

Preparation of nano-polyethylene fibers and floccules using MCM-41-supported metallocene catalytic system under atmospheric pressure

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Abstract

Under atmospheric pressure, nano-polyethylene fibers and floccules were prepared via ethylene extrusion polymerization *in situ* with MCM-41-supported metallocene catalytic system. The nano-fibers and floccules were the major morphological units in the resultant samples, and the nano-fibers aggregated uniformly into aggregates and bundles. The diameter of the single fiber was 80–100 nm. With the extension of the polymerization time, the number of floccules increased. The DSC results showed that the resultant samples had higher melting point, compared with polyethylene prepared by homogeneous metallocene catalytic system in the same conditions.

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1. Introduction

The discovery of homogeneous catalyst systems comprising of metallocene and aluminoxane opened a new era in the synthesis of polyolefin [1], of which polyethylene (PE) is the most widely-used synthesized polyolefin [2,3]. Recently, novel supported metallocene catalysts were being developed to control the morphology of PE [4–13].

Some researches have been carried out with regular arranged mesoporous silica materials (e.g. MCM-41, MSF, etc.) as carriers of metallocene catalysts. The polymers prepared using this catalyst reveal fiber morphology [14–17]. Usually, it is believed that if polymer chains are aligned in one dimension, the resultant polymer fiber exhibits an ultrahigh module, which is even greater than that of steel on a weight basis [18]. Aida and co-workers [19] first prepared fully extended-chain crystal polyethylene nano-fibers via ethylene extrusion polymerization *in situ*, with titanocene supported on mesoporous silica fiber (MSF) under a high polymerization pressure (10 atm), demonstrated the good potential of using nano-channels for the control of chain structure

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and material morphology. Subsequently, Ye et al. [18] also prepared PE nano-fibers with MCM-41 supported titanocene dichloride (Cp_2TiCl_2) under higher pressure (20 atm) and investigated the mechanical properties of the resultant PE fibers.

However, the preparation of nano-fibers using MCM-41 supported metallocene catalyst under atmospheric pressure has not been reported yet. The polymerization pressure may influence the chains structure and aggregates to obtain nano-fibers and floccules. The coexistence of nano-fibers and floccules would make it have not only high tensile strength but also good elasticity, so it may wide the potential practical application.

In this work, we prepared nano-polyethylene fibers and floccules via ethylene extrusion polymerization technology *in situ* with MCM-41-supported Cp_2ZrCl_2 catalytic system under atmospheric pressure. Here we mainly research the effect of polymerization time on the morphologies of the PE samples under atmospheric pressure, and elucidate the relation between the polymerization time and PE morphology.

2. Experimental

2.1. Materials

All manipulations involving air and/or water sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technology. Zirconocene dichloride (Cp_2ZrCl_2) was synthesized according to the literature [20]. Methylaluminoxane (MAO) was purchased from Aldrich as 10 wt.% aluminum solution in toluene and was used as received. Polymerization-grade ethylene was purified using three columns of KOH, CuO and 5 Å molecular sieves. Toluene was refluxed over sodium with benzophenone as an indicator and distilled under nitrogen atmosphere before use.

Aqueous ammonia (reagent grade, 25 wt.%), tetraethyl orthosilicate (TEOS, 98%) and cetyltrimethyl ammonium bromide (CTAB) were used as received.

2.2. The preparation of MCM-41

The MCM-41 was prepared by analogous method as reported in literature [21]. The as-synthesized powder was calcinated in air at 550 °C for 5 h to remove surfactants and to obtain MCM-41.

2.3. The preparation of the MCM-41 supported Cp_2ZrCl_2 catalyst

The MCM-41 was treated in flowing ultrahigh-purity nitrogen at 400 °C for 9 h before used. Then 0.55 g treated MCM-41 were mixed with MAO containing

0.55 mmol Al. The slurry was stirred for 2 h at room temperature. The resultant solid was filtered, collected and washed three times with 20 ml toluene. Subsequently, the MAO pretreated MCM-41 was mixed with 50 ml toluene solution containing 0.1 mmol Cp_2ZrCl_2 . After stirring for 1 h at 50 °C, the resultant solid was collected and washed three times with 20 ml toluene, and then dried in vacuum at room temperature. Spectrophotometric analysis indicates that Zr content is 0.16 mmol Zr/g catalyst.

2.4. The preparation of nano-polyethylene fibers and floccules

Nano-polyethylene fibers with floccules were prepared using the MCM-41-supported Cp_2ZrCl_2 catalyst at atmospheric pressure in 100 ml round bottom flask with a Teflon magnetic stirring bar. At selected polymerization temperature, toluene was introduced into the flask and saturated with ethylene monomer, then the required MAO was added and resultant mixture was stirred several minutes. Finally, the supported catalyst was added. The polymerization was terminated at fixed time by adding of acidified ethanol. The product was filtered, washed and dried in vacuum at 60 °C.

3. Characterization of MCM-41 and nano-polyethylene fibers and floccules

3.1. X-ray diffraction (XRD)

X-ray powder diffraction data were obtained on a D/max-3BX diffractometer using $CuK\alpha$ radiation of wavelength 0.154 nm. Diffraction data were recorded between 0° and 10°.

3.2. Nitrogen sorption

Adsorption and desorption isotherm of nitrogen was obtained at 77 K using an OMNISORP (TM) 100CX VER 1G adsorption apparatus. The MCM-41 sample was outgassed at 473 K for at least 8 h in vacuum before measurement.

3.3. Scanning electron microscopy

The MCM-41 and nano-polyethylene fiber samples were deposited on a sample holder and sputtered with gold. The morphology was observed on a scanning electron microscopy (SIRION, FEI, USA).

3.4. Differential scanning calorimeter (DSC)

A differential scanning calorimetry analysis was carried out on a Perkin-Elmer DSC 7 instrument. Ultrahigh

purified nitrogen was purged through the calorimeter. The PE sample (≈ 4 mg) was heated to 170 °C at a rate of 10 °C/min, it was then cooled to 40 °C at 10 °C/min. Subsequently, a second heating cycle was conducted at a heating rate 10 °C/min.

4. Result and discussion

4.1. Characterization of MCM-41

Typical X-ray diffraction patterns of MCM-41 usually show four Bragg peaks indicating the long-range order present in this material [21]. The XRD pattern of the MCM-41 prepared with cetyltrimethyl ammonium bromide as template is shown in Fig. 1. The Bragg peaks can be indexed assuming a hexagonal symmetry.

The adsorption and desorption isotherm of nitrogen on the MCM-41 sample shows the typical type IV isotherm according to the IUPAC nomenclature for MCM-41 (Fig. 2). Structure parameters of the MCM-41 samples are collected in Table 1.

Scanning electron microscopy is also used to determine the size and morphology of the MCM-41. Fig. 3 is the SEM micrograph of MCM-41. The image shows that the MCM-41 particles have tubular structure with 1–2 μm long and 0.2–0.3 μm in diameters, and each particle consists of many hexagonal nano-channels.

4.2. Ethylene polymerization

Four batches of PE samples were prepared at different polymerization time. Table 2 lists the polymerization conditions and results. The results of the ethylene polymerization reveal that the supported catalyst has high catalytic activity (10^6 g PE/mol Zr h atm). DSC characterization results show that the melting point of the sam-

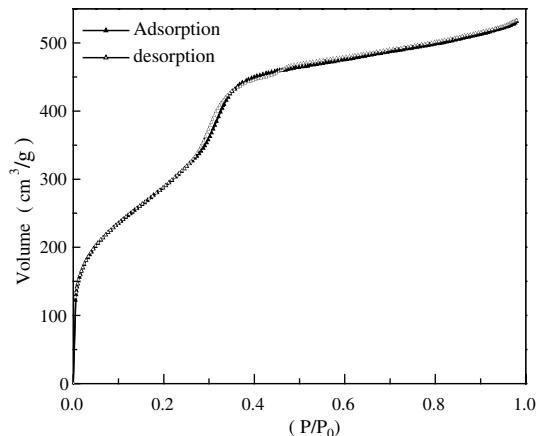


Fig. 2. Nitrogen adsorption desorption isotherm of MCM-41.

Table 1

Structure parameters of MCM-41 obtained with cetyltrimethyl ammonium bromide as template

Support	S_{BET} (m^2/g)	V_p (ml/g)	d_p (\AA)	d_{100} (\AA)	b_p (\AA)
MCM-41	1082	0.79	29	41	9.2

S_{BET} , BET specific surface area; V_p , specific pore volume; d_p , average pore diameter, obtained from BJH adsorption data, $d_p = 4V_p/S_{\text{BET}}$; d_{100} , XRD interplanar spacing; b_p , Pore wall thickness, $b_p = (a_0 - d_p)/2$, $a_0 = (2/\sqrt{3})d_{100}$.

ples produced with the supported catalyst is higher than that of the sample produced with homogeneous catalytic system in the same condition, which can suggest the existence of extended-chains structure. Compared with the results of different polymerization time, we also find that the melting point is similar with the extension of

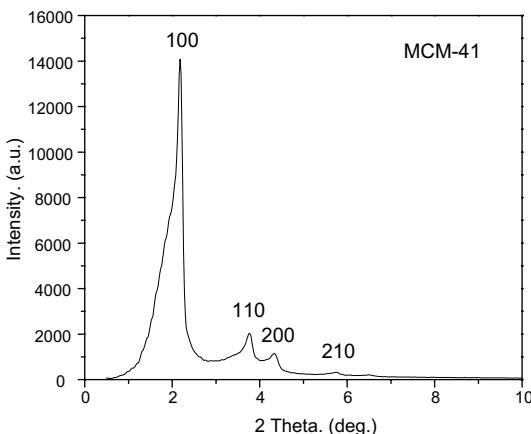


Fig. 1. X-ray diffraction pattern of MCM-41.

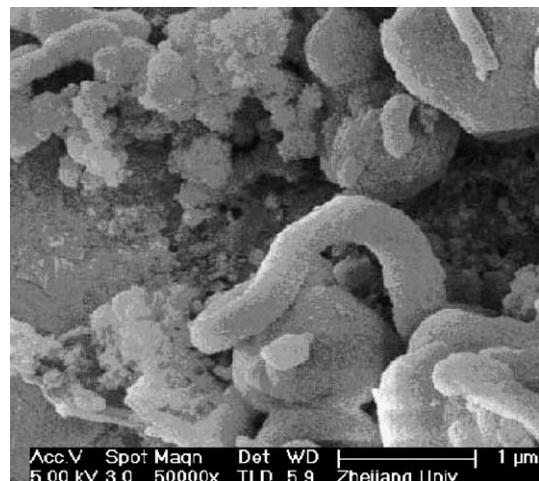


Fig. 3. SEM micrograph of MCM-41 sample.

Table 2

Ethylene polymerization using MCM-41-supported Cp_2ZrCl_2 catalytic system^a

Run	Pressure (atm)	Time (min)	Temperature (°C)	Activity ^b	T_m (°C)	
					First scan	Second scan
1	1	10	50	0.97	134	134
2	1	30	50	0.49	134	135
3	1	60	50	0.50	133	133
4 ^c	1	30	50	1.54	129.7	131.7

^a Polymerization conditions: toluene = 50 ml; $[\text{Al}]/[\text{Zr}]$ = 2000.^b $\times 10^6$ g PE/mol Zr h atm.^c Homogeneous metallocene catalytic system.

polymerization time and the melting point of first scan also is similar to the second scan.

4.3. Effect of polymerization time on morphology of nano-polyethylene fibers and floccules

To evaluate the influence of polymerization time on the nano-fibers and floccules, we observed the samples prepared at different time with SEM. Fig. 4 shows the SEM micrographs with different magnification of the sample produced in Table 2 run1 (10 min).

Fig. 4 shows that the PE sample mainly takes on fiber morphology, which consists of the aggregates of micro-fibers (a, b), bundles of nano-fibers (c) and single nano-fibers (d). In Fig. 4(a) and (b), a large number of PE

micro-fibers with the diameters of 0.5–1 μm aggregate together to form fiber aggregates. The parallel aggregates of the micro-fibers in the aggregation are uniform and orderly. Besides the micro-fibers aggregates, compactly packed bundles of single fibers can be observed and the diameter of the bundle is nearly 5 μm , as shown in Fig. 4(c). In the magnified view of Fig. 4(d), the single nano-fibers with the diameters of 100 nm can also be observed, and the surface of the single nano-fibers is smooth.

In addition to the fiber morphology, the floccules morphology can be observed among the PE fibers, shown as in Fig. 4(a)–(c). The floccules are the random aggregation of PE folded-chains. For the size of micro-porous in MCM-41 are not large enough to contain

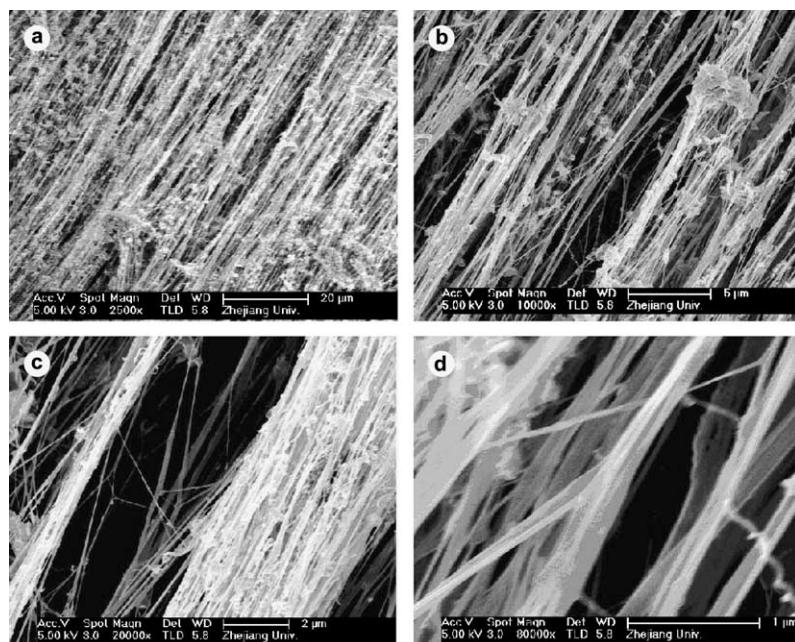


Fig. 4. SEM images of the PE fiber sample produced in Table 2 run 1 (10 min): (a) parallel aggregates of PE fibers with floccules among them, (b) magnified view of (a), (c) magnified view of (b), showing compactly aggregated fiber bundles with floccules among them, (d) magnified view of (c), showing parallel aggregate of single nano-fibers of PE.

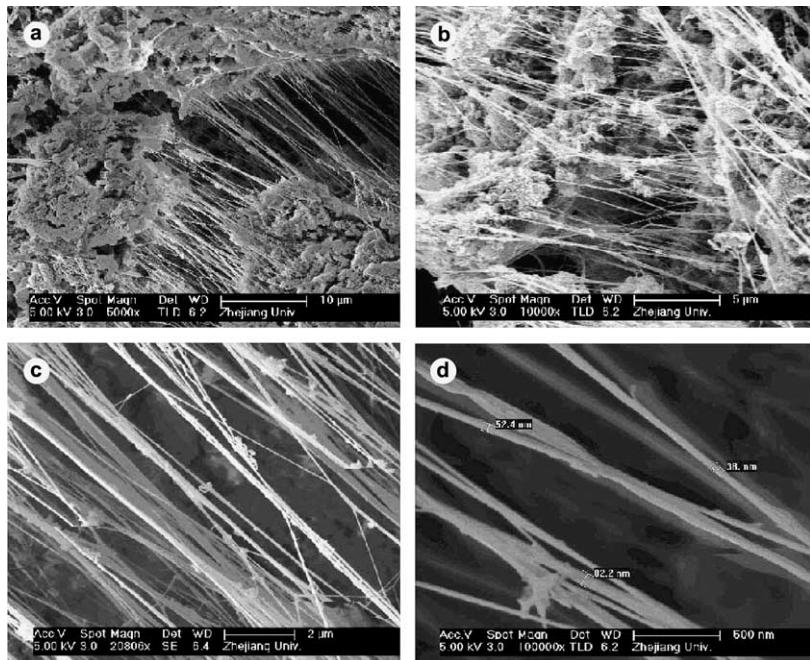


Fig. 5. SEM micrographs of the PE sample produced at polymerization time of 30 min: (a, b) the fibers and floccules morphologies of the sample with different magnifications, (c) magnified view of (b), showing compactly aggregate bundles of PE fibers, (d) magnified view of (c), showing single nano-fibers of PE.

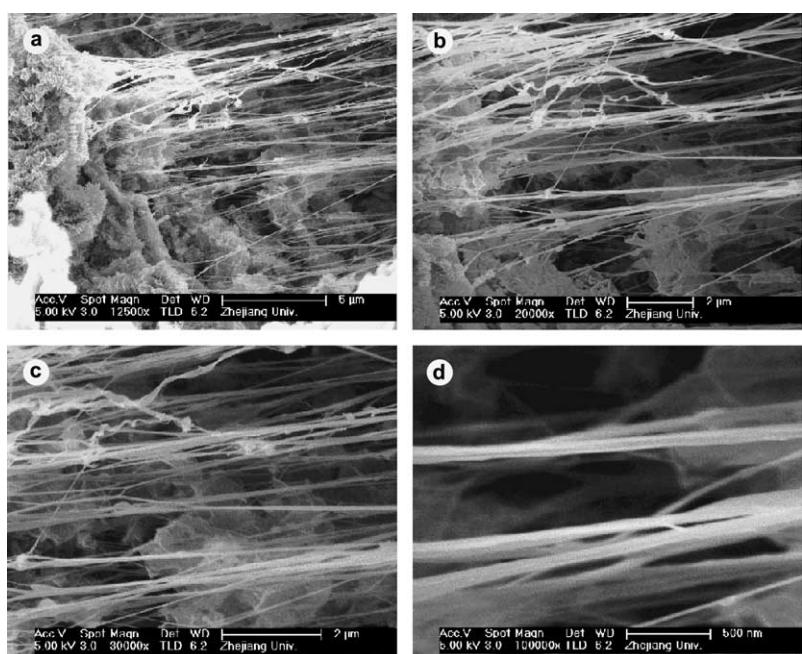


Fig. 6. SEM micrographs of the PE sample produced at polymerization time of 60 min: (a, b) the fibre and floccules morphologies of the PE sample with different magnifications, (c) magnified view of (b), showing fiber bundles with floccules among these bundles, (d) magnified view of (c), showing single nano-fibers of PE.

the PE chains, it can't confine the direction of PE chains propagation to obtain extended-chains, so that the folded-chains aggregate randomly to form PE floccules. Some floccules also result from the extended-chains not aggregating into fibers immediately.

At the polymerization time of 30 min, the micrographs with different magnification are shown in Fig. 5. In Fig. 5(a) and (b), there appear more PE floccules at the end of PE micro-fibers. In Fig. 5(c), the fiber bundles can also be observed; there are still some floccules among the bundles. When magnified, the single PE fibers with smooth surface can be observed clearly, the diameter of the single fiber is about 80 nm, as shown in Fig. 5(d).

Although similar fiber and floccules morphologies can be observed in the PE sample produced at the polymerization time of 60 min, the number of floccules increases, as shown in Fig. 6. Fig. 6(a) and (b) show the micro-fiber with the PE floccules at the end of the fibers, Fig. 6(c) shows the fiber bundles with the floccules among them and Fig. 6(d) shows the single nano-fibers with the diameter of 80 nm.

It is evident from these results that PE nano-fibers and floccules are the major morphologies in the PE samples. With the extension of polymerization time, the number of PE floccules is increasing.

The PE nano-fibers result from the control of MCM-41 nano-channels to the direction and dimension of PE chains propagation. For the MCM-41 consists of honeycomb shaped array of unidimensional, hexagonal pores [22] and the pore diameter (29 Å) is much smaller than the lamellar thickness (270 Å) of the folded-chain crystals of ordinary polyethylene [23]. These nano-channels can serve as template to suppress the kinetically favored chain folding process and obtain PE extended-chains. Then these extended-chains growing out of MCM-41 nano-channels aggregate and crystallize to form nano-fibers (Fig. 7) [19]. Then the nano-fibers aggregate further to form fiber aggregates and bundles, as shown in Fig. 8.

The appearance PE floccules results from the changing of polymerization rate; at the beginning of polymer-

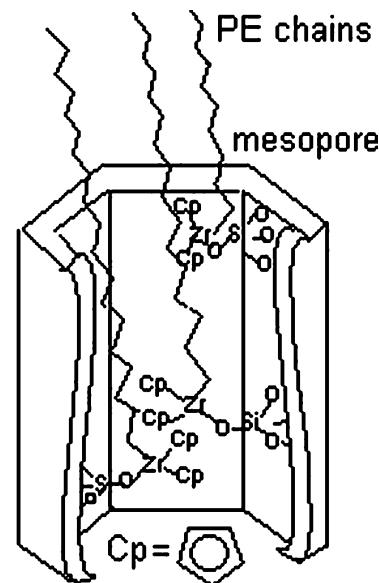


Fig. 7. Conceptual scheme for the formation of PE nano-fibers by MCM-41 mesopores extrusion polymerization.

ization, the polymerization rate of the ethylene is high; many extended-chains grow out of MCM-41 channels simultaneously and aggregate easily to form fibers. With the extension of the polymerization time, the polymerization rate decreases, the simultaneously produced extended-chains are not enough to aggregate, and then the extended-chains may change into another folded-chains to form PE floccules; and with the extension of polymerization time, the floccules increase (Fig. 9).

From the result we can find that the proportion of nano-fibers and floccules in the PE samples can be controlled by the change of polymerization time. This material may have special mechanical properties for the coexistence of nano-fibers and floccules—the nano-fibers can increase the intensity, while the floccules can increase the elasticity.

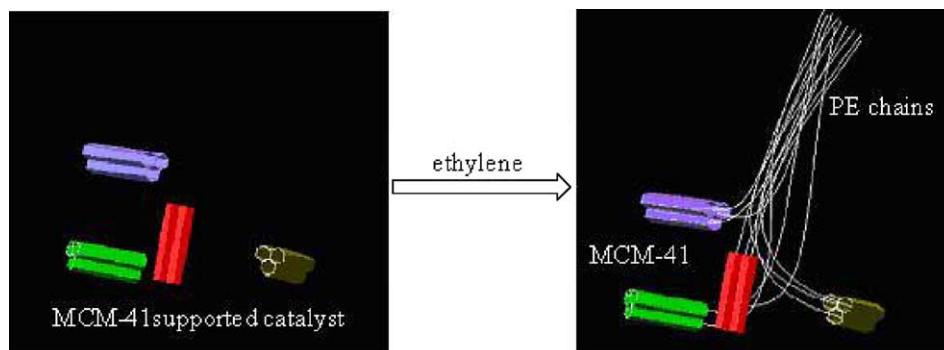


Fig. 8. The formation process of the fiber aggregates and bundles.

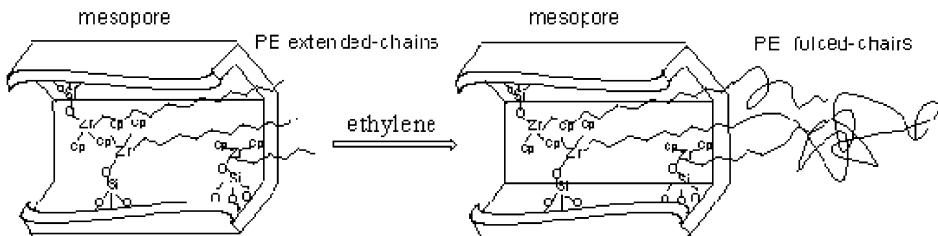


Fig. 9. The formation process of the floccules at low polymerization rate.

As is known to us, no nano-fibers and floccules were reported under atmospheric pressure; and only cocoon-like solid mass consisting of nano-fibers with diameters of 30–50 nm and parallel nano-fibers with diameter of 60 nm were prepared under high pressure [18,19]. Contrary to their researches, the PE floccules in our nano-fibers samples can also be observed at the end of fibers and the number increases with the extension of the polymerization time. This discrepancy may be due to the difference of polymerization conditions, especially the difference of polymerization pressure. In their work, the polymerization pressure is 10 and 20 atm, respectively.

5. Conclusions

Under atmospheric pressure, nano-polyethylene fibers and polyethylene floccules were prepared via ethylene extrusion polymerization in situ with MCM-41-supported Cp_2ZrCl_2 catalytic system. The nano-fibers and floccules were the major morphologic unit in the samples. The diameter of the nano-fibers is 80–100 nm, these nano-fibers aggregated uniformly to form fiber aggregates and bundles. With the extension of polymerization time, the number of the PE floccules increased, which could be used to control the proportion of nano-fibers and floccules in the samples and changed the PE properties. The melting point of the PE with nano-fibers was higher than that of common polyethylene.

Acknowledgments

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