

TIME-RESOLVED X-RAY STUDIES OF STRESS INDUCED CHANGES IN POLYMER STRUCTURE

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Purpose designed instrumentation has allowed time-resolved X-ray diffraction at the Daresbury Laboratory Synchrotron Radiation Source (SRS) and the European Synchrotron Radiation Facility (ESRF) to be used to characterize changes in molecular conformation and organization in response to mechanical stress over a range of temperatures in a variety of polymer materials. The high brilliance of the synchrotron sources has allowed small (SAXS) and wide (WAXS) angle diffraction patterns to be recorded with time-resolutions as short as 40 msec. Instrumentation has been developed which allows SAXS, WAXS and a video image of the specimen to be recorded simultaneously allowing determination of the strain at the point from where the X-ray diffraction data was recorded. Novel analytical techniques have been developed which have allowed distinct relaxation modes to be distinguished from WAXS data recorded during and subsequent to deformation of films of poly(ethylene terephthalate) (PET). Simultaneous SAXS and WAXS data recorded from a variety of grades of polyethylene have allowed changes in polymer conformation in response to mechanical stress to be related to changes in polymer organization. A novel micro-stretching device capable of recording stress/strain data has been used at the microfocus beamline ID13 at the ESRF with beam dimensions as small as a few microns to relate changes in mechanical properties of struts from polyurethane foams to structural transitions characterized in simultaneously recorded X-ray diffraction.

Keywords: SYNCHROTRON POLYMER DEFORMATION

EQUILIBRIUM & NON-EQUILIBRIUM CONFORMATIONS IN LIQUID CRYSTALLINE POLYMERS: A NEUTRON SCATTERING APPROACH

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Recognition that polymers may exhibit liquid crystalline properties dates back only 25 years. The first tailored side chain liquid crystalline polymers (SCLCPs) were then discovered by inserting a spacer in between the main-chain and lateral mesogens graftings. Much of the subsequent research has sought to control the properties of these tailored systems and to understand the nature of the coupling between the polymer main-chain and the mesogen.

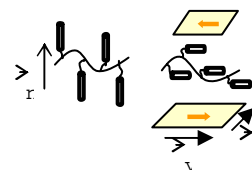
These materials are also technologically interesting because of their ease of processing. However, in contrast with the equilibrium state, the flow behaviour of such polymers is almost not explored. These polymers are nevertheless expected to show original rheological behaviours, which are beyond simple shear induced phase orientations as observed in small liquid crystalline molecules [1] since they should reflect a mixture of their polymeric and mesomorphic characters.

Among the numerous techniques developed to characterise the structure of the matter, Neutron Scattering (SANS) still remains the only method to access to the conformation of polymers in the melt. We will examine the 3-D conformation of side-chain liquid crystalline polymers, firstly in their equilibrium state and then, under shear flow. We will prove that the shear flow acts at a local scale selecting a main-chain/mesogen orientation no more defined by the molecular field [2] but by the flow parameters. An example of transition from smectic A phase to smectic C phase is given. Another example in the nematic phase shows that the polymer main-chain executes a flow induced 90° reorientation with respect to the director.

Finally, in the isotropic phase, we show that the flow is even responsible of the appearance of non-equilibrium phases [3]. These shear-induced behaviours will be presented in the frame of an experimental approach using rheomicroscopy, non-linear rheology and SANS techniques.

References

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POLYMERS AT CURVED INTERFACES: MICROEMULSIONS DROPLETS DECORATED BY BLOCK COPOLYMERS

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We report small-angle x-ray scattering (SAXS) results on microemulsions consisting of oil (decane), water and the nonionic surfactant C12E5 decorated with the block copolymer Brij700 (C18E100). The microemulsions form spherical droplets covered with a brush of hydrophilic E100 chains. Scattering data have been obtained on the new, modified NanosSTAR instrument at the University of Aarhus, which uses a rotating anode source and which is flux optimized for solution scattering. From the SAXS data we can by extensive modeling obtain information on the droplet structure, the corona shape of the E100 chains and the interaction between the droplets. The model is based on expressions derived from Monte Carlo simulations by Svaneborg and Pedersen.

Keywords: GRAFTED POLYMERS CURVED INTERFACE SMALL-ANGLE X-RAY SCATTERING

THE EFFECT OF SHEAR ON THE STRUCTURE OF THERMOPLASTIC ELASTOMER GELS

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Triblock copolymers in a solvent selective for their middle blocks provide the basis for the formation of novel physical networks where cross-links are formed by self-assembled domains of the end-blocks. Triblock copolymers of poly(styrene)-poly(ethylene/butylene)-poly(styrene) (SEBS) dissolved in a mixture of aliphatic and alicyclic compounds constitute such a network system. We present combined mechanical and structural data on such SEBS gels as studied using a Rheometrics RSA-2 instrument modified for in situ measurements of small-angle neutron scattering and rheology. The self-association of the PS-blocks does not only promote formation of highly interconnected end-block domains, but within a limited temperature range these domains constitute a network with body-centered cubic (bcc) microstructure. The thermodynamic stable cubic phase is at high temperature limited by an order-disorder transition and at low temperature by the glass transition of polystyrene. Upon exposure to large amplitude oscillating shear the polycrystalline soft gel can be aligned into a cubic ordered mono or twin domain texture, depending on shear amplitude.

Keywords: BLOCK COPOLYMER GELS NEUTRON SCATTERING