ELLIPSOMETRY MEASUREMENTS OF CHEMICAL REACTIONS AND
DIFFUSION PROCESSES IN POLYMER FILMS

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ELLIPSOMETRY MEASUREMENTS OF CHEMICAL REACTIONS AND
DIFFUSION PROCESSES IN POLYMER FILMS

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Chemical crosslinking of layer-by-layer assembled films promotes mechanical stability and robustness in a wide variety of environments, which can be a challenge for polyelectrolyte multilayers in saline environments or for multilayers made from weak polyelectrolytes in environments of pH extremes. Heating branched poly(ethylene imine)/poly(acrylic acid) (BPEI/PAA) multilayers at sufficiently high temperature drives amidization and dehydration to covalently crosslink the film, but this reaction is rather slow with hours of heating typically required for appreciable crosslinking to occur. Here, more than an order of magnitude increase in the amidization kinetics is realized through microwave heating of BPEI/PAA multilayers on ITO/glass substrates. The crosslinking reaction is tracked using infrared spectroscopic ellipsometry to monitor the development of the crosslinking products. For thin films (c.a. 500 nm), microwave crosslinking generates a more uniform network as determined by ion diffusion during electrochemical impedance spectroscopy than does conventional heating, and for thick films (c.a. 1500 nm), gradients in the crosslink density can be readily identified by infrared ellipsometry. Such gradients in crosslink density are driven by the temperature gradient developed by the localized heating of ITO by microwaves. This significant acceleration of reactions using microwaves to generate a homogeneous crosslink network as well as being a simple method to develop graded materials should open new applications for these polymer films and coatings.
As the infrared ellipsometry can detect the graded extinction coefficient which due to the graded crosslink density, IR ellipsometry can also use to measure the inter diffusion between different polymers. In this study, a new model using graded extinction coefficient through the bilayer system is introduced. Polymers used in this study are two types of polycarbonates (PC), which is a versatile material, have many applications in different aspect. Those two types of PC have different $T_g$. This material have several good properties such as high impact, temperature resistance, transparency and good electrical insulation properties. Several theory have tried to explain diffusion. However those theory are not perfect. Ellipsometry is an excellent way to observe the diffusion because it is a non-contact and non-destructive measurement. From the result obtained, an obvious interfacial film broadening can be observed. When the heating temperature is higher than $T_g$ of both polymers, both polymers exhibit high mobility. Moreover, when the heating temperature $T_{g1} < T < T_{g2}$ (1 and 2 represent two different PC respectively, specific material are introduced in Chapter III), PC-1 shows a much higher mobility than PC-2. The interface broadening are most contributed by PC-1 as it moves much faster than PC-2.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>ix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Ellipsometry</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 UV-Vis-NIR ellipsometer</td>
<td>1</td>
</tr>
<tr>
<td>1.1.2 IR ellipsometer</td>
<td>6</td>
</tr>
<tr>
<td>1.1.3 Ellipsometric measurement in reaction kinetics</td>
<td>8</td>
</tr>
<tr>
<td>1.2 Microwave</td>
<td>8</td>
</tr>
<tr>
<td>1.2.1 Microwave heating mechanisms</td>
<td>8</td>
</tr>
<tr>
<td>1.2.2 Properties of microwave heating</td>
<td>10</td>
</tr>
<tr>
<td>1.3 Polymer diffusion</td>
<td>11</td>
</tr>
<tr>
<td>1.3.1 Theory- Rouse model and Reptation model</td>
<td>11</td>
</tr>
<tr>
<td>1.3.2 Experiment method</td>
<td>12</td>
</tr>
<tr>
<td>1.3.3 Ellipsometric measurement in polymer diffusion</td>
<td>13</td>
</tr>
<tr>
<td>II. RAPID CROSSLINK OF POLYELECTROLYTE MULTILAYERS THIN FILMS BY MICROWAVE HEATING AND THE COMPARISON BETWEEN CONVENTIONAL HEATING AND MICROWAVE HEATING</td>
<td>15</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>15</td>
</tr>
<tr>
<td>2.2 Experimental</td>
<td>17</td>
</tr>
<tr>
<td>2.2.1 Materials</td>
<td>17</td>
</tr>
<tr>
<td>2.2.2 Sample preparation</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Characterization</td>
<td>19</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Schematic of an ellipsometric experiment, showing the p- and s- direction from a linear polarized incident beam Reproduced with permission</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Visualization of the characteristic changes in the polarization state of light upon reflection off the sample. The changes from linear polarization with electric-field strengths $E_p$ and $E_s$ to elliptical polarization with $E_{rp}$ and $E_{rs}$ are captured by the amplitude ratio $\tan \Psi$ and the phase difference $\Delta$ between parallel and perpendicular component with respect to the plane of incidence</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Polarization ellipse, described by the ellipsometric angles $\Psi$ and $\Delta$. The polarized wave propagates in the positive sense of the $z$ axis, which points towards the reader</td>
<td>4</td>
</tr>
<tr>
<td>1.4 Optical layout and principle of infrared ellipsometry designs. They have the advantage of a high throughput combined with measuring of all spectral elements during a whole scan cycle</td>
<td>7</td>
</tr>
<tr>
<td>1.5 Schematic of the sputtering process caused by an impinging primary ion</td>
<td>12</td>
</tr>
<tr>
<td>2.1 The extinction coefficient ($k$) and refractive index ($n$) for the (BPEI/PAA)$_6$ in the UV-visible-NIR region determined from fit of the data in Figure 2.2 A both (blue) before and (purple) after crosslinking</td>
<td>22</td>
</tr>
<tr>
<td>2.2 Change in the ellipsometric angle $\Psi$ for (BPEI/PAA)$_6$ films from microwave crosslinking (180 °C, 15 min) in the (A) UV-Vis-NIR and (B) IR spectra. The best fit of these data are shown by the dashed lines with a Cauchy model sufficient to describe the (BPEI/PAA)$_6$ film in the UV-Vis-NIR, while an oscillator model that includes the absorption from bending and stretching vibration is required in the IR</td>
<td>23</td>
</tr>
<tr>
<td>2.3 The extinction coefficient for the (BPEI/PAA)$_6$ in the IR region determined from fit of the data in Figure 2.2B both (A) before and (B) after crosslinking. The dashed lines are the individual oscillators included in the model. The band that indicates the carboxylic group (~1560 cm$^{-1}$) decreases, while the amide I band (~1600 cm$^{-1}$-1700 cm$^{-1}$) increases</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Comparison of conversion obtained from disappearance of reactant (black symbols) and appearance of the amide I bond (color symbols) at (A) 180 °C and (B) 200 °C</td>
<td>25</td>
</tr>
</tbody>
</table>
2.5 Impact of heating method on conversion using (A) conventional heating and (B) microwave heating at (□,■) 180 °C and (○,●) 200 °C for 450 nm thick film of (BPEI/PAA)₆ ..................................................................................................................... 26

2.6 Nyquist plots of the impedance associated with (BPEI/PAA)₆ crosslinked to different extents by conventional (+) and microwave heating (○). Nominal conversions of 30 %, 65 % and 80 % are examined to compare conventional and microwave heating. 27

2.7 Comparison of the ellipsometric angle, Ψ, of thicker (BPEI/PAA)₁₇ after crosslinking using (A) conventional heating at 180 °C for 510 min and (B) microwave heating at 180°C for 5 min. These conditions should yield similar conversion based on (BPEI/PAA)₆ data in Figure 3. The black dashed line is the best fit of the data using the same model as for the (BPEI/PAA)₆ film with significant error (as evidenced by the residual greater than 1) in the fit for the microwave heating sample. For these samples, a graded model improves the fit (blue dashed line) with the residual shown by the blue line. (C) The conversion profile from the best fits for both (open symbols) conventional heating and (closed symbols) microwave heating through the thickness of the film...... 30

2.8 Impact of PEM thickness on the average conversion at 180 °C using (□) (BPEI/PAA)₆ and (△) (BPEI/PAA)₁₇ using (A) conventional and (B) microwave heating. The extent of the gradient in the (BPEI/PAA)₁₇ films with microwave heating are illustrated for the (+) top and (-) bottom of the (BPEI/PAA)₁₇ film................................. 32

3.1 Bisphenol-A polycarbonate chemical structure .......................................................... 36

3.2 Bisphenol-TMC polycarbonate chemical structure .................................................... 37

3.3 Schematic of spin coating ........................................................................................... 38

3.4 Schematic of floating .................................................................................................. 39

3.5 Schematic of the change of bilayer during the diffusion. Before diffusion, the interfacial film was narrow and the thickness was small. So that interfacial film were seen as interface ........................................................................................................................ 42

3.6 Schematic of graded for bilayer system....................................................................... 43

3.7 The extinction coefficient (k) of APEC1797 (red) and Makrolon2205 (black) in IR range ................................................................................................................................. 44

3.8 Evolution of depth profile of bilayer system diffusing at 275°C.................................. 45

3.9 Evolution of depth profile of bilayer system diffusing at 250°C.................................. 46

3.10 Evolution of depth profile of bilayer system diffusing at 225°C............................... 47

3.11 Relation between interface thickness and time at 225°C, 250°C, 275°C ............... 47
3.12 Interface thickness vs time\(^{1/2}\) at 225°C, 250°C, 275°C

3.13 Interface thickness vs time\(^{1/2}\) at 225°C, 250°C, 275°C with linear fit

3.14 The extinction coefficient (k) of APEC1797 (red) and Makrolon2205 (black) in UV-visible range

3.15 Evolution of depth profile of bilayer system diffusing at 225°C

3.16 Relation between interface thickness and time at 225°C and 250°C

3.17 Relation between interface thickness and time\(^{1/2}\) at 225°C and 250°C with linear fit
1.1 Ellipsometry

Ellipsometry measures the change of polarization state upon reflection or transmission of light at a sample. The name ellipsometry is derived from the fact that the final state is usually elliptical polarization. It is a non-destructive method that allows one to determine absolute sample properties without a reference standard. Ellipsometry is used for analyzing processes and materials on surfaces and inside the thin films. Most of the materials studied by the ellipsometer are alloy, semiconductors, polymers, etc. In this research work, ellipsometers are mostly used for observing polymeric material.

1.1.1 UV-Vis-NIR ellipsometer

Ellipsometry is a sensitive, non-destructive and contactless optical technique that utilizes polarized light to determine the optical constants and thickness of thin films. It earns the sensitivity from the determination of the relative phase change in a beam of reflected polarized light. Since ellipsometry only measures the polarization state of a light beam (Figure 1.1), it does not have to measure the absolute intensity of the reflected light, which improves sensitivity and accuracy.
Figure 1.1 Schematic of an ellipsometric experiment, showing the p- and s- direction from a linear polarized incident beam Reproduced with permission from Ref [1].

UV-Vis-NIR ellipsometry measures the change of polarization state upon reflection or transmission of light at UV-Vis-NIR range. The variables of ellipsometry are often wavelength-dependent. A phase shift may be induced as the polarized light is reflected from a surface at non-normal incidence, changing the ellipticity of the polarized light. This change is dependent on the surface properties of the material. It is the essence of ellipsometry to analyze the reflected light in order to determine what the surface did to the light beam and to hence draw conclusions about the material.
Figure 1.2 Visualization of the characteristic changes in the polarization state of light upon reflection off the sample. The changes from linear polarization with electric-field strengths $E_{ip}$ and $E_{is}$ to elliptical polarization with $E_{rp}$ and $E_{rs}$ are captured by the amplitude ratio $\tan \Psi$ and the phase difference $\Delta$ between parallel and perpendicular component with respect to the plane of incidence.

Ellipsometry use this change in polarization to acquire information such as refractive index, extinction coefficient and thickness of thin films. As shown in Figure 1.3, the elliptical polarization of linearly polarized light is caused by the difference in reflectivity between the incident beam’s component that is parallel ($p$) to the plane of incidence and the component that is perpendicular ($s$) to the plane of incidence.
The ellipsometer measures the ratio of the two Fresnel reflection coefficient $R_p$ and $R_s$. This ratio is represented as the complex reflectance ratio $\rho$:

$$\rho = \frac{R_p}{R_s} = \tan^\Psi \times e^{i\Delta} \quad \text{Eq.(1.1)}$$

In this equation, $\Psi$ is the amplitude parameter and $\Delta$ represent the phase shift. In general, the $\Psi$ and $\Delta$ cannot be converted directly into the optical constants or the thickness of the samples. Different model is used to analyzing the ellipsometric data to obtain the optical properties and film thickness. (This was discussed in the following section).

Figure 1.3 Polarization ellipse, described by the ellipsometric angles $\Psi$ and $\Delta$. The polarized wave propagates in the positive sense of the $z$ axis, which points towards the reader.
An visual schematic explanation of the Eq.(1.1) for the polarization ellipse is shown in Fig. 1.1. The wave is assumed to propagate along the z axis of the right-handed Cartesian coordinate system x–y–z. The amplitudes of the electric field in the x and y directions are denoted by X and Y, respectively; both of them are real, non-negative quantities.

Usually, a layer model is established for analyzing the ellipsometric data. An iterative procedure with varied unknown optical and/or thickness parameters was used to calculate corresponding Ψ and Δ. The calculated Ψ and Δ that match the experimental data best provide physical properties (optical constants, thickness and anisotropy et al.) of the sample. Additionally, an infrared ellipsometer is best for thick films (100 nm – 50000 nm) as the IR light have a long wavelength, while the visible and ultra-violet wavelengths are best for thinner films (0.1nm – 1000 nm) as the wavelength of visible and ultra-violet light is relatively short compare to the IR light.

Moreover, if the optical constant at each wavelength is known, it can be used to enforce some type of dispersion model (Cauchy or Lorentz et al.) to determine the results. The combination of variable angle of incidence and spectroscopic measurement provide the ability to acquire large amounts of data from a given sample. More importantly, by choosing the best incident angle, it can also optimize the condition for data acquisition.

There are three main advantages of ellipsometry compared to reflectance:

1. Ellipsometry measures two parameters (Ψ and Δ) compared to the single parameter of reflectance.

2. Ellipsometry measures phase information not available from reflectance.
3. Ellipsometry measures a ratio of intensities, whereas reflectance measures absolute intensity.³

1.1.2 IR ellipsometer

The main investigation technique used to obtain the results presented in this work was infrared spectroscopic ellipsometry because the resonance between chemical bands and IR can be used to identify specific chemical group in polymer. The IR ellipsometric experiment is also non-invasive, contact-free, and does not depend on special requirements such as (ultra-high) vacuum. Many organic compounds do not exhibit characteristic electronic transitions in the VIS spectral range because the energy of vibration of chemical bonds is lower than the energy of the VIS light. Thus, a detailed structural characterization is often not possible from VIS ellipsometric spectra. On the other hand, IR ellipsometry is extensively used for this purpose because characteristic IR bands associated with vibrations of specific molecular groups are noticed. The band amplitudes and shapes in the IR ellipsometric spectra are directly related with the directions of transition dipole moments of specific molecular vibrations.

Infrared spectroscopy is energy limited by the radiation energy of the glow bar, which has a temperature of about 1600 K. To overcome this problem Fourier transform spectrometers (FTS) have been used.
Infrared ellipsometry is only practicable in combination with an FTS. The sequence of the devices FTS-PE (PE – photometric ellipsometer) is advantageous, because for an opposite order the measurement would be disturbed by the thermal radiation of the sample. The principle of the photometric measurement is shown in Fig. 1.4.

IR ellipsometry widens the scope of traditional IR spectroscopy. More information such as the spectral (real) refractive index and extinction coefficient in the IR range can be obtained. Ellipsometric studies of isotropic materials typically are based on reflection, and therefore samples can be studied even if their absorptivity prevents transmission measurements. Note that IR ellipsometry spectra are not the same as IR transmission spectra because there is no flat baseline in ellipsometry spectra.
1.1.3 Ellipsometric measurement in reaction kinetics

In the work of Simpson\(^5\), the IR ellipsometer is applied to determine the reaction rate of crosslink reaction in poly(dimethyl siloxane) as the information of chemical bond can be obtained in IR range. A limitation of visible-light ellipsometry is that it offers little chemical sensitivity, unless there is a large difference in refractive index between chemical compounds. Thus, in this work, the IR Ellipsometry Spectroscopy were used as when IR radiation is used for ellipsometry, information about the nature of the chemical groups present can be obtained from the study of the characteristic absorption bands.

1.2 Microwave

1.2.1 Microwave heating mechanisms

Microwave irradiation is a rapid way of heating materials for domestic, industrial and medical purposes. Microwaves offer a number of advantages over conventional heating such as non-contact heating (reduction of overheating of material surfaces), energy transfer instead of heat transfer (penetrative radiation), material selective and volumetric heating, fast start-up and stopping, and, last but not least, reverse thermal effect, i.e., heat starts from the interior of material body\(^6\).

As the microwave is electromagnetic wave with frequencies between 300 to 3000 Mhz (wavelength between 1m to 0.01m). For most material, electric component of the electromagnetic wave primarily contributes to the microwave heating effect. These microwave heating effects mainly result from the interaction of the electric component of the MW field with charged particles such as ions or permanent dipoles in a material (sometimes, magnetic dipoles may interact with the magnetic component of the
There are two types of interactions: dipolar polarization and conduction heating.\textsuperscript{7}

In materials where the charges are bound as dipoles, the electric field induces motion until it is balanced by electrostatic interactions. This is known as dipolar polarization. The motion mentioned in this interaction is short range\textsuperscript{8}.

In materials whose charge carriers are mobile, such as free electron and fast ion conductors, the alternating MW field gives rise to a current moving in material and causing resistive heating in the sample. This is known as conduction heating.\textsuperscript{7} The movement of charge carriers is long range and during the movement, the charged carriers collide with other species\textsuperscript{8}, which can generate heat. Generally, this mechanism is the dominant effect in solid materials if the material has free charged carriers. The conduction heating is the dominant interaction in this research because the ITO/glass that have abundant free electrons was used in this work.

Those two interactions result in the fast increase of temperature, which can explain the advantages of microwave described above.

To describe the microwave heating quantitatively, the dielectric properties are utilized. The dielectric properties of a material can also be used to determine the amount of power absorbed, $P$:

$$P = \sigma |E|^2 = 2\pi f \varepsilon_0 \varepsilon'' |E|^2$$

Eq.(1.2)

where $\sigma$ is the total effective conductivity, $E$ is the magnitude of the internal electric field, $\varepsilon_0$ is the permittivity of free space, $\varepsilon''$ is the loss factor of the material and $f$ is the microwave frequency.\textsuperscript{7} $P$ can estimate the ability of absorbing microwave energy and transferring to heat energy of a material.
Another key aspect of microwave heating solid state material is the penetration depth, \( D_p \) which refers to the distance into the sample at which the electric field is attenuated to \( 1/e \) of the value on surface:

\[
D_p = \frac{\lambda_0 \sqrt{\varepsilon'}}{2n\varepsilon''}
\]

where \( \lambda_0 \) is the wavelength of the microwave radiation.\(^7\)

1.2.2 Properties of microwave heating

Based on the equations in the last section, some properties of microwave heating would be easy to explain. Selective heating, instantaneous heating, volumetric heating and direct heating can be described as the properties of microwave heating. Direct heating indicates the microwaves directly induces the molecular polarization which result in the temperature increasing. Volumetric heating refers to the uniformity of heating throughout the sample. Instantaneous heating refers to the rapid rise of temperature upon applying microwaves and that the heating instantaneously stops when microwave is no longer applied to the sample. Selective heating can be achieved owing to the susceptibility difference between different materials.

Another unique features of microwave heating is the inverted temperature profile. In contrast to conventional heating, microwave-heated materials usually shows higher temperatures in their interior than on the surface. This can be explained by the surface emissivity. As many materials have sufficient values of \( \varepsilon'' \) to allow the microwave have a deep penetration in that material, the microwave energy can be absorbed on the surface as well as in the interior by the material. However, the microwave energy can escape from the surface. Surface radiation occurs more rapidly (especially at high temperatures) than
thermal conduction can deliver heat from the interior and, consequently, the surface remains cooler.

1.3 Polymer diffusion

1.3.1 Theory- Rouse model and Reptation model

The simplest picture of the dynamics of a random coil chain is given by the Rouse model. In this model, the polymer chains are seen as a linear series of beads connected by springs. The diffusion coefficient calculated from Rouse model is:

\[ D_{\text{Rouse}} = \frac{kT}{N\zeta} \approx M^{-1} \]  

where \( k \) is the Boltzmann’s constant, \( T \) is the temperature, \( \zeta \) is the friction coefficient that can shows the degree that how beads interact frictionally with the surrounding medium, \( N \) is the numbers of beads in the chain, \( M \) is the molecular weight. The linear correlation of \( D_{\text{Rouse}} \) and \( M^{-1} \) shows that each bead in the chain faces to the same frictional environment. In this model, friction coefficient gives a reasonable description of polymer dynamics when the chains are not too long. This model is good for some diffusion which happen in a low molecular weight polymer media. However, Rouse model is confinement to the diffusion of the long polymer chains.

Reptation model is proposed by de Gennes which is used to describe the entanglement and additional dynamic interaction among the chains at high molecular weight. Those phenomena cannot be explained by the Rouse model. In the Reptation model, the polymer chain is seen as a tube. The diffusion coefficient for Reptation model can be expressed:

\[ D_{\text{reptation}} = \frac{kT N\zeta}{N^2} \approx M^{-2} \]  

Eq.(1.5)
where $N_e$ is the number of monomers in a molecular between entanglements\textsuperscript{11}.

1.3.2 Experiment method

S. J. Whitlow\textsuperscript{12} and Lin\textsuperscript{13} used the SIMS (secondary-ion mass spectroscopy) which is sensitive to both hydrogen and deuterium to investigate the diffusion of polymer. This feature makes it useful for tracer studies of polymer inter-diffusion. The primary advantages of SIMS are that it has excellent depth resolution and it is able to directly measure a concentration profile. Most SIMS applications used the static (low-energy primary beam) mode to characterize polymer surfaces by their mass spectra. This is to protect the polymer material to be burned by the incident beam.

Figure 1.5 Schematic of the sputtering process caused by an impinging primary ion. With the permission from Ref [12].

However, the main difficulty for measuring polymer material is that polymers are insulators and they charge when bombarded with ion. Therefore, when the secondary electrons lost during sputtering, a net positive charge is leaved in the sample. This influences the interaction between the incident beam and sample.\textsuperscript{12}

Neutron total reflection can also be utilized to study polymer diffusion.\textsuperscript{14, 15, 16} In neutron total reflection experiments, information is acquired about the neutron refractive index profile to the reflection surface. This refractive index depends on the neutron
scattering length density. Isotope can change the neutron scattering length. So if the molecular are marked by isotopes, it can be easily traced by neutron. The information provided by Neutron reflection is the concentration profile perpendicular to the reflecting surface. If the contrast between layers are big enough and the design of the sample are reasonable, the accuracy would increase to sub-nanometer.

1.3.3 Ellipsometric measurement in polymer diffusion

Ellipsometers also can measure the diffusion between polymers. In the research work of Leonld K. Fillppov\textsuperscript{17}, the ellipsometer are used to study the small molecular diffuse in the polymer film. The reason why ellipsometer can measure the diffusion is ellipsometer can use the difference of refractive index between the small molecular and the polymer as contrast to distinguish the small molecular and the polymer. In this research, the small molecular is chloroform and the polymer is poly(methyl methacrylate). The refractive index of poly(methyl methacrylate) is greater than that of chloroform. This allow the ellipsometer to investigate the process of chloroform diffusing into poly(methyl methacrylate). the change and evolution of the solvent concentration in the polymer and the change of thickness of solvent/polymer interface during the diffusion process can be obtained by analyzing the ellipsometric data. (The procedure of analyzing the ellipsometric data are described in Chapter 3.) By analyzing relation between interface thickness and diffusion time, the diffusion coefficient and the activation energy of diffusion can be obtained. Those value can be used to estimate extent of the interaction between polymer and small molecular.

The diffusion process between miscible polymer bends is also studied by the ellipsometers. In the work of Yukioka\textsuperscript{18}, the system of a poly (methyl methacrylate )/poly
(styrene-co-acrylonitrile) (PMMA/SAN) are used in this research work. By choosing a suitable content (9.5 ~ 33 wt%)\textsuperscript{18} of the acrylonitrile (AN) in SAN, PMMA and SAN are miscible. Also, a four-layer model\textsuperscript{18} was used in this work, which is used to describe the increase of the interface thickness. The refractive index of the PMMA/SAN interface is assumed to be equal to the half of the sum of the refractive index of that two polymers. Thus, by using the Drude equation\textsuperscript{19}, the relation between interface thickness and diffusion time can be obtained. This method can also be used to study the diffusion between immiscible polymers. In another work of Yukioka\textsuperscript{20}, the system of amorphous nylon (polyamide)/ poly(styrene-co-maleic anhydride) was used to study the diffusion process. The same ellipsometric analysis model was used to calculate the growth of the interface. As the change of the refractive index shown in the Uv–NIR range, reliable measurements can be obtained by using Uv-Vis-NIR ellipsometer.

However, more information such as what chemical component exist in materials can be obtained from the IR ellipsometer sine the vibration of chemical can absorb IR light. P. Duckworth\textsuperscript{21} used IR ellipsometer to observe the diffusion between miscible polymers. The system used in this work was poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF). As the refractive index of those two types of polymer are similar in the visible range, which means the contrast between the two polymer is relatively small, the Uv-Vis-NIR ellipsometer cannot be used to observe the diffusion process take place in that system. However, in the infrared region, the difference of the refractive index between the different is large, which can generate big contrast. That contrast can be used for ellipsometry analysis.
CHAPTER II
RAPID CROSSLINK OF POLYELECTROLYTE MULTILAYERS THIN FILMS BY MICROWAVE HEATING AND THE COMPARISON BETWEEN CONVENTIONAL HEATING AND MICROWAVE HEATING.

2.1 Introduction

Polyelectrolyte multilayers (PEMs) are thin films or coatings created by the directed complexation of oppositely charged polyelectrolytes, often assembled by sequential deposition steps in a process known as layer-by-layer (LbL).22, 23 These materials have been proposed for potential applications as barrier materials,24 water purification materials,25, 26 anti-reflection coatings,27 coatings to modulate surface wettability,28 and in a range of biomedical devices29 such as patches for drug delivery30 or coatings for stents or microneedles31 for ultrasonic drug delivery. However, in some of the aforementioned applications, the reversible nature of the ionic crosslinks that comprise these films may not be suitable. For example, polyelectrolyte multilayers are commonly swollen significantly in water or even dissolved in salt solutions due to effective charge screening.32, 33 This reversibility of the crosslinks may be particularly relevant in biomedical applications30 or salt water treatment,34 for which PEMs are often proposed. For environments like these, some degree of covalent crosslinking may be desirable in order to provide sufficient mechanical stability and robustness.35
PEMs containing amine and carboxylic acid groups can be crosslinked through amidization, by methods such as heating\textsuperscript{36, 37, 38, 39} the multilayers, which has limited efficiency in the solid state, or EDC coupling,\textsuperscript{36} which also has limited efficiency because it is a heterogeneous reaction. As a result, crosslinking even small, thin films can take over ten hours.

While lengthy crosslinking times may be acceptable for fundamental research, any commercial application would require significant reductions in the reaction time. One example of polymer technology that has been commercially enabled by reductions in reaction time is patterning of photoresists used in the microelectronics industry.\textsuperscript{40} Initial photoresist platforms were based on the direct chemical conversion of light to induce differential solubility for patterning,\textsuperscript{41} but catalyst driven chemical amplification\textsuperscript{42} has allowed for further miniaturization of this technology due to significant improvements in the photon efficiency and throughput.\textsuperscript{43} Similarly, the need for fast directed self-assembly of nanostructures\textsuperscript{44} has led to the development of a wide variety of rapid annealing technologies, including rapid thermal processing,\textsuperscript{45} photothermal treatment,\textsuperscript{46} laser spike annealing,\textsuperscript{47} and microwave\textsuperscript{48} annealing. These rapid processing techniques enable processing at temperatures above the degradation temperature of the polymer if the duration is sufficiently short.\textsuperscript{49} Moreover, microwaves treatment have been shown to effectively enhance the reaction kinetics to generate metal oxides in inorganic-organic hybrid films.\textsuperscript{50}

In this work, we report on the efficacy of microwaves in accelerating the amidization of PEM films made from branched poly(ethylene imine) and poly(acrylic acid) (BPEI/PAA) on ITO substrates. The ITO substrates efficiently absorb the microwave
energy to rapidly heat (<5 s) to the temperatures of interest (≤ 200 °C) for the crosslinking. In comparison to conventional heating, the conversion to the amide is effectively accelerated using microwaves at the same processing temperature, which decreases the required reaction time by more than an order of magnitude. The conversion of the reactant (–NH3+) to amide is kinetically limited to approximately 85%, irrespective of the heating procedure. The localized heating at the ITO substrate from the microwaves leads to gradients in the crosslink density through the film thickness that can be resolved by IR spectroscopic ellipsometry. This gradient is almost negligible for thin PEM films (ca. 500 nm), but for thick films (ca. 1.5 μm) the conversion at the surface can be less than half of that near the substrate. These gradients do not occur under conventional heating and may offer potential to engineer the properties of PEMs through modulation in the local crosslink density. Moreover, the ability to dramatically accelerate reactions in polymeric films using microwave technique may open new routes for the fabrication of high performance coatings and thin films.

2.2 Experimental

2.2.1 Materials

The materials used in this work is branched polyethylenimine (BPEI, Mw = 25 000 g mol⁻¹), ethanol (ACS reagent, 99.5%), sodium hydroxide (ACS reagent, ≥97%) and hydrochloric acid (ACS reagent, 37%), which were purchased from Sigma-Aldrich. Also, poly(acrylic acid) (PAA, Mw = 50 000 g mol⁻¹; 25 wt% aqueous solution) was obtained from Polysciences. All chemicals were used as received without further purification. All water used was purified with a MilliQ DQ-3 system (Millipore, Bedford, MA) to produce water with a resistivity of 18.2 MΩ. Indium tin oxide (ITO) on glass (CG-51IN-S115)
substrates were purchased from Delta Technologies and were cleaned initially using an ultrasonic cleaner (B25000-DTH, VWR) for 10 min in ethanol and then water. The cleaned ITO was dried with N2 jet. Directly prior to use, the ITO substrates were subjected to a plasma cleaning (PDC-32G, Harris Plasma) in air at for 5 min.

2.2.2 Sample preparation

For the fabrication of the PEMs, stock aqueous polyelectrolyte solutions with controlled pH were made. The BPEI solution was prepared at 80 mM with respect to the amine group of BPEI in DI water with the pH adjusted to 9.5 by 0.1 M HCl. The PAA solution was prepared at 60 mM with respect to the carboxyl group of PAA in DI water with the pH adjusted to 4.5 by 0.1 M NaOH. All PE solutions were stirred overnight prior to pH adjustment and filtered (Corning® 250mL Vacuum Filter/Storage Bottle System, 0.45μm Pore 19.6cm² Cellulose acetate Membrane) prior to their deposition.

The assembly of PEMs proceeded sequentially at room temperature using a StratoSequence VI dipper (NanoStrata Inc.). Briefly, the clean ITO substrates were first exposed to the BPEI solution for 10 min and then washed by three separate DI water rinse baths of 1 min each. Subsequently, these substrates were exposed to the PAA solution for 10 min and washed with DI water in an identical manner. By repeating this BPEI/PAA deposition cycle n times, the desired number of BPEI/PAA bilayers, denoted as (BPEI/PAA)_n hereafter, were deposited on the ITO glass. These PEM films were dried at room temperature (≈ 23 °C) for 24h.

Two distinct thermal treatments, conventional and microwave, were used to crosslink the PEM films through amidization at 180°C and 200°C. For the microwave heating (Discover SP-D, CEM) of the PEM films, the films were cut to the desired size (1
cm × 1.25 cm) and placed in a borosilicate tube. The power, set temperature, and time of exposure were controlled during the microwave heating. The temperature of the substrate was confirmed independently using a thermal camera (Testo 875-1, Testo). The conventional heating process was performed using a preheated muffle furnace (Ney Vulcan 3-130) as a control for comparison. For the conventional heating, the sample was heated by the furnace for a given duration (total heating times of 30, 90, 150, 210, 270, 330, 390, 540, 660, 780 min at 180°C and 40, 70, 90, 150, 210, 270, 330, 510, 630, 750 min at 200°C). When the films were removed from the furnace, the samples were quickly placed onto an aluminum block at room temperature to quench the reaction. For the microwave heating, the sample was heated by microwave for a given duration (total heating times of 1, 2, 5, 9, 15, 23.5 min at 180 °C and 1.5, 3, 6, 12, 20 min at 200 °C). When the films were removed from the microwave, the samples were quenched in the same manner as conventional heated samples, although the temperature decrease is generally quite rapid on cessation of microwave energy.51

2.3 Characterization

The thickness of the (BPEI/PAA)ₙ films was determined using a UV–visible–NIR ellipsometer (VASE, M-2000, J. A. Woollam Co.) using 240-1700 nm light. Incidence angles of 65°, 70° and 75° were used in this measurement. For fitting of these ellipsometric data, a Cauchy layer was used for the optical properties of the BPEI/PAA film to determine the film thickness as the film is transparent at the UV-Vis-NIR range.52

An IR ellipsometer (Mark II, J. A. Woollam Co.) was used to determine the film thickness and optical constants over the wavelength range from 1.7-30 μm. The IR-ellipsometry measurements were performed ex-situ as the crosslinking rate is negligible at
ambient temperature. The samples were measured by the IR-ellipsometer prior to heating to obtain the initial state of the films. The IR spectra of the PEMs was obtained with a spectral resolution of 2 cm\(^{-1}\) at an incident angle of 75° and were fit using WVASE software (J.A. Woollam Co.). The optical constants were modeled using Gaussian oscillators to describe the IR absorption by the molecular vibrations of the PEM films. These oscillators can be directly associated with the chemistry of the film. For the amidization reaction, oscillators \((r\text{-reactant})\) at 1500 cm\(^{-1}\) and 1560 cm\(^{-1}\), corresponding to \(-\text{NH}_3^+\) and \(-\text{COO}^-\) respectively, provide direct evidence for the reaction. As the film densifies during the crosslinking reaction, the oscillator at 1400 cm\(^{-1}\) associated with the \(-\text{CH}_2\) group is used to normalize the area changes of the other oscillators as this group does not participate in the crosslinking reaction. Additionally, there are three distinct oscillators associated with the formation of the Amide I bond in the crosslinking product at 1620.7, 1637.7, and 1668.6 cm\(^{-1}\). These three oscillators are associated with the different chemical environment around the Amide I bond. To determine the crosslinking conversion, the sum of the area of these three amide I oscillators \((p\text{-product})\) normalized by the \(-\text{CH}_2\) peak area \((i\text{-invariant})\) provides a simple expression for the conversion as:

\[
conversion(t) = \frac{P_t - P_0}{P_{\text{finite}}}, \quad \text{Eq.}(2.1)
\]

where the \(t\) subscript refers to the area of the oscillator at time \(t\), \(0\) subscript infers the initial area for the oscillator, and \(P_{\text{finite}}\) is the expected normalized area if the reaction goes to completion (100% conversion). As the crosslinking is kinetically limited, \(P_{\text{finite}}\) was estimated based on the consumption of the \(-\text{NH}_3^+\) denoted as the peak area of oscillator \(r\):
where the final subscript refers to the peak areas at the longest time examined for the reaction.

Electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation (CHI660D, CH Instruments) with a conventional three-electrode setup. The working electrode was the (BEPI/PAA)\textsubscript{6} on ITO, while a platinum wire was used as the counter electrode. An Ag/AgCl (3M KCl) reference electrode was used for all measurement. A mixture of 1M KCl and 1mM K\textsubscript{3}[Fe(CN)\textsubscript{6}] was used as electrolyte. The EIS was performed over the frequency range of 0.01-10\textsuperscript{5} Hz with the amplitude of the applied sine wave potential as 0.416 V.

2.4 Result and discussion

Figure 2.2 illustrates the change in the ellipsometric angle, ψ, upon crosslinking of a (BPEI/PAA)\textsubscript{6} film. Even in the UV-Vis-NIR range (Figure 2.2A), there are clear changes in the ellipsometric angle after only 15 min of exposure to microwave radiation to heat the film to 180 °C. The dashed line illustrates the excellent fit of the data to a simple optical model (Cauchy) for the (BPEI/PAA)\textsubscript{6} films; the difference between initial film and crosslinked film is primarily the thickness reduction from 571.27 nm to 459.02 nm, as there is only a minor increase in the refractive index from 1.552 to 1.589 at 633 nm which is shown in Figure 2.1.
The chemical change on crosslinking does not generate absorption in the UV-Vis-NIR, so the Cauchy model still sufficiently describes the optical properties of the (BPEI/PAA)₆ film. This limits the ability of this ellipsometer to assess the crosslinking reaction. Conversely even qualitatively, there is a significantly greater change in the IR range on crosslinking of the film after the same microwave exposure (Figure 2.2B). In this case, the optical properties of the film include oscillators associated with the vibrations of chemical bonds in the (BPEI/PAA)₆ film. In order to fit the ellipsometric data in Figure 2.2B, a significant change in the oscillators is necessary (Figure 2.4); these changes are consistent with prior FTIR studies of the crosslinking of (BPEI/PAA)₆ films. With ellipsometry, the absorbance in the film is determined recursively and the consistency with prior studies validates this approach to quantify crosslinking.
Figure 2.2 Change in the ellipsometric angle $\psi$ for (BPEI/PAA)$_6$ films from microwave crosslinking (180 °C, 15 min) in the (A) UV-Vis-NIR and (B) IR spectra. The best fit of these data are shown by the dashed lines with a Cauchy model sufficient to describe the (BPEI/PAA)$_6$ film in the UV-Vis-NIR, while an oscillator model that includes the absorption from bending and stretching vibration is required in the IR.

Figure 2.3 illustrates the extinction coefficient, $k$, of these (BPEI/PAA)$_6$ films obtained from the fit of the ellipsometric data (Figure 2.2). The extinction coefficient is the sum of nine oscillators from these fits as shown by the dashed lines. These oscillators can be directly attributed to the bonding in the film including the asymmetric (1398.7 cm$^{-1}$) and symmetric (1552.3 cm$^{-1}$) stretching vibrations of –COO$^-$, the asymmetric deformation vibration of –CH$_2$- in PAA (1449.9 cm$^{-1}$) and BPEI (1477.0 cm$^{-1}$), symmetrical deformation vibration of –NH$_3^+$ (1495.9 cm$^{-1}$), the stretching vibration of –COOH (1707.0 cm$^{-1}$) and bending vibration of –NH at 1632 cm$^{-1}$. As shown in Figure 2.3A, the initial (BPEI/PAA)$_6$ film lacks the oscillator at 1668.5 cm$^{-1}$ which is associated with the formation of amide I bond. However, there small oscillators at 1617.5 cm$^{-1}$ and 1637.3 cm$^{-1}$ that are also associated with the amide I bond. These features are common in the IR spectra of BPEI/PAA multilayer films.
Figure 2.3 The extinction coefficient for the (BPEI/PAA)$_6$ in the IR region determined from fit of the data in Figure 1B both (A) before and (B) after crosslinking. The dashed lines are the individual oscillators included in the model. The band that indicates the carboxylic group (~1560 cm$^{-1}$) decreases, while the amide I band (~1600 cm$^{-1}$-1700 cm$^{-1}$) increases.

After microwave heating for 15 min (Figure 2.3B), the oscillators associated with the –NH$_3^+$ and –COO$^-$ groups decrease in intensity, while an oscillator emerges at ~1670 cm$^{-1}$ and the other two oscillators associated with the amide bonds increase in intensity. These changes provide direct evidence for the amidization and crosslinking of the (BPEI/PAA)$_6$ film in the microwave. The relative decay in the area of the oscillators associated with the –NH$_3^+$ group and the –COO$^-$ group can be used to provide insight into which component is the limiting reactant for the amidization. Qualitatively, the strength of the –COO$^-$ oscillator remains quite large after the microwave heating, while the oscillator associated with the –NH$_3^+$ group is almost eliminated. As the film densifies on crosslinking, comparison of the oscillator areas involves normalized by an invariant, in this case the area of the oscillator associated with the –CH$_2$- groups that do not participate in the reaction. The fractional consumption of the –COO$^-$ and –NH$_3^+$ are determined by the ratio of the normalized oscillator area after microwave heating to the initial film to be 43.2% and 89.2%, respectively. This indicates that the –NH$_3^+$ is indeed the limiting reactant and this should be used to calculate the conversion of the amidization. Using the area of
the green shaded oscillator $r$ in Figure 2A associated with the $–\text{NH}_3^+$, the conversion can be calculated as:

$$\text{conversion}(t) = 1 - \frac{r_t}{r_0},$$

**Eq.(2.3)**

where the $t$ subscript refers to the area of the oscillator at time $t$, $0$ subscript infers the initial area for the oscillator. The conversion can be obtained from both disappearance of reactant by using equation (2.3) and appearance of the amide I bond by using equation (2.1) and (2.2). The comparison between the conversions obtained from those two ways mentioned above is shown in Figure 2.4. A good agreement of the result obtained from different ways can be observed. However, the limited intensity of this oscillator leads to some uncertainty about the conversion. The absorption associated with the amidization products are more prominent (oscillators shaded blue in Figure 2.3B) and thus provide a more accurate pathway to calculating conversion using equations (1) and (2).

![Figure 2.4](image)  
Figure 2.4 Comparison of conversion obtained from disappearance of reactant (black symbols) and appearance of the amide I bond (color symbols) at (A) 180°C and (B) 200°C.
Figure 2.5 Impact of heating method on conversion using (A) conventional heating and (B) microwave heating at (□, ■) 180°C and (○, ●) 200°C for 450 nm thick film of (BPEI/PAA)₆.

Figure 2.5 illustrates the temporal evolution of the conversion based on the appearance of the amide I bond from the IR ellipsometry data, which is consistent with the conversion determined by the consumption of the limiting reactants (Figure S3). For conventional heating in a furnace at 200 °C, the conversion increases rapidly to 30.6% in the first 30 min, but then slowly increases over the next 420 min to a plateau conversion of 84.7% (Figure 3A). This behavior is in contrast to the very rapid crosslinking in the microwave when heating nominally to the same temperature as shown in Figure 3B. At the same temperature (200 °C) greater than 77.5% conversion is obtained in 1.5 min. With the microwave heating, the plateau conversion (84.2%) is similar to that for conventional heating, but within only 5 min of heating. This represents more than an order of magnitude increase in the amidization kinetics with the microwave heating. Even when decreasing the crosslinking temperature to 180 °C, the same plateau conversion is obtained within 10 min. This significant difference in the crosslinking kinetics suggests that microwave heating of the ITO substrate only partially describes the microwave interactions that promote crosslinking. Microwave processing of polymer films tends to rely solely on substrate heating, but here the order of magnetic difference in kinetics is more consistent with prior
arguments associated with the ‘microwave effect’. Water, which is a reaction by-product, is known to have a large microwave cross-section. Additionally, the components of this PEM system are hydrophilic and in these films water is known to be present in as high a quantity as 10 wt% after fabrication, even after vacuum drying. Thus, the enhancement in kinetics could be explained by the localized heating of water to dehydrate the film to drive the crosslinking reaction (Le Châtelier's principle).

![Figure 2.6 Nyquist plots](image)

Figure 2.6 Nyquist plots of the impedance associated with (BPEI/PAA)₆ crosslinked to different extents by conventional (+) and microwave heating (○). Nominal conversions of 30%, 65% and 80% are examined to compare conventional and microwave heating.

Defects in chemical crosslinked hydrogel networks, which can be tuned through kinetically controlling the crosslinking reaction, can impact mechanical properties. Similarly, the significant increase in the crosslinking rate of (BPEI/PAA)₆ film may be expected to impact the topology of the network that forms. In order to assess whether there are any differences in the structure imposed by the two different heating mechanisms, the permeability of ions through the crosslinked (BPEI/PAA)₆ film was examined by electrochemical impedance spectroscopy (EIS). EIS enables dynamics of electrochemical processes to be elucidated through the application of a small amplitude oscillatory potential
to the system at equilibrium. Orders of magnitudes in times scales are probed with EIS through changing the AC frequency of the perturbation. The impedance provides a measure of the resistances in the system. The Nyquist plot in Figure 2.6 shows how the impedance of (BPEI/PAA)$_6$ coated electrodes is impacted by crosslinking using either microwave or conventional heating. The effective resistivity (impedance) of (BPEI/PAA)$_6$ increases as the conversion (associated with the reaction to amide) increases for both heating methods, which is consistent with decreased ion mobility through the crosslinked film.$^{59}$ Similar EIS measurements on non-colvalently crosslinked PEMs show significantly lower impedance (nearly 2 orders of magnitude) and semi-infinite diffusion of ions through the membrane to enable determination of the ion diffusion coefficients. For all the (BPEI/PAA)$_6$ examined, semi-infinite diffusion of ions is not observed (lack of a sloped straight line at low frequency) even with the measurements extended down to 0.01 Hz. The high impedance and only semicircular features in the Nyquist plot are indicative of the low ion mobility within the crosslinked (BPEI/PAA)$_6$ films. Therefore in this case, EIS is only used to elucidate information about the charge transfer resistance associated ion diffusion through the PEM films.

Examining films with similar conversion, the high frequency behavior is not impacted by the selection of methodology for crosslinking with the high frequency intercept associated with the ohmic resistance invariant across all samples ($Z' \sim 1-3$ $\Omega$). This behavior is due to the similarity in the resistance of the electrolyte. The high frequency slope in the Nyquist plot increases as the conversion increases, which is indicative of increasing resistance of ion transport in the PEM. At intermediate and low
frequency, there is a marked shift in the shape of the spectra depending on the heating method used with a smoother, more rounded curve observed for the films crosslinked using the microwave heating. These smooth curves in Nyquist plots have been associated with the homogeneity of coatings,\textsuperscript{60} which suggests that the crosslinked network that forms from microwave heating is more homogeneous than that obtained from conventional heating. At high conversion (> 75\%), the impedance spectra are both almost semi-circular associated with resistive behavior, which implies limited ion mobility in the film over the time scales of the measurement (slower than 0.1 Hz).\textsuperscript{38} As the conversion decreases, the differences between conventional and microwave heating becomes more obvious, especially in the low frequency region. At 30\% conversion, impedance for the film crosslinked with microwaves exhibits pseudo-inductive behavior.\textsuperscript{61} Using conventional heating to 32\% conversion, the impedance spectra is more complex with an inflection at intermediate frequency; this inflection is consistent with two distinct resistances in the film and has been observed previously in failed corrosion resistant organic coatings.\textsuperscript{62, 63, 64} The crosslink network formed by conventional heating appears to become more homogeneous as the conversion increases. As the number of the potential and actual crosslinking sites can be assumed to be fixed, the distribution of the segment lengths between crosslinks should become narrower at high crosslink density, which is consistent with the EIS data. The microwave heating seems to lead to a much more homogeneous network, which we attribute to the localized heating of the hydroxyls by the microwaves that could provide a similar energy landscape for the reaction across all potential crosslinking sites.
Figure 2.7 Comparison of the ellipsometric angle, $\Psi$, of thicker (BPEI/PAA)17 after crosslinking using (A) conventional heating at 180 °C for 510 min and (B) microwave heating at 180°C for 5 min. These conditions should yield similar conversion based on (BPEI/PAA)6 data in Figure 3. The black dashed line is the best fit of the data using the same model as for the (BPEI/PAA)6 film with significant error (as evidenced by the residual greater than 1) in the fit for the microwave heating sample. For these samples, a graded model improves the fit (blue dashed line) with the residual shown by the blue line. (C) The conversion profile from the best fits for both (open symbols) conventional heating and (closed symbols) microwave heating through the thickness of the film.

Considering the heating during microwave processing is commonly localized at the inorganic substrates rather than within the polymer film,$^{50, 53}$ the heat transfer through the BPEI/PAA PEM could lead to a temperature gradient in a sufficiently thick film that may impact the crosslinking reaction at different depths into the film. Figure 2.7 illustrates
the ellipsometric angle, $\Psi$, of a (BPEI/PAA)$_{17}$ film after crosslinking to approximately 60% conversion with both conventional and microwave heating (based on conditions for the (BPEI/PAA)$_6$ film). The (BPEI/PAA)$_{17}$ film is approximately 1800 nm thick prior to crosslinking. The same oscillator model as used previously for the thinner PEM can adequately fit the IR ellipsometric data for conventional heating (Figure 2.7A). The residual has an absolute value less than one for all wavelengths and spikes in the residual correspond to large changes in $\Psi$ in a short wavelength range for the ellipsometric data (Figure 2.7A). However, for the (BPEI/PAA)$_{17}$ film crosslinked by microwave, this oscillator model (black dashed line) leads to a substantial residual between 1600 and 1680 cm$^{-1}$ (Figure 2.7B, shown by the blue shaded region). The residual reaches a maximum offset of $\sim$1.9° at $\sim$1640 cm$^{-1}$, which is similar to the peak position for an oscillator associated with the amide product. Moreover, the large residual occurs in a region where the ellipsometric angle, $\Psi$, does not vary sharply with wavelength. The residual in this wavelength range can almost be eliminated by inclusion of a linear gradient in the optical properties of the PEM (blue line in Figure 2.7B). This gradient can be converted directly to the local conversion in the film using equations 1 and 2. Figure 2.7C illustrates the spatial dependencies in the conversion from the best fits of the ellipsometric angles in Figure 2.7A and 2.7B. The conventional heating does not lead to a gradient in the crosslink density and the conversion is approximately 60% through the full film thickness. This is consistent with the expected conversion from the thin film (Figure 2.5). Conversely, there is a large
gradient in the conversion across the film when microwave heating is employed. The conversion near the substrate is approximately 60%, but the conversion drops to nearly 30% at the free surface of the (BPEI/PAA)17 film for the microwave heating. This large gradient in the crosslink density can be rationalized by the localized heating of the ITO by the microwave, which provides a majority of the heat load to the sample. The low thermal conductivity of polymers limits the heat transfer from the surface of the ITO through the film thickness, which results in the gradient in the crosslinking density. It should be noted that the improvement in the fit of the ellipsometric data for the thin films ((BPEI/PAA)6) with inclusion of a gradient is negligible, so the gradients in the crosslink density can only be resolved in thicker films.

![Figure 2.8](image)

Figure 2.8 Impact of PEM thickness on the average conversion at 180 °C using (□) (BPEI/PAA)6 and (Δ) (BPEI/PAA)17 using (A) conventional and (B) microwave heating. The extent of the gradient in the (BPEI/PAA)17 films with microwave heating are illustrated for the (+) top and (-) bottom of the (BPEI/PAA)17 film.

The difference between the conventional and microwave heating is distinguished when examining the influence of film thickness on the conversion. Figure 6 illustrates the temporal evolution of the conversion based on the appearance of the amide I bond for both (BPEI/PAA)6 and (BPEI/PAA)17. The conversion is independent of film thickness using
conventional heating (Figure 6A), as is expected for an isothermal, non-interfacial reaction. This independence in the conversion shows that the intermixing of the layers in this exponentially growing system does not impact the reaction kinetics significantly. For microwave heating, the difference in conversion can be significant. For the thin film, the conversion reaches a plateau of 85.3% in 9 min, but the average conversion for the thick film is only 59.9% after the same microwave heating. The average conversion is based on the integration of the conversion profile (see Figure 5C as an example) normalized by the film thickness. The extremes of the crosslinking provide insight into the nature of the crosslinking as well as the microwave gradient. Near the substrate, the conversion is similar to that obtained for the thin films. The conversion near the surface of the (BPEI/PAA)17 films plateaus at approximately 44%. This suggests that the conversion in the films is equilibrium limited as the gradient is maintained, but the conversion does not increase. This behavior is counter to the expectation for kinetically limited conversion whereby the interconnectivity of the PEM after sufficient crosslinking prohibits additional amidization kinetically due to the local connectivity and mobility of the reactive species. Nonetheless, the microwave heating leads to well-defined gradients in the crosslink density if the PEM film is sufficiently thick to inhibit heat transport.

2.5 Conclusion

The amidization of BPEI/PAA films supported on ITO/glass substrates can be accelerated by using microwaves which locally heat the ITO substrates. This process is shown to enhance the reaction kinetics for the conversion to the amide by more than an order of magnitude over conventional heating at the same temperature, perhaps in part due to the large amount of water present in these films and the efficiency of microwaves for
heating water. To the best of our knowledge, this represents the first report for accelerating the processing of PEMs with microwaves. Impedance (EIS) measurements of thin (BPEI/PAA)6 films indicate that the morphology of the network at similar crosslink density is substantially different between microwave and conventional heating. Using microwaves appears to generate a more homogeneous network based on the diffusion of the ionic probe used for the EIS measurement. Moreover, the localized heating from the substrate when using microwaves can be exploited to generate gradients in the crosslink density when using thicker (BPEI/PAA)17 films. The covalent crosslink density (as defined by the conversion to the amide) can vary by nearly a factor of two between the top and bottom of the (BPEI/PAA)17 film. These gradients do not occur under conventional heating. The dramatic acceleration in the amidization kinetics, change in the diffusional behavior through the films, and the ability to generate gradients makes microwave processing a promising alternative for the manipulation of PEMs.
CHAPTER III

OBSERVATION OF INTER-DIFFUSION IN MISCIBLE POLYCARBONATE COPOLYMERS BILAYERS

3.1 Introduction

3.1.1 Motivation

Studying the mechanism of diffusion between APEC and Makrolon (will introduce in the following section) can help to determine the condition of industrial processing such temperature, processing time and the route of processing. Suitable processing condition can be determined relatively easily by knowing the properties of polymer diffusion. Appropriate processing condition is important for manufacturer because processing condition influence the polymer properties a lot.

Several technics have been used to investigate the diffusion process of polymers. S. J. Whitlow\textsuperscript{12} and Lin\textsuperscript{13} used the SIMS (secondary-ion mass spectroscopy) which is sensitive to both hydrogen and deuterium to measure the diffusion of polymers. However, SIMS would make some damage on the surface of the sample. Neutron total reflection can also be utilized to study polymer diffusion.\textsuperscript{14, 15, 16} However, to generate the contrast between two kinds of polymer to distinguish two different polymers, one of the polymer need to be deuterium-marked which indicates the complexity of this measurement.

Ellipsometry is an excellent way to observe the diffusion as the ellipsometer is non-contact and non-damage measurement. Moreover, ellipsometer can distinguish different
polymer by its own optical properties (refractive index and extinction coefficient). However, the model for fitting is not perfect for diffusion. In this study, a new model will be built up. This is important because new model can give other people a guiding direction for using ellipsometry to study other material diffusion. This study can also extent the application of ellipsometry.

3.1.2 Polycarbonate

There are two types of polycarbonate are used in this research work. One of them is Makrolon which is a Bisphenol-A polycarbonate (structure shows in Figure 3.1).

![Bisphenol-A polycarbonate chemical structure.](image)

Bisphenol-A polycarbonate has been commercially available since the 1960s. It possesses a broad range of physical properties that enable it to replace glass or metal in many products. Polycarbonate offers a combination of moisture absorption capability, good heat resistance, rigidity, impact strength, and toughness that helps prevent potentially life-threatening material failures. In addition, it provides good visual clarity. As a result of such properties polycarbonate is used in load bearing applications, armored vehicles, rail cars and architectural applications. The $T_g$ of this polycarbonate is 150°C. Although the impact strength is high enough for commercial applications, much work have be done to increase the $T_g$ to improver heat resistant properties.

Another one is Bisphenol-TMC polycarbonate (structure shows in Figure 3.1, space-filling model shown in the left). Bisphenol-TMC polycarbonate have improved properties that mentioned above with a higher $T_g$ (239°C). The main advantage of this
polycarbonate is the combination of high Tg, and good impact strength with good melt flow\textsuperscript{69}, which make this material have a large demand to the commercial marketing.

![Bisphenol-TMC polycarbonate chemical structure]

3.2 Experiment section

3.2.1 Materials: Makrolon and APEC

Makrolon is Bisphenol A polycarbonate, a homopolymer also made by Covestro. The specific type in this study was Makrolon 2205. APEC is a copolymer that us manufactured by Covestro. The specific type used in this study was APEC 1797 which is colored green by a small molecular dye that is blended in the copolymer. Both polymers are commercially available.

3.2.2 Film fabrication

Both APEC and Makrolon films were spin-coated on polished silicon wafers (University Wafer). The thickness of the silicon wafer used for both polymer is 1mm. The wafers size used for APEC was 1.5cm×1.5cm. The wafer size used for Makrolon was 3cm×3cm. The silicon wafer was first cleaned with deionized water to remove dust. All water used was purified with a MilliQ DQ-3 system (Millipore, Bedford, MA) to produce water with a resistivity of 18.2 MΩ. Then the wafer was cleaned with a UV-ozone cleaner (Jelight Co. Inc., model no. 42) for 2 hours. This cleaning step is used to modify the surface properties from hydrophobic to a hydrophilic surface.
For the spin-coating solutions, Makrolon2205 was dissolved in 1,4-dioxane (anhydrous, 99.8%) with a weight percent 4 wt% and APEC1797 was dissolved in 1,4-dioxane (anhydrous, 99.8%) with a weight percent 6.5 wt%. Thin films were spun-cast onto silicon wafers from Makrolon2205 and APEC1797 solution mentioned above at 4000 rpm for 1 min.

Figure 3.3 Schematic of spin coating

Then both films were then first characterized by the UV-Vis-NIR ellipsometer and IR ellipsometer to determine the film thickness and optical properties in different spectrum range (the characterization details is discussed in Section 3.3) with any further actions.

3.2.3 Floating for bilayer generation

In this bilayer system, the 1st layer on the silicon wafer is a Makrolon film and the 2nd layer is an APEC. A film floating technique in water was used to remove the APEC film and float itself onto the Makrolon film. The sides of the APEC coated wafer are scored with a razor blade. This allows the release of the APCE film onto the deionized water from the silicon wafer.
Then the Makrolon coated wafer was submersed and brought up under the floating APEC film to generate the bilayer system. (shown in FIG.3.4) The resulting bilayers were kept under vacuum at room temperature for 16 hours to remove excess water that may be trapped between the two layers during the floating process.

3.2.4 Diffusion control

The diffusion processing was performed using a preheated muffle furnace (Ney Vulcan 3-130). The sample was heated by the furnace for a given duration (total heating times of 1, 2, 4, 8, 16, 32, 64, 128, 256min at 225°C, 250°C, 275°C). The bilayer system was heating on a crucible in furnace. Both crucible and furnace were per-heated to the aimed temperature. As the $T_g$ of both polymers are much higher than the ambient temperature, the diffusion process is negligible at ambient temperature. The bilayer samples were remove from the furnace after the set time and rapidly quenched to room temperature by placing on a cool aluminum block. The bilayer film was then measured by both UV-visible-NIR and IR ellipsometer after each period of heating.
3.3 Characterization

The thickness of both APEC1797 and Makrolon2205 polycarbonate film was determined using UV-visible-NIR ellipsometer (VASE, M-2000, J. A. Woollam Co.) using 240nm-1700nm light. Incidence angle of 65°, 70° and 75° were used in this measurement. This ellipsometer was used to observe the dye diffusion in the bilayer system as the dye molecular can generate contrast of optical properties in the UV-visible-NIR range.

An IR ellipsometer (Mark II, J. A. Woollam Co.) was also used to determine the film thickness and optical constants over the wavelength range from 1.7μm -30μm. A spectral resolution of 2cm⁻¹ and an angel of 75° was used in the IR ellipsometry measurement. This ellipsometer was used to observe the polymer-polymer diffusion as the different chemical structural can generate contrast of the optical propertied in the IR range.

All the ellipsometric data were fit using WVASE software (J.A. Woollam Co.). For the UV-visible-NIR ellipsometric data analysis of single Makrolon and APEC film, a simple oscillator model was used to determine the film thickness and optical properties for both Makrolon and APEC as both films are polycarbonate that can block the UV light. Therefore, an oscillator around 260nm was used to describe the extinction coefficient for both film. However, due to the existence of dye in APEC, another oscillator at 254nm need to be added to modify the extinction coefficient for APEC. For the UV-visible-NIR ellipsometric data analysis of bilayer system, a simple graded model was used to describe the initial bilayer system and the change of the bilayer system during the diffusion. Due to the dye in APEC, the extinction coefficient of Makrolon and APEC are different, which can generate contrast at this range. Thereby, by using oscillator model, the extinction
coefficient of both APEC and Makrolon can be obtained. By using the graded model, the depth profile of extinction coefficient for the bilayer system can be obtained.

As the APEC1797 have a higher extinction coefficient at 254nm than Makrolon2205 due to the dye absorption, by following the Beer–Lambert law:

\[ k \propto C_{\text{dye}}. \quad \text{Eq. (3.1)} \]

Then, by using effective medium approximation theory, the volume fraction of dye can be calculated by the following equation:

\[ v_{\text{dye}} = \frac{k - k_{\text{Makrolon2205}}}{k_{\text{APEC1797}} - k_{\text{Makrolon2205}}}, \quad \text{Eq. (3.2)} \]

where \( k \) is the total extinction coefficient of the bilayer system at 254nm; \( k_{\text{Makrolon2205}} \) is the extinction coefficient of Makrolon 2205 at 254nm; \( k_{\text{APEC1797}} \) is the extinction coefficient of dye and APEC 1797 at 254nm.

For the IR ellipsometric data, the graded model was also used to describe the bilayer system and the change of the bilayer system during the diffusion. Before using the simple graded model to describe the bilayer, each APEC and Makrolon layer was fitted by a simple oscillator model using Gaussian oscillators. The main range focused on is 2900\,\text{cm}^{-1} - 3000\,\text{cm}^{-1}. This is because there are more \(-(\text{CH}_2)\)- and \(-\text{CH}_3\) group in APEC compare to the Makrolon. As the vibration of \(-(\text{CH}_2)\)- and \(-\text{CH}_3\) group generate more absorption in that range, more contrast can be obtained in that range. By using the simple oscillator model, the extinction coefficient for both Makrolon and APEC can be obtained. By using the graded model, the extinction coefficient for the bilayer system can be obtained. By knowing those value, the volume fraction of APEC can be obtained. For the accuracy, the
extinction coefficient at 2950 cm\(^{-1}\) was used in the following calculations. By following the Beer–Lambert law:

\[
  k_{ir} \propto C_{APEC}, \tag{3.3}
\]

The volume fraction was calculated by the following equation:

\[
  v_{APEC} = \frac{k_{ir} - k_{\text{Makrolon2205--ir}}}{k_{\text{APEC1797--ir}} - k_{\text{Makrolon2205--ir}}} \tag{3.4}
\]

where \(k_{ir}\) is the total extinction coefficient of the bilayer system at 2950 cm\(^{-1}\); the \(k_{\text{Makrolon2205--ir}}\) is the extinction coefficient of pure Makrolon2205 at 2950 cm\(^{-1}\); the \(k_{\text{APEC1797--ir}}\) is the extinction coefficient of pure APEC1797 at 2950 cm\(^{-1}\).

The following paragraph is to give a brief introduction of graded model mentioned above. The grading of the optical properties of a film along the direction of the film normal (from top to bottom through the film) is usually described by breaking the film up into many much thinner layers, each of which is itself uniform, but with the properties of each layer slightly different from the layers above and below.

Figure 3.5 Schematic of the change of bilayer during the diffusion. Before diffusion, the interfacial film was narrow and the thickness was small. So that interfacial film was seen as interface.
With the development of the diffusion, the interfacial layer would be a graded layer, which means the optical properties is variable along the direction of diffusion. When using the graded model, the thickness is a parameter that describe the total thickness of Makrolon film, interfacial film, and the APEC film. Because during the diffusion process, individual thickness of each film is variable. The strategy that see those thicknesses as a total thickness can reduce the number of parameters, which simplify the fitting procedure.

New parameters are need to be added to describe the position of Makrolon-interface boundary and the position of interface-APEC boundary. First, the bottom of Makrolon film is defined as the 0% positon. The top of APEC film is defined as the 100% position. Second, the new Parameter-Node-1 is defined as the positon of Makrolon-interface boundary, the new parameter-Node-2 is defined as the position of interface-APEC boundary. (see Figure 3.6)

Figure 3.6 Schematic of graded for bilayer system.
3.4 Result and discussion

3.4.1 IR ellipsometric result

Figure 3.7 The extinction coefficient (k) of APEC1797 (red) and Makrolon2205 (black) in IR range.

Comparing the extinction coefficients in Figure 3.7, we can see significant a difference between APEC and Makrolon in the range of 2860cm\(^{-1}\)~2960cm. The peak near 2967cm\(^{-1}\) is corresponding to the –CH\(_3\) in both APEC and Makrolon. This peak of both APEC1797 and Makrolon 2295 is basically the same, which indicates the concentration of the repeat unit of both polymer is basically the same. The biggest contrast is at 2950cm\(^{-1}\). The peak at 2950cm\(^{-1}\) is corresponding to one of –CH\(_3\) in APEC as the chemical environment around this –CH\(_3\) is different to the –CH\(_3\) that describe before. The big contrast in this contrast was used to study the diffusion.
As we can see from the Figure 3.8 above, at the position that 4000 Å away from the substrate, the volume fraction of APEC1797 decreased with the increasing heating time, which indicates the Makrolon2205 diffused into APEC1797 layer at 275°C. Meanwhile, at the position that 2500 Å away from the substrate, the volume fraction of APEC1797 increased with the increasing heating time, which indicates the APEC1797 diffused into Makrolon 2205 layer at 275°C. Moreover, the Makrolon2205 move all way through the APEC1797 layer while the APEC1797 only permeated about 900 Å into Makrolon2205. This is because the heating temperature is high than the T_g of both polymer which means both polymer are rubbery state. Both polymer have high mobility. However, Makrolon 2205 diffuse much faster than APEC 1797. This is because the T_g (239°C) of APEC1797 is much higher than the T_g (150°C) of Makrolon2205.
From the Figure 3.9 above, at 250°C, we can see Makrolon2205 diffuse into APEC1797 layer a lot but just a few APEC1797 diffuse into Makrolon 2205 layer. As the T_g(239°C) of APEC1797 is comparable to the diffusion process temperature, the polymer is more like glassy state. Therefore the APEC 1797 have a low mobility which means the movement of the polymer chain is restricted. This was also shown in Figure 3.9: After heating 128min, the Makrolon2205 permeated all way through the APEC1797 layer meanwhile the thickness that the APEC1797 permeated into Makrolon2205 is only around 300 Å. That resulted that only a few APEC diffuse into Makrolon layer. However, the T_g(150°C) of Makrolon 2205 is much lower than the diffusion process temperature, which means this polymer is rubbery state at that temperature. Therefore, the Makrolon 2205 have a high mobility which result in diffusing a lot into APEC layer.
From the Figure 3.10, at 225°C, only the Makrolon 2205 diffuse into APEC layer as the diffusion temperature was still much higher than the T_g of Makrolon. However, basically none of the APEC 1797 diffuse into the Makrolon. This is because the diffusion temperature is lower than the T_g of the APEC 1797, which indicates the polymer is glassy state. In this state, the polymer chain is frozen.

As the result shown in the Figure 3.11 above, with the increase of the diffusion temperature, the diffusion rate increase. At 275°C, the interface broadens fast in the first
8min and then the increase rate decrease. At 250°C, the interface first grown to a plateau. After 16min, the interface thickness increase again and then the increase date decrease.

Figure 3.12 Interface thickness vs time\(^{1/2}\) at 225°C, 250°C, 275°C.

In the Figure 3.12, tow stage of the diffusion process at each diffusion temperature can be distinguished. The final stage (small slope) of the diffusion process shown up after 8min at 275°C, 32min at 250°C and 64min at 225°C. The final stage can be seen that the diffusion process comes to the end. Therefore, the diffusion coefficient can be calculated before the final stage.

Figure 3.13 Interface thickness vs time\(^{1/2}\) at 225°C, 250°C, 275°C with linear fit.
The equation used for fitting is:

\[ \sigma(t) = k t^\frac{1}{2} + \sigma_0 \]  \hspace{1cm} \text{Eq. (3.5)}

Where \( \sigma \) is the interface thickness, \( k \) is the slope, \( t \) is the diffusion time and \( \sigma_0 \) is the initial thickness of the interface.

Then the diffusion coefficient can be calculated by the following equation\textsuperscript{72}:

\[ D = \frac{(\sigma(t)-\sigma_0)^2}{2t} \]  \hspace{1cm} \text{Eq. (3.6)}

From the fitting result in Figure,

\[ D_{275^\circ C} = 1.17 \times 10^{-14} m^2/min \]

\[ D_{250^\circ C} = 1.43 \times 10^{-15} m^2/min \]

\[ D_{225^\circ C} = 5.46 \times 10^{-16} m^2/min \]

The diffusion coefficient increase with the increase of the diffusion temperature.

3.4.2 UV-visible-NIR ellipsometric Result

![Graph showing extinction coefficient (k) of APEC1797 and Makrolon2205](image)

Figure 3.14 The extinction coefficient (k) of APEC1797 (red) and Makrolon2205 (black) in UV-visible range.
Comparing the extinction coefficients in Figure 3.14, we can see significant a difference between APEC1797 and Makrolon2205 in the range of 240nm~500nm/cm. The peak near 260nm in Makrolon and the shoulder in APEC1797 is corresponding to benzene part on the carbon skeleton of both polymers. The peak near 250nm is corresponding to the dye in both APEC and Makrolon. As there is no dye molecular in the Makrolon 2205, there is no peak at 250nm for Makrolon 2205. This peak of dye generates big contrast which allow us to observe the dye diffusion.

Figure 3.15 Evolution of depth profile of bilayer system diffusing at 225°C

At 225°C, the Figure 3.15 it clear shows that the dye in the APEC 1797 layer diffuse into Makrolon 2205. However, basically none of the APEC 1797 diffuse into the Makrolon. Moreover, as more and more dye diffusion into Makrolon 2205 layer, the concentration (volume fraction) of dye molecular in the APEC1797 decreased. This clearly indicates UV-visible-NIR ellipsometer detect the dye diffusion.
As the result shown in the Figure 3.16, with the increase of the diffusion temperature, the diffusion rate decrease. At 225°C, the interface broadens fast in the first 4 min and then the increase rate decrease. At 250°C, the interface broadens fast in the first 16 min and then the increase rate decrease. However, the interface of the final stage at 250°C is much smaller than the final stage interface at 225°C, which may indicates the dye molecular have attractive interaction with the polymer in APEC 1797 and with the increase of temperature, the interaction also increase.

Figure 3.17 Relation between interface thickness and time\(^{1/2}\) at 225°C and 250°C with linear fit.
The same method (for IR result) was used for the calculation of diffusion coefficient from UV-visible-NIR ellipsometer.

From the fitting result in Figure 3.17,

\[ D_{250°C} = 6.36 \times 10^{-17} m^2/min \]
\[ D_{225°C} = 1.76 \times 10^{-15} m^2/min \]

Compare to the result obtained from IR ellipsometric data, at 225°C, the polymer chain diffusion is slower than the dye diffusion. This is because the polymer chain is relatively bigger than the dye molecular. The big chain need to overcome more fiction and need more energy to move. However, at 250°C, as the interaction between dye and polymer in APEC 1797 increase, the diffusion of dye become more and more difficult. Therefore, the diffusion coefficient of dye is smaller than the diffusion coefficient of polymer chain.

3.5 Conclusion

Due to the different chemical structure, the absorption of APEC 1797 and Makrolon 2205 in the IR range is different. This difference can generate contrast on the extinction coefficient (k) which are used to describe the light absorption behavior quantitatively. The contrast of k can be used to study the diffusion between polymer in APEC1797 AND Makrolon 2205. When polymer in APEC 1797 is in glassy state and the polymer in Makrolon 2205 is in rubbery state, the polymer chain in APEC1797 is still frozen at this temperature which means the movement of this polymer is limited. As the polymer in Makrolon 2205 is in rubbery state, the chain mobility is high. Therefore, the polymer in Makrolon 2205 diffuses into APEC 1797 layer. When both polymers are in rubbery state, the polymer in APEC 1797 can diffuse into Makrolon 2205 layer meanwhile polymer in Makrolon 2205 can diffuse into APEC 1797. Also, because the chain mobility increases
with the increase of temperature, the diffusion coefficient increases with the increase of temperature.

Due to the dye small molecular in APEC1797, the APEC1797 have a higher absorption of the UV light compare to the Makrolon 2205. The difference can generate contrast of k which can be used to study the dye diffusion behavior. At 225°C, polymer in APEC 1797 is in glassy state and the polymer in Makrolon 2205 is in rubbery state. The dye diffuses form APEC 1797 to Makrolon 2205. However, at 250°C, the polymer is in rubbery state in APEC 1797, the interaction between dye and polymer increases. Although the dye still diffuses into the Makrolon 2205, the interface thickness at 250°C is smaller than the interface thickness at 225°C. Also the diffusion coefficient at 250°C is relatively small compared to the diffusion coefficient at 225°C.
CHAPTER IV
FUTURE WORK

For the work associated with Chapter II, metal nanoparticle can be added in the BPEI/PAA thin film or thick film on normal glass and free standing films. Then, use microwave oven to crosslink the BPEI/PAA film. As free electrons exist in metal nanoparticles which distribute in BPEI/PAA film, a good crosslink performance can be obtained by microwave heating.

For the work associated with Chapter III, exchange the position of APEC and Makrolon to see if it shows any difference on the evolution of concentration profile. Different temperature should be try on the existed bilayer system. The diffusion processing at 265°C, 270°C, 280°C and 285°C would provide us a clear concentration profile that shows the mutual polymer diffusion as those temperatures are higher than the T_g of both Makrolon2205 and APEC1797. Therefore, diffusion at those temperatures should be investigated. The diffusion processing at 205°C, 210°C and 215°C would provide us a clear concentration profile that shows only the Makrolon 2205 diffusion as those heating temperature is above T_g of Makrolon2205 but under T_g of APEC1797. Furthermore, Makrolon with different molecular weight should also be investigated because the relation between molecular weight and diffusion coefficient can indicate if the polymer can be described by Rouse model or reputation model.
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