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Relaxation dynamics of small-world degree-distributed treelike polymer networks

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HIGHLIGHTS

- We create a new type of treelike polymer networks with a small-world degree distribution.
- We study the relaxation dynamics of these networks in the framework of generalized Gaussian structures.
- We monitor the transition from a linear-like structure to a disordered hyperbranched structure by means of one parameter, p.
- In the intermediate frequency region the loss and storage moduli show constant slopes for small values of p.

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ABSTRACT

Hyperbranched polymers are typically treelike macromolecules with a very disordered structure. Here we construct hyperbranched polymers based on the degree distribution of the small-world networks. This algorithm allows us to study a transition from monodisperse linear chains to structurally-disordered dendritic polymers by varying the parameter p ($0 \leq p \leq 1$), which measures the randomness and the degree of branching of the network. Employing the framework of generalized Gaussian structures, we determine for the obtained structures the relaxation spectra, which are exemplified on the mechanical relaxation moduli (storage and loss moduli). We monitor these physical quantities for networks of different sizes and for various values of the parameter p. In the intermediate frequency domain, we encounter macroscopically distinguishable behaviours.

1. Introduction

Hyperbranched polymers belong to one of the most rapidly growing fields in polymer science [1]. From the point of view of their topology they are usually treelike or loopless structures. Various polymeric materials with treelike architectures were synthesized, such as dendrimers and dendritic structures [2–5], hyperbranched polymers [6–12] or star polymers [13–16]. As objects of theoretical investigations, hyperbranched polymers can be divided in deterministic structures [17–19], such as dendrimers [20,21], or in architectures with structural disorder [22,23]. Dendrimers as networks have a small-world feature: Their molecular weight grows exponentially with the generation g while the longest path between two nodes grows linearly with g. Small-world networks attract a lot of interests [24–30], to name only a few. The first model of small-world networks was proposed by Watts and Strogatz [24], based on the famous experiment of Milgram [31].

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Due to its huge importance in modelling the real complex networks other small-world network models were developed. From the vast number of applications of small-world networks we cite real networks such as technological and economic networks [32], chemical-reaction networks [33], food webs [34], social networks [35,36], and computer networks [37].

Here we built the polymers having a small-world degree-distribution using a similar procedure which we implemented in constructing treelike scale-free networks [22,38–40]. The main difference between the models is given by the degree distribution, which in this article is of the small-world network model developed by Newman and Watts [29,41]. The degree of each node will be given by following this degree distribution, but our algorithm will create treelike structures. The difference in degree distribution of the two algorithms, small-world and scale-free type, respectively, will permit us to create a totally different type of treelike polymer networks. Also it is worth stressing that our algorithm enables us to monitor in detail the transition from a linear-like chain to hyperbranched structures only by changing a parameter, different than other small-world network models from the literature. Our model enables during the network's construction the minimum allowed degree equal to two, the nodes of degree one are added only at the last step of construction according to the degrees of open nodes. This procedure guarantees that the node-by-node construction of the network never stops by itself, but only when we reach the desired structure's size.

In order to study the dynamics of polymers with complex architectures we consider the method of generalized Gaussian structures (GGS) [17,18,42,43], which is an extension of the Rouse model for linear chains [44]. The GGS Rouse-type model keeps all the restrictions of its ancestor: it does not include the hydrodynamic interactions, the excluded volume interactions, the entanglement effects nor the stiffness effects. It is worth to mention that there are other Gaussian models which consider some of the interactions named above [45,46]. Nevertheless, the GGS Rouse-type model is a powerful tool which can treat polymers with complex architecture in a transparent way: In this model, the monomers of the polymeric systems are modelled as beads, experiencing viscous friction, and connected to each other by means of elastic springs. Here we focus on the GGS Rouse-type model which considers only interactions between nearest neighbour beads and it is assumed that all beads endure the same friction constant with the solvent. The dynamics of polymers in this framework is determined by knowing the full eigenvalues' spectrum of the connectivity (Laplacian) matrix. Many theoretical studies of the GGS model focused on polymers with complex architectures, such as dendrimers and their derivatives [18,20,21,47,48], star polymers [3,18,49], hyperbranched polymers [19,50,51], fractal polymer networks [52], other small-world network models [17,26,28], and treelike scale-free networks [22]. In this article we expand this research topic by introducing a new kind of network, constructed from the degree distribution of the small-world networks of Refs.[29,41], in which all bonds which form a loop are cut on two bonds, so that the obtained networks are tree-like. From the wealth of applications, which make use of the eigenvalues spectrum, we choose the dynamical complex modulus [17,53,54], with its real and imaginary parts, the loss and the storage moduli, respectively.

The paper is structured as follows: In Section 2 we introduce the algorithm used to construct treelike polymers with a degree distribution of the small-world networks. In Section 3 we recall briefly the GGS formalism and we briefly remind the basic equations for the mechanical relaxation of polymers. In Section 4 we study the relaxation patterns of polymers modelled in Section 2. Here, we study the eigenvalues spectra of our networks and then we focus on the size influence on the dynamics of polymer networks with the same p, which is a parameter related to branching degree and to disorder of a structure. Then we vary the value of p and study its effect on the relaxation patterns. This paper ends up with conclusions.

2. Network construction

In this section we introduce an algorithm which creates a new class of treelike networks from a small-world networks degree distribution. First we present some general features of a small-world network model, recalling the model with additional links described in Refs. [26,29,41]. The construction starts from a ring lattice with N_0 nodes, which are connected symmetrically to its two nearest neighbours. Then we add to each of the nodes a new bond with probability p. The other end of the link will get attached with equal probability to any of the nodes, except itself. This model of small-world networks leads to the distribution of degrees (functionalities) to the following normalized form [41]:

$$p_k = \mathrm{e}^{-2p}\frac{(2p)^{k-2}}{(k-2)!}, \tag{1}$$

which is valid for $k \geq 2$, while $p_1 = 0$. In the last equation p_k is the probability that a node has k bonds emanating from it or, equivalently, it has k nearest neighbours. From the functional form of Eq. (1), it follows that for $0 < p < 0.5$ it is most probable to have in the network the beads of degree $k = 2$. For $p = 0.5$ the beads of degrees 2 and 3 appear with equal, highest probability, for $p = 1$ the beads of degrees 3 and 4 are most common. As can be inferred from Eq. (1), with growing p the distribution $p_k(p)$ gets broader, i.e. the degrees for higher values of the parameter p are distributed more randomly. All these properties can be understood from the analysis of Eq. (1). For a better illustration we depict in Fig. 1 the probabilities p_k (for degrees $k = 2, \ldots, 8$) for $p = 0.01$, 0.1, 0.2, 0.5, 0.8, and 1.0. For very small values of p we have a very high probability to get nodes with degree 2 and extremely low probabilities to have nodes with higher degrees. Thus, we will obtain networks with a predominant linear-like spacers. On the other hand, for $p = 1.0$ the probability of having nodes with degree 2 is lower than the probabilities to get nodes with degree 3, 4, or 5. In this way we expect to get more structurally-disordered networks with shorter linear spacers. Some useful informations about the networks can be found by

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