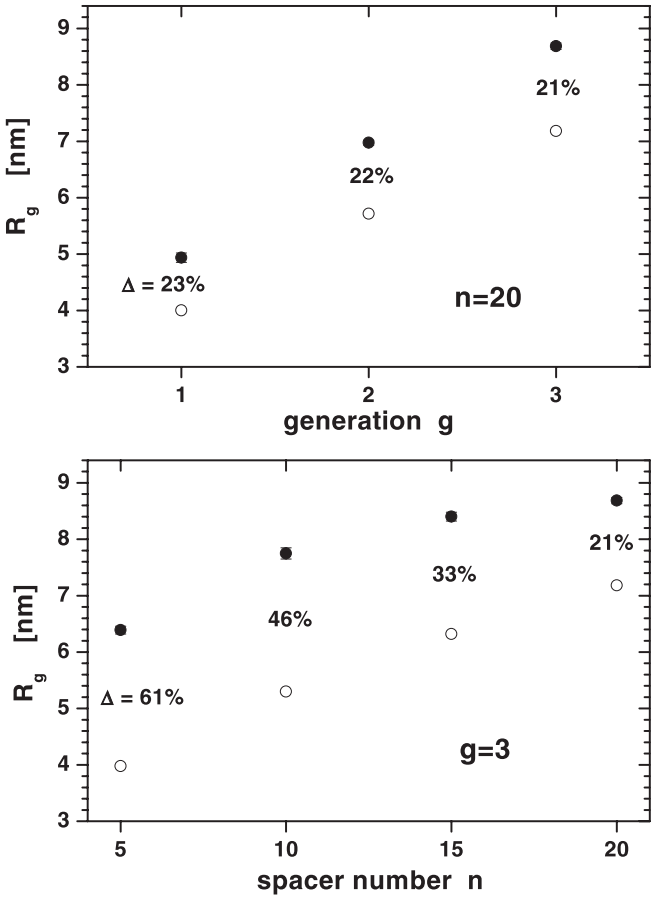

Fig. 3. Radius of gyration R_g versus dendrimer generation g ($n = 20$) (top) and spacer number n ($g = 3$) (*bottom*). The *solid circles* show the results of a fit of the SANS spectra using the Beaucage model. The *open circles* mark the theoretical results for a Gaussian dendrimer

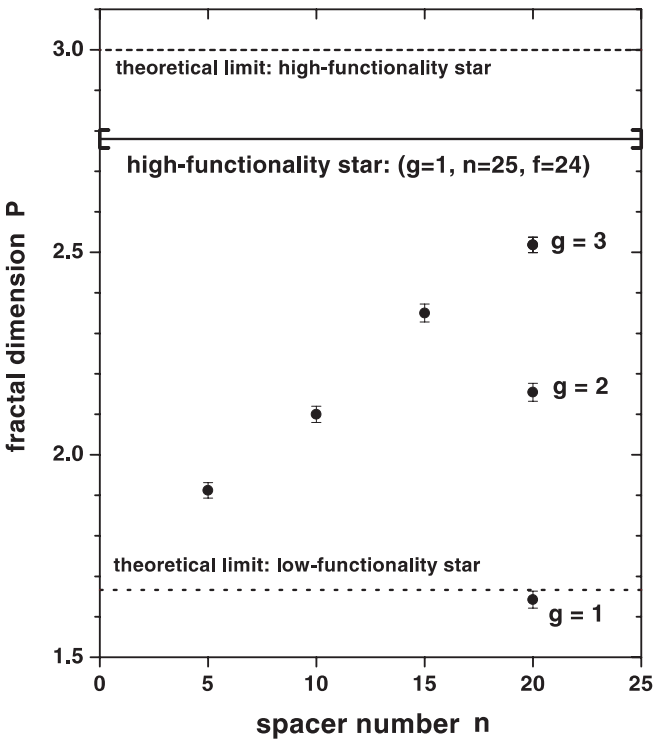

Fig. 4. Fractal dimension P as a function of the dendrimer generation g and the spacer number n (markers). The *solid line* marks the experimental result obtained for a high-functionality star. The *dashed lines* show the theoretical limits for a low- and a high-functionality star

mer we obtained the radius of gyration. For the homopolymer via the relation $R_g = \sqrt{N/6}\,l$ with $N = 144$ being the degree of polymerisation the segment length $l = 1.1$ nm of the corresponding freely jointed chain can be derived. Insertion of $l = 1.1$ nm into (5) leads to the theoretical results for the dendrimer radii R_g^G shown in Fig. 3. Since La Ferla assumes a dimensionless core ($g = 0$) we added the core radius $r \approx 0.66$ nm, estimated by the sum of the bond lengths in the core molecule, to the calculated values. Following this procedure deviations between the theoretical predictions and the fit results ($\Delta = R_g^{fit}/R_g^G - 1$) can be directly related to a stretching of the dendrons relative to the conformation of the homopolymer. The deviation of $\Delta = 23\%$ between the theoretical and the experimental value for the low-functionality star ($g = 1$, $f = 6$, $n = 20$) indicates that the arms in the star are already slightly stretched compared to the conformation of the linear chain. However increasing the generation from $g = 1$ to $g = 3$ with keeping the number of spacer units fixed to $n = 20$ does not cause any additional stretching of the dendrons. In fact Δ decreases slightly down to 21% indicating that the gain in accessible volume certainly compensates the increasing sterical crowding in the outer shells. Reducing the number of spacer units or analogously reducing the accessible volume in the $g = 3$ dendrimer results in a rather drastic relative increase of maximal $\Delta = 61\%$ for the smallest spacer number ($n = 5$) investigated.

In Fig. 4 the fit results for the fractal dimensions P of the dendrimers are plotted as a function of the dendrimer generation g ($n = 20$) and the number of spacer units n ($g = 3$). The dashed lines show the theoretical limits for a low- ($P = 5/3$) and a high-functionality star ($P = 3$) under good solvent conditions reflecting the transition from a loose, polymeric structure to a rather compact object with increasing arm number [8]. The solid line represents the fit result for a star ($g = 1$, $n = 25$) with an arm number ($f = 24$) equal to the number of terminal units in the $g = 3$ dendrimer. The dimension of the low-functionality star ($g = 1$, $f = 6$) is with 1.64 ± 0.021 close to the theoretical value. The fractal dimension of the high-functionality star is with 2.78 ± 0.022 still lower than the theoretical limit but significantly higher than the dimension of the $g = 3$ dendrimer ($P = 2.52 \pm 0.019$). The dendrimer has a less compact shape with a less well defined outer surface than the high-functionality star. The fractal dimension of the dendrimers decreases with decreasing generation number as well as with decreasing spacer number. The latter might reflect the fact that the dendrons are stretched and a space filling arrangement is prevented.

References

1. S. Rathgeber, T. Pakula, V. Urban: ACS PMSE preprints **84**, 935 (2001)
2. G. Beaucage: J. Appl. Cryst. **28**, 717 (1995)
3. G. Beaucage: J. Appl. Cryst. **29**, 134 (1996)
4. H. Benoit: Comput. Rend. **245**, 2244 (1957)
5. M. Daoud, J.P. Cotton: J. Physique **43**, 531 (1982)
6. M. Trollsås, L.J. Hedrick: J. Am. Chem. Soc. **120**, 4644 (1998)
7. R. La Ferla: J. Chem. Phys. **106**, 688 (1997)
8. M. Adam, D. Lairez: Fractals **1**, 149 (1993)