INTRODUCTION
Abrasive wear of UHMWPE is considered to be one of the factors that contributes to aseptic loosening of total hip replacements. In this study, the abrasive wear resistance of a wide range of linear polyethylenes and ethylene copolymers will be evaluated and compared. Samples with molecular weights ranging from 14,000 to several million g/mol, polydispersities from about 1 – 25 and comonomer contents from 0 to 11 % were selected for this study, offering the opportunity to determine the ideal molecular architecture that combines both excellent wear performance and convenient melt processing.

MATERIALS AND METHODS
Materials
For this project, 18 linear polyethylenes (further referred to as PE-1 to PE-18), some of them commercially available, and 22 ethylene copolymers (LLDPE-1 to LLDPE-22), all especially synthesized by different partners for this study and available only in small quantities, were examined. 26 of the 40 grades were obtained from Ticona GmbH, Germany. The remaining 14 grades were supplied by the following companies or institutions: PE-6, PE-16 and PE-18 from DSM, The Netherlands; narrow-distributed standards PE-12 and PE-17 from National Institute of Standards and Technology (NIST), USA; LLDPE-4 to LLDPE-7, LLDPE-10, LLDPE-11, LLDPE-14 and LLDPE-22 from the group of Geoffrey W. Coates at Cornell University, USA; and LLDPE-2 from Mitsubishi Chemical Corp., Japan. Four of the 22 copolymers contained 0.9 – 10.8 mol% propene, five comprised 0.25 – 1.35 mol% cyclopentene and the remaining 13 samples 0.2 – 3 mol% hexene.

Methods
The GPC measurements were conducted according to DIN 55672 using a Waters 2000 instrument. 1H NMR spectra were recorded at 130 °C on a Bruker UltraShield spectrometer at a frequency of 300MHz. Small-angle x-ray scattering (SAXS) measurements were performed at the Dutch-Belgium beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Abrasive wear was measured using a custom-modified micro-scale abrasive wear tester (CSEM, Switzerland), according to the specifications and the method described by Trezona et al. [1]. In this test, a rotating tungsten-carbide ball is abrading a thin sample of polyethylene at a normal force of 0.27 N, using a silicon carbide slurry as abrasive medium. The wear volume as a function of the sliding distance of the ball follows from the diameter of the hemispherical crater. Archard’s law is finally used to calculate the wear coefficient of the polymeric film.

RESULTS
In the present work, the resistance to abrasive wear of 18 linear polyethylenes and 22 ethylene copolymers, predominantly non-commercial, experimental grades, was investigated. The results conspicuously show that it is possible to combine ultra-high wear resistance with facile melt processing by introducing minor amounts of propene, hexene or cyclopentene into the polyethylene backbone. Several ethylene copolymers with weight-average molecular weights below 400 kg/mol, allowing processing from the melt at modest shear rates, surpassed the wear resistance of commercial-grade, essentially intractable UHMWPE. From the examined variety of different linear polyethylenes and ethylene copolymers, a molecular architecture for the most promising candidates, with respect to superior mechanical properties and processability, can be formulated: generally, the (co)polymer would exhibit $M_w$ between 200 and 400 kg/mol and a polydispersity around or below 2. As comonomer, propene and hexene would be preferred to cyclopentene, since the latter led to a higher reduction of both melting temperature and crystallinity. Finally, the comonomer content would ideally take a value between 1 and 2 mol%, as higher comonomer contents led to softening of the material, observed for LLDPE-1 with a comonomer content of 3 mol%. The most attractive polymer for use in commercial applications among the present set is melt-processable LLDPE-2 ($M_w = 370$ kg/mol, polydispersity = 2.1 and comonomer content = 2.3 mol%), which has a wear coefficient of 2.1 mm3/Nm, superior to commercial-grade intractable UHMWPE. Also LLDPE-9 and LLDPE-10 revealed promising thermal and mechanical properties.

The investigation of the present linear polyethylenes confirmed earlier results reported by Tervoort et al. [2], in which a correlation between the resistance to abrasive wear of polymers and the effective number of physical crosslinks per macromolecular chain was proposed. The vast majority of all polyethylene grades examined in this work displayed a high resistance to abrasive wear. All ethylene copolymers and most of the linear polyethylenes exhibited wear coefficients around or below 3.5 mm3/Nm. This is indeed remarkable, since commercial-grade UHMWPE, which is reported to have the highest abrasion resistance of all thermoplastic polymers, has a wear coefficient around 2.8 mm3/Nm.

Figure 1. Typical wear diagram of polyethylene with corresponding micrographs of wear craters after 3,000, 6,000, 9,000 and 12,000 revolutions.

Figure 2. Wear resistance of all samples with $M_w > 50$ kg/mol in dependence of $M_w$ and comonomer content. The size of the circles corresponds to the wear resistance (large circle is equivalent to high wear resistance) of the material. The circle marked with a cross denotes the commercial-grade UHMWPE Stamylan® UH 210. The dotted line separates intractable (right) from melt-processable (left) materials.

REFERENCES