Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Dynamics of internally functionalized dendrimers

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Here we provide a brief information about static properties of the SFD and of the homogeneous dendrimers. Also we look at dielectric relaxation forms in the absence of stiffness conditions.

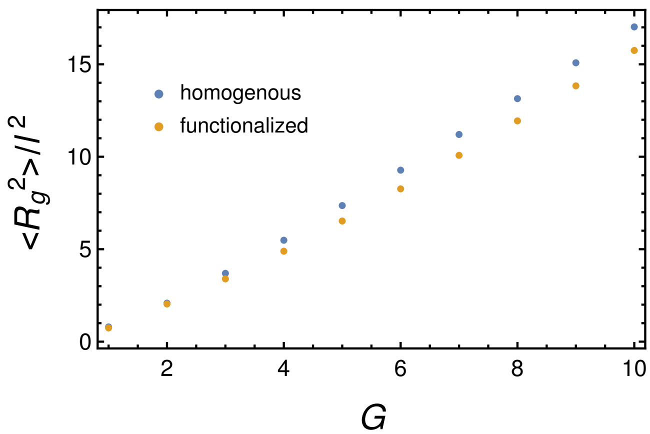

Fig. 1 Gyration radius $\langle R_g^2 \rangle$ for the SFD of functionalities $f_C = 3$ and $f = 4$ and stiffness parameters $q_C = 0.48$ and $q = 0.32$ and for the corresponding homogeneous dendrimers ($f = 4$ and $q = 0.32$).

The gyration radius $\langle R_g^2 \rangle$ can be directly calculated using the eigenvalues of the matrix $\mathbf{A}^{\rm STP}$,[1]

$$\langle R_g^2 \rangle = \frac{l^2}{N} \sum_{j=2}^{N} \frac{1}{\lambda_j}, \tag{1}$$

where the sum runs over nonvanishing eigenvalues $\{\lambda_j\}$ of $\mathbf{A}^{\rm STP}$. Equation (1) shows that for the $\langle R_g^2 \rangle$ the lowest nonvanishing eigenvalues are fundamental, as we have also discussed in the main text. In Fig. 1 we plot the gyration radius as a function of generation number G for the SFD of functionalities $f_C = 3$ and $f = 4$ and stiffness parameters $q_C = 0.48$ and $q = 0.32$ and for the corresponding homogeneous dendrimers ($f = 4$ and $q = 0.32$). As can be inferred from the figure, in both cases the gyration radius grows with G. The homogeneous dendrimer, having higher molecular mass, displays a larger gyration radius. We note that for free-draining case the intrinsic viscosity η is proportional to the gyration radius, $\eta \sim \langle R_g^2 \rangle$.[2] However, the situation changes, if one includes hydrodynamic interactions.[3,4] In the non-draining case the viscosity of dendrimers experiences a maximum and become lower with high G, whereas the gyration radius still grows with G.[3,4]

Finally, we present in Fig. 2 the imaginary part of complex dielectric susceptibility for different shells g of fully-flexible (i.e., $q_C = q = 0$) dendrimers (homogeneous ($f = 4$) and internally functionalized ($f_C = 3$ and $f = 4$)) of generation $G = 5$. The figure shows that for lower g a secondary peak develops, as it was observed earlier for homogeneous, fully-flexible dendrimers.[5] For the internally functionalized dendrimer the left peak is at higher frequencies than for the homogeneous dendrimer, reflecting the smaller size of the internally functionalized dendrimer. The intermediate minimum for the homogeneous dendrimer (for $g = 1,2,3$) is somewhat deeper that this for the internally functionalized one. This could be an indication of some additional process for the internally functionalized dendrimer. On the other hand, this could be also be due to the closeness of both maxima for the internally functionalized dendrimer. Therefore, in contrast to the semiflexible structures, there is no clear evidence of an additional process in the dielectric relaxation forms for internally functionalized dendrimers in the fully-flexible case.

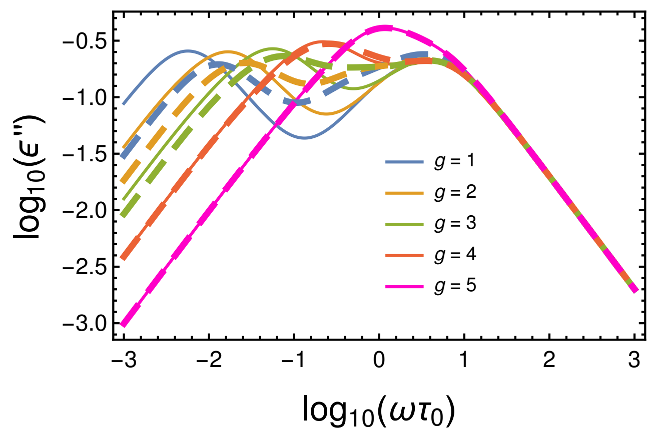

Fig. 2 Imaginary part $\varepsilon''(\omega)$ of the complex dielectric susceptibility for different shells g of fully-flexible (i.e., $q_C = q = 0$) dendrimers of generation $G = 5$. The solid lines correspond to the homogeneous dendrimer ($f = 4$) and the dashed lines to the internally functionalized dendrimer ($f_C = 3$ and $f = 4$).

References

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