A NOVEL STRAIN HARDENING INDEX SHI FOR LONG-CHAIN BRANCHED POLYMER MELTS

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ABSTRACT

Strain hardening of polymer melts in extensional flows is considered as a desirable rheological feature because it stabilizes homogeneity of free surface flows such as, e.g., film blowing, blow molding and fiber spinning. Relating strain hardening to molecular characteristics has been a long-standing challenge in rheology, but while long-chain branching (LCB) is known to be a decisive feature to enhance strain hardening, a quantitative relation between strain hardening and molecular topology is still missing. We propose a novel strain hardening index SHI that can be used to assess the strain hardening behaviour and to compare strain hardening of polymer melts with different topologies and different chemistries investigated at different temperatures.

INTRODUCTION

The standard method of measuring strain hardening is via the strain hardening factor (SHF), i.e., by taking the ratio of the elongational stress growth coefficient to the linear-viscoelastic start-up viscosity. The SHF indicates the change of *transient* strain hardening with strain rate in start-up elongational flow at a prescribed Hencky strain and at a particular experimental temperature for the specific polymer system considered. However, as the SHF does not contain a material time constant, it cannot be used to compare the strain hardening potential of polymer systems with different chemistries and different topologies.

Recent progress in living anionic polymerization technology has enabled the synthesis of well-defined model polystyrene (PS) polymer systems such as pom-pom polymers (**Fig. 1**) in quantities allowing extensive elongational characterization. We have shown that the elongational viscosity of these systems is well described by the Hierarchical Multi-mode Molecular Stress Function (HMMSF) model or the Enhanced HMMSF (EHMMSF) model[1] up to the steady-state elongational viscosity or in case of fracture, the maximal elongational viscosity. These models take into account hierarchical relaxation and dynamic dilution of the backbone by the side arms. We consider the maximal elongational viscosity of pom-poms as a function of the Weissenberg number Wi_d based on the disengagement time. We show that the maximal elongational viscosity normalized by the zero-shear viscosity is a useful measure of strain hardening, and we define a novel strain hardening index SHI. We discuss the effect of molecular topology, i.e. the effect of molecular weight of backbone as well as number and molecular weight of side arms on the strain hardening behaviour. In addition, we compare the strain hardening behaviour of pom-poms to the strain hardening of several polydisperse (commercial) LDPE melts. We show that the normalized elongational viscosity reaches a maximal value at $Wi_d \approx 2-8$, and we show that the experimentally measured strain hardening index SHI_m can be used to assess the strain hardening behaviour and to compare strain hardening of polymer melts with different topologies and different chemistries. From a one-mode HMMSF model, we derive a relation for the strain hardening index SHI, which is in nearly quantitative agreement with SHI_m up to SHI≈100.

MATERIALS

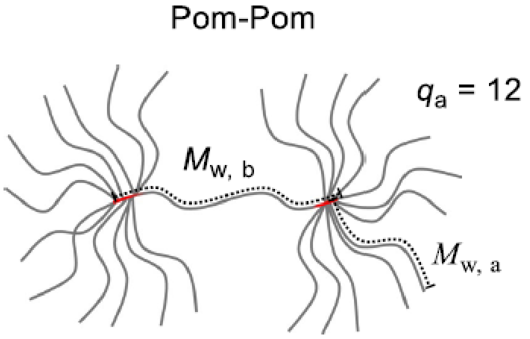

Fig. 1. Schematic representation of pom-poms.

A pom-pom polymer consists of a backbone chain of molecular weight $M_{w,b}$ with only one branch point at each end having q_a side arms of molecular weight $M_{w,a}$ (**Fig. 1**). We consider here the elongational viscosity of a series of 12 PS pom-poms as reported by Hirschberg et al.[2,3] comprising a wide range of $M_{w,a}$, $M_{w,b}$, and q_a (**Table 1**).

Table 1. Molecular characteristics of PS pom-poms.

Pom-Poms	**$M_{w,b}$ [kg/mol]**	**$M_{w,b}/M_n$ [-]**	**$M_{w,a}$ [kg/mol]**	**$M_{w,a}/M_n$ [-]**	**q_a [-]**	**M_w [kg/mol]**	**M_w/M_n [-]**
Pom-Pom $M_{w,b}$ – 2xq_a – $M_{w,a}$							
100k-2x12-24k	100	1.05	24	1.05	2x12	600	1.18
100k-2x12-40k	100	1.05	40	1.08	2x12	1060	1.16
100k-2x14-50k	100	1.05	50	1.20	2x14	1500	1.27
100k-2x22-25k	100	1.05	25	1.15	2x22	1200	1.15
220k-2x9-25k	220	1.06	25	1.08	2x9	670	1.08
220k-2x10-40k	220	1.06	40	1.10	2x10	1020	1.09
280k-2x22-22k	280	1.04	22	1.07	2x22	1248	1.15
400k-2x9-23k	400	1.10	23	1.14	2x9	814	1.15
400k-2x13-40k	400	1.10	40	1.15	2x13	1360	1.15
300k-2x24-40k	300	1.40	40	1.03	2x24	2220	1.40
100k-2x5-25k	100	1.05	25	1.05	2x5	350	1.12
220k-2x3-70k	220	1.06	70	1.04	2x3	640	1.11

The elongational rheology of the model PS pom-poms will be compared to the maximal viscosity of 6 commercial LDPE melts investigated by Wagner et al.[4] (2022) and Wagner and Hirschberg[1] (2023). The molecular characteristics of the LDPEs are summarized in **Table 2**.

Table 2. Characterization of LDPE melts.

Characteristics	**LDPE A**	**LDPE B**	**LDPE C**	**DOW150R**	**1840H-V**	**3020D**
Producer	Dow	Dow	Dow	Dow	BASF	BASF
M_w [kg/mol]	160	320	180	242	89	300
M_w/M_n	11	22	15	11	4	8
ρ_{RT} [g/cm^3]	0.920	0.919	0.918	0.921	0.920	0.94
MFR [dg/min]	2.0	8.5	3.9	0.18	-	-
E_a [kJ/mol]	65	65	65	-	-	64

THE STRAIN HARDENING INDEX SHI

As we will show in the following, the strain hardening index SHI depends on the product of two terms, one depending on the linear-viscoelastic (LVE) characterization of the melt in terms of the relaxation modulus *G(t)*, the other being a representative measure of stretch of chain segments. From the 1st and 2nd moment of the parsimonious relaxation time spectrum, the zero-shear viscosity η_0, the disengagement time τ_d and the steady-state compliance J_s^0 are obtained by

$$\eta_0 = \sum_i g_i \tau_i \tag{1a}$$

$$\tau_d = \frac{\sum_i g_i \tau_i^2}{\eta_0} \tag{1b}$$

$$J_s^0 = \frac{\sum_i g_i \tau_i^2}{\eta_0^2} \tag{1c}$$

To elucidate the essence of strain hardening, we simplify the HMMSF model to a one-mode model with relaxation time τ_d and modulus G_d representing the value of the relaxation modulus *G(t)* at time $t = \tau_d$,

$$G_d = G(t = \tau_d) \tag{2}$$

The stress tensor equation is then

$$\sigma(t) = \int_{-\infty}^{t} G_d / \tau_d \exp[-(t-t')/\tau_d] f^2(t,t') \mathbf{S}_{DE}^{IA}(t,t') dt' \tag{3}$$

and the evolution of stretch f is given by

$$\frac{\partial f}{\partial t} = f\,(\mathbf{K}:\mathbf{S}) - \frac{f-1}{\tau_d}(1-w_d^2) - \frac{(f^5-1)}{5\tau_d}w_d^2 \tag{4}$$

w_d is the dynamically diluted polymer fraction

$$w_d = (G_d / G_D)^{1/2} \tag{5}$$

with G_D being the dilution modulus of the HMMSF model[1,4]. In fast elongational flow and large values of $Wi_d = \dot{\varepsilon}\tau_d$, the elongational stress is obtained from Eq. (3) as

$$\sigma_E(Wi_d) \cong 5 f^2(Wi_d) G_d \tag{6}$$

At large Hencky strain, the square of the steady-state stretch $f^2(Wi_d)$ is obtained from Eq. (4) as

$$f^2(Wi_d) \cong \sqrt{5Wi_d} / w_d \tag{7}$$

From Eq. (6), the elongational viscosity is then given by

$$\eta_E(Wi_d) = \frac{\sigma_E(Wi_d)}{\dot{\varepsilon}} = \frac{\sigma_E(Wi_d)\tau_d}{Wi_d} \tag{8}$$

Normalized by the zero-shear viscosity η_0, this results in

$$\frac{\eta_E(Wi_d)}{\eta_0} \cong 5 f^2(Wi_d)\frac{G_d\tau_d/\eta_0}{Wi_d} = \frac{5}{w_d}\sqrt{5Wi_d}\,\frac{G_d J_s^0}{Wi_d} \tag{9}$$

From the right-hand side of this equation, we see that $\eta_E(Wi_d)$ decreases with increasing Wi_d according to $\eta_E(Wi_d) \propto Wi_d^{-1/2}$, and we note that this relation is often observed experimentally. The strain hardening index **SHI** is now defined as the normalized elongational viscosity $\eta_E(Wi_d)/\eta_0$ at $Wi_d = 1$,

$$\mathrm{SHI} = 5 f_d^2 G_d J_s^0 \tag{10}$$

with

$$f_d^2 = f^2(Wi_d = 1) = \sqrt{5}/w_d = \sqrt{5G_D/G_d} \tag{11}$$

While the term $5G_d J_s^0$ in Eq. (10) is determined by the LVE characterization of the melt, the representative stretch f_d depends on dynamic dilution according to Eq. (5). We also note that for pom-poms with q_a>5, the dilution modulus G_D is equal to the plateau modulus G_N^0 (**Table 3**), and therefore for these polymer systems, the SHI is fully determined by the LVE characterization[4].

COMPARISON TO EXPERIEMTAL DATA

For the 12 model PS pom-pom melts of **Table 1**, the normalized elongational viscosity $\eta_{E,\max}/\eta_0$ as a function of Weissenberg number $Wi_d = \dot{\varepsilon}\tau_d$ is shown in **Fig. 2**. Limited strain hardening is observed for pom-poms having only a few side arms at the two branched points such as 220k-2x3-70k ($\mathrm{SHI_m}$=6) and 100k-2x5-25k ($\mathrm{SHI_m}$=10), irrespective of the length of the side arms. We call $\mathrm{SHI_m}$ the experimentally observed or measured SHI. In contrast, pom-

pom 300k-2x24-40k with many side arms and the largest value of J_s^0 shows the highest strain hardening potential with $\mathrm{SHI_m}$=90. Most of the other pom-poms fall in a narrow band with $\mathrm{SHF_m}\approx 30$. Surprisingly, there is only a minor increase of $\mathrm{SHF_m}$ with increasing backbone molecular weight $M_{w,b}$ from 100 to 400 kg/mol, but with similar numbers of arms (q_a=10-13) and the same side arm molecular weight of $M_{w,a}$ = 40 kg/mol. Increasing the molecular weight of the side arms from 24 to 40 kg/mol at constant molecular weight of $M_{w,b}$ = 100 kg/mol and q_a=12 does not change strain hardening significantly, but a further increase of $M_{w,a}$ to 50 kg/mol increases $\mathrm{SHF_m}$ to 47 (**Table 3**). We note that for $M_{w,a}$ =50 kg/mol, the combined molecular weight $2M_{w,a}$ of two side arms is equal to the backbone molecular weight of $M_{w,b}$=100 kg/mol with the consequence that the entanglements of the arms act in a similar way as the entanglements of the backbone, thereby broadening the relaxation time spectrum and thus increasing the value of the steady-state compliance J_s^0 significantly. As seen from **Table 3**, $5G_d J_s^0$ is of the order 1 for all pom-poms considered and there is general agreement of the observed $\mathrm{SHI_m}$ and the strain hardening index SHI calculated from Eq.(10).

Table 3. Weight fraction φ_b of backbone, plateau modulus $\boldsymbol{G_N^0}$, dilution modulus $\boldsymbol{G_D}$, relaxation modulus $\boldsymbol{G_d}$, zero-shear viscosity η_0, disengagement time τ_d, steady-state compliance J_s^0, diluted polymer fraction $\boldsymbol{w_d}$, square of representative stretch f_d^2, strain hardening index SHI (Eq. (10)), and observed strain hardening index $\mathrm{SHI_m}$ (**Fig. 2**) for PS pom-poms at T = 160 °C.

Pom-Pom	φ_b [-]	G_N^0 [kPa]	G_D [kPa]	G_d [kPa]	η_0 [kPa s]	τ_d [s]	J_s^0 [kPa^{-1}]	$5G_d J_s^0$ [-]	w_d [-]	f_d^2 [-]	SHI [-]	$\mathrm{SHI_m}$ [-]
100k-2x12-24k	0.15	270	270	1.75	26	3.18	0.12	1.05	$8.0\cdot10^{-2}$	27.8	29.3	30
100k-2x12-40k	0.09	190	190	1.45	56	7.67	0.14	1.00	$8.7\cdot10^{-2}$	25.6	25.5	27
100k-2x14-50k	0.07	110	110	0.21	220	201	0.90	0.93	$4.4\cdot10^{-2}$	51.4	48.0	47
100k-2x22-25k	0.09	310	310	1.54	17	2.29	0.14	1.05	$7.0\cdot10^{-2}$	31.7	33.2	33
220k-2x9-25k	0.33	260	260	1.05	$1.5\cdot10^{3}$	313	0.21	1.11	$6.4\cdot10^{-2}$	35.1	39.1	35
220k-2x10-40k	0.22	190	190	1.46	$3.5\cdot10^{3}$	679	0.19	1.42	$8.8\cdot10^{-2}$	25.5	36.2	31
280k-2x22-22k	0.22	290	290	0.39	830	308	0.37	0.71	$3.6\cdot10^{-2}$	61.3	43.7	41
400k-2x9-23k	0.49	170	170	3.60	$1.9\cdot10^{4}$	1406	0.07	1.32	$1.5\cdot10^{-1}$	15.4	20.3	19
400k-2x13-40k	0.28	190	190	1.16	$3.5\cdot10^{4}$	7512	0.21	1.22	$7.8\cdot10^{-2}$	28.7	35.1	34
300k-2x24-40k	0.14	150	150	0.039	$1.0\cdot10^{3}$ *)	3441 *)	3.35	0.64	$1.6\cdot10^{-2}$	140	90.1	90
100k-2x5-25k	0.29	180	40	3.67	330 *)	20.8 *)	0.06	1.15	$3.0\cdot10^{-1}$	7.38	8.46	10
220k-2x3-70k	0.34	190	3	0.99	$3.0\cdot10^{5}$ *)	70945 *)	0.23	1.32	$5.7\cdot10^{-1}$	3.40	4.50	6

*) T=140°C

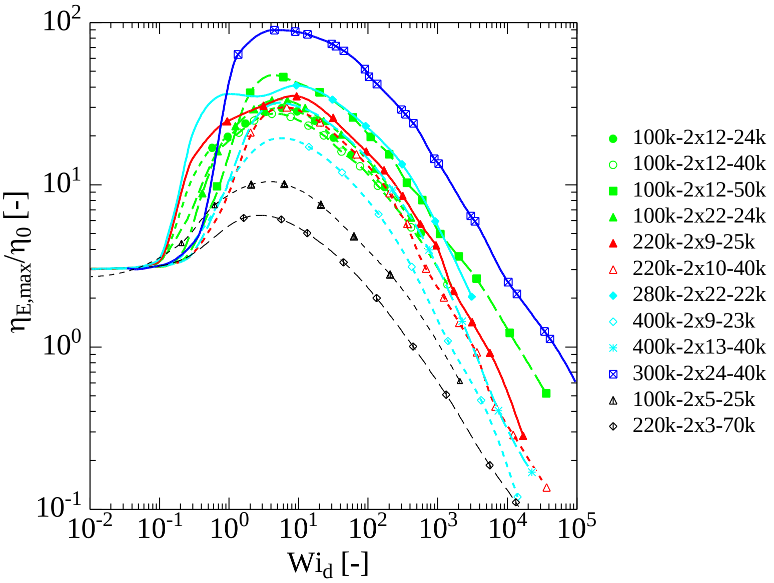

Fig. 2. Normalized maximal elongational viscosity $\eta_{E,\max}/\eta_0$ as a function of Weissenberg number $Wi_d = \dot{\varepsilon}\tau_d$ for PS model pom-poms $M_{w,b}$-2xq_a-$M_{w,a}$. Lines are calculated by the HMMSF model. Symbols indicate the calculated values at the experimental strain rates.

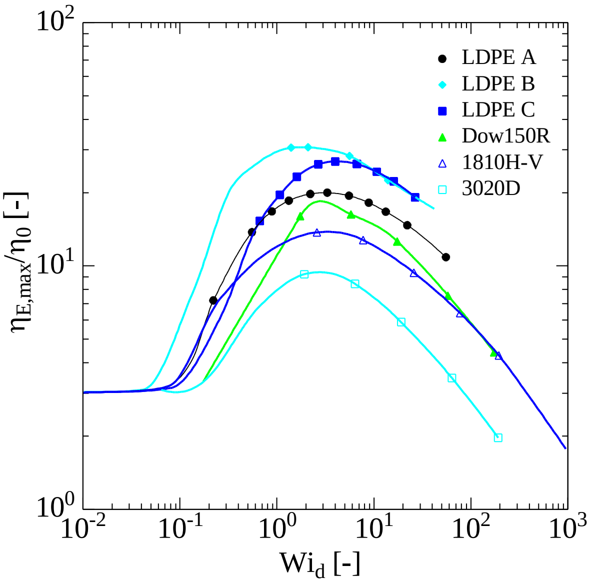

Fig. 3. Normalized maximal elongational viscosity $\eta_{E,\max}/\eta_0$ as a function of Weissenberg number $Wi_d = \dot{\varepsilon}\tau_d$ for six LDPE melts. Lines are calculated by the HMMSF model. Symbols indicate the calculated values at the experimental strain rates.

The normalized elongational viscosity $\eta_{E,\max}/\eta_0$ as a function of Weissenberg number $Wi_d = \dot{\varepsilon}\tau_d$ for the 6 LDPE melts of **Table 2** and measured at temperatures between 130 and 160 °C is presented in **Fig. 3**. Except for LDPE B, the LDPE melts show elongational stress overshoot in start-up elongational flow. The maximal elongational viscosity $\eta_{E,\max}/\eta_0(Wi_d)$ is therefore taken as the maximum of $\eta_E^+(t,Wi_d)$. LDPE B with the highest polydispersity shows the highest strain hardening with a peak of $\mathrm{SHI_m}$=30 at $Wi_d \approx 2$, while 3020D with the highest room temperature density of $\rho_{RT} = 0.94 g/cm^3$ and therefore the smallest amount of branching has the lowest strain hardening index of $\mathrm{SHI_m}$=9 at $Wi_d \approx 3$ (**Table 4**). As shown in **Fig. 4**, the maximal elongational viscosity $\eta_{E,\max}/\eta_{0d}(Wi_d)$ of LDPE C is similar to that of two PS model pom-poms with $M_{w,b}$ =100 kg/mol, q_a=12, and $M_{w,a}$=24 and 40 kg/mol.

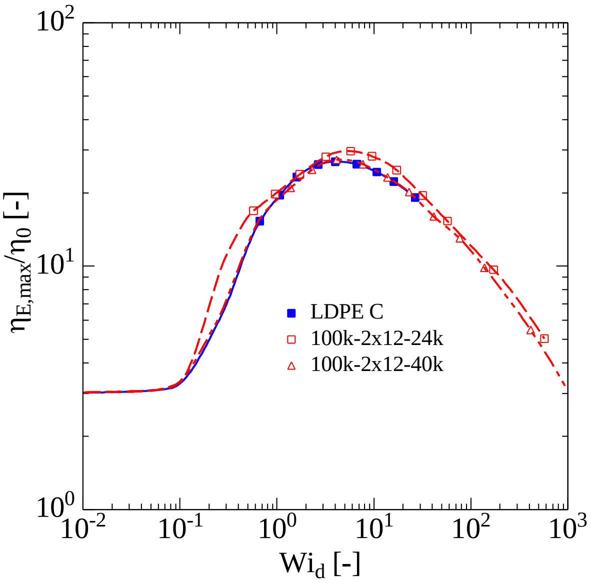

Fig. 4 Comparison of normalized maximal elongational viscosity $\eta_{E,\max}/\eta_{0d}(Wi_d)$ of LDPE C and PS model pom-poms with $M_{w,b}$ =100 kg/mol, q_a=12, and $M_{w,a}$=24 and 40 kg/mol.

Table 4. Dilution modulus G_D, relaxation modulus G_d, zero-shear viscosity η_0, disengagement time τ_d, steady-state compliance J_e^0, diluted fraction w_d, square of representative stretch f_d^2, strain hardening index SHI (Eq. (10)), and observed strain hardening index $\mathrm{SHI_m}$ for LDPE melts at measurement temperatures T.

LDPE	G_D [kPa]	G_d [kPa]	T [°C]	η_0 [kPas]	τ_d [s]	J_e^0 [kPa^{-1}]	$5G_dJ_e^0$ [-]	w_d [-]	f_d^2 [-]	SHI [-]	$\mathrm{SHI_m}$ [-]
LDPD A	30	0.170	150	31.4	22.1	0.70	0.61	$7.5\cdot10^{-2}$	29.7	17.8	20
LDPE B	30	0.049	150	7.07	14.0	1.98	0.49	$4.0\cdot10^{-2}$	55.3	26.9	30
LDPE C	30	0.012	150	22.0	26.7	1.22	0.71	$6.2\cdot10^{-2}$	35.9	25.4	27
Dow 150R	10	0.084	160	379	581	1.53	0.64	$9.1\cdot10^{-2}$	24.4	15.7	18
1810H-V	10	0.018	150	36.2	25.9	0.72	0.65	0.13	16.7	10.8	14
3020D	5	0.239	130	978	637	0.65	0.78	0.22	10.2	7.95	9

DISCUSSION AND CONCLUSIONS

We have quantified the strain hardening potential of PS pom-poms and LDPE melts by considering the maximal value of the normalized elongational viscosity $\eta_{E,\max}(Wi_d)/\eta_0$ corresponding to the normalized steady-state elongational viscosity or the normalized maximal elongational viscosity reached in the case of fracture or tensile stress overshoot, as a function of Weissenberg number $Wi_d = \dot{\varepsilon}\tau_d$. We found that $\eta_{E,\max}(Wi_d)/\eta_0$ reaches a maximal value at $Wi_d \approx 2-8$, and we showed that this experimentally observed maximal value of $\eta_{E,\max}/\eta_0$ =$\mathrm{SHI_m}$ can be used to assess the strain hardening behaviour investigated at different temperatures and across polymer systems with different topologies and different chemistries.

From a one-mode HMMSF model, we derived a relation for the strain hardening index $\mathrm{SHI} = 5 f_d^2 G_d J_s^0$ (Eq. (10)), which shows the same tendency as the measured $\mathrm{SHI_m}$, and is in nearly quantitative agreement with $\mathrm{SHI_m}$ up to SHI≈100. Interestingly, the temperature independent LVE factor $5G_d J_s^0$ with $G_d = G(t = \tau_d)$ is of the order of 1 for both polymer systems considered. The square of the characteristic stretch $f_d^2 = \sqrt{5}/w_d$ (Eq. (11)) depends on hierarchical relaxation and dynamic dilution with the diluted polymer fraction $w_d = (G_d / G_D)^{1/2}$ (Eq. (5)). Polymers with a large value of the steady-state compliance J_s^0, i.e., a rather broad relaxation time spectrum and therefore a low value of G_d and a small polymer fraction w_d, show large values of the strain hardening index SHI. From the comparison of pom-poms and LDPE melts considered here, we may conclude that the strain hardening potential of a typical LDPE such as LDPE C is equivalent to that of a pom-pom consisting of a backbone (largely independent of its length) and $2q_a$=24 side arms with a length corresponding to 2 to 3 times the entanglement length. Further research is in progress to extent these findings to polymer combs and to other chemistries.

REFERENCES

1. Wagner H.M.; Hirschberg V. Experimental validation of the hierarchical multi-mode molecular stress function model in elongational flow of long-chain branched polymer melts. *J. Non-Newtonian Fluid Mech.* ***2023,*** *321:105130.*
2. Hirschberg V.; Schusmann M.G.; Ropert M.C.; Wilhelm M.; Wagner M.H. Modeling elongational viscosity and brittle fracture of 10 polystyrene Pom-Poms by the hierarchical molecular stress function model. *Rheologica Acta* ***2023*** *62:269–283.*
3. Hirschberg V.; Schusmann M.G.; Ropert M.C.; Goeke A.; Wilhelm M.; Wagner M.H. Elongational rheology of 2, 3 and 4 polymer stars connected by linear backbone chains. *Rheologica Acta* ***2024*** *63:407-423.*
4. Wagner M.H.; Narimissa E.; Poh L.; Huang Q. Modelling elongational viscosity overshoot and brittle fracture of low-density polyethylene melts. *Rheologica Acta* ***2022*** *61: 281–298.*