ESRF	**Experiment title:** Influence of crystal sizes in phase transition: a gel study	**Experiment number:** SC-270
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Names and affiliations of applicants (* indicates experimentalists):

S. Rastogi *
J.G.P. Goossens*
T. Corstjens*

Report:

In-situ wide-angle X-ray scattering (WAXS) experiments have been performed to study the phase behaviour of syndiotactic polystyrene (sPS) with three solvents, i.e., decalin, benzylmethacrylate, and cyclohexylmethacrylate. The in-situ structural changes have been followed together with DSC, SAXS and Raman spectroscopy. From here, it has emerged that two different structural modifications exist within the solvent-included helical δ-phase, known to be a polymer-solvent compound. In the first modification, δ', the solvent molecules (intercalated between the phenyl rings of sPS) are ordered, whereas in the second modification, δ", disordering of the solvent molecules within the helices occurs. The existence of the δ' phase depends on the phenyl ring interaction between sPS and the solvent. The γ-phase (the solvent-free helical phase) is not observed in this study which is in contrast to earlier reported results on sPS/solvent systems measured by conventional methods. The transformation from the helical (δ") to the planar zigzag (β) occurs via melting and recrystallisation. Under specific conditions, the β-phase could be metastable, even in its thermodynamically stable region.

Figure 1 is a composite picture showing the presence of δ', δ" and β phases in sPS/BzMA system. These phases are seen in figures 1a,b,f respectively for 20wt% of sPS/BzMA and 1d,e for 40wt%. Figure 1c shows polymerized BzMA. It may be noted that the inner broad reflection in 1c, can be observed in figures 1a,1d (marked as 1) in the case of unpolymerized BzMA due to its intercalation with the polymer. The d-value for this reflection matches with the molecular length of BzMA. The origin of broad reflection in figure 1c is explained as interchain distance in polymerized BZMA, in figures 1a and 1d due to solvent ordering and its absence in 1b and 1e due to solvent disordering at high T. Polymerization in the ordered solvent will result into molecular helnding.

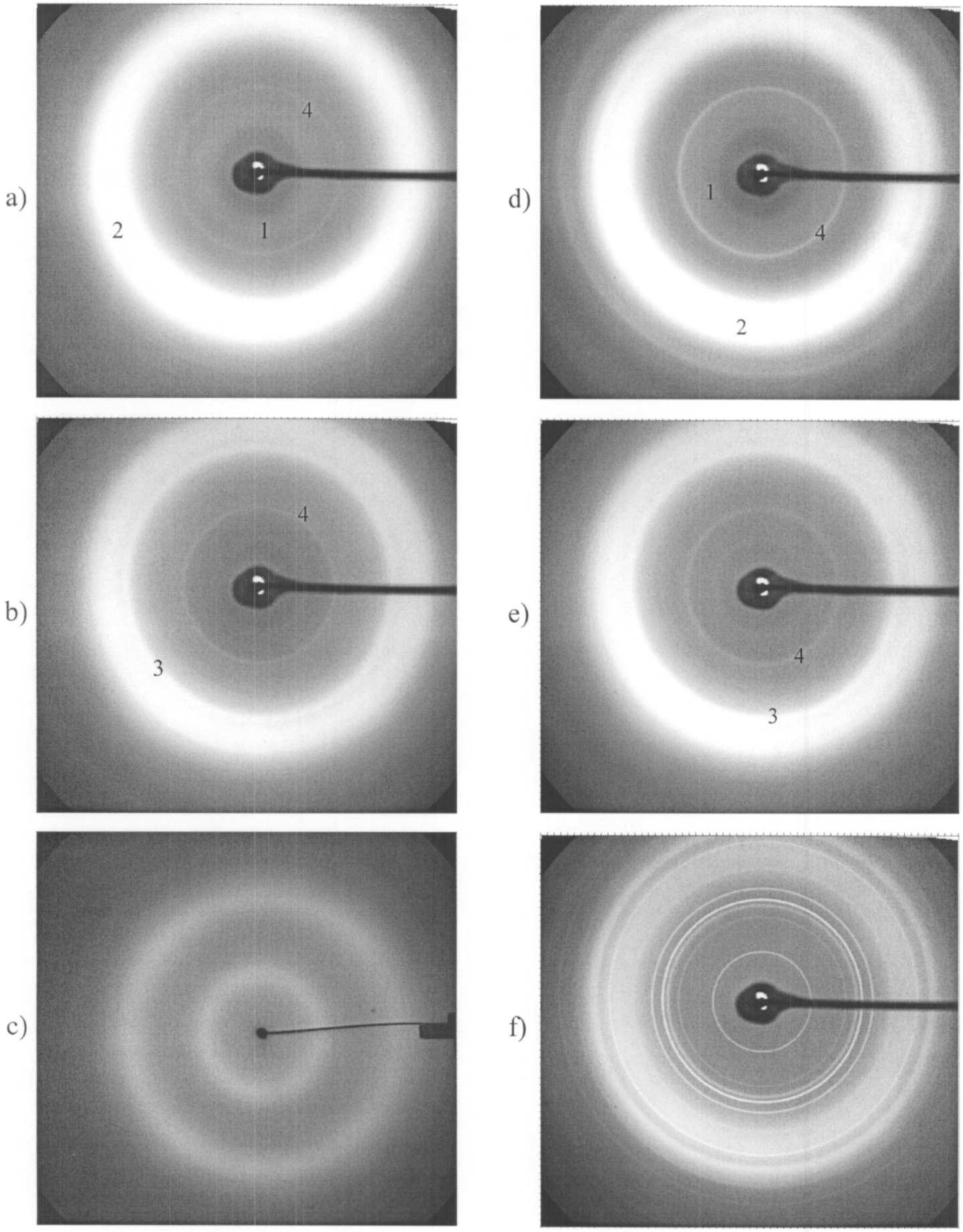

Figure 1: WAXS data: a) 20 wt% sPS at 70°C (δ'), b) 20 wt% sPS at 130°C (δ''), c) PBzMA, d) 40 wt% sPS at 55°C (δ'), e) 40 wt% sPS at 115°C (δ''), and f) 20 wt% sPS at 180°C (β').