



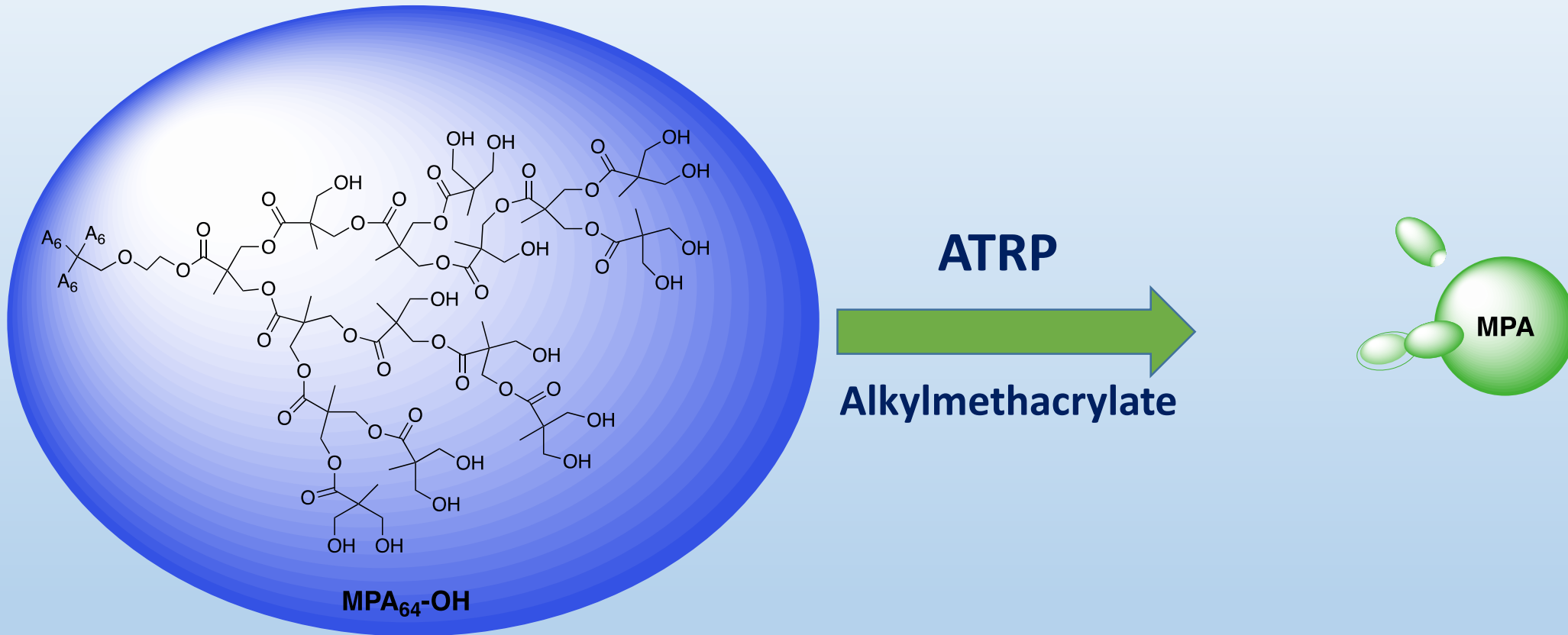
Molecular Design and Shear Stability Correlations of Dendritic Polymethacrylates

Journal:	<i>Molecular Systems Design & Engineering</i>
Manuscript ID	ME-ART-07-2019-000081.R2
Article Type:	Paper
Date Submitted by the Author:	25-Sep-2019
Complete List of Authors:	Cosimbescu, Lelia; PNNL, Energy and Efficiency Division Malhotra, Deepika; PNNL, Energy Processes and Materials Division Campbell, Kristen; Pacific Northwest National Laboratory Swita, Marie; Pacific Northwest National Laboratory, Kennedy, Zachary; Pacific Northwest National Laboratory,

SCHOLARONE™
Manuscripts

Design, System, Application Statement

This work revolves around understanding how molecular properties, influence macro properties in the bulk, such as rheology and shear of the polymers in lubricants containing them. This topic is truly interdisciplinary in nature, crossing the boundary between chemistry, polymer science and engineering. The research is significant in that it increases the stability of polymers and thereby imparting durability to the systems/applications comprising them, such as fluid power, engine oils, industrial hydraulic fluids. This durability translates into machine/equipment efficiency, in the form of mechanical efficiency or fuel efficiency, depending upon the application.



Effect of number of arms of dendritic methacrylates on rheology and shear stability of polymer solutions

Molecular Design and Shear Stability Correlations of Dendritic Polymethacrylates

Lelia Cosimbescu^{†*}, Deepika Malhotra, Kristen B. Campbell, Marie S. Swita, Zachary C.

Kennedy

[†]Pacific Northwest National Laboratory, Richland, WA 99352

lelia.cosimbescu@pnnl.gov

Abstract

Highly branched poly(alkyl methacrylate)s with and without crystalline polycaprolactone segments were designed and prepared via a *core-first* strategy from commercially available hyperbranched cores, then evaluated with respect to their rheology and shear stability performance. The main focus of this work was to study the effect of branching on mechanical shear stability, as it relates to the durability of viscosity index improvers. A secondary goal was to study the influence of the side chain length and polycaprolactone segment on rheology and shear stability. The polymers were prepared from 16, 32, 64-arm functionalized macroinitiators then subsequently subjected to AGET-ATRP (Activator Generated by Electron Transfer – Atom Transfer Radical Polymerization) conditions with dodecyl methacrylate (DMA) or 2-ethylhexyl methacrylate (EHMA). The inclusion of polycaprolactone appears to have enhanced the viscosity index in several samples. Although hyperbranching is thought to increase shear stability, several analogs provided competitive viscosity index (VI) values as well. The caprolactone (CL) hard segments appeared to have a detrimental effect on shear, as compared to their non-CL counterparts. Surprisingly, EHMA showed decreased shear stability versus DMA analogs, despite the shorter polymer side chain (C6 versus C12) and presumably less side-chain entanglements. Overall, the trend is very clear for non-CL polymers, with shear stability

increasing as arm number increased from 16, to 32 to 64, despite the substantial increase in molecular weight.

Keywords: polymethacrylates, shear stability, hyperbranched polymers, star polymers, multi-arm, viscosity modifiers, viscosity index improvers.

Introduction

Hydraulic fluid formulations are increasingly moving away from monograde that contain no viscosity index improvers (VII), to multigrade that include additives to maintain performance, such as friction modifiers, antiwear additives, antioxidants, antifoam agents, corrosion inhibitors and viscosity modifiers. Viscosity index improvers (VIIs) or viscosity modifiers (VMs) are added to hydraulic fluids and lubricants to mitigate viscosity losses occurring at high temperatures. Throughout their lifecycles, hydraulic fluids experience a wide range conditions such as mechanical shear and temperature changes. The resistance of oil's change in viscosity over a temperature range is measured by its viscosity index (VI). This improvement is directly correlated to the type of polymer added to the lubricant's formulation, its architecture, composition, and molecular weight. A detailed review that discusses VIIs designs and the subsequent fluid properties can be found in the literature.¹ Although high VIs can be achieved with linear polymers at large molecular weights, they are prone to bond cleavage under elevated mechanical stress environments (shear). Several reports²⁻³ indicate the resistance of hyperbranched structures to shear.

In our previous study, we investigated the viscosity behavior and shear stability of several polymers with various architectures including linear polymers, hyperbranched polyethyleneimine, and polyesters.⁴ Previous findings showed that higher molecular weight additives provide larger VI improvement. In polycaprolactone grafted polymers however, this trend was enhanced, and

those polymers appeared to provide an even greater VI increase. Our results challenged the conventional belief that a hyperbranched architecture has a positive influence on shear stability when long pendant alkylmethacrylates were part of the design. Increasing intra-arm entanglements via long lipophilic pendant chains or increased number of arms were not beneficial towards shear stability. Instead shear stability appeared to be mainly governed by molecular weight. Overall, strategies such as incorporation of a semi-crystalline segment and shorter methacrylate pendants appeared to increase shear stability. This effort builds on previous work, while conducting a systematic study of polymers containing 16, 32, and 64 arms, with and without caprolactone segments. It is possible that in less stressed systems (i.e. shorter pendants) increased number of arms has a positive influence on shear stability, so 2-ethylhexyl methacrylates are included in the current study to probe this hypothesis. A high viscosity index (VI) is directly influenced by the solubility of the polymer. Studies^{5,6,78} show that when they have a solubility depression at low temperature and remain in a coiled form, polymers contribute very little to the viscosity. However when hot, the polymer is more soluble and expands, thus contributing more to the viscosity of the solution. Thus introducing a semicrystalline segment in the polymer backbone is expected to result in an overall solubility depression at low temperature, and obtain the effect described above, evident by the higher VI.

Our work utilized the “core-first” sequential polymerization strategy to synthesize multi-arm star block copolymers comprising an oil insoluble hyper-branched core with linear lipophilic arms on the boundary. Molecular weight, conformation, chain length, and geometry of the polymer play a critical role in imparting additional benefits of improved viscosity and shear stability. The surface congestion of dendritic molecules, coupled with the high degree of branching, is expected to reduce and even prevent inter-arm entanglements.^{9,10} Of course, dendritic molecules are costly and

laborious to produce whereas their hyper-branched analogs have become, commercially available in recent years. Furthermore, a core-first synthetic strategy requires only a small amount of a hyper-branched macroinitiator to grow arms from, thereby making such molecules economically feasible. To the best of our knowledge, there is only one report of a similar strategy employed in the design of VIIs, and that is our own previous work.⁴

Methods

General considerations

Hyperbranched bis-MPA polyester-16-hydroxyl (MPA-OH16), methoxypolyethylene glycol (\bar{M}_n 350 g/mol), copper bromide (Cu(I)Br/Cu(II)Br) N,N,N',N'',N'''-pentamethyldiethylene-triamine (PMDETA), tin(II)octoate, α -bromoisobutyryl bromide (BiBB), were purchased from Sigma Aldrich and used as received. The monomers dodecyl methacrylate (DMA) and 2-ethylhexyl methacrylate (EHMA) were purchased from Sigma Aldrich and passed through a neutral alumina plug to remove inhibitors. Caprolactone (CL) was purified by heating over CaH₂ for 2h, followed by distillation under reduced pressure. Inhibitor-free tetrahydrofuran was used for polymerization reactions. Reaction equipment was oven dried, placed under vacuum while cooling, and backfilled with argon. Regular solvents, such as methanol (MeOH), dichloromethane (DCM), tetrahydrofuran (THF) were purchased from Fisher. Neutral base oils 100R and 220R were kindly donated by Chevron. The benchmarks are commercial viscosity modifiers kindly donated by Evonik Industries and employed here as comparative examples.

Characterization

Nuclear magnetic resonance (NMR) spectra were obtained using an Agilent-Oxford 500 MHz spectrometer at the following frequencies: 500 MHz (¹H) and 125.7 MHz (¹³C {¹H}). The chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane

(TMS) and coupling constants for small molecules are reported in Hertz (Hz). Samples were prepared in deuterated chloroform (CDCl_3). Relative molar mass distributions were obtained by size exclusion chromatography (SEC) analysis. The molar masses were determined relative to the elution volumes of *linear* poly(methyl methacrylate) standards pushed through two columns of Jordi Resolve DVB Medium Mixed bed (300 mm x 7.8mm) in THF (mobile phase) and detected via a refractive index detector. Due to the different hydrodynamic volume of high molecular weight hyperbranched polymers versus linear polymers, the molecular weights are well underestimated via SEC, existing in-house capability. We have searched for hyperbranched polymers to use as standards, however only modest molecular weights are commercially available around 10 kDa – 50 kDa, (kg/mol), that by far fall below the highest possible molecular weight of our polymers, as high as 3,000 kDa. Values reported are the average of two runs. The samples were dissolved in THF, and if the solution appeared cloudy, a small amount of DCM was added to fully dissolve the polymer. THF blanks were run in between all polymer runs, and standard checks every five runs. Dynamic light scattering (DLS) measurements were recorded using a Brookhaven Nanobrook Omni instrument equipped with a 640 nm 40 mW red diode laser. Polymer samples were dissolved in THF, passed through a PTFE filter (0.45 μm for **P6**, 0.1 μm for **P9**) directly into a clean, de-dusted quartz cuvette with a path length of 1.0 cm, then capped before measurement. Measurements were performed in triplicate at 25 °C with a scattering angle of 90 ° for a duration of 180 seconds and the average hydrodynamic radius (R_H) is reported.

Synthesis: The syntheses for all macroinitiators, including the polycaprolactone-containing ones are presented in the SI. Briefly the caprolactone macroinitiators were prepared from commercial hyperbranched cores, via caprolactone ring opening, in presence of the tin(II) catalyst, until all caprolactone was consumed.

General Polymerization Procedure

The monomer, initiator, CuBr_2 , and CuBr were combined in a two-neck reaction flask then degassed with vacuum-argon cycles or stirred under Ar for 2 hours (convenience). If the initiator was a solid, it was added at the beginning along with all other reagents; if the initiator was an oil, then it was added as a THF solution after degassing. Tin(II)2-ethylhexanoate was added last under a stream of N_2 , as the reducing agent.¹¹ Typically, the reaction mixture started becoming viscous in *ca.* 30 minutes, and the reaction was generally stopped when the viscosity impeded stirring. In some cases, particularly for the analogs with 32 and 64 arms, the reaction was intentionally stopped before full thickening and at lower conversions, otherwise the polymer became insoluble in DCM or oil. The reaction flask was opened to air which effectively terminated the polymerization. The crude polymer was dissolved in THF or DCM and precipitated into methanol, followed by decantation of the solvent. An aliquot from the DCM solution of the crude polymer was analyzed to determine conversion. These details are presented for each polymer in the SI. This process was repeated until a clean polymer with less than 5 mol % of monomer was obtained, typically two times. Monomer removal was monitored via thin-layer chromatography (TLC) of the polymer solution, and washing was continued until monomer was no longer detected via TLC. Notably, clean polymers may contain up to but not to exceed 5% monomer. It is important to note that ^1H NMR measures molar ratios, not weight ratios, so 5% moles of monomer versus the polymer translates into an insignificant weight of the monomer, considering the molecular weight difference between the two, which does not affect any of the parameters measured.

Rheology measurements

Polymers were dissolved in a mixture of two base oils, 70%100R/30%220R at a concentration of 2% w/w and the resulting blends were measured by a spindle viscometer to determine dynamic viscosity (centipoise, $\text{cP} = \text{mPa}\cdot\text{s}$) at 40 and 100 °C. The dynamic viscosity values were converted into kinematic viscosity (KV) values ($\text{cSt} = \text{mm}^2\cdot\text{s}^{-1}$) by dividing the centipoise value by the density of the blend ($0.848 \text{ g}\cdot\text{cm}^{-3}$ at r.t.). The densities of the blends were roughly the same, independent of the polymer used. We only measured densities at RT. Previous work where we measured densities at both temperatures, showed that KVs only change very slightly, while the trend is maintained, and VIs do not change at all. Therefore, even if KVs might be offset by 1-2 cSt, the VIs remain the same. A Brookfield digital (LVDV-E) spindle viscometer was fitted with a cooling/heating jacket that was continuously flowing with oil supplied by an external cooling/heating bath that regulated the jacketed temperature at 40 or 100 °C. A rotating spindle (ULA code 00; 0.3–100 RPM) was submerged into the blended oil at the regulated temperatures for 30 minutes. This standard practice for calculating viscosity index (VI) from the acute viscosity at 40 and 100 °C is described in standard ASTM D2270 and was used to generate viscosity index values. Given the low rotating speed of the spindle, viscosity reported are zero-shear viscosity values.

Shear Stability Measurements

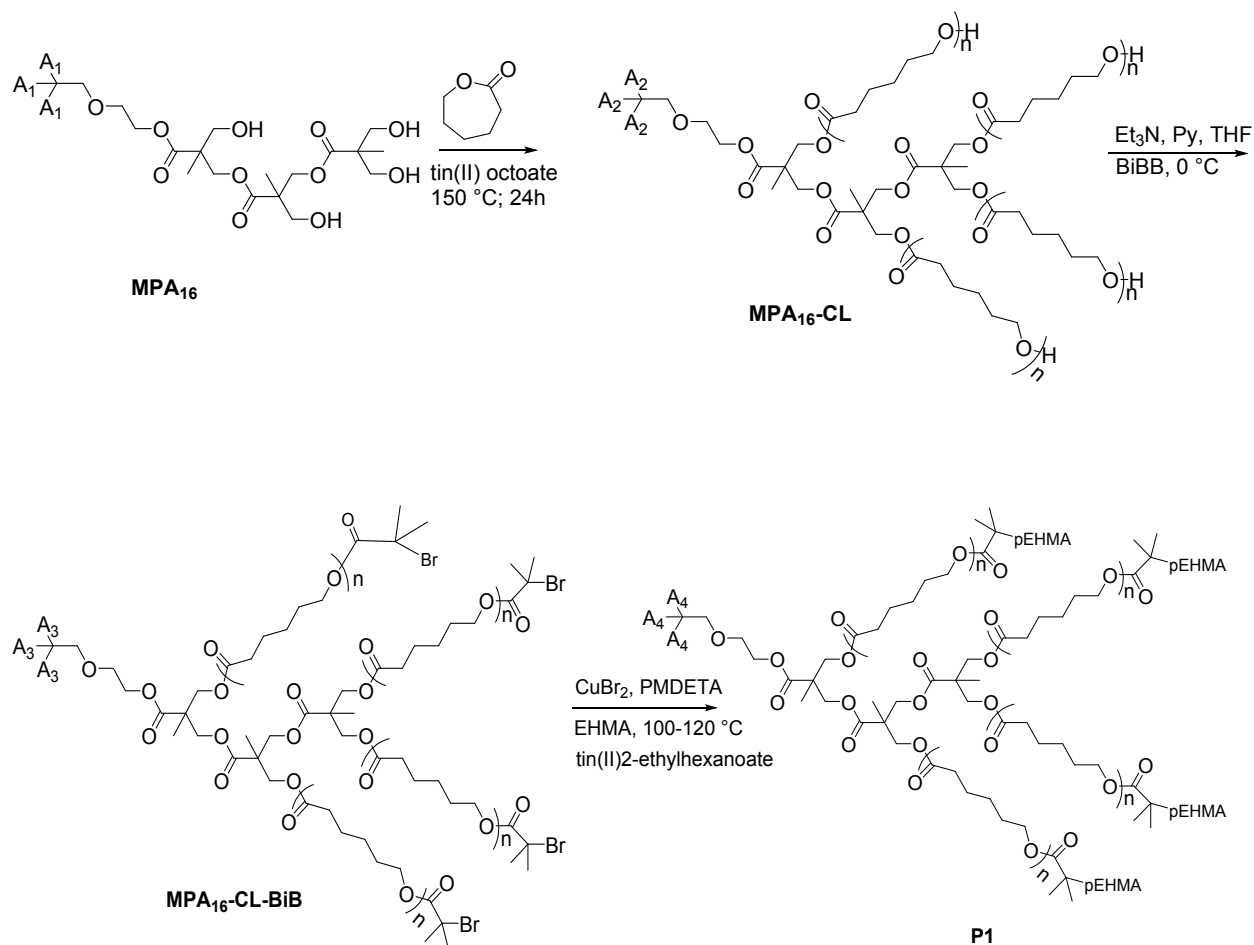
Shear stability is a measurement of a lubricant's resistance to viscosity loss when it is subjected to high shear stress or passed through narrow passageways in components such as bearings or gears. A common test for this property is the Taper Roller Bearing Rig (KRL) test CEC-L-45-99. This test was the most convenient for us as it is fast, requires small amounts of sample (80 mL), and provides valuable shear stability data to establish trends. Test oil is run in a fitted tapered roller bearing for 20 hours under design load. Unsheared and sheared viscosity measurements were

obtained and used to generate permanent viscosity loss (PVL). The measurements were conducted at Southwest Research Institute. The blends had their concentrations adjusted (by dilution with the 100R/220R base stock) to have similar KV40s (+/- 2) cSt, such that the both VIs and % viscosity losses could be compared.

Results and Discussion

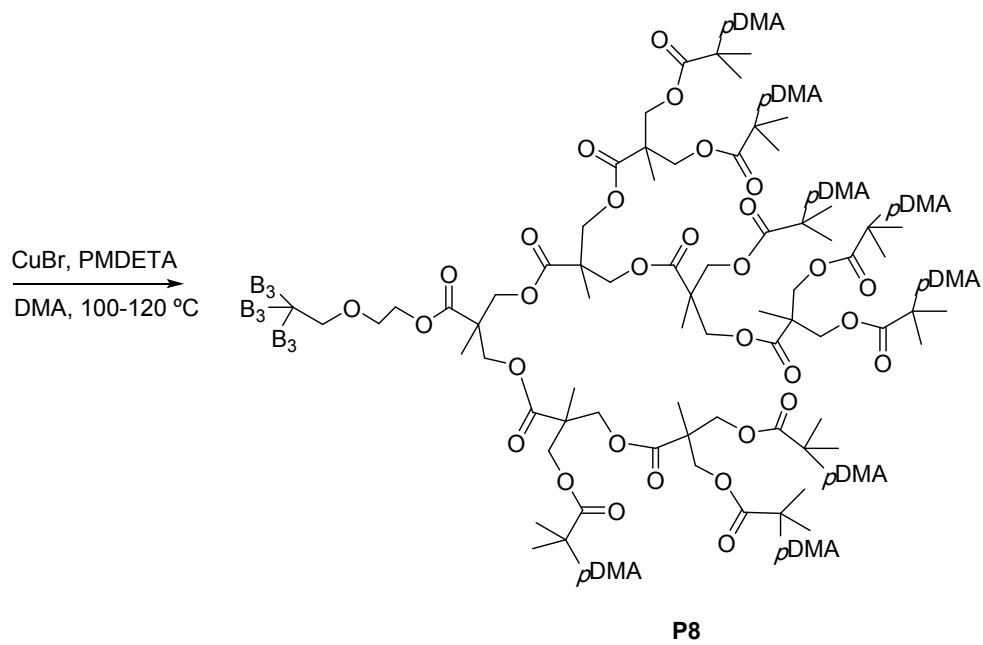
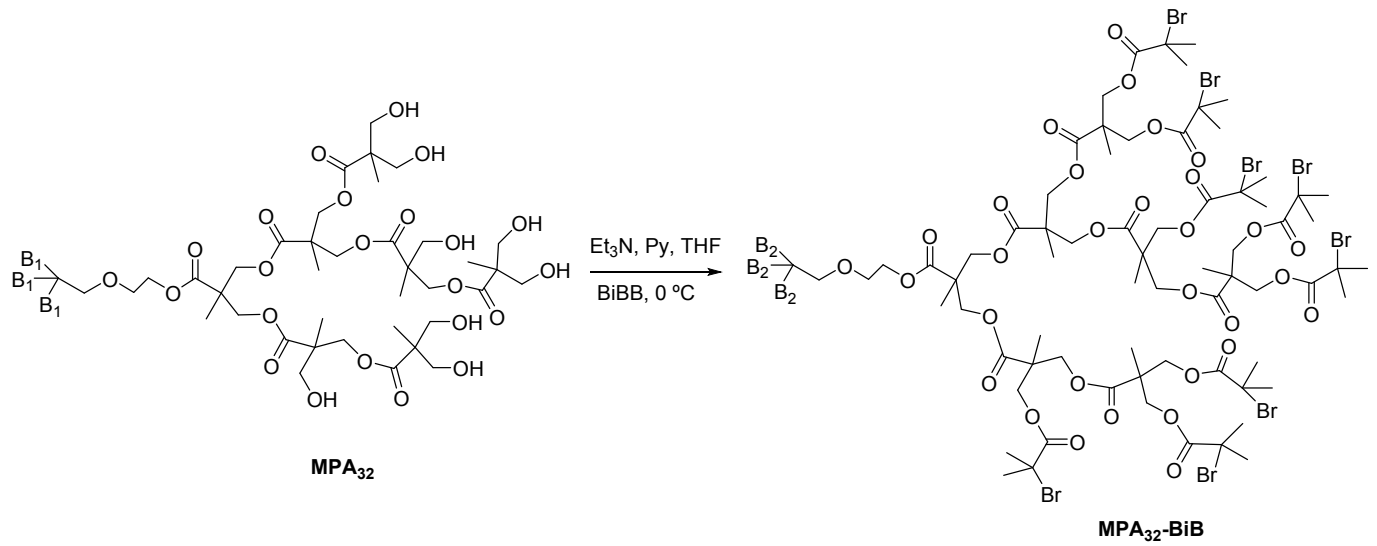
Molecular Design and Synthesis

The focus of the molecular design was to explore the influence of a highly branched core architecture and crystalline segments on shear stability and viscosity. A *core-first* strategy was employed to prepare multi-arm stars from hyper-branched cores with and without semi-crystalline segments: MPA-(caprolactone-CL) (MPA-CL-OH, generation 2, -OH \approx 16, generation 3, -OH \approx 32; generation 4, -OH \approx 64) 2,2-bis(methylol)propionic acid hyperbranched polyester (MPA; generation 2, -OH \approx 16; generation 3, -OH \approx 32; generation 4, -OH \approx 64). All cores were hydroxy-terminated and were treated with α -bromoisobutyryl bromide (BiBB) and subsequently utilized as a head group for atom transfer radical polymerization (ARGET ATRP) with DMA or EHMA. MPA-CL was prepared as an extended core to promote a viscosity index enhancement by utilizing the crystalline segment polycaprolactone, as an inner block. The synthesis of the MPA₁₆ – CL and subsequent ATRP macroinitiator is captured in **Scheme 1**, as an illustrative example. The synthesis of MPA₃₂-CL-BiB and MPA₆₄-CL-BiB and their EHMA and DMA respective polymers, **P2**, **P3**, **P5** and **P6** is analogous to the one shown, except different cores were used as starting materials (MPA₃₂ and MPA₆₄). Those molecules become quite large when caprolactone is affixed, so the drawing is not shown in interest of space and clarity.



Scheme 1: Illustrative synthesis and structure of precursor and initiator **MPA₁₆-CL**, **MPA₁₆-CL-BiB**, from which polymer **P1** and **P4** were made. A₁, A₂, A₃ and A₄ are identical arms to the one drawn from the nearest quaternary carbon, Analogous compounds have been prepared to generate **MPA₃₂** (**P2** and **P5**) and **MPA₆₄** (**P3** and **P6**) polymers.

The direct functionalization of **MPA₁₆**, **MPA₃₂** and **MPA₆₄** with BiBB, led to a polymer growth directly from the hyperbranched core, as illustrated in **Scheme 2**. The scheme only displays the 32- arm analog synthesis of DMA polymers, **P8** and **P9**, while a similar 16-arm polymer with DMA was reported before, **P7**.⁴ Analogous polymers were prepared with EHMA monomer as well (**P10**, **P11**, **P12**).



Scheme 2. Synthesis and structure of Initiator **MPA₃₂-BiB** and Polymer **P8**. B₁, B₂, B₃ are identical arms to the one drawn from the quaternary carbon. The same sequence was repeated to make the EHMA analog, polymer **P11**, as well as analogous intermediates to generate MPA₁₆ (**P7** and **P9**) and MPA₆₄ (**P10** and **P12**) polymers.

In a previous study, EHMA showed improved performance versus DMA not only with respect to friction and wear, but also shear stability.¹² The shear stability of EHMA polymers was twice that of the DMA polymers, which was attributed to the shorter pendant chain, hexyl versus dodecyl. The same effect was probed here, with the expectation that EHMA would produce a more shear stable polymer versus that containing DMA alone. The molecular weight of each arm was normalized, in that EHMA had more repeating units versus DMA by 1.28, to account for the difference in molecular weight of the two monomers. The initiators employed in this work, their compositions, average molecular weights, polydispersity index (\mathcal{D}_M), and degree of hyperbranching, are summarized in **Table 1**.

Table 1: Composition and characterization of synthesized macroinitiators and their precursors.

Compound and composition	\bar{M}_n^{app} and \bar{M}_w^{app} (kg/mol) ^a	Maximum # of arms	\mathcal{D}_M	# BiBs per molecule ^b
<i>MPA₁₆-CL</i>	13.9 (20.4) 29.8	16	2.14	na
<i>MPA₃₂-CL</i>	15.6 (48.5) 41.2	32	2.64	na
<i>MPA₆₄-CL</i>	22.3 (113)	64	2.52	na

	56.2			
MPA ₁₆ -BiB	4.3 (4.5) 6.2	16	1.44	14.3
MPA ₃₂ -BiB	3.7 (9.2) 6.7	32	1.81	29
MPA ₆₄ -BiB	5.0 (18.1) 9.7	64	1.94	56
MPA ₁₆ -CL- BiB	13.5 (22.8) 29.8	16	2.21	11.3
MPA ₃₂ -CL- BiB	12.9 (53.4) 43.6	32	3.37	25.6
MPA ₆₄ -CL- BiB	28.0 (123) 72.8	64	2.60	54

^aMolecular weight measured by size exclusion chromatography (SEC); ^b The number of BiBs per molecule were estimated from ¹H NMR. The molecular weights of all hyperbranched systems are highly underestimated, as the standards are linear polymethacrylates, and the more hyperbranched the system is, the higher the deviation. This is evident from the calculated M_w versus measured in the 32- and 64-arms analogs. The estimated M_n from ¹H NMR, which appears to more accurately represent M_w versus SEC, is reported in parentheses.

The chemical composition of starting materials and intermediates, as well as final polymers were verified by standard NMR spectroscopy. Relative molecular weights, as compared to polymethylmethacrylate (PMMA) standards, were acquired by SEC. All NMR and GPC data/spectra may be found in the supporting information, whereas the polymer characterization results are shown in **Table 2**. Due in part to the polydispersity of the starting materials and precursors, as evident from Table 1, the final polymers are rather non-uniform themselves, despite the use of a controlled polymerization technique. The CL-containing macroinitiators, in particular, have increased polydispersities. Competing polymerization events such as cross-coupling between

macroinitiators may have also contributed to the broad molecular weight. Further, in multifunctional initiators, not all arms will grow equally due to steric crowding. On the other hand, as stated earlier, due to the confinement of the architecture to a globular state, which significantly deviates from the linear standards, the M_w measurements and their polydispersity are strictly *relative*. This is suggested also by the M_w of the macroinitiators, particularly MPA₃₂-CL-BiB and MPA₆₄-CL-BiB. Surprisingly, the M_n of the subsequent polymer is not much larger than that of the initiator, although conversions were 80% or higher with the exception of few cases where polymerization was intentionally stopped prematurely to avoid insoluble polymer formation. We arbitrarily chose 200 repeating units per arm, with the exception of **P3** and **P7**, both MPA₆₄ extended with semi-crystalline polycaprolactone units, to mitigate the insolubility of the hyperbranched core and of the caprolactone in oil. When 200 repeating units were utilized in P3 and P7, the polymers had limited solubility in the base oil of study even at 1% (w/w).

Table 2. Characterization of highly branched polymers.

Analog	Composition	repeating units per arm	\bar{M}_w^{app} ^a (kg/mol)	\bar{M}^b	Conversion (%)	M_w^c (kg/mol)
P1	MPA ₁₆ -CL-EHMA	200	194	5.6	85	412
P2	MPA ₃₂ -CL-EHMA	200	351	4.6	95	1,069
P3	MPA ₆₄ -CL-EHMA	400	299	7.9	66*	2,946
P4	MPA ₁₆ -CL-DMA	156	279	3.1	72	346
P5	MPA ₃₂ -CL-DMA	156	315	3.6	62*	686
P6	MPA ₆₄ -CL-DMA	312	272	5.1	70*	3,123
P7	MPA ₁₆ -DMA	156	269	3.3	93	530.8
P8	MPA ₃₂ -DMA	156	290	3.4	84	973

P9	MPA ₆₄ -DMA	156	391	3.2	80*	1,789
P10	MPA ₁₆ -EHMA	200	365	3.2	93	547
P11	MPA ₃₂ -EHMA	200	421	3.4	80*	1,071
P12	MPA ₆₄ -EHMA	200	337	3.4	72*	1,614

a) Apparent number-average molecular weight (\overline{M}_n^{app}) and apparent weight-average molecular weight (\overline{M}_w^{app}) were determined via SEC against poly(methy methacrylate) standards and are expressed in either kg/mol or kDa; b) Molar dispersity (\mathcal{D}_M) was calculated from $\overline{M}_w^{app} / \overline{M}_n^{app} = \mathcal{D}_M$; c) The values reported are an average of two runs for each polymer; d) The number of repeating units were adjusted for DMA, to have a constant molecular weight feed, and correct for the difference in M_w of EHMA versus DMA (by a factor of 1.28). e) The calculated molecular weights were generated as follows: the number of repeating units were multiplied by the respective molecular weight of the monomer, multiplied by the number of arms and multiplied by the respective polymerization conversion; to this number, the M_w of the macroinitiator was added (without the Br loss correction). * These polymers were intentionally formed at lower conversions otherwise the resulting polymers became insoluble.

In an effort to elucidate more accurate M_w of the polymers with in-house resources, a static light scattering (SLS) single angle (90 °) measurement approach was considered as it is able to generate absolute molecular weights with a Debye plot. The details of this work and specific results are presented in the SI (page 47), in interest of space and clarity of the overall paper. Notably the DLS data did however provide further confirmation that the SEC measured M_w values are only relative and suggested the calculated M_w values may be most useful for comparison across the analog series. For example by SEC, **P6** appears smaller than **P9** (272 kDa versus 391 kDa), which is not expected, based on the last column of Table 2, whereas the DLS size ratio (2.08) between these two polymers correlates more so to the calculated M_w based on conversion (1.75).

Rheology performance

The polymeric solutions were first prepared at 2% (w/w) concentrations in 70%100R/30%220R. This combination of base oils is commonly used in hydraulic fluid applications. Their dynamic viscosities (DV) were measured by a Brookfield viscometer at 40 and 100 °C. **Table 3** includes

the measured (dynamic - DV) and calculated viscosities (kinematic - KV) at 40 and 100 °C, at zero shear, for the 2% w/w blends. These numbers were utilized to generate viscosity index (VI) values using ASTM D2270. The polymers whose KVs were very high were adjusted to bring within +/- 0.5 cSt at 100 °C, so the blends could be more accurately compared. Those values are reported in **Table 3**, with the heading “adjusted”.

Table 3. Viscosity performance of 2% (w/w) and then adjusted [additive]/[70%100R/30%220R] blends versus benchmark.

Analog	KV40 (cSt)	KV100 (cSt)	VI	Relative Thickening Power ^b	Dilution (wt.%)	KV40 adjusted	KV100 adjusted	VI adjusted
70%100R/30% 220R	24.35	4.80	119	0	--			
Benchmark ^a	29.94	6.15	160	n/m	--			
P1	37.11	7.77	186	6.38	1.44%	33.05	6.83	172
P2	46.30	10.71	231	10.9	1.00%	33.16	7.02	180
P3	33.68	6.95	173	4.66	--			
P4	35.27	7.00	164	5.46	1.85%	34.4	6.81	161
P5	33.26	6.67	162	4.45	--			
P6	76.00	15.55	218	25.8	0.75%	31.99	6.29	151
P7	34.04	6.88	168	4.84	--			
P8	34.11	6.88	167	4.88	--			
P9	32.94	6.69	165	4.29	--			
P10	34.87	7.29	181	5.26	1.80%	34.28	7.07	174
P11	36.94	7.90	193	6.29	1.54%	33.52	7.14	184
P12	33.33	6.87	172	4.49	--			

Viscometer recorded dynamic viscosity in centipoise (cP) at 40 and 100 °C. Kinematic viscosity measured in centistokes (cSt) was derived for 40 and 100 °C by dividing DV by the density of the blend, 0.8487 g/mL, essentially the same for all polymers. ^aThe concentration of the benchmark was unknown, so we used enough polymer to reach roughly a KV40 of 30cSt. ^b The thickening power of each polymer was calculated by dividing the difference in KV40s of the polymer solution versus base stock, by the concentration of the polymer (2% in all cases).

It is well accepted that hyperbranched polymeric architectures enhance shear stability while having a minimal influence on the viscosity or thickening power. For the same molecular weight, the linear polymer has the ability to uncoil, whereas a hyperbranched dendritic molecule has a fixed chain length, and the only variation in hydrodynamic volume is caused by side chains collapsing/expanding. The length of the polymer is rather fixed with little room for conformational changes. The PCL is an exception, as it has the potential for a linear expansion, and that is the reason for potential of differing solubility and conformation at different temperatures. This effect is supported by our data, particularly for systems that do not possess a semi-crystalline segment, as in compounds **P7** through **P12**. Regardless of the branching increasing from 16 to 64, the VIs are not increasing at all, particularly for DMA analogs, despite the substantial increase in M_w . It appears that EHMA, the shorter chain monomer, may actually have a positive effect on VI. VI is directly linked to the polymer opportunity for conformational changes with temperature, which allow for the polymer chains to expand or contract in a ball-like fashion. The observed behavior could be explained by the fact that DMA being longer than EHMA (C12 versus C6), it is more prone to side-chain entanglements among various arms. EHMA however may form more distinct arms, with less inter-arm entanglements, that then can expand and contract under temperature variations, and thus results in a higher VI.

Compounds **P1-P6** that contain caprolactone semi-crystalline segments, were designed to probe the potential differential solubility of the various segments shown in other systems^{13,14,15,6,7} to provide a boost in viscosity index, as compared to their non-CL counterparts. The crystalline segment, i.e. the amount of PCL, was expected to augment the VI, as seen in other systems referenced above. Only polymers **P2** and **P6** show a VI boost, bringing the VI up to 230. The pair of compounds that illustrates this effect best is **P2** and **P10**, both polymers contain EHMA, both

had similar conversions (95% and 93% respectively), both had the same # of arms (32), yet their VIs are very different. It is important to note that most of the nearly dendritic polymers that contain caprolactone, MPA₃₂ and MPA₆₄ had to be stopped at very low conversions to achieve a soluble polymer. This indicates that the CL played a major role in the solubility of the final product. The PCL containing polymer **P2** has a VI of 231 versus the one without, **P11**, which has a VI of 193. The same effect is observed in a side by side comparison of the MPA₆₄ analogs **P6** (with caprolactone) and **P9** (without caprolactone), both having DMA as terminal chains, and both having ~64 arms, having very different VIs, 218 versus 165 respectively. The # of arms, type of monomer, and % conversion result in a complex mix of molecular weight, solubility and architecture which are difficult to decouple and that mask the effect of the crystalline segment. It is important to note that most of the nearly dendritic polymers that contain caprolactone, MPA₃₂ and MPA₆₄ had to be stopped at very low conversions to achieve a soluble polymer. This indicates that the PCL segment played a major role in the solubility of the final product. It is likely that due to the architecture of the polymer and subsequent density of the arms in the overall macromolecular system, the PCL is somewhat hindered by the polymethacrylate portion which may prevent conformational changes and therefore PCL effect is minimized.

A potential explanation of the EHMA and DMA differing behavior can be attributed to the branched structure of the EHMA which prevents ordering of the alkyl side chains (as will be the case for DMA analogs) and potentially increases the polymer solubility. Ultimately this would lead to more expanded polymer coils that are more efficient viscosity improvers, simply because of their larger hydrodynamic volume.

Shear Stability

The main focus of this work, following previous published work, is the effect of highly branched systems on shear stability along with a fundamental understanding of structural features that influence shear. Previous work studied the effect of linear and branched polymers with various cores, and degrees of branching.⁴ Our previous conclusions were biased towards the molecular weight being the major factor in permanent shear loss of a polymer, as branching did not appear to consistently provide a benefit. Herein, we took a systematic approach where three types of highly branched cores were functionalized via polymerization with or without spacers or hard segments and their idealized architectures are illustrated in Figure 1. Previously synthesized linear analogs were used for comparative purposes with respect to shear stability, see Table 4.

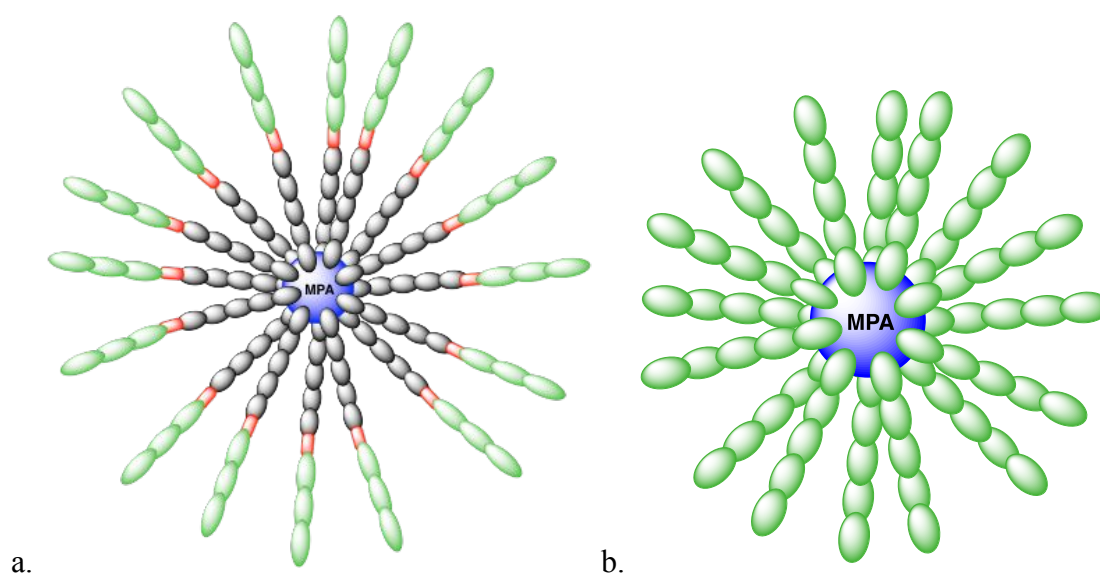


Figure 1: General architecture of polymers under study: a. compounds **P1-P6**, with caprolactone spacers (grey) then polymer grown from them (green); b. compounds **P7-P12**, with polymers grown directly from the MPA core (green).

Shear stability is a complex result of polymer molecular weight, concentration in the base oil, polymer architecture, and composition.^{16,17,18} In this study, the polymer solutions were subjected to harsh conditions as they might encounter in gears (100 °C, under mechanical shear), which can break down the polymers thereby resulting in permanent viscosity losses. The results are reported

as % viscosity loss and can be found in **Table 4**, which summarizes other relevant polymer data such as VI, KV100, and architecture. The oil solutions were roughly normalized to a similar KV100 so that the % viscosity loss can be compared among the various analogs and structure-property relationships can be assessed.

It is well accepted that molecular weight has a significant influence on the shear stability, with viscosity loss increasing with increased molecular weight. Unfortunately, the polymers under current study have much higher molecular weights than measured via SEC. Due to the polymers dendritic architectures, the M_w and shear stability correlations are difficult to assess. To further complicate the issue, a solvophobic effect is also conceivable: THF is a better solvent for the CL segments but not for the EHMA/DMA polymers which causes them to become collapsed; in oil solution the opposite is true. Overall, their hydrodynamic volume seems to be roughly the same in their collapsed state, particularly for **P7-P10**. This hypothesis is further supported by their respective VIs which appears to remain relatively constant independent of the degree of branching or expected M_w .

The 2% polymer solutions in oil were diluted to roughly normalize the KV100 values, such that the % viscosity loss due to shear is comparable among various polymers. The caprolactone and EHMA containing polymers display a viscosity loss of 26, 26 and 23%, for the respective 16, 32 and 64-arm. The hard segments (CL) appear to have a detrimental effect on shear, if compounds P1-P3 are compared to compounds **P10-P12**. That same trend is observed for caprolactone and DMA polymers versus their counterparts without CL, compounds **P4-P6** and **P7-P9**. The caprolactone segments extends the polymer backbone and it may cause scission of the caprolactone segments. The DMA-caprolactone polymers appear to have a less consistent shear trend behavior, potentially due to enhanced chain entanglements of the DMA, but overall these

polymers have a higher shear stability than the EHMA containing ones. EHMA, although has a shorter chain length, it has an ethyl branch, which can be more prone to shear. In addition, the EHMA polymers are expected to have more distinct arms as compared with DMA that may be more susceptible to shear. Regardless, the shear does not appear to be influenced by the M_w of the polymers (the expected M_w should be considered and not the measured values by SEC). Even the high molecular weight MPA₆₄ analogs tend to have a lower viscosity loss than the linear benchmarks used for comparison (Benchmarks 2 and 3). Therefore, hyperbranching appears to off-set M_w differences, and is shown to increase shear stability.

In the compounds without caprolactone, the same trends are visible and more pronounced. In both EHMA and DMA-containing polymers, the shear stability increases from 16-arm, to 32-arm to 64-arm analogs, despite the substantial increase in M_w . The EHMA again, shows a detrimental effect on shear, versus DMA analogs, with viscosity loss values consistently higher (23, 20 16 versus 18.6, 16.5, 14.2), presumably for the same reasons mentioned above. Benchmark 1 and 4 are commercial products of unknown architectures, topologies, and molecular weights, one designed for hydraulic fluid applications while the other for engine oil applications. Benchmark 4 clearly shows the penalty of high VI (238) at the expense of shear stability (31% viscosity loss). Benchmarks 2 and 3 are linear polymers of differing topologies and molecular weights. Benchmark 2 has both a high M_w and VI, but the shear stability is low (33% loss). Benchmark 3 contains caprolactone segments, but has a modest M_w which results in a reasonable viscosity loss by comparison.

Hyperbranched systems such as poly(methyl methacrylate)s,¹⁹ polyethylenes,²⁰ 6-arm poly(methyl methacrylate)s²¹, and styrene copolymers²² have been studied by others for shear stability purposes but few²³ of the reported literature included *long alkyl chain* methacrylates other

than our previous work. Notably, Van Ravensteijn⁷ et al. conducted prolonged measurements on mildly dendritic polymers (9 arms) using the high-speed surface force apparatus which indicate that the additives can withstand high shear rates ($\sim 10^7$ s⁻¹). Increased shear stability can be partly explained by the significantly lower chain overlap due to the more compact conformation of hyperbranched polymers in solutions relative to linear polymers of comparable molecular weight. We observed the same trend in the present work, versus most linear polymer Benchmarks. Benchmark 1 is likely a very low M_w linear polymer that displays very high shear stability. This is another strategy for improving shear stability which we are currently exploring at the moment and results will be reported in a future manuscript.

Finally, highly branched polymers seem to provide a shear benefit as compared to linear polymers, even at very high molecular weights. Their molecular architecture appears to induce a “molar bearings”- like behavior²⁴, and overall enhance shear stability as supported by the MPA₁₆, 32, 64 without a caprolactone chain extender. This is however true up to a point, because their high molecular weight still comes into play, and they still suffer viscosity losses versus very low molecular weight analogs.

Table 4. Architecture and composition versus viscosity loss under shear.

Polymer ^a	KV100	# arms ^b	Composition	VI	Viscosity loss ^c (%)
P1	6.83	11.3	MPA ₁₆ -CL-EHMA	172	26
P2	7.02	25.6	MPA ₃₂ -CL-EHMA	180	26
P3	6.95	54	MPA ₆₄ -CL-EHMA	173	22
P4	6.81	11.3	MPA ₁₆ -CL-DMA	161	19.2
P5	6.67	25.6	MPA ₃₂ -CL-DMA	162	15.4
P6	6.29	54	MPA ₆₄ -CL-DMA	151	23.5
P7	6.88	14.3	MPA ₁₆ -DMA	167	18.6
P8	6.88	29	MPA ₃₂ -DMA	167	16.5
P9	6.69	56	MPA ₆₄ -DMA	165	14.2

P10	7.07	14.3	MPA ₁₆ -EHMA	174	23
P11	7.14	29	MPA ₃₂ -EHMA	184	20
P12	6.87	56	MPA ₆₄ -EHMA	172	16
Benchmark 1	6.15	—		160	2.5
Benchmark 2	13.40	linear	DMA	235	33
Benchmark 3	7.01	linear	PCL-DMA	219	17.5
Benchmark 4 (1.7%)	7.69	—	—	238	31

^aPolymers under study **P1-P12** were tested as dilute solutions in 70%100R/30% 220R and normalized to close KV100; Benchmarks 1 and 4 are commercial products of unknown architecture and M_w ; Benchmarks 2 and 3 are compounds prepared in-house of various M_w and topologies: Benchmark 2 has a M_w of 362 kDa while Benchmark 3 has a M_w of 118 kDa. ^bThe viscosity loss (%) was calculated from viscosity loss during shear, divided by the viscosity before shear, times 100.

Conclusions

The main focus of this work was to investigate the effects of the chain composition and architecture on the shear stability of highly branched polymers based on poly(dodecyl)methacrylates (pDMA) and poly(ethylhexyl)methacrylates (pEHMA). In addition, the influence of topology and composition on viscosity index was also studied due to its relevance in lubricant applications. Rheology and shear stability are important parameters in hydraulic fluid design and have a critical impact on its performance and durability. Multiple analogs with hyperbranched architectures were prepared via the *core-first* strategy from commercially available hydroxyl-terminated hyperbranched cores MPA_{16,32,64}. Linear analogs were previously prepared and reported but utilized here to afford comparative benchmarks for shear stability performance study. The hyperbranched polyesters (MPA-OH_{16, 32, 64}) were either first extended with polycaprolactone or directly functionalized to generate multi-arm macro ATRP initiators. Polymerizations were carried out in the presence of dodecylmethacrylate or 2-ethylhexyl methacrylate. The compounds were characterized via NMR and GPC-SEC, while their solutions in a base oil (70%100R/30%

220R) were evaluated and analyzed for rheology and shear stability, via established methods. It is known that in general hyperbranched polymeric architectures enhance shear stability while having a minimal influence on the viscosity or thickening power. This effect is well supported by our data, particularly for systems that do not possess a semi-crystalline segment, as in compounds **P7** through **P12**. For the polycaprolactone-containing polymers, was expected to augment the VI, only **P2** and **P6** show a VI boost, bringing the VI up to 230. We believe that due to the architecture of the polymer and subsequent high density of the arms in the overall macromolecular system, the PCL is somewhat hindered by the polymethacrylate portion which may prevent conformational changes and therefore PCL effect is minimized.

. EHMA polymers display a higher VI throughout all compounds versus their DMA counterparts, which we attributed to the fact that they may form more distinct arms and increase the opportunity of contracting/expanding with temperature.

The polycaprolactone (CL) crystalline segments appear to have a detrimental effect on shear, if compounds **P1-P3** are compared to compounds **P10-P12**. That same trend is observed for caprolactone and DMA polymers versus their counterparts without PCL, compounds **P4-P6** and **P7-P9**. Surprisingly, although EHMA has a shorter side chain length than DMA, DMA polymers have a higher shear stability than the EHMA ones. EHMA, although has a shorter chain length, it has an ethyl side branch, which can be more prone to shear. In the polymers without PCL, the same trends are visible and more pronounced. In both EHMA and DMA-containing polymers, the shear stability increases from 16-arm, to 32-arm to 64-arm analogs, despite the substantial increase in M_w . Hyperbranching appears to off-set M_w differences and is shown to increase shear stability. All of the analogs show an improved shear stability versus linear polymers of similar M_w , or same shear stability despite their very high molecular weight. The exception is Benchmark 1 which

displays a relatively low VI, but also a remarkable shear stability, with only 2.5% viscosity loss. We speculate that this is a very low M_w linear polymer, as we have seen this trend in previous work.²⁵ It is possible that in less stressed systems (i.e. shorter pendants, such as methyl) shear stability of similar analogs would be much higher which also could be due to a corresponding lower molecular weight. However, such systems could not find application as additives in hydraulic fluids or most lubricants due to their limited solubility in non-polar media. Future work will include linear copolymers of DMA and EHMA respectively, with various polar co-monomers, to probe not only for shear stability, but efficacy of polar groups against friction or wear.

Supporting Information: synthetic details, spectroscopic characterization (¹HNMR, ¹³CNMR) data for each compound and intermediate; GPC chromatograms of final polymers.

Acknowledgements

This project was funded by the Office of Vehicle Technology (VT) of the U.S. Department of Energy (US DOE), (VT0604000-05450-1004897). PNNL is proudly operated by Battelle for the U.S. DOE (under Contract DE_AC06-76RLO 1830).

Author contributions statement

LC proposed the original material design, synthesized compounds and analyzed results. DM performed rheology measurements. KC performed the spectroscopic analysis of all intermediates and products. MS performed GPC-SEC analysis of all macroinitiators and polymers. ZK performed light scattering measurements. All authors contributed to and reviewed this manuscript.

Conflict of Interest Disclosure

The authors declare no competing financial interest.

References

- ¹ Martini, A.; Ramasamy, U. S.; Len, M. Review of Viscosity Modifier Lubricant Additives. *Tribol. Lett.*, 2018, **66**, 58.
- ² Wang, J.; Ye, Z.; Zhu, S. Topology-engineered hyperbranched high-molecular-weight polyethylenes as lubricant viscosity-index improvers of high shear stability. *Ind. Eng. Chem. Res.*, 2007, **46**, 1174-1178.
- ³ Xue, L.; Agarwal, U. S.; Lemstra, P. J. Shear degradation resistance of star polymers during elongational flow. *Macromolecules*, 2005, **38**, 8825-8832.
- ⁴ Cosimbescu, L.; Robinson, J. W.; Page, J. P. Polymer Architecture: Does It Influence Shear Stability? *Ind. Eng. Chem. Res.* 2018, **57**, 3511858-11867.
- ⁵ Stambaugh, R.L., Kinker, B.G.: Viscosity index improvers and thickeners. In: Mortier, R.M., Fox, M.F., Orszulik, S.T. (eds.) *Chemistry and Technology of Lubricants*. Springer, Dordrecht (2010).
- ⁶ Selby, T. W. The non-Newtonian characteristics of lubricating oils. *ASLE Transactions* 1958, **1**, 68-81.
- ⁷ Van Ravensteijn, B. G. P.; Zerdan, R. B.; Seo, D.; Cadirov, N.; Watanabe, T.; Gerbec, J. A.; Hawker, C. J.; Israelachvili, J. N.; Helgeson, M. E. Triple Function Lubricant Additives Based on Organic-Inorganic Hybrid Star Polymers: Friction Reduction, Wear Protection, and Viscosity Modification. *ACS Appl. Mater. Interfaces* 2019, **11**(1), 1363-1375.
- ⁸ Covitch, M. J.; Trickett, K. J. How polymers behave as viscosity index improvers in lubricating oils, *Adv. Chem. Eng. Sci.* 2015, **5**, 134.
- ⁹ Covitch, M. J. How Polymer Architecture Affects Permanent Viscosity Loss of Multigrade Lubricants. *SAE Technical Paper 982638*, 1998, doi:10.4271/982638.
- ¹⁰ Wang, J. L.; Ye, Z. B.; Zhu, S. P. Topology-engineered hyperbranched high- molecular-weight polyethylenes as lubricant viscosity-index improvers of high shear stability. *Ind Eng Chem Res.* 2007, **46**, 1174-1178.
- ¹¹ Matyjaszewski, K., Dong, H., Jakubowski, W., Pietrasik, J., & Kusumo, A. Grafting from surfaces for “everyone”: ARGET ATRP in the presence of air. *Langmuir*, 2007, **23**(8), 4528-4531.
- ¹² Arce, E.; Nieto, P. M.; Díaz, V.; Castro, R. G.; Bernad, A.; Rojo, J. Glycodendritic structures based on Boltorn hyperbranched polymers and their interactions with Lens culinaris lectin. *Bioconjugate ch.* 2003, **14**, 817-823.
- ¹³ Savoji, M. T.; Zhao, D.; Muisener, R. J.; Schimossek, K.; Schoeller, K.; Lodge, T. P.; Hillmyer, M. A. Poly (alkyl methacrylate)-Grafted Polyolefins as Viscosity Modifiers for Engine Oil: A New Mechanism for Improved Performance. *Ind. Eng. Chem. Res.*, 2018, **57**, 1840-1850.
- ¹⁴ Wang, T. Y.; Tsiang, R. C. C.; Liou, J. S.; Wu, J.; Sheu, H. C. Preparation and characterization of a star-shaped polystyrene-b-poly (ethylene-co-propylene) block copolymer as a viscosity index improver of lubricant. *J. Appl. Polym. Sci.*, 2001, **79**, 1838-1846.
- ¹⁵ Bezot, P.; Hesse-Bezot, C.; Elmakoudi, B.; Constants, B.; Faure, D.; Hoornaert, P. Comparison of hydrodynamic and rheological properties of dilute solutions of a styrene-hydrogenated butadiene copolymer in aliphatic solvents by light scattering and viscometric techniques, *J. Appl. Polym. Sci.* 1994, **51**, 1715-1725.
- ¹⁶ Zolper, T. J.; He, Y. F.; Delferro, M.; Shiller, P.; Doll, G. LotfizadehDehkordi, B.; Ren, N.; Lockwood, F.; Marks, T. J.; Chung, Y. W.; Greco, A.; Erdemir, A.; Wang, Q. Investigation of Shear-Thinning Behavior on Film Thickness and Friction Coefficient of Polyalphaolefin Base Fluids With Varying Olefin Copolymer Content. *J Tribol-T Asme*, 2017, **139**, 021504/1-021504/9.
- ¹⁷ Jeong, S. H.; Kim, J. M.; Baigg, C. Rheological Influence of Short-Chain Branching for Polymeric Materials under Shear with Variable Branch Density and Branching Architecture. *Macromolecules*, 2017, **50**, 4491-4500.
- ¹⁸ Kim, C. A.; Kim, J. T.; Lee, K. Choi, H. J.; Jhon, M. S. Mechanical degradation of dilute polymer solutions under turbulent flow. *Polymer*, 2000, **41**, 7611-7615.
- ¹⁹ Wheeler, J. S.; Longpré, A.; Sells, D.; McManus, D.; Lancaster, S.; Reynolds, S. W.; Yeates, S. G. Effect of polymer branching on degradation during inkjet printing. *Polym. Degrad. Stab.*, 2016, **128**, 1-7.
- ²⁰ Wang, J.; Ye, Z.; Zhu, S. Topology-engineered hyperbranched high-molecular-weight polyethylenes as lubricant viscosity-index improvers of high shear stability. *Ind. Eng. Chem. Res.*, 2007, **46**, 1174-1178.
- ²¹ Xue, L.; Agarwal, U. S.; Lemstra, P. J. Shear degradation resistance of star polymers during elongational flow. *Macromolecules*, 2005, **38**, 8825-8832.
- ²² Pu, K. Y.; Li, K.; Shi, J.; Liu, B. Fluorescent single-molecular core- shell nanospheres of hyperbranched conjugated polyelectrolyte for live-cell imaging. *Chem. Mater.*, 2009, **21**, 3816-3822.

²³ Jukić, A.; Rogošić, M.; Janović, Z. Optimization of Alkyl Methacrylate Terpolymer Properties as Lubricating Oil Rheology Modifier. *Ind. Eng. Chem. Res.* 2007, **46**, 3321–3327.

²⁴ Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Frechet, J. M. Molecular ball bearings: the unusual melt viscosity behavior of dendritic macromolecules. *J. Am. Chem. Soc.* 1995, **117**, 4409-4410.

²⁵ Cosimbescu, L., Vellore, A., Ramasamy, U. S., Burgess, S. A., & Martini, A. Low molecular weight polymethacrylates as multi-functional lubricant additives. *Eur. Polym. J.*, 2018, **104**, 39-44.