



Single chain polymer nanoparticles as shear-resilient viscosity modifiers for lubricating oils

Sinai Aharonovich, Charles E. Diesendruck*

Schulich Faculty of Chemistry and Grand Technion Energy Program, Technion-Israel Institute of Technology, Haifa 3200008, Israel

ARTICLE INFO

Keywords:

Single-chain polymer nanoparticles
Lubricating oils
Viscosity modifiers
Mechanochemistry

ABSTRACT

Lubricants are crucial to the reduction of erosion and energy loss in systems that include moving surfaces. Two basic requirements for lubricants, viscosity and viscosity-temperature response, are achieved by adding polymers known as viscosity modifiers (VMs). During service, the lubricant's viscosity decreases due to mechanochemically-induced fragmentation of the macromolecules. Herein, we demonstrate how folding the linear polymers into single chain polymer nanoparticles hinders the macromolecule's fragmentation, leading to retention of the lubricant's viscosity properties. Mechanochemical scission in the folded polymer gradually unfolds it, causing the polymer to gain hydrodynamic size and, as a result, these lubricants display *permanent viscosity gain*. Given the enormous production volume of the lubricant industry, this new class of shear-resilient VMs may lead to considerable financial and environmental benefits.

1. Introduction

Lubricating oils are of paramount significance in many systems that include moving surfaces, one example of many, for instance, is internal combustion engines [1]. Their economic and environmental importance in reduction of erosion-corrosion, energy losses to friction, and in other roles [2], which also facilitate attaining governmental emission and fuel economy regulations [3] is reflected in the projected annual global production of lubricating oils and greases of $1.24 \cdot 10^{10}$ gal by 2020 [4]. When choosing lubricating oils for most applications, two fundamental parameters which are considered are viscosity values and viscosity-temperature response, that allow both adequate pumpability at cold temperatures, and formation of oil film with adequate thickness on surfaces at high temperatures [2].

A quantitative measure of the temperature response of the kinematic viscosity ν of the oil is given by its viscosity index (VI) [5], which increases with smaller $\Delta\nu/\Delta T$. Since the oil's viscosity depends strongly on temperature, a basic design requirement of lubricating oils is satisfactory VI values. To this end, polymers known as viscosity modifiers (VMs) are commonly added to oil formulations. Different oil soluble polymer classes have been used over the last decades for this purpose, common examples being olefin copolymers (OCP), and poly(methacrylates) (PMAs), particularly with long alkyl chains [6]. A plausible reason for the VI elevation caused by the VMs is the decrease in activation entropy for viscous flow of their solution compared to the pure

oil [7, 8]. For PMAs, but not in the case of OCPs [9], increase of the hydrodynamic volume by coil expansion is another contributing factor for the observed VI elevation [6, 7, 10]. The larger intrinsic viscosity thus obtained (via Einstein's viscosity equation) [11] is connected to the increase in the polymer solution's viscosity through the Huggins [12] and Kraemer [13] equations.

During service, the viscosity of the lubricating oil decreases transiently and/or permanently. Whereas transient viscosity loss is caused by the effects of solvodynamic shear forces on non-covalent interactions and/or on the conformations/alignment of the macromolecules in the solution, the majority of the permanent viscosity loss (PVL) is due to mechanochemically-induced, irreversible, scission of covalent bond/s in the polymer chain which results in splitting of the macromolecule to smaller fragments [14]. Since the intrinsic viscosity of a polymer solution relates to the molecular weight through the Mark-Houwink equation [15], and since the VI depends on the size of the macromolecule [16, 17], the shear induced mechanochemistry of the VM macromolecules results in the doubly undesired decrease of both the thickening power and the VI of the lubricant.

Mechanochemical studies have established that under the effect of shear force fields, the coil of the polymer chain in solution is initially stretched, and if sufficient mechanical energy is transmitted to the macromolecule, chain fragmentation may eventually result [14, 18, 19]. In linear polymers, chemical bond scission occurs above a limiting degree of polymerization (DP_{lim}), and its probability increases with

* Corresponding author.

E-mail address: charles@technion.ac.il (C.E. Diesendruck).

<https://doi.org/10.1016/j.reactfunctpolym.2018.07.018>

Received 29 May 2018; Received in revised form 23 July 2018; Accepted 25 July 2018

Available online 27 July 2018

1381-5148/ © 2018 Elsevier B.V. All rights reserved.

larger DPs [14]. The corresponding limiting chain length is governed by the magnitude of the cumulative shear forces the translating solvent molecules apply on the polymer's coils parallel to main chain direction, which depends on factors such as the shear field source, solvent and polymer type and structure in solution, viscosity and temperature [20–22].

Hence, one tactic to improve the VM is to change its topology in order to increase the polymer's hydrodynamic size (and therefore viscosity) without affecting its rate of mechanochemistry. VMs with nonlinear architectures such as branched [23–26], or star [27, 28], have therefore been developed, some of which are represented in high-end commercially used VMs nowadays. However, given a certain backbone length, there are geometric considerations (see Supplementary data) that confine the maximal size gain that can be achieved in these topologies [29], as above the limiting main chain length, mechanochemical degradation of viscosity properties would occur. For example, excellent results have been shown with hyperbranched structures, in which main-chain fragmentation seem not to have such a significant effect on viscosity, probably due to their low Mark-Houwink parameter [23]. On the other hand, when the degradation occurs through arm-loss, the mechanochemical decay is more severe compared to a linear chain, since each coil-to-stretch transition (CST) will present similar rate of rupture compared to previous ones, as the main chain length is similar [22, 30].

Herein, we demonstrate a different approach to improve VMs which is independent of the previous strategy: address directly the mechanism of chain fragmentation. We have recently showed that folding linear polymers with sacrificial covalent intra-chain bonds to single chain polymer nanoparticles (SCPN) [31–35] significantly improves their mechanochemical stability in solution [36, 37]. Thus, the mechanical energy is spread among degenerate bonds, analogously to the loads dispersion by a truss, and when a certain bond cleaves in an individual macromolecule the result is not a “catastrophic failure” (Scheme 1). In addition, folding the chain may hinder CST. More importantly, unlike the previously described strategy, regular scission of these “sacrificial” bonds leads to gradual unfolding, causing the chain to *gain* hydrodynamic size in response to shear forces [38]. As a result, these SCPNs solutions not only display reduced PVL, but, *unprecedentedly, also* show permanent *viscosity gain*, when subjected to strong shear forces.

2. Experimental

2.1. General

Toluene, isopropanol, and melted stearyl methacrylate (SMA) were passed through a short column of neutral alumina prior to use. Copper wire ($D = 0.02''$) was flattened to strips, filed with a sand paper, and washed with acetone. Ethylene bis(2-bromoisobutirate) was prepared according to a modified procedure (see Supplementary data) [39]. Additional solvents, reagents, and monomers were used as received.

Dynamic viscosity was measured in a Brookfield type digital viscometer model SNB1 from Shanghai Nirun Intelligent Technology Co. Density was measured using a 2 mL graduated flask at the relevant temperature. For GPC analysis of the unsheared polymers, 4 mg of the polymer sample were dissolved in THF. For GPC of solutions of polymers in oil, a sample of the solution is diluted by THF until a concentration of 2–3 mg/mL of the polymer is obtained. GPC analysis was done in a Thermo LC system equipped with Tosoh's TSKgel Guard Column HHR-L and 4 TSKgel G4000HHR columns in sequence. Detection was obtained with a pentadecarboxylic acid system including Dionex DAD-3000 PDI UV-Vis Detector, Wyatt Viscostar II, Wyatt OPTILAB TrEX, Wyatt MALS DAWN HELEOS II 8 + TR and WyattQELS DLS. GPC data analysis and polymer properties calculation were conducted using Wyatt's Astra 7 software. Ultrasonication was done using a SONICS Vibra-cell ultrasonic processor 500 W, tuned to $9.57 \text{ W}\cdot\text{cm}^{-2}$. Sonication of the oil solution is performed at RT in a 50 mL Kimble flask

in accordance to ASTM D2603 [40], at 20% amplitude, with pulsed sonication (1:2 s irradiation:idle ratio). NMR spectra were recorded using an AVANCE II 200, 300 or 400 MHz Bruker spectrometer at the Technion NMR facilities.

2.2. Typical procedure for preparation of poly(SMA-co-AAEMA) (polymer C)

Melted SMA (16.20 g, 47.8 mmol), AAEMA (2.59 g, 12.1 mmol), and a 1:4 v/v mixture of isopropanol and toluene (32 mL) were added to a 250 mL flame-dried Schlenk flask. A toluene solution (1 mL) of tris[2-(dimethylamino)ethyl]amine (Me_6TREN) (17 mg, 71.6 μmol) was added, and the solution was deoxygenated by argon bubbling for 15 min, followed by 4 freeze-pump-thaw cycles. Copper strips freshly made from 15 cm of wire were then added, and the mixture was thermostated at 40 °C. The reaction was started by addition of a deoxygenated toluene solution (1 mL) of the di-initiator (27 mg, 74.2 μmol) through a syringe. Reaction progress was followed visually by the increase in viscosity and by ^1H NMR and GPC of aliquots. After 1160 min, the pale green reaction mixture was diluted with pentane (400 mL) and eluted through a short neutral alumina column. The mixture was then concentrated to ca. 100 mL, then dichloromethane (100 mL) was added, and the polymer was purified from the unreacted monomers by 3 cycles of precipitation from methanol (1 L). The polymer was collected on a fritted Büchner funnel, crushed with a glass rod, dried by air and vacuum (11.33 g, 75.2%).

2.3. Typical procedure for intramolecular cross-linkage of poly(SMA-co-AAEMA) with trimethylolpropane triacrylate (TMPTA) (polymer A-SC)

In an Erlenmeyer flask thermostated to RT, polymer A (0.75 g) was dissolved in THF (750 mL) during 15 min under argon bubbling. A MeOH solution (1 mL) of KOH (18 mg, 0.32 mmol) was added, and the mixture was kept stirred for additional 10 min under Ar, after which a MeOH solution (0.5 mL) of TMPTA (43 mg, 0.146 mmol) was added. The flask was sealed and the reaction was stopped after 212 h by addition of aqueous H_2SO_4 (0.35 mL, 0.5 M). The reaction mixture was concentrated under reduced pressure to ca. 30 mL, and the polymer was purified by precipitation from methanol (300 mL). The polymer was collected on a fritted Büchner funnel, crushed with a glass rod, dried by air, and by vacuum. (0.76 g, 8.8 mol% cross-link, $M_n = 233\text{KDa}$).

2.4. Typical procedure for measurement of dynamic viscosity of polymer solutions and calculation of PVL and VI

In a 50 mL beaker, polymer (243 mg) was stirred with oil (24.05 g) at 90 °C during 1 h. The resulted clear solution is left unstirred for additional 15 min at the same temperature. At least 4 viscosity measurements at 40 °C and 100 °C are taken for the calculation of permanent viscosity loss (PVL) and viscosity index (VI). After sonication, the polymer solution is placed at 120 °C for 15 min prior to viscosity measuring. VI is calculated according to ASTM D2270 [5]. PVL is calculated according to ASTM D2603 [40].

3. Results and discussion

As an initial point in our VM design, we choose simple poly(methacrylate esters), due to their easily tunable properties via selection of their alcohol part. The established living radical polymerization methods for methacrylates [41–43] readily allow tight control over important properties such as molecular weight, distribution of comonomers and incorporation ratio. Key required properties of the VM are not only oil solubility, but also presence of polar and hydrogen bond forming moieties. The later requirement improves thickening and VI achieved by the additive [8], together with additional benefits such as better adherence to metal surfaces and prevention of deposit formation

Download English Version:

<https://daneshyari.com/en/article/7826064>

Download Persian Version:

<https://daneshyari.com/article/7826064>

[Daneshyari.com](https://daneshyari.com)