ELUCIDATION OF CHAIN-FOLDING STRUCTURE OF ISOTACTIC POLY(3-METHYL-BUTENE-1) IN BULK AND SINGLE CRYSTALS BY SOLID-STATE NMR

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ELUCIDATION OF CHAIN-FOLDING STRUCTURE OF ISOTACTIC POLY(3-METHYL-BUTENE-1) IN BULK AND SINGLE CRYSTALS BY SOLID-STATE NMR

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ABSTRACT

Since the discovery of single crystals of polyethylene by Keller using transmission electron microscopy (TEM)\textsuperscript{1}, various methods have been developed to unravel detailed chain-level structures (chain-folding) of semi-crystalline polymers in both bulk and single crystals. Nevertheless, understanding of molecular structure basis, is still a controversial issue due to experiment limitations. Such experimental situations are largely different from theory or simulations. Recently, our group developed a unique approach, which can investigate the chain trajectory of the synthetic polymer in bulk crystals, using $^{13}$C–$^{13}$C double quantum (DQ) NMR combined with $^{13}$C labeling samples\textsuperscript{2}.

In this thesis, we propose systematic research on chain-level structure of a semi-crystalline polymer prepared under different conditions. We investigated chain-trajectory of $^{13}$C CH$_3$-labeled isotactic poly(3-methyl-butene-1) (iP3MB1) in melt-grown crystals and solution-grown single crystals blended with non-labeled iP3MB1 using solid-state NMR. Comparisons of $^{13}$C - $^{13}$C double quantum (DQ) NMR results with spin dynamics simulation revealed individual chains in melting grown crystals fold in three different directions and chains in single crystals prefer direction parallel to the long side (crystallographic $a$ axis) of the rectangle-size single crystal is determined.
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CHAPTER I

INTRODUCTION

Since the discovery of single crystals of polyethylene by Dr. Keller in 1957,\(^1\) polymer crystallization has been a central topic in polymer physics company with the developments of different characterization tools in the last half century.\(^3-7\) It is understood that the process of structural change of polymer chains from random coils in the melt and solution states to folded chains is essence of polymer crystallization. However, there is a long deviate for basic understanding of chain-folding structure and process as follows: i) When do polymer chains fold during crystallization? ii) How do polymer chains fold in the crystals? Generally, a slow crystallization leads to well defined single crystal with regular shapes from dilute solution, however, a rapid crystallization results in spherulites with rounded shapes. From these morphology observation, it is believed that kinetics is an important function of polymer crystallization. So far, well-developed scattering, diffraction, and microscopy techniques have been successfully applied to provide detailed structures of packing, conformation, lamellae thickness, morphology of single crystals and spherulites with a function of crystallization time.\(^8-11\) On the other hand, there is still something missing in molecular structural basis for polymer crystallization due to experiment limitations. Understanding of chain-level structure, especially the chain-folding structure
in both bulk and single crystals is still missing. The main problem is that experimental situations are always largely different from theory or simulations. There are many theories and simulations to approach the chain-folding structure. Well-known Lauritzen-Hoffman theory provides information related to chain-level structure in different regimes, where competition between secondary nucleation rate ($i$) and the growth rate ($g$) determines the chain trajectory on the growth front.\textsuperscript{12-13} Recent computer simulations have been developed to successfully investigate the molecule-level structures of individual chains during crystallization, and commonly suggest that intra-chain interactions via an adjacent re-entry structure play dominant roles in the secondary nucleation of polymer crystals.\textsuperscript{14-16} However, these theories and simulations cannot meet together and give out the consequence. So we really need new experimental techniques which can elucidate the chain structures and to confirm the simulation results and structures predicted from theory.

In the previous work, our group proposed a novel approach using $^{13}$C-$^{13}$C double quantum (DQ) NMR combined with selective isotopic $^{13}$C labeling.\textsuperscript{2} This strategy can determine (1) the re-entrance sites of folded chains, (2) the adjacent re-entry fraction - F, (3) the successive folding number, n, of a semi-crystalline polymer in bulk and solution-grown single crystals as a function of crystallization temperature ($T_c$). We now have an ultimate tool for accessing the three-dimensional structure of synthetic polymers at the molecular levels. Our aim is to deeply understand the vital issues in fundamental polymer systems using advanced Solid-State (SS) NMR having atomic scale resolutions.

So far, our experiments have focused on lateral polymers including isotactic Polypropylene (iPP)\textsuperscript{17} and isotactic Poly(1-butene) (iPB1). In this thesis, we treat with another semi-crystalline polymer, Poly (3-Methyl-Butene-1). Through this project, we will
experimentally and theoretically confirm whether our strategy can determine chain-folding structure of Poly (3-Methyl-Butene-1) in melting grown bulk crystals and solution grown single crystals.

1.1 Former Approaches to Chain-folding Structure

In the last half century, many differently special techniques were used “observe” the chain-level structures of polymer crystallization. Neutron scattering (NS) and Infrared Radiation (IR) are two common tools used to analysis chain-folding structure. Because $^2$H and $^1$H atoms show different neutron scattering lengths and vibration frequencies, when polymer chains with $^2$H and $^1$H atoms are mixed together, if one kind of chain is very dilute and surrounded by another, it will be easy to “observe”. However, this strategy has two serious shortcomings to detect structural information of polymers on a molecular level: (i) Most experiments on $^2$H-/$^1$H-PE have to be performed under rapid cooling conditions because of the mixing induces segregation during slow crystallization. $^{18}$ (ii) The spatial resolution of these techniques are very low. Other techniques can also give out evidence to chain-folding structure. A recent approach to direct observe polymer chains using atomic force microscopy (AFM). $^{19}$ Computer simulation works give out many theories and models of polymer crystallization as well.

1.1.1 Neutron Scattering

In NS, $^2$H and $^1$H atoms show different neutron scattering lengths and “isolated” polymer chains in the mixed blends can provide structure information.
Keller et al. first propose “chain trajectory” of polymer chains. They investigated how the average radius ($R_g$) of a polymer chain in single and bulk crystals changes with molecular weight ($M_w$). The $R_g$ in single crystal is much smaller than the $R_g$ in melt state, and slightly increase with increasing molecular weights. These results suggested the super-folding structures in the single crystals.\textsuperscript{20}

For single crystal, Flory et al. suggested that polymer chains adopt super-folding structures with stem dilutions but have a very small adjacent re-entry fraction (25%).\textsuperscript{21} Later, Sadler et al. calculated the NS curve up to a larger $q$ range, which suggested 75% adjacent re-entry structure in single crystals.\textsuperscript{22} (Figure 1.)

![NS curve in Kratky Plot and simulations of different ratio adjacent re-entry structure in single crystal of blend of $^2$H- and $^1$H-PE](image)

**Figure 1.** NS curve in Kratky Plot and simulations of different ratio adjacent re-entry structure in single crystal of blend of $^2$H- and $^1$H-PE

We can see from Figure 1, the points below the plots show a kind of situation of 75% and 25% adjacent re-entry models. In small $q$ range, 25% model fits the experimental data
more but in large q range, 75% model fits more. Both calculated curves are not well consistent with experimental data in the entire range.

For melting grown crystal, Flory suggested switchboard moles with an adjacent re-entry fraction of 0 %,\textsuperscript{21} whereas Sadler et al. reported 46 %.\textsuperscript{23} In a nutshell, NS analysis can only give out statistical consequence. Therefore, it is difficult to explain detailed local chain-folding structures.

Recently, Ungar et al. utilized “monodisperse homo-oligomer” with end group selectively labeled by $^2$H. This kind of special chemical design successfully improved NS resolutions and led to sharp scattering peaks.\textsuperscript{24} This work successful uses NS to detect structural changes of oligomers with a function of supercooling. On the other hand, this strategy still cannot detect the inter-stem interactions, which can prove adjacent re-entry structure. Another weakness is that it can only works on oligomer which cannot present the property of polymer.

1.1.2 Infrared Radiation

The spatial resolution of IR spectroscopy is not such high because IR band shape in a limited range of $\sim 10 \text{ cm}^{-1}$ which is comparable to the line width.\textsuperscript{25,26} If an isolated $^2$H polymer chain is surrounded by $^1$H polymer chains, an isolated $^2$H chain gives a single peak on IR spectra. So IR can detect local inter-stem interactions. But chain-folding directions also influence the spectra a lot. For PE, the adjacent re-entry folding direction along (100) plane gives singlet, while folding along (010) provides doublet signals. This makes the analysis much more difficult. Additionally, doublet and singlet peaks will contribute to the
overlapped line shapes in limited spectral range. For these reasons, it’s hard to do detailed analysis of chain-level structures to use IR spectroscopy.

1.1.3 Atomic Force Microscopy

Another approach is the direct observation of polymer chains using atomic force microscopy (AFM). This experiment uses a very special polymer isotactic-poly (methyl methacrylate) (iPMMA) and make it a monolayer on the substrates. Two iPMMA helical chains tied together to make one strand. In Figure 2, black lines clearly show the adjacent re-entry structure of these strands. But it’s a shame that this polymer is too special and we can only see two-dimensional crystals oriented.

![Figure 2. AFM images of iPMMA helical chains](image)

Recently, Hobbs et al. proposed a new AFM strategy on PE with a spatial resolution of 3.9 Å. This technique clearly detected long loop chain-folding structures of PE.
However, it’s still not clarified enough to show the tight adjacent re-entry folds which are believed by most people by this advanced technique.

1.1.4 Simulation for Molecular Level Structure

It’s very common that the experimental situations differ from theoretical and simulation works. But simulation works are still helpful to approach the chain-folding structure. Computers can even do what experiment cannot do.

To our knowledge, the previously described techniques have never consider how crystallization temperature ($T_c$) effects on chain-folding structures because of insufficient spatial resolution and sample limitations. But computer can simulate it. Allegra firstly use computer simulation to proposed bundle models in which aggregates consist of 10-20 stems by folding in the pre-stage of crystallization. Muthukumar et al. also developed anisotropic aggregation models, where individual molecules make folded structures in the pre-stage of crystallization from dilute solution. And these structures will decide the final morphology under various $T_c$. Sommer et al. described that coarse-grained polymer chains fold once or twice in the pre-stage using Monte Carlo Dynamic (MD) simulation. These three models are all based on computer simulation and give out a pre-folded chain theory to include the function $T_c$.

1.2. Solid-state NMR Approach to Chain-folding Structure

$^{13}$C–$^{13}$C dipole-dipole interactions are used to detect the chain trajectory of dilute labeled polymers in non-labeled polymers blend. Dipolar interactions are inversely
proportional to the third power of the inter-nuclear distance, $1/\langle r \rangle^3$. If two labeled carbon
$^{13}\text{C}^{13}\text{C}$ are very close to each other, $^{13}\text{C}^{13}\text{C}$ dipolar interaction will be large and show a
high Double Quantum (DQ) efficiency on the spectra. In the dilute labeled chain sample,
if labeled chain does chain-folding, the evaluation of relatively inter-stem $^{13}\text{C}^{13}\text{C}$
correlations will be detected. The labeling position can be controlled by selection of a site
(e.g., side chain) and concentration (statistics).

![Diagram](image)

**Red line:** $^{13}\text{C}$ labeled chain
**Black line:** non-labeled chain

**Figure 3.** Basic strategy (a) diluted blend sample (b) adjacent re-entry and (c)
random re-entry model

Figure 3. shows the basic strategy which we used to approach chain-folding structure
of a polymer chain. We use diluted blend sample, the red line is labeled chain and black
line is non-labeled chain in (a). And (b), (c) show two models for chain-folding structures.
Left one is adjacent re-entry model, and the right one is switchboard or random re-entry
model. The blue lines represent $^{13}\text{C}$-labeled chains and black lines are non-labeled chains.
The red circles are $^{13}\text{C}$ labeling sites. If it follows adjacent re-entry model, $^{13}\text{C}^{13}\text{C}$ inter-
estem dipolar interactions will be large and show a larger DQ efficiency in the spectra. If it
follows switchboard model, inter-stem interaction will be small because the distance
between $^{13}\text{C}-^{13}\text{C}$ is larger. From this difference, we can determined how the chain folding in the lamellar.

![Graphs showing Distance Effect and Topology Effect](image)

Figure 4. Double quantum build-up curves for (a) distance effect for two spin system and (b) topology effect for three spin system.

Figure 4. shows the most important data (curve) we used in our DQ SSNMR analysis. In the bottom graphs, x axis is excitation time which we can set in our experiment. Y axis is Double Quantum efficiency which reflects the $^{13}\text{C}-^{13}\text{C}$ inter-stem dipolar interactions, can be tested by the machine at a certain excitation time. (a) and (b) are both simulation data by SPINEVOLUTION. This software can do the simulations of DQ efficiency curve by receiving the atomic coordination of any $^{13}\text{C}$ system. All the circles upper the graphs are $^{13}\text{C}$. The red one is the reference carbon we used to be the center of such $^{13}\text{C}$ system. (a) shows the distance between two $^{13}\text{C}$ (red and blue circle) change will lead to some influence to the curve. If the distance is larger than 6Å, DQ efficiency is so small which we can ignore. This is the reason we only focus on all the $^{13}\text{C}$ in the system which are not
farer than 6Å to the reference carbon. (b) shows the topology effect of a simple 3-carbon system. By changing the angle between them, we can also see the difference in the curve.

In different models, such as Figure 3. (b) and (c), both distance and topology effect influence the DQ efficiency curve for each reference $^{13}$C. We can use SPINEVOLUTION to simulate all possible models then compare with the NMR experimental data and finally determine the chain-folding structure of each polymer.

1.3. Crystal Structure of isotactic Poly(3-Methyl-Butene-1)

Figure 5. $^{13}$C high-resolution (a) melt-state and (b) SS NMR spectra for iP3MB1

Isotactic Poly(3-Methyl-Butene-1) (iP3MB1) is one of the isotactic polyolefins, which is also semicrystalline polymer. Figure 5. shows the recent NMR result of iP3MB1.31 Left of the picture is the chemical structure. There are 5 carbons in every monomer unit, which are named by C1~C5. (a) and (b) show the melt and solid-state NMR
spectra. In the melt state, two methyl groups C4 and C5 show the same chemical shift due to the fast conformational transition between two states. On the contrary, in solid state, they are different and C4 divided into 5 peaks and C5 divided into 4 peaks, due to the Right/Left Up/Down structures in stems which will be explained later.

1.3.1. Crystal Unit Cell Investigated by XRD Analysis

The crystal structure of isotactic poly(3-methyl-butene-1) (iP3MB1) has been investigated by XRD. The most recent XRD investigation by Corradini, P. et al. \(^{32}\) revised that four uniform 4\(_1\) helices are packed into a P21/b monoclinic space group with unit parameters of \(a = 9.55\), \(b = 17.08\), \(c = 6.84\) Å, and \(\gamma = 116.5^\circ\). The crystal system is Tetragonal.

Figure 6. Crystal structure of non-statistic iP3MB1 (a) ab plan (b) ac plan
Figure 6 illustrates the non-statistic structure of the \(ab\) (a) and \(ac\) (b) plan of iP3MB1. Number 1~5 is signed to name C1~C5. From then on, green is always used to sign C4 and red used to sign C5.

![Diagram of C4 and C5](image)

Figure 7. Difference between C4 and C5

Figure 7 shows the difference between C4 and C5. In Figure 5, we can see C4 and C5 signals show a chemical shift separation of 6 ppm in solid state. The C5 carbon shows gauche-gauche conformations with respect to the two C1 carbons in the \(\gamma\) positions, whereas the C4 carbon has a trans-gauche conformation with respect to the two C1 carbons. Therefore, the observed upfield shift of the C5 signals is interpreted in terms of one additional \(\gamma\) gauche effect. In the figure, C4 is much more perpendicular to c axis and C5 is much more parallel to c axis.
Isotactic polyolefin chains in the crystalline regions adopt helical conformations with right (R) or left (L) handed senses, and it is possible for the chains to independently adopt upward or downward orientations along c-axis. Upward(u) and downward(d) orientations are defined in terms of differences between the z coordinate of the first lateral carbon, which is directly connected to the mainchain CH carbon, and the z coordinate of the mainchain CH carbon. This disorder commonly occurs in stereoregular crystalline polymers. In iP3MB1, such a Right or Left, up or down disorder also exist. The XRD analysis and a recent SSNMR analysis both lead to the conclusion that the melting grown crystal of iP3MB1 is a totally statistic disorder structure (Ru, Rd, Lu, Ld disorder). Figure 8. shows such a statistic disorder structure of iP3MB1.

Fortunately, such a statistic disorder structure will not influence the chain-folding at any direction when the chain-folding number is not so large.
Figure 9. Chain-folding law in disorder isotactic polyolefins

Figure 9. shows the chain-folding law of such a series of disorder isotactic polyolefins. Using Ru as an example, it cannot fold to itself and Ld, but it can fold to Lu and Rd. If the chain is not folded too long, it can fold at any direction and finally the structure in a large region, including many chains, is still statistical disorder.

In this part, the structure of melting grown crystals of iP3MB1 is well known. On the other hand, the structure of single crystal is still missing although the single crystal is not hard to get.
Both the labelled and non-labelled sample is synthesized by Wei Hu\textsuperscript{34} in 2006 using the C2-Symmetrical Zirconocene/MAO catalyst system. Figure 10. shows the formula of the synthesis of labelled sample. Since the monomer is one side methyl group labelled, C4 and C5 each have 50\% to be $^{13}$C in the polymer. Mw=23000±7000 is detected by SSNMR side group analysis.

2.1. Bulk and Single Crystals Sample Preparation

Melting grown crystals and solution grown single crystals are both made into two groups: (1) all $^{13}$C labelled sample (2) dilute sample (blend ratio label : non-label = 1 : 9).

Melting Grown Crystal:
• Melting at 330 °C with \( \text{N}_2 \) protection.

• Crystalline at 285 °C for 2hr.

Solution Grown Single Crystal:\(^{35}\)

• Single crystals of poly-3-methyl-butene-1 were grown from 0.01% solutions in tetralin.

• The solutions were maintained at the boiling point for 5-6 hr. and directly pull in Dewar vessels.

2.2. Characterization of iP3MB1 Bulk and Single Crystals

AFM for single crystals

Prepare: Sample solution drop on silicon base and dry

Machine: Veeco icon Atomic Force Microscopy

Mode: Tapping mode

Software: Nanoscope Analysis

TEM for single crystals

Prepare: Sample solution drop on Copper grid and dry

Observations were made with a Philips CM12 electron microscope operated at 120 kV.
The patterns were recorded with a Megaview III digital camera from soft imaging system(SIS).

The ‘Compass’ were mostly used in the conformational and packing analyses.

Solid-State NMR for bulk and single crystals

Prepare: single crystals take out from solvent by 25um diameter pole filter. Then packing into 4mm NMR tube.

$^{13}$C CPMAS NMR and DQ NMR

SS-NMR experiments were carried out by Bruker Avance 300 MHz NMR equipped with a 4 mm double resonance VT CPMAS probe. The $^1$H and $^{13}$C carrier frequencies are 300.1 and 75.6 MHz, respectively. The MAS frequency was set to 5102 ± 3 Hz. The chemical shift was referenced to the CH signal of adamantine (29.46 ppm) as an external reference. The 90° pulses for $^1$H and $^{13}$C were 4.5–5.0 μs. The recycle delay and crosspolarization (CP) time were 2 s and 1 ms, respectively.
CHAPTER III

RESULTS AND DISCUSSION

Through this chapter, we are going to show all the characterization results and do further discussion.

3.1. AFM Analysis of iP3MB1 Single Crystals

![AFM images of iP3MB1 single crystals](image)

Figure 11. AFM images of iP3MB1 single crystals (a) several single crystals (b) one isolated crystal (c) thickness of the crystal

Figure 11. show the AFM images of iP3MB1 single crystals. (a) shows all the single crystals are similar size. The morphology is near rectangle. The average size of them is
8.9*3.6 \text{um}^2. (b) shows one isolated single crystal. Long sides of the rectangle is much smoother than short sides. (c) shows the thickness of the single crystal in (b). The average thickness is 10.5 nm.

Now we get information about the single crystal as: (1) Mw=23000±7000 (2) Depth=10.5 nm (3) Unit Cell c=6.84 Å (4) 4 repeat units per unit stem. We can calculate that the maximum chain-folding number: n = 7.

3.2. TEM Analysis of iP3MB1 Single Crystals

![TEM simulation and experimental images of iP3MB1 single crystals](image)

Figure 12. TEM simulation and experimental images of iP3MB1 single crystals (a) simulation pattern of statistic disorder structure (b) simulation pattern of Ru-Lu order structure (c) experimental pattern (d) experimental image

In Figure 12, (a) and (b) are corresponding simulated electron diffraction pattern ((hk0) reflections) of statistic disorder structure and Ru-Lu order structure. Order structure
contains more information and the pattern is denser. (c) is the experimental pattern of iP3MB1 single crystal. Compare (a) with (c), we can see they are very similar. Dots beside (400) and upper (-620) disappear. From this evidence, we can say the single crystal of iP3MB1 is also statistic disorder structure.

(d) is the corresponding image to (c), we can easily find that (010) direction is exactly along the long sides of the rectangle. Long side of single crystal is parallel with crystallographic \( a \) axis.

3.3. Double Quantum Solid-State NMR Analysis of Bulk and Single Crystals

In NMR part, we should first do packing refinement to know the unit cell we build is correct or not. Then using the atomic coordination after refinement to approach chain folding structure.

3.3.1. Packing Refinement

In our simulation, we should first define a reference methyl carbon to be center \(^{13}\text{C}\) and consider all the methyl carbons which may be \(^{13}\text{C}\) around it in 6 Å. The center \(^{13}\text{C}\) plus the surrounding carbons are considered as the system for chain-packing analysis.

In Figure 13 (a), the red circle center green C4 is the reference carbon for example. Each of the C4 and C5 in the 6 Å sphere has 50% possibility to be \(^{13}\text{C}\). The probability of finding \( m \) spins (\( m \) is the number of \(^{13}\text{C}\) in the sphere system) is calculated considering the combination and labeling ratio, respectively. We give SPINEVOLUTION all the atomic coordinates of the system determined by XRD\(^{33}\). Individual curves are summed up by
weighting the probability of finding the spin topology in \( m \) spins (Figure 13 (b)). It is the average curve of all conditions with different spin systems (number, distance, and topology). Subsequently, individual summed DQ sub-buildup curves for \( m \) spin systems are further weighted by each possibility and finally get the red line in Figure 13 (c). The black line in Figure 13 (c) are the experimental data of all labeled sample. We can see it does not fit the red line well. So we should do the packing refinement of the atomic coordinates. We tried to expand the crystal unit cell and change atomic coordinates. Finally, we found after expand 2.5%, in right picture, the red line fits the experimental data best. The corrected atomic coordinates of CH\(_3\) carbons are used for further chain-folding analysis.

Figure 13. Packing refinement of iP3MB1 (a) example for C4 center (b) individual curves for each spin number (c) simulation build-up curve (red) and experimental curve (black) before and after expand.
3.3.2. Determination of Chain-folding Structure

The most important parameters we use is $n$: successive folding number, which means how many times one chain do adjacent re-entry fold.

Figure 14. Possible chain-folding structure as iP3MB1. Red: chain-folding OA (along $a$ axis), Green: chain-folding OB (along $b$ axis), Blue: chain-folding AB (along the diagonal of $a$ and $b$ axis).

In Figure 14, there are four possible linear adjacent re-entry model. OA, OB and AB stand for three different direction linear chain-folding model.

In order to know the chain-folding structure, we should do the DQ experiment and simulation with the dilute sample. In Figure 15 and Figure 16, the open red circles are experimental $^{13}$C–$^{13}$C DQ curves of $^{13}$C-labeled iPB1 diluted with non-labeled chains (1:9). The blue lines are simulation data considering different folding topology based on OA, OB...
and AB chain-folding models with different chain-folding number. C4 (left) and C5 (right) show different result here. Number n written in the picture is the most fitting chain-folding number for each picture.

Figure 15. Chain-folding for melting grown crystal

In Figure 15, experimental and calculated DQ curves are possible to support all of the three model as reasonable chain-folding topologies with a small chain-folding number. We can go on our simulation to fit the experimental data most by changing the parameter n and the combination ratio of different models. In melting grown crystals, average of the three models with small chain-folding number (n=2) is the possible way for folding.
In Figure 16, only model OA can fit the experimental data for both C4 and C5 when n=6. In AFM analysis part, we calculated that the maximum chain-folding number for single crystal is 7.

On the other hand, both AFM and TEM results show that the morphology of single crystal is near rectangle. Long sides of it are very smooth, but short sides are rough. (Figure 17 (a)). And from TEM pattern, we learned the long sides are exactly parallel with crystallographic $a$ axis, which is exactly the direction of chain-folding OA model. So we can come to the conclusion, OA is the main direction for the folding in single crystal. OB and AB may also exits which make short sides rough. In Figure 17 (b), we propose some
multi-direction chain-folding pieces, which is dominated by OA, are possible for the chain-folding structure in solution grown single crystal.

Figure 17. Morphology and chain-folding (a) sketch for the near rectangle morphology of single crystal (b) possible multi-direction chain-folding pieces dominated by OA

This quantitative analysis of DQ efficiency indicates that DQ NMR is a potential tool for characterizing the chain-folding structure with parameter $n$. We successfully use it in analysis the chain-folding structure of iP3MB1.
CHAPTER IV

CONCLUSION AND FUTURE WORKS

In this thesis, we can come to the conclusion as below:

• Through electron diffraction pattern analysis, single crystal of iP3MB1 is also statistic disorder structure, which will not influence the folding structure in any direction.

• In melt grown crystal, all the three direction is possible to fold. Even multi-direction folding in one chain is possible. Average chain folding number is 2.

• In single crystal, chain folding direction OA (crystallographic a axis) is the main direction. Other two direction is possible to occur combine with OA. Average chain folding number is 6. Several possible chain-folding pieces are proposed.

• iP3MB1 really do folding in both bulk and single crystal. Solution grown single crystals fold more times than melting grown crystals. Molecular level chain-folding direction is possible to influence the morphology in single crystal.
Although we briefly solved the chain-folding structure in $i$P3MB1, we did not touch the paradox of the statistic disorder packing structure of $i$P3MB1. There are still many unresolved questions about the $i$P3M1B crystal structures.

On the other hand, we have used our DQ NMR strategy on many polymers, including $i$PP, $i$PB1 and $i$P3MB1, to solve chain-folding structure. We have the confidence to say if we have enough money and time, after well-designed experiment and simulation, we can approach the chain-folding structure of any other polymers. But the strategy now is not powerful enough to totally know the molecular level chain-folding structure. The resolution of our experiment cannot tell the difference between each models. We need new ideas to overcome this weakness. In this case, $i$P3MB1 is a little bit different from $i$PP and $i$PB1, there are two sites C4 and C5 labelled. Multiple labelled sites can give out more information on the 2D spectrum. It is a shame that the statistic disorder paradox in this polymer is so difficult that we can hardly get useful information from the interaction between C4 and C5. But if we can find another simple polymer (or well-designed polymer), we may try more sites and get more information which can help us to tell more stories.

In Figure 18, a kind of low PEO single crystal, with low PDI and certain MW=5000, annealed at high temperature below melting temperature. Left picture shows the perfect square morphology before annealing. Middle picture shows annealing at a lower temperature, chain moves and rearrange to a larger thickness. Right picture is after annealing at a higher temperature, which shows 3 times lamellar thickness than the left one. The models below directly show how the chain fold in one single lamellar and how it thickening during annealing.
During annealing at a high temperature below $T_m$, polymer chains are possible to move. It is just like the process of melting and recrystallization. Is this lamellar thickening phenomenon occurs on $iP3MB1$? Does chain-folding number change during such a process? These topics will be a part of my future works. I will also do annealing at proper temperature and use both AFM and SSNMR to investigate this phenomenon.
REFERENCES


