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The Relaxation Spectra of Polymer Networks with Different Types of Topology, Ordering, Heterogeneity

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Summary: Many characteristic features of the relaxation spectra of the different types of polymer networks (meshlike and tree-like) manifesting in experimental behaviour are determined by manifold types of local and long-range irregularities or inclusions existing even in the simplest network structures. These irregularities in the local topology, in the fluctuations of the local orientational order existing due to stretching of the chains in the bulk elastomers (even in the non-ordered elastomers), also due to possible LC-ordering, the distribution of chain lengths between junctions and possible existence of cross-link agglomerations and domains at random cross-linking and the influence of the position of the chain element relative to junctions lead to variety of relaxation spectra, frequency and time-dependencies The long-range hydrodynamic effects in bulk network can also lead to drastic variation of relaxation spectra. The inclusion of elongated rigid particles in polymer gels and network leads to the appearance of new branches of relaxation spectra changing and overlapping the relaxation spectra of the primary network system.

Keywords: networks, heterogeneous polymers, nematic elastomers, rods in a gel, relaxation

Introduction

The real polymer network systems are in general very non-uniform irregular systems with different types of chemical and physical structural irregularities. These irregularities manifest in many physical and mechanical properties (mechanical and dielectric relaxation, NMR and dynamic light scattering, IR-spectra, etc.). The dynamic heterogeneity displays either in intrachain small-scale motions (between junctions) or in comparatively large-scale relaxation characteristics (if the scale of motion is greater than the distances between neighbouring junctions).

Many problems have been solved in the framework of dynamic network models consisting of multi-segmental Rouse chains between junctions and of "coarse-grained" network models. In latter type of dynamic models, a polymer chain between network junctions in modelled by a

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single spring, and the friction constant of a junction mimics the friction of network chains which are directly attached to a given junction. The coarse-grained network models have been used to describe long-range (long-time) dynamics typical for network systems. The estimation and comparison of contributions of intrachain and specific network collective relaxation processes to viscoelastic local dynamic characteristics of 2D and 3D Gaussian networks were made in Refs.[1-4]

The other reason of the dynamic heterogeneity is the heterogeneity of "domains" type. The transition from "power-low" to "stretched exponential" low of time dependencies (for relaxation modulus etc.) for polymer networks was investigated by the authors and Prof. Kilian.[5-7] A polymer network is presented as an ensemble of non-interacting cross-linked agglomerations (domains) of different sizes, the domains have the similar regular internal structure. To a first approximation, these domains are treated independently of each other. Relaxation modulus, storage modulus, and loss modulus of the heterogeneous polymer network are calculated. For the purpose of averaging over all network domains the exponential number distribution of chain segments in domains is used.[8-11] This type of distribution has been previously proposed in the frame of aggregation model.[9-11] It is shown[5-7] that a structure heterogeneity introduced into a network model according to the above domain approach leads at long times to the stretched exponential type of time dependence of relaxation modulus instead of power-law dependence predicted by the theories dealing with regular networks. Stretched exponential time dependencies is widely observed in polymer systems and discussed by many authors.[12-17] The network heterogeneity also leads to the more rapid decrease of the storage modulus in the region of low frequencies as compared with regular polymer networks. Assuming a broad size distribution of the domains in cross-linked polymers due to a random character of cross linking, we demonstrate a stretched exponential time behaviour of the relaxation modulus on scales larger than the average size of inhomogeneities in the polymer. This general approach can be applied to some special cases of cross-linked polymers, namely to polydisperse polymer networks, to inhomogeneous mesh-like networks, and to inhomogeneously cross-linked polymeric gels.[7]

Another problem is related to properties of an effective viscous medium which produces a dissipative background for specific network motions. The problem of long-range hydrodynamic interactions in polymer network dynamics exist. The long-range (quasi-macroscopic) hydrodynamic effects in bulk networks lead to the cut-off of long-scale relaxation and to the existence of the dynamical independent regions (domains) in the network.

The dynamic heterogeneity increases due to long-range hydrodynamic interactions leading to the sweeping along of the effective viscous medium in polymer network. This effect results in the cut-off of the collective interchain relaxation spectra and creates “kinetic domains”.[3,18,19] If these quasi-independent kinetic domains posses different number of segments, chains, different cross-linked agglomerates they will be active as independent dynamical element that increases the dynamical heterogeneity of the network.

The additional difference in the types of the relaxation processes observed in the networks may be connected with the differences in the relaxation properties of longitudinal and transversal elements in the polymer chains, especially in the chain with high bending and rotational rigidity. The motion of transverse elements can described by means of the dynamic model of plane rotators and was considered in the papers of Gotlib and Toshchevikov.[15,16] In these papers, a theory of high-frequency transverse torsional-vibration relaxation processes was developed for heterogeneous polymer systems with a distribution of chains over the degrees of polymerisation. Different types of exponential distribution were considered, which can be due both to certain polymerisation mechanisms and the structural heterogeneity of domain-type polymers. The chain model of elastically coupled rotators was used to describe the high-frequency dynamics of macromolecules. Time dependences for an autocorrelation function of the order parameter of a selected chain element averaged over all elements in a given chain and over all chains of the heterogeneous system were obtained. The character of the time dependence for the autocorrelation function of the order parameter of a heterogeneous system is determined by both a distribution function and the ratio between the average degree of polymerisation of chains in the system and the number of rotators in a rigid chain fragment characterising the torsional rigidity of the chain. At long times, a change in the order-parameter autocorrelation function obeys the stretched exponential law $\sim \exp[-(t/\tau_*)^{\alpha}]$, where the index α is defined by the degree-of-polymerisation distribution function of chains.[16]

The fixed average volume of the network and fixed average distances of the chain ends as well as orientational order existing in ordered parts of the network, especially in LC elastomers also can lead to additional dynamic heterogeneity. These problems was recently considered by the authors.[20,21] Some dynamic properties of LC elastomers are discussed in the next section.

Heterogeneity of the local dynamics due to the chain stretching between network junctions and ordering of LC-type in nematic elastomers

Local dynamics of polymer networks may be heterogeneous due to different stretching of network strands and because of orientational interactions of LC-type between chain segments. The interactions of this type are manifested in statistical properties of nematic elastomers.[22-26] To describe local mobility of rod-like chain segments in nematic elastomers we use "three-chain" network model[22] and two chain models for network strands. One of those is freely-jointed-rod chain model. Another chain model is simpler and consists of freely-jointed Gaussian subchains with fixed mean-square lengths of each subchains.[27,28] In this model, it is assumed that the elasticity constant of each elastic chain segment changes with ordering in such a way that the mean-square length of the segment remains constant. The variation of elasticity constants with ordering describes a change in reaction forces (and in corresponding Lagrange multipliers[29,30]) which affect the rigid mesogenic segments of chains in a real liquid crystal.

The relaxation times for both dynamic models considered contain two factors

$$\tau_\alpha(\Psi) = \zeta_\alpha(\Psi) \cdot \frac{1}{2K_\alpha[1-\cos\Psi]} \qquad (1)$$

where Ψ has the meaning of phase shift between neighbouring chain elements for a certain normal mode and the index $\alpha = x, y, z$ designate three directions along which we consider relaxation of chain segments projections. The first ("dynamic") factor, $\varsigma_\alpha(\Psi)$, is determined by dissipative effects (external and internal friction, influence of potential barrier, etc.). The second factor ("statistical" factor), K_α, is determined by statistical mean-square fluctuations of segment projections b_α on three axis of rectangular frame of reference.

The statistical factor K_α for two chain models considered as a function of the order parameter, $S = (3 < \cos^2 \vartheta > -1)/2$, and of the degree of chain stretching between network junctions may be calculated. Here ϑ is angle between the directions of a segment and the director. Degree of chain stretching and degree of cross-linking are characterised by dimensionless parameter $\gamma \equiv h_0 / Nl$ where Nl is contour length of each chain and h_0 is the average end-to-end distance of network strands between junctions. For undeformed network the average distances between chain ends in "three-chain" cell are identical and equal to h_0.

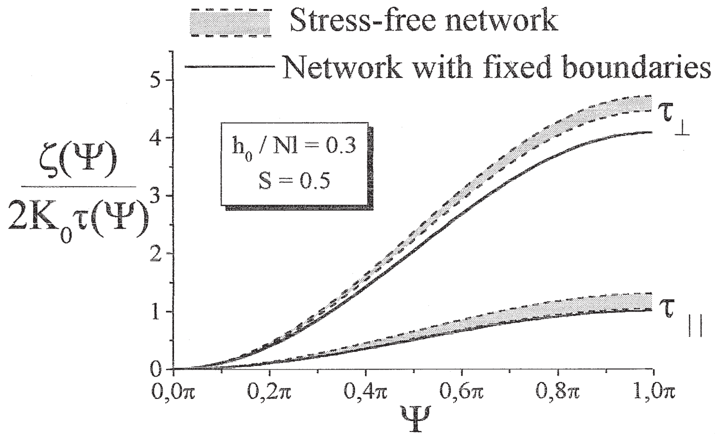

Figure 1. The dependences of inverse reduced relaxation times on the wave number Ψ for stress-free network and for the network with fixed boundaries.

In ordered network, the set of relaxation times splits into two branches, $\tau_{||}$ and $\tau_{\perp}$, corresponding to relaxation of segment projections along and normal to the director, respectively. "Gaussian" subchain model with fixed mean-square lengths of segments predicts the following form of the relationship between order parameter and statistical parameters $K_{||}$ and $K_{\perp}$ corresponding to relaxation times $\tau_{||}$ and $\tau_{\perp}$, respectively (see Equation (1)):

$$\frac{K_0}{K_{||}} = (1-\gamma^2)+2S, \quad \frac{K_0}{K_{\perp}} = (1-\gamma^2)-S \tag{2}$$

where $K_0 = 3kT/l^2$ is the elasticity constant of a free chain the segments of which have the mean-square length l. In the framework of this model, relaxation times $\tau_{||}$ and $\tau_{\perp}$ for undeformed network with uniformly stretched chains do not depend on the direction of chain stretching and are described by Equations (2) for all chain in the network.

However, relaxation times for a chain consisting of rods depend on the direction of chain stretching. It leads to additional splitting of branches $\tau_{||}$ and $\tau_{\perp}$ in relaxation spectrum of nematic elastomer due to chaotic orientation of end-to-end chain vectors in the network. However, for Gaussian networks with not strongly stretched chains between junctions ($h_0/Nl < 0{,}1$) the relative breadth of each continuous spectral line (both for $\tau_{||}$ and for $\tau_{\perp}$) is smaller than *1%*. This result confirms the correctness of describing dynamics of real rod-like mesogenic groups in elastomers in terms of simplified chain model consisting of Gaussian segments with fixed average lengths. For non-Gaussian networks ($h_0/Nl > 0{,}1$), it is necessary to take into account the splitting of branches in relaxation spectrum due to rigidity of chain segments.

Fine structure of relaxation spectrum of a nematic elastomer may be also caused by distribution of end-to-end lengths of chains between network junctions. Especially, this distribution takes place in stress-free elastomer when the ordering is accompanied by spontaneous stretching of the elastomer along the director. This effect leads to a shift of the dispersion curves for both $\tau_{||}$ and $\tau_{\perp}$ to lower times (Figure 1). Moreover, each spectrum line for stretched network becomes continuos. The relaxation times of a given chain depend on the degree of chain stretching and the degree of chain stretching is different for the chains with differently oriented end-to-end vectors in the stretched network. The difference in the structure of relaxation spectra for network with fixed boundaries and for stress-free network should lead to the difference in time and frequency dependencies of physical quantities for these systems.

The model theory of the relaxation spectra for the dynamic cross-linked gel containing included rod-like particles

A simplified visco-elastic "coarse-grained" network model can be used for describing the dynamic properties of polymer networks and gels with included rigid rod-like particles.[31] In this model, the real polymer network is distributed into cells the scale of which is near to the average distance between the centres of mass of the neighbouring rod-like particles.

The hard rods are characterised by the length l and parameters determining rotational and translational friction of the rod on the background of the effective viscous medium in which the primary component network and the rods are embedded. The interaction of the rods and gel are described by effective elastic potential characterised by the constant K_1 (Figure 2), that prevents the translational displacements of the rod on the distances which are smaller than the average distance between roads and hinders the rotational mobility of the rod. Even this simplified dynamic model gives qualitative and quantitative description of the fine structure of the relaxation spectra.

The dynamics of rigid rod component was described by the introducing of the effective quasi-elastic element in which the Lagrange multiplier in the equation of motion is replaced by its average value leading to the given mean square length equal to the length of the hard rod. There is introduced internal viscosity ς_1 which is determined by the ratio of the translational

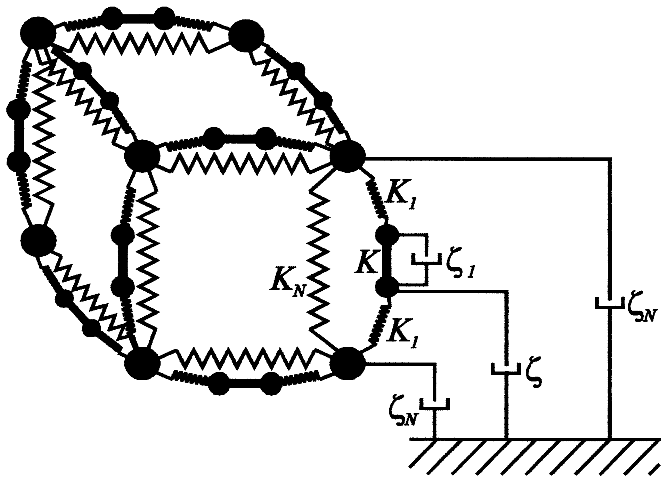

Figure 2. The cell of 3-dimensional regular cubic model network with included rod-like particles.

and rotational diffusion coefficients for the hard rod. In this case the ration $\varsigma_1 = \varsigma / 4$, where ς is the external friction coefficient of the rod.[29,30]

The visco-elastic model of the system is shown on the Figure 2. The solution of the equations of motion of this model system leads to relaxation spectrum consisting at least of five branches. Three branches correspond collective motions and relaxation times of these branches ($\tau_1(\theta^*)$, $\tau_2(\theta^*)$, $\tau_3(\theta^*)$ - see Figure 3) depend on the wave vector $\vec{\theta}(\theta_1, \theta_2, \theta_3)$ of the motion (i.e. on the phase shift between neighbouring cells of the network). Two another degenerated branches correspond to intracell motion (τ_4, τ_5 – see Figure 3). The junctions of the network doesn't take part in the last types of intracell motion.

The form and width in the time scale of the collective branches and the values of the times of intracell motions depend on the viscoelastic parameters of the primary network (gel) i.e. on the length of the chain forming the network, on their average friction, and on the effective elasticity coefficient K_1, that restricts the motion of the rod in the network. The average force reaction constant K is a complicated function of the elastic constant of the network (K_N), of K_1 and of the length of the rod l (see Figure 2). The values of $K(K_1, K_N, l)$ were calculated. If the elastic constant K_1 tends to zero we obtain the independent relaxation of the network and that of the rods. In this case only one collective branch of relaxation times of the network (for "coarse-grained" network model) and simple rotation and translation of rods remain (τ_1, τ_4, and τ_5).

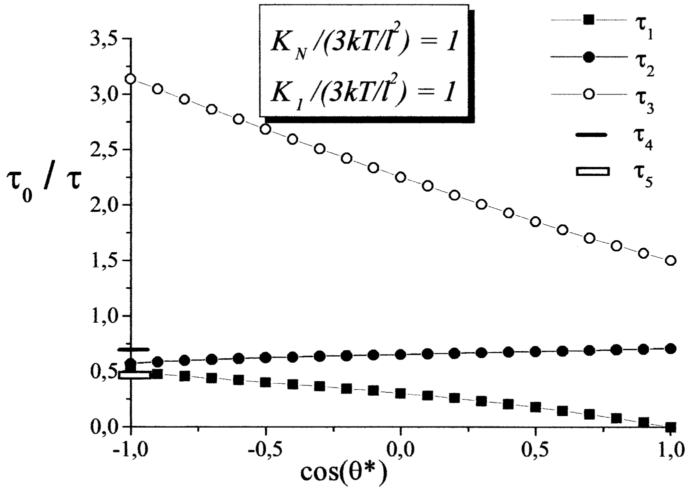

Figure 3. Dependence of inverse relaxation times on cos(θ^*) for cross-linked gel containing included rod-like particles. Here $\tau_0 = \varsigma l^2 / 6kT$ and $\cos(\theta^*) = \left(\cos\theta_1 + \cos\theta_2 + \cos\theta_3\right)/3$ where θ_j ($j=1, 2, 3$) are the phase shifts between neighbouring network junctions along axes *x,y,z*, respectively.

Conclusion

The theories of the relaxation properties of the tree-like networks (dendrimers) were considered by many authors: Graessley,[32] Kloczkowski et al.,[33] Cai and Chen,[34] Golovachev,[35] Blumen et al.,[36] Gotlib, Markelov[37] and Neelov.[38] One of the reasons of the additional dynamic heterogeneity of the polymeric network is connected with the simultaneous existence of meshlike and tree-like (without cycles) parts in the real network and gel system. This problem was treated in many papers and should be considered separately (see Ref.[39]). Thus the relaxation properties of the real elastic polymeric networks are very sensitive to the topology, type of order and different forms of heterogeneity of the network structure and on the existence of hard-rod inclusions.

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