

## Supporting Information

### Direct route to colloidal UHMWPE by including LLDPE in solution during homogeneous polymerization of ethylene

S. Ronca<sup>1\*</sup>, G. Forte<sup>1</sup>, A. Ailianou<sup>2</sup>, J. A. Kornfield<sup>2\*</sup>, S. Rastogi<sup>1</sup>

1) *Department of Materials, Loughborough University, Loughborough, LE11 3TU, Leicestershire, UK;* 2) *Department of Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, USA.*

\*Corresponding authors emails: s.ronca@lboro.ac.uk, jak@cheme.caltech.edu

### Experimental methods

Materials: All manipulations of air and moisture-sensitive compounds are performed under nitrogen or argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. Ethylene (grade 3.0) is purchased from BOC, and bis[N-(3-tert-butylsalicylidene) pentafluoroanilate]titanium (IV) dichloride is obtained from MCat; both are used as received. Toluene (anhydrous 99.8%) and Methylaluminoxane (10 %wt toluene solution) are purchased from SigmaAldrich®.

Synthesis: A 1.5 l jacketed Pyrex glass reactor assembled for polymerisation is equipped with a magnetic stirrer, a temperature probe, a gas inlet and a rubber septum for catalyst injection. The oven-dried reactor is purged from air with three vacuum-nitrogen (moisture- and oxygen-free) cycles. The desired amount of ethylene-butene copolymer is introduced in the reactor under nitrogen stream and dissolved in the desired amount of toluene at 80°C for 2 hours prior to cooling to 50°C; this step is skipped for the polymerisation of pure UHMWPE.

Methylaluminoxane (MAO, 10%wt in toluene) and ethylene (partial pressure = 1 bar) are added, followed by injection through the rubber septum of precatalyst Bis[N-(3-tert-butylsalicydene)-pentafluoroanilate]titanium (IV) dichloride dissolved in 2 ml of toluene/MAO solution. The reaction is carried on for the required time under vigorous stirring and constant feed of ethylene, controlled by means of a Buchi pressflow gas controller bpc 6002. After 12-15 minutes, the reaction is quenched by addition of methanol. In order to perform the SEM and DSC analyses, the polymer is filtered and dried in a vacuum oven at 40°C for one night.

Scanning Electron Microscopy: SEM Investigations on morphologies of nascent reactor powders are carried out with a high resolution FEG SEM (Carl Zeiss Leo 1530 VP) operated at 5 keV. As-polymerized particles are carefully deposited on SEM stubs and the samples are coated with gold by a sputtering technique.

Differential Scanning Calorimetry: Analyses are performed using a TA Instruments Q2000. Samples of 1.0-2.0 mg mass are weighed with a Mettler-Toledo XS3DU precision balance and crimped in Tzero Aluminum pans of known mass. An identical empty pan is used as reference. A standard heating rate of 10°C min<sup>-1</sup> has been used for heating/cooling/heating cycles from 50 to 160°C. Nitrogen is purged at a rate of 50 ml min<sup>-1</sup>. DSC is calibrated using indium.