

Investigation of the shear induced macroscopic Alignment of Diblock Copolymers with combined In-Situ Methods

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The mechanical macroscopic alignment of diblock copolymer melts under large amplitude oscillatory shear (LAOS) was investigated utilizing unique in-situ methods as Rheo-SAXS^[1] and Rheo-Dielectric^[2]. Both methods provide essential information enabling the correlation of the mechanical response with structural and molecular dynamic processes. In detail we were able to follow the kinetic pathway of the macroscopic orientation process of lamellar Polystyrene-block-Polyisoprene diblock copolymers revealing new insights in the mechanical alignment process. 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 -1.8 for the structural changes studied by 2D-SAXS and the mechanical response. Further the excellence of the macroscopic orientation for higher shear amplitudes 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.1a). By means of our unique Rheo-Dielectric setup 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.1b). 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.

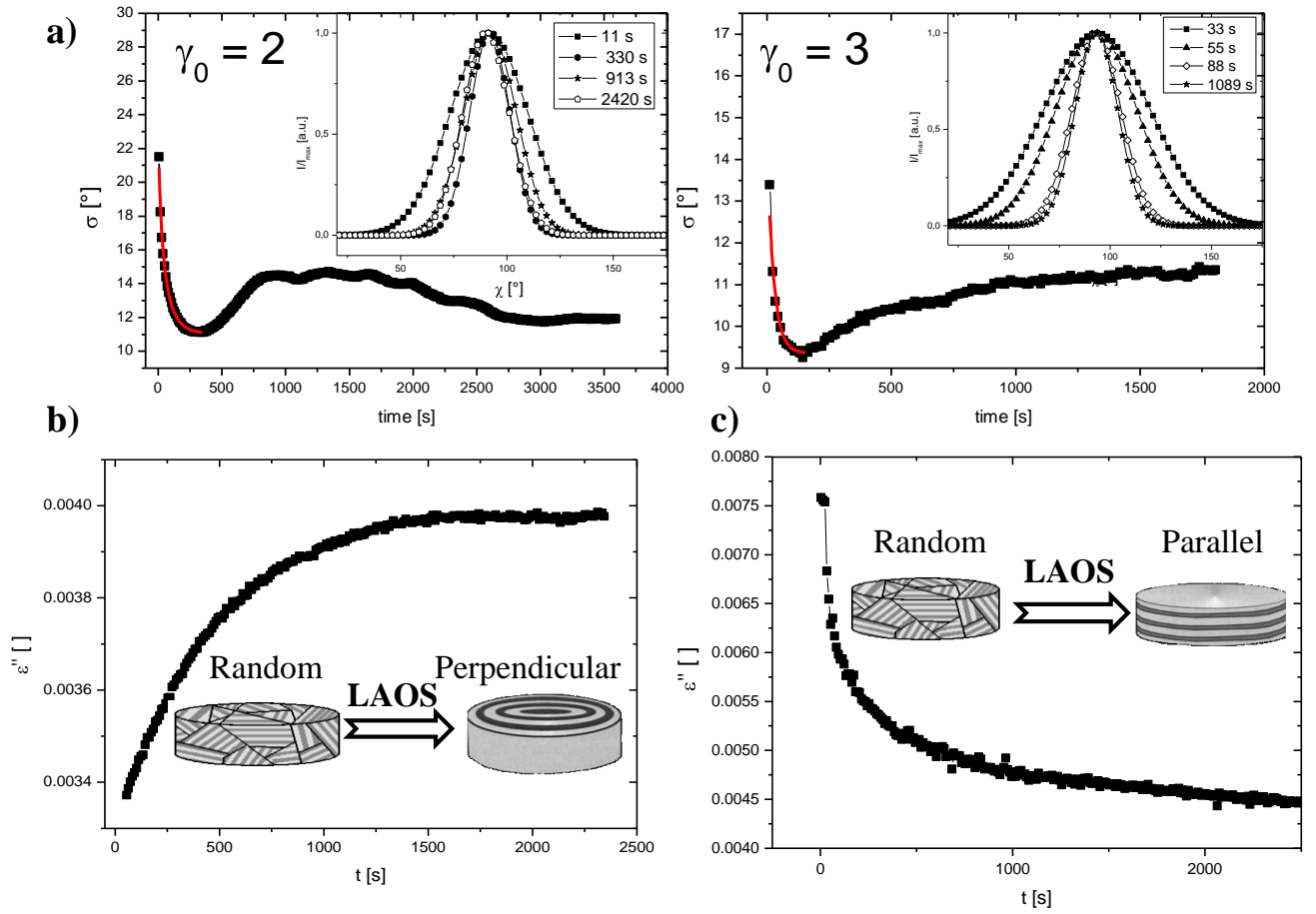


Fig. 1: a) time dependence of the standard deviation σ calculated by fitting the scattered reflexes at 270° of the 2D-SAXS images with a Gaussian function (LAOS: 1 Hz, 150°C). The insets represent the scattered reflexes at characteristic times during the mechanical excitation. b) and c) time dependence of the dielectric loss modulus ε'' for the macroscopic (b) perpendicular (LAOS: 5 Hz, 100%, 160°C) and (c) parallel (5 Hz, 100%, 130°C) orientation.

References

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