



What is the effect of lipophilic polymeric ionic liquids on friction and wear?

Abhijeet P. Bapat^a, Robert Erck^b, Bryan T. Seymour^c, Bin Zhao^c, Lelia Cosimbescu^{a,*}

^a Pacific Northwest National Laboratory, Richland, WA, United States

^b Argonne National Laboratory, Lemont, IL, United States

^c Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States



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ABSTRACT

In this work, methacrylate-type ionic liquid (IL) monomers containing a quaternary ammonium cation and two different counter-anions were synthesized and used as *co*-monomers to obtain functional poly(alkyl methacrylates) (PAMAs). They were then evaluated as friction and wear reducing additives for lubricants. The effect of molecular weight, polymer topology (random or diblock), and IL counter anion on friction and wear behavior of polymer PAO (poly-alpha olefin) solutions have been investigated. The results were compared to those of PAO solutions additized with a small molecule, non-polymeric ionic liquid, or non-ionic copolymers containing 2-(dimethylamino)ethyl methacrylate (DMAEMA) as the polar comonomer. No clear correlation between polymer molecular weight and friction or wear behavior was observed. Random ionic liquid copolymers led to lower wear volumes than their block counterparts. Polymers containing dicyanamide (DCA) counter anion showed lower wear volume compared to those containing bis((trifluoromethyl)sulfonyl)imide (TFSI) anion. Surprisingly, none of the IL copolymers studied outperformed the DMAEMA containing block copolymer in terms of wear volume reduction, suggesting the IL moiety had no beneficial effect on wear.

1. Introduction

Lubricants are essential for minimizing friction between sliding pairs of machine parts, thereby preventing mechanical failure and also improving the energy efficiency of the equipment [14]. Internal combustion engines, like all machines, rely on effective lubricants to ensure their smooth and efficient operation, a long service life, and minimal impact on the environment [9]. Modern lubricants are a complex combination of functional additives such as viscosity modifiers or viscosity index improvers, friction modifiers, antiwear additives, dispersants, pour point depressants, antioxidants, and so on, blended into the base fluid for optimal performance and maximum service life.

The continuous drive to improve the energy efficiency of machines requires the use of low-viscosity lubricants that form extremely thin hydrodynamic films between sliding pairs [14]. A low viscosity lubricant often operates in the mixed-boundary, or boundary lubrication regimes where the incorporation of friction modifiers and antiwear additives is necessary to minimize friction and wear of the moving parts [10, 14, 15]. As the name suggests, friction modifiers (FMs) reduce the friction between surfaces in contact. While FMs may reduce wear, additional antiwear agents that minimize the surface damage resulting from friction are often added to the fully formulated lubricants.

FMs can be classified into two main categories, namely 1)

organomolybdenum compounds, and 2) organic friction modifiers. Organic FMs can be further classified as low-molecular-weight amphiphilic molecules, and polymeric FMs [14]. Similarly, common antiwear agents include organic compounds containing nitrogen, sulfur, phosphorous, halogens, or boron [10]. Both FMs and antiwear agents have the ability to form protective monolayers or thicker barrier films on the sliding metal-component surfaces via physical or chemical adsorption [10, 14, 15].

Since the publication of the first study reporting the effectiveness of ionic liquids (ILs) as universal lubricants, a significant amount of research investigating ILs as lubricant additives has been undertaken [1, 13, 17, 22]. Room temperature ILs are organic or hybrid organic/inorganic molecules that commonly exist as molten salts at mild temperatures due to the destabilization of the solid-phase crystal [4]. The ion-pair structure of ILs can be chosen to enable them to be highly conductive [6], dissolve enzymes [12] and biomass [19], and catalyze chemical reactions [2]. A vast choice of anions and cations that can be combined to obtain tailor-made ILs with desired properties, presents a myriad of possibilities. The negligible volatility, non-flammability, and high thermal stability of ILs make them highly suitable as lubricant additives. It is believed that the high polarity of ILs facilitates strong adsorption and tribochemical film formation, resulting in their enhanced anti-wear performance [8, 11].

* Corresponding author: Pacific Northwest National Laboratory, 902 Battelle Blvd., MSIN K2-44 Richland, WA, United States.

E-mail address: lelia.cosimbescu@pnnl.gov (L. Cosimbescu).

While several studies investigating small-molecule ILs as lubricant additives have been reported [21], only one report involving polymeric ILs is available [20]. This is remarkable, considering that polymeric ILs have been widely investigated for other applications such as electrolytes for electrochemical devices, dispersing agents, anion-sensitive smart surfaces, and precursors to polymeric nanofibers and graphitic materials [7, 18].

In this paper we present the synthesis and investigation of oil-soluble random and diblock copolymers of dodecyl methacrylate and ionic liquid methacrylates containing a quaternary ammonium cation and two different counter anions as potential friction-and-wear reducing additives in lubricants. The effect of molecular weight, polymer topology, and counter anion on the friction-and-wear behavior of the copolymers was studied. The results were also compared with those for an oil-soluble small molecule IL, and tertiary amine functional non-IL copolymers having random and block topology.

2. Experimental section

2.1. Materials

All reagents including silver nitrate, sodium dicyanamide, 2-(dimethylamino)ethyl methacrylate (DMAEMA), bromoethane, lithium bis((trifluoromethyl)sulfonyl)amide (LiTFSI), 2,2'-azobis(2-methylpropionitrile) (AIBN), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT), dodecyl methacrylate (DMA), tetrabutylammonium bromide, and tetradodecylammonium bromide were purchased from either Sigma Aldrich, Alfa Aesar, or TCI America and used as received. All solvents including acetonitrile, THF, methanol, acetone, and dichloromethane were purchased from either Sigma Aldrich, VWR Scientific, or Fischer Scientific and used as received. DMA, DMAEMA, and THF used for polymerizations were de-inhibited by passage through basic alumina prior to use. PAO basestock oil was obtained from Exxon Mobil. This additive-free hydrogenated olefin oligomer mixture had kinematic viscosity 4.1 cSt at 100 °C and 19 cSt at 40 °C, and is referred to as "PAO4."

2.2. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded using an Agilent-Oxford 500 MHz spectrometer at the following frequencies: 500 MHz (^1H) and 125.7 MHz ($^{13}\text{C}\{^1\text{H}\}$). 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 , CD_3CN , acetone- d_6 , or mixtures of these solvents. Size exclusion chromatography (SEC) of the polymers, including both polymeric ionic liquids (PILs) and polymers without ionic liquid moieties, was performed at ambient temperature using a PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) equipped with a refractive index detector, one PLgel 5 μm guard column (50 \times 7.5 mm), and two PLgel 5 μm mixed-C columns (each 300 \times 7.5 mm, linear range of molecular weight from 200 to 2,000,000 Da). For PILs with TFSI counter-anions, THF containing 10 mM LiTFSI was used as the eluent, whereas for PILs with dicyanamide (DCA) counter-anions, THF containing 10 mM tetrabutylammonium dicyanamide was used as the eluent. The SEC samples were prepared by mixing both the polymer and the respective IL-containing THF in a 4.0 mL vial. The mixtures were placed on a shaker plate overnight to allow the polymers to dissolve. For polymers not containing ionic liquid moieties, pure THF was used as the eluent. The polymer concentrations were about 4 mg/g, and all samples were passed through a 0.45 μm PTFE filter before injection into the system. The flow rate for SEC analysis was set at 1.0 mL/min. The SEC system was calibrated with narrow disperse polystyrene standards (Scientific Polymer Products, Inc.), and the data was processed using Cirrus GPC/

SEC software (Polymer Laboratories, Inc.).

2.3. Synthesis and Physico-chemical characterization

2.3.1. Reversible addition-fragmentation chain transfer (RAFT) random copolymerizations

The IL monomer, DMA, AIBN, and CPDT were dissolved in a suitable solvent in a two-necked reaction flask fitted with an air condenser and rubber septum. The reaction flask was degassed using freeze-pump-thaw-nitrogen fill cycles ($\times 3$) and maintained under nitrogen flow. Reactions were initiated by heating to the desired temperature in a temperature-controlled oil bath. An aliquot of the reaction mixture was periodically analyzed by ^1H NMR spectroscopy to monitor the progression of the polymerization. Reactions were stopped by cooling to room temperature (RT) and opening the flask to air. The polymer was isolated by precipitation from a concentrated THF solution into methanol (or other non-solvent where specifically mentioned). This process was typically carried out two times, or until a clean polymer with < 5 mol% of monomer was obtained.

2.3.2. Reversible addition-fragmentation chain transfer (RAFT) mediated block copolymerizations

All the RAFT block copolymerization reactions were carried out in two sequential steps in one pot. In the first step, the IL monomer, AIBN, and CPDT were dissolved in a suitable solvent in a two-necked reaction flask fitted with an air condenser and rubber septum. The reaction flask was degassed using freeze-pump-thaw-nitrogen fill cycles ($\times 3$) and maintained under nitrogen flow. Reactions were initiated by heating to 80 °C in a temperature-controlled oil bath. An aliquot of the reaction mixture was periodically analyzed by ^1H NMR to monitor the progression of the polymerization. Additional degassed AIBN solution was added if required, to ensure $> 95\%$ conversion of the IL monomer was achieved. In the second step, a degassed solution of DMA, and AIBN in a suitable solvent was added and stirring was continued at 80 °C. After a DMA conversion of $\sim 95\%$ was achieved, the heating was stopped, the mixture cooled to RT, and the flask was opened to air. The polymer was isolated by precipitation from a concentrated THF solution into methanol. This process was repeated until a clean polymer with < 5 mol% of total monomer was obtained, typically two times.

2.4. Tribology measurements

A modified Plint reciprocating tribometer was used to conduct friction measurements of the test oils. A ball-on-flat geometry was employed in which the stationary upper specimen was a hardened type 52,100 steel (62 HRC with $S_a = 15$ nm) ball $\frac{1}{2}$ " dia, and the reciprocating lower specimen was a type 52,100 steel (hardened to 62 HRC) flat polished to mirror finish ($S_a = 6$ nm).

The testing temperature was 100 °C. The stroke length was 20 mm and the reciprocation rate was 2 Hz. Tests were nominally one - hour long. In all cases, the measured resistance between ball and flat was near zero, i.e., the contact resistance was very low. A load of 15.6 N was used to produce a peak initial static Hertzian pressure of 1 GPa. Although using different loads may appear beneficial, it is important to do a test in a pressure range the material would experience in actual use. Utilizing extremely high loads would lead to a pressure exceeding anything in use, and one runs the risk of changing the wear mechanism from mild wear (controlled mostly by oil properties) into severe wear (controlled mostly by the shear strength of the metal itself). That would not provide useful information for this application. The time-average coefficient of friction was calculated in software and shown as a function of time on graphs. Post-test optical images were obtained using an Olympus microscope. Post-test profilometrical images and quantitative wear data were obtained using a Bruker GTK white-light interferometer. Wear on the ball was calculated by mathematically removing the curvature of the ball.

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