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Structure, Dynamics and Properties of Materials with Polymers Having Complex Architectures

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Summary: Various non-linear highly branched polymers such as multiarm stars, block copolymer micelles and bottlebrush-like polymers have been studied in order to analyze their intramolecular structure and effects of spatial ordering resulting from their specific macromolecular architecture. These polymers constitute a class of compact macromolecules which, due to the high intramolecular density, interact strongly, excluding each other in space. Investigations of the structure and dynamics in such systems, using various experimental methods as well as computer simulations, have been performed. Small angle X-ray scattering is used to characterize the structure and mechanical spectroscopy is used for the detection of the dynamic behavior of the systems. Simulations have been performed using the cooperative motion algorithm with lattice polymers equivalent to the considered macromolecules. Results of both experiments and the simulation seem to support the concept of slow structural cooperative rearrangements controlling the flow in such systems. The effects are analogous to those related to flow in low molecular liquids but take place on another size scale. The new slow relaxation processes creates new super soft-states which are characterized by shear modulus plateau lower than 10^4 Pa.

Keywords: complex polymer architectures; dynamics; relaxation processes; soft materials; structured melts

Introduction

New complex macromolecular architectures are of particular interest when they lead to new material properties. A large variety of macromolecules differing by topology of bond skeletons and by distributions of monomers of different types have been synthesized [1-4]. In many cases, such macromolecules constitute self-assembling systems in which a supramolecular order can result in modified dynamics and, consequently, in new properties [5,6]. In the simplest case of linear polymers, joining monomeric units into linear chains results in a dramatic change of properties. Whereas a system consisting of monomers can usually be only liquid-like or solid (e.g. glassy), the polymer can additionally exhibit a rubbery

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state, with properties that make these materials extraordinary in a large number of applications. This new state is manifested by the very slow relaxation of polymer chains in comparison with the fast motion of monomers, especially when the chains become so long that they can entangle.

Knowledge of the mechanical behavior for complex macromolecular architectures is not as comprehensive as for the linear polymers. In this paper, some effects of macromolecular architecture on mechanical properties will therefore be illustrated and discussed. The structures considered are illustrated in Figure 1.

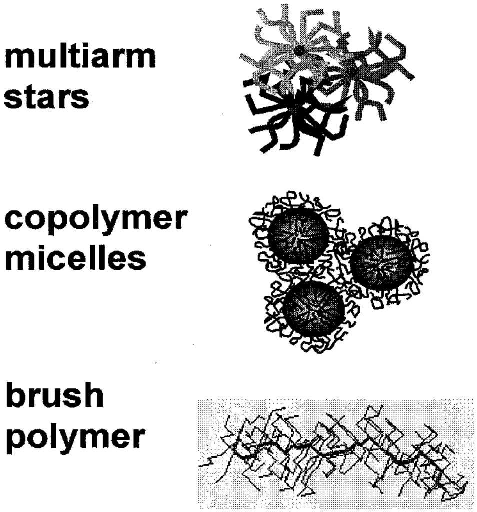

Figure 1. Illustration of the macromolecular architectures considered in this paper.

Experimental Results

Mechanical manifestation of relaxations taking place in a linear polymer melt in comparison with the behavior of a low molecular system is illustrated in Figure 2. The dynamic mechanical characteristics of the two materials indicate a single relaxation in the monomer system in contrast to the two characteristic relaxations in the polymer. The rubbery state, characteristic of entangled polymers, extends between the segmental (monomer) and the chain relaxation frequencies and is controlled by the chain length determining the ratio of the two relaxation rates. In the rubbery state the material is much softer than in the solid state. If expressed by the real part of the modulus, the typical solid-state elasticity is of the order of 10^9 Pa or higher, whereas the rubber like elasticity in bulk polymers is of the order of 10^5-10^6 Pa.

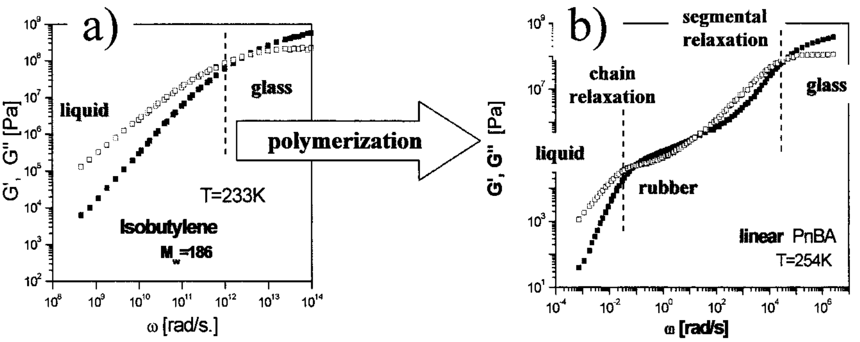

Figure 2. Real (G') and imaginary (G'') parts of the complex shear modulus vs. frequency for (a) an isobutylene oligomer and (b) a melt of linear p(n-butyl acrylate), p(nBA), chains.

An example of the behavior of multiarm stars in the melt is illustrated in Figure 3, where the mechanical results indicate three relaxation processes. The slowest is related to rearrangements within the supramolecular order, documented by means of the small angle X-ray scattering result presented in the insert [7].

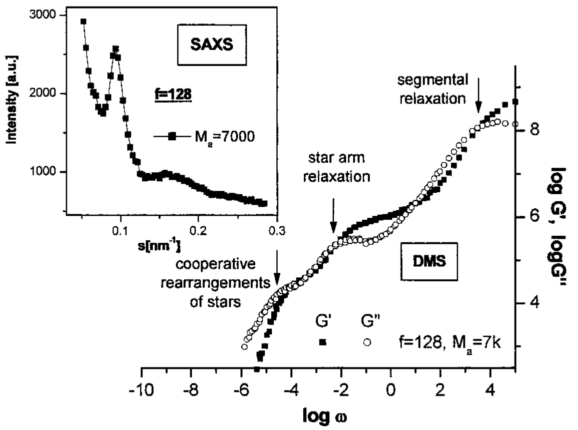

Figure 3. An example of the small angle X-ray scattering (SAXS) and dynamic mechanical spectroscopy (DMS) results for a polybutadiene melt of multiarm stars. The scattering peak indicating star ordering and various modes in the mechanical relaxation can be seen.

It is interesting to notice that there is a new dynamic state in this system between the relaxation of the arms and the structural relaxation. In this state, the melt of multiarm stars shows a new elastic plateau with the G' level which is considerably lower than that characteristic of the entangled linear polymers.

Another example of the same type of behavior is illustrated in Figure 4. In this case, spherical micelles of polyisoprene-b-polystyrene block copolymers dispersed in a polyisoprene matrix show ordering, which depends on the micel concentration, as illustrated in Figure 4c. The dynamic mechanical results indicate that with the increasing order a new slow relaxation process is created which, also here, can be attributed to structural relaxation [8]. For the system containing 50% micelles this structural relaxation becomes so slow that the G' plateau at the level of 10^3 Pa extends to the lowest detectable frequencies.

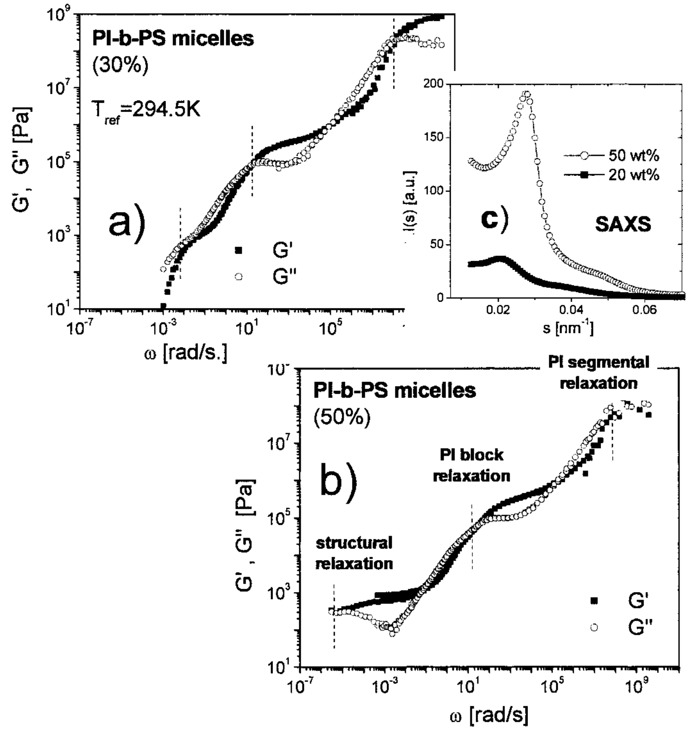

Figure 4. Master curves of G' and G'' vs. frequency for PI-b-PS spherical micelles dispersed in PI matrix with concentration (a) 30% and (b) 50%. Vertical dashed lines indicate the relaxation processes as assigned in (b). In (c) the SAXS intensity distributions for the two systems are shown.

In the example given in Figure 5, viscoelastic properties determined for the melt of brush-like macromolecules are presented as master curves of G' and G'' determined for the reference temperature, 254 K [9]. The results indicate a presence of three relaxation ranges: the high frequency relaxation corresponds to segmental motion, the intermediate relaxation is attributed to the reorientation rates of the side chains and the slowest process is the global macromolecular relaxation in this system, which controls the zero shear flow and the corresponding viscosity. The rate and nature of this relaxation must be dependent on the length of the backbone. For short backbone chains these macromolecules can behave similarly to stars, for which translational motion dominates the slow dynamics, but for longer backbones, the reorientation possibilities should become slower than translation [10].

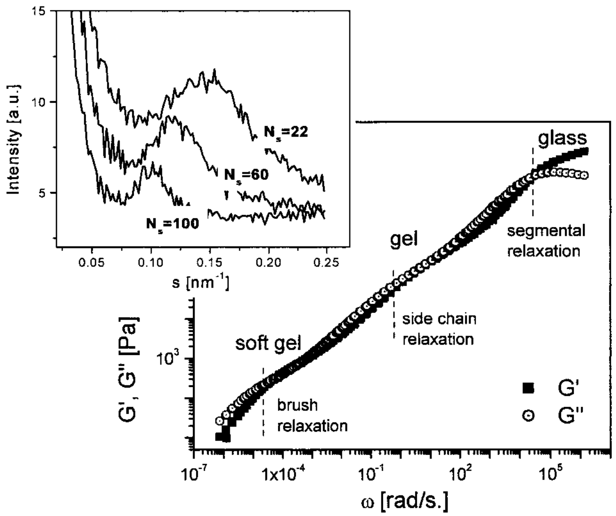

Figure 5. Frequency dependencies of the storage (G') and loss (G'') shear moduli (master curves at T_{ref}=254 K). The insert: Small angle X-ray scattering from melts of p(nBA) brush like polymer with various side chain length.

Discussion

Complex polymeric systems such as the discussed melts of multiarm stars or melts of micelles in microphase separated block copolymers seem to show a complex dynamic behavior resulting from the ordering of stars or micelles. The results presented indicated that in both these cases three relaxation processes are detected, the slowest one of which must be related to the structural rearrangements. Dense systems of stars considered as examples of macromolecules of this kind have been simulated using the cooperative motion algorithm [7,11]. Results have shown that the structure in such systems develops due to strong excluded volume effect on the macromolecular scale, because the multiarm stars (with number of arms greater than 25) fill locally the space, becoming impenetrable. Development of the structure leads to additional dynamic slow relaxation modes, which can be considered as having similar origin for both stars and hairy micelles. The flow of such systems becomes controlled not by the relaxation of polymeric arms but by the additional slow relaxation process, which is attributed to cooperative rearrangements of the larger elements (stars or micelles) within the ordered state. This leads to a slowing down of the decay of the position correlation of the stars or micelles which, for a large number of polymeric arms, becomes considerably slower than the relaxation of the arms and constitutes in this way an extra slow mode in the translational relaxation. This relaxation, although taking place on the macromolecular size scale, seems to have many similarities with the cooperative rearrangements considered in the dynamics of small molecules in the simple liquid [12]. The degree of order in the studied systems is mainly controlled by the ratio of the core radius to corona thickness which evidently depends on various molecular parameters, such as length and number of arms. For stars or miceles with a large number of short arms, the highest degree of ordering should be expected, whereas, stars or micelles with long arms could show a limited order even when the number of arms is high. These effects have been observed both in real and in simulated systems [7,8,13].

The type of order observed in the multiarm star melts can be described as liquid-like on the macromolecular scale. Neither in real nor in simulated systems have any clear signatures of lattice formation been detected. This probably results from the deformability and related form fluctuations of the star coronas. They consist of flexible arms and remain soft spheres even when the number of arms is large and the core radius is large. The latter is well confirmed both by the dynamic properties of the stars and in polymer melt filled with spherical copolymer micelles.

Qualitatively, the simulation results concerning dynamics seem to be in good agreement with the experimental observations. Both the relaxations detected by means of the viscoelastic measurements and the suggested assignments are reflected in the simulation. Two relaxations, one related to segmental motion and the other to arm relaxation, have been observed in all systems. The relaxation rate of the first one is independent of the structure parameters both in experiments and in the simulation. On the other hand, the arm relaxation has been observed to be considerably dependent on the arm length but essentially independent of the arm number. The most interesting effect observed both in the simulated and in the real systems was the additional slow relaxation process appearing in systems with clear ordering. The analysis of the simulation results concerning dynamics, as well as a direct observation of star motions in these systems (Fig. 6), leads to the conjecture that the slow process can be related to translational cooperative rearrangements of stars within the ordered state which are of the same character as those suggested for the rearrangements in low molecular liquids. This might be a cooperative process on the macromolecular scale with the mechanism analogous to that postulated for liquids in the dynamic lattice liquid model [12,14]. This model postulates that the rearrangements of macromolecules take place along closed loops as a result of preservation of local continuity in the dense ordered system.

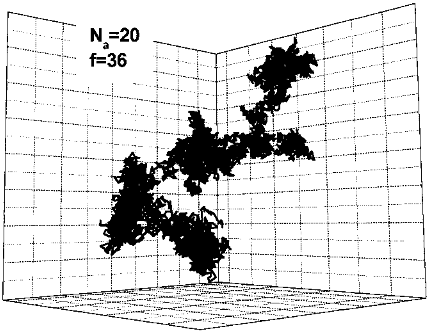

Fig. 6. Typical star center of mass trajectory recorded for a multiarm star in the simulated melt. The trajectory consists of blobs related to a longer residence of the star at some well distinguishable places which are distributed along the trajectory and are connected by other trajectory fragments related to faster displacements between the localized states.

This mechanism of relaxation can be considered for stars, hairy micelles and probably for short brush macromolecules which are not much different from the stars. For longer brush macromolecules, the orientational relaxation should become the slowest and for the brushes with the backbone sufficiently long to form entanglements the entanglement, relaxation should become dominant.

In all the studied systems, the intermediate relaxation which is attributed to motion of arms or hairs, plays an important and specific role. If the arms or "hairs" are short, this relaxation is responsible for a drop of modulus to a level considerably lower than that characteristic for conventional polymers. The states between the longest relaxation and the arm relaxation constitute a possibility to create new mechanical properties, which can be classified as super-soft [15]. Depending on structural parameters of the systems, the proportions between relaxation rates corresponding to three distinguished processes can be influenced. This should lead to various properties of materials in frequency ranges corresponding to modulus plateaus related to various unrelaxed states i.e. glassy, rubbery or the super-soft state. For example, extension of side chain length to the range where they can entangle should extend the frequency range of the modulus plateau at the typical level for polymer rubber elasticity, i.e. at 10^5-10^6 Pa (in detail, depending on the chemical nature of the monomer). On the other hand, extension of the backbone with not yet entangled side chains can lead to an extension of the frequency range with the super-soft elastic plateau with a modulus level below 10^4 Pa [15].

Conclusions

It is pointed out that some polymers with complex architectures represent model soft objects, which order on a macromolecular scale because of strong steric interactions. This is a consequence of their complex topology, which leads to specific intramolecular monomer density distributions. It is shown that signatures of the structures formed appear in the dynamics of these systems as extra slow relaxation processes, which can control the terminal rheological behavior as well as lead to new properties of unusually soft bulk materials. The simulation results are able to represent the structure and dynamics of the considered systems.

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