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Feature Article

Recent developments in polymer dynamics investigations of architecturally complex systems

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Dedicated to Professor Nikos Hadjichristidis in recognition of his contribution to polymer science.

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ABSTRACT

The tube model for linear and branched architectures is nowadays able to predict in high precision the linear viscoelastic relaxation time spectrum. For linear chains, the involved time scales fit to the commonly accessible dynamic scattering techniques. This makes it possible to microscopically investigate the correlation between structures and relaxation processes. In branched systems, however, the hierarchical nature of relaxations limits direct investigation via these microscopic methods as the dynamic processes are prolongated to much longer relaxation times that are no more accessible to usual dynamic scattering methods. A way to overcome this difficulty is offered by the use of static small angle neutron scattering. Here, the combination of annealing and quenching steps after a step deformation provides unique information of the structure at particular times along the relaxation spectrum. This, however, necessitates the availability of architecturally clean and specifically deuterium labelled model polymers due to the sensitivity of the scattering method. Therefore, we outline in this contribution first the current status on the synthesis and analysis of such compounds with relation to neutron scattering. Secondly, we present exemplary neutron scattering results from *in situ* stress relaxation studies inside the neutron beam on linear and H-shaped branched polymers which were molecularly designed to highlight specific relaxation processes. We discuss the relevance of the tube model parameters in linear and non-linear studies.

1. Introduction

Information of polymers on a molecular scale and their mechanical and rheological properties can be gained by observing the relaxation behaviour after a sudden deformation, away from its equilibrium state. The typical response is viscoelastic and is characterized by both elastic, strain-dependent and viscous, time-dependent components.

In the linear regime, i.e. after small deformations, the microscopic origin of elastic properties probed at short times or high frequencies is the mutual entangling of polymer chains. At long times, slowly varying perturbations, however, cause polymers to flow. De Gennes, Doi and Edwards, as leading authors in this field [1,2] approximated this many-chain problem with the tube model solution that accounts for the interaction between chains. In this model, each chain is thought to be confined or restricted inside a tube or channel, made up of the identical chains. Its topological length scale, termed tube diameter is the respective mesh size of a temporary network of entanglements. Sub-tube diameter motions are taken unconstrained and exhibit so-called Rouse motion from the similarity of motion in a heat bath whereas above the confinement length scale the dynamics of a chain is mainly a curvilinear segmental one-dimensional Rouse motion along the average contour called tube axis. In this concept the transversal fluctuations around the tube axis are fully developed already at the Rouse entanglement time scale τ_e, where a chain segment has explored the tube. Relaxation processes at later time are one-dimensional longitudinal Rouse motions along the tube that give

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rise to fluctuations of the tube length (contour length fluctuations (CLF) with the chain Rouse time τ_R) and the diffusion of the chain as a whole (termed reptation with the reptation time τ_d). Additionally, constraint-releasing motion of the surrounding chains (CR), which constitute the tube affects the dynamics of a given chain. This picture allowed a quasi-full description of the relaxation modulus for linear chains basing on molecular principles [3,4]. The described approach is therefore also called molecular rheology and is today well established [5].

Whereas by now the dynamics of simple linear chains is rather well understood, the behaviour of architecturally more complex chains and their blends is still matter of intensive investigation, not only because of their importance in nowadays prominent plastics and materials [5–11,35–38]. The incorporation of any low level of branching inside the molecule, e.g. is observed to extend the long time behaviour already drastically. A single knot or branch point blocks several relaxation modes and shifts the relaxation spectrum by decades [4,10]. Similar as for the linear chain [3], now tube models for branched systems have been developed which differ slightly in their details depending on the schools and are now being used already for predictive purposes. The main difference with linear chains is the hierarchical nature of relaxation. Whereas for linear chains a single loss peak in $G''(\omega)$, characteristic for the longest, i.e. reptation time is observed, now each level of branching, from outside inwards to the center of the molecule, will cause more or less separated maxima in the loss modulus. Star polymers are the simplest branched structures without hierarchy, showing, however, all details of the influence of the branch point. The next level in complexity, e.g. an H-shaped polymer can be regarded as two stars coupled from two sides to a central backbone. The relaxation of the latter is inhibited until all arms have freed themselves by arm retraction and associated tube-depopulation. To help overcome the entropic barrier for retraction to the branch point the tube is believed to widen in time by the already relaxed ends which, being solvent-like on the time scale of the unrelaxed sections, dilute the network of entanglements or swell the tube equivalently [10,36]. This process is called dynamic tube dilution. As soon as the arms have reduced to isotropic disoriented segments now with localized friction, the branch points can now be integrated as part of the backbone. The new structure now resembles a linear chain, which continues to relax but in a wider, dilated tube [6–8,14]. Star, H and related pompom geometries have thus been extensively studied and rheology curves were described in the past [6,35–38]. The tube model has been extensively treated elsewhere and we refer to the specific literature. Even the non-linear responses have been proposed. As before, all approaches base on a specific molecular model that deals with the different time and corresponding length scales. However, all approaches are lacking the last, final microscopic proof.

Neutron scattering on these materials now enables an ultimate insight in the structure on the microscopic level of polymers which is out of reach but complementary to the observed rheological answer. The technique of neutron scattering has therefore become one of the most powerful methods for soft matter investigations. By partial deuteration – taking profit of the different scattering lengths of hydrogen and deuterium atoms – single chains or parts of them can be made visible. In this way the focus can be put on different length scales. This is due to the fact that the scattering vector, i.e. the observable inverse spatial length scale as well the energy, i.e. the observable inverse time scale of the chains are ideally suited: small angle neutron scattering (SANS) instruments allow explorations of space between roughly 1 and 1000 nm and the energy resolution is such that times up to 500 ns can now be resolved directly using quasi-elastic neutron spin echo spectroscopy (NSE). For comparison with the complex shear modulus $G^*(\omega)$, the NSE technique limits investigations to roughly 1–5 tube diameters wide, thus enough to probe local and transitional dynamics within less than $\sim$500 ns. The time scale can be extended at will, however, through transient experiments using SANS, e.g. after step-strain deformations and relaxation, and by quenching the relaxed states at longer times [6,7,9,12–15]. In this way comparably long times to the rheological investigations can be achieved with the exclusive advantage that the corresponding molecular structures and details can be caught. The quenching technique decouples effectively the microscopic and laboratory time frame.

However, the absolutely necessary requirement to achieve this last goal is the availability of suitably labelled linear and branched model polymers for the sake of quantitative comparison to predictions following the molecular rheology rules. The needed polymers must be composed of building blocks having defined molecular weights and low molecular weight distributions. In addition, the locations and functionalities of the branch points must be defined. Such exact architectures can be synthesized by coupling anionically polymerized building blocks with chlorosilane compounds [16,17]. The advantage of anionic polymerization is that this technique allows synthesizing polydienes like polybutadiene and polyisoprene up to high molecular weights. In addition, segments of the polymer chains can be labelled by sequentially polymerizing deuterated and hydrogenous monomer. This is the utmost requisite for detailed neutron scattering studies.

In this contribution, basing on some specially designed architectures, relaxation modes of polymers will be investigated after a fast uniaxial step strain deformation using the method of small angle neutron scattering from quenched samples. Examples of microscopic investigations into the assumptions of the rheological descriptions will be provided on two model architectures, i.e. linear and H-shaped. Only the shown synergy of chemical synthesis, molecular rheological characterization and neutron scattering provides the strength to extract structure–property relationships which can be applied for industrial process optimization and controlled and enhanced polymer properties.

2. Synthesis and analysis of branched model architectures

Model polymers of high structural quality are required to allow the development and a deeper understanding of