

Preparation of Nanopolyethylene Wire with Carbon Nanotubes-Supported Cp_2ZrCl_2 Catalyst

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ABSTRACT: Nanowires were prepared by ethylene polymerization in situ with carbon nanotubes (CNTs)-supported Cp_2ZrCl_2 catalyst. It was found that the metallocene catalyst was first adsorbed on the surface of the CNTs and then the polymerization of ethylene was initiated. The resulting PE could encapsulate on the surface of the CNTs to form nanowire. The diameter of nanowire could be controlled

easily by the polymerization conditions. The possible mechanism of formation of nanopolyethylene wire is proposed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1291–1294, 2006

Key words: carbon nanotube; nanopolyethylene wire; metallocene catalyst; encapsulation polymerization

INTRODUCTION

The preparation of high-strength polyethylene (PE) fibers is an important topic for researchers, both in industry and in academia, which leads to a large number of investigations¹. The crystal structure and orientation of the PE chain strongly affect the fiber properties. Aida and coworkers² first catalyzed the synthesis of crystalline linear polyethylene nanofibers by ethylene polymerization with mesoporous silica fiber-supported titanocene in situ, and termed the mechanism as extrusion polymerization. The polyethylene chains can grow out of the nanochannels and assemble to form extended-chain crystalline fibers with diameter in the range of 30–50 nm. Subsequently, Ye et al.³ also prepared PE fibers by ethylene extrusion polymerization with MCM-41-supported titanocene catalyst. PE fibers of this kind have high crystallinity and good mechanical properties.

Aida and coworkers and Ye et al conducted experiments in which the PE fibers were of high crystallinity, and the polymerizations were performed under high ethylene pressure. Here we report on the preparation of nanopolyethylene wires by ethylene encapsulation-polymerization in situ using carbon nanotubes (CNTs) supported by Cp_2ZrCl_2 catalyst under atmospheric pressure. The nanotube enwrapped in the nanofibers might increase the mechanical and electrical properties of the fibers. The possible mechanism of formation of nanopolyethylene wire is proposed.

EXPERIMENTAL

Materials

All manipulations were carried out under argon atmosphere using the standard Schlenk technology. Cp_2ZrCl_2 was synthesized according to the literature⁴. Methylaluminoxane (MAO) was purchased as 10 wt % in toluene from Aldrich. Polymerization-grade ethylene was further purified through 4-Å molecular sieves. Toluene was refluxed over sodium with benzophenone as an indicator and distilled under nitrogen atmosphere. CNTs were provided by Professor Xiaobin Zhang.

Preparation of CNTs-supported Cp_2ZrCl_2 catalyst

CNTs were dried at 80°C under vacuum for 8 h to remove the adsorbed water. The pretreated CNTs were suspended in toluene solution of MAO while stirring at room temperature for 2 h. The toluene solution of Cp_2ZrCl_2 was then added under stirring. Two hours later, the supported catalyst was dried in vacuo.

Polymerization

A 100-mL glass reactor equipped with a stirrer, an ethylene inlet, and a vacuum line outlet was purged three times with argon. At a selected polymerization temperature, toluene was introduced into the reactor and saturated with ethylene monomer. Subsequently, the required MAO and CNTs-supported catalysts were added to start the polymerization. The polymerization was terminated at a fixed time by the addition of acidified ethanol. The product was filtered, washed, and dried in vacuum at 60°C.

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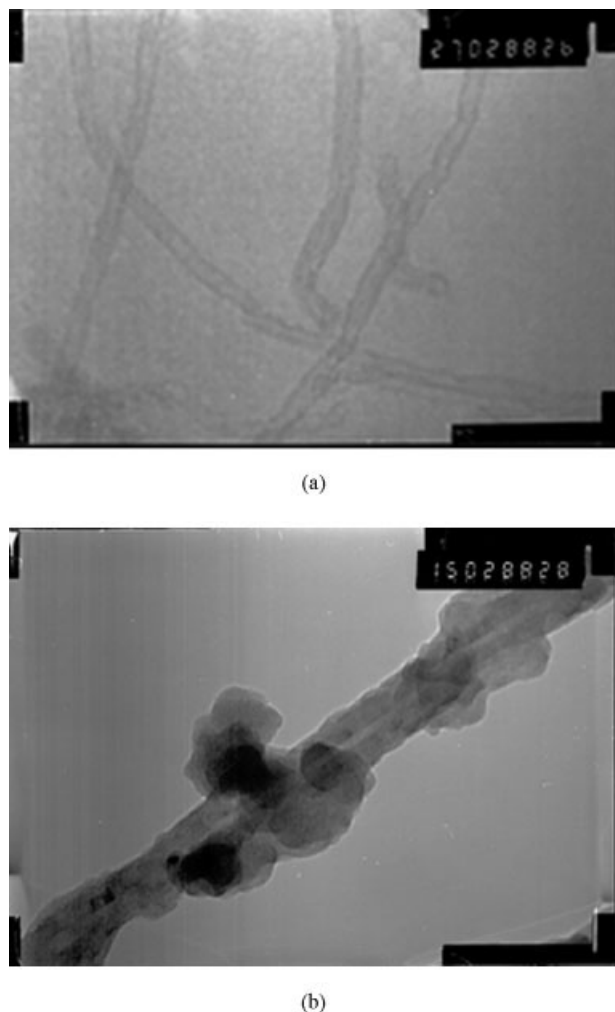


Figure 1 TEM micrograph of CNTs before (a) and after (b) the addition of supporting catalysts.

Characterization

Morphologies of the CNTs before and after addition of the supporting catalysts were investigated using a JEOL model 1200EX transmission electron microscope (TEM). The Raman spectrum at excitation laser wavelength of 514 nm was examined on Almega Dispersive Raman instrument. Scanning electron microscope (SEM) was used to investigate the morphologies of the resultant polyethylene. The surface of the PE was sputter-coated with gold before viewing, and the instrument used was SIRION, FEI SEM.

RESULTS AND DISCUSSIONS

Morphology of CNTs before and after addition of supporting catalysts

CNTs were used as support for Cp_2ZrCl_2 catalysts in this work. TEM analysis revealed that this kind of CNTs presented a slender fibrous structure, as shown in Figure 1(a). The average diameter of a single CNT

was about 30 nm, and the length of a CNT was between several hundreds of nanometers to several micrometers.

Figure 1(b) shows the structure of the CNTs after the addition of supporting Cp_2ZrCl_2 catalysts. The external surface of the CNTs was covered with some particles, which indicated that the catalysts had been adsorbed on the external surface of the CNTs. The average diameter of a single CNT supporting Cp_2ZrCl_2 was similar to the pristine CNT. This result came from the fact that the CNTs were long and slender fibers wherein the walls of the tubes were hexagonal carbon (graphite structure) and capped at each end⁵, the catalyst Cp_2ZrCl_2 could not disperse into the pore of the carbon tubes, and could only be adsorbed on the exterior of the carbon tube.

To investigate the nature of the interaction between the Cp_2ZrCl_2 catalysts and CNTs, the Raman spectrums of the CNTs before and after the addition of supporting Cp_2ZrCl_2 catalysts were examined at excitation laser wavelength of 514 nm, as shown in Figure 2. On comparing spectral data in Figure 2(a) with that of Figure 2(b), the CNTs had similar Raman signals, which indicated that the Cp_2ZrCl_2 catalysts did not destroy the structure of the CNTs, and had only been adsorbed on the surface of CNTs.

Polymerization of ethylene

Ethylene polymerization was carried out with CNTs-supported Cp_2ZrCl_2 catalysts at different temperatures. Figure 3 shows the influence of $[\text{Al}]/[\text{Zr}]$ molar ratio on polymerization activities. The results indicated that the supported catalysts had high polymerization activity ($10^6 \text{ g PE}^{-1} \text{ mol}^{-1} \text{ Zr}^{-1} \text{ h}^{-1}$). With the increase of $[\text{Al}]/[\text{Zr}]$, the activity of catalyst increased.

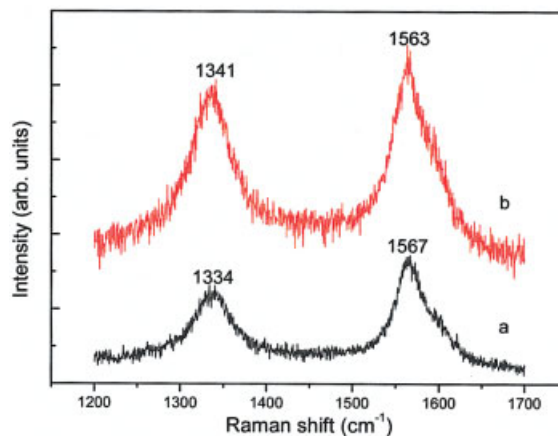


Figure 2 Raman spectra of CNTs before (a) and after (b) the addition of supporting Cp_2ZrCl_2 catalysts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

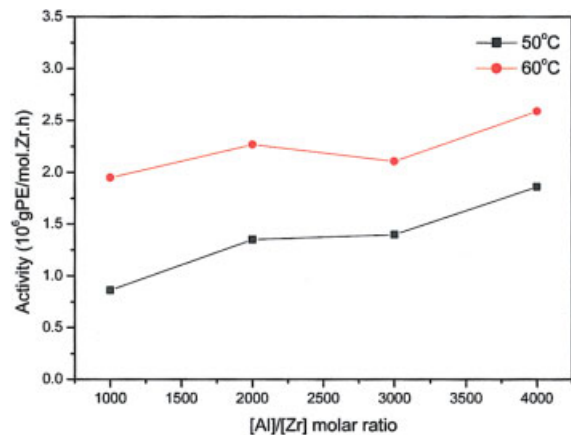


Figure 3 Influence of [Al]/[Zr] molar ratio on polymerization activity, ([Zr] = 3×10^{-5} , ethylene pressure = 1 atm, t = 30 mins, toluene = 50 mL). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Morphology of the resultant nanopolyethylene wires

Figure 4 shows the SEM micrograph of the resulting polyethylene prepared via ethylene encapsulation-polymerization in situ, using CNTs-supported Cp_2ZrCl_2 catalyst. It was clear that the polymer had fibrous structure. The diameters of the fibers were mostly in the range of 50–200 nm, which were much larger than that of the pristine CNTs (30 nm). In addition, most of the fibers had smooth surface. The changes in diameters and surface possibly indicated that the polyethylene had encapsulated on the exterior of the CNTs. This might be due to the fact that the CNTs were the carriers of catalysts and the polyethylene could encapsulate on the exterior of CNTs to form fibrous morphology. The possible schematic process of ethylene encapsulation-polymerization in situ is shown in Figure 5.

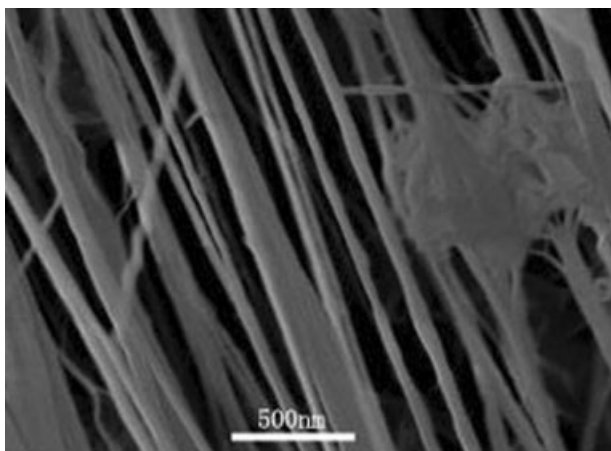


Figure 4 SEM micrograph of the resulting polyethylene wires ($T = 50^\circ\text{C}$, [Al]/[Zr] = 1000).

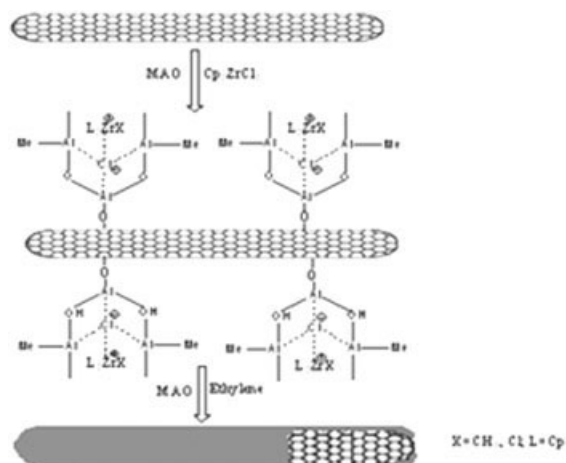


Figure 5 Possible process of formation of nanopolyethylene wire using CNTs-supported Cp_2ZrCl_2 catalyst.

To investigate the influence of the MAO concentration on the morphology of nanopolyethylene, we prepared another polyethylene wire using [Al]/[Zr] in the molar ratio of 4000. Figure 6 shows the SEM micrograph of the resulting nanowires. From the image, we could see that the polymer also had fibrous morphology, but the surface of the fibers became rough and the diameters of the fibers increased when comparing with the fibers shown in Figure 4. This phenomenon resulted from the increase of ethylene polymerization activity with the increase of [Al]/[Zr] molar ratio, so there was more PE encapsulated on the surface of CNTs. This result also showed that the thickness of the PE shell could be controlled easily with the polymerization conditions.

When compared with the method of simply dispersing a nanotube in polyethylene by extrusion in the melt, the ethylene polymerization with CNTs-supported catalyst could obtain good nanopolyethylene wires. The di-

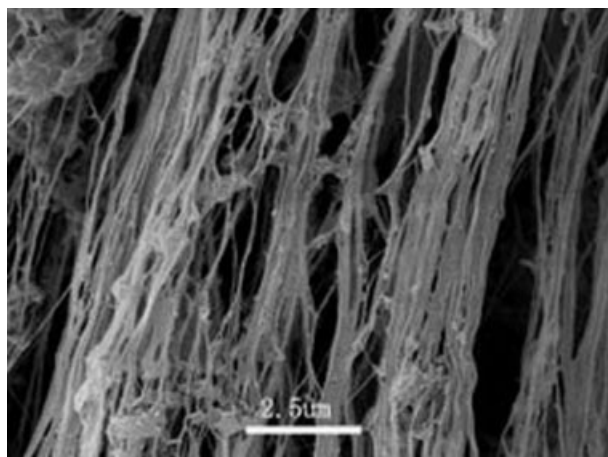


Figure 6 SEM micrograph of nanopolyethylene wires ($T = 50^\circ\text{C}$, [Al]/[Zr] = 4000).

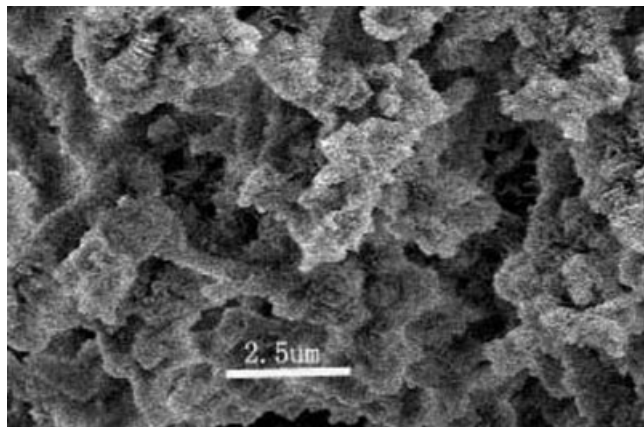


Figure 7 SEM micrograph of PE prepared with homogeneous Cp_2ZrCl_2 catalyst ($T = 50^\circ\text{C}$, $[\text{Al}]/[\text{Zr}] = 1000$).

iameter of the wires could be controlled by the polymerization conditions easily. Owing to the existence of nanotube in the wires, the nanofibers could have good mechanical and electric properties. At the same time, the ethylene polymerization in situ could make the nanotubes disperse uniformly in the PE.

In contrast, the PE prepared with homogeneous Cp_2ZrCl_2 catalyst has no fiber morphology, as shown in Figure 7, which indirectly indicated that the PE could encapsulate on the surface of the CNTs very well to form nanopolyethylene wire.

CONCLUSIONS

The nanopolyethylene wires could be prepared by ethylene encapsulation-polymerization in situ using CNTs-supported Cp_2ZrCl_2 catalytic system. The metallocene catalyst could be absorbed on the external surface of nanotube and, therefore, had high polymerization activity. The results of SEM showed that the diameters of the resultant wires are 50–200 nm. And the diameters of the nanopolyethylene wires could be easily controlled by the polymerization conditions. This novel approach represents a new route towards high-performance nanomaterials.

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