Dynamic Nanostructures in Amorphous Materials

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In recent years increasing evidence of partial ordering of amorphous systems on the nanometer scale has been obtained. For instance, polymers composed of rigid backbones and flexible sidegroups often exhibit layered structures accessible to x-ray or neutron scattering. The packing differences also manifest themselves in different mobilities of structural elements, amenable to methods capable of elucidating the dynamics of the different building blocks. Particularly informative are slow molecular and collective motions because their motional rates will be significantly different for systems with only slight differences in density.

Advanced solid state NMR provides particularly selective information in this regime. Such experiments have established the concept of dynamical heterogeneities, measuring their time and length-scales. In computer simulations of amorphous systems consisting of hard spheres without any further interaction, the formation of such dynamic heterogeneities has been confirmed, and a resulting dynamic structure could be visualized. These heterogeneities exhibit a highly cooperative dynamic behavior and have been observed in polymeric and low-molecular glass formers using multi-dimensional NMR techniques. Due to the lack of periodicity, these nano-scaled structures have not yet been observed in scattering experiments.

**Keywords:**
- Nanostructure
- Cooperativity
- Dynamic Heterogeneity
- Computer Simulation

**Cross-links to other projects:**
- Heterogeneous Polymers
- Solid-State NMR Spectroscopy
- Supramolecular Architectures

Another indication for order resulting from collective dynamic behavior of polymers in the molten state is obtained by high resolution double-quantum NMR. Due to topological constraints, the chain motion is not completely isotropic and local chain stretching results in dynamic order parameters, which in poly(butadiene), PB, melts were found to be much higher than predicted by current statistical models for entangled polymer melts.
When one or both chain ends are fixed by attaching them to a rigid poly(styrene), PS, block in a PS-PB or PS-PB-PS block copolymer the order is stabilized for long times, because translational chain motion is hindered. Remarkably, however, the local order parameter substantially increases, when the PB chains are confined to a layer in a block-copolymer.

The observation of significantly enhanced crystallization on similar restrictions of translational chain motion also suggests the presence of substantial local chain ordering in the melt that facilitates conformational rearrangements necessary for crystallization. These and other findings are rationalized by proposing a nanodomain structure, which is partially ordered on a local scale and completely disordered on larger scales.

**Scheme of nanodomain structure in polymer melts and block copolymers**

### References: