

A Theoretical Reasoning on Why Coordination Catalysts Supported on Mesoporous Supports 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

E-mail addresses: nejabat@iaushiraz.ac.ir, ghnejabat@yahoo.com

Received: 28 January 2018, Accepted: 21 April 2018

DOI: 10.22063/poj.2018.2122.1111

ABSTRACT

Since 1999 when Takuzo Aida proposed the preparation of high density polyethylene (HDPE) crystalline nanofibers through polymerizing 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 reach polyolefins with crystalline nanofiberous morphology were not 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 about 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.

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

INTRODUCTION

One of the applications of mesoporous silicas like MCM-41 is their using as the support for different types of coordination catalysts 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 polyethylene fibers consist 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]. After this exceptional observation, many scientific groups developed 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 was that the said catalysts could not produce isotactic polypropylene nanofibers. The main reason which was suggested for this observation was the probable confinement effect of nano-tubes on the crystallization of iPP [7, 8] without presenting any calculation or experimental evidences. In the present article another probable reason is proposed for this observation. It is 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. As shown in Figure 1 most of the papers have considered a planar zigzag structure for HDPE molecule and a helical structure for iPP molecule to ensure the lowest amount of spatial hindrance [9-12].

HDPE crystallizes ideally in 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 the final macroconformation becomes helical (Figure 1). iPP has three propene units per one turn (3_1 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 as is reported in many papers is near 30 \AA [5,13,14] and for SBA is around 36 to 54 \AA [15,16]. HDPE can crystallize in three forms including orthorhombic, monoclinic and hexagonal (Figure 2) [9]. The orthorhombic unit cell dimensions are reported to be $a=7.4 \text{ \AA}$, $b=4.93 \text{ \AA}$ 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 of alpha, beta, gamma 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 $a= 19 \text{ \AA}$, $b= 19 \text{ \AA}$, $c= 6.5 \text{ \AA}$ 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 clear 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 is 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 a good reason.

Here another possible reason is proposed. As is 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 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 this alternating upward and downward oriented helices in the nanotubes is so low (may be either due to low space available in the pores or kinetic aspects of chain growth and spontaneous polymerization of catalyst sites located in the tubes) that 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 which are in planar zigzag conformations and can crystallize beside each other without conformational restrictions.

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Figure Captions:

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

Figure 2. The proposed unit cells of HDPE and iPP by researchers.

Figure 3. The 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 d which is around 36 to 50 Å for SBA-15 channels.

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

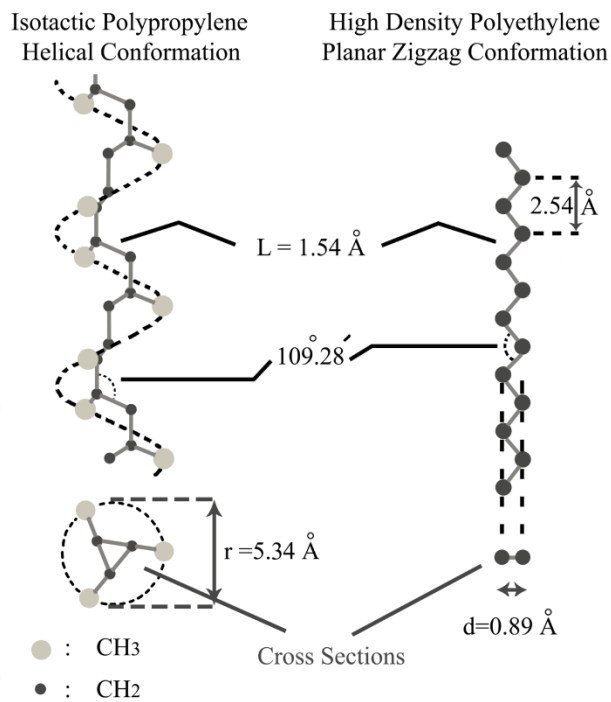


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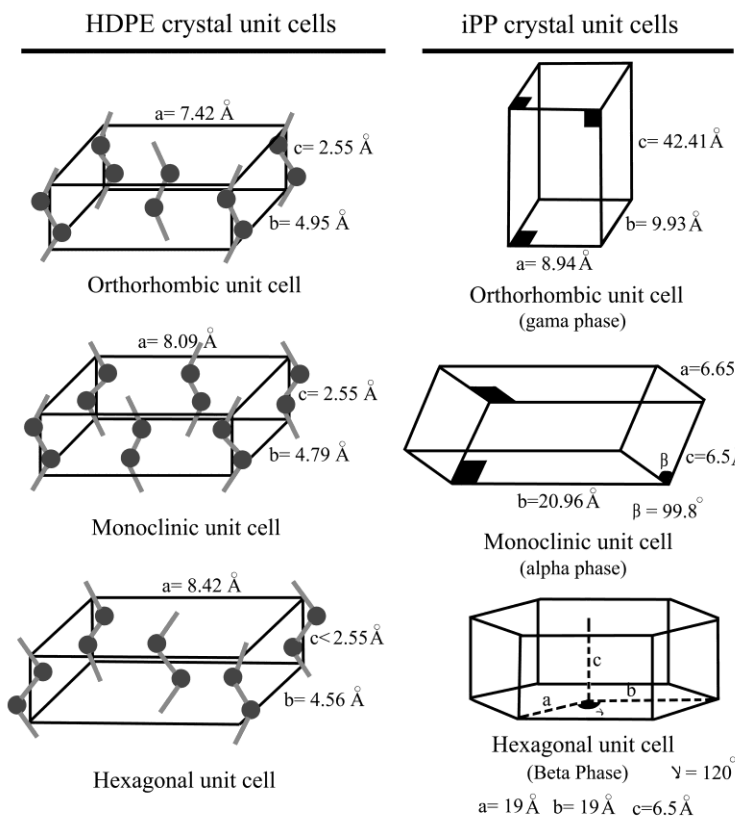


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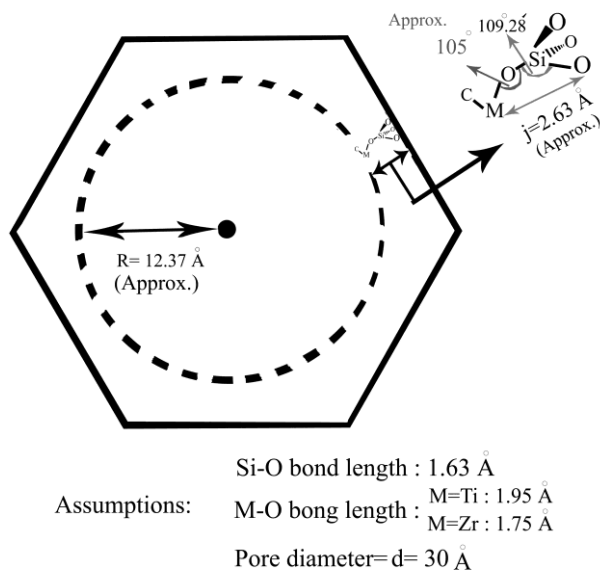


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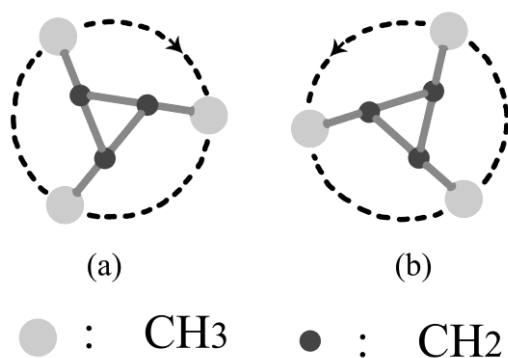


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