Macromol. Symp. ***146**, 33–39 (1999)*

The Superstructure of Carbosilane Dendrimers with Perfluorinated End Groups in Bulk and in Solution.

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Abstract

Carbosilane dendrimers of generation 1 to 4 are functionalized with perfluorinated (-C_6F_{13}) end groups. Extending the spacer between the central Si and the first layer of branching points allows the synthesis of the 4th generation. The superstructure of these systems in bulk observed with X-ray scattering is the result of the microphase separation between the carbosilane scaffold and the end groups. It varies with generation from a layered to a columnar structure. In dilute solution only the second generation dendrimer shows a tendency for aggregation. The others form compact particles consisting of single molecules with a core shell structure.

Introduction

Dendrimers as a novel type of macromolecular architecture open new perspectives in the research in macromolecular chemistry and physics. Dendrimers are superior by their well-defined, highly branched structure: Emanating from a central point with functionality f linear blocks of uniform length are attached. The end of such a block represents a new branching point. Each such step of growth is called a generation. In this nomenclature g=0 consists only of the functional centre and f arms. The synthesis and the characterisation of the carbosilane dendrimers used in this study were reported in a recent publication[1]. The molecules consist of a highly flexible carbosilane core which is unable to crystallise do to the branched structure of the dendrimer. The end groups are perfluorohexyl (-C_6F_{13}). These end groups are immiscible with the core and may be considered to be rigid rods. The result of this microphase separation is a superstructure which is strongly dependent on the generation of the dendrimer. In consequence of this domain structure one expects different dynamics for the end groups and the dendritic core, respectively. In the first part of this contribution we will review experimental results confirming this expectation.

The structure of flexible dendrimers in solution has been subject to controversial discussion in recent years[2]. Recent experimental results[3] support the idea of a compact structure with a maximum of density in the centre of the dendrimer. We cannot expect our dendrimers to comply with the same model. Due to their core-shell structure they will rather be expected to ressemble a unimolecular micelle. In the second part of this contribution we will present

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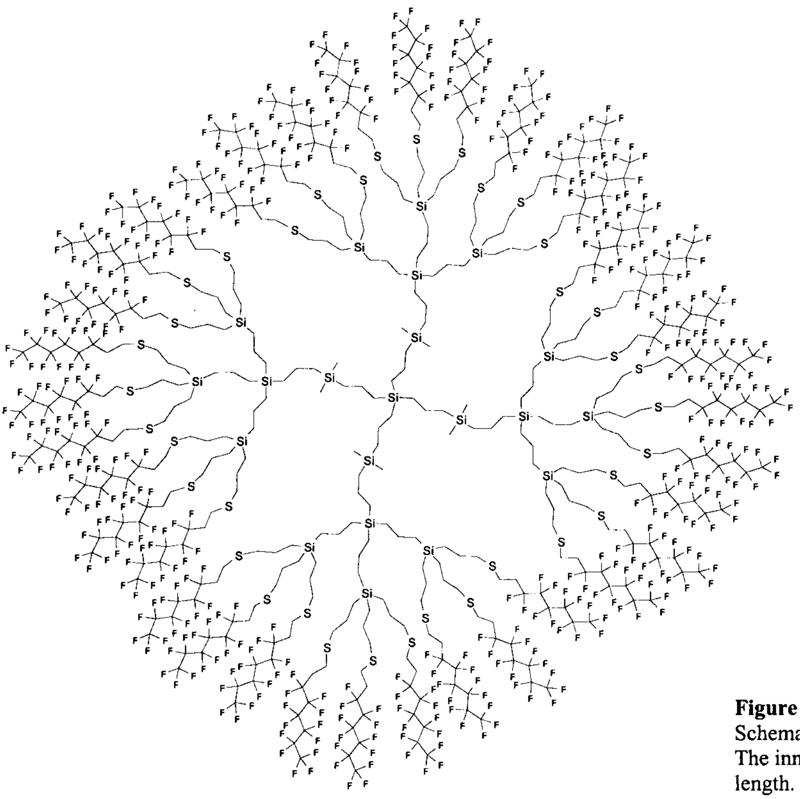

Figure 1
Schematic structure of G2ext
The innermost spacer is of double length.

experimental evidence for the existence of such compact particles in dilute solution that comprise only one dendrimer molecule.

Experimental

Three generations of a carbosilane dendrimer denoted GxRF6 (x=1,2,3) were prepared and functionalized with $-C_6F_{13}$ end groups on the surface. Their synthesis is described elsewhere[1]. An additional series of dendrimers of generation 1 to 4, Gxext was prepared along the same lines with an additional spacer in the first generation. The structure of these dendrimers is schematically given in figure 1 for the example of the second generation.

In addition to the previously synthesised dendrimers we have now extended the innermost spacer in order to increase the size of the dendritic core and thus be able to obtain higher generation numbers. Using this approach we were able to synthesise up to generation 5 of the dendrimer. In the present report, however, we restrict attention to generation 1 to 4. As an example of the structure of the dendrimer we show G4ext in Figure 1. The samples with short spacer are denoted just as in our previous publication as GxRF6.

Structure and segmental dynamics in bulk

The molecular architecture of the dendrimers is of spherical symmetry. Their end groups, on the other hand are stiff rods and tend to form layered structures. These opposing factors influence the formation of structure in bulk and in solution. One expects their weight to be dependent on the generation of the dendrimer.

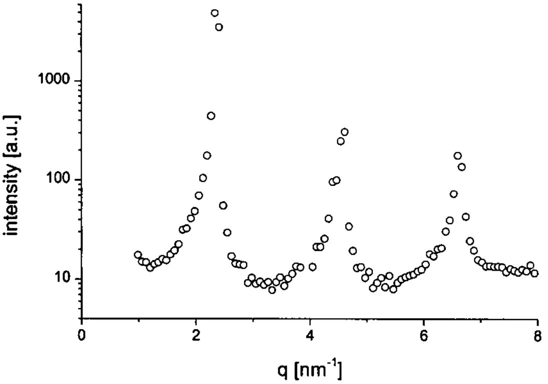

Figure 2
SAXS diagram of G2RF6 in the ordered state

In Figure 2 we display the x-ray scattering diagram of G1RF6 at T=-50°C. At this temperature the material shows a smectic type pattern in the microscope between crossed polarizers. A transition from a smectic to an isotropic state is seen in DSC at T=-15°C[1]. The scattering diagram exhibits three reflections at equidistant positions in the scattering vector q in accordance with the assumption of a layered structure. The layer spacing is 2.73(±0.05) nm as obtained from the second and third order reflection. The reflections in Figure 2 display a shoulder at small q which is caused by an additional period in the sample structure which is 5% larger in size. The end groups may in tilted in some domains of the sample and perpendicular to the layers in others. We therefore conclude that for the first generation dendrimer the end groups dominate in the formation of a superstructure.

With increasing generation number, however, this clear structure does no longer prevail[4]. For G2RF6 one does not find a well-defined superstructure. G3RF6 then shows a structure of different symmetry. It is characterized as cylindrical domains arranged on a two dimensional hexagonal lattice. In order to fit into this structure the dendrimer has to adopt a flat plat like structure with the end groups protruding perpendicular to the axis of the cylinder. This structure is to be considered as a compromise between the spherical architecture of the dendritic core and the smectic tendency of the end groups.

The segmental dynamics of these dendrimers has been investigated using dielectric spectroscopy[5] and quasielastic neutron scattering. Neutron scattering is a particularly useful technique for our dendrimers as they are intrinsically labelled by their chemical structure: scattering from the dendritic core is dominated by the incoherent scattering length of hydrogen whereas the end groups consist of the coherent scatterers C and F. The neutron scattering experiments are thus able to provide separate access to the dynamics of the end groups and to the segmental dynamics in the dendritic core. In accordance with the picture of the end groups as rigid rods it was found that their dynamics is a rotational diffusion. The experiments show a weak decrease of the rotational diffusion coefficient with generation by about a factor of 0.8. The segmental diffusion of the dendritic core on the other hand is found to show a cross over with scattering vector from a translational diffusion to a q independent, local relaxation. This behavior may be modelled with a jump diffusion model[6]. The dynamics is then described by a diffusion coefficient and a local relaxation time τ. D decreases with generation. The increase is not as strong as predicted by theory[7] The parameters D and τ define a length $l^2_s = 6D\tau$ which turns out to be the same for the dendrimers under study. As this length is a local property of the dendritic core it is a function of the chemical structure which is the same.

Dilute solution of the dendrimers

In the previous section we have shown that structure and dynamics in bulk are strongly influenced by the mesogenic nature of the end groups. We will now turn to the properties of dilute solutions with the intention to investigate the single molecule's structure and dynamics. The dendrimers used in this study are particularly useful for this purpose as the nature of their end groups is not likely to induce aggregation in solution. The solvent used is perfluorohexane which is chemically identical with the end groups. The core shell structure of the molecule which is already apparent in bulk will be supported by this solvent as it is selective for the end groups.

In Figure 3 we show the result of a small angle neutron scattering (SANS) experiment on G2ext, G3ext and G4ext in dilute solution. The experiments were performed using the instrument D11 at the ILL, Grenoble. A series of concentrations has been measured to assure that intermolecular interference does not affect the data shown in the figure. The data shown in Figure 3 refer to c=1.25%. It is seen that within this series of dendrimers the static structure factor is smoothly decaying for the second and third generation but exhibits several maxima for the fourth generation. The curves drawn through the data points are fits of the structure factor for ellipsoidal particles[8] (2nd and 3rd generation) and a spherical particle for the 4th generation. Also included in the fitting procedure is a gaussian distribution of the radius which accounts for the observed smearing of intensity in the regime of the minima of the structure factor. The radius of G4ext is thus found to be 2.7 nm.

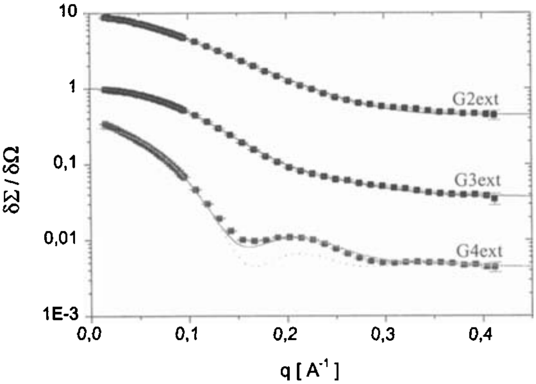

Figure 3
SANS pattern of dilute solutions of the dendrimers (c=1.25%, T=25°C)

As a result we find a quantitative description of the static scattering in the model of single particle scattering. The radii observed for G3ext and G4ext are in accordance with those expected on the basis of single molecules forming the scattering particles. G2ext displays a structure which is too large for a single molecule. We may therefore conclude that the 2nd generation dendrimer aggregates in solution whereas the higher generations form particles with an ellipsoidal or spherical particles in thermal average. The fit of the spherical form factor in Figure 3 for G4ext may be improved if one allows for a variation of scattering length density in radial direction (full line). The dotted curve in the figure is calculated for a constant density. This supports the picture of a core shell particle consisting of a flexible core formed by the carbosilane scaffold of the dendrimer and a shell of rod like end groups. Further analysis of the data is in progress.

A second experiment giving access to the size of the dendrimers in solution is photon correlation spectroscopy (PCS). For the simple situation of a particle undergoing translational diffusion the normalized autocorrelation function of the intensity is given as

$$g_2(t) = f \exp(-2Dq^2t)$$

q is again the modulus of the scattering vector and t the correlation time. The factor f is an apparative property. As a consequence of polydispersity of the particles one often observes deviations from this simple exponential decay which are taken into account by fitting a KWW function to the data:

$$g_2(t) \approx f \exp(-(t/\tau)^{\alpha}$$

α then is a measure of the polydispersity of the scatterers.

The experimentally observed correlation functions at all scattering vectors and for the three dendrimers Gxext are all well described by a single exponential decay. The KWW exponent α is in all cases $0.96<\alpha<1$. Moreover the parameter τ is strictly proportional to q^{-2}. We therefore observe the translational diffusion of single particles with very low polydispersity.

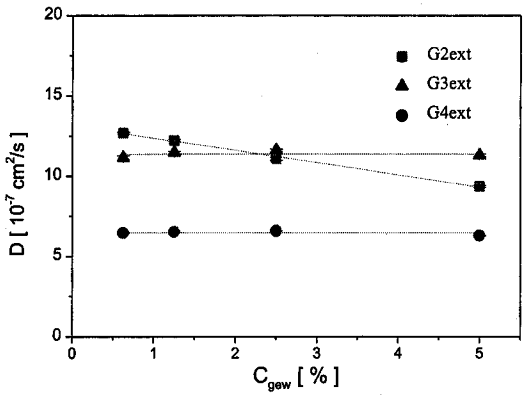

Figure 4
Apparent diffusion coefficient of the dendrimers in dilute solution as obtained from PCS.

In Figure 4 we show the results for the apparent diffusion coefficients thus determined for Gxext in a series of concentrations. Whereas the diffusion coefficient for G3ext and G4ext does not depend on concentration one observes a significant decrease of D_{app} for G2ext. This confirms the aggregations already seen in the SANS experiments for the second generation dendrimer. The hydrodynamic radii R_H calculated from the diffusion coefficients are 2.4 nm, 2.8 nm, and 4.9 nm for the three generations. They are larger than the radii for the dendritic core determined with SANS as the end groups contribute to R_H.

In conclusion we have found a superstructure in bulk of the carbosilane dendrimers with perfluorinated end groups which is the result of the microphase separation between the dendritic scaffold and the end groups. The symmetry of the superstructure depends on generation and is the result of the spherical architecture of the molecules and the tendency of the end groups to form a layered structure. The same principles govern the structure of the single molecules in solution. For generation 2 and 3 we find ellipsoidal particles but for generation 4 the average form of the molecule is spherical. The molecules are compact structures of the core shell type and show only a weak tendency for aggregation.

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