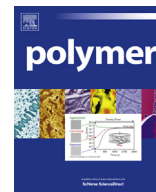




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## Mixtures of polymer architectures: Probing the structure and dynamics with neutron scattering

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### ABSTRACT

We review some of our latest contributions in the field of neutron scattering of polymers with linear and non-linear architecture. On the one hand, the reviewed Small Angle Neutron Scattering investigations cover dilute mixtures of dendritic polymers and linear polymers that were investigated during relaxation after a fast step strain or *in situ* during a strain ramping. The focus was on the otherwise not accessible long time dynamics of the inner branches. The parameters of the model are those of the tube model and include the evolution of liberated chain ends, the size and time dependence of the confining tube diameter and branch-point related dynamics. The case of deformed tube diameters could be obtained from a permanently-linked network state as the limiting case of a deformed melt. On the other hand, recently, cyclic polymers as a special class of branched architectures showed to be of high significance to detect similar features directly from equilibrium measurements by means of quasi-elastic Neutron Spin Echo spectroscopy. We show that by means of polymer rings as a probe different aspects of the tube concept can be distinguished in a unique way.

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### 1. Introduction

A profound understanding of mechanical and rheological polymer properties can be achieved by accessing their relaxation behavior on a molecular level. Small Angle Neutron Scattering (SANS) [1] and Neutron Spin Echo (NSE) spectroscopy [2] are complementary techniques that allow such a microscopic focus on the molecular configuration and the related dynamics. The advantage and inherent importance is that both methods are intimately related and study the spatial and temporal properties of different correlation functions at the same length scales. As is well known, the typical response of a polymeric or rubbery material is viscoelastic, i.e. characterized by a simultaneously elastic and a viscous component which depends on the response to deformation with time [3]. After infinitely small deformations in so-called linear response at short times, the presence of entanglements between polymer chains can be related to macroscopic variables like the elasticity modulus. At long times, polymers flow as a result of slow relaxation processes and the respective parameters can be related to the zero shear rate melt viscosity. As a state of the art model, each

chain moves or reptates through a confinement channel or so-called tube that is composed of identical neighboring chains [3,4]. The topological length scale in this mean-field approximation of inter-chain interactions can be interpreted as the cross-section or the pore-size of a temporary network of such entanglements. The diameter and dynamics of the tube is intrinsically time-dependent since the tube itself is built by the moving chains. Motions at a scale smaller than the tube size are unconstrained and are 3D-Rouse-like, i.e. described by bead motion in a heat bath [5]. At intermediate length scales and times, the chain performs a curvilinear Rouse motion along its tube. This 'local reptation' sets in after the time, where fluctuations, perpendicular to the tube axis, have abundantly explored the tube diameter, defining the entanglement time scale  $\tau_e$ . The subsequent 1D-longitudinal Rouse motions along the tube give rise to fluctuations in the tube length (so-called contour length fluctuations (CLF)) and decay with the characteristic Rouse time  $\tau_R$ , the longest relaxation time of the chain within the tube. Finally, the motion reduces to the diffusion of the chain as a whole out-of-the-tube with the characteristic reptation time  $\tau_d$  and accompanied by additional constraint-releasing motion of the surrounding chains (CR).

Whereas today the dynamics of simple linear chains are rather well understood and are described in various standard works and text books [3,6–8], the behavior of architecturally more complex

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chains and especially their mixtures with linear polymers has initiated recently a new effort into more intensive investigations, since new properties for new materials may emerge. In this context we mention branched polymers [9] and especially cyclic or ring polymers [10,11]. Branched polymers have been shown to effectively modify shear and extensional viscosities, a fact that can be advantageous for enhanced industrial processing and stabilization purposes compared to classical linear polymers [9]. Cyclic polymers have become available only recently in high quality and reasonable quantities for research [12–14]. In particular, deuterium-labelled rings from our lab for the first time allowed studies like those reviewed here for their linear or branched counterparts. Aside of academic fundamental interest and the similarity of ring organization in the melt with the packing of biological material in e.g. cells [15], practical applications for novel materials if any are totally un-explored yet. Similar as for linear chains, tube models for branched systems in various levels of sophistication and maturity for linear and/or non-linear flow behavior have also become available and applied for predictive purposes [9,16,17]. The hierarchical structure that reflects very often closely also the chemical synthesis involved and the associated relaxations lead to well-distinguishable dissipation mechanisms recognizable in the rheological loss modulus  $G''(\omega)$ . In the past, star- and H-shaped polymers [18,19] have been the principal prototypes for the study of the respective mechanisms of stress relaxation. There, arm motion towards a branching point, which is the branched analog of the contour length fluctuation mechanism in linear polymers is undisputedly accompanied with freeing segments out of their mean-field tube-like engagement through a first-passage time treatment. The entropic penalty for the arm retraction in direction of the branching point, however, requires the tube to widen. On the time scale of the ‘deeper’ unrelaxed tube parts in today’s models the relaxed chain ends are considered as solvent-like and ‘dilute’ the network of entanglements accordingly [7,9]. This process is called dynamic tube dilution and leads to the mentioned enhanced tube diameter, where the factor of enhancement contains the unrelaxed fractions and a conformational parameter that distinguishes between good solvent or  $\theta$ -state conditions [7,9,16,17]. These tube models have been extensively discussed in the literature. However, this is by no means applicable for cyclic polymers. The existence of a comparable tube-like conformation for pure rings is highly unlikely. This already leads to a well-defined different rheological response [20]. In this respect, cyclic polymers are devoid of any comparable mechanism in linear polymers where all dynamics relies on the presence of chain ends. Instead, no entanglement or intermediate elasticity due to topological interactions between different pure ring molecules is observed [12–14]. This is compatible with the observation of a structurally rather mass fractal-like behavior, which compacts rings into non-Gaussian states [21–23]. The dynamic equivalent is a seemingly close-to-Rouse-like relaxation modulus  $G(t)$  following an approximate  $t^{-2/5}$  dependence [24]. This situation changes, however, if such cyclic polymers are dilute dispersed in long linear matrices [14].

In this small review of our own current efforts in the field of interacting topologies, we present results, obtained from time-resolved or quenched SANS investigations and/or NSE methods on exemplary model systems of mixed architectures to complement the former investigations. The emphasis will be entirely on the interpretation of the scattering data and for details on the non-scattering physics we refer to the vast basic literature. Therefore, the review is not meant to be complete in neither aspect but tries to bridge the general text book science for linear polymers to more advanced and architecturally complex polymer structures and their blends. We emphasize the absolutely necessary requirement of

suitably labelled linear, cyclic and branched model polymers to achieve a quantitative comparison to the predictions following molecular rheology rules of the specific components [25]. In this contribution, basing on such especially designed architectures, on the one hand, the relaxation modes of well-defined polymers in mixtures with linear matrix chains are described. In order to track these, neutron and rheological experiments were devised such that the process of interest is active and visible in the experimental time frame. Therefore, applicable to the anisotropic studies, the applied rates of deformation need to be considerably higher than the corresponding relaxation rates under study. The description of such Rheo-SANS experiments and the equipment to do so *in situ* in the neutron diffractometer is documented well in the literature [25–28]. On the other hand, cyclic polymers as ingredient in the mixture are studied in quiescent state by means of quasi-elastic scattering. Therewith, features of microscopic investigations will be provided on two non-linear model architectures, i.e. dendritic and ring-shaped polymers. For all these, the linear-linear architecture combination of rather well-known dynamics serves as a proof-of-principles and provides a simple reference frame for the applicability of the suggested techniques.

## 2. Experimental

All model polymers in this review, i.e. polyisoprene and polyethyleneoxide were obtained from elaborate high-vacuum anionic polymerization techniques in both hydrogenous and deuterated forms yielding very monodisperse products, fully characterized in our lab and specified in the corresponding references. If applicable, their linear rheology was measured using an Advanced Rheometric Expansion System (ARES, Rheometric Sci, USA) in typically plate-plate geometry and isothermal frequency sweeps over several decades at varying temperatures were mastered via the time-temperature-superposition principle (TTS) to arrive at a WLF master curve for a selected reference temperature, an acronym after its inventors Williams-Landel-Ferry [8]. These - in the architectural blends only “effective”- WLF parameters were extensively used in the computation of the thermal history during relaxation ramps concurrent with the SANS experiments at mainly the diffractometers *KWS2* at the MLZ Garching, Germany and the *D11* at the ILL Grenoble, France. For selected samples NSE measurements of the dynamic structure factors were obtained from the quasi-elastic spectrometers *IN11* and *IN15* at the ILL, Grenoble, France.

### 2.1. Neutron scattering for molecular rheology

Neutron scattering enables one in a unique way to intrude into the local and global structure and dynamics on the microscopic level of polymers in bulk state, which is out of reach for light- or X-ray scattering techniques [1,29]. Neutrons deliver the complementary molecular aspect to the very frequently used rheological response as the signature of dynamic processes of stress relaxation. Neutron scattering therefore has become one of the most powerful methods for soft matter investigations and today several excellent reviews exist [30]. The high rank that neutrons take among scattering probes is due to the fact that the accessible scattering vectors  $q$ , i.e. the observable inverse spatial length scale as well as the energy, i.e. the observable inverse time scale of the chains are ideally suited for such systems. They match those of the structure and the internal dynamics of polymers: Small Angle Neutron Scattering (SANS) instruments allow explorations of length scales between roughly 1 and 1000 nm. Additionally, the energy resolution of high resolution quasi-elastic Neutron Spin Echo spectroscopy (NSE) is such that Fourier times up to almost 0.7  $\mu$ s can already be resolved directly nowadays [72]. The scattering vector  $q$  is

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