Unsolved Problems in the Theory of Dynamics in Homogeneous and Heterogeneous Polymer Networks

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SUMMARY: A brief review related to some unsolved problems of the dynamic theory of polymer networks and to possible ways of solving them is presented. The comparative role of small-scale intrachain and long-scale collective interchain relaxation processes, the influence of long-range hydrodynamic interactions between the network elements and the effective viscous medium, and the problem of the structure heterogeneity of polymer networks are considered. New approaches for theoretical treatment of these problems are proposed and discussed.

Introduction

The dynamics of polymer networks is a very interesting and not completely understood problem of physics of macromolecular compounds. The chains in a polymer network are connected with each other by means of chemical crosslinks and form a unified spatial structure. As a result, the long-range collective motions of polymer chains in the network appear. The existence of these collective network motions having characteristic scales greater than the average distance between neighbouring crosslinks can lead to the considerable difference between relaxation properties of polymer networks and these of polymer solutions or melts, consisting of uncrosslinked macromolecules.

In most theories dealing with network dynamics (especially, with long-time network dynamics) a polymer network has been modelled as a collection of long flexible chains connected by crosslinks (junctions).[1-17] A polymer network is assumed to be regular and to consist of "bead and spring" Rouse chains.[18] In the coarse-grained network model [4,11,14-16] each multisegmental polymer chain between neighboring junctions is modeled by a single Gaussian spring. The coarse-grained network model allows only the interchain large-scale relaxation to be described. The proceeding dynamic models of polymer networks are able to provide important information concerning, for example, the comparative role of intra- and interchain relaxation processes in a network, the influence of the hydrodynamic viscous

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interactions between network elements and the effective viscous medium, the influence of structure heterogeneity on dynamic properties, etc. In the frame of a network model consisting of "bead and spring" Rouse chains, some problems of network dynamics may be considered as unsolved because their treatments are still under development. Some approaches to network dynamics, which were developed in recent publications of the authors, are briefly reviewed here.

Comparative Role of Intra- and Interchain Relaxation Processes in Polymer Networks

The existence of collective chain motions determines the main difference between relaxation properties of crosslinked and uncrosslinked polymer systems. The relative contributions of intra- and interchain relaxation processes were considered for the treatment of viscoelastic dynamic characteristics[19] as well as for the local translational and orientational displacements manifested in NMR, dielectric relaxation, polarized luminescence, etc.[17] We shall consider here for example the dynamic viscosity $\eta'(\omega)$ of polymer network. A regular cubic network consisting of "bead and spring" Rouse chains embedded in an effective viscous medium is considered. We study the viscoelastic response of the polymer network to an external stress producing a longitudinal velocity gradient in the effective viscous medium.

It should be especially emphasised that a certain characteristic time exists in a polymer network, namely, the maximum relaxation time τ_{ch} of a network chain between neighbouring crosslinks. This relaxation time "separates" the network motions of different scales. The intra- and interchain motions have characteristic times smaller and greater than τ_{ch}, respectively. The smallest relaxation time τ_0 is the relaxation time of a single Gaussian subchain.

In the region of high frequencies $1/\tau_{ch} << \omega << 1/\tau_0$, the dynamic viscosity $\eta'(\omega)$ of a polymer network is mostly determined by the intrachain relaxation processes and has a behaviour typical of uncrosslinked macromolecules.[20,21] With a decrease of frequency, the influence of the intrachain motions on the frequency dependence of the dynamic viscosity $\eta'(\omega)$ becomes weaker. At $\omega \leq 1/\tau_{ch}$ the intrachain relaxation processes begin to provide only a constant contribution, independent of frequency. In the region of low frequencies, $\omega \leq 1/\tau_{ch}$, the frequency dependence of $\eta'(\omega)$ is governed by the interchain relaxation

processes. It is key that the contributions of intra- and interchain relaxation processes to the dynamic viscosity $\eta'(0)$ of a polymer network at zero frequency are shown to be approximately equal. This means that the intrachain motions provide a noticeable contribution to the macroscopic viscoelastic characteristics of a polymer network, even in the low-frequency region, corresponding only to large-scale, interchain relaxation. In contrast, the local dynamic characteristics of the network are mostly governed by the interchain motions only on a scale greater than the average distance between cross-links.[17)]

It is very interesting to compare the macroscopic viscoelastic properties of a polymer network consisting of multisegmental "bead and spring" Rouse chains with the properties of a simplified coarse-grained network model (which describes only the interchain network relaxation), and with the properties of a melt consisting of uncrosslinked chains at the same number of chains per unit volume as in polymer network. Such a comparison has been made in ref. [19)] and indicates that the frequency dependence of dynamic viscosity of a polymer network may be described to a good approximation by a coarse-grained network model (at low frequencies $\omega \leq 1/\tau_{ch}$) and by a melt of uncross-linked macromolecules having the same molecular weight as polymer chains between junctions in the network (at high frequencies $\omega > 1/\tau_{ch}$). The contribution from intrachain motions to the total dynamic viscosity of a polymer network cannot be omitted even in the low-frequency interchain region. This intrachain contribution is practically not changed at sufficiently low frequencies and is shown to be very close to the dynamic viscosity at zero frequency of a melt of uncross-linked macromolecules.

Hydrodynamic Interaction Effects

Since the possibility of a simplified description of the viscoelastic properties of a polymer network in terms of a coarse-grained network model and a melt consisting of uncrosslinked chains has been demonstrated, we can use this simplified description to study in more detail some fine effects related to network dynamics. The dynamic network model described in the previous section neglects the hydrodynamic interactions between the network elements and the effective viscous medium. In this case, we need only the velocity gradient in an effective viscous medium to excite the mechanical relaxation spectrum; the relaxation times themselves correspond to those of a network at zero velocity gradient (immobile viscous medium).

If the hydrodynamic interactions are taken into account, the relaxation becomes more complicated. When we consider the scales of motions smaller than the distance between neighbouring crosslinks, the dynamic behaviour of network chains is very close to that of uncrosslinked macromolecules in a melt and the results obtained in the theory of dynamic properties of polymer melts may be used for the intrachain relaxation of a network. In a polymer melt, the motion of a single macromolecule is considered as motion in an effective medium.[20] The viscosity η_m of the medium is assumed to be close to the viscosity of a liquid of monomers of the polymer. On a large scale, the velocity profile obeys macroscopic hydrodynamics, namely, the velocity of the medium should decrease as $1/r\eta$ where η is the macroscopic viscosity of the melt. If $\eta_m < \eta$ the velocity field falls rapidly and so-called hydrodynamic screening takes place. [20] As a result of the screening, the dynamics of a single macromolecule in a melt becomes Rousean. Thus, for the sufficiently small relaxation times corresponding to the intrachain network motions, the hydrodynamic interactions are negligible.

If we consider scales of network motions larger than the distance between crosslinks, the contribution of hydrodynamic interactions becomes noticeable. For large-scale collective network motions, the hydrodynamic interactions between the network and the effective medium may be important. These interactions are controlled by the viscosity close to that of a melt of uncrosslinked chains. To study the effect of hydrodynamic interactions, a simplified coarse-grained network model describing only the cooperative interchain relaxation may be used. A bulk crosslinked polymer as a whole is an incompressible system, i.e. its volume and average distances between neighbouring crosslinks are well defined. One can assume that an effective viscous medium in a network system has the properties of a real incompressible liquid. Therefore, the combined consideration of the interacting continuous model of a network and a mobile incompressible medium can be carried out.[22,23]

The relaxation spectrum that is excited in such a network system is shown to depend strongly on the compressibility of the network component of a "network and incompressible medium" system. In general, the network component may be either compressible or incompressible because the elements of a network (junctions in the case of coarse-grained network model) do not include all the degrees of freedom of an incompressible bulk polymer. As a result, the hydrodynamic interactions between the network and the incompressible, effective viscous

medium lead to the appearence of two branches (or types) of relaxation spectrum. In the case when the network component itself represents a compressible system, the set of relaxation times is shown to be the same as that of a network model in which the hydrodynamic interactions are neglected.[22,23] This branch of the relaxation spectrum corresponds to the spectrum of the network moving in an immobile viscous medium. The viscous medium does not take part in this relaxation because the symmetry of this type of network motion is in contradiction with the symmetry of motion of an incompressible medium. The forces acting from the network on the effective viscous medium are compensated for by the internal pressure in the medium. If the network component itself is incompressible, another, more "non-trivial" set of relaxation times $\tau^{*}(\vec{\theta})$ is excited.[22,23]

$$\frac{1}{\tau^{*}(\vec{\theta})} = \frac{1}{\tau(\vec{\theta})} + \frac{1}{\tau^{**}}$$

Here $\tau(\vec{\theta})$ are the relaxation times corresponding to the case of a compressible network component, $\vec{\theta}$ is the interchain wave vector describing the phase shift between neighbouring cells of a coarse-grained network model, and $\tau^{**} = h_0 \eta / K$ where η is the viscosity of an effective viscous medium, K is the elasticity constant of a Gaussian spring between cross-links of a coarse-grained network model, and h_0 is the average distance between neighbouring network junctions. It is obvious that this relaxation spectrum is restricted by the finite maximum relaxation time equal to τ^{**}. For this type of network motion, the cooperative motions of network elements satisfy the condition of incompressibility. The effective viscous medium is partly carried along by the motion of the network, so that for motions with longest time scales the network and the medium move synchronously. The corresponding relaxation times are located in a relatively short time interval, and the width of the relaxation spectrum is very narrow.

The case of an incompressible network component seems to be a more realistic situation because a crosslinked polymer in bulk has a fixed average volume and density. Then only the narrow relaxation spectrum exists.

Problem of Structure Heterogeneity of Polymer Networks

The comparison of predictions of regular network models with experiment is often difficult because real crosslinked polymers usually have a heterogeneous structure. Therefore, the

problem of structure heterogeneity is of great importance in the theoretical consideration of viscoelastic properties of polymer networks. There are a great number of possible types of network heterogeneity (or irregularity), for example, the distribution of molecular weights of network chains between crosslinks, the existence of regions with different topologies and crosslink densities, the existence of uncrosslinked amorphous domains, dangling chains, etc. We shall confine ourselves here to the consideration of one example of network heterogeneity.

The random character of a crosslinking process may lead to the existence of crosslinked as well as uncrosslinked regions in a real network polymer. The crosslinked regions of different sizes may be separated by regions containing uncrosslinked macromolecules. A first, simplest approximation is the independent treatment of different cross-linked regions. The simple dynamic model of a heterogeneous polymer network is proposed.[24)] A polymer network as a whole is presented as an ensemble of crosslinked regions (domains) of different sizes, that relax independently of each other. It is assumed that each domain has an internal regular structure, namely a regular cubic network of finite size, consisting of Rouse chains. The contour lengths of the network chains between crosslinks are the same for all domains forming a heterogeneous network; the domains differ from each other only by the number of cubic network cells they contain. We assume also that the cubic network domains are embedded in an effective viscous medium that is "common" for all domains.

The viscoelastic behavior of a collection of network domains may be imitated by the behavior of a number of generalized Maxwell viscoelastic models [21)] connected in parallel. Therefore, the total dynamic modulus of a heterogeneous polymer network is the weighted sum of the dynamic moduli of the network domains. The relative weights (contributions) should be determined by the distribution of domain sizes. For the averaging over all the domains of a heterogeneous network, different types of distribution functions of domain sizes may be used. Since we consider the independent relaxation of non-interacting network domains, the domain model of a heterogeneous polymer network seems to be similar to the model of reversible aggregation,[25-27)] which has been proposed for describing the relaxation of amorphous polymers. For the heterogeneous polymer network, the number distribution function of the aggregation model that obeys an exponential law will be used.

In the case of a regular cubic network of infinitely large size, the relaxation modulus of a polymer network at short times ranges from the relaxation time of a single Gaussian subchain τ_0 to the maximum relaxation time of a chain between neighboring junctions τ_{ch} according[17,24] to a power-law time behaviour that is typical of a single Rouse chain.[18,20,21]

$$G(t) - G_e \cong \text{const} \cdot \left(\frac{\tau_{ch}}{t} \right)^{1/2}$$

At greater times, the relaxation modulus of an infinitely large regular network also has a power-law time behaviour, but it decreases more rapidly:[1,3,14-17]

$$G(t) - G_e \cong \text{const} \cdot \left(\frac{\tau_{ch}}{t} \right)^{3/2}$$

The relaxation modulus of a single network domain of finite size has the same time behaviour as that of an infitely large regular network in the region of "intradomain" relaxation, i.e., at times smaller than the maximum relaxation time of a network domain of finite size. However, at greater times, the relaxation modulus of a network domain has an exponential decay because the relaxation spectrum of a given domain is limited by the finite maximum relaxation time of the domain as whole.[24]

In the case of a heterogeneous polymer network with domain structure, the relaxation modulus represents a result of averaging over all the domains forming the network. The network heterogeneity considered is a long-range one manifested on a scale greater than the size of an elementary network cell. Therefore, the relaxation modulus of a heterogeneous polymer network as a whole, at times (t) smaller than the relaxation time of a network chain τ_{ch}, has the same behavior as that of an infinitely large regular polymer network. However, at $t >> \tau_{ch}$ the time dependence of a heterogeneous polymer network is drastically changed as compared with that of a regular network. At sufficiently large $t >> \tau_{ch}$, the relaxation modulus of a heterogeneous network is shown to have the following asymptotic behaviour:[24]

$$G(t) - G_e \cong \text{const} \cdot \left(\frac{t}{\tau_{ch}} \right)^{3/10} \exp\left[- \left(\frac{t}{\tau^*} \right)^{3/5} \right]$$

The characteristic relaxation time τ^* in the stretched exponential term is close to the maximum relaxation time of a network domain of average size

The structure heterogeneity introduced into a dynamic network model according to the proceeding approach using domains leads, at sufficiently long times, to the stretched exponential type of time dependence of relaxation modulus instead of the power-law dependence predicted by theories dealing with conventional networks. It should be especially emphasized that the stretched exponential time dependence of relaxation modulus of a heterogeneous network system appears because the averaging over all network units (domains) is performed using a number distribution function containing a exponential term. Besides the number distribution function of the aggregation model[25-27] used here, there are many other examples of exponential distributions. The exponential distribution seems to be the general origin of time dependence of a stretched exponential type in polymer systems having domain structure. For instance, a time dependence of such a type can appear due to the distribution of molecular weights of network chains, which also obey an exponential law.[28] Another example is a network with domain structure, in which the number of crosslinks inside domains fluctuates due to the random character of the crosslinking process and, therefore, is governed by the Gaussian distribution.

Note that complex polymer systems often show decay obeying the stretched exponential law. Examples include local segmental motions in non-crystalline polymers, motions of polymer chains in entangled polymer melts, and other relaxation phenomena in complex correlated systems. [29] In such systems, the strong correlations between relaxing units have an effect at slowing down the relaxation. In our case, the origin of the appearance of stretched exponential relaxation is related to the distribution of non-interacting relaxing units (domains) in a heterogeneous network. This is similar to the situation in disordered orientational glasses [30,31] where non-exponential relaxation is also caused mostly by heterogeneous broadening.

Conclusion

We have considered some problems of the theoretical description of dynamic properties of polymer networks. All the treatments disscussed are under development at the present time. For example, one of the further problems which could be considered is related to the effects of direct interchain friction which is not included in the interactions of network chains with an effective viscous medium.[13,14,16] Also the dynamic problems of polymer networks with intra- or interchain orientational interactions, networks built of semiflexible chains and nematic elastomers have not been solved and present a very interesting and promising field of study.

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