

A New Generation of High Performance Viscosity Modifiers Based on Comb Polymers

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ABSTRACT

Viscosity index improvers based on poly(alkyl methacrylates) as well as polyolefins have been well known to the industry as key additives to formulate lube oils for decades. Recent efforts to combine these two chemistries to prepare well-defined comb polymer architectures have led to a performance breakthrough. Specifically, the concept of temperature dependent comb polymer coil expansion and collapse allows to achieve extraordinary viscosity temperature properties. Viscosity indices and thickening efficiencies are well beyond the levels achievable by conventional chemistries at the same shear stability level.

After a general introduction of viscometric key properties, the paper describes synthetic pathways towards these novel comb polymers. Standard radical polymerization of polyolefin macromonomers with alkyl methacrylate backbone comonomers is the most straightforward process for their preparation, and allows for an easy transfer to manufacturing. This versatile chemistry enables the design of comb polymers for all kinds of modern base fluids and lubricant applications. The superior viscometric properties of these copolymers are illustrated for selected lube oil formulations such as modern driveline fluids and fuel economy engine oils. The unique viscometric properties of these materials lead to a number of significant performance advantages, for instance improved low temperature viscosity as well as improved efficiency and reduced fuel consumption. Consequently, the novel technology helps meet the stringent current and future requirements of automobile manufacturers regarding fuel economy and CO₂ emissions.

INTRODUCTION

POLYMERS IN SOLUTION - Textbooks on polymer science outline generally the behavior of polymers in solution [1]. If e.g. a poly(methyl methacrylate) chain of molecular weight 100,000g/mol (ca. 1000 repeat units) was fully stretched, it would represent a length of 1250nm with a diameter of 0.3nm [figure 1]. But the described state is only theoretical and will never occur in solution. Due to thermodynamic reasons the same poly(methyl methacrylate) chain dissolved in toluene will

take up the form of a coil with a diameter of 50nm. Polymeric viscosity index improvers (VII) dissolved in baseoil (solvent dewaxed or hydro-treated mineral oil, poly(α -olefine), ester oils, etc.) display typical characteristics of polymers in solution. The extent of chain expansion, i.e. the hydrodynamic coil volume V_h , is dependent on the molecular weight of the polymer chain; and also on the type of polymer chemistry, the solvent and the temperature. This principle is described by the Mark-Houwink equation $V_h = K \cdot M_\eta^\alpha$ with M_η representing the viscosity-average molecular weight, which mostly can be approximated by the weight-average molecular weight M_w , that is accessible from GPC measurements. K and α are called Mark-Houwink parameters and deliver the link to the dependencies on polymer chemistry, solvent and temperature. A library of Mark-Houwink parameters is given in the literature [2].

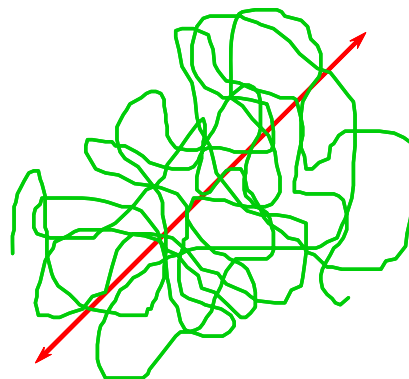


Figure 1. Polymer in solution. A poly(methyl methacrylate) chain of 100,000g/mol represents a coil of only 50nm despite fully extended length of 1250nm (1nm=10⁻⁹m).

The polymeric VII defines three key properties of lube viscometrics [3,4]:

- thickening efficiency (i.e. polymer treat rate required for defined kinematic viscosity KV100 at 100°C, ASTM D445),
- viscosity/temperature V/T relationship (i.e. both viscosity index VI between 100°C and 40°C, ASTM D2270, and BF-40 Brookfield viscosity at -40°C, DIN 51398) and
- shear stability (i.e. the permanent shear stability index PSSI).



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With increasing temperature the solvency power of the lube oil increases, leading to increased coil expansion and thickening efficiency. With this expansion, the polymer counteracts the intrinsic thinning of the pure baseoil (as given for any solvent). Thus, the viscosity differences between high and low temperatures get smaller [figure 2]. This reversible principle can easily be envisioned by the linearized Ubbelohde-Walther plot [4]. The lube industry continues to use the VI as defined in ASTM D2270.

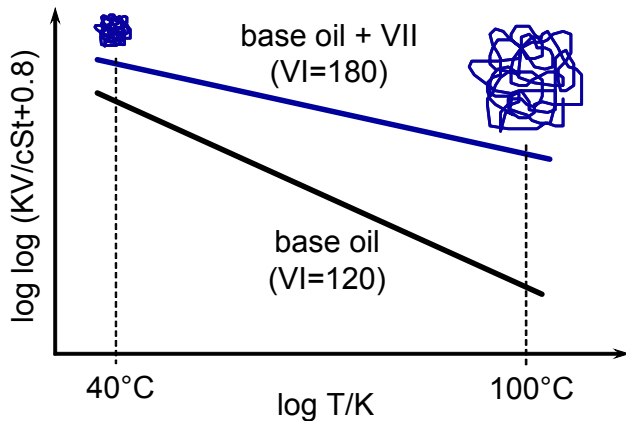


Figure 2. V/T relationship in linearized Ubbelohde-Walther plot. In the presence of VII viscosities are lifted. The coil expansion at higher temperatures counteracts the thinning of baseoil, resulting in better (higher) VI.

Mechanical degradation in lube oil application leads to irreversible loss of thickening efficiency and VI activity (figure 3). Several methods to mimic mechanic shear in the field exist. The tapered roller bearing (Kegelrollenlager KRL, DIN 51350-6) is more severe than ultra sonic shear (ASTM D5621) and Bosch injection pump (DIN 51382). The magnitude PSSI defines the fraction of viscosity contribution by polymer, which is lost after shear.



Figure 3. Irreversible mechanical degradation results in loss of thickening efficiency.

Within the performance window of a given polymer chemistry, the molecular weight M_w is the key design parameter. The higher the M_w , the lower the treat rate for given KV100, the better the V/T relationship (the higher the VI and the lower the - in fact treat rate driven - BF-40) but the higher the PSSI [3,4].

It is well known that different VII chemistries act in different windows (figure 4) of the performance space [3,4]. On the one hand polyolefin (hydrocarbon) polymers like olefin copolymer OCP, poly(isobutylene) PIB

and hydrogenated styrene-diene copolymer HSD are well known for their high thickening efficiency and low treat rate. On the other hand ester polymers like poly(alkyl methacrylate) PAMA, styrene fumarate copolymer and α -olefin fumarate copolymer are applied where good V/T behavior is required. However, none of the chemistries is able to deliver excellent performance for all of the three viscometric magnitudes in parallel.

polyolefin / hydrocarbon polymers:

- olefin copolymer, OCP
- poly(isobutylene), PIB
- hydrogenated styrene diene copolymer, HSD

ester polymers:

- poly(alkyl methacrylate), PAMA
- styrene fumarate copolymer
- alpha-olefin fumarate copolymer

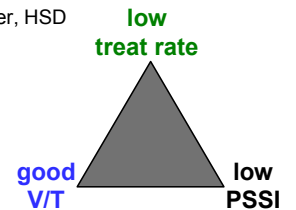


Figure 4. Each type of polymer chemistry acts in a different corner of the performance space.

Additionally, it is also well known that changes in architecture also can lead to significant changes in the values of the Mark-Houwink parameters K and α [2]. Non-linear architectures such as stars, combs, hyper-branched or network structures (figure 5) offer the opportunity to change these parameters. Especially stars have been thoroughly evaluated as VII in lube application, e.g. as hydrogenated styrene diene copolymers HSD [3,4]. The present publication now sheds particular light onto another of these defined architectures: comb polymers.

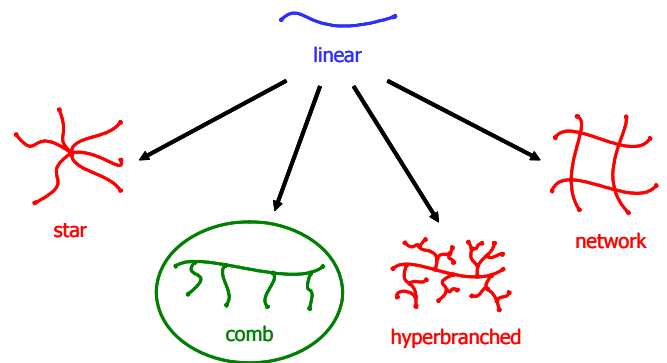


Figure 5. Architecture defines performance window.

MAIN SECTION

NOVEL COMB POLYMERS - Alkyl methacrylates (AMA) are prepared via direct or transesterification of synthetic or natural C8-18 alkyl alcohols. Conventional radical polymerization of a well-defined AMA mix and additional methyl (MMA) or butyl methacrylate is the process of choice to prepare polymeric PAMA VII [3,4]. The present