

NUCLEATION AND PARTICLE GROWTH OF POLY(3-ALKYLTHIOPHENES)

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Introduction

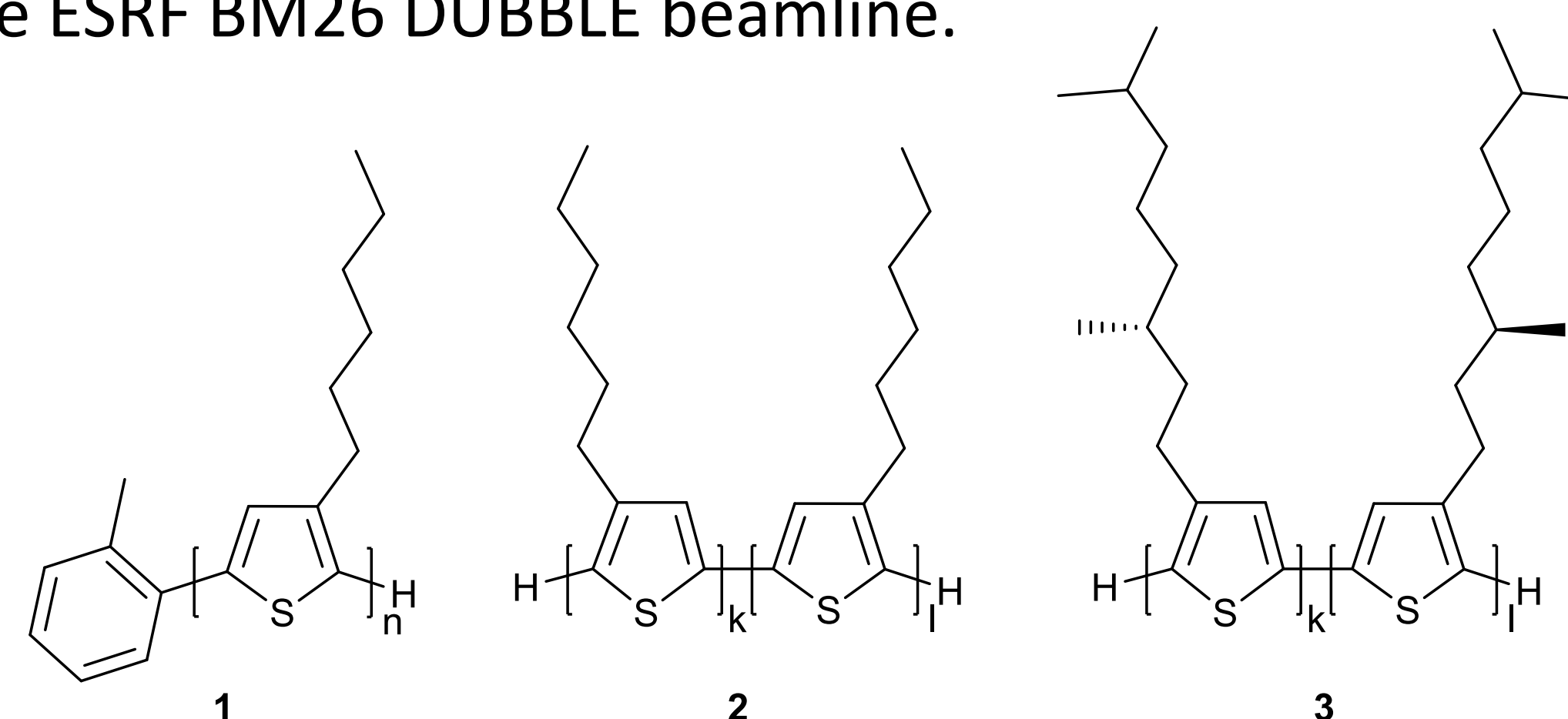
Nucleation – the initial step of the crystallization – is still rather unexplored, while this step **has a major impact on the outcome** [1]. One of the possible systems for studying nucleation are organic polymers, namely **polythiophenes**, where nucleation and particle growth has recently been examined by non-linear optics (NLO) [2].

In this research, dynamic **small-angle X-ray scattering (SAXS)** experiments are used for nanoscale information about size, structure and morphology of monomers/aggregates in the initial stages of the particle growth.

Experimental

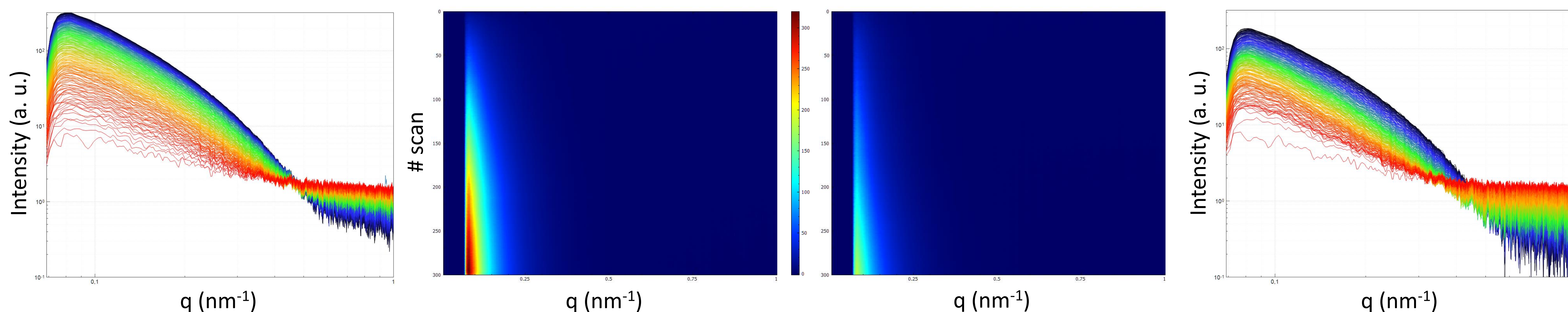
In total, 3 poly(3-alkylthiophenes) were studied by sealing various concentrations of the polymer in a mixture of a THF solvent and MeOH anti-solvent. The polymer mixtures were dissolved by heating, and the aggregation with subsequent particle formation was observed during the cooling period. In-house trials were succeeded by synchrotron experiments at the ESRF BM26 DUBBLE beamline.

- Poly(3-hexyl)thiophene, with initiator (**1**)
- Poly(3-hexyl)thiophene, no initiator (**2**)
- Poly(3-(3,7-dimethyloctyl)thiophene, no initiator (**3**)

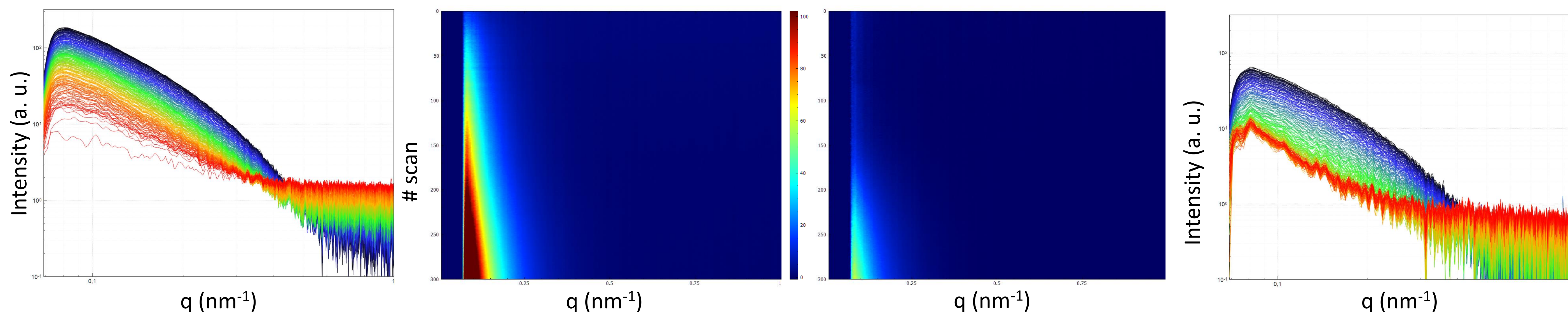


SAXS

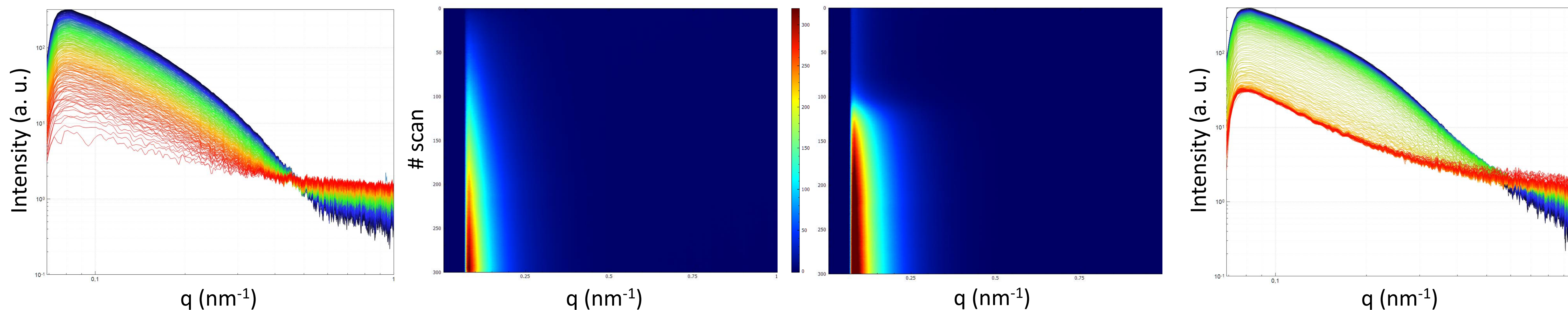
Poly(3-hexyl)thiophene, with initiator (**1**), comparison of different concentrations of the feeding solution: 5 mg/ml left, 2.5 mg/ml right.



Poly(3-hexyl)thiophene, with initiator (**1**), comparison of different anti-solvent shares at 2.5 mg/ml: 55% MeOH left, 45% MeOH right.



Poly(3-hexyl)thiophene, comparison of initiator effect at 5 mg/ml: with the initiator (**1**) left, without the initiator (**2**) right.



Conclusions

Results are showing differences in particle formation between the types of the polymers, based on the concentration, side-chain, presence of defects in the backbone of the polymer or the ratio of solvent/anti-solvent in the mixture. Aggregation of polymers is also observed prior to the precipitation of particles.

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References

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- [2] Moris, Michèle et al. Harmonic light scattering study reveals structured clusters upon the supramolecular aggregation of regioregular poly(3-alkylthiophene). *Communications Chemistry*. 2:130 (2019).