In collaboration with:

Detecting different types of long chain branching by means of extensional characterization

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INTRODUCTION

High cis-polybutadiene represents one of the most important raw materials for tire industry. It is commonly used in a variety of parts of the tire, like sidewall, tread and rim strip.

Improving the knowledge about its mechanical behavior and how this is related to the molecular structure allows improving the processability of uncured rubber compounds and also the performance (low hysteresis, high tensile strength and resistance to wear) of cured rubber compounds.

The polymers used in this work are characterized by different molecular architecture in terms of molecular weight, branching content, and polydispersity. The investigation started with tests conducted in the linear viscoelasticity field and then moved into the range of nonlinear viscoelasticity with extensional rheology experiments.

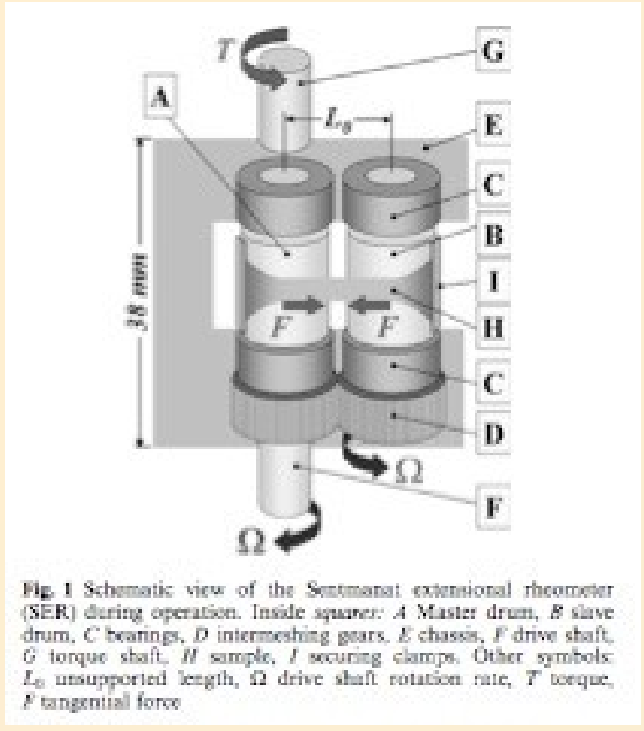
In order to better distinguish the samples response, we conducted experiments on raw polymers as well as on their concentrated, entangled solutions.

Intriguing results were obtained in particular for two of the four investigated samples as they showed very different extensional behavior in solution although the undiluted and diluted polymers had practically the same dynamic-mechanical spectrum. Furthermore, the ranking of strain hardening was even inverted in the solutions with respect to the undiluted polymer. This observation in our opinion allows speculating that, due to entanglement dilution, the presence of multiple branching points becomes more evident in solution when the polymer has a complex branched structure (e.g. comb-like).

MATERIALS AND METHODS

Table 1

SAMPLE	M_w g/mol	MWD	1,4 CIS %
PBR-HMW (High Molecular Weight)	470000	3.9	95.7
PBR-WD (Wide Distribution)	424000	4.1	97
PBR-HB (High Branching)	389000	3.0	96
PBR-MB (Moderate Branching)	338000	2.6	95



Sentmanat et al., Rheol Acta (2004)

MATERIALS

The polybutadiene samples used in this work were produced by Versalis S.p.A. through a stereospecific polymerization mechanism with metal-alkyls based catalysts. The concentrated solution were prepared with squalene as solvent and cyclohexane as co-solvent. Three different concentrations (weight of polymer/total weight of solution) were used: 70%pol, 50%pol, 30%pol. Molecular structure data was evaluated through GPC analysis and they are collected in Table 1.

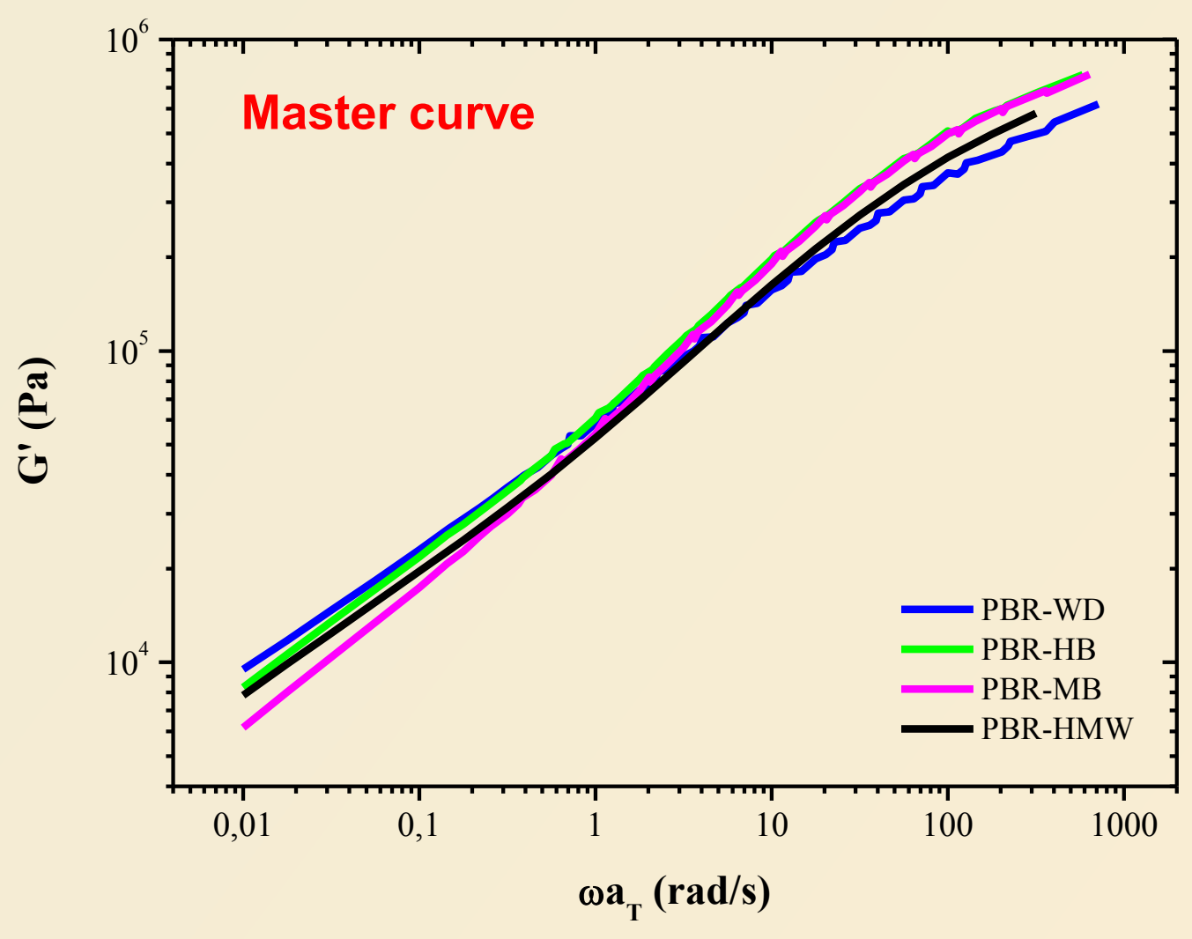
METHODS

Small Amplitude Oscillatory Shear measurements were performed on both raw polymers and solutions with a rotational rheometer RMS800 (Rheometrics Inc.). A parallel-plate configuration (D= 8 mm) was adopted in order to investigate the dynamic-mechanical behavior with the following temperatures: 35°C, 50°C, 70°C, 90°C and 110°C. Then, master curves were realized with T=110°C as reference temperature.

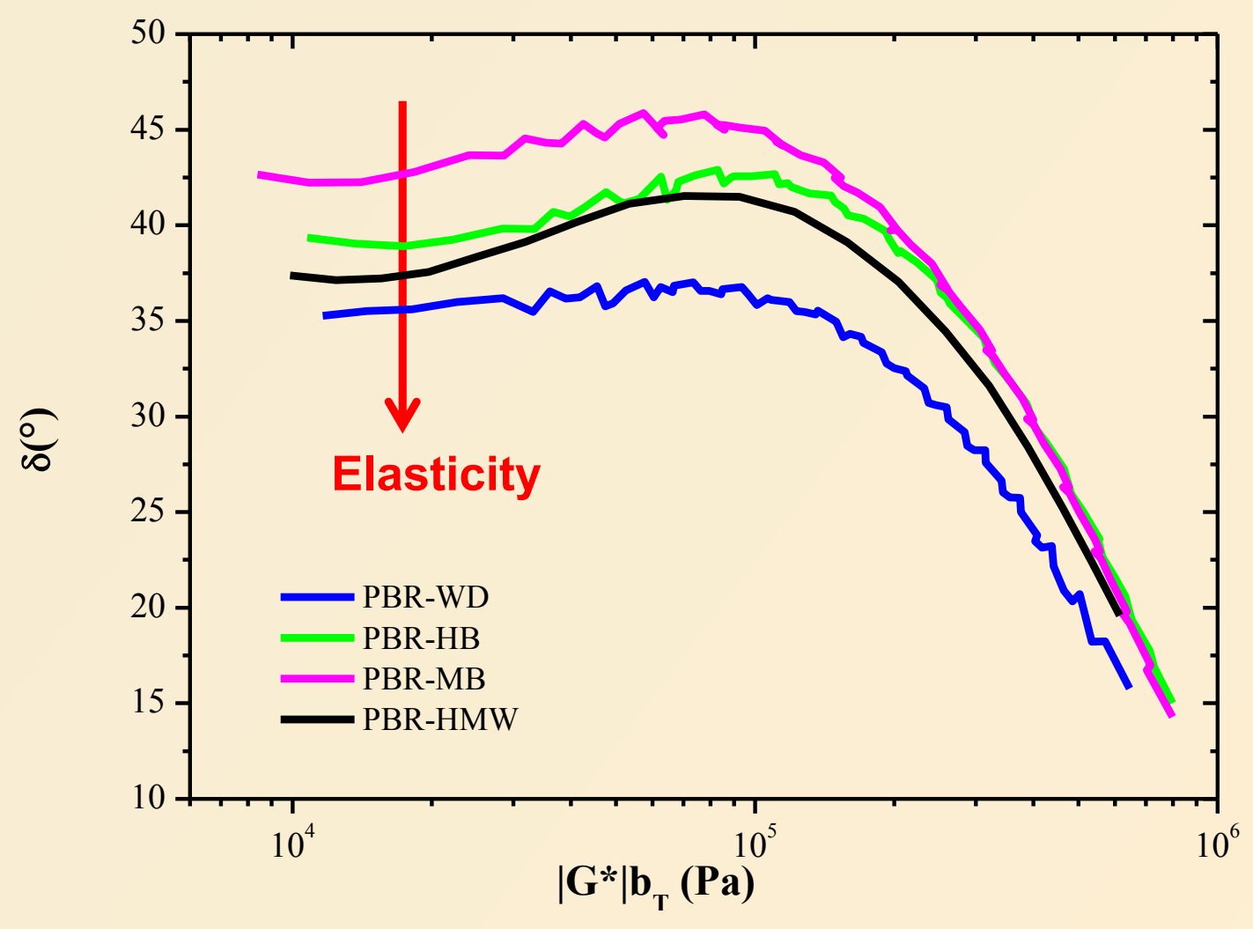
Extensional stress growth measurements were performed for both undiluted and diluted polymer samples, with a rotational rheometer Anton Paar-Physica MCR501 equipped with SER (shown above). The tests were performed at T=25°C with different Hencky strain rates in the range 0.001 [1/s] - 1 [1/s], using two different sample geometries. In almost all tests a Hencky strain of 3.5 was achieved but in some cases larger values were reached adopting an initial slightly oblique positioning of the polymeric fiber on SER drums.

Results and Discussion

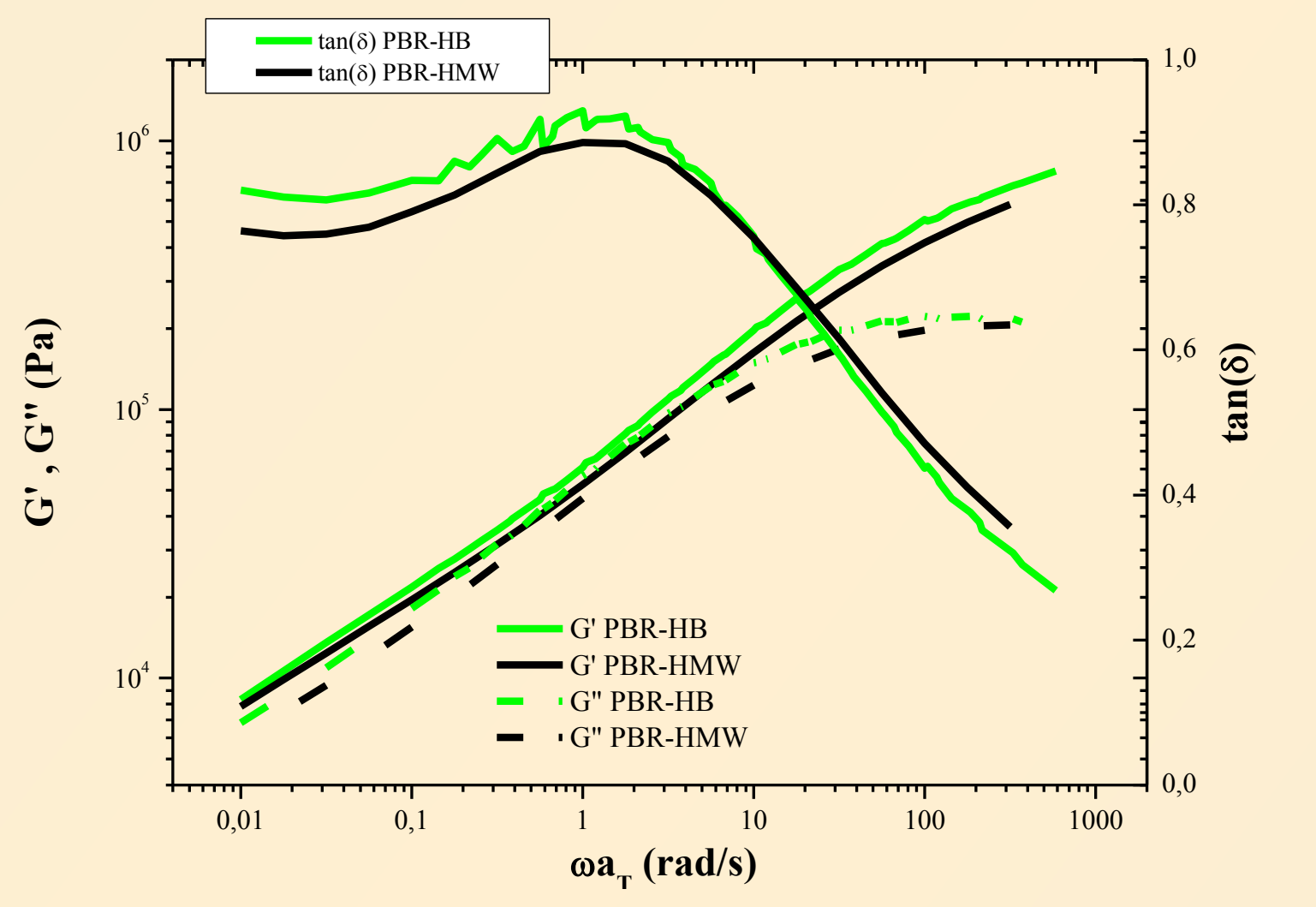
Linear Viscoelasticity of undiluted polymers



The DMA spectrum is quite similar for all the tested samples, due to the combined effect of molecular weight, branching and polydispersity.

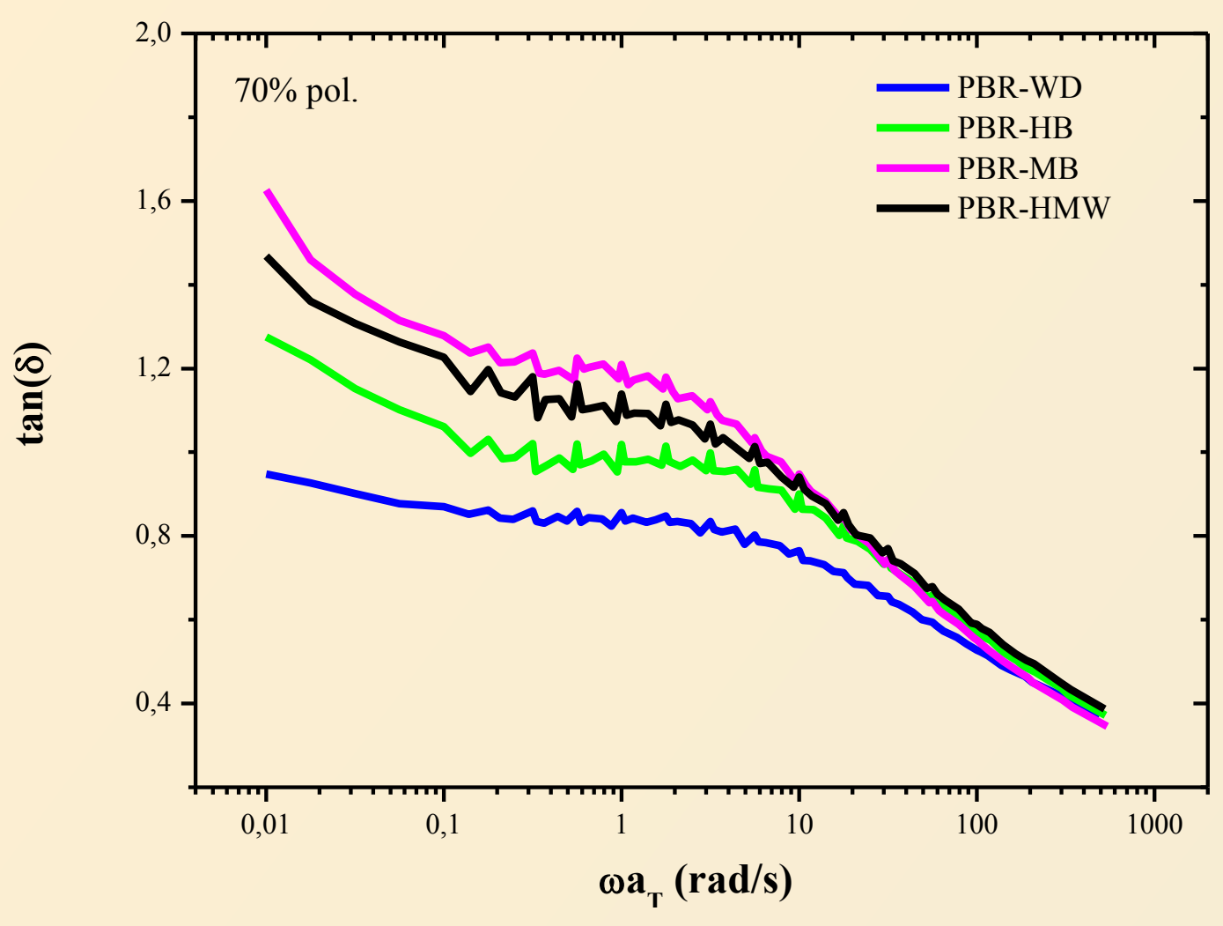


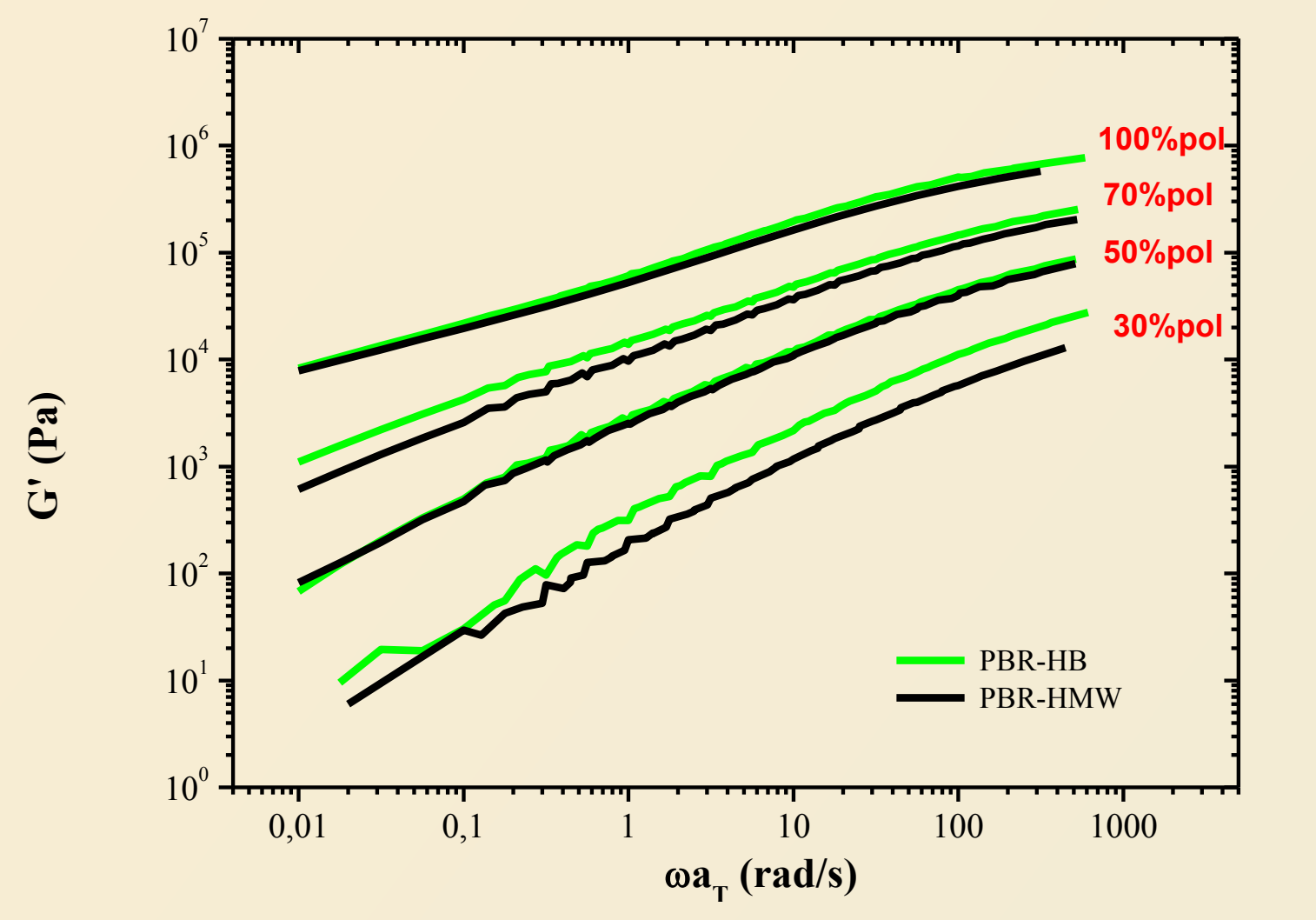
The van Gurp - Palmen plot is frequency-independent and highlights the architectural and polydispersity differences, in particular the effects of LONG CHAIN BRANCHING.



In particular, two samples with high branching content and high molecular weight have different branching patterns though showing almost the same dynamic-mechanical behavior.

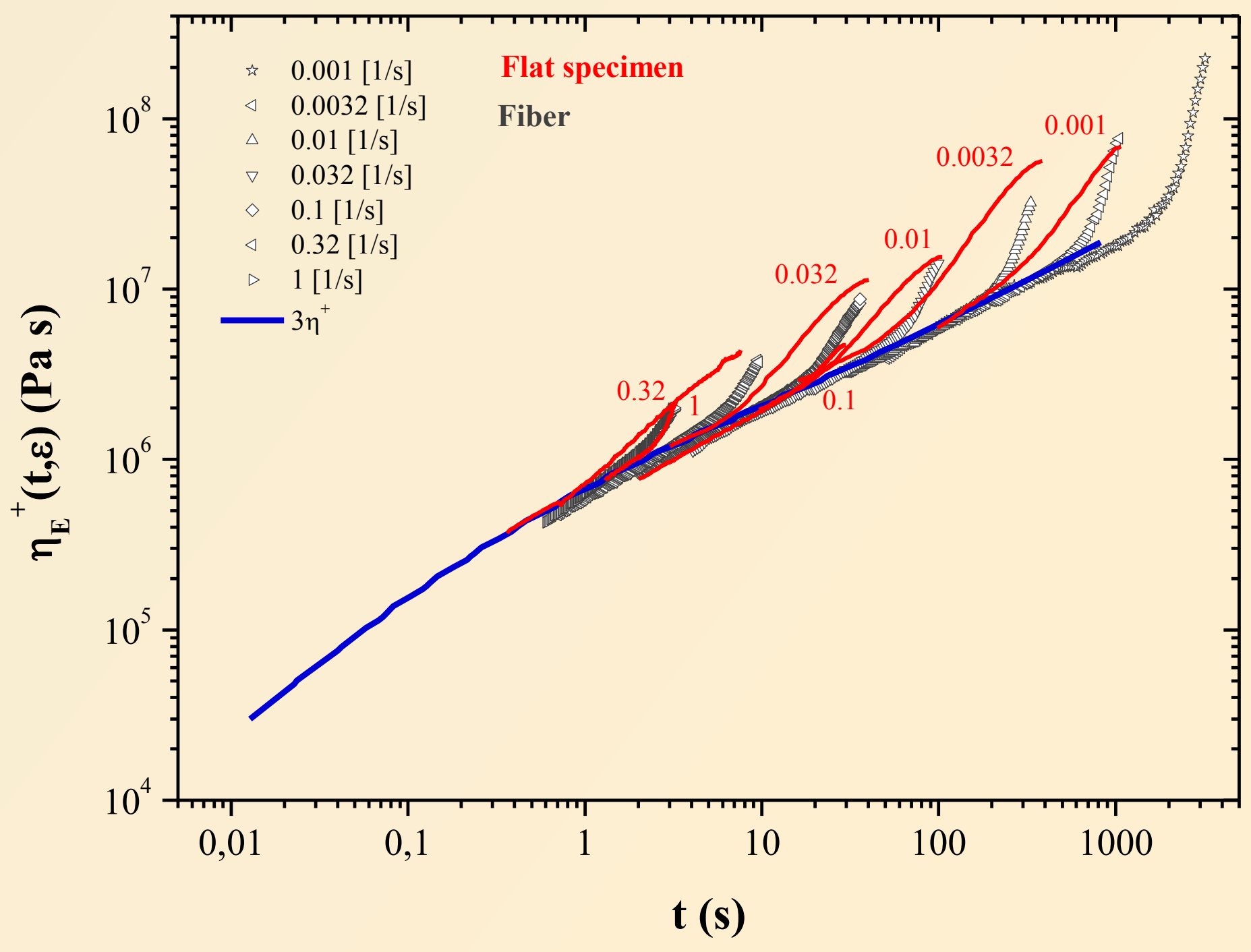
Linear Viscoelasticity of entangled solutions





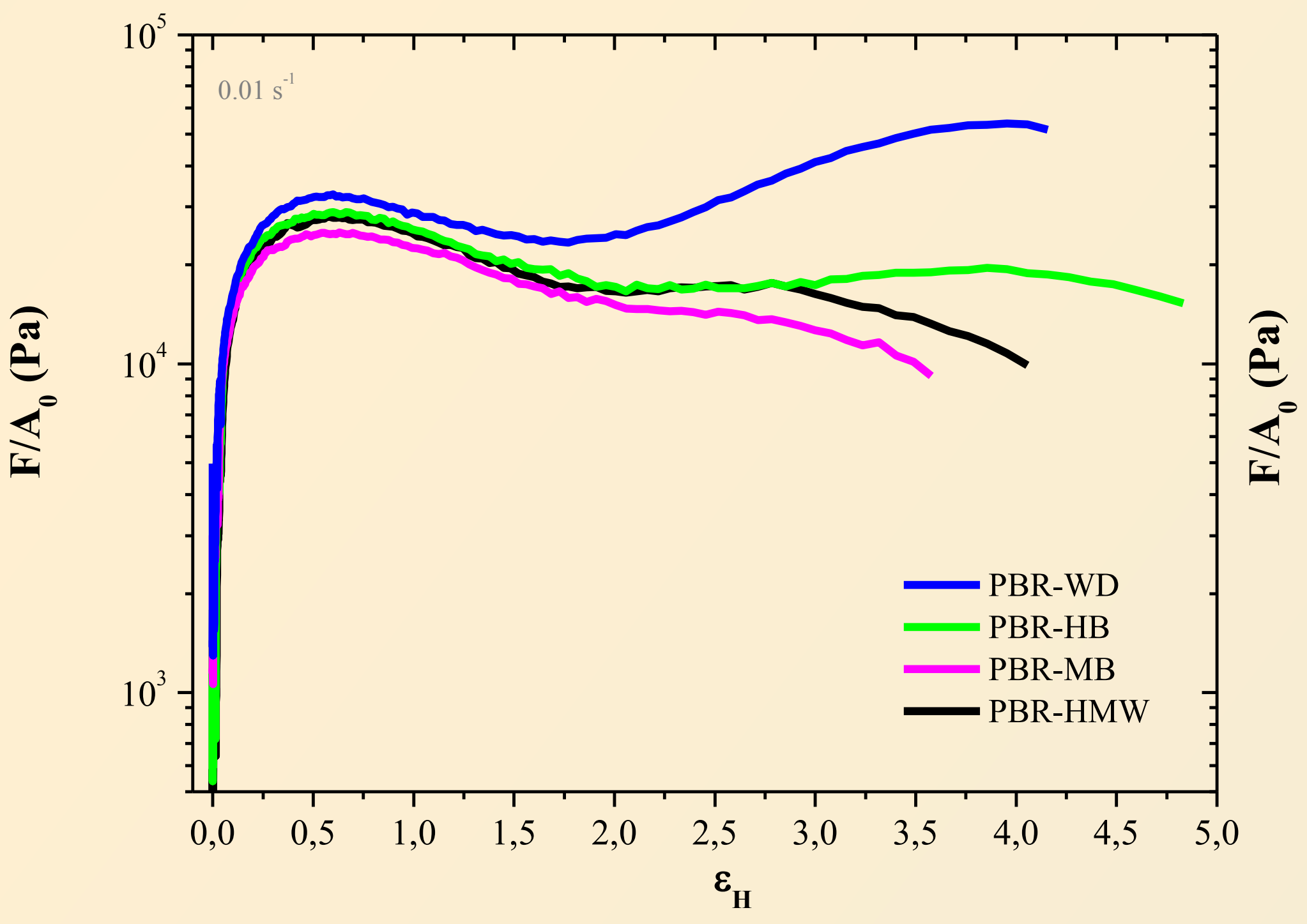
Dilution allows better appreciating the differences between the polymers because the rheological effects of branching points become more relevant with dilution.

Geometry effect in extensional tests

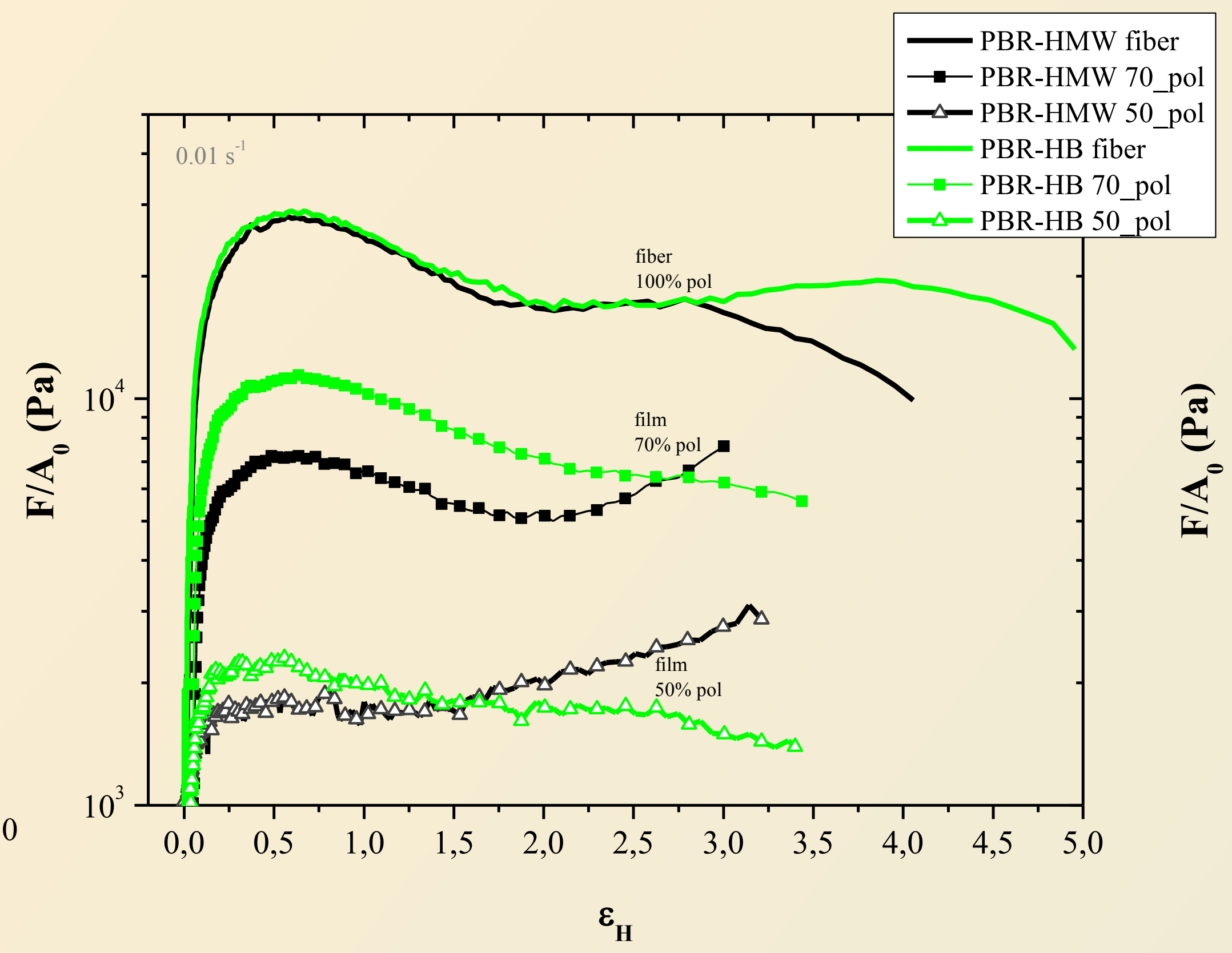


Fiber geometry allows achieving a homogeneous uniaxial extensional flow due to the symmetry of the specimen cross-section. This also allows obtaining an excellent reproducibility of data as well as higher elongations at break when compared to flat specimens.

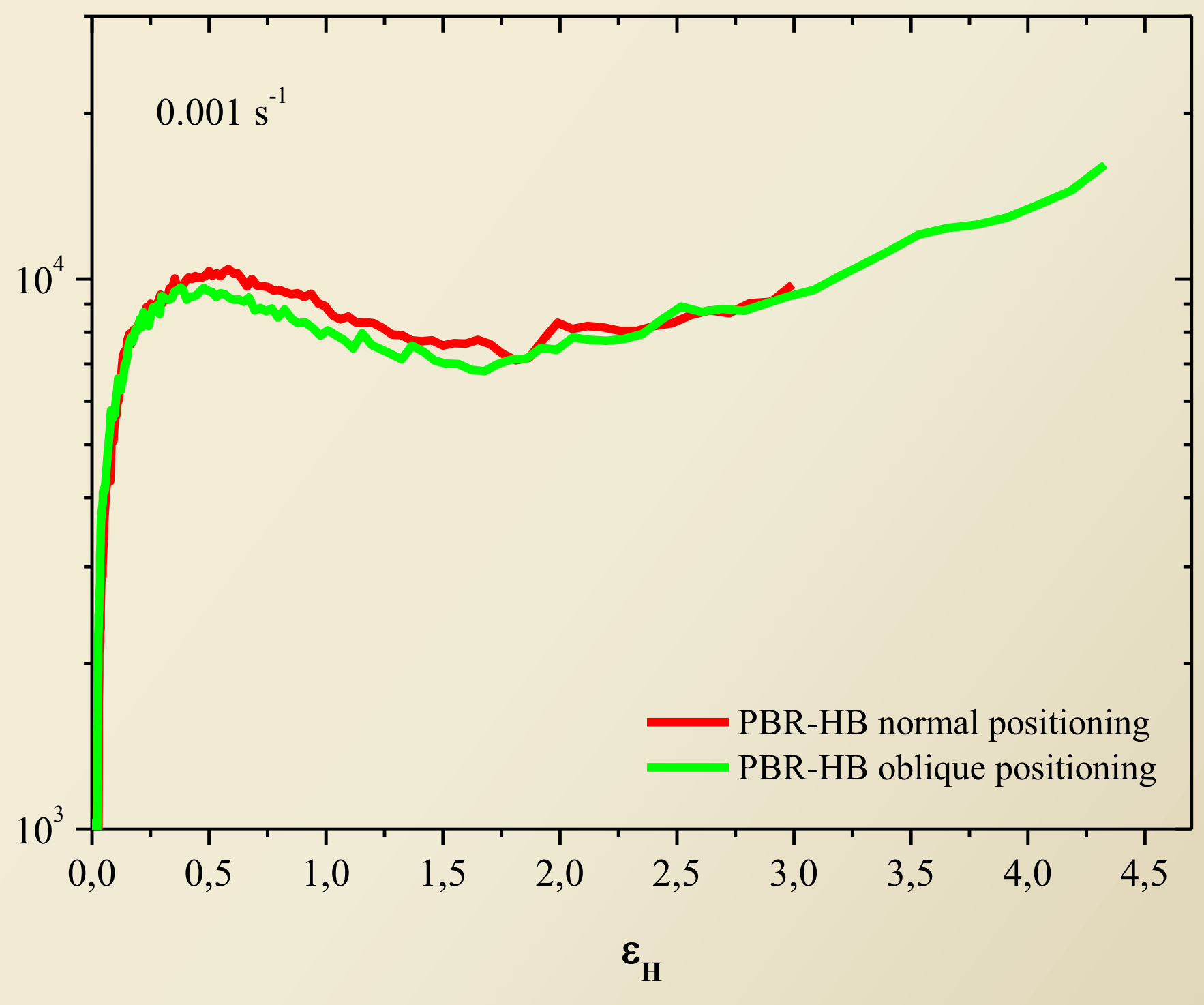
Extensional rheometry



The strain at break of the investigated samples is large. This allows testing the rheological response at very large strain where also the differences between polymer samples are large.



Dilution can change completely the ranking in terms of strain hardening. In solution, the PBR-HMW sample, having a higher branching point density, shows larger strain hardening compared to sample PBR-HB. This indication is in accordance with the light scattering characterization of PBR-HMW sample.



The oblique positioning of the fiber specimen on SER drums allows reaching larger deformations, needful to investigate the type of long chain branching of polymer samples.

CONCLUSIONS

When the polymer structure is not known *a priori*, it is generally very difficult to relate the rheological behavior to a specific structural characteristic. When dealing with commercial polymers, it is indeed hard to discriminate the combined effects of MW, branching and polydispersity. In this work we have shown that testing entangled solutions can be very helpful for highlighting the different effects of different branching point densities. Furthermore, using fiber specimens and adopting a slightly oblique positioning of the specimen on the SER drums, we have been able to extend significantly the "standard" range of Hencky strain (<3.5 ca). This is particularly important with polymers showing large strain at break.