

Combined methods in Rheology: Rheo-SAXS, Rheo-NMR and Rheo-Dielectric to bridge length and time scales

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ABSTRACT

Rheology as the science of flow and deformation of matter in general measures forces (torque and normal forces) and displacement of materials. Regularly Rheology can establish the interplay of molecular structure and mechanical properties. Both quantities differ in their internal length scale starting from 10^{-9} m to 10^{-2} m and time scales covering 10^{-8} s to 10^{+2} s. Furthermore mechanical deformation e.g. shear can lead to oriented structures or crystallization if non-linear shear is applied. Consequently there is a need to conduct *in-situ* molecular characterization techniques during rheological measurements if non-linear shear, e.g. large amplitude oscillatory shear (LAOS) in combination with FT-Rheology is applied.

This contribution presents three recent developments within our group to investigate short length scale dynamic measurements ($< 1\text{-}2$ nm) via Rheo-Dielectric (end-to-end vector), Rheo-NMR, molecular size (R_g) measurements (ca. $10 - 50$ nm) and structural correlations via Rheo-SAXS measurements. The experimental realization and first experiments will be presented in detail.

INTRODUCTION

The rheological properties of materials are usually characterized by two classes of flow: the linear viscoelastic experiments (e.g. $G'(\omega)$, $G''(\omega)$) and the non-linear viscoelastic experiments (e.g. $\eta(\dot{\gamma})$), which can be preformed and analyzed in various ways¹. Among these non-linear experiments, large amplitude oscillatory shear (LAOS) has attracted increasing interests in recent years¹. The development of high sensitive Fourier Transform rheology (FT-Rheology) by Wilhelm et al.², allows the precise analysis of the non-linear mechanical response with respect to the phase angle and relative intensities of the higher odd harmonics I_n/I_1 . Recent investigations have shown substantial correlations between the non-linear mechanical response and the microstructure of the materials^{3, 4} or the molecular topology of polymer chains^{5, 6}. The knowledge on the macroscopic flow behavior or changes in the microstructure caused by large deformation is an essential factor for processing control and advanced practical applications, such as membranes or anisotropic charge and photon conductivity.

For a better understanding of the rheological behavior, the need of simultaneous acquisition of information on the microstructure and molecular dynamics in the sample arises.

In this contribution we report three new and unique combined methods: The Rheo-SAXS⁷, Rheo-Dielectric⁸ and Rheo-NMR⁹ combinations. These methods allow in-situ studies of dynamics and structural changes with a high time resolution and directly correlate them to the non-linear mechanical response. Additionally the latest results on the non-linear flow behaviour of complex materials such as block copolymers, obtained by in-situ measurements, will be presented herein.

RESULTS AND DISCUSSION

A) Rheo-SAXS Combination

In-situ Rheo-SAXS measurements were carried out at the beamline BW1 of the DORIS III storage ring at HASYLAB (DESY, Hamburg, Germany)⁷, at a wavelength of 0.1267 nm. In order to achieve a well defined mechanical excitation as well as precisely detecting the mechanical response, the beamline is equipped with a commercial stress controlled rheometer (Mars II, Thermo Scientific). We developed a custom made Vespel® comprised parallel plate geometry with a diameter of 36 mm containing thin windows of 0.3 mm thickness at 15.5 mm distance from the center of the plate ($\gamma_{\text{local}} = 86\% \gamma_0$), to minimize scattering and absorbance effects, which reduces beam intensity. To redirect the intrinsically horizontal synchrotron X-ray beam by 90°, a diamond (004) reflection (see Fig. 1) is used⁷. The rheometer is equipped with a custom made cylindrical heating cell, operating with nitrogen as an inert gas to avoid oxidative decomposition of the polymer melts. The accessible temperature range lies between room temperature and 250 °C, with an accuracy of

0.5 °C. The scattered intensities were recorded by a 2D detector (Pilatus 1000k) which can be positioned at a distances between 30 cm and 2.50 m above the sample. The acquisition time necessary for each 2D-SAXS frame was down to 11 s (10 s exposure plus 1 s delay time for data storage and triggering). At the new storage ring Petra III at DESY, the acquisition time for each frame could be reduced to the millisecond range due to the high flux.

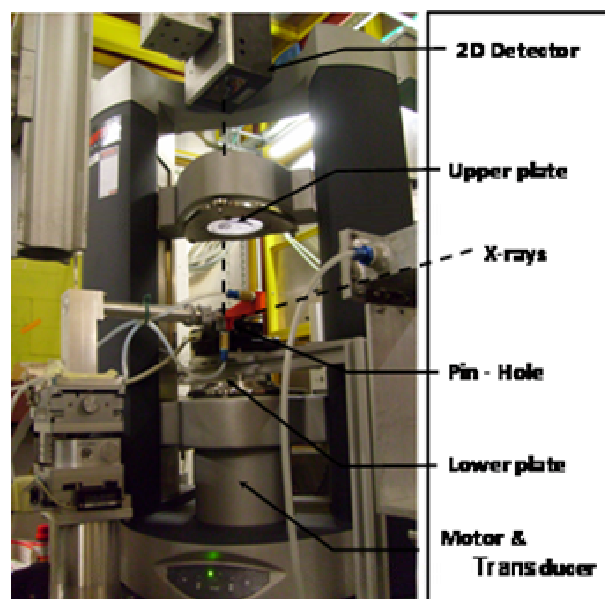


Figure 1 Photograph of the Rheo-SAXS apparatus. The oscillatory shear is applied by the lower sample plate at which also the transducer is located. The upper sample plate remains fixed during the experiments. The setup which is located at the beamline BW1 at HasyLab.

The Rheo-SAXS combination is an ideal method to characterize shear-induced structural changes on a mesoscopic length scale (1 nm to 100 nm) in-situ measuring the mechanical parameters under precise rheological conditions.

Rheo-SAXS of PS-b-PI

The kinetic pathway of the macroscopic orientation process of lamellar Polystyrene-block-Polyisoprene (PS-b-PI) diblock

copolymers ($M_n = 28000$ g/mol, $f_{PS} = 50\%$, $PDI = 1.04$) was investigated by Rheo SAXS (see Fig. 2).

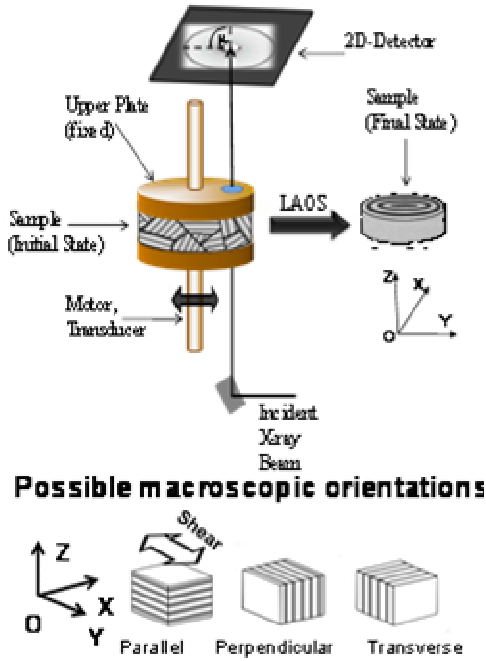


Figure 2 Schematic representation of the experimental setup, the Cartesian coordinate OXYZ is defined such that the vertical reflected X-ray beam is parallel to the OZ axis. The oscillatory shear is applied by the lower sample plate at which also the transducer is located. The upper sample plate remains fixed during the experiments.

Our first results revealed new insights in the mechanical alignment process. For the first time we could show that the excellence of the macroscopic orientation for higher shear amplitudes ($\gamma_0 > 1$) showed to be a function of the mechanical excitation time, resulting in a better orientation for shorter mechanical excitation times whereas longer experimental times caused a reduction in the degree of orientation (see Fig. 3b). This phenomenon was detected as an increase of the non-linear mechanical response followed by the time dependence of $I_{3/1}$ (see Fig. 3a). Additionally, we examined a significant dependence of the orientation time to the applied strain amplitude γ_0 , showing power

law dependence with an exponent close to -2 for the structural changes studied by 2D-SAXS and the mechanical response.

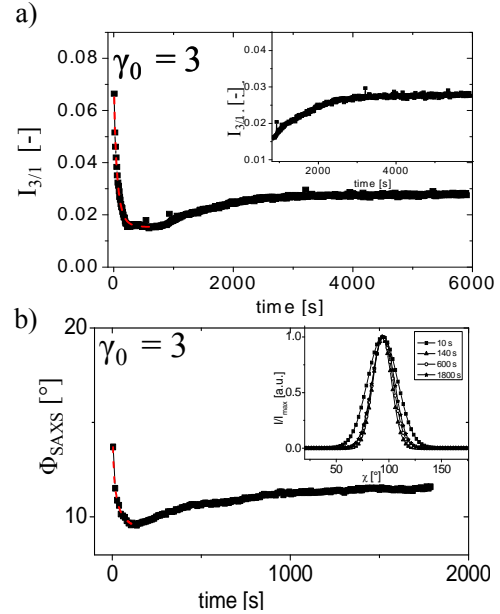


Figure 3 a) Time dependence of the relative intensity of the third harmonic measured by FT-Rheology. The inset represents an enlargement of the de-orientation area. b) Time dependence of the standard deviation σ calculated by fitting the scattered reflexes at 270° of the 2D-SAXS images with a Gaussian function. The insets represent the scattered reflexes at characteristic times during the mechanical excitation. (LAOS: 1Hz, 150°C , $\gamma_0 = 3$).

B) Rheo-Dielectric Combination

For the Rheo-Dielectric experiments a very sensitive setup was built using a combination of an ARES II-Rheometer (TA Instruments) and a dielectric ALPHA-Analyzer (Novocontrol Technologies)⁸ (see Fig. 4). The ALPHA-Analyzer is able to measure about 12 orders of magnitude frequency range (3×10^{-5} to 1×10^7 Hz), 16 orders of impedance range (10^{-2} to $10^{14} \Omega$) and 15 orders of capacity range (10^{-15} to 1 F). These ranges exceed the capacitance bridges used in former Rheo-Dielectric measurements by several decades in each quantity. Furthermore the ALPHA-Analyzer

allows a $\tan\delta$, phase shift between input voltage and output current, resolution of $\pm 3 \times 10^{-5}$ to $\pm 10^{-3}$, depending on the used capacity. The ceramic insulation between the parallel plate and fixture is very brittle and has a low thermal expansion coefficient. Thus INVAR steel with an extremely low temperature coefficient of $1.3 \times 10^{-6} \text{ K}^{-1}$ (in comparison to $13 \times 10^{-6} \text{ K}^{-1}$ in conventional steel) is used as a new measuring plate and fixture. This is specifically helpful for measuring various temperatures. The sample plates with 8, 15, and 25 mm in diameter are connected to the electronic wire with a bolt, and the other end of the wire is connected with a BNC connector. The BNC connector is installed outside of the oven. All parts of the electrode inside oven. This allows temperature control and electronic noise shielding environment.

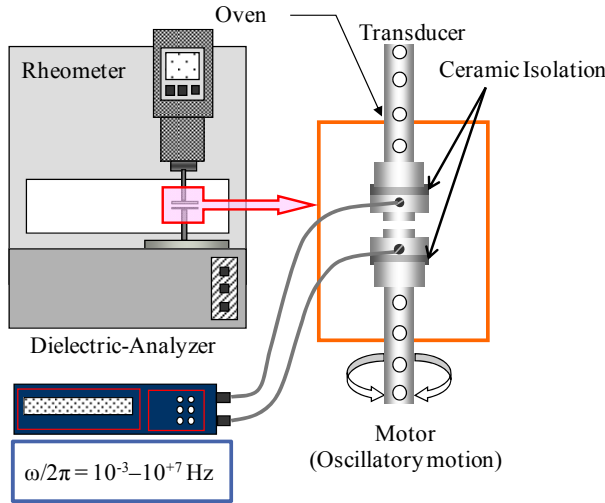


Figure 4 Schematic representation of the Rheo-Dielectric setup.

Rheo-Dielectric of PS-b-PI

A “Type A” (Stockmeyer classification) polymer, such as polyisoprene, consist of monomer units which exhibit a dipole moment $\vec{\mu}_i$ parallel to the polymer

backbone. The resulting total dipole moment:

$$\vec{\mu}_{total} = \sum_{i=1}^N \vec{\mu}_i \quad (1)$$

corresponds to the end-to-end vector of the polymer chain. As we showed in recent work, the influence of LAOS to the molecular dynamic of polyisoprene chains can be in-situ studied by Rheo-Dielectric⁸. In our recent work we investigated the shear-induced macroscopic alignment of PS-b-PI. We found that the macroscopic orientation of symmetric diblock copolymers with their lamella normal parallel respectively perpendicular to the shear flow exhibit different responses in the time evolution of the dielectric loss modulus ϵ'' (see Fig. 5). For the perpendicular orientation we observed an increase in the dielectric loss whereas for the parallel macroscopic orientation the dielectric loss is decreased. As the dielectric response of the sample is mainly attributed to global chain dynamics of the PI-block a first speculation about the dynamics governing these phenomenon could be that due to the tethered polymer chains the end to end vector of the PI-chains preferably directs perpendicular to the lamella normal resulting in the observed increase for the perpendicular and decrease for the parallel orientation, respectively.

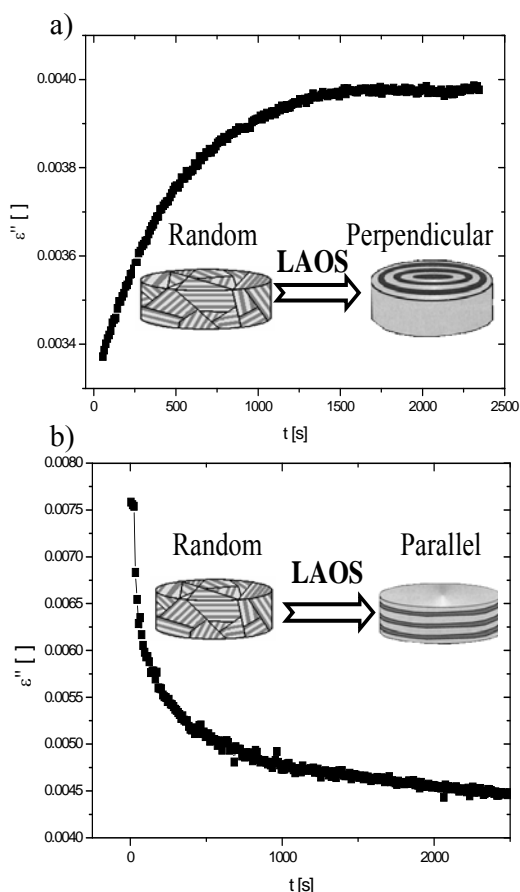


Figure 5 Time dependence of the dielectric loss modulus ϵ'' for the macroscopic a) PS-b-PI ($M_n = 24000$ g/mol, $f_{PS} = 53\%$, $PDI = 1.03$) perpendicular (LAOS: 5 Hz, 100%, 160 °C) and b) PS-b-PI ($M_n = 24000$ g/mol, $f_{PS} = 53\%$, $PDI = 1.03$) parallel (5 Hz, 100%, 130 °C) orientation.

C) Rheo-NMR Combination

Flow dynamics have long been investigated by means of new "Rheo-NMR" under constant shear in different geometries, but the study of highly viscous or rubber-like polymers is impeded by the strong stray field of cryogenic high-field magnets, in which precision actuator and transducer motors, as used in oscillatory rheometry, esp. for LAOS and FT-Rheology, cannot be used reliably.

Nearly all bulk polymers have a high content of the susceptible proton nuclei, and can thus be probed by NMR in fields of less

than 1 T, as can be reached by the use of permanent magnets. While spectroscopic resolution is hard to gain with these, the relaxational behaviour, which strongly depends on the molecular mobility, is easily observed in field homogeneities not better than a few hundred ppm.

We have built a permanent magnet of the Halbach type showing a flux of 0.7 T (~ 30 MHz ^1H) in a 40 mm bore, outer dimensions of just 200 x 200 x 120 mm, and a homogeneity better than 700 ppm in the sample volume of a 20 mm plate-plate geometry. This allows combined measurements of mechanical properties and NMR relaxation parameters like T_1 , T_2 etc. as a function of a wide range of experimental parameters like $\omega_1/2\pi$, γ_0 or temperature.



Figure 6 30 MHz Halbach magnet with magnetic shielding set in an ARES II rheometer.

The magnet was equipped with an appropriate ^1H probe head, and adaptation with magnetic shielding to fit into an regular ARES II rheometer. To avoid NMR signal distortion, non-conduction geometries (20 mm plate-plate) were made out of PTFE for room temperature measurements.

To test for the unhampered sensivity of the rheometer, viscosity standards were measured with and without the magnet in place, and also with a standard 25 mm steel geometry.

The curing kinetics of a commercially available two-component epoxy-glue, as used in an earlier work of our group with a 10 MHz prototype of the magnet⁹, was measured as a test-bed example. The T_2 -relaxation of the sample was measured with a CPMG pulse sequence, where eight scans with a recycle delay of 2.5 s were used, that is, a time resolution of 20 s was possible.

Fig. 7 shows measured curves for different curing times. The decrease in T_2 is due to dipolar coupling between protons becoming stronger as the sample becomes more rigid, and the mobility of the polymer coil is diminished. The same reason is valid for the lowered overall intensity of the signal, as the CPMG sequence only quantitatively shows spins with a high mobility. The T_2 parameters are fitted from the CPMG trains using a stretched exponential

$$I(t) = I_0 \exp(t/T_2)^\beta$$

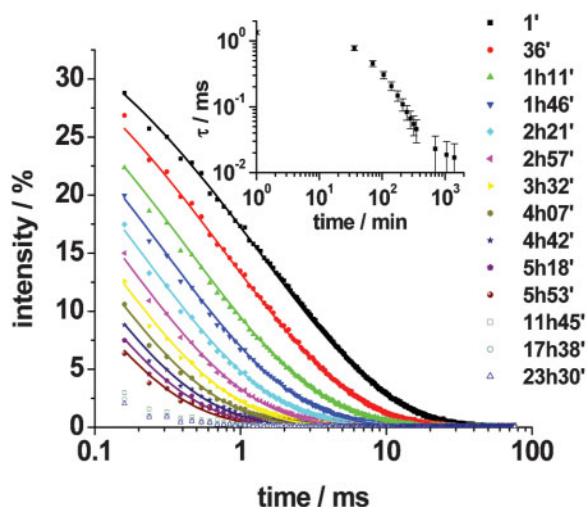


Figure 7 shows measured CPMG curves for different curing times. The inset shows the fitted $\tau=T_2$ parameters

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