

m37.p01

## Evidence for a mesomorphic phase in precisely branched polyethylenes

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**Keywords:** SAXS polymers, SALLS, polymer crystallization

Recently several authors suggested the presence of a transient mesomorphic phase to explain the crystallization-induced morphological changes in polyethylenes [1-2]. Up to now the assumed layer-like mesomorphic phase could not be observed by scattering techniques, probably because the amount is too low or its lifetime prior to conversion into crystalline material too short. In the group of K. Wagener precisely branched polyethylenes were synthesized using Acyclic Diene Metathesis (ADMET) polycondensation chemistry [3]. Here, the focus is on the temperature dependent morphology of two ADMET polyethylenes with precisely positioned hexyl branches every 21st and 15th carbon along the polyethylene backbone. During its crystallization the polyethylene with 1 hexyl branch at every 21st carbon atom organizes into paracrystalline stacks of monodisperse crystalline layers, separated by amorphous matter. Small and Wide angle synchrotron X-ray and small angle light scattering experiments reveal that the ethylene sequences in the layers are tilted approximately 45° with respect to the layer normal and that they are arranged in a monoclinic fashion after a rapid transition from amorphous (mesomorphic) precursor layers in which the ethylene sequences are not tilted. The thickness of these precursor layers closely agrees with the value predicted by the Strobl crystallization line for polyethylene [4]. A polyethylene with 1 hexyl branch every 15th carbon atom crystallizes just before vitrification without passing a mesomorphic layer phase. The formed, unidentified - presumably crystalline - structures melt closely after devitrification. However, upon further heating, amorphous layers are formed with a density deviating from that of the matrix. The fraction of the layers increases with annealing time and the layers melt at the stability limit of mesomorphic layers with a thickness identical to the stretched ethylene sequences and predicted by the Strobl crystallization line [4]. For this particular sample, X-ray scattering experiments support the presence of non-crystalline, mesomorphic layers in a rather wide temperature range.

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m37.p02

## Time-resolved SAXS study of the formation of resorcinol-formaldehyde aqueous gels

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**Keywords:** SAXS, sol-gel materials, time-resolved analysis

Sol-gel processes consist in the polymerization of precursors in a solvent until the system solidifies; after removal of the solvent a porous solid is obtained [1]. According to the specific conditions, different materials can be synthesized with potential application as catalysts supports, adsorbents, insulators etc. [2]. In the literature, a two-step mechanism is generally reported consisting (i) in the formation of a colloidal suspension called a sol and (ii) its aggregation until the clusters touch each other, at which moment a gel is obtained [1]. For some systems, however, the final structure of the material after drying is hardly compatible with this scenario [3]. In the case of resorcinol-formaldehyde gels, the gel formation mechanism is unclear, although some authors propose that the structure of the gels forms *via* a reaction-induced phase separation [4]. As the molecular weight of the polymerizing species increases, their solubility in the solvent decreases which eventually triggers demixing. Generally, cluster formation by aggregation and phase separation can occur simultaneously and competitively [5]. The rate of both phenomena certainly depends on the reaction conditions. In particular, organic materials with a great variety of pore textures (micro, meso and/or macroporous solids) can be obtained depending mainly on the pH of the precursors' solution [6]. To gain insight into the mechanisms of gel formation, the gelation of resorcinol-formaldehyde aqueous mixtures prepared at various pH was followed by time-resolved SAXS. The pH of the solution was adjusted between 2.0 to 8.0, to cover the whole possible pore texture range of the final material. The reported data were obtained in DUBBLE, the Dutch-Flemish beamline at the European Synchrotron Radiation Facility in Grenoble, France. The SAXS patterns are analyzed in the frame of the aggregation or phase separation mechanisms.

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