

A theoretical reasoning on why coordination catalysts supported on mesoporous supports can produce HDPE crystalline nanofibers but not iPP crystalline nanofibers

Gholam-Reza Nejabat*

Department of Polymer Engineering, Shiraz Branch, Islamic Azad University, Shiraz, P.O. Box: 71993-3, Iran

Received: 28 January 2018, Accepted: 21 April 2018

ABSTRACT

Since 1999, when Takuzo Aida proposed the preparation of high density polyethylene (HDPE) crystalline nanofibers through polymerization of ethylene by a $Cp_2TiCl_2/MCM-41$ catalyst, many researchers have published various papers on different aspects of the idea. The published researches show that the endeavors to polymerize other types of alpha olefins, especially propylene, to obtain polyolefins with crystalline nanofiberous morphology have not been successful and no one has reported such morphology for them. In the present article, a possible reason behind these observations is proposed. Comparing the direction of the growth of HDPE chains and isotactic polypropylene (iPP) helices to become appropriate for making polymer crystals shows that HDPE chains are able to form crystal unit cells without concerning upward or downward chain growth direction, while the growth direction of adjacent iPP chains might be responsible for unsuccessful synthesis of crystalline iPP nanofibers in confined channels of the mesoporous catalysts. iPP helices can crystallize beside each other only in the form of anticline isochiral helices. **Polyolefins J (2018) 5: 153-156**

Keywords: HDPE crystalline nanofibers; iPP; crystal unit cell; helical chain.

INTRODUCTION

One of the applications of mesoporous silicas like MCM-41 is their use as the support for different types of coordination catalysts that are used in α -olefin polymerization [1]. For the first time in 1999 Aida et al. showed that crystalline nanofibres of linear polyethylene can be formed by polymerization of ethylene with titanocene catalyst supported on mesoporous silica fibre (MSF). X-ray scattering showed that the polyethyl-

ene fibers consisted predominantly of extended chain crystals. This observation indicated a potential utility of the honey-comb-like mesoporous framework as an extruder for nanofabrication of polymeric materials [2]. This exceptional observation provided a new challenge for developing this novel field using other mesoporous silicas as the support of different types of coordination catalysts to reach polyolefinic nanofibers [1, 3-6].

One of the features of these types of catalysts that attracted the attention of researchers is that isotac-

* Corresponding Author - E-mail: ghnejabat@yahoo.com

tic polypropylene nanofibers cannot be produced by them. The main reason suggested for this observation is the probable confinement effect of nano-tubes on the crystallization of iPP [7, 8], without presenting any calculation or experimental evidences. However, on the basis of such observation we have suggested that the nanotubes of the mesoporous materials affect the direction of growth of iPP helices in such a way that they cannot orient in an appropriate manner to form crystalline unit cells.

DISCUSSION

Various papers have been published on the microstructures of iPP and HDPE concerning the spatial arrangement of hydrogen and methyl groups around the axis of the polymer chains. According to the literature, most of the papers have considered a planar zigzag structure for HDPE molecule and a helical structure for iPP molecule, as shown in Figure 1, to ensure the lowest amount of spatial hindrance [9-12].

HDPE crystallizes ideally in the all-trans conformation (linear zigzag, Figure 1), while the size of substituents R in isotactic poly(α -olefins) $[-(\text{CH}_2-\text{CHR})_n-]$ forces the microconformation around each second chain bond to adopt a gauche position, and therefore,

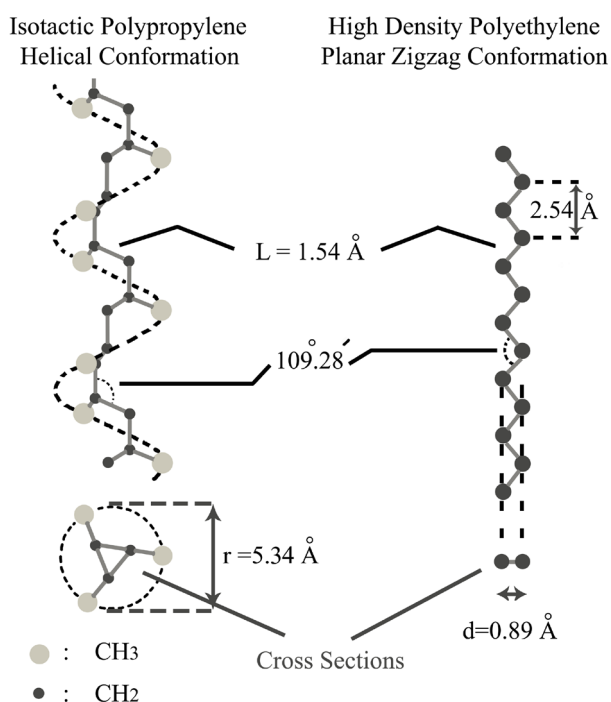


Figure 1. Spatial arrangement of atoms in HDPE and iPP molecules.

the final macroconformation becomes helical (Figure 1). iPP has three propene units per one turn (31 helix). The conformational angles are zero for trans and 120° for gauche conformations. In other members of the family it is said that the larger and longer the side group, the larger the diameter of the helix [12].

Comparing the internal diameter of the pores of MCM-41 or SBA-15 or other similar materials with the unit cell dimensions of HDPE and iPP shows that there is no confinement effect (regarding space available for crystal growth in the nanotubes of these mesoporous materials). The internal diameter of the pores of MCM-41 and SBA, as is reported in many papers, is, respectively, near 30 \AA [5, 13, 14], and around 36 to 54 \AA [15, 16]. HDPE can crystallize in three forms including orthorhombic, monoclinic and hexagonal (Figure 2) [9]. The unit cell dimensions reported for the orthorhombic are $a=7.4 \text{ \AA}$, $b=4.93 \text{ \AA}$ and $c=2.1 \text{ \AA}$, while for the monoclinic are $a= 8.09 \text{ \AA}$, $b= 4.79 \text{ \AA}$, $c= 2.55 \text{ \AA}$ and for the hexagonal unit cell are $a= 8.42 \text{ \AA}$, $b= 4.56 \text{ \AA}$, $c= 2.55 \text{ \AA}$ [9]. iPP can crystallize in three forms called α , β , and γ with the unit cells of monoclinic, hexagonal and orthorhombic, respectively (Figure 2). As is clear in the figure, the cell dimensions are $a=6.65 \text{ \AA}$, $b=20.96 \text{ \AA}$ and $c=6.5 \text{ \AA}$ for the monoclinic unit cell, $a= 8.94 \text{ \AA}$, $b= 9.93 \text{ \AA}$, $c= 42.41 \text{ \AA}$ for the orthorhombic unit cell and $a= 19 \text{ \AA}$, $b= 19 \text{ \AA}$,

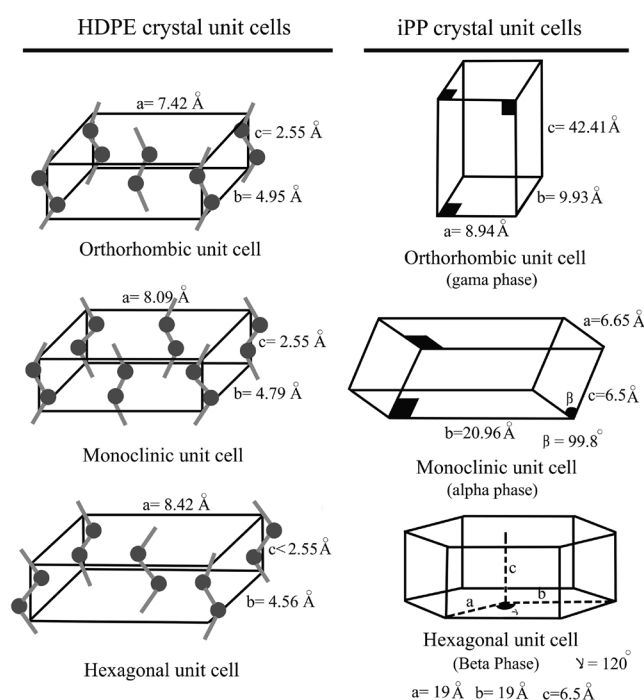


Figure 2. Unit cells of HDPE and iPP proposed by researchers.

$c = 6.5 \text{ \AA}$ for the hexagonal unit cell [9]. By comparing the dimensions given above and the space available in supported catalysts on mesoporous supports (Figure 3) it is clear that all kinds of iPP unit cells or HDPE unit cells can be formed in MCM-41 channels without experiencing any confinement effects (The chains are allowed to grow in the c direction). As is obvious from Figure 3, the spaces which can be provided in MCM-41 channels for the growing polymer chains are tubes with diameters of around 24.74 \AA which are big enough to accommodate all types of unit cells, presented in Figure 2, in them. Therefore, here the confinement effect proposed by researchers [7, 8] may not be meaningful.

However, here an alternative reason is offered. As was mentioned by Lotz et. al. [9], the crystallization of iPP occurs in a manner that the crystal structure includes statistical occupation of every chain site by either an up- or a down-pointing chain (anticline isochiral helices). In other word, two adjacent helices cannot have similar upward or downward orientations (Figure 4). This ensures that the methyl groups of two adjacent helices tend to be located as far from each other as possible. Now, by considering the nanotubes in mesoporous supports it can be said that the probability of the formation of these alternating upward and downward oriented helices in the nanotubes is so low that (may be either due to low space available in

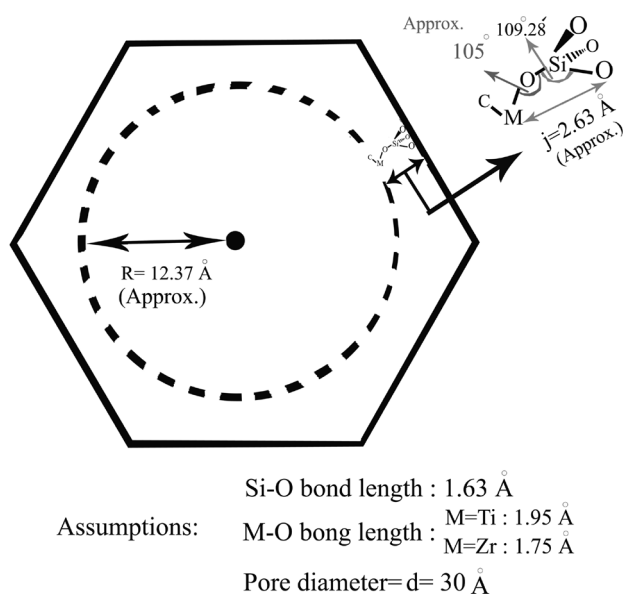


Figure 3. Cross-section of one of the channels of MCM-41. This cross-section can also be considered for SBA-15 with a little modification of SBA-15 channels diameter which is around 36 to 50 \AA .

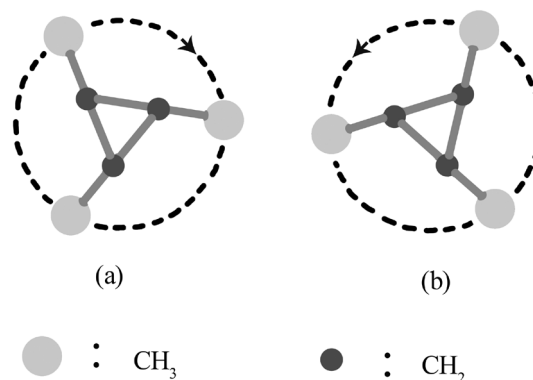


Figure 4. Cross-section of up and down pointing iPP chain helices (anticline isochiral helices). a. right-handed helix, b. left-handed helix.

the pores or kinetic aspects of chain growth and spontaneous polymerization of catalyst sites located in the tubes) the chains cannot orient appropriately beside each other in any of the crystalline unit cells. This issue does not happen for HDPE chains because they can grow in upward or downward direction without any conformational difference between them.

CONCLUSION

Comparing the dimensions of HDPE and iPP crystal unit cells with the dimensions of pores of different mesoporous supports showed no considerable spatial confinement effects on the growth or crystallization of HDPE or iPP. By considering the helical conformation of iPP chains in its crystal unit cells a probable reason was proposed. Since all the helices have to be right-handed and left-handed beside each other to make crystal unit cells and this feature is not reachable in mesopores (the probability of formation of alternating left-handed and right-handed helices beside each other in the tubes is low), therefore iPP cannot crystallize in these types of pores. These restrictions are not applicable for HDPE chains with planar-zigzag conformations which can crystallize beside each other without conformational restrictions.

REFERENCES

1. Ye Z, Zhu S, Wang W-J, Alsyouri H, Lin YS (2003) Morphological and mechanical properties

- of nascent polyethylene fibers produced via ethylene extrusion polymerization with a metallocene catalyst supported on MCM-41 particles. *J Polym Sci Pol Phys* 41: 2433-2443
2. Kageyama K, Tamazawa JI, Aida T (1999) Extrusion polymerization: Catalyzed synthesis of crystalline linear polyethylene nanofibers within a mesoporous Silica. *Science* 285: 2113-2115
 3. Dong X, Wang L, Wang W, Yu H, Wang J, Chen T, Zhou Z (2005) Preparation of nano-polyethylene fibers and floccules using MCM-41 supported metallocene catalytic system under atmospheric pressure. *Eur Polym J* 41: 797-803
 4. Dong X, Wang L, Jiang G, Zhou Z, Sun T, Yu H, Wang W (2005) MCM-41 and SBA-15 supported Cp_2ZrCl_2 catalysts for the preparation of nano-polyethylene fibers via in situ ethylene extrusion polymerization *J Mol Catal A Chem* 240: 239-244
 5. Dong X, Wang L, Zhou J, Yu H, Sun T (2006) Preparation of nano-polyethylene fibers using $TiCl_4/MCM-41$ catalytic system. *Catal Commun* 7: 1-5
 6. Semsarzadeh MA, Aghili A (2008) Novel preparation of polyethylene from nano-extrusion polymerization inside the nanochannels of MCM-41/ $MgCl_2/TiCl_4$ catalysts. *J Macromol Sci A* 45: 680-686
 7. Dong X, Wang L, Wang J, Zhou J, Sun T (2006) Evidence of nanoconfinement effects of MCM-41 on propylene polymerization catalyzed by MCM-41 supported metallocene catalyst in the presence and absence of β -Cyclodextrin. *J Phys Chem B* 110: 9100-9104
 8. Delmon B, Yates JT (2005) *Studies in surface science and technology*, Elsevier, Vol. 158, 1443-1443
 9. Lotz B, Wittmann JC, Lovinger AJ (1996) Structure and morphology of poly(propylenes): A molecular analysis. *Polymer* 37: 4979-4992
 10. Sperling LH (2006) *Introduction to physical polymer science*. 4th ed, John Wiley and Sons, 254-254
 11. Androsch R, Di Lorenzo ML, Schick C, Wunderlich B (2010) Mesophases in polyethylene, polypropylene, and poly(1-butene). *Polymer* 51: 4639-4662
 12. Elias H-G, Mulhaupt R (2016) *Plastics, General Survey*, 1. Definition, molecular structure and properties. In: *Ullmann's polymers and plastics: Products and processes*, 7th ed., Wiley-VCH, Hamburg, 3-149
 13. Nekoomanesh M, Nejabat GR, Arabi H, Emami M (2009) A comment on "preparation of nano-polyethylene fibers using $TiCl_4/MCM-41$ catalytic system". *Catal Commun* 10: 859-860
 14. Nejabat GR, Nekoomanesh M, Arabi H, Emami M, Aghaei-Nieat M (2010) Preparation of polyethylene nano-fibres using rod-like MCM-41/ $TiCl_4/MgCl_2/THF$ bi-supported Ziegler-Natta catalytic system. *Iran Polym J* 19: 79-87
 15. Dong X, Wang L, Wang W, Jiang G, Chen Y, Zhao Z, Wang J (2005) Preparation of nano-polyethylene fibers and floccules by extrusion polymerization under atmospheric pressure using the SBA-15-supported Cp_2ZrCl_2 catalytic system. *Macromol Mater Eng* 290: 31-37
 16. Ahmadi E, Mohamadnia Z, Rahimi S, Armanmehr MH, Heydari MH, Razmjoo M (2016) Phillips catalysts synthesized over various silica supports: Characterization and their catalytic evaluation in ethylene polymerization. *Polyolefins J* 3: 23-36