Experimental report

25/09/2017

Proposal:	**9-11-1799**	**Council:**	4/2016
Title:	Tunability of branching design andsolution properties of hyperbranched polyethylene		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Albena LEDERER**
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Samples: (C2H4)n

Instrument	Requested days	Allocated days	From	To
D11	2	2	26/09/2016	28/09/2016

Abstract:

Modern catalysts allow the synthesis of well-defined and precisely tuned polyolefin architectures. Yet, profound knowledge of the connection between synthetic mechanism, structure and properties of these polymers is still limited. Our work is focused on a comprehensive investigation of the complete structure-property relation of diversely branched polyethylene by putting together an interdisciplinary research group with a vast knowledge in different expert fields. So far, experimental light scattering as well as viscosity measurements gave necessary information about the molecular properties in solution on a global scale. However, size limitations of these techniques prevent the investigation at lower polymerization degrees and determination of the topology on a segmental level. Hence, SANS is the ideal method to receive insight into the local structure of polyethylene with different degree of branching and size. The correlation with light scattering and viscosity measurements would enable to evaluate the complete molecular structure in solution and will significantly contribute to the understanding of the synthetic mechanism and the tunable design of polyolefin architecture.

Experimental report

Polyethylene (PE) occurs in numerous topological variations enabling a broad range of possible material properties, which is why it is still one of the most consumed plastics to date. By the invention of late transition metal catalysts a completely new class of PE was developed.[1] Here controlled variation of molecular topology leads to polyethylene with special rheological properties, which is fully soluble at room temperature in contrast to polyolefins synthesized by other approaches. However the distinct influence of the macromolecular structure on solution properties of these materials has not been fully investigated. So far, light scattering experiments as well as viscosity measurements revealed the basic connection between synthesis parameters and solution properties.[2,3] But by using static and dynamic light scattering one reaches rapidly resolution limits when examining the respective hyperbranched PE (hbPE) in detail. Consequently, small angle neutron scattering (SANS) was the method of choice to investigate topological characteristics not only on a global but also on a local scale (< 10 nm). The extraordinary contribution of SANS to evaluate segmental conformation of dendritic polymers was very well demonstrated in our previous experiments performed at ILL.[4–6]

This study was targeted at the complete elucidation of structure-property relations of hbPE synthesized using chain walk catalysts. We performed standard characterization method size exclusion chromatography coupled to viscosity, static and dynamic light scattering and refractive index detectors which allowed the determination of physical parameters such as molar mass, intrinsic viscosity, radius of gyration and hydrodynamic radius as well as the evaluation of solution properties on a global scale at sizes higher than 30 nm diameter. Moreover, we were able to assess topological features like shape and compactness by molecular parameters by the ratio R_G/R_H, power law exponents or the contraction factor.

During SANS experiment we investigated 10 samples of PE which were synthesized using Pd(II)-chelate catalyst but different reaction conditions such as pressure, temperature, time and catalyst concentration.[7] Each sample contained 5 different polymer concentrations (1-5 % w/v) to enable Zimm data treatment. The samples were dissolved in pure THF-d8. The dissolution of the samples as well as the performance of SANS experiments took place at ambient temperature. The measurements were carried out at the D11-experiment of ILL in Grenoble with a wavelength of 4.6 and 6 Å and two detector distances of 8 and 1.4 m. The detector distances covered a *q*-range from 0.04298 – 0.45 $Å^{-1}$ (at 1.4 m) and 0.00753 – 0.08617 $Å^{-1}$ (at 8 m) with a good overlap of the two *q*-regimes. The exposure time was 10 min per sample. The scattering intensities are normalized with a standard water measurement after the required transmission measurements have been carried out. The solvent THF-d8 and the empty glass cuvette were separately measured, normalized and subtracted from the data of the sample solutions.

Figures 1 – 3 show the scattering curves of different PE sample series in which only one reaction parameters varies. This way the correlation between synthesis conditions and polymer structure becomes transparent. To evaluate topological properties, the fractal dimension d_f is a helpful parameter. It can be derived from the negative slope of the scattering curve on double-logarithmic scaling (log I(q) vs. log q). For linear chains the fractal dimension can vary from $d_f = 1.8 – 2.0$ whereas homogeneously branched structures range between $d_f = 2.0 – 2.5$.

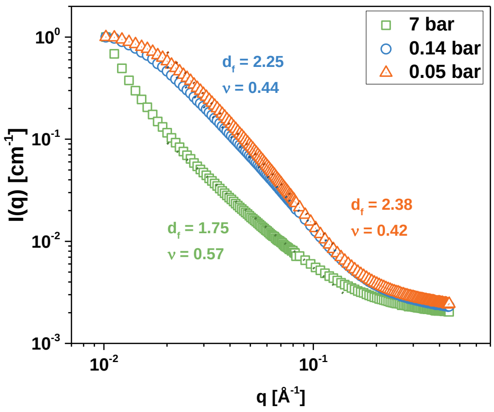

Figure 1: Scattering intensity as a function of the momentum transfer q of hbPE synthesized at different pressure.

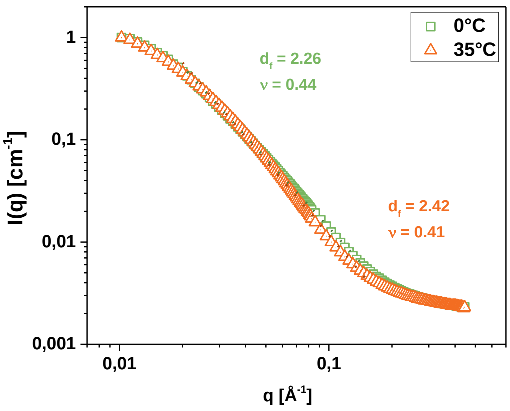

Figure 2: Scattering intensity as a function of the momentum transfer q of hbPE synthesized at different temperature.

The fractal dimension of PE synthesized at high pressure (7 bar) is 1.75, which indicates a linear topology. PE samples from low reaction pressure display d_f values of 2.25 and 2.38, respectively, referring to a polymer with high branching density. The topological difference of PE with different reaction temperature is less pronounced. PE from 0 °C and 35 °C show d_f values of 2.26 and 2.42, respectively. However, it is obvious that the branching density grows with increasing temperature. Another affecting parameter is the time of polymerization. The conduct of d_f indicates that the branching density increases with higher synthesis duration as $d_f = 1.52$ after 3 h but $d_f = 1.75$ after 20 h.

Consequently one can sum up that the production of PE with linear topology is favored at high pressure, low temperature and longer polymerization whereas compact and highly branched PE topologies are obtained at low pressure, elevated temperature and short reaction time.

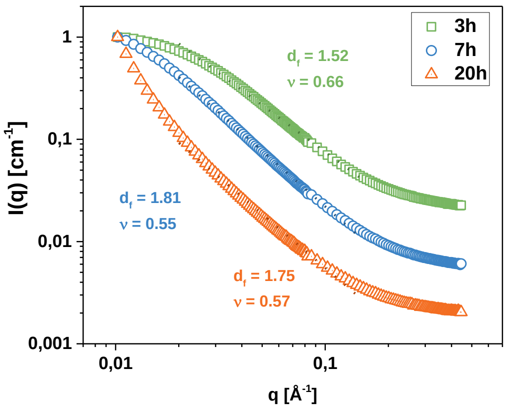

Figure 3: Scattering intensity as a function of the momentum transfer q of hbPE synthesized at different duration.

These results are correlated with the experiments based on HT-SEC, DLC, SLS and solution viscosity measurements as well as computer simulation. The interpretation leads to novel insights into the development of the branching structure under the late transition catalytical reaction and is currently under preparation for publication.

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