

Silver nanoparticles in isotactic polypropylene*)

Part II. Molecular modelling of polypropylene chains arrangement on the surface of silver nanoparticles

Daniel Hybiak^{1, **}, Sylwia Chmielewska¹, Józef Garbarczyk^{1, 2)}

DOI: [dx.doi.org/10.14314/polimery.2015.700](https://doi.org/10.14314/polimery.2015.700)

Abstract: Molecular modelling (MM) was used to explain the mechanism of formation of polymorphic β form of isotactic polypropylene (iPP) at the surface of the silver nanoparticles (nAg). Geometrical optimization of iPP chains and unit cell of Ag systems was made with the use of MM+ force field in vacuum. According to the results, the arrangement of methyl groups in the (110) contact plane implies a lateral packing of helices with a periodicity $a \approx 19 \text{ \AA}$, which is a characteristic feature of the complicated packing of helices in β iPP. Partial charges calculated on the basis of the hybrid potential BLYP revealed the possibility of electrostatic interactions between hydrogens from methyl groups and silver atoms at the edge of unit cell. Analysis of the optimized iPP/Ag system confirmed that the formation of the polymorphic β iPP can be explained by the epitaxial mechanism.

Keywords: polymorphism, epitaxy, molecular modelling.

Nanocząstki srebra w izotaktycznym polipropylenie. Cz. II. Modelowanie ułożenia łańcuchów polipropylenu na powierzchni nanocząstek srebra

Streszczenie: W celu wyjaśnienia mechanizmu tworzenia się formy β izotaktycznego polipropylenu (iPP) na powierzchni nanocząstek srebra (nAg) wykorzystano modelowanie molekularne (MM). Wykonano optymalizację geometryczną układów iPP z nAg przy użyciu pola siłowego MM+ w próżni. Stwierdzono, że ustawienie grup metylowych w płaszczyźnie kontaktu (110) ujawnia boczne upakowanie helis z okresowością $a \approx 19 \text{ \AA}$. Jest to cecha charakterystyczna dla upakowania helis w formie β iPP. Wyniki obliczeń ładunków cząstkowych przy użyciu potencjału hybrydowego BLYP wskazują na możliwość występowania oddziaływań elektrostatycznych między wodorami z grup metylowych łańcuchów iPP i atomami srebra leżącymi na krawędziach komórki elementarnej. Analiza optymalizowanych układów potwierdziła, że oddziaływanie atomów srebra z makrocząsteczką iPP może się przyczynić do tworzenia polimorficznej formy β na drodze mechanizmu epitaksjalnego.

Słowa kluczowe: polimorfizm, epitaksja, modelowanie molekularne.

Isotactic polypropylene (iPP) can exist in the crystalline phase in 3 polymorphic forms: monoclinic α , triclinic γ and trigonal β [1, 2]. The rotation of 3_1 helices of the conformation of $(TG)_3$ or $(TG^*)_3$ macromolecules and of the repeat distance 6.5 \AA along the helices axis has been found in all polymorphic forms of iPP. The structure of α form has been determined as monoclinic, with param-

eters $a = 6.65 \text{ \AA}$, $b = 20.96 \text{ \AA}$, $c = 6.5 \text{ \AA}$ [2]. The gamma form is built of triclinic cells which are the subcells of a much larger face-centred orthorhombic unit cell with parameters $a = 8.54 \text{ \AA}$, $b = 9.93 \text{ \AA}$, $c = 42.41 \text{ \AA}$. The β form has been for the first time described by Keith and co-workers to have hexagonal unit cells [3]. Recently, this form has been determined by Meille *et al.* [4] and by Lotz *et al.* [5] to have trigonal unit cells with parameters $a = b = 11.01 \text{ \AA}$, $c = 6.5 \text{ \AA}$. The appearance of β form can be stimulated by specific low molecular weight organic or inorganic compounds added to the molten polypropylene matrix [6–10]. The best known and most effective compounds of this type are the pigment Red E3B [11], as well as calcium salts of pimelic and suberic acids [12]. According to Lotz and co-workers [13], the formation of β form iPP is connected with epitaxy. Epitaxy refers to the process of growing of a crystalline overlayer on a crystalline substrate. The deposited material forms a crystalline over-

¹⁾ Poznań University of Technology, Institute of Chemical Technology and Engineering, ul. Berdychowo 4, 60-965 Poznań, Poland.

²⁾ Hipolit Cegielski State College of Higher Education in Gniezno, ul. Ks. Kard. Stefana Wyszyńskiego 38, 62-200 Gniezno, Poland.

*) Material contained in this article was presented at the IX International Conference "X-Ray investigations of polymer structure", 3–6 December 2013, Zakopane, Poland.

**) Author for correspondence; e-mail: daniel.j.hybiak@doctorate.put.poznan.pl

layer that has defined orientation with respect to the substrate crystal structure. This phenomenon takes place when the dimensions of unit cells of the crystal lattices of both crystals are similar. The dimensional lattice matching theory proposed by Lotz for helical polymers has been used to explain the structural relationship between the surface of nucleating agents and the β form iPP lattice [13]. According to Kawai and co-workers, epitaxy occurs when relative difference between the lattice parameters of the substrate (nucleating agent) and the macromolecule is less than 15 % (parameter f_m) [14]. For the helical polymers Lotz has proposed to consider matching between the substrate lattice and the interchain or repeat distance on the chain axis [13]. Stocker and co-workers have suggested that (110) contact face of β iPP is involved in the epitaxies on both γ -quinacridone and N,N' -dicyclohexylterephthalamide (DCHT) [10].

Recently, it has been noted that also some metallic nucleating agents having nanometric dimensions can influence the polyolefin chains during the crystallization process [15–19]. In the above cited works, the formation of β polymorph was a result of a simultaneous effect of metallic nanoparticles and physical factors (shear forces) [16–19]. Therefore, a direct role of metallic nucleating agents in the formation of β polymorph isotactic polypropylene remains an open question.

In our previous study [20] we have found that the content of β iPP is strongly related to the amount of silver nanoparticles added as well as temperature conditions of crystallization. The highest amount of β form (k parameter) [21] was observed in the samples containing 0.6 wt % nAg after isothermal crystallization at 125 °C and 130 °C ($k \approx 70$ %) as well as in the sample obtained under non-isothermal conditions ($k \approx 67$ %). On the basis of these observations we suggested the epitaxial mechanism. We have put forward a hypothesis that the protons from methyl groups of iPP chains can interact with Ag atoms located in unit cells (space group F) at repeat distances which are the multiplicities of the a parameter. The distance between protons of methyl groups from adjacent chains in the unit cells of β form iPP is close to 19.07 Å [4, 5], however the distance between the neighbouring Ag atoms which is equal to the parameter a mul-

tiplied by 5 is 20.43 (5×4.0853 Å) (Fig. 1). The ratio f_m calculated on the basis of these values is 6.6 %.

The present article is a continuation of our previous study published as Part I [20]. The aim of this study was to check the above mentioned hypothesis and show the possible arrangements of iPP chains on the surface of silver.

COMPUTATIONAL PROCEDURES

The first step in our calculation was to propose the initial model of the iPP chain layer on the Ag surface. The iPP chain (3_1 helix of TG conformation) containing 14 mers was modelled by Hyperchem software [22] and silver unit cell (space group F) with parameter $a = 4.0853$ Å was modelled by the Crystal Builder options in the same program [22]. Positions of silver atoms in the unit cell were blocked in order to maintain the structure F of unit cell. The calculations were performed for two systems: one of seven unit cells of silver with four polypropylene chains (7ucAg4iPP) and the other of seven unit cells of silver with twelve polypropylene chains (7ucAg12iPP). Before optimization process, the iPP chains were assumed to be parallel to each other and to Ag surface. This arrangement of iPP chains does not correspond neither to α nor β form (see Fig. 2a and 3a). All systems were optimized with the use of the MM+ force field in vacuum with the help of Hyperchem program [22].

Partial charges were calculated using the method BLYP/3-21G in the Gaussian 09 package [23]. According to [24–26] the potential of the hybrid BLYP well describes organometallic systems and its use reduces the cost of computation time. Partial charges were calculated before and after geometry optimization of the system 1ucAg1iPP.

RESULTS AND DISCUSSION

After optimization of system 7uc4iPP (Fig. 2b) the surface of the silver unit cells forces the arrangement of the first layer of iPP chains presented in Fig. 2.

As a result of optimization, the iPP chains were rearranged and adopted a structure approaching that of the rigonal beta form. It can be better seen when the calculation was made for the subsequent layers as well (Fig. 3b).

The arrangement of the first layer of iPP chains enforces the arrangement of the second layer of iPP chains. In the second layer two isochiral, isocline chains at the corners assume different positions with respect to the middle chains. The above different azimuthal orientations of the two middle chains with respect to the corner ones generates a structural periodicity $a \approx 19$ Å in the contact (110) plane (horizontal aspect). This arrangement of iPP chains in the presence of silver nanoparticles makes a structure characteristic of β form and is consistent with the unit cell specified by Lotz [5].

Unexpectedly, during optimization, the Ag nanocrystal (containing 7 unit cells) was rotated by about 45 degrees in relation to the (110) iPP plane (Fig. 4), which

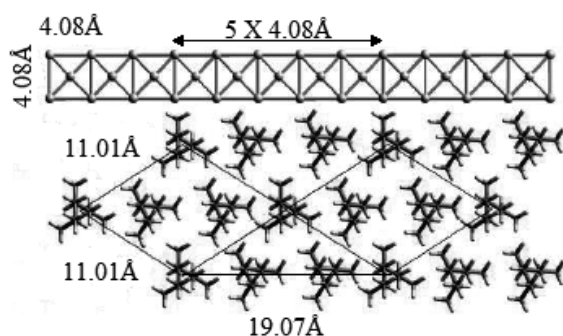


Fig. 1. Dimensional lattice matching between Ag surface and β form iPP (projection onto the 001 Ag plane)

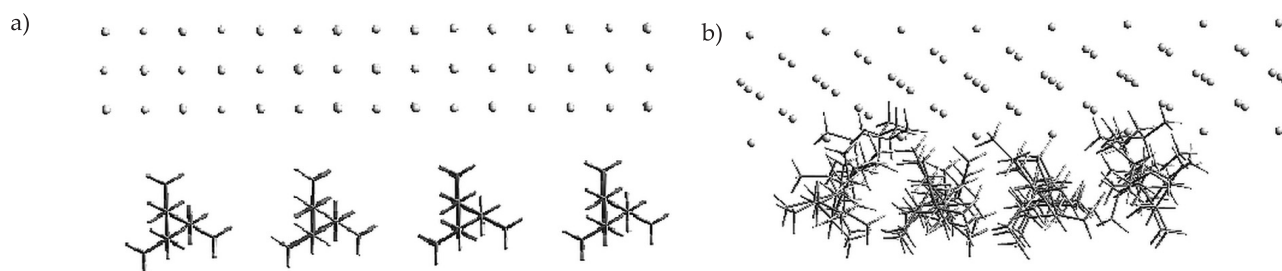


Fig. 2. Model of 7ucAg4iPP initial arrangement: a) before, b) after optimization (perpendicular projection in the direction of the c-axis of polypropylene chains)

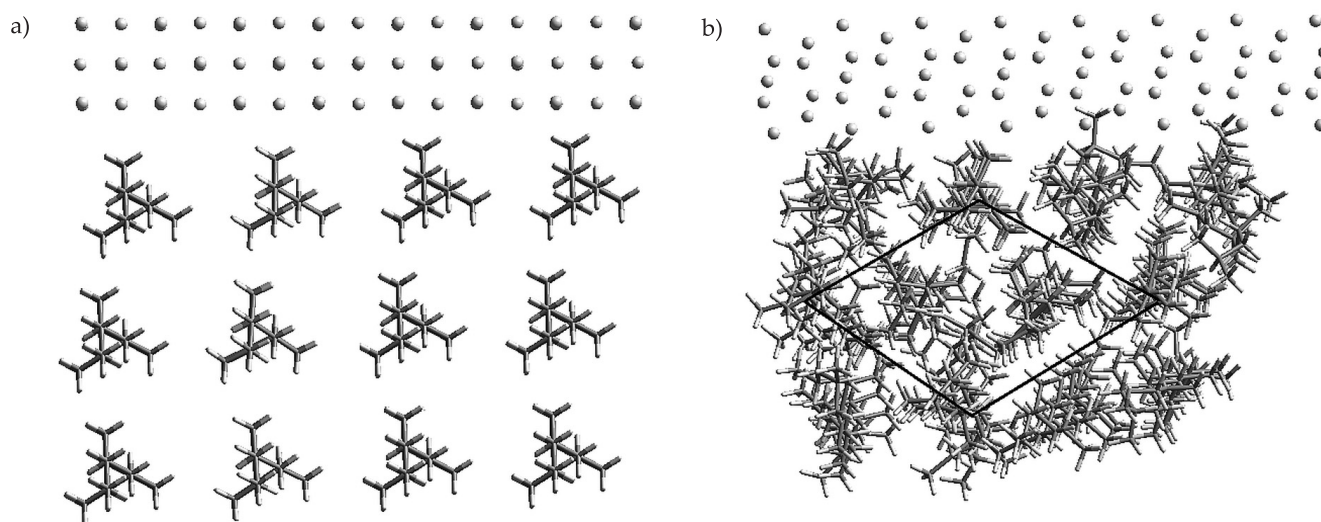


Fig. 3. Model of 7ucAg12iPP initial arrangement: a) before, b) after optimization (projection perpendicular to c-axis of polypropylene chains)

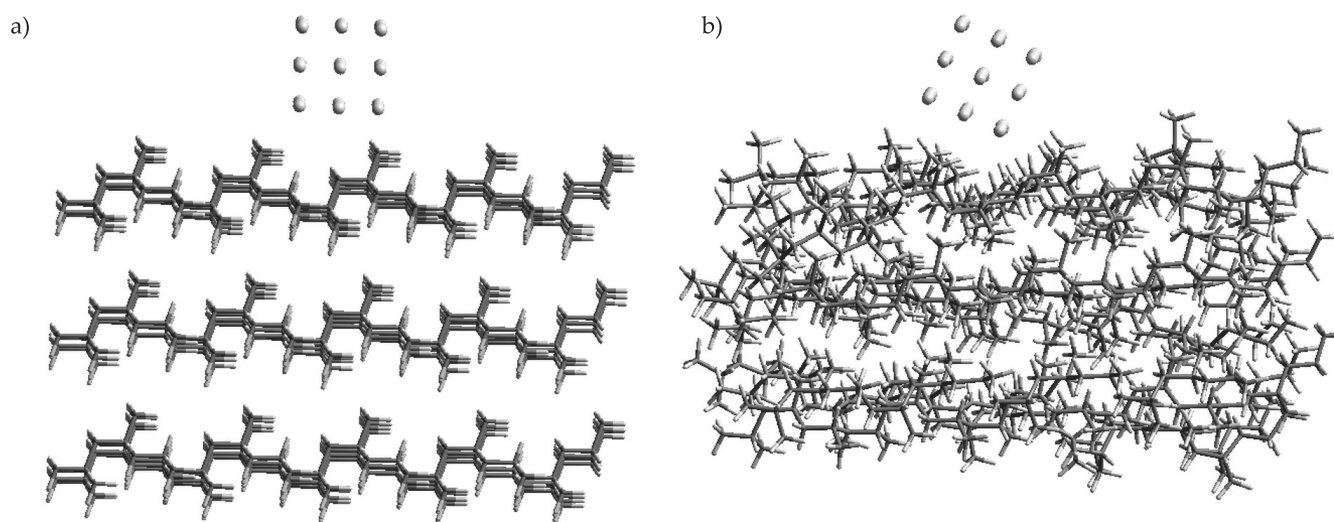


Fig. 4. Model of 7ucAg12iPP initial arrangement: a) before, b) after optimization (projection in the direction of c-axis polypropylene chains)

revealed the most effective interaction between protons from methyl groups iPP chains and silver atoms situated on the edge of silver crystal unit cell.

In order to clarify this observation, the partial charges were calculated in a simple system consisting

of one unit cell of silver and one polypropylene chain (1ucAg1iPP).

According to the calculations of partial charges for the system 1ucAg1iPP before optimization by MM+, the charges at the corners of the unit cell of silver were nega-

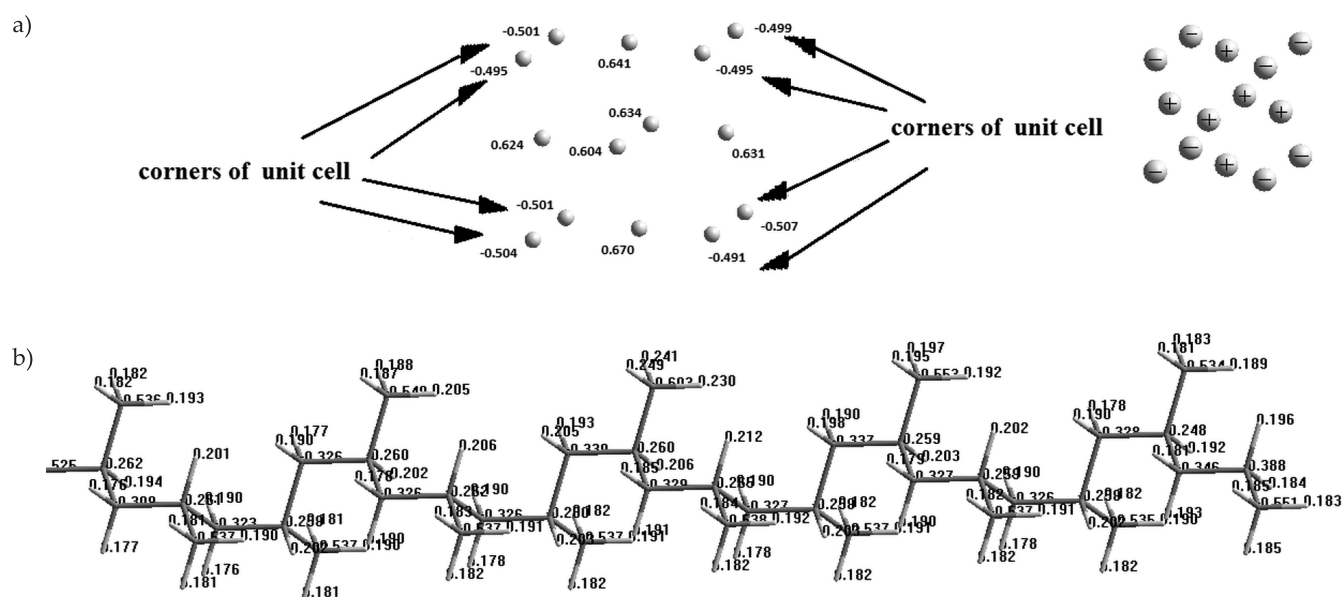


Fig. 5. Part of the model of 1ucAg1iPP before optimization by MM+ with the partial charges calculated for this system: a) unit cell of silver, b) part of iPP chain

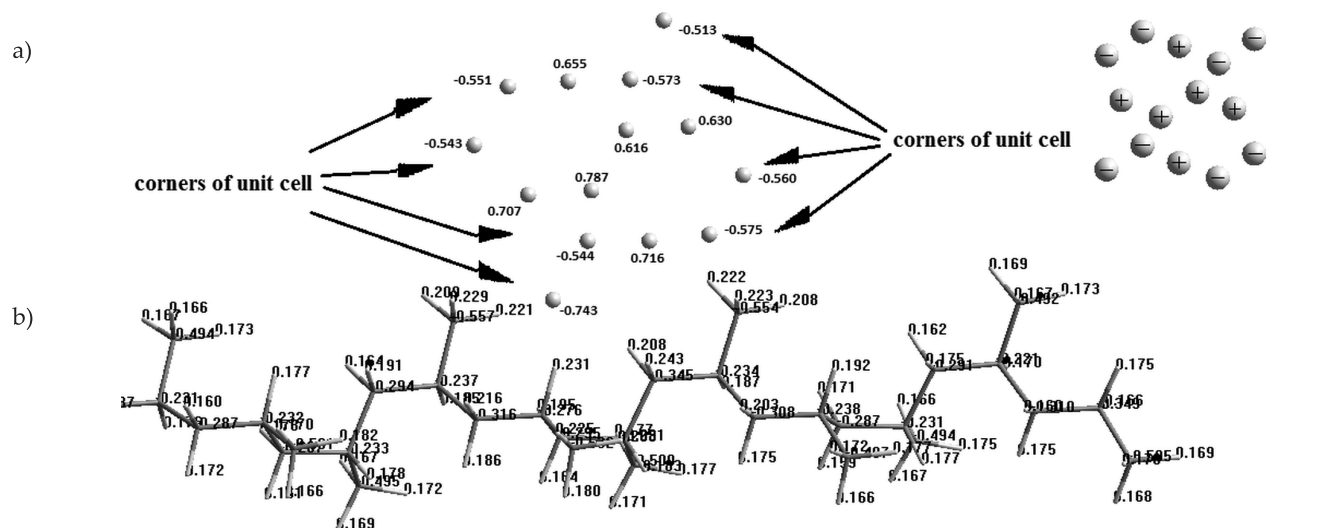


Fig. 6. Part of the model of 1ucAg1iPP after optimization by MM+ with partial charges calculated for this system: a) unit cell of silver, b) part of iPP chain

tive, and oscillated around values from -0.495 to -0.507, while, the remaining atoms of silver on the face centred unit cell had positive sign ranging from 0.607 to 0.670 (Fig. 5a). The polypropylene chain was found to have negative charges located at the carbon atoms and positive charges at the hydrogen atoms (Fig. 5b).

After geometry optimization the values of partial charges changed a little (Fig. 6). The hydrogen atoms from CH_3 groups, which were close to the unit cell of Ag, had greater positive partial charges (0.209–0.230) than the hydrogen atoms from the other groups in iPP (0.166–0.173). However, the atoms of silver on the edge of the unit cell were found to have more negative partial charges (-0.743). This result may indicate the possibility of specific interactions between C, H and Ag atoms. This type of interactions between the metal and hydrogen

have been also noted by Baetzold and classified as dipole-dipole interactions [27].

Figure 7 shows that the hydrogen atoms from CH_3 groups are located between three adjacent silver atoms in

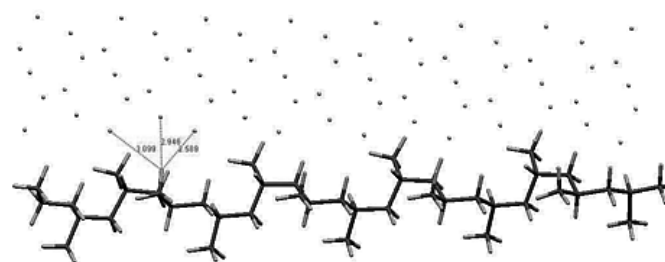


Fig. 7. The distances between the hydrogen atoms from the methyl groups of iPP and the 3 silver atoms from the unit cell

the unit cell. The distances between the hydrogen atom and the silver atoms are in the range 2.5–3.1 Å. These values also indicate that weak hydrogen bonds [28] between H atoms from CH₃ group and Ag atoms are very likely.

CONCLUSIONS

The study reported in this paper was undertaken to answer the question why the β form of iPP develops in the presence of Ag nanoparticles. Molecular modelling investigation indicates that the β iPP (110) plane is probably the contact plane. Simulations of arrangement of iPP chains showed that the arrangement of methyl groups in the (110) contact plane implies a lateral packing of helices with the periodicity $a \approx 19$ Å, which is a characteristic feature of the complicated packing of helices in β iPP. During optimization the Ag nanocrystal (containing 7 unit cells) was rotated by about 45 degree in relation to the (110) iPP plane. Indicated the best interactions between protons from methyl groups iPP chains and silver atoms situated on the edge of unit cell. The partial charges as well as distances between silver atoms of the unit cell and hydrogen atoms of CH₃ groups iPP indicate the possibility of weak C–H–Ag interactions.

On the other hand, a comparison of the distances between the chains arranged in the (001) plane in the α form and the lengths of multiplicity of the parameter a of silver unit cell, the conditions for epitaxy are also satisfied. Experimental data presented in [20] showed that besides the majority of β iPP the samples studied contained about 30 % of α form. However, it is well known that α iPP can be formed with no need of any additives. Therefore, the explanation of the role of nAg in formation of α polymorph requires further detailed analysis.

This research was supported by Grant of Poznan University of Technology 03/32/DSPB/0503/2015. The calculations were carried out at the Poznan Supercomputing – Networking Centre. Number of project: 179; Topic of project: Analysis of the arrangement of the molecules in the crystal.

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Received 15 I 2014.