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Block Copolymer Nanoparticles Prepared via Polymerization-Induced Self-Assembly Provide Excellent Boundary Lubrication Performance for Next-Generation Ultralow-Viscosity Automotive Engine Oils

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Supporting Information

ABSTRACT: Core cross-linked poly(stearyl methacrylate)—poly(benzyl methacrylate)—poly(ethylene glycol dimethacrylate) [S_{31}–B_{200}–E_{20}] triblock copolymer nanoparticles were synthesized directly in an industrial mineral oil via polymerization-induced self-assembly (PISA). Gel permeation chromatography analysis of the S_{31}–B_{200} diblock copolymer precursor chains indicated a well-controlled reversible addition–fragmentation chain transfer dispersion polymerization, while transmission electron microscopy, dynamic light-scattering (DLS), and small-angle X-ray scattering studies indicated the formation of well-defined spheres. Moreover, DLS studies performed in THF, which is a common solvent for the S and B blocks, confirmed successful covalent stabilization because well-defined solvent-swollen spheres were obtained under such conditions. Tribology experiments using a mini-traction machine (MTM) indicated that 0.50% w/w dispersions of S_{31}–B_{200}–E_{20} spheres dramatically reduce the friction coefficient of base oil within the boundary lubrication regime. Given their efficient and straightforward PISA synthesis at high solids, such nanoparticles offer new opportunities for the formulation of next-generation ultralow-viscosity automotive engine oils.

KEYWORDS: block copolymer nanoparticles, polymerization-induced self-assembly, reversible addition-fragmentation chain transfer polymerization, boundary lubrication, tribology

INTRODUCTION

Recently, the automotive industry has seen a concerted drive toward ultralow-viscosity oils because such fluids enable greater fuel economy to be achieved.1 However, formulating such ultralow-viscosity oils is highly problematic. This is because the addition of oil-soluble polymers, which are normally essential to boost performance and durability, makes it impossible to maintain a sufficiently low overall oil viscosity. In principle, this problem can be addressed by adding polymers in the form of sterically stabilized spherical nanoparticles, which make a negligible contribution to the overall oil viscosity.2

In this context, Liu and co-workers reported that cross-linked acrylic block copolymer nanoparticles can act as boundary lubricants for base oil.3 Lubrication tests performed in a mini-traction machine (MTM) indicated a remarkable reduction in the friction coefficient within the boundary lubrication regime, in which opposing surfaces become sufficiently close to produce frequent metal-on-metal asperity contacts.4 5 This typically occurs under high loads and/or when the rate of flow of the lubricating fluid through such contacts is sufficiently low, e.g., for engine start-up at relatively low temperatures. This paradigm-breaking result is potentially highly significant, but unfortunately the synthetic route reported by Liu and co-workers is far from optimal with regard to scale-up.6 More specifically, acrylic copolymers are highly susceptible to ester hydrolysis over long time scales within the normal operating temperature of the internal combustion engine (typically 90–120 °C), but up to 250 °C for brief periods under certain conditions.7 Moreover, the block copolymer synthesis involved multiple steps and the use of various solvents (toluene, 2-butane, THF, and pyridine) over the course of a week prior to nanoparticle self-assembly in a Group II base oil at 80 °C for 13 h. Furthermore, the copolymer chains were prepared via atom transfer radical polymerization (ATRP) using a copper catalyst—the deliberate addition of this transition metal is normally considered unacceptable for automotive engine oil applications because its...
**Experimental Section**

**Materials.** A 4 cSt American Petroleum Institute (API) Group III mineral oil (2.82% aromatic content) and glycerol monooleate were kindly provided by The Lubrizol Corporation Ltd. tert-Butyl peroxyc-2-ethylhexanoate (T21s) initiator was purchased from AkzoNobel (The Netherlands). Cumyl dithiobenzolate (CDB), benzyl methacrylate (BzMA), CDCl₃, and all other reagents were purchased from Sigma-Aldrich (U.K.) and were used as received, unless otherwise noted. Stearyl methacrylate (SMA) was purchased from Santa Cruz Biotechnology (Heidelberg, Germany). THF, n-heptane, and toluene were purchased from Fisher Scientific (U.K.). CD₂Cl₂ was purchased from Goss Scientific (U.K.).

**Synthesis of Poly(stearyl methacrylate) Macromolecular Chain Transfer Agent (mMacro-CTA) via RAFT Solution Polymerization of Stearyl Methacrylate.** The synthesis of the poly(stearyl methacrylate) (S₁₁) macro-CTA has been previously reported by Derry et al.³¹

**Synthesis of Poly(stearyl methacrylate)–Poly(benzyl methacrylate)–Poly(ethylene glycol dimethacrylate) Triblock Copolymer Spheres via RAFT Dispersion Polymerization.** The synthesis of core cross-linked triblock copolymer spheres via RAFT dispersion polymerization at 20% w/w solids was conducted as follows. Benzyl methacrylate (BzMA; 2.29 g; 13.0 mmol), T21s initiator (2.82 mg; 13.0 μmol; dissolved at 10.0% v/v in mineral oil), and S₁₁ macro-CTA (0.7 g; 65.0 μmol; macro-CTA/initiator molar ratio = 5.0; target PBzMA DP = 200) were dissolved in mineral oil (11.96 g). The reaction mixture was sealed in a 50 mL round-bottomed flask and purged with nitrogen gas for 30 min. The deoxygenated solution was then placed in a preheated oil bath at 90 °C and stirred magnetically. After 2 h (BzMA conversion = 98%): Mₑ = 280 kg mol⁻¹, Mₛ = 340 kg mol⁻¹, Mₛ/Mₑ = 1.22), ethylene glycol dimethacrylate (EGDMA; 0.245 mL; 1.30 mmol; target PEGDMA DP = 20) and additional mineral oil (1.03 g) were added, and the resulting dispersion was stirred at 90 °C for a further 2 h to afford a 20% w/w dispersion of core cross-linked S₁₁–BzMA–EGDMA spheres in mineral oil.

**¹H NMR Spectroscopy.** ¹H NMR spectroscopy studies were conducted as previously reported by Derry et al.³¹

**Gel Permeation Chromatography (GPC).** GPC analyses were conducted as previously reported by Derry et al.³³ Dynamic Light-Scattering (DLS). DLS studies were performed at 25 °C using a Zetasizer NanoZS instrument (Malvern Instruments, U.K.) at a fixed scattering angle of 173° as previously described by Derry et al.³³ Copolymer dispersions were diluted to 0.10% w/w using either n-heptane (viscosity at 25 °C = 0.39 mPa·s) or THF (viscosity at 25 °C = 0.46 mPa·s) prior to light-scattering studies.

**Transmission Electron Microscopy (TEM).** TEM analysis was conducted as previously reported by Derry et al.³³ Small-Angle X-ray Scattering (SAXS). SAXS analyses were conducted as previously reported by Derry et al.³³ SAXS patterns were recorded over a q range of 0.003 Å⁻¹ < q < 0.13 Å⁻¹ (sample-to-detector distance 5.104 m), where q = (4π sin θ)/λ is the length of the scattering vector and θ is one-half of the scattering angle.

**Lubrication Testing.** Striebeck curves were obtained using a PCS Instruments mini-traction machine (MTM) consisting of a 19.05 mm diameter steel ball and a 46 mm diameter steel disk. The steel ball and disc are driven independently to create a rolling/sliding contact ratio or slide-to-roll ratio (SRR) of 1:5 (20%) at a constant applied load of 35 N. Tribology measurements were conducted at entrainment speeds ranging from 10 to 3000 mm s⁻¹ using a 4 cSt API Group III mineral base oil in either the presence or absence of 0.5% w/w additives at 100 °C.

**Viscosity Measurements.** The measurements were performed using an Anton Paar MCR502 rheometer equipped with a Peltier
Indeed, it is known that the solvophobic formulation.

**RESULTS AND DISCUSSION**

RAFT dispersion polymerization in mineral oil at 90 °C was used to prepare core cross-linked poly(stearyl methacrylate)—poly(benzyl methacrylate)—poly(ethylene glycol dimethacrylate) (S_{31}−B_{200}−E_{20}) triblock copolymer spheres, according to Scheme 1. GPC traces recorded for the S_{31} macro-CTA and the corresponding linear S_{31}−B_{200} diblock copolymer precursor are shown in Figure 1. Narrow molecular weight distributions were obtained in both cases, and a high blocking efficiency (>95%) was achieved for the RAFT dispersion polymerization of benzyl methacrylate in mineral oil at 90 °C. These data indicate excellent RAFT control, as expected for this PISA formulation.

TEM studies of the linear and core cross-linked nanoparticles confirmed a well-defined spherical copolymer morphology in both cases (see Figure 2a and 2b). This technique can only visualize the nanoparticle cores - the poly(stearyl methacrylate) stabilizer chains cannot be detected. DLS was used to examine the particle size distributions of dispersions of the precursor S_{31}−B_{200} spheres and final S_{31}−B_{200}−E_{20} spheres after a 40-fold dilution with n-heptane (see Figure 2c). This technique determines the overall hydrodynamic size of the nanoparticles, which includes the steric stabilizer layer. These linear and cross-linked nanoparticles exhibited intensity-average diameters of 42 and 48 nm, respectively. In both cases relatively narrow size distributions were obtained (DLS polydispersity index <0.05). Diluting the core cross-linked S_{31}−B_{200}−E_{20} spheres using THF rather than n-heptane prior to DLS studies led to the formation of highly swollen nanogels with an intensity-average diameter of 78 nm. The latter observation confirmed successful core cross-linking using the EGDMA comonomer: if cross-linking had been unsuccessful then nanoparticle dissolution would have occurred to produce molecularly-dissolved copolymer chains because THF is a good solvent for both blocks. TEM analysis of grids prepared using the same dilute nanoparticle dispersion in THF provided further evidence for successful cross-linking (see Figure S2). Such covalent stabilization is believed to be essential for automotive engine oil applications because it substantially enhances the structural integrity of the nanoparticles under demanding conditions, particularly high temperatures. Indeed, it is known that the solvophobic PBzMA block can become sufficiently plasticized on heating in mineral oil to induce a morphological transition. SAXS is a powerful structural characterization technique for colloidal dispersions. It can provide detailed information on particle size, morphology, and interparticle interactions. SAXS patterns recorded for 1.0% w/w dispersions of linear S_{31}−B_{200} spheres and core cross-linked S_{31}−B_{200}−E_{20} spheres in mineral oil at 25 °C (black squares) and 100 °C (open red circles). Dashed lines represent data fits using an established spherical micelle model. For clarity, SAXS patterns are offset by an arbitrary factor, as indicated.
for non-interacting spheres. The SAXS patterns could be fitted using a well-known spherical micelle model (see dashed white traces in Figure 2d). This model indicated core diameters of 27.6 ± 2.1 and 29.4 ± 2.4 nm and mean aggregation numbers of 218 and 234 for the linear and core cross-linked nanoparticles, respectively (see Table S1 for summary of fitting parameters). Importantly, the SAXS pattern obtained at 100 °C for the same 1.0% w/w dispersion of S11–B200–E20 spheres in mineral oil is essentially identical to that collected at 25 °C (see Figure 2d).

Liu and co-workers reported that their acrylic core cross-linked spherical nanoparticles enhanced the lubricant performance of a Group II base oil. More specifically, a significant reduction in the friction coefficient was observed in the boundary lubrication regime at low entrainment speeds when constructing Stribeck curves using a mini-traction machine (MTM). According to Zheng et al., the spherical nanoparticles are drawn into the asperity contact area, where they undergo elastic deformation and hence prevent direct contact between the two moving surfaces. This so-called “ball-bearing” effect has also been proposed for spherical inorganic nanoparticle additives. In the present study, we utilize precisely the same experimental conditions to assess the lubricating performance of the cross-linked S11–B200–E20 spheres prepared directly in a Group III base oil.

In an MTM experiment, the friction generated between the rotating steel ball and disk is manifested as the maximum force that can be applied before slippage is observed. The relationship between the friction coefficient (μf), friction force (Ff), and the normal force (Fn) is given by Ff = μfFn. Glyceryl monooleate (GMO) is widely used as a friction modifier for automotive engine oil formulations. When present at 0.5% w/w, this additive reduces the friction coefficient of the base oil within the boundary lubrication regime. However, using 0.5% w/w core cross-linked S11–B200–E20 spheres of 48 nm diameter clearly leads to a much more dramatic reduction in the friction coefficient at entrainment speeds below 50–60 mm s⁻¹. Indeed, the Stribeck curve shown in Figure 3 is strikingly similar to that reported by Liu and co-workers when using 0.5% w/w cross-linked acrylic copolymer spheres of 35 nm diameter under the same operating conditions. At an entrainment speed of 10 mm s⁻¹, the friction coefficient observed for the S11–B200–E20 spheres is approximately 0.02, which is a remarkably low value. Importantly, the addition of 0.5% w/w S11–B200–E20 spheres results in a negligible change in the solution viscosity at both 25 and 100 °C compared to mineral oil. Moreover, the nanoparticle dispersion exhibited Newtonian rheological behavior at both temperatures (see Figure S3).

RAFT polymerization was developed by Rizzardo and co-workers, who have demonstrated its versatility and excellent tolerance of a wide range of monomer functionality. However, one important barrier to commercialization of formulations and processes based on this chemistry is the organosulfur-based RAFT agent, which confers both color and malodor. In principle, the RAFT chain-ends can be removed via several routes including the addition of excess initiator. Moreover, this post-polymerization modification can be achieved for block copolymer nanoparticles. It is perhaps worth emphasizing in this context that commercial engine and gear oils typically already contain low levels of organosulfur-based additives; indeed, scientists at the Lubrizol Corporation have already demonstrated that RAFT end-groups can be tolerated in star copolymers designed to act as viscosity modifiers for such fluids.

CONCLUSIONS

In summary, the methacrylic core cross-linked spheres reported herein offer excellent boundary lubrication performance. Given their highly convenient synthesis via RAFT dispersion polymerization and bearing in mind that RAFT end-group removal is not required for this particular application, these nanoparticles appear to be well-suited for the formulation of next-generation ultralow-viscosity automotive engine oils that significantly reduce friction in the boundary lubrication regime, thus delivering enhanced energy efficiency (i.e., greater fuel economy).

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12472.

1H NMR spectra; TEM study of cross-linked nanoparticles dispersed in THF; SAXS data for cross-linked nanoparticles dispersed in mineral oil at 25 and 100 °C; SAXS models (PDF)

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Notes

The authors declare no competing financial interest.
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