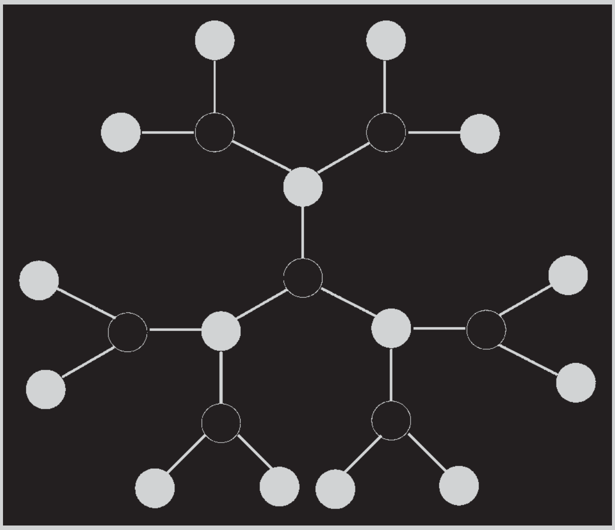
Summary: In this study we extend our previous work concerning the Rouse dynamics of linear alternating copolymers (*Macromolecules* **2003**, *36*, 486) to tree-like structures and focus on copolymeric dendrimers built from monomers of two kinds A and B; as before, we let the monomers differ in their interaction with the solvent. In the framework of generalized Gaussian structures (GGS), we consider alternating arrangements of monomers over the dendritic structures. We develop a semi-analytical method to determine for such structures (of arbitrary functionality, f, and number of generations, g), the eigenfrequencies (relaxation times). The method allows us to compute readily the storage, $[G'(\omega)]$ and the loss, $[G''(\omega)]$ moduli. These quantities show a multitude of features which mainly depend on the difference in the mobilities, or, equivalently, in the friction coefficients ζ_A and ζ_B of the A- and B-beads. These features range from the presence of large plateau-type regions in $[G'(\omega)]$ to the appearance of double-peaks in $[G''(\omega)]$. In contrast to linear alternating copolymers, the behavior of the dynamic moduli of copolymeric systems with dendritic topology can shed light into their composition, i.e. into the relative numbers of A- and B-beads. We discuss these aspects in view of their experimental relevance.



A system under study: a dendrimer of third generation ($g = 3$) with functionality $f = 3$, composed of alternating beads.

Relaxation of Copolymeric Dendrimers Built from Alternating Monomers

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Introduction

Dendrimers are man-made, synthetic polymers characterized by a well-defined, unidisperse, molecular architecture. Their unique properties derive from their regular structure, which starts by growing from a central core f branches; in the next generation, the process continues by growing $(f - 1)$ branches from each site added in the previous generation. The process stops then after g generations.[1–11] The interest in dendrimers is also due to the wide range of applications suggested for them:[12–15] these extend from using them as units for supramolecular assemblies, as laser-printing toners and as biological agents. In fact, one of the most exciting ideas involves the use of dendrimers in biological host-guest systems, say for the delivery of DNA into cells.[16] In our field, dendrimers are increasingly employed as building blocks in the design of new macromolecular materials with complex architecture, say by incorporating them into polymer networks.[17–19] Another recent development concerns dendritic polymers consisting of different monomers; an example are copolymeric dendrimers, consisting of two kinds of monomers. Being constructed

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from monomers of different chemical and physical properties, such macromolecules combine the unique dendrimer properties with features well-known from the study of linear and star copolymers.[20–27]

In this work, we study theoretically the viscoelastic relaxation of copolymeric dendrimers. In an earlier work, we have evaluated theoretically the dynamics of linear and cross-linked copolymers in the free-draining limit.[28] Remarkably, even this rather simple ''free-draining'' model of an alternating copolymer chain built from two (*A*- and *B*-) kinds of beads reveals a multitude of new dynamical features when the difference in the mobility of the different kinds of beads is large. These features include the appearance of a plateau-type behavior in the storage modulus and of an additional peak in the loss modulus.[28] Here we extend our approach to copolymers whose topology follows a tree-like, dendrimer pattern. As before,[28] we are mostly interested in alternating copolymers. In dendrimers this implies that the *A*- and *B*-monomers alternate when going from a generation to the next. Apart from the fact that such dendritic copolymers are of general theoretical interest, our considerations have also a clear experimental motivation: Such copolymeric dendrimers were recently synthesized, see e.g. ref.,[21] where the systems reported display along their bonds, alternatingly, amines and ethers.

On the theoretical side we model our systems through generalized Gaussian structures (GGS), a method already used in the study of several classes of polymers.[29–36] We investigate in how far the presence of different *A*- and *B*-monomers affects the dynamics. In the GGS framework, the monomers are modeled by beads; these are connected with each other by elastic springs and undergo viscous friction in the solvent. Clearly, the GGS approach extends the familiar Rouse model[37,38] developed for linear chains, by allowing the structures to be very general; in this way the beads may have functionalities larger that 2. In a way similar to the extension of the Rouse to the Zimm model, one can also incorporate hydrodynamic interactions into the GGS-formalism. Here, we consider for simplicity free-draining structures, i.e. we do not take the hydrodynamic interactions into account. We also dispense with other monomer-monomer interactions, such as leading to excluded-volume aspects, and with other forces (possibly attractive or repulsive) between monomers of different kinds. In this way our treatment is restricted to copolymers which do not microphase-separate, examples of which are, for instance, block copolymers of styrene and α-methyl-styrene[39–42]and polystyrene-*block*-polyisoprene-*block*-polystyrene copolymers.[43] Such copolymers are called homogeneous. Moreover, also the proper choice of the solvent may lead to copolymer homogeneity.[44,45] Clearly, the above assumptions simplify our problem. Nonetheless, even such simplified models lead to complex features in the mechanical relaxation patterns, as we proceed to show.

The paper is organized as follows: In the next section we recall the GGS model and the form of the main dynamical quantities of interest, namely of the storage $G'(\omega)$ and of the loss $G''(\omega)$ moduli. In the section *''General Method''* we show how to determine the eigenvalues (relaxation times) of dendrimers built from alternating *A*- and *B*-monomers. The section *''Results and Discussion''* presents $G'(\omega)$ and $G''(\omega)$ for alternating dendrimers whose generation g ranges from 1 to 8. The paper ends with our *''Conclusion''*.

The Model

As already pointed out, we focus on objects of dendritic topology, consisting of subunits of two different (*A*- and *B*-) kinds, modeled as beads. In dendritic structures, letting the beads alternate, automatically leads to an alternation from generation to generation. All beads are connected to their neighbors by elastic springs with the same elasticity constant *K*. The friction constants of the beads differ, however, being ζ_A and ζ_B respectively.

An example of a dendrimer with alternating beads (or, equivalently, generations) is shown in Figure 1. The central bead (core) represents by itself the generation 0, i.e. $g = 0$; its bead is taken to be of type *A*, with friction constant ζ_A. From our assumptions, it follows that all beads which belong to *even* generations are of type *A* and also have ζ_A as their friction constant. The rest of the beads (belonging to *odd* generations) are of type *B* and their friction constant is ζ_B.

Now, the Langevin equation of motion for the *i*-th bead reads:

$$\zeta_i \frac{d\mathbf{R}_i(t)}{dt} + K \sum_{j=1}^{N_{\text{tot}}} A_{ij}\mathbf{R}_j(t) = \mathbf{f}_i \tag{1}$$

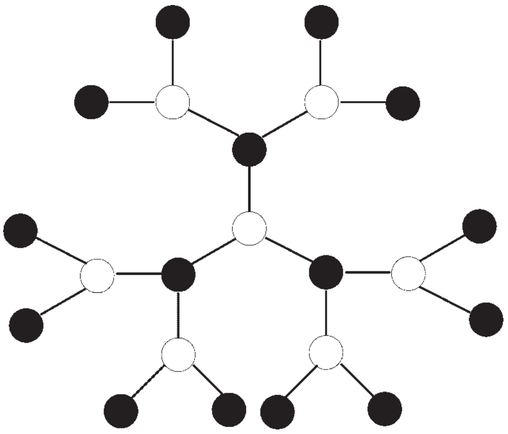

Figure 1. A system under study: a dendrimer of third generation ($g = 3$) with functionality $f = 3$, composed of alternating beads.

Here $\mathbf{R}_i(t)$ is the position vector of the ith bead, ζ_i is its friction constant, $\mathbf{f}_i$ represents the sum of stochastic forces acting on the ith bead, and N_{tot} is the total number of beads in the system. Moreover, $\mathbf{A} = (A_{ij})$ is the so-called connectivity matrix (or Laplace-matrix). For $i \neq j$ the element A_{ij} equals (-1) if the ith and jth beads are connected and is 0 otherwise; A_{ii} equals the number of bonds emanating from the ith bead.

Of particular interest are the relaxation times τ_j of the system, which are related to the eigenvalues λ_j of Equation (1) via $\tau_j = 1/\lambda_j$. To determine these eigenvalues, it is sufficient to focus on the homogeneous part of Equation (1), i.e. to set its right-hand-side to zero. Then we introduce τ_0 through $\tau_0 \equiv \zeta_A/K$ and note that τ_0 is a characteristic relaxation time of the problem.

Now we can rewrite the homogeneous part of Equation (1) in the form:

$$\frac{d\mathbf{R}_i(t)}{dt} + (1/\tau_0)\sum_{j=1}^{N_{\text{tot}}} \tilde{A}_{ij}\,\mathbf{R}_j(t) = 0 \tag{2}$$

by setting

$$\tilde{A}_{ij} = \sigma_i A_{ij} \tag{3}$$

where the σ_i are given by

$$\sigma_i = \frac{\zeta_A}{\zeta_i} \tag{4}$$

Note that this transformation leads to the new matrix $\tilde{\mathbf{A}} = (\tilde{A}_{ij})$. Now $\tilde{\mathbf{A}}$ is obtained from $\mathbf{A}$ by multiplying its rows with σ_i. Given that for the B-beads σ_B equals ζ_A/ζ_B, which is, in general, different from unity, the new matrix $\tilde{\mathbf{A}}$ is not symmetric anymore. Nonetheless, as we have shown in our previous publication,[28] all eigenvalues λ_i of this matrix are also real and nonnegative. Given that we have only two kinds of beads, σ_i in Equation (4) can adopt only two values, namely $\zeta_A/\zeta_A = 1$ and ζ_A/ζ_B for the A- and the B-beads, respectively.

An experimentally readily accessible quantity is the complex dynamic modulus, $G^*(\omega)$, which is usually determined by applying an external harmonic strain to the system. Even more familiar are the storage $G'(\omega)$ and the loss $G''(\omega)$ moduli, which are simply the real and the imaginary components of $G^*(\omega)$. As discussed before,[28,38] in the GGS model of Equation (1) and (2), $G'(\omega)$ and $G''(\omega)$ are proportional to the reduced storage and loss moduli:

$$[G'(\omega)] = \frac{1}{N_{\text{tot}}}\sum_{i=2}^{N_{\text{tot}}} \frac{(\omega\tau_i)^2}{1+(\omega\tau_i)^2} \tag{5}$$

and

$$[G''(\omega)] = \frac{1}{N_{\text{tot}}}\sum_{i=2}^{N_{\text{tot}}} \frac{\omega\tau_i}{1+(\omega\tau_i)^2} \tag{6}$$

the difference between very dilute and dilute solutions being in general only a matter of different, ω-independent, prefactors; however, in the concentrated regime additional features (such as entanglements) may enter, which will change the picture. In the range of validity of Equation (5) and (6) we are interested in the shapes of $G'(\omega)$ and $G''(\omega)$ and not in their prefactors, and will consider in the following only the reduced moduli $[G'(\omega)]$ and $[G''(\omega)]$. In Equation (5) and (6) we have assumed that the vanishing eigenvalue is λ_1, i.e. that $\lambda_1 = 0$, so that the sum runs only over the other eigenvalues. As previously discussed, in order to evaluate Equation (5) and (6) one needs only to know the relaxation times τ_i or, equivalently, the eigenvalues λ_1 of the linear homogeneous system given by Equation (2).

General Method

As stated, we have to determine the eigenvalues of dendrimers consisting of alternating beads. A dendrimer is characterized by its functionality f and by the number g of generations. The number N_{tot} of beads of the dendrimer is then:

$$N_{\text{tot}} = f\,\frac{(f-1)^g - 1}{f-2} + 1 \tag{7}$$

We note that $f = 3$ is the lowest f value which leads to nontrivial dendrimers; in general we take f to be $f > 2$. Furthermore, here all beads of *even* generations are assumed to have ζ_A as friction constant, whereas all beads of *odd* generations have friction constant ζ_B. Figure 1 shows a particular example for an alternating copolymeric dendrimer, for which $f = 3$ and $g = 3$.

For true dendrimers, $f \geq 3$, we proceed along ideas put forward by Cai and Chen[7] for $f = 3$ and developed further, for arbitrary f, in ref.,[36] ref.[46] and ref.[47]. One can namely categorize the normal modes of the dendrimer into two groups: (i) modes in which the core is mobile and (ii) modes in which the core is immobile.[7] In this way we can follow the procedure of ref.,[36] ref.[46] and ref.:[47]

Mobile Core

Here, as a rule, all beads are involved in the motion. Based on the structure of the dendrimer (where every inner bead is connected with one bead from the previous and with $f-1$ beads from the next generation), the following equation of motion holds for the inner beads:

$$\zeta_j \frac{d\mathbf{R}_{j,m}(t)}{dt} + K\left[f\mathbf{R}_{j,m}(t) - \mathbf{R}_{j-1,n}(t) - \sum_{l=1}^{f-1}\mathbf{R}_{j+1,l}(t)\right] = 0 \tag{8}$$

Here $\mathbf{R}_{j,m}(t)$ is the position vector of the m-th bead of generation j, and the sum over l involves the nearest neighbors to $\mathbf{R}_{j,m}(t)$ in the generation $(j+1)$. For the inner beads the index j obeys $0 < j < g$; $\zeta_j = \zeta_B$ if j is *odd*, and $\zeta_i = \zeta_A$ if j is *even*. Using $\sigma_j = \zeta_A/\zeta_j$ as in Equation (4), and $\tau_0 = \zeta_A/K$, Equation (8) can be written as:

$$\tau_0 \frac{d\mathbf{R}_{j,m}(t)}{dt} + \sigma_j \left[f\mathbf{R}_{j,m}(t) - \mathbf{R}_{j-1,n}(t) - \sum_{l=1}^{f-1} \mathbf{R}_{j+1,l}(t) \right] = 0 \tag{9}$$

Paralleling the procedure of ref.,[36] one can now separate the time dependence and also use a normal mode expansion. The form is that of Equation (A2) of ref.:[36]

$$\mathbf{R}_{j,m}(t) = \sum_k \mathbf{C}_k \Phi_k(j,m) \exp(-\lambda_k t/\tau_0) \tag{10}$$

Here $\mathbf{C}_k$ are j-independent constant vectors, λ_k are the eigenvalues, and $\Phi_k(j, m)$ are the eigenfunctions of Equation (8). Inserting Equation (10) into Equation (9) we arrive at (for $0 < j < g$):

$$(-\lambda_k)\Phi_k(j,m) + \sigma_j \times \left[f\Phi_k(j,m) - \Phi_k(j-1,n) - \sum_{l=1}^{f-1} \Phi_k(j+1,l) \right] = 0 \tag{11}$$

which differs from the corresponding expression, Equation (A3) of ref.,[36] by the appearance of σ_j. A further simplification arises from the symmetry of the dendrimer: In the case of a mobile core, beads belonging to the same generation move in the same manner.[7,36,46] Hence $\Phi_k(j, m) = \Phi_k(j)$, which reduces considerably the number of equations to be considered; Equation (11) leads to:

$$(-\lambda_k)\Phi_k(j) + \sigma_j[f\Phi_k(j) - \Phi_k(j-1) - (f-1)\Phi_k(j+1)] = 0 \tag{12}$$

Additional relations hold for the central bead ($j = 0$) and for the beads of the last generation, $j = g$:

$$(-\lambda_k)\Phi_k(0) + f\Phi_k(0) - f\Phi_k(1) = 0 \tag{13}$$

and

$$(-\lambda_k)\Phi_k(g) + \sigma_g[\Phi_k(g) - \Phi_k(g-1)] = 0 \tag{14}$$

The coupled system of Equation (12)–(14) is the one from which one now obtains the eigenvalues. The eigenvalue $\lambda_1 = 0$ is always present (for it all $\Phi_1(j)$ are equal), and it corresponds to the translation of the GGS as a whole. Note that the eigenvalues of this group of normal modes are non-degenerate; this differs from the situation in the case of an immobile core, to whose discussion we now turn to.

Immobile Core

When the core, or even larger inner portions of the dendrimer are immobile, the normal modes can be envisaged as involving two branches (wedges) moving against each other.[7,36,46,47] Here a wedge is defined as consisting of an inner bead and of all its descendants. For a normal mode in which the core is immobile, but a bead of the first generation moves, there is another bead of the first generation moving in the opposite direction. These two moving beads have each their wedges; inside each wedge again all beads of the same generation move in the same way. Starting point of the corresponding system of coupled equations is now a variant of Equation (12), with $\Phi_k(0) = 0$, so that

$$(-\lambda_k)\Phi_k(1) + \sigma_1[f\Phi_k(1) - (f-1)\Phi_k(2)] = 0 \tag{15}$$

whereas all other equations for larger j stay unchanged.

Now, even larger groups of inner beads may be immobile, say all beads up to generation n, where $1 \leq n < g - 1$. Then the starting equation is based on Equation (12) with $\Phi_k(n) \equiv 0$, and reads (for $1 \leq n < g - 1$):

$$(-\lambda_k)\Phi_k(n+1) + \sigma_{n+1}[f\Phi_k(n+1) - (f-1)\Phi_k(n+2)] = 0 \tag{16}$$

Finally, when only peripheral beads move, i.e. for $\Phi_k(g-1) \equiv 0$, one has from Equation (14):

$$(-\lambda_k)\Phi_k(g) + \sigma_g\Phi_k(g) = 0 \tag{17}$$

One may note in Equation (16) and (17) the appearance of σ_j. Focusing on Equation (17) we observe that it describes a large number of degenerate eigenvalues; they obey $\lambda = \sigma_j$, and hence their value depends on whether g is *even* or *odd*.

As a function of n we have with Equation (12), Equation (14), and Equation (15)–(17) a set of equations which lead to the complete eigenvalue spectrum for the case of an immobile core. We note that these eigenvalues are degenerate, but that their degeneracy can be easily determined. Thus, e.g., if a bead next to the immobile core is mobile, its wedge also moves. We can then choose as independent normal modes the ones in which this particular bead and, since the forces on the core are balanced, another one but only one of the other $(f-1)$ neighbors of the core (plus its corresponding wedge) moves. The degeneracy of the corresponding eigenvalue is then $(f-1)$. In the same way, each immobile bead at the nth stage ($n \geq 1$), whose outwards nearest neighbors are moving, gives rise to $(f-2)$ independent normal modes. To determine the total degeneracy of normal modes with immobile beads up to and including the nth generation, we have to multiply the above mentioned factor $(f-2)$ with the total number of beads in the nth generation, namely with $f(f-1)^{n-1}$. The total degeneracy of such modes is hence $f(f-2)(f-1)^{n-1}$.

To conclude, using the theoretical scheme described in this section makes it possible to get all the eigenvalues of the copolymeric dendrimer under study in a straightforward way, even for very large g. It is not difficult to show (see also the *Appendix*) that applying this approach to a dendrimer of generation g reduces the dynamical problem to solving polynomials of maximal degree equal to g. Hence, we call our approach ''semi-analytical'', because in the case of large dendrimers we also have to use numerical procedures, but which only involve finding the roots of polynomials. To illustrate the method, we apply it in the *Appendix* to the cases $g = 1$ and $g = 2$, for which we readily find all the eigenvalues analytically. For larger g one has to evaluate the roots numerically.

The big advantage of the method just developed is that it offers a very effective means for obtaining the eigenvalues' spectrum, method which bypasses the direct diagonalization of the corresponding (asymmetric) connectivity matrix, Equation (3). The method is especially suitable for very large g, where, because of the exponential increase of N_{tot} with g (see also the *Appendix*), limits on computer time and, especially, on computer memory render soon a brute-force diagonalisation (note that we need *all* the eigenvalues) unfeasible. Even for moderately large g our method has advantages, because it can be readily implemented on small PCs using existing programs, such as MATHEMATICA or MAPLE.

As a check on the precision of our method, we verified the results obtained with it (values of the eigenvalues and their degeneracies), through a comparison to the eigenvalues which follow from a direct numerical treatment of the corresponding asymmetric connectivity matrix given by Equation (3). We used the procedures given in ref.[48] to determine the eigenvalues: First we employed ''subroutine balanc'' to balance the asymmetric matrix under scrutiny; the idea of balancing is to use similarity transformations to make corresponding rows and columns of the matrix have comparable norms, thus reducing the overall norm of the matrix while leaving the eigenvalues unchanged. Then, through ''subroutine elmhes'' we brought the matrix to Hessenberg form. The eigenvalues were then obtained through ''subroutine hqr'', which implements the QR-algorithm for real Hessenberg matrices. Finally, we sorted the eigenvalues obtained in ascending order through a variant of ''subroutine eigsrt''. The agreement between the results obtained in this way and those achieved using Equation (12) and (15) to (17), which are based on the symmetry of the dendrimers, is extremely good; for dendrimers up to the sixth generation we obtain the same eigenvalues, to an accuracy of five digits. It may be worthwhile to stress that the analytical approach provides *all* the eigenvalues; also the degeneracies of the numerically determined eigenvalues follow precisely our analytical predictions.

Results and Discussion

We are now ready to apply the formalism discussed above in order to compute the mechanical moduli, $[G'(\omega)]$ and $[G''(\omega)]$, of dendrimers built from alternating monomers. We choose trifunctional dendrimers, $f = 3$, because this class (to which the *poly*(*amidoamine*) (PAMAM) dendrimers[16,49–51] belong) was much investigated. We focus on the dependence of $[G'(\omega)]$ and $[G''(\omega)]$ on the dendrimer structure, i.e. on g, and on composition, i.e. on $\sigma = \zeta_A/\zeta_B$. In so doing we will also compare the alternating copolymeric dendrimers to linear alternating copolymers built from the same A- and B-monomers.

We start with the storage modulus $[G'(\omega)]$ for a dendrimer at the sixth generation, $g = 6$, and study the influence of changes in σ, which we let vary from 0.01 to 100. The case $\sigma = \zeta_A/\zeta_B = 1$ corresponds to the homopolymer situation and reproduces what one finds in the GGS-model for a ($f = 3$, $g = 6$)-dendrimer:[52,53] The storage modulus $[G'(\omega)]$ displays a non-scaling (non-power-law) behavior in the domain of intermediate frequencies, which correspond to the internal (''intra-dendrimer'') relaxation.

Now, even a slight departure of $\sigma = \zeta_A/\zeta_B$ from 1 (by which one is in a copolymer situation), drastically changes the $[G'(\omega)]$-behavior; larger changes in σ lead even to the appearance of pronounced quasi-plateaus in $[G'(\omega)]$, see the $[G'(\omega)]$-curves in Figure 2 for $\sigma = 0.01$ and $\sigma = 100$. Here the plateaus are to the left (to the right) from the curve with $\sigma = 1$, when σ is smaller (larger) than unity. Noting that we present our results in terms of the dimensionless frequency $\omega\tau_0$, where $\tau_0 = \zeta_A/K$ is the characteristic relaxation time of the A-beads, the reason is evident: For $\sigma \gg 1$, i.e. for $\zeta_A/\zeta_B \gg 1$, the B-beads are considerably more mobile than the A-beads, and the response of the system starts earlier than that of the homopolymeric dendrimer, $\sigma = 1$. At high frequencies only the B-beads move, whereas the A-beads are practically immobile. When $\sigma \gg 1$ one has to go to much lower frequencies, in order to approach the domain where the A-beads start to move. This scale separation leads to the plateau in $[G'(\omega)]$. On the low frequency scale, at the left of the plateau in the direction of the terminal relaxation, one finds a domain where $[G'(\omega)]$ follows closely the non-scaling behavior of homopolymer dendrimers ($\sigma = 1$). This low-frequency behavior of $[G'(\omega)]$ has a simple physical interpretation: On very large scales (at low frequencies) we are beyond the domain of the interplay between the two kinds of beads with their different mobilities. In other words, one sees here a ''coarse-grained'' behavior, in which the A-beads and the neighboring B-beads of the next generation combine to a new entity, a ''coarse-grained'' homopolymer dendrimeric object, whose generation number g' and general functionality f' obey $g' = g/2$ and $f' = (f-1)^2 + 1$, while the functionality of its core equals $f(f-1)$. Turning now to the case $\sigma \ll 1$, considerations similar to those expressed above render clearly that now the plateau appears to the *left* of the curve corresponding to the homopolymer dendrimer, see Figure 2.

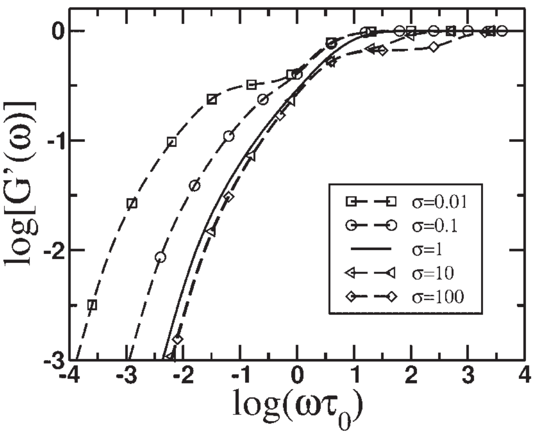

Figure 2. The reduced storage modulus $[G'(\omega)]$ plotted in double logarithmic scales versus the reduced frequency $\omega\tau_0$. Shown are results for a dendrimer with $f = 3$ and $g = 6$, for which the parameter σ ranges from 0.01 to 100.

These conclusions are similar to those derived in our previous study of linear alternating copolymer chains.[28] The main difference resides here in the fact that for copolymeric dendrimers, the plateau values of the storage modulus $[G'(\omega)]$ in the extreme cases $\sigma \ll 1$ and $\sigma \gg 1$ are not anymore equal, see Figure 2. This contrasts strongly with the findings for copolymer chains.[28] To render this point clear, we display in Figure 3 for the two cases $\sigma = 0.01$ and $\sigma = 100$ the behavior of $[G'(\omega)]$ for the dendrimer with $f = 3$ and $g = 6$, hence where $N_{\text{tot}} = 190$. In the same Figure we also plot $[G'(\omega)]$ for an alternating copolymer chain, where we took $N_{\text{tot}}^{\text{ch}} = 191$; for symmetry reasons we have to take $N_{\text{tot}}^{\text{ch}}$ *odd* and we took it as close as possible to N_{tot}. We remark that for the chain the plateau is situated around 0.5, a clear indication that at high frequencies only half of the beads move (note that a long alternating chain with *odd* N_{tot} contains almost the same number of A- and B-beads). In the case of dendrimers, the number of beads in each generation increases exponentially with g; for an alternating structure one of the species dominates, depending on whether g is *even* or *odd*. Note that for $f = 3$ the number of beads in the last generation alone (the peripheral beads), $N_{\text{per}} = 3 \times 2^{g-1}$, accounts for more than half of the total number of beads, $N_{\text{tot}} = 3 \times 2^g - 2$. Hence, if the central bead (the core) is of type A, for g *even* the majority of the beads are of A-type and for g *odd* are of B-type. Hence, for a given g there is an asymmetry between the A- and the B-beads, asymmetry which becomes clear when one interchanges the role of the slow beads, as happens for instance by first taking $\sigma = 100$ and then taking $\sigma = 0.01$. It is this asymmetry which leads to the observed difference in the plateau values of $[G'(\omega)]$ for $\sigma = 100$ and for $\sigma = 0.01$; one should note that for the same choice of σ, the curves for the linear alternating chains are (for all practical reasons) only shifted with respect to each other, the shift being due to the fact that τ_0 is defined in terms of ζ_A.

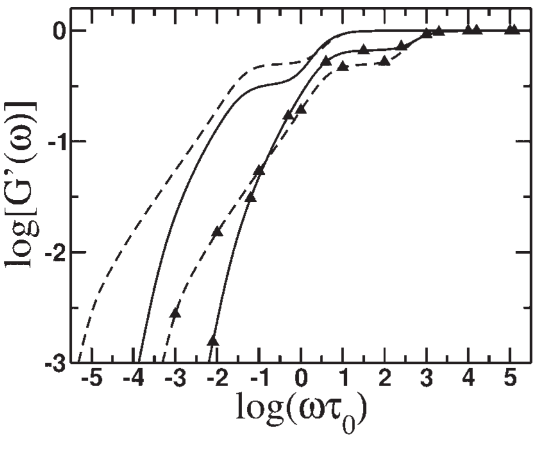

Figure 3. The reduced storage modulus $[G'(\omega)]$ plotted in double logarithmic scales versus the reduced frequency $\omega\tau_0$. Shown are results for a copolymeric dendrimer with $f = 3$ and $g = 6$, hence with $N_{\text{tot}} = 190$ beads, and for an alternating copolymer chain with $N_{\text{tot}}^{\text{ch}} = 191$ beads. In both cases the parameter σ takes either the value $\sigma = 0.01$ or $\sigma = 100$. The dashed lines indicate the results for the linear chain, the solid lines correspond to the dendrimer results. The triangles stand for $\sigma = 100$, lines with no symbols are for $\sigma = 0.01$.

Furthermore, the above feature is even more clearly revealed when one studies the influence of g, the number of generations, on the storage modulus $[G'(\omega)]$. In Figure 4 we plot $[G'(\omega)]$ for the particular value $\sigma = 0.01$, which is small enough to guarantee pronounced plateaus in $[G'(\omega)]$. By increasing g from $g = 3$ to $g = 8$, the plots of Figure 4 demonstrate that the plateaus of the $[G'(\omega)]$ – curves cluster close to two values, and that they are near the one or the other value depending on whether g is *even* or *odd*; We recall that dendrimers with *even* g consist mainly of A-beads, whereas the opposite is true for *odd* g. For our choice of σ,

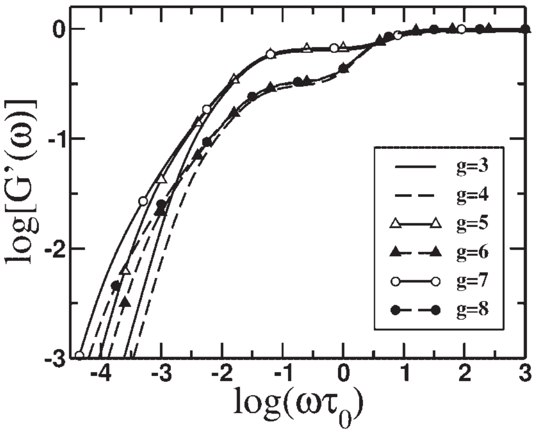

Figure 4. The reduced storage modulus $[G'(\omega)]$ plotted in double logarithmic scales versus the reduced frequency $\omega\tau_0$. Shown are results for alternating copolymeric dendrimers. The parameters are $f = 3$ and $\sigma = 0.01$; g ranges from 3 to 8.

which implies that the *A*-beads are more mobile than the *B*-beads, it follows that the $[G'(\omega)]$ curves for *g even* have their plateau at a lower value than the $[G'(\omega)]$ curves for *g odd*, a fact which is also evident from Figure 4. At very low frequencies and in the logarithmic scale of Figure 4, the $[G'(\omega)]$ get to be parallel to each other, with slope 2; their position is then mainly determined by the number of *A*- and of *B*-beads. Also this feature is well-obeyed by the curves in Figure 4.

Now we turn to consider the loss modulus $[G''(\omega)]$. As a general feature, $[G''(\omega)]$ displays (at least) one maximum, since it goes as ω at small ω-values and as ω^{-1} at large ω-values. As we have shown in ref.,[28] the separation of the scales of motion in copolymer systems may lead both to a plateau type behavior in the storage modulus $[G'(\omega)]$ and also to the appearance of more than one peak in the loss modulus $[G''(\omega)]$. As we proceed to show, this also holds in the case of dendrimers made out of alternating monomers. In Figure 5 we display $[G''(\omega)]$ for copolymeric dendrimers with $f = 3$ and $g = 6$ (as noted above, such dendrimers have more *A*- than *B*-beads) and for σ varying between 0.01 and 100. Again, the case $\sigma = 1$ corresponds to the GGS, Rouse-type, homopolymeric dendrimer. As in the case of alternating copolymer chains,[28] we find that also here $[G''(\omega)]$ may develop two peaks. The main peak (located around $\omega = 10/\tau_0$) corresponds to the *A*-beads, which are in majority. The second peak is due to the *B*-beads and lies on the left side or on the right side of the main peak, depending on σ, i.e. on the quotient of the mobilities of the *A*- and of the *B*-beads, see Figure 5.

Finally for dendrimers with $f = 3$, we plot in Figure 6 the loss modulus $[G''(\omega)]$ for $\sigma = 0.01$, while letting g range from $g = 3$ to $g = 8$. At such a low σ value, one observes two peaks in $[G''(\omega)]$. Again, there is a separation of the $[G''(\omega)]$-curves into two families, depending on whether g is *even* or *odd*. It is noteworthy that the composition of the dendrimer is now directly reflected in the relative weight of the two peaks: The highest peak corresponds to the energy loss due to the friction against the viscous medium of the majority of the beads. Thus, the A- and *B*- composition of the dendrimers leads to very typical features, both in $[G'(\omega)]$ and also in $[G''(\omega)]$, and may be readily revealed through mechanical dynamic measurements.

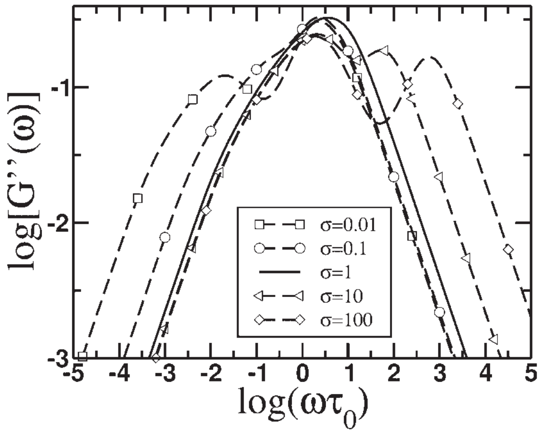

Figure 5. The reduced loss modulus $[G''(\omega)]$ plotted in double logarithmic scales versus the reduced frequency $\omega\tau_0$. The parameters are as in Figure 2.

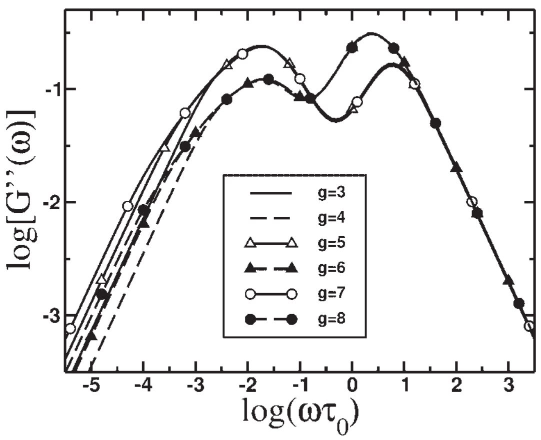

Figure 6. The reduced loss modulus $[G''(\omega)]$ plotted in double logarithmic scales versus the reduced frequency $\omega\tau_0$. The parameters are as in Figure 4.

Conclusion

In this work we presented a theoretical study of the mechanical dynamic properties of dendrimers built from monomers (beads) of two different types, which we called *A* and *B*. We performed our analysis in the framework of generalized Gaussian structures (GGS) and we assumed (as a first step), that the *A*- and *B*-beads differ only in their friction constants. The GGS procedure does not include finer aspects, such as the influence of the excluded volume or hydrodynamic interactions. However, the GGS-procedure allows us to readily treat very large systems and to display the basic dynamical aspects, while also following our previous study[28] in which we considered linear *alternating* copolymer chains in the framework of the Rouse-model. Here we take the dendrimers to be made of *alternating* monomers, which implies that the *A*- and *B*-monomers alternate from generation to generation; we note that such substances have been recently synthesized and experimentally investigated.[21]

To treat the dynamics of such copolymeric dendrimers of an arbitrary functionality, *f*, and number of generations, *g*, we made use of some methods previously developed for homopolymeric dendrimers and dendritic wedges.[7,36,46,47] A great advantage of these methods is that they allow us to avoid the direct, large-scale numerical diagonalization of the corresponding connectivity matrices. Essentially, the main idea is to use the underlying symmetry of the dendritic structure in order to strongly reduce the problem of finding the eigenvalues of the corresponding connectivity matrix: The linear system to be treated reduces from being exponential in g (of order $(f-1)^g$) to being linear in g.

The application of this method to dendrimers built from trifuctional monomers ($f=3$) shows that the storage $[G'(\omega)]$ and the loss modulus $[G''(\omega)]$ directly reveal fundamental features of the underlying geometry: It turns out that if the mobilities of the A- and the B-beads differ considerably, then there appear plateaus in the $[G'(\omega)]$ curves. What is new here, compared to linear alternating copolymers, is that changing the σ parameter to $1/\sigma$, i.e. interchanging the roles of the A- and the B-beads, does not result in a symmetric situation. This asymmetry in behavior reflects the fact that in dendrimers made of alternating monomers the type of the beads in majority changes from generation to generation; this alternation leads to the separation of the corresponding curves into two families, depending on whether g is *even* or *odd*.

As for the loss modulus $[G''(\omega)]$, it reflects such changes in an even more pronounced way than the storage modulus $[G'(\omega)]$. For σ very different from unity, say for $\sigma=0.01$, such a difference in the A- and the B- mobilities leads to the appearance of a second peak in $[G''(\omega)]$. Remarkably, the relative height of the two peaks also sheds light into the A- and B- composition of the dendrimer, since the height of the peaks is revealing of the number of beads of one kind involved in the energy dissipation around a given frequency. Therefore, measurements of the storage and loss moduli of copolymeric dendrimers can unveil a large number of structural details, when the underlying building blocks (i.e. the beads) markedly differ in their properties.

Appendix

Given that in the homopolymer case the analytical determination of the eigenvalues of the dendrimers can be pushed quite far,[7,36,46,47] we sketch here the reasons why the procedure gets difficult in the case of an alternating arrangement of two monomers species. We take here f to be arbitrary and consider the cases $g=1$ and $g=2$.

(a) $g=1$. Here there are no inner beads, one has only the core and f peripheral beads, so that $N_{\text{tot}}=f+1$. For a mobile core one has to solve Equation (13) and (14), which, setting $\sigma_1=\sigma$, we rewrite as:

$$\begin{pmatrix} f-\lambda_k & -f \\ -\sigma & \sigma-\lambda_k \end{pmatrix}\begin{pmatrix} \Phi_k(0) \\ \Phi_k(1) \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{A1}$$

Setting the determinant in Equation (A1) equal to zero allows to rewrite the condition for non-trivial solutions as a characteristic polynomial:

$$\lambda^2-\lambda(f+\sigma)=0 \tag{A2}$$

whose roots are the two, non-degenerate eigenvalues $\lambda_1=0$ and $\lambda_2=f+\sigma$.

When the core is immobile, the single equation still to be taken care of is Equation (17), which, as discussed in the main text, leads to the solution $\lambda=\sigma$, which is $(f-1)$-fold degenerate, see section *"General Method"*. Together with the two previously determined eigenvalues, we have $N_{\text{tot}}=(f+1)$ eigenvalues, i.e. all of them.

(b) $g=2$. Here N_{tot}, the total number of beads, is from Equation (7) $N_{\text{tot}}=f^2+1$.

In the case of a mobile core, we have to solve Equation (12), (13) and (14). The corresponding matrix relation is:

$$\begin{pmatrix} f-\lambda_k & -f & 0 \\ -\sigma & \sigma f-\lambda_k & -\sigma(f-1) \\ 0 & -1 & 1-\lambda_k \end{pmatrix}\begin{pmatrix} \Phi_k(0) \\ \Phi_k(1) \\ \Phi_k(2) \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{A3}$$

Non-trivial solutions obtain when the determinant of Equation (A3) vanishes, which leads to the following characteristic polynomial:

$$\begin{aligned}&(f-\lambda)(\sigma f-\lambda)(1-\lambda)-\sigma f(1-\lambda)-\sigma(f-1)(f-\lambda)\\&\quad\equiv-\lambda^3+\lambda^2(f+\sigma f+1)-\lambda(f+\sigma f^2-\sigma f+\sigma)=0\end{aligned} \tag{A4}$$

From Equation (A4) one has by inspection the eigenvalue $\lambda_1=0$; the other two eigenvalues are solutions of the remaining quadratic polynomial:

$$\begin{aligned}\lambda_{2,3}&=[(f+\sigma f+1)\\&\quad\pm\sqrt{(f+\sigma f+1)^2-4(f+\sigma+\sigma f^2-\sigma f)}]/2\end{aligned} \tag{A5}$$

All three eigenvalues are non-degenerate; their total number, given as a function of g, is again $(g+1)$.

In the case of an immobile core one has now two possibilities: Either the first-generation beads are all immobile or not. In the first case only the peripheral beads are moving; as discussed in the section *"General Method"*, the corresponding value for λ_4 is $\lambda_4=1$, which is $f(f-2)$-fold degenerate. The equations for the second case (where beads of the last two generations are moving) are Equation (15) and (16), which lead to

$$\begin{pmatrix} \sigma f-\lambda_k & -\sigma(f-1) \\ -1 & 1-\lambda_k \end{pmatrix}\begin{pmatrix} \Phi_k(1) \\ \Phi_k(2) \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{A6}$$

The characteristic polynomial is now

$$\lambda^2-\lambda(\sigma f+1)+\sigma=0 \tag{A7}$$

which leads to the eigenvalues

$$\lambda_{5,6}=[(\sigma f+1)\pm\sqrt{(\sigma f+1)^2-4\sigma}]/2 \tag{A8}$$

both of them being $(f-1)$-fold degenerate. Thus, we have obtained $3+2(f-1)+f(f-2)=f^2+1=N_{\text{tot}}$ eigenvalues, i.e. all of them.

From our procedure it becomes obvious that there is not much to be gained by continuing analytically in this way, given that the maximal degree of the characteristic polynomials involved equals $(g+1)$ (or g, if one remarks that the polynomial of highest degree has $\lambda_1=0$ as eigenvalue). To proceed analytically further, one has to find an additional symmetry in the system of Equation (12)–(14) and in the related expressions, Equation (15)–(17), a symmetry which we did not find so far. As shown by ref.[36], the case $\sigma=1$ is more symmetric. Nonetheless, already these relations drastically simplify the numerical determination of the eigenvalues; to compute all eigenvalues for a copolymeric dendrimer of generation g the most arduous task is to find the roots of polynomials of degree up to g, instead of having to diagonalize $N_{\text{tot}} \times N_{\text{tot}}$ matrices, with N_{tot} given by Equation (7), i.e. $N_{\text{tot}} \sim (f-1)^g$. For our part, based on the equations just mentioned, we calculated for large g the eigenvalues numerically.

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[1] [1a] A. D. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **1990**, *102*, 119; [1b] *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.
[2] M. C. Moreno-Bondi, G. Orellana, N. J. Turro, D. A. Tomalia, *Macromolecules* **1990**, *23*, 910.
[3] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638.
[4] C. J. Hawker, J. M. J. Fréchet, *Macromolecules* **1990**, *23*, 4726.
[5] J. M. J. Fréchet, *Science* **1994**, *263*, 1710.
[6] J. Roovers, B. Comanita, *Adv. Polym. Sci.* **1999**, *142*, 179.
[7] C. Cai, Z. Y. Chen, *Macromolecules* **1997**, *30*, 5104.
[8] R. La Ferla, *J. Chem. Phys.* **1997**, *106*, 688.
[9] Z. Y. Chen, C. Cai, *Macromolecules* **1999**, *32*, 5423.
[10] F. Ganazzoli, R. La Ferla, G. Terragni, *Macromolecules* **2000**, *33*, 6611.
[11] F. Ganazzoli, R. La Ferla, G. Raffaini, *Macromolecules* **2001**, *34*, 4222.
[12] G. R. Newkome, C. N. Moorefield, F. Vögtle, "*Dendritic Molecules: Concepts, Syntheses, Perspectives*", VCH, Weinheim 1996.
[13] K. Lorenz, H. Frey, B. Stühn, R. Mülhaupt, *Macromolecules* **1997**, *30*, 6860.
[14] F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681.
[15] O. A. Matthews, A. N. Shipway, J. F. Stoddart, *Prog. Polym. Sci.* **1998**, *23*, 1.
[16] D. Luo, K. Haverstick, N. Belcheva, E. Han, W. M. Saltzman, *Macromolecules* **2002**, *35*, 3456.
[17] V. Percec, C.-H. Ahn, G. Ungar, D. J. P. Yeardley, M. Möller, S. S. Sheiko, *Nature* **1998**, *391*, 161.
[18] S. Jahromi, V. Litvinov, B. Coussens, *Macromolecules* **2001**, *34*, 1013.
[19] F. Gröhn, G. Kim, B. J. Bauer, E. J. Amis, *Macromolecules* **2001**, *34*, 2179.
[20] M. Nanjo, A. Sekiguchi, *Organometallics* **1998**, *17*, 492.
[21] Y. Pan, W. T. Ford, *J. Org. Chem.* **1999**, *64*, 8588.
[22] L. Balogh, A. de Leuze-Jallouli, P. Dvornic, Y. Kunugi, A. Blumstein, D. A. Tomalia, *Macromolecules* **1999**, *32*, 1036.
[23] D. Yan, C. Gao, *Macromolecules* **2000**, *33*, 7693.
[24] C. Gao, D. Yan, *Macromolecules* **2001**, *34*, 156.
[25] C. Gao, D. Yan, *Macromolecules* **2003**, *36*, 613.
[26] G. E. Rios, G. T. Pickett, *Macromolecules* **2003**, *36*, 2967.
[27] F. Ganazzoli, Y. A. Kuznetsov, E. G. Timoshenko, *Macromol. Theory Simul.* **2001**, *10*, 325.
[28] C. Satmarel, A. A. Gurtovenko, A. Blumen, *Macromolecules* **2003**, *36*, 486.
[29] J.-U. Sommer, A. Blumen, *J. Phys. A* **1995**, *28*, 6669.
[30] H. Schiessel, *Phys. Rev. E* **1998**, *36*, R5775.
[31] Ch. Friedrich, H. Schiessel, A. Blumen, in: "*Advances in the Flow and Rheology of Non-Newtonian Fluids*", D. A. Siginer, D. DeKee, R. P. Chhabra, Eds., Elsevier, Amsterdam 1999, p. 429.
[32] H. Schiessel, Ch. Friedrich, A. Blumen, in: "*Applications of Fractional Calculus in Physics*", R. Hilfer, Ed., World Scientific, Singapore 2000, p. 331.
[33] A. A. Gurtovenko, A. Blumen, *J. Chem. Phys.* **2001**, *115*, 4924.
[34] A. Blumen, A. A. Gurtovenko, S. Jespersen, *J. Non-Cryst. Solids* **2002**, *305*, 71.
[35] A. A. Gurtovenko, A. Blumen, *Macromolecules* **2002**, *35*, 3288.
[36] A. A. Gurtovenko, Y. Y. Gotlib, A. Blumen, *Macromolecules* **2002**, *35*, 7481.
[37] P. E. Rouse, *J. Chem. Phys.* **1953**, *21*, 1272.
[38] M. Doi, S. F. Edwards, "*The Theory of Polymer Dynamics*", Clarendon, Oxford, UK 1986.
[39] M. Shen, D. R. Hansen, *J. Polym. Sci., Symp. 46*, **1974**, 55.
[40] D. R. Hansen, M. Shen, *Macromolecules* **1975**, *8*, 343.
[41] S. Krause, in: "*Block and Graft Copolymers*", J. J. Burke, V. Weiss, Eds., Syracuse University Press, Syracuse, NY 1973, p. 143.
[42] L. M. Robeson, M. Matzner, L. J. Fetters, J. E. McGrath, in: "*Recent Advances in Polymer Blends, Grafts, and Blocks*", L. H. Sperling, Ed., Plenum Press, New York 1974, p. 281.
[43] C. D. Han, D. M. Baek, J. K. Kim, T. Hashimoto, S. Okamoto, *Macromolecules* **1991**, *24*, 5408.
[44] L. A. Utracki, R. Simha, *Macromolecules* **1968**, *1*, 505.
[45] H. Ohnuma, T. Kotaka, H. Inagaki, *Polym. J.* **1970**, *1*, 716.
[46] Y. Y. Gotlib, D. A. Markelov, *Polym. Sci., Ser. A (translated from Vysokomol. Soedin., Russia)* **2002**, *44*, 1341.
[47] A. A. Gurtovenko, D. A. Markelov, Y. Y. Gotlib, A. Blumen, *J. Chem. Phys.* **2003**, *119*, 7579.
[48] W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, "*Numerical Recipes – The Art of Scientific Computing*",

Cambridge University Press, Cambridge 1986, Chap 11, p. 348–376.

[49] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117.

[50] A. Topp, B. J. Bauer, D. A. Tomalia, E. J. Amis, *Macromolecules* **1999**, *32*, 7232.

[51] G. Sui, M. Micic, Q. Huo, R. M. Leblanc, *Langmuir* **2000**, *16*, 7847.

[52] [52a] P. Biswas, R. Kant, A. Blumen, *Macromol. Theory Simul.* **2000**, *9*, 56; [52b] P. Biswas, R. Kant, A. Blumen, *J. Chem. Phys.* **2001**, *114*, 2430.

[53] R. Kant, P. Biswas, A. Blumen, *Macromol. Theory Simul.* **2000**, *9*, 608.