

Electronic Supplementary Material (ESI) for RSC Advances.

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## Supporting Information

### **Confined Polymerization: Catalyzed Synthesis of High $T_m$ , Nanofibrous Polyethylene within Porous Polymer Microspheres**

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## **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 (MB SPS-800) prior to use. Polymerization-grade ethylene was obtained from Beifang Special Gas Corporation (Changchun, China).  $\text{Cp}_2\text{TiCl}_2$  and Lauryl chloride (CD for short) were 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.

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## **General information**

### **Textural**

characterization of polymer support and corresponding heterogeneous catalyst was done by N<sub>2</sub> absorption/desorption isotherms. Field emission scanning electron microscope (FESEM, XL30 ESEM FEG) was used for the observation of morphology. The titanium loading was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES). Polymer melting points ( $T_m$ ), crystallization temperatures ( $T_c$ ) and crystallinities ( $X_c$ ) were determined by differential scanning calorimetry (DSC) with A Mettler Toledo, DSC 1 Stare system. Heating scans at 10 °C /min in the temperature range 30 °C to 160 °C were carried out. The heating cycle was performed twice. Molecular weight and molecular weight distribution of the samples were determined by gel permeation chromatography (GPC) at 135°C on a PL-GPC 220 with dichlorobenzene as the solvent using polystyrene calibration. XRD measurement was performed on a Bruck D8 X-ray Thin Film Reflector at 293 K using *Cu-K $\alpha$*  radiation at 40 kV and 35 mA. The N<sub>2</sub> absorption/desorption isotherms were measured with NOVA-1000. The surface areas, pore volume, and average pore diameter were calculated with the NOVA Enhanced Data Reduction Software Ver.2.13. SAXS experiments were carried out on a modified Xeuss system of Xenocs France equipped with a semiconductor detector (Pilatus 100K, DECTRIS, Swiss) attached to a multilayer focused Cu K $\alpha$  X-ray source (GeniX3D Cu ULD, Xenocs SA, France), generated at 50 kV and 0.6 mA. The wavelength of the X-ray radiation was 0.154 nm. The sample-to-detector distance was 2485 mm, and the effective range of the scattering vector  $q$  ( $q = 4\pi(\sin\theta)/\lambda$ , where  $2\theta$  is the scattering angle and  $\lambda$  is the wavelength) was 0.05–1.12 nm<sup>-1</sup>. Each SAXS pattern obtained in the center of the sample was collected within 60 minutes which was then background corrected and normalized using the standard procedure.

The scattering patterns after calibration were averaged over all directions at a constant  $q$ , resulting in one-dimensional (1D) scattering intensity curves. Because of the isotropic distributed stacks of parallel lamellar crystallites in the system, a Lorentz correction (multiplication of  $I$  by  $q^2$ ) was performed in order to calculate the long spacing of the lamellar stacks.<sup>1</sup>

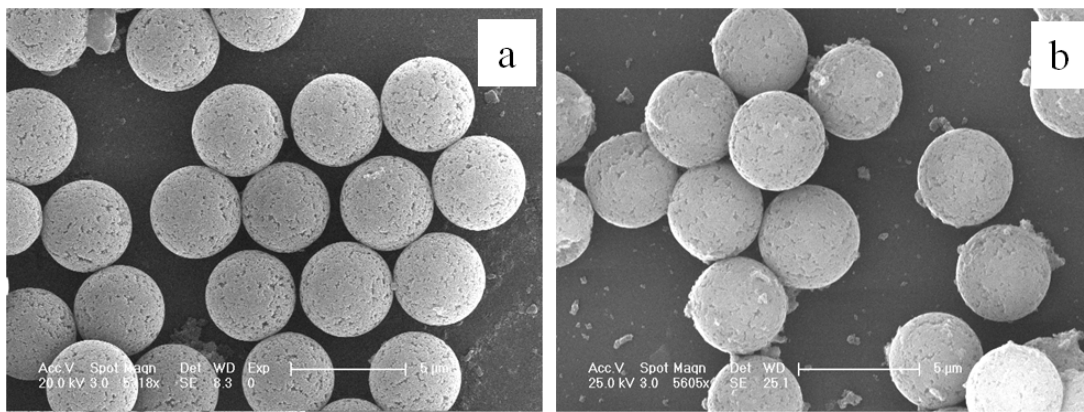
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## Preparation

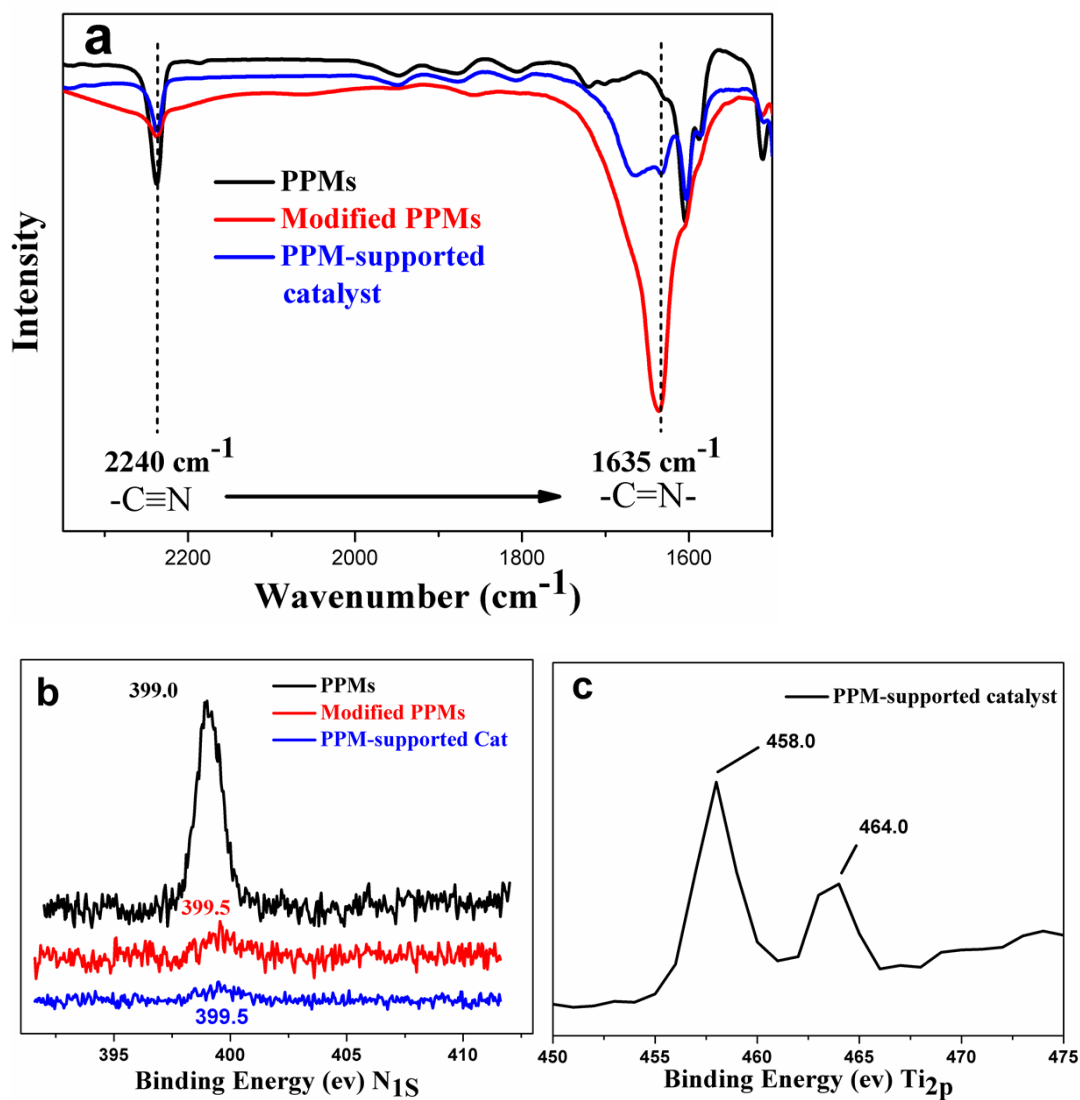
All experimental operations involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere using a standard Schlenk technique. Prior to catalyst fixation, the prepared PPMs were activated at 60 °C for 12 h under vacuum conditions. The weighed PPMs were mixed with MMAO in 60 mL of toluene. After being stirred for 12 h at 50 °C, the slurry was filtered through a fritted disk. The resultant solid was washed thrice with toluene. Subsequently, the solid obtained was mixed with  $\text{Cp}_2\text{TiCl}_2$  in 60 mL of toluene. The slurry was filtered after stirring for 12 h at 50 °C. The resultant solid was collected and washed five times with toluene. The supported catalyst was dried in vacuum at room temperature. The bulk Ti content in the supported catalysts was measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

## Ethylene polymerization

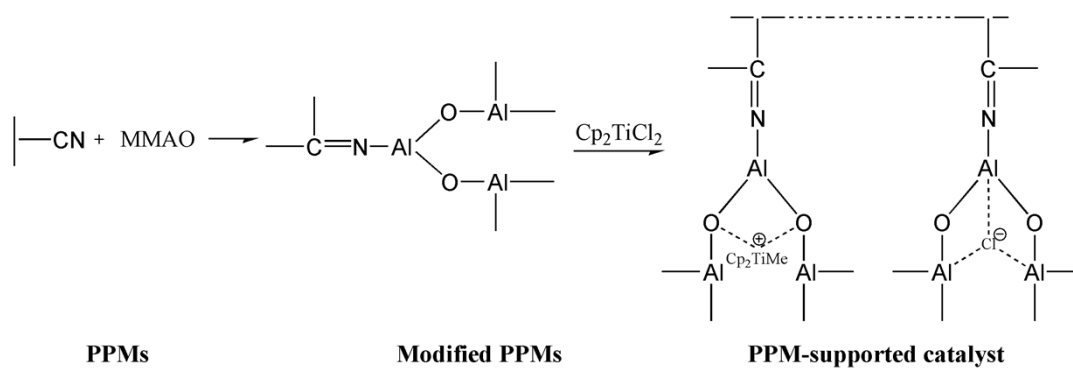
Ethylene slurry polymerization with homogeneous or supported catalysts was conducted in a 1 L or a 0.1 L autoclave stainless steel reactor, equipped with mechanical stirring and inlets for catalyst suspension and the monomer. Before polymerization, the reactor was heated and allowed to cool down under vacuum. Hexane and MMAO solution were added into the reactor under nitrogen protection. The mixture was stirred for 5 min with heating up to the reaction temperature. The catalyst solution or suspension was injected into the reactor; the system was stirred for 5 min and then pressurized to the desired ethylene pressure to start the polymerization. After 30 min, the polymerization was terminated by quenching with acidified (HCl) ethanol. The polyethylene (PE) product was collected by filtration, washed several times with ethanol, and then vacuum dried at 60 °C for at least 12 h. Polymerization was also carried out using the unsupported metallocene catalyst under identical reaction conditions.



**Figure S1.** SEM images of PPMs (a) and PPM-supported catalyst (b). Scale bars: (a and b) 5 $\mu$ m.



**Figure S2.** The FTIR spectra of the PPMs, Modified PPMs and PPM-supported catalyst (a), XPS spectra of the PPMs, Modified PPMs and PPM-supported catalyst (b and c)



**Scheme S1.** Schematic diagram for the preparation of PPM-supported catalyst.

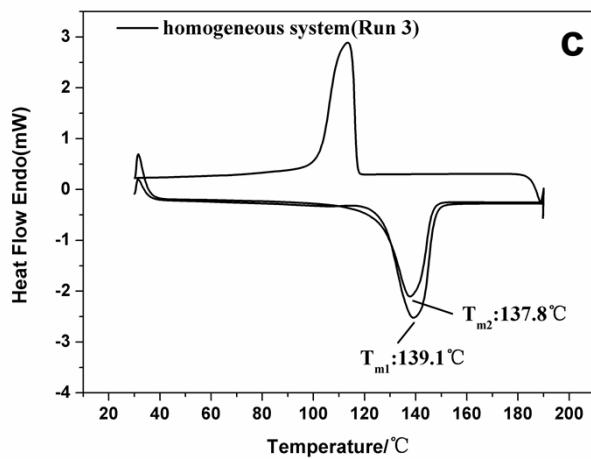
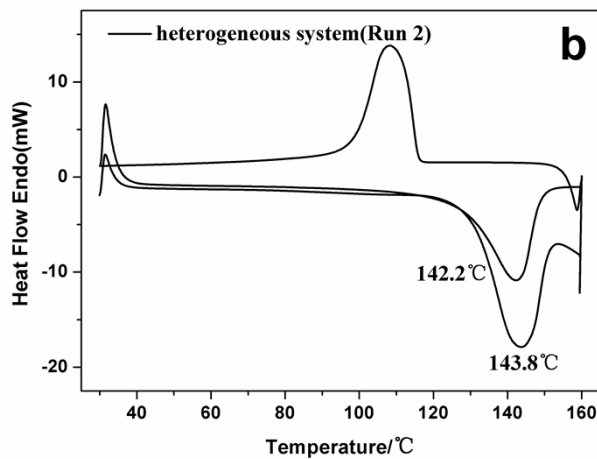
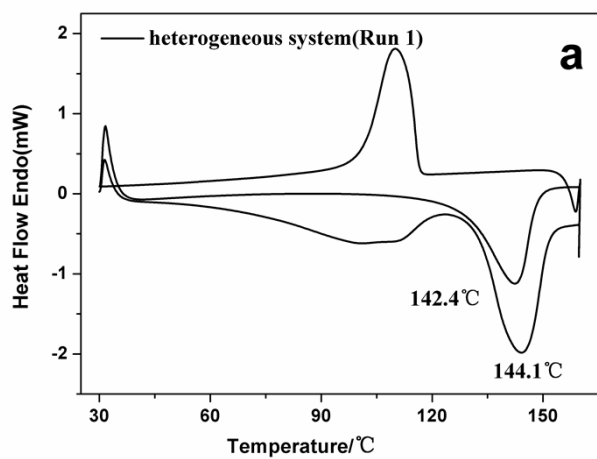


Figure S3. DSC curve of the product polyethylene



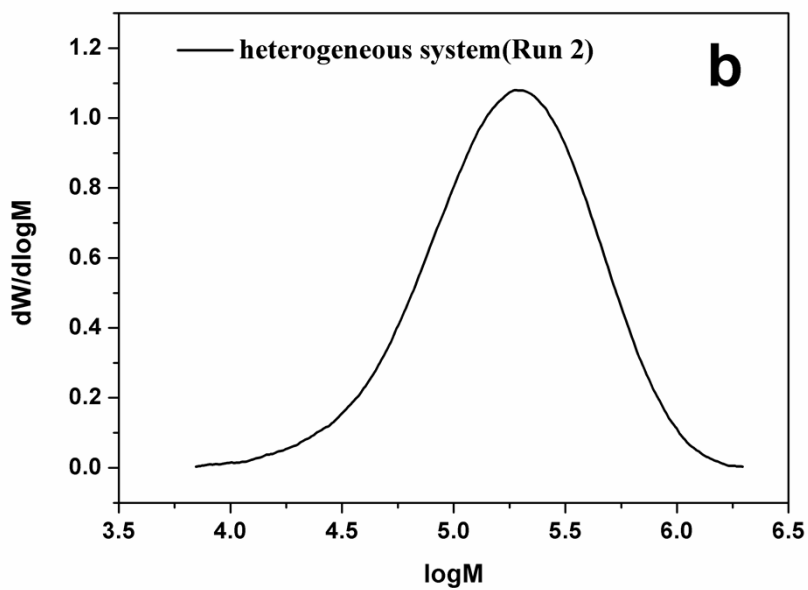
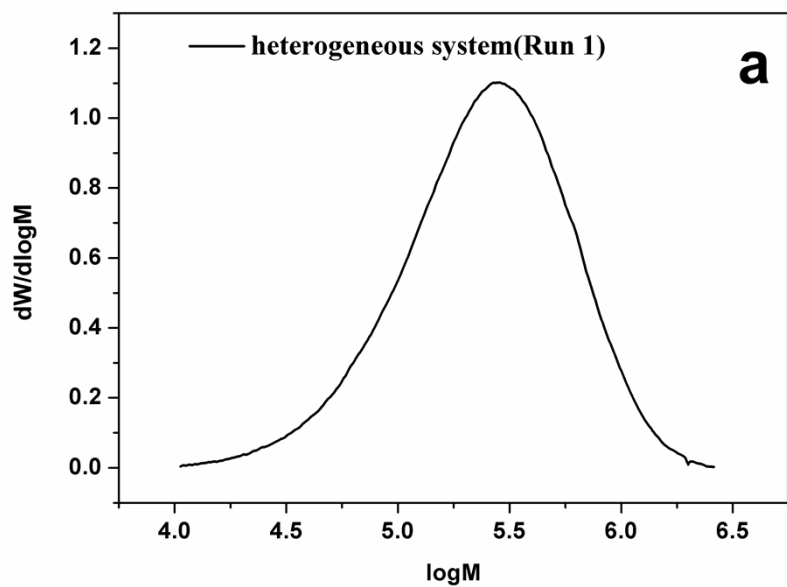
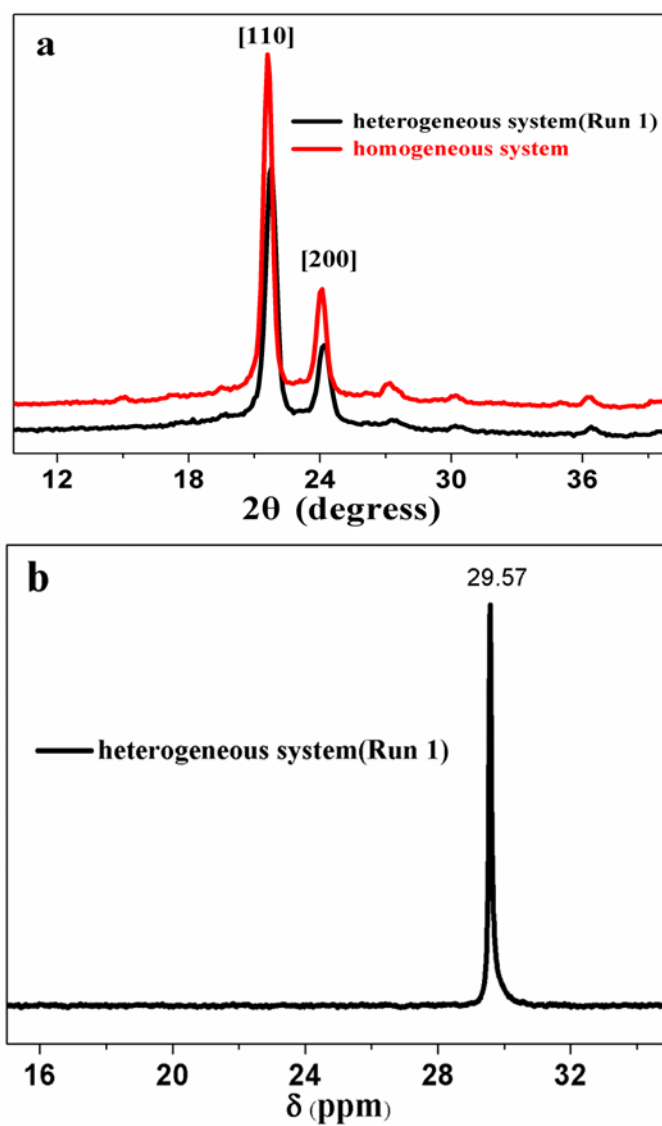


Figure S4. GPC results of the product polyethylene



**Figure S5.** the XRD spectra of the PE samples prepared with PPM-supported and homogeneous catalytic systems (a) and  $^{13}\text{C}$  NMR spectra of the PE prepared with PPM-supported catalyst (b).

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## References

1. Glatter, O.; Kratky, O. *Small-Angle X-ray Scattering*; Academic Press: London, 1982