

Supporting Information

Controlled individual and partial polyethylene nanofibers with high T_{m2} prepared by PPM-supported Cp_2TiCl_2 catalysts

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General information

Materials

Modified-methylaluminoxane (MMAO) was purchased from Shanghai Ziegler Co. China as 1 mol/L aluminum solution in hexane. Toluene and hexane (analytical reagents; Beijing Chemical Factory) as solvents were purified by the MBRAUN Solvent Purification System prior to use. Polymerization-grade ethylene was obtained from Beifang Special Gas Corporation (Changchun, China). Titanium tetrachloride was purchased from Shanghai Sinopharm Chemical Reagent co., LID (chemical pure). Lauryl chloride (CD for short) was purchased from Alfa Aesar Chemical Corporation (Tianjin, China) and used as received. Styrene (St for short, analytical reagent; Beijing Reagents Factory), Acrylonitrile (AN for short, Chemical pure, Shanghai Reagent Factory) and 1,4-divinylbenzene (DVB for short; analytical reagent; Tianjin Reagents Factory) were distilled in vacuum. benzoyl peroxide (BPO for short, Beijing Chemical Factory) were recrystallized in methanol before use.

Preparation of porous polymer microspheres (PPMs)

We employed seeded polymerization to produce monodisperse cyano-functionalized porous polymeric beads (PPMs for short). Firstly, polystyrene (PS) seed particles, prepared by dispersion polymerization, were dispersed into 0.25 wt% SLS water/EtOH (5/1, g/g) solution (SE solution) using a 250 ml four-necked round bottom flask equipped with a reflux condenser, nitrogen inlet apparatus and a mechanical stirrer. The CD emulsions in the SE solution were poured into the seed dispersion. The stirring speed and temperature were fixed at 200 rpm and 30 °C throughout the swelling process. After complete disappearance of the CD droplets, the second monomer mixture (St/DVB/AN), BPO and diluent (toluene/heptane) were emulsified and added into the reactor for another 12 h of swelling. The swollen particles were stabilized with a 5 % PVP K-30 aqueous solution, and then polymerized at 80 °C for 12 h. The resulting particles were washed repeatedly using water and ethanol. Subsequently, the soxhlet extraction was followed by methylene chloride for 24 h to eliminate the seed particle and porogen.

All experimental operations involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere using a standard Schlenk technique. Prior to catalyst fixation, the prepared PPMs were activated at 60 °C for 12 h under vacuum conditions.

Table S1. The reagent amounts of prepared PPMs supports

PPMs-1#	Characteristic of polystyrene seed particles	Styrene /g	Divinyl benzene /g	Acrylonitrile /g	Toluene /g
PPMs-1#		2	7	1	10
PPMs-2#	M_w : 3.1×10^4 g/mol, particle size: 1.5 μm	2	6	2	10
PPMs-3#		5	3	2	10



Figure S1. The reaction device used in the physical treatment

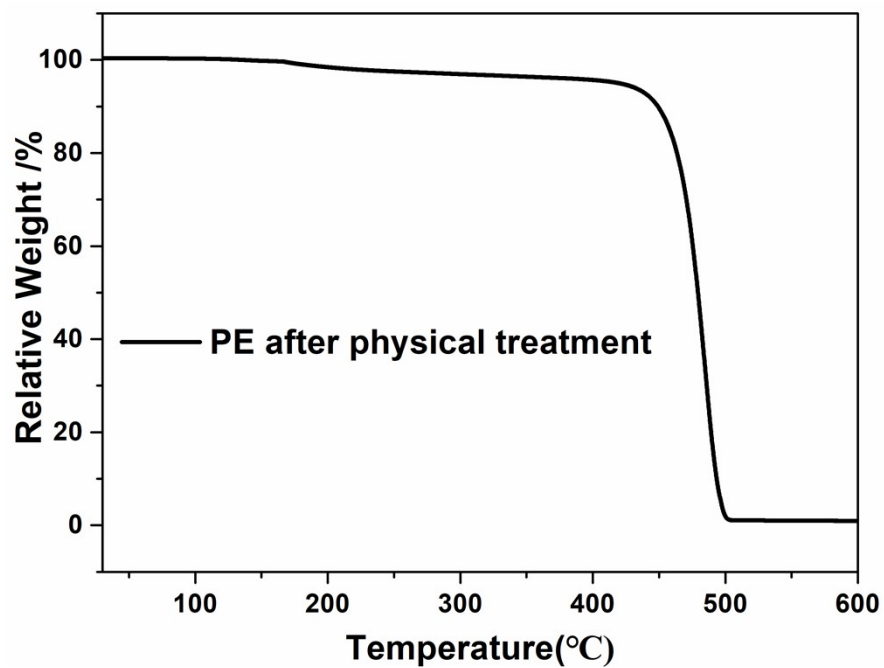


Figure S2. Thermal property of the polyethylene after physical treatment.

Table S2 DSC and SAXS data of polyethylene by Cp₂TiCl₂ and Cp₂ZrCl₂ catalysts

Polyethylene by catalyst	T _{m2} (°C.)	q	d _{ac} (nm)	X _c %	d _c (nm)	d _a (nm)
Cp ₂ TiCl ₂ PPM-supported (after physical treated)	142.5	0.130	48.3	44	21.3	27.0
Homogeneous	137.8	0.183	34.3	59	20.3	14.0
Cp ₂ ZrCl ₂ Homogeneous	134.0	0.197	31.8	61	19.4	12.4

$d_{ac}=2\pi/q$; $d_c=d_{ac} * X_c$; $d_a=d_{ac} - d_c$

Calculation of the outer surface area of PPMs

First of all, bulk density (ρ) and individual particle radius (R) of PPMs supports were obtained through test and SEM measurement, respectively.

Volume of individual porous polymer microsphere (PPM):

$$V = 4\pi R^3/3 \quad (1)$$

Quality of individual porous polymer microsphere (PPM):

$$m = \rho \times V \quad (2)$$

Outer surface area of individual porous polymer microsphere (PPM):

$$S = 4\pi R^2 \quad (3)$$

Total outer surface area of 1 gram porous polymer microspheres (PPMs):

$$S_t = S \times (1/m) \quad (4)$$

The calculated results are shown in Table S3. Based on the results, the theoretical outer surface area of 1g PPMs was just about 0.0016 m², which was much smaller than that of BET specific surface area. Therefore, the influence of the external catalyst on the polymerization results can be negligible because of the huge difference.

Table S3. Outer surface area of PPMs under theoretical condition

	Bulk density/g cm ⁻³	Particle radius/ μ m	Theoretical outer surface area of 1g PPMs/m ²	BET specific surface area of 1g PPMs/m ²
PPMs-1#	0.95	1.98	0.0016	278
PPMs-2#	0.96	2.10	0.0015	112
PPMs-3#	0.94	1.83	0.0017	55.2