

## High temperature quadruple-detector size exclusion chromatography for topological characterization of polyethylene

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## 1. Theoretical Background

The mean square radius of gyration  $R_G$  is a physical quantity to determine the size of a macromolecule and is defined as the average squared distance of any scattering point in the molecule from its center of mass.

$$R_G = \left( \frac{1}{N} \sum_k R_k^2 \right)^{1/2} \quad (S1)$$

The molar mass dependence on  $R_G$  is expressed by

$$R_G = K \cdot M^\nu \quad (S2)$$

where the exponent  $\nu$  shows values characteristic for the scaling of the macromolecules and  $K$  denotes a constant. The hydrodynamic radius  $R_H$  is related to the translational diffusion coefficient  $D$  by the Stokes-Einstein relation

$$R_H = \frac{k_B T}{6\pi\eta_0 D} \quad (S3)$$

where  $k_B$  is the Boltzmann's constant and  $\eta_0$  is the viscosity of solvent. Consequently  $R_H$  quantifies the size of polymer in solution including contributions from the solvation core. Another essential parameter for the structural analysis of dilute macromolecules is the viscosity of the solution. The intrinsic viscosity  $[\eta]$  is the reduced viscosity extrapolated to  $c = 0$  and is expressed as

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c) = 2.5 \frac{V}{m} = \frac{10\pi}{3} N_A \frac{R^3}{M} \quad (S4)$$

Here,  $\eta_{sp}$  denotes the specific viscosity. The relationship between the intrinsic viscosity and the molar mass of a polymer in solution can be expressed by the Kuhn-Mark-Houwink-Sakurada (KMHS) equation

$$[\eta] = K_\eta \cdot M^\alpha \quad (S5)$$

where exponent  $\alpha$  depends on the topology and conformation statistics of the molecule in solution similar to  $\nu$  in eq.(S2). The viscosity dependent spherical radius can be expressed as

$$R_\eta = \left( \frac{[\eta]M}{(10\pi/3)N_A} \right)^{1/3} \quad (S6)$$

The apparent density gives information about the global compactness of the molecule and can be derived from the molar mass and  $R_G$

$$d_{APP} = \frac{3}{4\pi N_A} \frac{M_W}{R_G^3} \quad (S7)$$

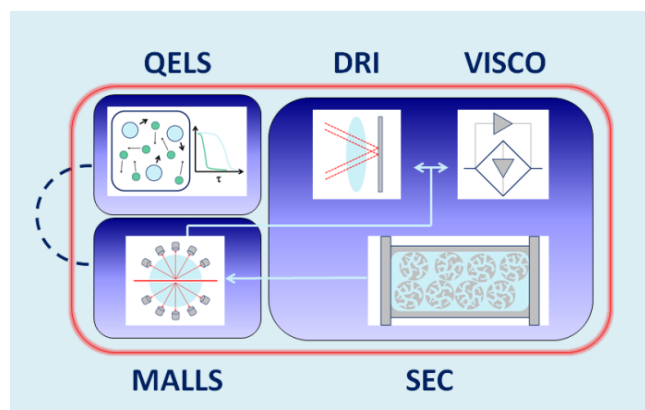
The degree of branching is given by

$$DB_{Frey} = \frac{2D}{2D + L} \quad (S8)$$

where  $D$  and  $L$  are the number of dendritic and linear units, respectively.

## 2. Experimental details

**Instrumentation:** High temperature size-exclusion chromatography (Figure S1) was performed with a PL-GPC 220 (Agilent Technologies, US) with an online degasser, an online preinjection filter and two PLgel Olexis (Agilent Technologies, US) columns packed with 13  $\mu\text{m}$  nominal particle size of polystyrene. Experiments were carried out at a flow rate of 1  $\text{mL min}^{-1}$  and an operating temperature of 150  $^{\circ}\text{C}$ . 1,2,4-trichlorobenzene (TCB, Aldrich, DE) was used as mobile phase. Threefold determination was applied to each sample which includes 3 separate dissolutions à 3 injections. The samples were dissolved in TCB with concentrations between 3.5-4  $\text{mg mL}^{-1}$ . The samples were dissolved between 1–3 h depending on the topology of the sample. The injection volume was set to 200  $\mu\text{L}$ . The SEC was coupled to four consecutive detectors: A DAWN Heleos-II 18 angle static light scattering photometer (MALLS, Wyatt Technology, US), DYNAPRO Nanostar (DLS, Wyatt Technology, US), a four-capillary viscometer (Agilent Technologies, US) and a differential refractometer (Agilent Technologies, US). It should be mentioned that the VISCEXperiment Details and DRI detector are in parallel arrangement and the mobile phase is split in half before. The DLS (known also as QELS, quasi elastic light scattering) is connected to the MALLS detector using an optical fiber which is positioned at detector channel number 12 ( $99^{\circ}$  relative to the incident laser beam). For normalization of MALLS photodiodes, interdetector delays as well as band broadening calculations measurement of Polystyrene-30 kDa (PSS, DE) with narrow molar mass distribution was performed. Polystyrene-200 kDa (PSS, DE) was used for calculating dRI-constant. Refractive index increment  $\partial n/\partial c$  for polyethylene ( $\partial n/\partial c = -0.104 \text{ mL/g}$  in 1,2,4-TCB at  $T = 135^{\circ}\text{C}$ ) was taken from literature.<sup>1</sup> The raw data was processed and analyzed using the software ASTRA (Wyatt Technology, US). Zimm model (fit degree 1) was applied for static light scattering calculations. All averages and standard deviations were calculated from 3 determinations. Parameters  $R_G$  and  $R_{\eta}$  are z-average values, whereas  $R_H$  is an uncertainty-weighted average. Viscosities were determined using model described by Huggins.<sup>2</sup>  $[\eta]$  are weight-average values.



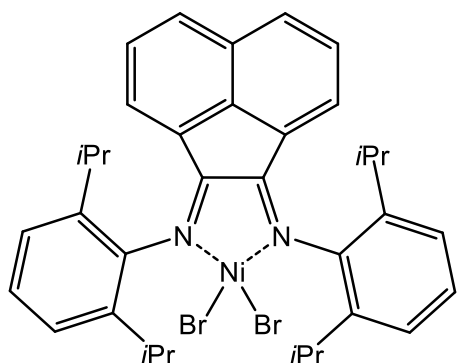
**Figure S1:** Measuring principle of quadruple detector HT-SEC.

**Chemicals:** 1,2,4-Trichlorobenzene was purchased from Sigma Aldrich with a purity of  $\geq 99\%$  and stabilized with 1  $\text{g L}^{-1}$  Butylated hydroxytoluene (Roth,  $\geq 98\%$ ) to prevent thermo-oxidative degradation. LLDPE and NIST1484a (NIST) polyethylene standard were purchased from Sigma Aldrich (DE). LDPE was purchased from VEB Leuna Werke (DE).

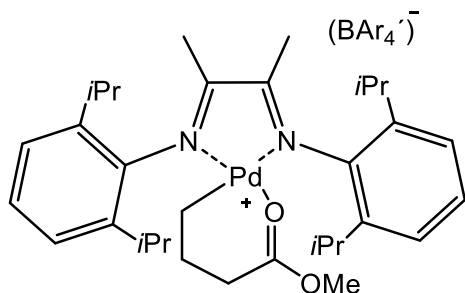
**Samples:** All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Toluene and chlorobenzene were dried over sodium and  $\text{CaH}_2$ , respectively, and freshly distilled before use. Ethylene (99.9 %, SIAD) was purified by passing through the column packed with deoxygenating

catalyst and molecular sieves.  $\alpha$ -diimine complexes [N,N'-bis(2,6-diisopropyl)-acenaphthenediimine] NiBr<sub>2</sub> (CAT1) and [(N, N'-bis(2,6-diisopropyl)butane-2,3-diimine)Pd(CH<sub>2</sub>)<sub>3</sub>COOCH<sub>3</sub>]<sup>+</sup> [BAr'<sub>4</sub>] (Ar'=3,5-bis(trifluoromethyl)phenyl) (CAT2) (for chemical structure see Supporting Information, S1) were prepared according to literature procedures.<sup>3</sup> Methylaluminoxane (MAO, 10 % wt toluene solution) was purchased from Aldrich and used as received for CAT1. *Procedure for PE using nickel catalyst (LINPE)*: A 250 mL glass pressure ampoule with a magnetic stirring bar was evacuated and placed under an ethylene atmosphere. Dry toluene (10-100 ml) and 1.3 mL (2.0 mmol) of MAO was added, and the solution was then allowed to stir under 1.5 bar of ethylene for 10 min at prescribed polymerization temperature. Polymerization was started by injection of nickel catalyst solution (1-10  $\mu$ mol). Pressure of ethylene was kept constant during reaction. After allotted polymerization time the reaction was terminated by pouring the polymerization mixture to a large excess of ethanol acidified by HCl. Polyethylene was separated by filtration, washed by ethanol and dried under vacuum overnight at 50 °C. *Procedure for PE using palladium catalyst (BPE, HBPE)*: A glass pressure ampule with a magnetic stirring bar was charged with the appropriate amount of solid catalyst CAT2. The desired volume of dry chlorobenzene was transferred via cannula to the reaction ampule. After stirring for 10 min at desired temperature, the polymerization was started by the saturation of reaction mixture with ethylene. Ethylene pressure was controlled by a gas regulator. For the polymerizations at 0.09 bar of ethylene, a mixture of ethylene and nitrogen was prepared and bubbled through the reaction mixture. After allotted polymerization time the ethylene pressure was released and the reaction was quenched by addition of 0.3 ml of triethylsilane. The chlorobenzene was evaporated on a rotary evaporator. Obtained polyethylene was dissolved in toluene and passed through a column packed with silica gel and alumina to remove the rest of catalyst. Then, the solvent was evaporated and obtained polymer was dried under vacuum overnight at 50 °C. (A summary of conditions used for sample preparation can be seen in Table S1.)

### 3. Chemical structure of catalysts



[N,N'-bis(2,6-diisopropyl)-acenaphthenediimine] NiBr<sub>2</sub> (CAT1)



[(N, N'-bis(2,6-diisopropyl)butane-2,3-diimine)Pd(CH<sub>2</sub>)<sub>3</sub>COOCH<sub>3</sub>]<sup>+</sup> [BAr'<sub>4</sub>]<sup>-</sup> (Ar'=3,5-bis(trifluoromethyl)phenyl) (CAT2)

### 4. Synthesis conditions used for branched PE preparation

Table S1: Summary of conditions used for branched PE preparation.

PE	Cat.	n(cat.) [μmol]	MAO/cat.	Volume [ml]	T [°C]	p(ethylene) [bar]	Time [h]	Yield [g]	Br./ 1000C <sup>a</sup>	T <sub>m</sub> <sup>b</sup> [°C]
<b>LINPE</b>	<b>CAT1</b>	<b>1.2</b>	<b>750</b>	<b>100</b>	<b>23</b>	<b>1.5</b>	<b>0.33</b>	<b>1.11</b>	<b>nd</b>	<b>74</b>
<b>HBPE</b>	<b>CAT2</b>	<b>2.1</b>	<b>-</b>	<b>12</b>	<b>35</b>	<b>0.09</b>	<b>21</b>	<b>0.39</b>	<b>100</b>	<b>Amorph.</b>
<b>BPE</b>	<b>CAT2</b>	<b>5.7</b>	<b>-</b>	<b>14</b>	<b>0</b>	<b>7</b>	<b>22</b>	<b>0.83</b>	<b>94</b>	<b>Amorph.</b>

<sup>a</sup> number of branches per 1000 C atoms determined by <sup>1</sup>H NMR

<sup>b</sup> melting temperature determined by DSC from 2<sup>nd</sup> heating run (10°C/min)

## 5. Appendix

**Table S2: Number-, weight and z-average molar mass, molar mass distribution ( $M_w/M_n$ ), radius of gyration, hydrodynamic radius, viscometric radius and intrinsic viscosity of PE samples determined using fourfold HT-SEC, including error estimations.**

	$M_n$ [kg/mol]	$M_w$ [kg/mol]	$M_z$ [kg/mol]	$\bar{D}$	$R_G$ [nm] <sup>a</sup>	$R_H$ [nm] <sup>b</sup>	$R_\eta$ [nm] <sup>a</sup>	$[\eta]$ [mL/g] <sup>c</sup>
LLDP	$54.8 \pm 5.2$ (9)	$123.7 \pm 4.5$ (7.9)	$217.8 \pm 34.2$ (59.3)	$2.26 \pm 0.24$ (0.42)	$35 \pm 2$ (3)	$16 \pm 3$ (5)	$22 \pm 2$ (4)	$140.7 \pm 9$ (15)
NIST	$105.5 \pm 5.6$ (9.7)	$108.4 \pm 5.0$ (8.6)	$111 \pm 14.7$ (25.4)	$1.03 \pm 0.02$ (0.03)	$30 \pm 3$ (5)	$14 \pm 4$ (7)	$15 \pm 1$ (1)	$172.3 \pm 12$ (20)
LDPE	$75.9 \pm 4.2$ (7.3)	$492.5 \pm 72.6$ (125.8)	$2928.2 \pm 355.9$ (616)	$6.62 \pm 1.22$ (2.12)	$58 \pm 3$ (5)	$30 \pm 6$ (10)	$40 \pm 3$ (6)	$97 \pm 4$ (7)
LINPE	$257.3 \pm 22.1$ (38.4)	$295.8 \pm 24.1$ (41.7)	$401.7 \pm 9.4$ (16.3)	$1.15 \pm 0.05$ (0.08)	$47 \pm 1$ (1)	$26 \pm 1$ (1)	$28 \pm 1$ (1)	$325.4 \pm 12$ (21)
BPE	$320.8 \pm 3.6$ (6.3)	$376.3 \pm 1.7$ (2.9)	$426.7 \pm 0.9$ (1.7)	$1.17 \pm 0.01$ (0.02)	$24 \pm 1$ (1)	$18 \pm 1$ (1)	$18 \pm 1$ (1)	$74.9 \pm 1$ (1)
HBPE	$161.3 \pm 16.6$ (26.7)	$210 \pm 8.8$ (15.3)	$272 \pm 5.9$ (10.3)	$1.30 \pm 0.08$ (0.14)	$16 \pm 1$ (2)	$12 \pm 1$ (2)	$11 \pm 1$ (1)	$28.9 \pm 2$ (4)

All values stated as followed: Average  $\pm$  standard error (standard deviation). All averages and uncertainties calculated from triple determination as stated in experimental section. <sup>a</sup>z-average value, <sup>b</sup>uncertainty-weighted average, <sup>c</sup>weight-average value.

**Table S3. Weight-average contraction factors  $g$  and  $g'$  of PE samples. Contraction factors  $g$ ,  $g'$  and drainage parameter  $\epsilon$  determined at  $M_w=150\text{kg/mol}$ .**

Sample	$g_w$	$g'_w$	$g$ (150kg/mol) <sup>a</sup>	$g'$ (150kg/mol) <sup>a</sup>	$\epsilon$ (150kg/mol) <sup>a</sup>
LLDPE	$1.15 \pm 0.08$ (0.14)	$0.90 \pm 0.03$ (0.04)	0.896	0.862	1.357
NIST	$1.01 \pm 0.06$ (0.11)	$0.85 \pm 0.02$ (0.04)	0.739	0.977	0.461
LDPE	$0.46 \pm 0.07$ (0.12)	$0.58 \pm 0.02$ (0.03)	0.413	0.507	0.769
LINPE	$1.14 \pm 0.06$ (0.11)	$1.04 \pm 0.09$ (0.16)	-	-	-
BPE	$0.37 \pm 0.02$ (0.03)	$0.18 \pm 0.01$ (0.01)	0.424	0.182	2.424
HBPE	$0.25 \pm 0.01$ (0.01)	$0.11 \pm 0.01$ (0.01)	0.233	0.110	1.516

Weight-averaged contraction factor stated as followed: Average  $\pm$  standard error (standard deviation). <sup>a</sup>To calculate  $g$  and  $g'$  linear sample LINPE was used as a linear reference.

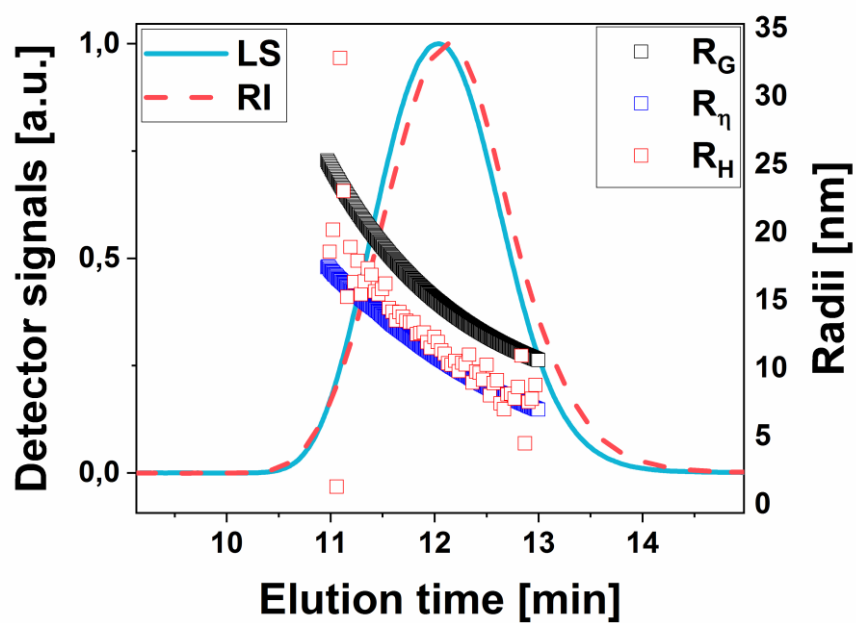


Figure S2. Radii  $R_G$ ,  $R_H$  and  $R_\eta$  versus elution time of sample LLDPE obtained by fourfold HT-SEC.

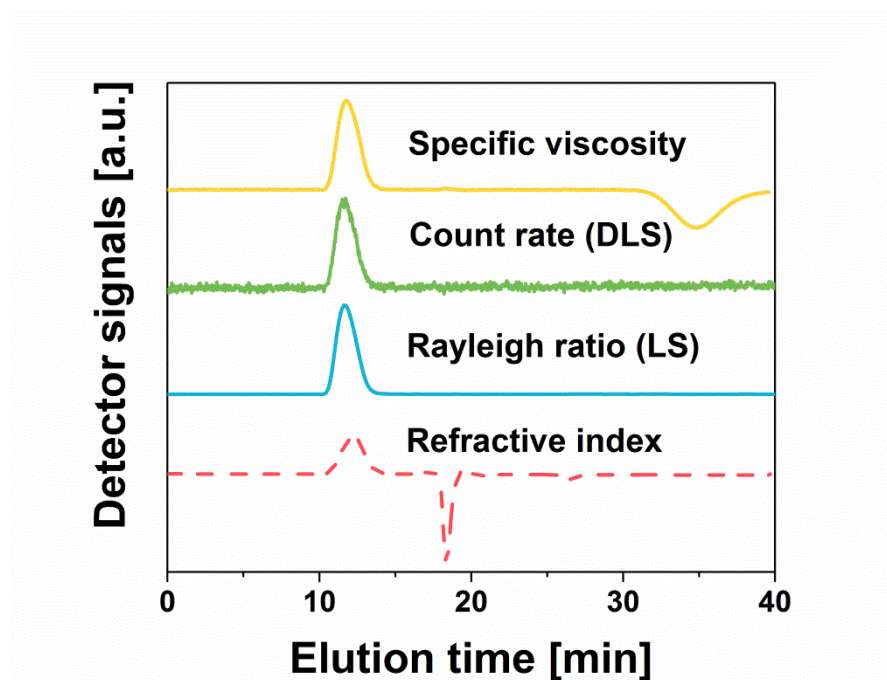
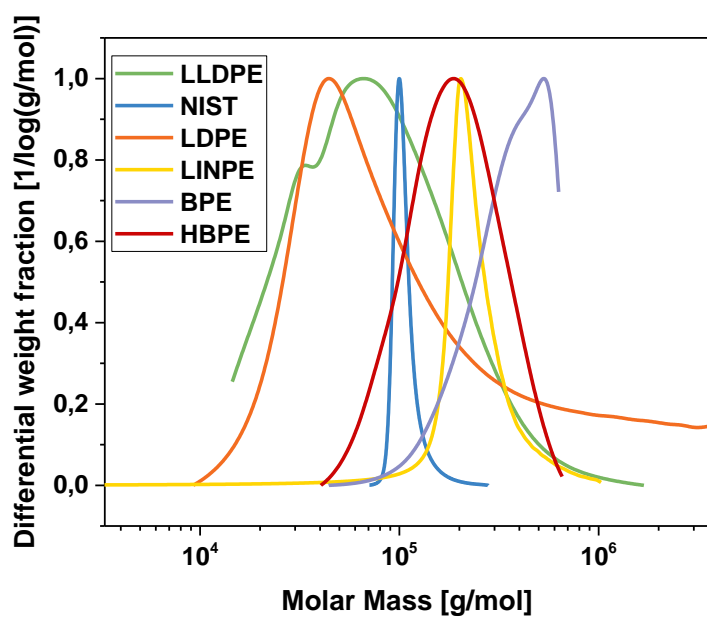
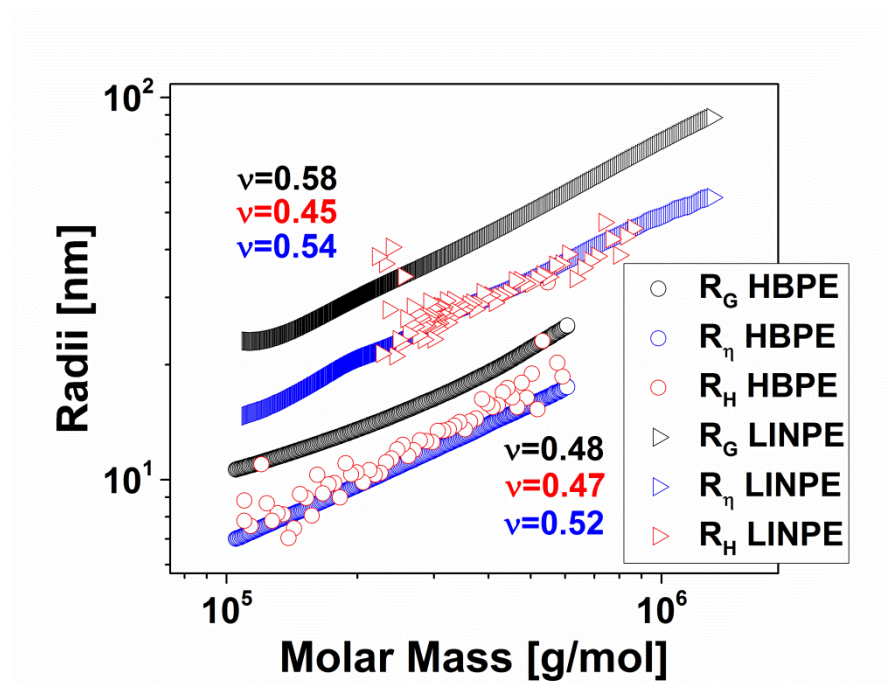


Figure S3. Chromatograms obtained by fourfold HT-SEC.

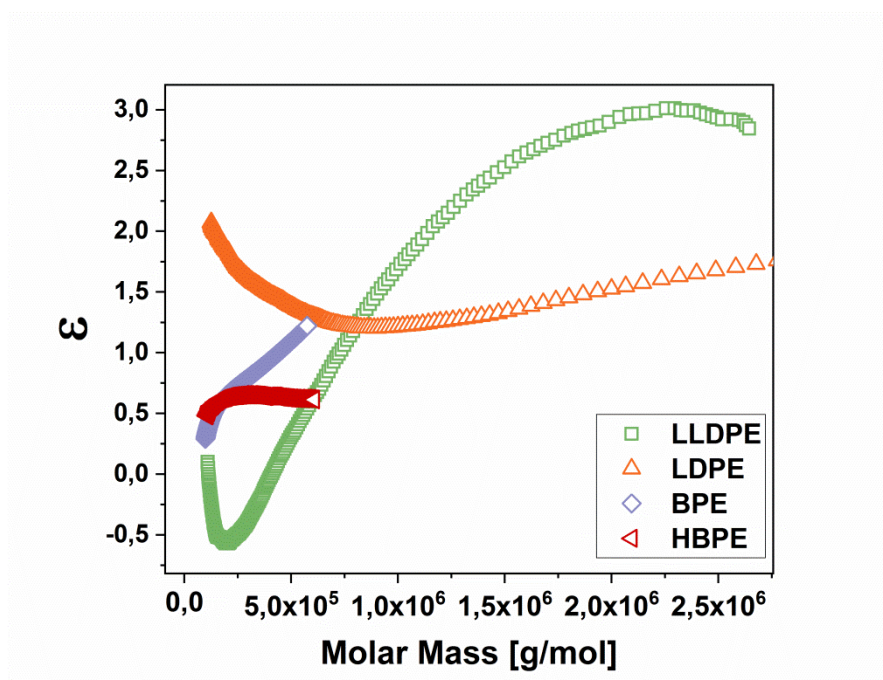


**Figure S4.** Molar Mass distribution determined using fourfold detector HT-SEC.



**Figure S5.** Conformation plots from different radii of samples HDPE (circles) and LINPE (triangles). The  $\nu$  values denote the slope of the respective plot.





**Figure S6.** Drainage parameter  $\varepsilon$  as a function of molar mass for samples LLDPE, LDPE, BPE and HBPE.

## References

- (1) S.Michielsen, Specific Refractive Index Increments of Polymers in Dilute Solution, Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; *Polymer Handbook*; 4<sup>th</sup> Edition, John Wiley & Sons, **1999**.
- (2) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, 64, 2716–2718.
- (3) Johnson, L. K.; Killian, C. M.; Brookhart, M.; Hill, C.; Carolina, N. *J. Am. Chem. Soc.* **1995**, 117, 6414–6415.