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Highly branched polyethylenes as lubricant viscosity and friction modifiers

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ABSTRACT

A series of highly branched polyethylene (BPE) were prepared and evaluated in a Group I base oil as potential viscosity and friction modifiers. The performance of these BPEs supports the expected dual functionality. Changes in polarity, topology, and molecular weight of the BPEs showed significant effects on the lubricants' performance with respect to viscosity index and friction reduction. This study provides scientific insights into polymer design for future lubricant development activities.

1. Introduction

Polymeric materials play a significant role towards the performance enhancement of lubricants, such as engine oils and transmission fluids. Ongoing development of the internal combustion engine (ICE) towards fuel efficiency, performance, and emission standards requires high performance lubricants to maintain effective lubricity of internal components over a range of temperatures and conditions. The primary utility of a lubricant is to absorb heat and reduce friction between surface asperities, thereby affording lower energy losses and greater fuel efficiency. In general, refined petroleum base fluids have a limited window of ideal conditions which afford optimal lubricity towards efficient energy transfers. Alternatively, synthetic liquid lubricants maintain performance over a broader range of temperatures and sliding surface velocities. Even with these advantages, synthetic lubricants still require performance enhancing additives that ultimately make them a high end, expensive product. Viscosity and friction modifiers are a substantial and essential component of engine oil formulations among other additives, which include detergents, oxidation inhibitors, rust and corrosion inhibitors, foam inhibitors, anti-wear additives, pour point depressants [1]. In particular, friction and viscosity modifiers influence tribology properties and bulk viscosity profiles.

Friction modifiers are typically amphiphilic molecules that adsorb onto metal surfaces promoting thin film formation between sliding surfaces [2]. Viscosity modifiers are polymers (i.e., non-uniformly dispersed macromolecules) which reduce the natural thinning effect lubricants experience with increasing temperature. Temperature dependent conformational and/or hydrodynamic volume (V_h) changes enhance the aforementioned effects [3]. To date, few lubricant polymer additives have been described in the literature as a dual friction and viscosity modifier [4,5].

Common viscosity modifiers include poly(isobutylene)s (PIB), hydrogenated styrene diene copolymers (HSD), alpha-olefin fumarate copolymers, poly(alkyl methacrylate)s (PAMA) and olefin co-polymers (OCP), with molar masses ranging from 20 to 500 kDa [1,6]. In particular, OCPs are a staple viscosity modifier in part due to their thickening efficiency and viscosity index value (vide infra) as well as their relatively low production cost. This class of polymers is typically a semi-crystalline polymer with linear topology [7]. More recently, non-linear topologies of amorphous OCPs prepared from palladium diimine catalysts were reported [8–10]. Significant to our research interests, Ye and coworkers demonstrated that viscosity index (VI) values diminished while shear stability improved alongside a shift in topology, from *linear* to *hyperbranched* polyethylenes [11]. Their research main focus was the efficiency of the palladium catalysts towards copolymerization of ethylene with polar co-monomers. They did not investigate effects of topology hybrids or polar copolymers on lubricant performance (i.e., viscosity and friction). In contrast, our focus is the performance of such hyperbranched structures, as lubricant additives, and the effect of enhanced polarity on friction. It is known that the inclusion of monomers that favor interaction with metal surfaces promotes film formation on surfaces [5].

To the best of our knowledge, highly branched OCPs have not been investigated as a dual viscosity and friction modifier for lubricants. OCPs are particularly attractive due to their common place as a viscosity

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modifier within the lubricant industry suggesting the infrastructure towards production already exists.

2. Experimental

2.1. Materials

Ethylene (99.98%), chloro(1,5-cyclooctadiene)methylpalladium(II), silver hexafluoroantimonate(V), sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate, anhydrous acetonitrile, anhydrous diethyl ether (Et_2O), anhydrous dichloromethane (DCM), Chromasolv® pentanes, 30% w/w hydrogen peroxide solution, basic alumina oxide were used as is from Sigma-Aldrich (St. Louis, MO). Methyl acrylate, 1-octene, and methyl 10-undecenoate (MU) were purchased from TCI America (Portland, OR). Celite Hyflo Super Cel and 2.0 M hydrochloric acid in Et_2O were purchased from Alfa Aesar (Haverhill, MA). 2,3-bis(2,6-di-i-propylphenylimino)butane was purchased from Strem Chemicals (Newburyport, MA). Additive-free Group I base oil was kindly donated by Afton Chemical (Richmond, VA). Group I base oil (ExxonMobil) was used to create a baseline for viscosity and friction measurements, clean between measurements, and prepare lubricant mixtures with synthesized polymers. Benchmarks 1 and 2 are commercial lubricant viscosity modifiers and were kindly donated by Lubrizol and Evonik, respectively. The benchmarks were employed as comparative examples.

2.2. Physical and chemical characterization

Nuclear magnetic resonance (NMR) spectra were obtained using an Agilent-Oxford 500 MHz spectrometer at the following frequencies: 499.8 MHz (^1H) and 125.7 MHz (^{13}C). The chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane (TMS) and coupling constants are reported in Hertz (Hz). Samples were prepared in deuterated chloroform ($CDCl_3$) containing TMS (0.3–1%, v/v). Relative molar mass distributions were obtained by size exclusion chromatography (SEC) conducted by PSS (Polymer Standards Service; Mainz, Germany). The molar masses were determined relative to the elution volumes of linear poly(styrene) standards pushed through three columns packed with PSS-SDV O (5 μm G; 50, 100, 1000 Å). Tetrahydrofuran (THF) was the mobile phase and had a flow rate of 1.0 mL/min. A dynamic refractive index (DRI) detector was utilized to identify elution volumes of the polymer relative to the solvent.

2.3. Synthesis

The diamine palladium catalyst with either a hexafluoroantimonate (V) or a tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion was prepared according to published procedures [10,12]. Likewise, highly branched polyethylenes with various topologies and olefin comonomers were prepared as described elsewhere [13,14].

In a typical procedure, a 0.1 M catalyst/DCM solution was prepared in a Parr apparatus and backed filled with argon, then the headspace was purged with ethylene 2 to 3 times prior to sealing the reaction vessel. The closed system was then charged with ethylene to the targeted pressure. In the case of a varied pressure (100↓ psi), the system was charged to 100 psi and recharged when the internal pressure reduced to ca. 15 psi due to the consumption of ethylene. For an isobaric pressure of 100 or 15 psi, a continuous feed of ethylene was provided with a regulator in between the bottle and apparatus. At atmospheric pressure (atm), the vessel was fitted with a balloon and recharged whenever the balloon appeared deflated. The transferred mass of ethylene was incrementally checked to target mass loadings towards the influence of molar mass of the polymer and subsequent viscometric properties. Once the ethylene was consumed (as determined by internal pressure drop), the crude material was transferred to a separate flask and treated with either 2.0 M HCl/Et2O, 30% w/w H_2O_2, or a celite/alumina oxide mixture to remove catalyst. In the case of acid or peroxide, an aqueous wash against water and saturated sodium bicarbonate was conducted to neutralize the reactive reagents. All volatile organics were removed by vacuum techniques. Typical gravimetric yields (as compared to ethylene mass loadings) were in the range of 20–50%. The isolated polymeric material was characterized by $^1H/^{13}C$ NMR and SEC.

2.4. Lubricant investigations

Polymers were dissolved into an additive free Group I base oil at a concentration of 2% by weight (w/w). The resulting oil solutions were measured by a Brookfield spindle viscometer which provided dynamic viscosity (centipoise, $cP = mPa \cdot s$) at 40 °C and 100 °C. The dynamic viscosity value was converted into kinematic viscosity (centistokes, $cSt = mm^2 \cdot s^{-1}$) by dividing the centipoise value by the density of the blend ($0.86\ g \cdot cm^{-3}$ at r.t.). The densities of the blends were roughly the same, independent of the polymer used. The 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 °C and 100 °C. A rotating spindle (0.3–100 RPM) was submerged into the blended oil at the regulated temperatures for 60 min. The dynamic shear was reported on the digital screen with a respective torsion percent. The cP value with the highest torsion percent was used for viscosity index calculations, once converted to cSt. An on-line calculator, well accepted by experts in the field, was used to generate viscosity index values, from kinematic viscosities at 40 °C and 100 °C (KV40 and KV100). A variable load-speed bearing tester (VLBT) was utilized to obtain Stribeck curves at room temperature and at 100 °C. A 50 N normal load was applied through a stiff spring. A 25.4 mm diameter rotating bar of AISI 8620 alloy steel was used to rotate against a 25.4 mm square coupon of A2 tool steel. The speed cycle started from 1.7 m/s and reduced to 0.2 m/s at 0.1 m/s per step. Neat Group I base oil was used before testing each blend to obtain a baseline.

3. Results and discussion

A series of highly branched polyethylenes (BPE), polyoctene, and their respective copolymers were prepared following published procedures [10,12–15]. Olefins (i.e., ethylene, octene, and undecenoic methyl ester) were combined with a palladium diimine catalyst in dichloromethane (Table 1). In the experiments where ethylene was utilized, a Parr apparatus was employed in which the pressure was either varied (100↓) with an initial charge of 100 psi or held constant (isobaric) at 100 or 15 psi. Elevated pressures of ethylene near 100 psi have been ascribed to produce *linear* (L) topologies whereas pressures near 15 psi or below lead to *hyperbranched* (B) topologies [9,16]. Hybrid chain topologies of *linear* and *hyperbranched* (L/B) polyethylenes were also obtained by Ye and coworkers when the pressure of ethylene was altered during the active polymerization [14]. Lastly, we prepared copolymers of ethylene with methyl 10-undecenoate (MU; <10 mol% to increase polarity and encourage polymer-surface interactions, potentially leading to friction reduction. This co-monomer was proven effective towards polymerization with the Pd chain walking catalyst by Ye and co-workers, referenced above.

Our early attempts produced fairly ineffective viscosity modifiers due to relatively low ethylene incorporation and low molecular weights. Analog **1** and **2** included the exposure of ethylene gas to a 0.1 M palladium catalyst/dichloromethane (DCM) at an elevated (100 psi) or atmospheric pressure (atm), respectively. These reaction vessels were repeatedly charged until a targeted mass (grams) of ethylene had been consumed. After purification, the polymers were dissolved in a Group I base oil to prepare, individually, 2% w/w blends. The KV values at 40 °C and 100 °C as well as the VIs were only slightly above the neat oil's viscosity (Table 2 and Fig. S7). Characterization of the neat