11-1-1998

Study of microwave annealing effects on polymer crystallization

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Study of Microwave Annealing Effects on Polymer Crystallization

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November, 1998

Thesis

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

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Study of Microwave Annealing Effects on Polymer Crystallization

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Acknowledgements

I would like to thank my advisor, Dr. Andreas Langner, for his advice and support. His extensive knowledge and creative ideas made it possible to initiate this thesis. His effective guidance and help taught me how to become a good researcher and experimentalist. His humor gave me a lot of fun during my studies.

I also would like to thank my graduate committee, Dr. Gerald Takacs, Dr. Joseph Hornak, and Dr. Massoud Miri, for all their help and support. I have benefited from their suggestions and questions. I would like to extend my thanks to Ms. Ruth Willerth for her help in the construction of the experimental set-up.

No words are enough to express my thanks to my parents. Without their understanding and support, I would never have finished this thesis. I also would like to express my thanks to my husband for all his help and love.
Abstract

In this project, the effect of melt annealing on the crystallization of poly(ethylene oxide), (PEO), was studied by comparing thermal annealing to microwave annealing. After the subsequent controlled crystallization, the crystalline morphology of films was characterized by Polarizing Light Microscopy (PLM); the melting curves for both films and bulk samples were measured by Differential Scanning Calorimetry (DSC). These measurements revealed significant differences between microwave and thermally annealed samples. We propose that microwave annealing has a “quantum effect” on polymer crystallization. The difference in morphology cannot be explained by a change in the temperature profile of the two annealing methods.

By investigating the difference between microwave annealing and thermal annealing, while changing the crystallization temperature, we found that microwave absorption could change the polymer chain conformation more efficiently. The application of microwaves accelerates the dipole moment oscillation thus speeding up rotation of polymer chain segments. In this way, microwave annealing could destroy the residual nuclei left from a prior crystalline morphology, decreasing the nucleation site density. Consequently, homogeneous nucleation becomes more important in the case of microwave annealing, and the morphology and melting behavior of the crystalline phase are both changed. As molecular weight of PEO was increased, the microwave effect became more evident. Some factors in the crystallization process which may mask the microwave effects are the surface area of the film samples, the cooling rate and the crystallization temperature.

It is believed that microwave annealing has potential to produce new crystalline polymeric materials with different solid state microenvironments, as compared to thermal annealing. It may give a method to control the crystallization process, and provide a new way to perform kinetic and thermodynamic studies on semicrystalline polymers.
# Table of Contents

**Chapter 1: Introduction**

**Chapter 2: Background**

2.1 Morphology of Crystalline Polymers 3
2.2 Nucleation and Growth Steps of Crystallization 6
2.3 Homogeneous and Heterogeneous Nucleation 7
2.4 Melting Behavior of Crystalline Polymers 8
2.5 Microwave Processing of Polymers 11

**Chapter 3: Experimental**

3.1 Poly(ethylene oxide) Samples 16
3.2 Experimental Set-up for Microwave Annealing 17
3.3 Morphology Characterization by PLM 18
3.4 Investigation of Melting Behavior of Crystalline Polymers by DSC 18

**Chapter 4: Results and Discussions**

4.1 Microwave Effects on PEO Crystallization 21
4.2 The Mechanisms of the Microwave Effects 24
4.2.1 Dependence of Microwave effects on Crystallization Temperature 25
4.2.2 Dependence of Melting Behavior on PEO Molecular Weight 42

**Chapter 5: Conclusions**

References 50
List of Figures

Figure 1: Theoretical plot of Tm* versus Tc for indicated chain length of linear polyethylene

Figure 2: Typical variation in dielectric constant and dielectric loss with frequency for polymers

Figure 3: Experimental set-up for microwave annealing

Figure 4: The calibration temperature of the polymer melts vs. setting temperature of the reservoir

Figure 5: Morphology of crystalline PEO, crystallized at 25 °C in air after a) thermal annealing, and successively b) microwave annealing

Figure 6: Morphology of crystalline PEO, crystallized at 25 °C in air after a) microwave annealing, and successively b) thermal annealing

Figure 7: Morphology of crystalline PEO, crystallized at -44 °C on dry ice after a) microwave annealing, b) thermal annealing

Figure 8: Morphology of crystalline PEO, crystallized 1 hr at 55 °C, after (a) microwave annealing, (b) thermal annealing

Figure 9: Morphology of crystalline PEO, crystallized 15 hr at 55 °C, after a) microwave annealing, b) thermal annealing

Figure 10: DSC thermograms of the film samples after different annealing treatments

Figure 11: DSC thermograms of the bulk samples after different annealing treatments
Figure 12: Morphology of crystalline PEO, crystallized at 0 °C, after a) microwave annealing, b) thermal annealing

Figure 13: Morphology of crystalline PEO, crystallized at 40 °C, after a) microwave annealing, b) thermal annealing

Figure 14: DSC thermograms of the bulk and film samples crystallized at -44 °C

Figure 15: DSC thermograms of the bulk and film samples crystallized at 0 °C

Figure 16: Morphology of crystalline PEO (Mn:2000 g/mol), crystallized at 25 °C in air, after a) microwave annealing; b) thermal annealing

Figure 17: Morphology of crystalline PEO (Mn:400,000 g/mol), crystallized at 25 °C in air, after a) microwave annealing; b) thermal annealing
List of Tables

Table 1: Comparison of microwave and thermal heating characteristics 12
Table 2: Sample characteristics of poly(ethylene oxide) 16
Table 3: Comparison of melting behaviors for film samples 26
Table 4: Comparison of melting behaviors for bulk samples 27
Chapter 1 Introduction

Crystalline polymers represent a class of materials that, in solid state, can develop complex morphologies for which ordered structures occur over a wide range of dimensions. Moreover, these ordered crystallites are often intimately mixed with amorphous domains producing a composite structure. A variety of microstructures of this kind provide a good possibility to design the crystalline polymeric materials with unique properties. Therefore, it is of importance to understand polymer crystallization to achieve better process control and obtain desired properties.

An important issue in the study of polymer crystallization is the annealing behavior of polymeric materials below and above their melt temperatures. In this work, "annealing" refers to heating the polymer above its melt temperature. In a previous study about the crystallization kinetics of poly(ethylene oxide), (PEO), a model had been proposed to simulate the exothermic behavior of its crystallization (1). The model fit the experimental data well for low molecular weight polymers, but not for high molecular weight polymers. One explanation for this disagreement was the memory effect of previous morphology on subsequent recrystallization. When crystalline polymers melt, polymer chains can locally break the bonds. However, it will take more time and energy for longer polymer chains to move around in a highly viscous melt. As a result, some partially ordered regions still exist after melting. The chains in these regions can rapidly revert back to form bonds when the crystallization occurs upon cooling. Because of this, the morphology of crystalline polymers usually exhibits a memory effect of prior
crystallization events. Conventional thermal annealing of polymer melts to eliminate this
local, partial ordering is tedious and time-consuming. Therefore, in this study, we attempt
to introduce microwave radiation to speed up annealing. By accelerating the rotation of
polymer chains, it is expected that microwave radiation will be able to heat the polymer
melt volumetrically and quickly, leading to rapid disordering of its molten phase, and
achieving better subsequent crystallization process control.

In this preliminary work, we have carried out parallel experiments to study the
effects of microwave annealing (MA) and thermal annealing (TA) on the PEO
crystallization. Sample morphology and the subsequent melting behavior were
characterized by polarizing light microscopy (PLM) and differential scanning calorimeter
(DSC), respectively. Each parallel experiment of MA and TA has been conducted under
the same cooling conditions. The effects of surface area, crystallization temperature, and
molecular weight on the morphology and melting behaviors of crystalline PEO, treated
by MA or TA, have also been investigated.
Chapter 2 Background

2.1. Morphology

It is well known that some polymer melts, at a certain degree of supercooling will rearrange themselves to form more ordered arrays characteristic of a crystalline state, resulting in specific morphologies. A detailed study of crystalline morphology will not only make it possible to better understand crystallization mechanism, but also help to achieve desired polymer properties. Here, we will discuss four typical morphologies for crystalline polymers, including the amorphous structure, lamellae, axialite and spherulite, as well as their relationship to crystallization conditions.

**Amorphous Structure:** One important feature of crystalline polymers, distinguishing them from small molecular crystalline solids, is that there is considerable fraction of a disordered, liquid-like, amorphous component. Usually, this component forms a continuous matrix in which the crystalline regions are embedded. The relative amount of the amorphous component varies considerably depending on the chemical nature of the polymer chains and on the crystallization conditions. Each polymer chain may be incorporated into, or pass through several crystalline regions. As a result, crystalline regions are tied together primarily by covalent bonds from segments of the chain in the amorphous region (2).

**Lamellae:** X-ray diffraction experiments of semi-crystalline polymers often give a very broad, noisy pattern. In general, only one peak associated with a repeat unit along the
chain is observed. On a larger scale, the "chain-folding lamellae" concept predicts that the representative structural element of the crystallite is the plate-like lamellae (3). It is typically about 100 Å in thickness, independent of molecular weight. The molecular chain axis or the C-axis of the unit cell lays in the direction of the thickness, perpendicular to the plane surface of the lamellae. Each constituent molecule traverses the lamellae many times. The thickness of the lamellae grown from a melt is reasonably uniform, and it is inversely related to the degree of supercooling at which the crystals were grown.

**Axialite and Spherulite:** Single crystal lamellae can be formed under extreme conditions. However, upon cooling of a polymer melt, many lamellae are generated. They may break-up, branching through screw dislocations, and finally impinge or interconnect with each other through chains which are anchored in more than one lamellae. Aggregate lamellar layers may link and align to take a characteristic shape, either sheaf-like or spherical. A sheaf-like morphology is referred to as either axialite or hedrite, while a spherical one is usually called a spherulite.

**Relationship between These Structures:** The multi-layered lamellar aggregates, formed through the action of screw dislocations about one axis, may appear sheaf-like (3) if viewed along the edges of the lamellae. Axialites result when all the lamellae grow to their final size without interconnection with each other except along the axis. Axialites are formed at a temperature near the melt temperature. They grow slower, and the constituent lamellae are much bigger than spherulites. In the vicinity of the center of an
axialite, all the layers tend to splay apart from each other, with non-crystallizable components in the growth front being rejected into the interstitial sites (2-3).

The maltese cross-section image of a spherulite, viewed under a polarizing light microscope, indicates that all the radii are equivalent. In practice, spherulites are composed of radial sequences of lamellae which are often linked by screw dislocations. The growth proceeds by the initial formation of an array of dominant lamellae, composed of the longest and most regular molecular chains present within the melt. Following the establishment of the dominant framework, subsequent subsidiary crystallization of less crystallizable material occurs at the interstitial sites of branched lamellae. Components or impurities unable to crystallize become trapped in amorphous domains if their diffusion is slow relative to the advancing growth front (2).

Axialites are believed to represent the precursor to a full spherulite. Lamella branching or interconnection may take place anywhere in the growth front, and screw dislocations may occur around any axis, when crystallization proceeds rapidly. Eventually, all solid angles will be filled and a near spherical envelope is generated. Therefore, the formation of axialites or spherulites, under a particular set of growth conditions, depends upon the frequency with which the branching occurs. These structures differ by degree rather than by any more fundamental aspect (3).

The precise arrangement of lamella and amorphous domains within the bulk polymer is of great importance in determining microscopic properties. For example, it has long been accepted that as the crystallization proceeds, the shorter, less crystallizable components of the melt tend to be rejected into the interstitial regions between
spherulites. As such inter-spherulitic regions constitute the sites of potential weakness, crack propagation, or dielectric break-down may start from these regions. In practice, spherulite size represents an important parameter for bulk property control (2).

2.2 Nucleation Step and Growth Step during Crystallization

Two steps are involved in the crystallization from a polymer melt. Initially, a nucleus of critical size must be formed. If the nucleus is too small, its high surface free energy prevents it from being stable long enough to make crystal growth possible. Nucleation can take place spontaneously in 3 dimension, or on an existing surface, i.e. in a growth front. Once the growth front is established, crystal growth can take place. During crystal growth stage, polymer chains must align themselves to the growth front. As chains continually add to the growth front, layers of polymers form the edge of the lamellae. It is believed that the morphology of the crystalline phase depends on the relative rate of nucleation to the rate at which polymer chains are “reeled in” to the growth front. The “reeling in” of the chains depends on the diffusion, or the reptation rate. At a small degree of supercooling, or a high crystallization temperature, the reptation rate of polymer chains is relatively high, and the lateral growth rate of a nucleus across the face of the crystal is much faster than the nucleation rate. This leads to full lateral growth of lamellae with little interconnections. As a result, axiallites are formed under these conditions. In contrast, if the degree of supercooling is sufficiently large, the nucleation rate will be much higher than the lateral growth rate. Multiple nucleation events take place simultaneously, and lateral growth of nuclei is retarded. Now the reptation or diffusion process is the rate-limiting step. Fine lamellae structures will splay,
bridge and impinge to form a much more complex morphology. The resulting structure is the spherulite (4).

2.3 Heterogeneous and Homogeneous Nucleation

Nucleation can be classified as homogeneous or heterogeneous. Homogeneous nucleation involves a spontaneous, 3-dimensional aggregation of polymer chains at a temperature below its melting point, in a manner which is reversible up to a point where its critical size is reached. Beyond this point, the subsequent addition of chains is irreversible, and the polymer aggregate will grow. Heterogeneous nucleation, on the other hand, arises from adventitious impurities, either randomly distributed throughout the bulk or possibly localized on a surface. Nucleation at the surface of the sample container is an example of the latter case (2). These sites are one example of residual nuclei, as mentioned earlier.

In some crystallization studies it was found that nucleation sites appear in similar positions during successive melting and re-crystallization cycles. This suggests that chemically different sites may not be necessary for heterogeneous nucleation to occur. Those regions of physical ordering may persist above the melting point, and take a long time to disperse. Some evidence (5) suggested that chain orientation in the polymer melt might indeed affect the rate of the subsequent crystallization process. It is likely that much of the data indicating a dependence on the melt history arise from this factor. These residual nuclei, defined by Sharples as “tiny regions with a high degree of order that may persist in a melt for a long time and will act as predetermined nuclei for re-crystallization upon cooling”, are also involved in a heterogeneous nucleation process (2). The number
of residual nuclei depends on the annealing conditions, such as annealing temperature, annealing time and annealing method.

The number of nuclei generated in the course of crystallization is of importance, because it determines the final size of the growth-units. This parameter is now recognized as being correlated with the optical and mechanical properties of semi-crystalline polymers. Therefore, a study of the nucleation process is necessary.

Considerable evidence indicates that heterogeneous nucleation predominates in practice. The majority of homogeneous nucleation events require a much higher degree of supercooling, (e.g. 50 °C) instead of 20 °C, which is usually needed for crystallization (2). The higher the nucleation rate, the smaller the size of the growth-units (either axiallite or spherulite). The nucleation rate will be the sum of the homogeneous nucleation rate and the heterogeneous nucleation rate.

2.4 Melting Behaviors of Crystalline Polymers

Although the melting of polymers is a first-order transition, unlike the sharp melting curves often observed for small molecules, the melting curves of crystalline polymers are quite broad. The broadening of the melting range can be attributed to a large variation of surface energy originated from crystal size distribution, and the complex morphology of polymers. The polymer morphology typically depends on processing conditions and molecular properties, such as end-group effect, molecular weight and polydispersity, and the extent of chain regularity. Thus, a detailed investigation of the polymer melting behavior may provide information about the nature of the crystalline morphology.
Moreover, the accurate measurement of the polymer melting temperature is of importance to calculating the degree of supercooling for both kinetic and thermodynamic studies.

A broad range of melting temperatures suggests that a large range of crystallite stabilities, or qualities are involved. The high quality crystals that are formed will melt at a higher temperature than more disordered crystals. When a crystal melts, it consumes energy. Therefore, an endothermic peak is observed on a DSC curve. \( T_m^* \) is usually defined as the melting temperature at which the melting is completed. \( T_m^* \) may increase with increasing heating rate, and with the crystallization temperature for a specific polymer sample. In this research, in order to investigate the effect of microwave annealing and compare it with thermal annealing, the heating rate and the crystallization temperature are kept the same in both cases. Therefore, if there exist different melting curves between microwave annealing and thermal annealing, it can be deduced that the differences are caused by the annealing conditions.

\( T_m \) is another characteristic melting temperature. It is defined as the equilibrium melting temperature of chains with finite molecular weight (4). Although \( T_m \) cannot be measured directly, it is an important parameter. It can be approached when a sample has been crystallized very slowly. When this equilibrium melting temperature is compared with those melting temperatures, \( T_m^* \), obtained for typical polymer systems, important morphological structure information can be deduced.
the melting temperature of the perfect crystal formed by infinite molecular weight polymers, is also a thermodynamic equilibrium melting temperature (4). It can be seen that \( T_m \) is a theoretical parameter under idealized conditions: no surface effects, no end-group effects. Chains are fully extended and equilibrium conditions are satisfied.

![Figure 1: Theoretical plot of \( T_{m*} \) against \( T_c \) for indicated chain length of linear polyethylene (6)](image_url)

The approach of Hoffman and Weeks (6) can be used to estimate \( T_m \) and \( T_{m*} \) based on the dependence of \( T_{m*} \) on \( T_c \), the crystallization temperature. The construction of the
Hoffman-Weeks method is given in Figure 1. A plot of $T_m^*$ vs. $T_c$ is made. The intersection of the extrapolated curves with the straight line $T_m^* = T_c$ gives the equilibrium melting temperature $T_m$. Moreover, an extrapolation to infinite molecular weight yields the thermodynamic equilibrium temperature $T_m^0$. However, the crystallinity level has been demonstrated to be important for obtaining accurate result (7).

2.6 Microwave Processing of Polymers

The use of microwave radiation for processing polymers offers a number of distinct benefits over conventional processing approaches. These include: enhanced polymerization rates (8), increased glass transition temperatures ($T_g$) of the cured epoxy (9), improved interfacial bonding between graphite fibers and their matrix, and increased mechanical properties of the resulting composites (10). The advantages of microwave heating over conventional thermal heating are summarized in Table 1 (11). The characteristics of microwave heating include: volumetric “inside to outside” heating, direct and quick heating, high selectivity, and high controllability. In addition to these thermal characteristics, there are so-called “microwave effects” which include anything that either is different from thermal processing or can not be predicted or easily explained by the different temperature profile (12). All of these characteristics have aroused a lot of research interests in exploiting microwave radiation to either produce new polymeric materials with desired properties, or use it as a new alternative technique for polymer processing. It has been discovered that some of these ideas indeed work, some do not. We
will not enumerate them here. However, a more detailed discussion about the mechanism of microwave heating will be helpful for understanding our experiment results.

**Table 1: Comparison of microwave and thermal heating characteristics**

(11)

<table>
<thead>
<tr>
<th></th>
<th>Thermal Heating</th>
<th>Microwave Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Rate</td>
<td><strong>Slow</strong>, controlled by heat transfer</td>
<td><strong>Fast</strong>, Direct coupling of energy into molecules</td>
</tr>
<tr>
<td>Selectivity</td>
<td><strong>No</strong>, Heating is due to temperature gradient</td>
<td><strong>Yes</strong>, Heating is proportional to material loss factor and input power</td>
</tr>
<tr>
<td>Heat movement</td>
<td><strong>Out to in</strong>, Surface driven heating from hot to cold</td>
<td><strong>In to out</strong>, Volumetric heating with boundary heat loss</td>
</tr>
<tr>
<td>Controllability</td>
<td><strong>No</strong>, Heat source can’t be readily controlled</td>
<td><strong>Yes</strong>, Microwave energy can be readily removed</td>
</tr>
</tbody>
</table>

The major mechanism (13) of coupling of microwave radiation to polymers is through dipole reorientation by the electric field (Figure 2). The relaxation of this reorientation has a maximum at a frequency of about 10E+7 Hz, but there is a high frequency tail, which reaches the microwave region (10E+11 Hz). However, the maximum value of this relaxation varies during a processing cycle, as the temperature increases. Put in other words, the dielectric loss factor, which is related to microwave absorption, is a function of both the frequency and the temperature. Consequently, as the temperature changes, the microwave absorption changes. Another consideration for the use of microwave heating is that the processing temperature for most polymers may be very close to the thermal degradation temperature of the polymer. Therefore, it is strictly required that the microwave system provide a very uniform temperature distribution.
throughout the part being processed, and it is necessary to precisely control the temperature of the part in order to avoid thermal run-away.

![Graph showing dielectric constant and dielectric loss vs. frequency](image)

**Figure 2: Typical variation in dielectric constant and dielectric loss with frequency for polymers** (13)

At the molecular level, when no electric field is present, the dipole moments are randomly oriented throughout the medium. But when an electric field is applied, there is a tendency for dipole moments to orient in the direction of the field to lower their energy. An imposed alternating electric field will cause oscillations of dipole moments, with the adjacent groups acting to inhibit the motion of the dipoles. The resulting friction generates heat.
The efficiency of this coupling depends on a number of factors, including the dipole strength, the mobility of the dipole and the mass of the dipole. Strong dipole coupling to the radiation leads to high efficiency for energy transfer. In the condensed state, the mobility of the medium around the dipole is also important. Small polar molecules obtain translational energy in addition to the energy from reorientation (rotational energy). This will dramatically increase the coupling of these molecules to the radiation field as compared with a segment of a large macromolecule. Similarly, a dipole that is a part of a pendent group will couple more strongly than a group in the main chain, due to its greater mobility. To summarize the behaviors for polymers, the melt couples the strongest followed by the rubbery state, glassy polymers and crystalline materials.

A mechanism for explaining the “microwave effect” on polymer processing has been proposed based on a non-equilibrium, non-uniform energy distribution between neighboring groups. For the solution imidization of a polymeric acid (12), microwave heating increased the “temperature” of the reacting groups by approximately 50°C, over the temperature range investigated. The energy couples directly with a reactive polar group in this system and dissipates through adjacent groups by random collisions. However, if the energy absorption is faster than energy transport, possible at the initial stages of reaction, there will be a non-uniformity in the temperature profile. This is consistent with some recent pulsed radiation studies (13), in which the pulsed repetition rate was set equal to rate of energy transfer along the chain. Theoretical calculations by Brook et al (14) predict that a small perturbation to the higher energy region of the energy distribution was sufficient to account for some “microwave effects” which have been observed in ceramics. The basis of these calculations is analogous to the mechanism
proposed for polymers, but the details are different. Polymer systems are not as highly ordered as ceramics systems. In this work, for the first time, we introduce microwave heating for annealing a polymer melt, and investigate the "microwave effect" on the subsequent crystallization process.
Chapter 3 Experimental

3.1. Sampling of Poly(ethylene oxide)

In this study, three types of poly(ethylene oxide), (PEO), were used. These materials were all commercially available PEO with narrow molecular weight distributions. Major information about the PEO samples is listed in Table 2.

Table 2: Sample characteristics of PEO

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Physical Description</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 g/mol</td>
<td>Waxy flakes</td>
<td>Fluka</td>
</tr>
<tr>
<td>20,000 g/mol</td>
<td>Waxy power</td>
<td>Fluka</td>
</tr>
<tr>
<td>400,000 g/mol</td>
<td>White fine power</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

The PEO powders were spread on glass slides and were molten on a hot stage to form liquid films. The films were annealed by either TA or MA, and then crystallized into solid films for further characterization. The bulk samples were prepared in glass tubes which were heated, annealed and subsequently, cooled. At the same time, film samples could also be prepared in the tubes, because a liquid film was automatically formed on the upper wall of the tubes when the powders in the tube melted and shrank. After annealing and crystallization, the tube was broken, and the polymer film on the glass wall was analyzed by PLM directly, then the film was scratched off the glass wall and collected for DSC characterization.
3.2 Experimental Set-up for Microwave Annealing

The experimental set-up for annealing of the polymer samples is shown in Figure 3. The sample tube was placed in a microwave oven (Multiwave, MA-693M, Goldstar Co.) The microwave oven was run at 100% power with a frequency of 1.47 GHz) surrounded by a paraffin oil bath. During microwave annealing, the temperature of the polymer sample could be controlled by the paraffin oil bath, which did not absorb microwave radiation. A recirculating isothermal water system was used to jacket the oil bath, and take excess heat out of the microwave oven in order to keep the sample at a constant temperature. After the annealing was complete, the temperature of the sample polymer melt was immediately measured with a digital platinum thermometer (Interstate Electric DT6) through a hole on top of the oven. Therefore, the calibration curve between the setting temperature of the isothermal reservoir and the temperature of the polymer melt could be obtained, as shown in Figure 4.

It was found that a steady temperature of the polymer melt could be achieved after the microwave power was turned on for a period of time. If the set temperature was above 60 °C, 10 minutes were usually needed to reach a steady temperature. At a lower set temperature, a longer time was required. As seen from Figure 4, an increase in the set temperature led to a smaller temperature difference between the polymer melt and the set temperature. At higher temperatures, the heat transfer was more efficient, and the temperature could be controlled more precisely.
Once the microwave annealing was completed, the polymer sample tube was quickly taken out of the microwave oven, and placed in a water bath, which was set at a specified temperature. By this way, the crystallization could be carried out isothermally. After the crystallization was finished, the samples were characterized using differential scanning calorimetry (DSC) and polarizing light microscopy (PLM).

For thermal annealing (TA), polymer sample tubes were placed in a controlled water bath. The temperature of the water bath was calibrated to maintain the same sample temperature as for MA. Crystallization was conducted as described above.

### 3.3 Morphology Characterization by PLM

A polarizing light microscope (Reichert-micro) with a JVC TK-10 video camera and a Metler FP-52 hot stage was used to characterize the morphology of film samples (magnification: 200X). The morphology of the bulk samples could not be examined by PLM because they were too thick for the light to pass through. An attempt to cross section bulk samples with a microtom led to unclear images.

### 3.4 Investigation of the Melting Behaviors for the Crystalline PEO by DSC

The differential scanning calorimetry (DSC) is a thermal analysis technique for accurate measurements of transition temperatures and heat capacities. The DSC curve, refered to as a thermogram, is proportional to the heat capacity of a sample. In our experiments, the melting curves of all the samples were measured at a heating rate of 5 °C/min. Although crystallization curves are preferred for investigating the effects of
different annealing methods, the difficulty in transferring a hot melt into the DSC pan prevented us from doing so. Instead, both film and bulk samples were characterized after the annealed melts were crystallized under controlled cooling conditions so that we could obtain the melting curves for both the film and the bulk samples under the same heating conditions. A Seiko Instrument Inc. DSC 220C Module was used here.

Figure 3: Experimental set-up for microwave annealing
Figure 4: The temperature calibration curve for the polymer melt and the reservoir
Chapter 4 Results and Discussions

4.1 Microwave Effects on PEO Crystallization

For comparison, we would like to maintain the same annealing temperature for both MA and TA samples. However, the energy can be coupled into the system directly, quickly and volumetrically using microwave annealing. In contrast, thermal annealing requires a longer time to achieve thermal equilibrium, because polymers are usually poor thermal conductors. Thus, we intentionally prolonged the annealing time for both MA and TA to eliminate potential temperature gradients inside the polymer melt, especially for TA samples.

All the bulk PEO samples (Mn: 20,000 g/mol) were annealed at 100 °C for various time periods, from 5 minutes to 2 hours. After annealing, they were all quenched at 25 °C in air until the crystallization was complete. DSC melting behavior for each bulk sample was characterized using ≈ 10 mg semi-crystalline specimens removed from the center of the sample tube.

It was found that DSC melting curves were superimposable for all the MA bulk samples when the annealing time was larger than 10 minutes, while the DSC melting curves were also superimposable for all the TA bulk samples when the annealing time was larger than 10 minutes. However, no DSC thermograms of the MA samples were superimposable on those of the TA samples. The fact that an annealing time longer than 10 minutes did not change the DSC melting behavior indicated that thermal equilibrium
had been reached by 10 minutes, no matter if MA or TA was used. Therefore, the difference between MA and TA cannot be explained by the difference of temperature gradient inside the polymer melt. There must be a fundamental difference between microwave annealing and thermal annealing, as evidenced by different DSC melting behaviors.

Figure 5: Morphology of crystalline polymers-PEO crystallized at 25 °C in air after (a) thermal annealing, and subsequent (b) microwave annealing
(Annealing temperature: 100 °C; annealing time: 10 min.; Mn: 20,000 g/mol.)

The effect of the annealing method on PEO crystallization became more evident when the crystalline morphology of film samples was examined using PLM. As seen in Figure 5a, a spherulite structure was formed after thermal annealing. However, after
subsequently annealing the same sample with microwaves, the fine texture in the image 5b was observed. Crystallization conditions for both micrographs were exactly the same.

![Image of PLM images](image)

(a)  
(b)

Figure 6: Morphology of crystalline polymers-PEO crystallized at 25 °C in air after (a) microwave annealing, and subsequent (b) thermal annealing

(Annealing temperature: 100°C; annealing time: 10 min.; Mn: 20,000 g/mol.)

When the order of annealing conditions was reversed, the resulting PLM images were also reversed. This is shown in Figure 6. Therefore, it could be concluded that different annealing methods gave rise to different crystalline morphologies. The result was reproducible, and was independent of the annealing order. This was a true "microwave effect".
As discussed in chapter 2, a Maltese cross pattern in a PLM image implied that the lamellae of the crystalline polymer aligned, branched and splayed in a spherical symmetry, which was observed in the PLM images of the TA samples. However, the fine texture in the PLM images of the MA samples implied that the structure might be anisotropic. Anisotropic mechanical property (15) had been reported for polyimide films, when microwaves were employed to assist the imidization. This could be explained by the inability for polymer chains to regularly align to the film plane when using microwave radiation.

4.2 Mechanism of Microwave Effects

Before we could compare the effects of microwave annealing and thermal annealing by investigating sample morphology and its melting behavior, subsequent crystallization had to be completed for all the samples. It is important to keep in mind that there are some other factors affecting the PLM and DSC results for PEO crystalline polymers, such as annealing temperature, annealing time, crystallization conditions, sampling type (bulk or film), and molecular weight. Here, we have changed one factor, and kept all the other conditions the same while studying the effects of MA and TA on PEO crystallization. In the next section, we will investigate the microwave effects on PEO crystallization by changing either the crystallization temperature or the molecular weight of PEO. Moreover, we will discuss the nature of microwave effects and specify the conditions required to observe these effects.
4.2.1 Dependence of microwave effects on crystallization temperature

Table 3 and Table 4 give a comparison of the melting behavior of MA and TA samples. The precision of these measurements is within ±2%. Similar trends were observed for both film and bulk samples, as exhibited in these tables. When the crystallization was carried out at -44 °C (dry ice bath), the extent of crystallinity for microwave annealing was much lower than for thermal annealing, as indicated by the enthalpy change during the melting transition. The enthalpy of melting, or ΔH of the MA sample at -44 °C was about 10% lower than that of the TA sample for both film and bulk samples. When the crystallization was performed in a water bath at higher temperatures, the difference of the enthalpy change between MA and TA becomes much smaller. This phenomenon was observed in both film and bulk samples. Based on these DSC results, if a difference in crystallinity existed for film samples between MA and TA, a similar difference would be expected to exist for bulk samples. The role of substrate surface area on the crystallization for film samples will be discussed in more detail later.

Although the melting curves for the MA and TA samples crystallized at 55 °C seemed to be similar, their crystallization kinetics were different. After annealing, the polymer melts were immediately transferred into a 55 °C water bath. Since the temperature was relatively high, the crystallization was slow, and could be observed by eye. For the sample 7-18-1 by MA, countable crystallites became visible after the melt was cooled for 10 minutes. However, the sample 7-18-2 by TA exhibited at least triple the amount of visible crystallites with the same mass of the melt after it was placed into the 55 °C water bath for just 4 minutes. This difference could be reproduced. It seemed
that microwave annealing decreased the nucleation density and retarded the rate of the crystallization process. Although the final extent of crystallinity, and the melting point did not change by changing annealing method, the kinetics of the crystallization process of MA and TA were different. This might explain why at the low crystallization temperature -44 °C, the crystallinity of microwave annealed samples was lower than that of thermal annealed samples. At such a low temperature, the crystal growth is diffusion (reptation) limited. As a result, the extent of crystallization depended on the number of nuclei. In the polymer melt annealed by microwaves, the nuclei density was low, because most of the residual nuclei were destroyed by microwave-assisted chain rotations.

**Table 3: Comparison of melting behavior for film samples**

<table>
<thead>
<tr>
<th>Crystallization Conditions</th>
<th>PEO Samples Number</th>
<th>Annealing Method</th>
<th>Melting Curves ΔH, mJ/mg</th>
<th>Tmp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry ice (-44°C)</td>
<td>7-08-1 7-08-2</td>
<td>MA TA</td>
<td>175 189</td>
<td>65.2</td>
</tr>
<tr>
<td>Ice water (0°C)</td>
<td>7-01-1 7-01-3</td>
<td>MA TA</td>
<td>183 178</td>
<td>65.1</td>
</tr>
<tr>
<td>Water (40°C)</td>
<td>7-02-1 7-02-2</td>
<td>MA TA</td>
<td>193 190</td>
<td>65.7</td>
</tr>
<tr>
<td>Water (55°C) 1hr</td>
<td>7-08-3 7-08-4</td>
<td>MA TA</td>
<td>203 200</td>
<td>67.7</td>
</tr>
</tbody>
</table>

(Annealing temperature: 78 °C; Annealing time: 10 min.; Mn: 20,000 g/mol; DSC heating rate: 5°C/min.; Tmp: melting point at the peak position.)

PEO chains possess large dipole moments at the hydroxyl terminated chain ends. An applied alternating electric field will cause the oscillation of these dipole moments, and initiate chain rotation. Therefore, the coupling of microwave radiation will increase the
rotation energy of the system, speeding up the elimination of residual nuclei in the melt. In contrast, energy is transferred by less efficient collision for thermal annealing, and chain conformations do not change as easily. Some residual nuclei will persist after annealing, and act as heterogeneous nuclei for subsequent crystallization.

Table 4: Comparison of melting behavior for bulk samples

<table>
<thead>
<tr>
<th>Crystallization conditions</th>
<th>PEO Samples Number</th>
<th>Annealing Method</th>
<th>Melting Curves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry ice (-44 °C)</td>
<td>7-08-1, 7-08-2</td>
<td>MA, TA</td>
<td>ΔH, mJ/mg T&lt;sub&gt;mp&lt;/sub&gt;, °C</td>
</tr>
<tr>
<td>Ice water (0 °C)</td>
<td>7-01-1, 7-01-3</td>
<td>MA, TA</td>
<td>172, 65.3, 190, 65.3</td>
</tr>
<tr>
<td>Water (40 °C)</td>
<td>7-15-1, 7-15-2</td>
<td>MA, TA</td>
<td>184, 64.3, 183, 65.1</td>
</tr>
<tr>
<td>Water (55 °C), 15hr</td>
<td>7-18-1&lt;sup&gt;(a)&lt;/sup&gt;, 7-18-2&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>MA, TA</td>
<td>189, 65.8, 194, 66.4</td>
</tr>
</tbody>
</table>

(Annealing temperature: 78° C; Annealing time: 10min.; Mn: 20,000 g/mol; DSC heating rate: 5°C/min.; T<sub>mp</sub>: melting point at the peak position.)

(a) Countable crystallites became visible at the 10th minutes after the melt was placed in 55 °C water bath.

(b) At least triple the amount of visible crystallites present in the same amount of melt as compared to (a) at the 4th minutes after the melt was placed in 55 °C water bath.

As discussed before, homogeneous nucleation takes longer time and requires lower temperatures than heterogeneous nucleation. Homogeneous nucleation appears to predominate in PEO crystallization following microwave annealing. This gives an explanation why the MA sample 7-08-1 has a lower crystallinity than the TA sample 7-


08-2. For the latter, heterogeneous nucleation may be the dominant mechanism. The comparison is given in Table 4.

Figure 7: Morphology of PEO crystallized at –44 °C on dry ice after (a) microwave annealing, (b) thermal annealing
(Annealing temperature: 78°C; Annealing time: 10 min.; Mn: 20,000 g/mol)

The morphologies of the film samples 7-08-1 and 7-08-2 were examined by PLM. As shown in Figure 7a, only one crystallite was observed for the MA sample, which implies a lower nuclei density. The even distribution of light and dark indicate that
lamellae were just locally aligned, not radially symmetric around the center. In contrast, as indicated in Figure 7b, more crystallites existed for the TA sample, implying more nuclei. The Maltese cross pattern indicate a radially symmetric lamellae structure.

Figure 8: Morphology of PEO crystallized for 1 hr at 55°C after (a) microwave annealing, (b) thermal annealing

(Annealing temperature: 78°C; Annealing time: 10 min.; MW: 20,000 g/mol)
Figure 8 represented the morphologies for the film samples for MA (7-08-3) and TA (7-08-4) crystallized at 55 °C in the water bath for one hour, then kept at 25 °C in air. For the microwave-annealed sample, as shown in Figure 8a, the lamellae are well defined, smooth and of a large size. There may be amorphous structures or less crystallized domains in the dark regions. Since the crystallization had not been finished for this sample within one hour, it continued to form crystals with poor quality during the cooling at 25 °C. However, the image of the thermally annealed sample in Figure 8b showed more uniform crystallites with a rough contoured texture. This could be attributed to a high crystallization rate due to a high residual nuclei density. The dark “river” in the image is a crack in the film.

If the samples were kept at 55 °C for a long enough time (e.g., 15 hours), it was observed that the morphologies of MA and TA samples became similar. This is revealed in Figure 9. During the longer time period, polymer chains had an opportunity to reorganize into a crystalline state close to thermal equilibrium. Since at such a high temperature, the chain reptation rate and impurity diffusion rate were both high, any small unstable or poor quality crystalline entities might dissipate, and re-crystallize into bigger crystal structures. Consequently, long crystallization times tended to eliminate the morphology difference between TA and MA.

Next, we closely examine the DSC thermograms of MA and TA samples as listed in Table 3 and 4. The thermograms for film samples are shown in Figure 10a-d, while those for the corresponding bulk samples are given in Figure 11a-d. As seen in Figure 10, a
comparison of thermograms of MA and TA film samples reveals that the MA melting curves are narrower than the corresponding TA curve. The crystallinity for the MA film sample is lower than for the TA film one, and the morphologies for these two film samples were different as indicated in Figure 7. For bulk samples, Figure 11a shows similar DSC behavior as compared with Figure 10a for the films. This implies that there

(a)  
(b)  

Figure 9: Morphology of PEO crystallized for 15 hr at 55°C, after (a) microwave annealing; (b) thermal annealing.  
(Annealing temperature: 78°C; Annealing time: 10 min.; Mn: 20,000 g/mol)
may be different morphologies for the two MA and TA bulk samples, just as was the case for the two film samples. We hypothesize that surface effects do not play an important role under the low temperature crystallization conditions.

Usually, crystallization rate depends on both diffusion rate (the rate of polymer chain reptation) and nucleation rate. The diffusion rate increases with the crystallization temperature, while the nucleation rate decreases with the temperature. Therefore, the maximum PEO crystallization rate is achieved at about 40°C (degree of supercooling: 25°C). At a low temperature, such as -44°C, the diffusion rate is very slow, and the nucleation rate is high. As a result, no extra nucleation center from the substrate is needed for the crystallization. That is why surface effects were not pronounced for these samples.

At a higher crystallization temperature, such as 0°C or 40°C, the glass substrate of the film samples could be used as heterogeneous nucleation sites for the crystallization, leading to a the fast crystallization rate. The nucleation rate of polymer melt is slow. This could explain why there was no big difference in morphology between MA and TA film samples at these temperatures (Figure12 and 13). Similarly, their DSC thermograms also tended to be close to each other, as depicted in Figure10b and 10c. However, Figure11b and 11c showed different thermograms for the bulk counterparts. Here, a surface effect is not important. The difference between TA and MA bulk samples could be attributed to the fact that a heterogeneous nucleation mechanism dominates for the TA bulk sample, while a homogeneous nucleation mechanism took control for the MA one. Again, homogeneous nucleation most likely dominated at a larger degree of supercooling (lower
Figure 10a: DSC thermograms of film samples after different annealing treatments (crystallized at $-44^\circ$C)

Figure 10b: DSC thermograms of film samples after different annealing treatments (crystallized at $0^\circ$C)
Figure 10c. DSC thermograms of film samples after different annealing treatments (crystallized at 40 °C)

Figure 10d: DSC thermograms of film samples after different annealing treatments (crystallized at 55 °C)

(Conditions for Figure 10a-d, Annealing temperature: 78 °C; Annealing time: 10 min.; Mn: 20,000 g/mol; DSC heating rate: 5 °C/min; Tc: the crystallization temperature.)
Figure 11a: DSC thermograms of bulk samples for different annealing treatments (crystallized at $-44 \, ^\circ C$)

Figure 11b: DSC thermograms of bulk samples for different annealing treatments (crystallized at $0 \, ^\circ C$)
Figure 11c: DSC thermograms of bulk samples for different annealing treatments (crystallized at 40 °C)

Figure 11d: DSC thermograms of bulk samples for different annealing treatments (crystallized at 55 °C for 15 hr)

(Conditions for Figure 11a-d: Annealing temperature: 78°C; Annealing time: 10 min.; Mn: 20,000 g/mol, DSC heating rate: 5 °C/min; T_c: the crystallization temperature.)
temperature) and less time was left for crystal growth. The resulting crystals may have smaller size and larger surface area. This could explain why the DSC melting curves for the MA samples showed lower melting temperatures.

At the crystallization temperatures of 0°C and 40°C, the microwave effect was observed for the bulk samples even in the DSC curves (Figure 11b and 11c), which, as mentioned before, a less sensitive technique than PLM to examine surface morphology. Very possibly, a big difference in morphology also exists between MA and TA bulk samples, although we could not directly characterize it with a suitable technique.

Figure 12: Morphology of PEO crystallized at 0°C
(a) microwave annealing; (b) thermal annealing

(annealing temperature: 78°C; annealing time: 10 min.; Mn: 20,000 g/mol)
At the highest crystallization temperature of 55 °C, the crystallization rate is dictated by nucleation. In this case, both heterogeneous and homogeneous nucleation would take a long time. It had been observed that it took 10 minutes for crystallites to emerge for the MA samples, while 4 minutes was needed for the TA samples. Possibly, the surface effect no longer played an important role in the crystallization at this extremely high temperature. Surface nuclei may sustain even after formation. Therefore, the different morphology as indicated in Figure 8 for the MA and TA samples was primarily caused by their different kinetics. When extending the crystallization time from 1 hour to 15 hours at 55 °C, the difference in DSC thermograms between MA and TA bulk samples was reduced, as shown in Figure 11d. This could be attributed to long time melting-recrystallization or reorganization of the crystallites at this high temperature. This result was consistent with the morphology examination for the film samples given in Figure 9.

Comparisons of DSC thermograms between the bulk and film samples at two crystallization temperatures are given in Figure 14a-b and Figure 15a-b using TA or MA, respectively. When the crystallization temperature was -44 °C, as shown in Figure 14a-b, the film thermogram was close to the bulk one, especially under the condition of thermal annealing (Figure 14a). As discussed earlier, the surface effect should not play an important role in the crystallization at this low temperature. Therefore, it is reasonable to assume that the structure of the bulk sample was similar to that of the corresponding film sample. If this is true, there should be different morphologies between TA and MA bulk samples, considering the fact that the morphologies between the TA and MA films samples were different, as indicated in Figure 7.
Figure 13: Morphology of PEO crystallized at 40°C
(a) microwave annealing; (b) thermal annealing

(annealing temperature: 78°C; annealing time: 10 min.; Mn: 20,000 g/mol)

Figure 15a-b shows that DSC thermograms of film samples are quite different from those of bulk ones at a crystallization temperature of 0°C. Therefore, the morphology of film samples cannot be representative of bulk ones. The surface effect for the film samples must be taken into consideration at this relatively high temperature. It was interesting to notice that different melting behavior between the film and bulk samples occurred at the lower temperature part of the melting curves for MA, and at the higher temperature part for TA. However, the reason for this difference is not clear.
Figure 14a: DSC thermograms of the bulk sample and the film sample, crystallized at \(-44^\circ\)C (after thermal annealing treatments)

Figure 14b: DSC thermograms of the bulk sample and the film sample, crystallized at \(-44^\circ\)C (after microwave annealing treatments)

(Conditions for Figure 12a-b: annealing temperature: 78\(^\circ\)C; annealing time: 10 min.; Mn: 20,000 g/mol; DSC heating rate: 5\(^\circ\)C/min; \(T_c\): the crystallization temperature.)
Figure 15a: DSC thermograms of the bulk sample and the film sample, crystallized at 0 °C (after thermal annealing treatments)

Figure 15b: DSC thermograms of the bulk sample and the film sample, crystallized at 0 °C (after microwave annealing treatments)

(Conditions for Figure15a-b: annealing temperature: 78° C; annealing time: 10 min.; Mn: 20,000 g/mol; DSC heating rate: 5 °C/min; T_c: the crystallization temperature.)
In summary, we propose the following hypothesis: when surface effects are not dominant during the crystallization, the morphology for the film sample is representative of the bulk one. Homogeneous nucleation dominated for the samples subject to MA while heterogeneous nucleation took control for the samples annealed thermally. The different crystallization mechanism between MA and TA led to different morphologies for both film and bulk samples. However, long crystallization times, especially at a high crystallization temperature, would mask the difference between MA and TA. In contrast, if the surface nucleation events are important for the film samples during crystallization, heterogeneous nucleation would dominate for the film samples for either MA or TA, with the substrate surface providing most of the nucleation sites. This could explain the similar morphologies for the film samples found for MA and TA, as revealed in their PLM images. However, the film morphology was not representative of the bulk one. Moreover, since the different DSC melting behaviors between MA and TA had been observed for the bulk samples, the morphology for these two bulk samples must also be different.

4.2.2 Dependence of Melting Behavior on PEO Molecular Weight

As discussed before, microwave annealing could reduce the number of residual nuclei in the polymer melt, through the coupling of the alternating electric field with the dipoles in the polymer chains. For poly(ethylene oxide), the largest dipole moments are located at the chain ends of the molecule. Therefore, it was expected that a melt of low molecular weight polymer should exhibit larger microwave absorption, because of its
higher density of chain ends. To test this hypothesis, the effects of microwave annealing on three PEO samples with different molecular weight ranges were studied.

As evidenced by different morphologies for MA and TA samples in Figure 4 and Figure 5, the microwave effect for PEO samples with a molecular weight of 20,000 g/mol was significant. However, under the same crystallization condition for the PEO samples with a molecular weight of either 2000 g/mol or 400,000 g/mol, the sample morphology by MA looked similar to that by TA, as exhibited in Figure 16 and 17.

The critical molecular weight for PEO is 3200 g/mol (1). Below this value, there is no polymer chain entanglement, and microwave absorption for this kind of polymer is larger than that for the polymer with a molecular weight higher than 3200 g/mol. However, the energy adsorbed by the low molecular weight polymer could easily dissipate through chain movement. Since its chains were short and easily extended, it was expected that there would be a small number of residual nuclei existing in the polymer melt even for thermal annealing. This could explain why the microwave effect was not pronounced for the polymer with a molecular weight of 2000 g/mol. On the other hand, as the molecular weight increased to 400,000 g/mol, there was little microwave absorption for this kind of polymer, because only a small amount of chain ends were available to couple to the microwave radiation. Therefore, the residual nuclei may persist even with MA. Most possibly, a balance was needed between the amount of microwave absorption and the number of potentially available residual nuclei, in order to achieve the maximum microwave effect. This explains why the PEO with a molecular weight of 20,000 g/mol demonstrated the strongest microwave effect.
Figure 16: Morphology of PEO (Mn: 2000 g/mol) crystallized at 25°C in air after (a) microwave annealing; (b) thermal annealing

(annealing temperature: 100°C; annealing time 10 min.)

Figure 17: Morphology of PEO (Mn: 400,000 g/mol) crystallized at 25°C in air after (a) microwave annealing; (b) thermal annealing

(annealing temperature: 85°C; annealing time 20 min.)
The incorporation of low molecular weight PEO into high molecular weight fraction (50%wt 20,000g/mol + 50% 400,000g/mol) had been studied to enhance annealing efficiency for PEO with high molecular weight. If the physical blend was thermally heated at 78°C for half an hour, then crystallized at 25°C in air, two kinds of structures were observed. Under the PLM. One was black, indicating a higher percentage of the low molecular weight fraction. The other looked white, indicating a higher percentage of the large molecular weight fraction. Its DSC curves exhibited two melting peaks, separated far away from each other. If the physical mixture was heated by microwave radiation, only one homogeneous structure in the crystalline materials was observed. The DSC curves of the crystalline mixture showed two melting peaks, but they were much closer to each other as compared to TA. Therefore, it was concluded that the polymer with high molecular weight could be microwave-annealed by blending it with the polymer having low molecular weight.
Chapter 5: Conclusions

In this preliminary study, we investigated the effects of microwave radiation on the crystallization of polymer melts. We discovered, for the first time, that microwave radiation could directly couple to molecular motion in this polymer. This was a true "microwave effect", rather than the result of a modified temperature profile.

By comparing microwave annealing to thermal annealing, it was found that the morphology and melting behavior of crystalline poly (ethylene oxide) were different using the two annealing methods, when other factors such as annealing temperature, annealing time, crystallization conditions, and sample type were all kept the same. This difference could be attributed to decreased residual nuclei in the microwave-annealed samples, as compared to those that were thermally annealed. It was believed that by accelerating the dipole moment oscillation of polymer chains, and speeding up the rotation of polymer chain ends, microwave radiation could be used to enhance the reptation rate of polymer chains. As a result, heterogeneous nucleation due to residual nuclei became less important in the subsequent crystallization. In conclusion, microwave annealing could help eliminate the "memory" of a prior crystallization and produce a more homogeneous amorphous melt.

The effect of microwave absorption could be masked under certain conditions. When the substrate surface of the film samples dominated the crystallization by supplying heterogeneous nucleation sites, as was the case for fast crystallization, similar morphologies were obtained for both microwave annealing and thermal annealing.
Another observation was that different crystallite morphologies formed at 55 °C after microwave annealing and thermal annealing, appeared to restructure as the crystals were kept at such a high temperature for a prolonged period of time. The conditions distinguishing homogenous nucleation from heterogeneous nucleation could be used to maximize the microwave effect.

The microwave effect was also attenuated for high molecular weight fractions of PEO. Since the microwave absorption was not big enough for annealing the PEO polymer melts when its molecular weight was 400,000 g/mol, incorporation of PEO of low molecular weight was helpful to increase the annealing efficiency. We found that the difference in DSC melting behavior and morphologies between microwave annealing and thermal annealing was most pronounced for the 20,000 g/mol PEO sample.

In summary, it was found that microwave annealing could change the solid state micro-environment of a crystalline polymer as compared to thermal annealing. This could provide us with possibilities for modifying polymer properties related to morphology, such as mechanical, optical, electrical properties or even permeability and chemical reactivity. Further measurements on these properties should be of significance when comparing microwave annealing to thermal annealing. Fundamentally, this unique processing method could lead to new approaches for kinetic and thermodynamic studies, if the crystallization process was monitored immediately after microwave annealing, and a comparison of crystallization and melting behavior could be made. Crystallite morphology for pure homogeneous nucleation, or 100% amorphous solid polymers could
be possible by employing microwave annealing. Further work using microwave annealing on other polymer systems should be pursued.
References


