
Mufadal Ayubali-Mohamedali

Follow this and additional works at: http://scholarworks.rit.edu/theses

Recommended Citation

This Thesis is brought to you for free and open access by the Thesis/Dissertation Collections at RIT Scholar Works. It has been accepted for inclusion in Theses by an authorized administrator of RIT Scholar Works. For more information, please contact ritscholarworks@rit.edu.

Mufadal Ayubali-Mohamedali

June 2006

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

Approved: ______ Thomas W. Smith

Thomas W. Smith (Advisor)

_______ Terence Morrill

Terence C. Morrill (Department Head)

Department of Chemistry
Rochester Institute of Technology
Rochester, New York 14623-5603
Copyright Release Form:

I, Mufadal Ayubali-Mohamedali, hereby grant permission to the Wallace Memorial Library of Rochester Institute of Technology to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

Mufadal Ayubali-Mohamedali

Mufadal Ayubali-Mohamedali

June, 2006
# TABLE OF CONTENTS

LIST OF TABLES...........................................................................................................vi

LIST OF FIGURES.........................................................................................................vii

ACKNOWLEDGMENTS...................................................................................................x

ABSTRACT....................................................................................................................xi

1. INTRODUCTION & BACKGROUND........................................................................1

   1.1 Electro-optical material......................................................................................2

   1.2 Potassium dihydrogen phosphate (KDP)..........................................................3

   1.3 KDP nanocrystals..............................................................................................4

   1.4 Thesis objective................................................................................................4

       1.4.1 Major challenges.....................................................................................4

       1.4.2 Strategy....................................................................................................6

       1.4.3 Block polymer micelle & morphology.....................................................6

2. BACKGROUND TO EXPERIMENTAL TECHNIQUES...........................................10

   2.1 Light Scattering................................................................................................10

       2.1.1 Dynamic Light Scattering.......................................................................10

           • Theory.....................................................................................................11

       2.1.2 Static Light Scattering............................................................................16

           • Theory.....................................................................................................17

   2.2 Viscometry.........................................................................................................20

       • Theory........................................................................................................21

   2.3 Differential Scanning Calorimetry (DSC)........................................................24

       • Theory........................................................................................................25
3. EXPERIMENTAL DESIGN AND SAMPLE PREPARATIONS

3.1 Material and Sample Preparation

3.1.1 Synthesis of PS-b-POE block polymer

3.1.2 Solution Preparation: Light Scattering & Viscometry

3.1.2.1 Selection of block polymers

3.1.2.2 Solution Preparation

3.1.3 PS_b_PEO/K+H2PO4- Solution

3.1.4 Film preparation: DSC

3.1.5 Film preparation: AFM

3.1.6 AFM measurements

3.2 Instrumental Set Up

3.2.1 Light Scattering

3.2.2 Viscometry

3.2.3 Differential Scanning Calorimetry

4. RESULTS

4.1 Dynamic Light Scattering

4.2 Static Light Scattering

4.3 Viscometry

4.4 Differential Scanning Calorimetry

4.5 Atomic Force Microscopy

5. DISCUSSION OF RESULTS

5.1 Light Scattering & viscometry
5.2 Differential Scanning Calorimetry ................................................................. 73
5.3 Atomic Force Microscopy .............................................................................. 74

6. SUMMARY & CONCLUSION ............................................................................ 76
7. REFERENCES .................................................................................................... 78
8. APPENDICES .................................................................................................... 80
   • Appendix i .................................................................................................... 80
   • Appendix ii .................................................................................................. 82
List of Tables

Table 1: Block copolymer solution compositions .......................................................... 28

Table 2: Summary of hydrodynamic radius of the particles in solution with all the acid doping .................................................................................................................. 46

Table 3: Summary of radius of gyration for various solution concentration for all acid doping .................................................................................................................................................. 54

Table 4: Summary of intrinsic viscosities for all the acid doped solution of bock copolymer .................................................................................................................................................. 59
List of Figures

Figure 1: Structure of Potassium dihydrogen phosphate molecule..........................3

Figure 2: A random order to an ordered array morphology of KDP nanocrystals.........5

Figure 3: Orientation of dipoles within the KDP nanocrystals under application electric field.................................................................5

Figure 4: morphology block copolymer relative to their volume fractions...............7

Figure 5: Overview of synthesis steps and processes........................................8

Figure 6a-d: graph of autocorrelation functions versus delay time for 33\% PEO block copolymer.................................................................34

Figure 7a-d: graph of autocorrelation function versus \(Q^2t\) graphs for 33\% PEO block copolymer.................................................................36

Figure 8a-d: graph of autocorrelation functions versus delay time for 11\% PEO block copolymer.................................................................37

Figure 9a-d: graph of autocorrelation function versus \(Q^2t\) graphs for 11\% PEO block copolymer.................................................................38

Figure 10a-d: graph of autocorrelation functions versus delay time for 51\% PEO block copolymer.................................................................39

Figure 11a-d: graph of autocorrelation function versus \(Q^2t\) graphs for 51\% PEO block copolymer.................................................................40

Figure 12: graph of normalized intensity at 90° versus Log of inverse relaxation times for 11\%PEO block copolymer systems.................................42

Figure 13: graph of normalized intensity at 90° versus Log of inverse relaxation times for 33\%PEO block copolymer systems........................................43

Figure 14: graph of normalized intensity at 90° versus Log of inverse relaxation times for 51\%PEO block copolymer systems.................................43
Figure 15a-d: Graph of Inverse characteristics relaxation times verses $Q^2$ to measure the apparent diffusion coefficient for 33% PEO block copolymer..........................44

Figure 16a-d: Graph of effective diffusion coefficient versus concentration to extrapolate diffusion coefficient at infinite dilution for the 33% PEO block copolymer systems.....45

Figure 17a-d: Graph of excess Rayleigh ratio versus Concentration for 11% PEO block copolymer.................................................................48

Figure 18a-d: Graph of excess Rayleigh ratio versus Concentration for 33% PEO block copolymer.................................................................49

Figure 19a-d: Graph of excess Rayleigh ratio versus Concentration for 51% PEO block copolymer.................................................................50

Figure 20: Graph of inverse Rayleigh ratio versus $Q^2$ for 11% PEO block copolymers (20% and 50% acid doped solutions)..............................52

Figure 21: Graph of inverse Rayleigh ratio versus $Q^2$ for 33% PEO block copolymers (20% and 50% acid doped solutions)..............................53

Figure 22: Graph of inverse Rayleigh ratio versus $Q^2$ for 51% PEO block copolymers (20% and 50% acid doped solutions)..............................53

Figure 23a-c: Graph of radius of gyration versus solution concentration g/mL for the 20% acid doped solution.......................................................55

Figure 24a-c: Graph of specific viscosity versus solution concentration g/mL for the 11%, 33% and 51%PEO block copolymer solutions.................................57

Figure 25: DSC scan for the acid doped films of 11% PEO block copolymer...........61

Figure 26: DSC scan for the acid doped films of 33% PEO block copolymer...........62

Figure 27: DSC scan for the acid doped films of 51% PEO block copolymer...........62

Figure 28: DSC scan for the neutralized film doped with 10 mole% phosphoric acid (33% PEO block copolymer)..............................................64

Figure 29: DSC scan for the neutralized film doped with 20 mole% phosphoric acid (33% PEO block copolymer)..............................................65
Figure 30: DSC scan for the neutralized film doped with 50 mole% phosphoric acid (33% PEO block copolymer).................................................................66

Figure 31: Height and phase contrast AFM micrographs for the 33% PEO block copolymer film annealed @150C for 1hrs.................................................67

Figure 32: Height and phase contrast AFM micrographs for the 33% PEO block copolymer film doped with 20% acid and annealed @150C for 1hr......................68

Figure 33: Height and phase contrast AFM micrographs for the 33% PEO block copolymer film doped with 20% acid, neutralized and annealed @150C for 1hr.........69

Figure 34: Height and phase contrast AFM micrographs for the 33% PEO block copolymer film doped with 20% acid, neutralized and annealed @180C for 20min......70
ACKNOWLEDGMENTS

This thesis is dedicated to my mother and my wife Duriya from whom I have gained lot of confidence and inspiration in my life. I want to thank my parents for their support and patience since coming to the United States for my education.

I would like to express my deep gratitude to my advisor Professor Thomas Smith for giving me the opportunity to work with him, understanding me, and providing me with guidance, support, encouragement during the course of my master’s degree. I learned a great deal about polymer chemistry through his teaching and research and he has been very dear to me as a mentor. Without him, the completion of my education would not have been possible.

A heart felt appreciation to Professor Andreas Langner whose courses made chemistry very interesting at RIT. He always found time to teach, answer many of my questions and his valuable suggestions and encouragement fostered my confidence. I have always considered him as one of my advisors.

I also would like to thank Professor Michael Kotlarchyk for his guidance and support, teaching me the light scattering techniques and letting me work in his lab. Grateful thanks to my committee member, Professor Christopher Collison for his help and suggestions, and Professor Surendra Gupta for teaching me the Atomic Force Microscopy instrument.

I want to extend my thanks to Dr. Terence Morrill, the Chemistry Department Head for providing me support for my study at RIT and the faculties and graduate students in the chemistry department where I spent most of the time.

Finally, I want to thank all my team members in Dr Smith’s research group with whom I shared the laboratory, especially Jinghang Wu for giving me motivation and encouragement during the course of my master’s degree.
ABSTRACT

Potassium Dihydrogen Phosphate (KDP) nanocrystals were synthesized in micellar solutions of block copolymers of polystyrene (PS) and poly(ethylene oxide) (PEO) in toluene/Dimethoxyethane solvent. The synthetic procedure entailed the doping of the block copolymer solutions with phosphoric acid and the stochiometric neutralization of the acid-doped system with potassium hydroxide (KOH). The neutralization reaction was localized within the core of the micelle which in effect served as a nanoreactor or nanovessel for the reaction.

Micellization of the block copolymer molecules was induced upon doping the solution with phosphoric acid which resulted in ion dipole binding of the protons to the ethylene oxide molecules in the core of the micelle. The polystyrene segments of the copolymer surround the micelle core as a corona. Dynamic and static light scattering and solution viscometry were used to elucidate the micellization process and the extent of aggregation (micelle size) in the block copolymer solutions doped with phosphoric acid. Light scattering results indicated that acid doping, at levels of 20 mole% or higher, based on the concentration of ethylene oxide residues, induced complete micellization of copolymer molecules.

The acid-doped micellar solutions were neutralized with the KOH to form colloidal solutions in which $K^+H_2PO_4^-$ ions were ostensibly bound within the PEO core of the micelle. These neutralized colloidal solutions were precursors for the nanocrystallization of KDP. Solutions were puddle cast on glass slides and dried at $\sim50^\circ$ C to yield films that were subsequently annealed to promote crystallization of KDP. Differential scanning calorimetry (DSC) and atomic force microscopy (AFM), respectively, were used to study the
crystallization of KDP and the morphology of thin films spin coated from the micellar solutions.

The objective of this thesis was to synthesize an ordered array of KDP nanocrystals within the block copolymer film. DSC scans on the annealed films in some cases showed the presence of crystalline KDP in the composite film. AFM micrographs also showed the formation of nanosized particles of KDP. However, these nanocrystals were polydisperse in sizes and were randomly distributed. The random distribution and polydispersity indicated the crystallization of KDP material was not confined within the core of micelle.
CHAPTER 1
INTRODUCTION & BACKGROUND

Noncentrosymmetric single crystals of potassium dihydrogen phosphate (KDP) materials are electro-optically active and are used to modulate light in electro-optic devices. However, large crystals of KDP are very fragile and expensive.\(^1\) Furthermore, in order to incorporate these materials within a microchip, hybrid composite materials are required\(^2,3,4\).

Polymer nanocomposites containing inorganic or organic electro-optical materials offer a solution to the problem of integration\(^3,5\). The advantage is that the synthesis of the polymer nanocomposite is scalable and cost effective and thin films of composite materials can be easily incorporate in the microchip.

In this research, the synthesis of nanocrystalline potassium dihydrogen phosphate (KDP) was explored by growing the material from the molecular level in micellar solutions of block copolymers of polystyrene and polyethylene oxide (PS-b-POE). When toluene solutions of PS-b-POE are doped with phosphoric acid, aggregation or micellization of the copolymer molecules is apparently induced and copolymer micelles with a POE core and a PS corona are ostensibly formed. It is believed that the ethylene oxide (POE) residues in the micellar core are complexed with H\(_3\)PO\(_4\) and the acid-doped micelle core serves as a nanoscopic vessel for a subsequent neutralization reaction. Ultimately, crystalline KDP would be nucleated within the POE domains of nanostructured films cast from neutralized solutions of the acid-doped block copolymer. Depending on the mole fraction of ethylene oxide residues in the block copolymer and the number of copolymer molecules per micelle, the core will have the ability to bind with different amounts of phosphoric acid. When this micellar solution is subsequently neutralized with potassium hydroxide (KOH), the
neutralization reaction is confined to core of the micelle. By controlling the molar mass of the poly ethylene oxide segment and the level of acid doping, the amount of the $K^+H_2PO_4^-$ generated and the size of the KDP nanocrystals obtained upon drying and annealing can be systematically varied.

Similar approaches for synthesizing gold, platinum$^6$ and titania$^7,8$ nanoparticles in diblock polymer films have been reported.

1.1.1 Electro-optical Materials

Electro-optical materials show a linear or a non-linear change in optical properties under the influence of an applied electric or a magnetic field. Change in refractive index, second harmonic effects, and polarization of light are three kinds of change in optical properties exhibited by electro-optical materials. The electro-optical activity of a material is due to the field-induced polarization of electrons. The polarization of electrons within the material is described by Equation 1, below.

\[
\text{Equation 1} \quad P = \chi^1(\omega) \ast E(\omega) + \chi^2(\omega) \ast E(\omega)^2 + \chi^3(\omega) \ast E(\omega)^3 + \ldots
\]

Where $\chi$ is the electric susceptibility of the material, and $E$ is the applied electric field.$^9$ The higher order terms for polarization shown in the equation are negligible for most materials. However, in electro-optically active materials, these terms become significant under an applied field and induced polarization of electrons can lead to a change in optical properties. Such is the case in noncentrosymmetric crystals like potassium dihydrogen phosphate, where the second term in the equation becomes significant and induces change in
refractive index under applied field. This effect is known as the Pockels effect and the change in refractive index $\Delta n$ in the material is given by Equation 2\textsuperscript{10},

$$\text{Equation 2} \quad \Delta n = \frac{r}{2} n^3 * E$$

Where $r$ is the electro-optical coefficient and $n$ is the normal refractive index.

1.1.2 Potassium dihydrogen phosphate (KDP)

Electro-optic activity in potassium dihydrogen phosphate is a result of the polarizability of electrons in the crystal lattice and the asymmetry of the crystal. The unit cell of the KDP crystal (elements of which are illustrated in Figure 1) is chiral and has two tetragonal lattice structures with two KH$_2$PO$_4$ units per lattice site.\textsuperscript{11}

![Figure 1: Structure of Potassium dihydrogen phosphate molecule\textsuperscript{11}](image)

It is important to emphasize that only single crystals of KDP exhibit the Pockels effect. In solution or in the amorphous state, KDP is not electro-optically active. The change in refractive index demonstrated by the bulk KDP single crystals is small with highest reported change in refractive index of $\sim0.04\%$\textsuperscript{5}. In addition, single crystals of KDP are fragile, and the process for manufacturing large crystals is very expensive\textsuperscript{1}. 
1.1.3 KDP nanocrystals

It is our hypothesis is that if nanoscopic single crystals of KDP can be synthesized and ordered in a regular array, and if some external force such as an applied field were used to impose asymmetric orientation on these crystals, then it might be possible to observe nonlinear optical activity, like that exhibited by bulk single crystals of KDP, in nanocystal/polymer composites. To test this hypothesis we needed to synthesis nanocrystalline KDP and fabricate an ordered array of these nanocrystals. Given an ordered nanocrystalline array, the final step would be the application of some external force (either an electric field or shear force or thermal gradient) to asymmetrically orient the nanocrystals within the confines of a glassy polymer.

1.4 Thesis objective

The objective of this research was therefore to synthesize a polymer nanocomposite containing an ordered array of KDP nanocrystals which, under an applied field, can be asymmetrically oriented. We expect that such a composite material will exhibit electro-optic activity and non linear optical properties similar to that shown by single crystal of bulk KDP.

1.4.1 Major challenges

The literature discloses a number of examples of the synthesis of nanoparticles of inorganic electro-optical materials\textsuperscript{12, 13}. In these processes, nanoparticles are typically synthesized by controlled precipitation from solutions of precursor molecules and the particles formed thereby tend to aggregate and sinter. Aggregates are typically milled or otherwise ground and redispersed in polymer binders. In the present research our strategy was to confine or localize the formation of nanoparticles in a self-assembling medium which would spontaneously form an ordered array of nanocrystals (perhaps a body centered cubic
lattice structure) that could subsequently be asymmetrically oriented. Figure 2 depicts the transition from a random spatial array to an array where asymmetric crystals are positioned in an ordered lattice.

![Image of lattice structure]

Figure 2: A random order of crystals to an ordered array of KDP nanocrystals

The system, of course cannot be electro-optically active without nematic or smectic orientation of the asymmetric nanocrystals in the lattice. In a system of randomly oriented particles, the overall polarization of the dipolar crystals would be negligible. Therefore to induce a nematic or smectic orientation one would need to apply an external forces such an electric field or shear force or thermal gradient. Figure 3 depicts the transition from an ordered array to an asymmetrically oriented smectic structure.

![Image of lattice structure]

Figure 3: Electric field induced orientation of asymmetric nanocrystals
1.4.2 Strategy

As was stated above, in the present research our strategy was to confine or localize the formation of nanoparticles in a self-assembling medium which would spontaneously form an ordered array of nanocrystals (perhaps a body centered cubic lattice structure) that could subsequently be asymmetrically oriented. In the early 80’s, Smith, et al.\textsuperscript{14,15} articulated a “locus control” process for the formation and stabilization of monodisperse colloidal and nano-sized dispersion of selenium and zero valent iron, respectively, with the agency of soluble functional polymers or surfactant micelles. Our specific strategy was to use micellar solutions of an ion-binding block copolymer to extend the locus control process to the formation of KDP nanoparticles.

Block copolymer morphology

Small organic molecules are most often miscible with each other in all proportions. Thus, ethylbenzene mixes freely with ethanol to form a homogeneous solution. Unlike small molecules, high molar mass polymers are typically immiscible with each other and form disordered composites whose components are distinctly phase separated. Simply considered, this is a result of the minimal contribution of entropy of mixing of high molar mass molecules. In a block copolymer, different high molar mass chain segments are covalently linked. As a result, the scale of phase separation of block copolymers in the solid state is limited to the dimensions of the order of the radius of gyration of the segments of the block copolymers themselves. In the solid state, the equilibrium morphology of an A-B diblock copolymer will be one of a small set of nanostructured minimal energy surface composites, with the specific morphology being determined by the relative molar volume of the A and B segments in the diblock polymer.\textsuperscript{16} In solution block copolymer molecules may dissolve
molecularly or as micellar aggregates, depending on the relative solubility of the chain segments in the solvent.

Figure 4 displays different structures adopted by block copolymers in solution (MIC and CYL) and in the solid state (BCC, HEX, LAM, MLAM, HPL or Ia3d), depending on the relative volume fraction of the block segments. For volume fraction of less that 20% spherical BCC structures are typically observed. As the volume fraction of the minor component is increased to 25-35% by volume, hexagonal arrays of cylindrical structures are formed. For block copolymers in which the volume fractions of the two segments are roughly equivalent lamellar (LAM, MLAM) or bicontinuous structures (HPL, Ia3d) may be observed (see Figure 4).

Figure 4: Morphology of block polymers relative to their volume fraction

Our strategy leverages micellar solutions of an A-B diblock copolymer to confine or localize the formation of KDP nanoparticles and the equilibrium nanostructured morphology of the block copolymer in the solid state to create an ordered array.
Specifically, KDP was synthesized in micellar toluene/ether solutions of block polymers of polystyrene and polyethylene oxide by neutralization of H$_3$PO$_4$ doped solutions with methanolic KOH. Poly ethylene oxide chain segments bind the acid and aggregate to form micelles with an acid-doped ethylene oxide core and a polystyrene corona. Thus, the core of the micelle serves as nanoreactors where the neutralization reaction is confined. The schematic shown in Figure 5 presents an overview of the locus control process as applied to the synthesis of KDP nanoparticles.

---

**Figure 5:** Schematic diagram for the overview of synthesis steps and processes

The block copolymer was molecularly dissolved in an 80:20 by volume mixture of toluene and dimethoxy ethane (DME). Upon doping with 100% phosphoric acid, ethylene oxide moieties are protonated and micellization or aggregation of block copolymer chains is
induced. The micelle core was acid-doped POE and the corona is PS. Stochiometric neutralization with potassium hydroxide yields a colloidal solution wherein $K^+H_2PO_4^-$ ions are sequestered in the PEO core. Films were subsequently cast from the neutralized solutions and were dried and annealed to create an ordered nanocomposite and to crystallize KDP. In order to develop a detailed understanding of the H$_3$PO$_4$-induced micellization process, light scattering and viscometry were employed. Differential scanning calorimetry was used to study the crystallization of the KDP. Atomic force microscopy of ultra thin films spin-coated from micellar, acid-doped, solutions and colloidal, KOH-neutralized, solutions provided evidence in support of predicted block copolymer morphologies and unexpected insight into nature of the crystallization process.
CHAPTER 2
BACKGROUND TO EXPERIMENTAL TECHNIQUES

2.1 Light Scattering

Light scattering techniques are used to measure the characteristic of particles in solution. Information such as particle size, shape, molecular weight and their interaction (virial coefficient) can be measured by passing a polarized light through the solution. When light interacts with particles, it scatters light at different angles. The intensity of the scattered light is measured by a photodetector positioned at different angles. Light scattering techniques are commonly used to study the characteristics of polymers and macromolecules such as proteins, DNA in solution. Information that can be realized depends on the nature of the solution and specific light scattering technique employed. In this research, quasi-elastic or dynamic light scattering (DLS) and the static light scattering (SLS) techniques were employed to study the state of aggregation of the block copolymer chains in solution.

2.1.1 Dynamic Light Scattering

In dynamic light scattering, the mutual diffusion of the particles in solution can be measured. The incident light must be from a monochromatic and coherent light source, i.e. a laser source. When such light is passed through a solution containing particles, light is scattered at different angles and recorded by a photodetector or a photon counter. Most importantly, due to the motion of the particles, the intensity of the scattered light changes with respective to time. The temporal variation of intensity therefore contains information about the random motion of the particle. This is the main principle of the dynamic light scattering technique, which records the fluctuation in intensity at discrete time intervals to measure the characteristic relaxation time and the diffusion coefficient associated with the
random motion of the particles. A digital autocorrelator uses information of the photon count intensity at different delay time intervals to produce an autocorrelation function. The autocorrelation function, as the name implies, is a measure of correlation of the intensity of scattered light at a give time $\tau'$, and the intensity after a delay time, $t$. Intensities at many discrete delay time intervals are recorded by the digital autocorrelator in their register or channels. The mathematical relationship for the average intensity will be shown in the theory section. The time required for the autocorrelation function to decay is the characteristic relaxation time. From the characteristic relaxation time, the diffusion coefficient of the particle is determined and then used in the Stokes-Einstein equation to calculate the hydrodynamic size of the particles. Different analysis algorithms such as cumulant-analysis or CONTIN analysis\textsuperscript{19} are used to analyze the autocorrelation decay curve. In this research, the CONTIN algorithm was used to extract the distribution of the characteristic relaxation times. Details of the CONTIN algorithms are discussed in the theory section.

**Theory**

In the dynamic light scattering experiment, the intensity of scattered light measured at a given angle changes with respect to time due to the kinetic motion of the particle. The intensity of scattered light is measured over a period of time in a discrete time intervals by the digital autocorrelator. The average intensity $\langle I(Q) \rangle$ is the sum of intensities at discrete time intervals at a given angle divided by the total time. At a constant angle, the average intensity $\langle I \rangle$ from this equation is represented as:

\[
\langle I \rangle = \lim_{T \to \infty} \frac{1}{T} \int I(t) dt \approx \lim_{n \to \infty} \frac{1}{n} \sum_{j=1}^{n} I(j \Delta t)
\]
T is the total duration of intensity measurements; and \( \Delta t \) is the sampling time for each consecutive measurements and \( n \) is the number of intensity measurements taken after every sampling time. The fluctuation of the intensity around the average intensity \( \langle I \rangle \) is used by the digital autocorrelator to produce the autocorrelation function \( C(t) \) and it is mathematically presented in Equation 4,

\[
\text{Equation 4} \quad C(t) = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} I(t')^* I(t'+t) dt' = \langle I(0) I(t) \rangle.
\]

The autocorrelation function \( C(t) \) is doing the autocorrelation between the intensity at an arbitrary time \( t' \) and the intensity after a time \( t'+t \). \( t \) is referred to as the delay time of the correlation function and \( T \) is the total time of the duration of measurement.

At \( t = 0 \), the value of autocorrelation function \( C(t) \) is maximum. When the delay time \( t \to \infty \) the intensities becomes uncorrelated or basically the \( C(t) \) is independent of \( t \) and is equivalent to the average intensity \( \langle I \rangle^2 \) called the baseline B. The autocorrelation function is presented by Equation 5,

\[
\text{Equation 5} \quad C(Q,t) = B \left[ 1 + f \left| g^{(1)}(Q,t) \right|^2 \right]
\]

At a constant angle, equation 5 is represented as \( C(t) = B \left[ 1 + f \left| g^{(1)}(t) \right|^2 \right] \); \( f \) is an instrumental constant which is \( 0 \leq f \leq 1 \), and \( g^{(1)}(t) \) is the electric field autocorrelation function. They are related by the normalized intensity autocorrelation function \( g^{(2)}(t) \) according to the Siegert relation as shown below in Equation 6,

\[
\text{Equation 6} \quad g^{(2)}(t) = \frac{\langle I(0)I(t) \rangle}{\langle I \rangle^2} = 1 + f \left| g^{(1)}(t) \right|^2
\]
The relation in equation 6 is valid for most cases except for very small number of scatterers or when the motion of the scatterers is limited\(^2\). The electric field autocorrelation function \(g^{(1)}(t)\) can be directly measured from the autocorrelator function. For a dilute solution, where the interparticle distance is large enough to ignore particle to particle interaction, and the solution contains a monodispersed sized, spherically shaped particles, the electric field autocorrelation function decay is exponential relative to time and is shown in Equation 7,

\[
\text{Equation 7} \quad \left| g^{(1)}(t) \right|^2 = \exp(-2\Gamma t)
\]

For a simple diffusing particle, the inverse characteristic relaxation time \(\Gamma\) or the spectral line width and the diffusion coefficients are related as

\[
\text{Equation 8} \quad \Gamma = DQ^2
\]

\(D\) is the translation diffusion coefficient of the particle and \(Q\) is the scattering wavevector given by Equation 9,

\[
\text{Equation 9} \quad Q = \frac{4\pi m}{\lambda_0} \sin(\theta/2)
\]

\(n\) is the refractive index of the solution, \(\lambda_0\) wavelength of the incident light in vacuum, and \(\theta\) the scattering angle. Therefore the intensity autocorrelation function in this condition can be represented as

\[
\text{Equation 10} \quad \left| g^{(1)}(t) \right|^2 = \exp(-2DQ^2t)
\]

In an ideal case, that is a solution containing monodispersed sized, non-interacting, spherically shaped particles, the graph of the autocorrelation function with delay time on a linear scale will be a single exponential decay at a given scattering angle. Additionally, if the
particles in solution are simple diffusing particles, then the graph of the autocorrelation decay curves with $Q^2t$ at different angles should collapse to a single exponential curve. When a solution contains a polydispersed sizes of particles, the autocorrelation decay curve is no longer a single exponential, instead is a sum many exponential terms. The number of the exponential terms and their significant contribution to the total autocorrelation depends on the distribution and sizes of the particle. Equation 11 describes the autocorrelation decay for a solution with polydisperse sized particles.

**Equation 11**  
\[ g'(t) = \lim_{n \to \infty} \frac{1}{n} \sum_{j=1}^{n} w_j(D_j) \exp(-D_j Q^2 t) \]

\(w_j(D_j)\) is the weighting function which is determined by the amount of particles in each size range $j$.

In this thesis, the CONTIN algorithm analysis was used to measure the characteristic relaxation times for solutions containing molecularly dissolved polymer chains and aggregated polymer chains. The CONTIN algorithm is an inverse Laplace transforms of the photon count intensity autocorrelation function. This function closely fits autocorrelation function’s multiplicity of exponential terms corresponding to the distribution of characteristic relaxation times or distribution of sizes of particles in solution as shown by S.W. Provencher, by Equation 12.

**Equation 12**  
\[ |g^{(t)}(\tau)| = \int \Gamma G(\Gamma) \exp(-\Gamma \tau) d(\ln \Gamma) \]

$G(\Gamma)$ is the line width distribution function. Using the CONTIN algorithm function, the distribution of characteristic relaxation times for the free chains and aggregation of polymer chains in solution was measured. The translation diffusion coefficient discussed in the spectral line width equation earlier is the apparent or the effective diffusion coefficient at a
given concentration. The value of translation diffusion coefficient is apparently affected by the interaction of particles even at relatively dilute solution. Specifically, for polymer solution, the interactions are due to entangling of polymer chains. The true diffusion coefficient is therefore, the diffusion coefficient of a particle at infinite dilution where there is no or minimal interaction. This can be extrapolated from the plot of apparent diffusion coefficient at corresponding solution concentration. The diffusion coefficient at infinite dilution $D_0$ is the extrapolated from the plot by taking the vertical-intercept or the D-intercept on the graph.

Using the Stokes-Einstein relationship, Equation 13, the hydrodynamic radius of the particle in solution can be calculated. Using the diffusion coefficient at infinite dilution, $D_0$ the hydrodynamic radius, $R_H$, of a particle is measured. Here $k_B$, $T$ and $\eta$ are the Boltzmann’s constant, absolute temperature and the solvent viscosity, respectively

$$\text{Equation 13 } R_H = \frac{k_B T}{6 \pi \eta D_0}$$
2.1.2 Static Light Scattering

The static light scattering (SLS) techniques is routinely used in the laboratories to measure the radius of gyration of the random coil structure, molecular weight and the viral coefficient of the polymer in solution. The intensity of the scattered light in the SLS contains information about the characteristics of these particles. The principle behind the scattering of light is derived from the Rayleigh scattering\(^2\), i.e. when incident light or an electric field impinges on a molecule and induces oscillation of dipoles within the molecule, the oscillating dipole generates a secondary field called the scattered light. Rayleigh scattering applies only to molecules without considering absorption or scattering from large particles such as colloidal sized particles. Therefore in the SLS techniques, the principle of Rayleigh scattering is extended to large sized particles such as macromolecules in solution. The scattered light contains information about the molecular weight, radius of gyration and interaction of the polymer chain (entangling) in dilute solution. In order to measure the radius of gyration of these particulates, the size of the particles should be at least \(1/20\)th size of the wavelength of the incident light.

The excess Rayleigh ratio is an absolute value of the light scattered by the particles in solution. The intensity of the scattered light for the solution \(I_{\text{solution}}\), solvent \(I_{\text{solvent}}\) and toluene \(I_{\text{toluene}}\) solution are recorded individually by measuring the number of photon per seconds at a given angle. The intensities are subtracted from the dark count and then corrected for the dead count at 25 nano seconds that is due to the limitation of the digital autocorrelator.

The excess Rayleigh ratio \(R_\theta\) was calculated according to the mathematical equation 14 below
Equation 14 \[ R_\theta = \left( \frac{I_{\text{solution}} - I_{\text{solvent}}}{I_{\text{Toluene}}} \right) \times 1.4 \times 10^{-5} \text{ cm}^{-1} \]

Where, \( 1.4 \times 10^{-5} \text{ cm}^{-1} \) is a known value of Rayleigh scattering of a pure toluene solution from the literature.

**Theory**

In principle, Rayleigh scattering is due to interaction of light with the molecules, i.e. the interaction of light induces an oscillation of a dipole within the molecule which generates a scattered light. The intensity of the transmitted light is therefore less than that of the incident light because some of the light is lost due to scattering. The scattered light, according to Rayleigh theory, is represented in Equation 15.

Equation 15 \[ \frac{i_\theta}{I_o} = \frac{2\pi^2 n^2 \left( \frac{dn}{dc} \right)^2 c}{N_A r^2 \lambda_o^4 \left( \frac{1}{M} + 2Bc \right) \left( 1 + \cos^2 \phi_x \right)} \]

\( \phi_x \) is the polarization angle measured between the XY plane and the vertical Z-axis in the spherical coordinates.

\[ i_\theta = \frac{i_s}{V} \] is the scattered intensity of light per unit volume at a given scattering angle \( \theta \) along the horizontal (XY) plane, \( I_o \) is the incident light. \( n \) is the refractive index, \( \frac{dn}{dc} \) is the refractive index increment, \( N_A \) is the Avogadro number, \( \lambda_o \) is the wavelength of the incident light source in vacuum, \( M \) is the molecular weight, \( B \) the virial coefficient and \( c \) the concentration in mass per volume.
The assumption in the Rayleigh scattering theory is that the molecules are isotropic, non-absorbing and the scattering is only due to molecules (free or micellized polymer molecules). Upon rearranging the terms, the above Equation 15 can be rewritten as follows

$$\textbf{Equation 16} \quad R_\theta = \frac{Kc}{\frac{1}{M} + 2Bc}$$

where $K$ is constant $K = \frac{2\pi^2 n^2(dn/dc)^2}{N_A \lambda_o^4}$,

and $R_\theta$ the Rayleigh ratio is

$$\textbf{Equation 17} \quad R_\theta = \frac{i_s r^2 \cdot}{I_0 (1 + \cos^2 \phi_x)}$$

$r$ is the distance from the detector to the sample and $\phi_x$ is the polarizing angle measured along the horizontal plane. Both, the distant of the detector from the solution $r$ is fixed and the angular angle $\phi_x$ along the vertical plane is set to 90° to measure the intensity at a set distance and at angles along the horizontal plane. Therefore, the excess Rayleigh ratio is finally $R_\theta = \frac{i_s \cdot r^2}{I_0}$ with a unit of cm⁻¹. According to the Rayleigh ratio from the equation 16, there is a direct relationship between the Rayleigh scattering ratio $R_\theta$ and the Molecular weight $M$ of the particle. Hence, larger particle or particle with larger molecular weight will scatters more light or have larger Rayleigh ratio. Therefore it is reasonable to assume that the scattering from the aggregates would be larger than that from the free chains. Secondly, assuming that the virial coefficient $B$ is very small number, there is also a direct relationship between the Rayleigh ratio and concentration. Therefore even in the dilute regime, higher concentration solution will have larger scattered intensity or Rayleigh ratios.

In the static light scattering, the light scattered is from large colloidal particles in a solution. Therefore the equation for the scattered light from the Rayleigh equation needs an
extension to include intraparticle interference effects due to the size and structure of the particles. This is achieved by adding an interference factor \( P(\theta) \)

\[
\text{Equation 18} \quad \frac{1}{P(\theta)} = 1 + \frac{1}{3} R_g^2 Q^2
\]

Therefore the final expression for the Rayleigh scattering in static light scattering becomes

\[
\text{Equation 19} \quad R_\theta = \left( \frac{Kc}{1/M + 2Bc} \right) \left( \frac{1}{1 + \frac{1}{3} R_g^2 Q^2} \right)
\]

Taking the inverse of Equation 19,

\[
\text{Equation 20} \quad \frac{Kc}{R_\theta} = \left( \frac{1}{1/M + 2Bc} \right) \left( 1 + \frac{1}{3} R_g^2 Q^2 \right)
\]

Equation 20 is called the Zimm expression. The Zimm expression is used to evaluate the radius of gyration of the free chains and aggregates in the micellar solution. The Rayleigh ratio or the excess Rayleigh ratio at a given angle \( \theta \) in the above Equation 20 is measured experimentally as shown in equation 14.

From equation 17, the Rayleigh scattering of a sample \( R_\theta(\text{sample}) \) with a fixed distance \( r \) is

\[
R_\theta(\text{sample}) = \frac{i_\text{sample}}{I_o} * r^2 \text{ and the Rayleigh scattering of a known solvent, toluene is}
\]

\[
R_\theta(\text{toluene}) = \frac{i_{\text{toluene}}}{I_o} * r^2 \]. Dividing both equation, \( \frac{R_\theta(\text{sample})}{R_\theta(\text{toluene})} = \frac{i_\text{sample}}{i_{\text{toluene}}} = \frac{I_s}{I_{\text{toluene}}}
\]

Therefore the excess Rayleigh scattering of a sample is
Equation 21 \[ R_g(\text{sample}) = \frac{I_z}{I_{\text{toluene}}} \times R_g(\text{toluene}) \]

Rayleigh scattering from a pure toluene is \(1.4 \times 10^{-5} \text{cm}^{-1}\). According to the Zimm expression, the plot of inverse Rayleigh ratio \(1/R_g\) versus the scattering angle square \(Q^2\) at a given concentration should be linear and the radius of gyration can be evaluated from the slope and vertical intercept of this linear plot. The linear expression is clearly represented in the rearranged Zimm expression in equation 21.

Equation 22 \[ \frac{1}{R_g} = \left(\frac{1}{M} + \frac{2Bc}{Kc}\right) + \left(\frac{1}{M} + \frac{2Bc}{Kc}\right) \left(\frac{1}{3} R_g^2 Q^2\right) \]

From this equation, the slope is \(\frac{1}{M} + \frac{2Bc}{Kc}\left(\frac{1}{3} \frac{R_g^2}{Q^2}\right)\), the Vertical-intercept is \(\frac{1}{M} + \frac{2Bc}{Kc}\), hence \(R_g = \sqrt{3 \left(\frac{\text{slope}}{\text{vertical - intercept}}\right)}\).

2.2 Viscometry

Viscosity is the measure of resistance to flow of a fluid. The intrinsic viscosity is inherent to the kind of solute. In a polymer solution, the viscosity is also affected due to swelling, molecular weight and interaction of the polymer chains at high solution concentrations. The viscosity is measured using a capillary viscometer which is calibrated such that the time required for the fluid to flow through the capillary tube is proportional the viscosity of the fluid. In a colloidal solution or liquid containing dispersed particles, the viscosity of a solute or a pure fluid is greatly affected by dispersed particles because more
energy per volume is dissipated to move or rotate the particles in solution. In particular, the intrinsic viscosity changes when the size of the particles in solution changes. This is in keeping with the Stokes-Einstein equation model where in the increase in viscosity can result either from changes in the size or concentration of the particles. In this research, we are trying to understand the transition of polymer chains to aggregation of the block copolymer solution when doped with phosphoric acid through the changes in viscosity. When the block copolymer solution is doped with the acid, micellization or aggregation of chains occurs because the proton binds with the ethylene oxide molecules on the polymer chains.

**Theory**

The flow of a pure fluid passing through a tube is described by Newton’s law of viscosity:

\[
\text{Equation 22 } \frac{F}{A} = \eta \frac{dv}{dy}
\]

where \( \frac{F}{A} \) is the shear rate, \( \frac{dv}{dy} \) is the velocity gradient and \( \eta \) is the viscosity of a fluid. This equation may also be presented as

\[
\text{Equation 23 } \frac{dE_v}{dt} = \eta \left( \frac{dv}{dy} \right)^2
\]

which states that the energy dissipated per volume to move a fluid is proportional to the square of velocity gradient. The principle of Newton's fluid flow is used, through the Poiseuille equation, to evaluate the viscosity of fluid in capillary viscometers. The viscosity is given as follows.

\[
\eta = \frac{\pi r^4 \langle h \rangle \rho g t}{8 V * L}
\]
The above equation can be rearranged and presented as follows,

\[
\eta = \frac{\pi R^4 P}{8 Q L}
\]

Equation 24

Where \( P \) or \( \rho g \langle h \rangle \) is the pressure head forcing the liquid through the capillary with a radius \( r \) and length \( L \) (usually, the hydrostatic pressure of the liquid itself). \( \eta \) is the viscosity of a liquid, \( Q \) is the volumetric flow rate \( \text{cm}^3/\text{s} \) of the liquid with volume \( V \) flowing through the capillary within in given time \( t \). The Ubbelohde viscometer is similar to the capillary viscometer but the bulb volume of the Ubbelohde viscometer is fixed. Thus, the flow rate, \( Q \), is just inversely proportional to the time between marks. \( P \), the hydrostatic pressure is proportional to the density of the fluid. Assuming that the dimensions of the viscometer are constant, the viscosity of a liquid is proportional to the density and time for the liquid to flow through the capillary tube. i.e. \( \eta = K \rho \ast t \). Using the proportionality the equation can be transformed to

\[
\text{Equation 25} \quad \frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} = \eta_{rel}
\]

From Equation 25, one can see that a relative viscosity, \( \eta_{rel} \), is obtained if the viscosity of a liquid is measured relative to another liquid whose viscosity is known (typically the solvent in which the polymer is dissolved or dispersed). Additionally, viscosity of a solution with colloidal sized particles can be measured similarly by comparing with the viscosity of the solvent.

Einstein's model of viscosity of a colloidal solution in dilute region is very similar to the above equation 25. According to the model, in a solution containing solid spherical
particles that are non-solvating and whose concentration is very dilute to the extent that any interaction between particles can be ignored, the viscosity of the colloidal solution is a function of the volume fraction \( \phi \), given by

\[ \text{Equation 26} \quad \frac{\eta}{\eta_0} = 1 + 2.5\phi + k_1\phi^3 + \ldots \]

Where \( \eta \) is the viscosity of the colloidal solution, and \( \eta_0 \) is the viscosity of the solvent.

At very low volume fraction \( \phi \), the third and higher terms become negligible. Hence, the plot of relative viscosity vs. the volume fraction, will show a linear increase of relative viscosity at low volume fraction region, and this region of low volume fraction may corresponds to the dilute or semi dilute region.

At higher volume fraction, the relative viscosity \( \phi \) according to equation 26, is nonlinear. This deviation is due to interaction of particles.

The volume fraction \( \phi \) can be expressed in terms of concentration \( c \) (mass per volume), i.e., \( \phi = c \left( \frac{\bar{V}}{M} \right) \) where \( M \) is the molecular weight and \( \bar{V} \) is the partial molar volume of the particles, respectively. Therefore Equation 26 may be expanded as shown in Equation 27,

\[ \text{Equation 27} \quad \frac{\eta}{\eta_0} - 1 = 2.5 \left( \frac{V}{M} \right) c + k_1 \left( \frac{V}{M} \right)^2 c^2 + \ldots = \eta_{sp} \]

Here \( \frac{\eta}{\eta_0} - 1 \), is the specific viscosity, \( \eta_{sp} \). According to the Einstein model, if the solution contains spherical particles, the slope of the plot of specific viscosity \( \text{versus} \) the concentration should be \( 2.5 \left( \frac{V}{M} \right) \); this value will depend ultimately on the volume and mass of the spherical
particle. If the colloidal particles are either non-spherical or solvating, the value of the slope will deviate in accordance with the shape or solvating characteristic of the particles.

For a solution of flexible polymer chains Equation 27 becomes.

\[
\text{Equation 28 } \frac{\eta}{\eta_0} - 1 = [\eta] c + k_H [\eta]^2 c^2 + \ldots
\]

\([\eta]\) is the intrinsic viscosity and is characteristic of the nature of polymer-solvent interaction, and \(k_H\) is the Huggins' constant. In the very dilute regime, i.e. when \(c \to 0\), the intrinsic viscosity can be evaluated by taking the slope of the plot of specific viscosity versus concentration.

The intrinsic viscosity \([\eta]\) is \(2.5 \left( \frac{V_s}{M_s} \right)\), here \(V_s = \frac{4}{3} \pi * R_h^3 * NA\) is the hydrodynamic volume of the particle and \(M_s\) is the molecular weight of the particles. Assuming that the molecular weight and intrinsic viscosity of the polymer solution is known, the hydrodynamic radius of the particles in the solution can be measured. However, the molecular weights of the block copolymer molecules, especially for the micellized structures remain unknown. Therefore the hydrodynamic radius of the aggregate structures cannot be calculated. While the intrinsic viscosity gives one a measure of the average size of polymer molecules in a solution, the distribution of sizes of particles in solution cannot be evaluated. Thus, viscometry measurements are complementary poor cousins to light scattering.

2.3 Differential Scanning Calorimetry (DSC)\(^{23}\)

DSC is used to measure phase transitions such as melt, crystallization and the glass transition temperatures in the material. The degree of crystallization in the polymeric
material can also be evaluated relative to the thermal history of the material. Phase transitions are measured by comparing the amount of heat supplied to an unknown sample relative to that supplied to a reference sample. The specific heat capacity is an inherent property for each material; hence the amount of heat absorbed or supplied to the material is associated with the molecular and morphological characteristic of the material. In this research, DSC scans were used to evaluate phase transitions in the PS-b-POE block copolymers. Pure block copolymer, block copolymer composites doped with phosphoric acid and block copolymer composites doped with phosphoric acid and neutralized with the base (KOH) to form ionic K⁺H₂PO₄⁻ were studied as a function of the composition of the block copolymer, the level of acid doping, and the thermal history of the materials. In DSC studies were particularly focused on elucidating how the crystallization of potassium hydrogen phosphate nanocrystals was induced and on identification of optimum condition for the formation of crystallization.

**Theory**

Differential scanning calorimetry is used to measure the phase transition in the material by measuring the differential heat transfer required to maintain a material with a given specific heat capacity, Cₚ at the same temperature as a reference. The thermodynamic phase transitions are described by the Gibbs energy \( G = H + TS \) or its first derivative with respect to temperature or pressure, i.e. the enthalpy H, entropy S and the volume V: i.e.

\[
G = H + T \left( \frac{dG}{dT} \right)_P \\
\text{.... first derivative, where } S = - \left( \frac{dG}{dT} \right)_P \text{ and } V = \left( \frac{dG}{dP} \right)_T
\]

In the second derivative of gibbs energy correspondingly lead to heat capacity Cₚ,

\[
C_P = - \left( \frac{dH}{dT} \right)_P
\]
During a phase or thermodynamic transition at a constant pressure, the Gibbs free energy change between phases at equilibrium is zero and is characterized by corresponding changes in these parameters, i.e.

\[ \Delta G = 0 = \Delta H + T \Delta S \quad \text{and} \quad \Delta G = \frac{\Delta H}{\Delta S} = \frac{dH}{dS} \]

The first order thermodynamic transition show a discontinuity in the first derivative of Gibbs free energy with temperature and the second derivative also has corresponding discontinuity. This type of transition is typified by the melting of a crystal.

The second order thermodynamic transition for the second derivative of the Gibbs free energy with temperature show a discontinuity with temperature. However, the first derivative of the Gibbs energy changes continuously with temperature. The second order transition are typified by the glass transition in an amorphous polymeric material.

The specific heat capacity, \( C_p \), at a constant pressure is \( C_p = \left( \frac{dH}{dT} \right)_p \). \( C_p \) is an inherent value for each material and therefore we can measure the phase transition of a material depending on its thermal history and morphology. The power input or the rate of heat transfer \( \frac{dH}{dt} \) supplied to the material is adjusted to keep the temperature constant. The difference in the heat capacity between the reference pan and the sample pan is used to measure the heating rate and time required to maintain a constant temperature, i.e.,

\[ T = T_0 + R \cdot t \]

\( T \) is the temperature at a given time \( t \), \( R \) the rate of heat supplied.

Therefore, \( \frac{dT}{dt} = R \) and the

\[ \text{Equation 29} \quad \frac{dH}{dt} = m \left( \frac{dH}{dT} \right)_p \cdot \frac{dT}{dt} = m \cdot C_p \cdot R \]
From the above equation the DSC signal or the heat supplied to a material of a given mass, \(m\), is a function of its heat capacity, \(C_p\) and heating rate, \(R\) at a given temperature, \(T\). During the thermodynamic transition, the specific heat capacity changes discontinuously for a second order transition (glass transition) and increases abruptly to a maximum for a first order transition (melting or crystallization). In the DSC scans, these changes are seen as changes in the amount heat supplied or removed from the material at a given rate at a particular temperature. This temperature is the melting, crystallization or glass transition temperature of the material.

CHAPTER 3
EXPERIMENTAL DESIGN AND SAMPLE PREPARATIONS

3.1 Material and Sample Preparation

3.1.1 Synthesis of PS-b-POE block polymer

PS-b-POE block copolymer was prepared by living anionic polymerization in tetrahydrofuran by Yijun Ye\(^\text{24}\) during the course of his PhD studies with T. W. Smith at the Xerox laboratories. Details of the synthesis can be found in Ye’s PhD thesis. The synthetic procedure was analogous to that employed by O’Malley and Marchessault.\(^\text{25}\) In the synthesis of PS-b-PEO diblock copolymers, the polystyrene (PS) block segment was synthesized first by living anionic polymerization using diphenylmethyl potassium initiator. Ethylene oxide was then added in different portions to vary molecular weight of the polyethylene oxide (PEO) segments. Prior to adding the ethylene oxide, the molecular weight and polydispersity of the polystyrene segments were characterized by gel permeation chromatography (GPC). After the synthesis of the block copolymer, the polyethylene oxide content was determined,
on the basis of relative integration of phenyl hydrogen atoms in the polystyrene blocks to all
the hydrogen atoms in the polyethylene oxide block, using $^1$H NMR.

3.1.2 Solution Preparation: Light Scattering & Viscometry

3.1.2.1 Selection of block polymers

PS-b-PEO block copolymers containing 11, 33 and 51 mole % ethylene oxide were
employed in the light scattering and viscometry studies. The number average molecular
weight of the PS segment was ~60,000 g/mole. The polydispersity of the block copolymers
was ≤ 1.3. Each of the three block polymer solutions was prepared with NO ACID and 10,
20 and 50 mole% H$_3$PO$_4$ relative to molar concentration of ethylene oxide residues. At a
given acid doping level, solutions ranging in concentration from 0.04g/mL to 0.001g/mL
were prepared for each of the three block copolymers. Accordingly a matrix of twelve
different copolymer acid-free and acid doped block copolymers compositions (outlined in the
Table 1, below) were analyzed.

The following table summarizes each case of the three block copolymer solutions at
different acid doping.

Table 1 – Block copolymer solution compositions

<table>
<thead>
<tr>
<th>Ethylene oxide content of block copolymers</th>
<th>H$_3$PO$_4$ Doping Level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO Acid</td>
</tr>
<tr>
<td>11mole%</td>
<td>11mole%</td>
</tr>
<tr>
<td>33mole%</td>
<td>33mole%</td>
</tr>
<tr>
<td>51mole%</td>
<td>51mole%</td>
</tr>
</tbody>
</table>
3.1.2.2 Solution Preparation

A stock solution of 5wt%/Vol (0.05g/mL) of block copolymer was prepared in 8:2 volume ratio of toluene: dimethoxyethane (DME) solution. Solutions were heated at 60°C for several minutes to ensure complete dissolution of crystalline POE polymer segments. The stock solutions were then doped with the requisite amount of 1 molar phosphoric acid solution in dimethoxyethane solvent. Solutions turned hazy momentarily upon adding the acid and soon became transparent upon rigorous shaking. All solutions were filtered through a 1-μm glass filters before further dilution.

The stock solution (0.05g/mL) was further diluted by using (80/20 Vol/Vol) toluene/DME stock solvent to concentrations ranging from 0.04g/mL to 0.001g/mL. Approximately 3-5mL of each concentration solution was filtered again with 1-μm glass filter before adding them into 12-mm round glass cells for light scattering experiments. Similarly for the viscometry, the acid doped stock solution was filtered prior to putting them in the Ubbelohde dilution viscometer. Then for the viscosity measurements at each concentration, the solutions were diluted by adding requisite amount of filtered stock solvent. Before taking any measurements from both the light scattering and viscometry experiments, the solutions were preheated to 60°C for at least five minutes to ensure complete dissolution of crystalline POE polymer segments and the solutions were then allowed to gradually cool and maintained at a temperature of 30°C during the experiment.

3.1.3 PS-b-PEO/K⁺H₂PO₄⁻ Solution

Phosphoric acid doped block polymer solutions from the stock (The 5wt%/Vol (0.05g/mL) were neutralized with requisite amount of 1 molar potassium hydroxide (KOH) in methanol. Upon neutralization, the solution turns milky momentarily and then translucent
upon thorough mixing. The solution were then rigorously agitated on a vortex mixture, and then centrifuged to remove any macroscopic particles. The solution was decanted from the centrifuge tube and filtered through a 1-μm glass filter. We found that the neutralized solutions were unstable over time. A dense milky solution was formed within three hours and macroscopic crystals were observed after few days of time. Light scattering and viscometry studies were therefore not performed on the neutralized solutions. Promptly after neutralization (within an hour) the filtered solutions were cast on glass slides. Films for differential scanning calorimetry (DSC) experiments were puddle cast and films for the atomic force microscopy (AFM) measurements were spin cast.

### 3.1.4 Film preparation: DSC

Films for the differential scanning calorimetry were prepared from neutralized block polymer solution in toluene/DME as described in Section 3. The neutralized solution of 0.05g/mL concentration was puddle cast on microscope glass slides and dried at 50°C overnight. The heat treatment or annealing of the films was done on the hot plate covered with a glass vessel with a steady flow of inert gas (nitrogen, argon) to suppress the possible oxidative degradation of PEO. Some films were annealed in vacuum. In order to prevent any possible reaction of acid with Al, gold-coated Aluminum pans were used in the DSC experiments.

### 3.1.5 Film preparation: AFM

Films for the atomic force microscopy were spin coated using a resist coater on a 1” x 1” microscope slide cover. A neutralized stock solution at a concentration of 0.05g/mL was prepared as described earlier in Section 3, and was subsequently diluted to 0.02 g/mL for the
spin coating. This concentration of 0.02g/mL was necessary for AFM measurements that resulted in films with thickness less than 200 nm which gave better sensitivity of AFM scans. Spin casting the stock solution concentration of 0.05 g/mL gave films thickness ~800nm measured from the profilometer. The heat treatment (thermal history) of the films prepared for AFM measurements was thermal history of thicker films studied by differential scanning calorimetry.

3.1.6 AFM measurements

Atomic Force Microscopy measurements were done using the Asylum Research corporation MFP-3D-CF combined confocal/Atomic Force Microscopy instruments. The AFM scans were taken using non contact mode, Force and tapping mode to get height and phase contrast images of the surface morphology of the material. The phase contrast images contrasted the soft and hard areas on the material by either attractive or repulsive forces on the tip. The soft regions or sticky surfaces were the polymeric and hard the or repulse to the tip were inorganic material.

Platinum coated tips were used for the Force and tapping mode AFM graphs which seemed to work well without sticking or contaminating material.

3.2 Instrumental set up

3.2.1 Light Scattering

The dynamic and static light scattering experiments were performed using a Brookhaven Instruments BI-200SM goniometer equipped with a 35mW, vertically-polarized Model 127 Spectra-Physics He-Ne Laser (wavelength, \( \lambda = 632.8\text{nm} \)) and an EMI-9863 photomultiplier. All polymer solutions were contained in 12mm round glass cells that were
immersed in decahydronaphthalene index-matching fluid. Measurements for the light scattering were performed at 30 ± 0.2°C using a water bath and at scattering angles of 30 to 150 degrees. Photon statistics for the dynamic light scattering were performed using a BI-9000AT digital autocorrelator. The delay time of 2μ seconds were taken at medium speed on the digital autocorrelator (80 channels) to record the photon counting. For each solution, the measurements were taken for at least three (3) minutes for a reasonable statistical purpose.

The autocorrelation data’s used in the autocorrelation graphs in the results sections are basically the normalized autocorrelation graphs because the raw autocorrelation data’s are divided by the average intensity or the baseline minus one and the divided by the fudge factor, $C(t) = B\left(1 = f|g^{(1)}(t)|^2\right)$, therefore $|g^{(1)}(t)|^2 = \frac{1}{f} \left(\frac{C(t)}{B} - 1\right)$.

In the static light scattering, the total photon counts were taken within a time period of five seconds at each angle for five times and then averaged. The intensity of the scattered light was calculated by taking the average of the photon count in 5 sec (counts per seconds). The Excess Rayleigh ratio was calculated according to the equation 14 in the theory section.

Because of nonlinearity with the concentration, it was not possible to measure the refractive index increments, dn/dc. Accordingly, the dn/dc value was set to 1.0 for all static light scattering experiments.

### 3.2.2 Viscometry

Viscometry experiments were performed using size 50 and 75 Ubbelohde dilution viscometer. All the viscometers were cleaned with chromic acid and rinsed with the solvent prior to use. The experiment temperature was set to 30°C by placing the viscometer in a glass constant temperature bath that was regulated with a water flow at 30±0.5C. For each block
copolymersolutionseries, the stock solution of 0.05g/mL doped with requisite amount of acid was filtered with 1-μm glass filters and placed in the viscometer. Dilution was done by adding requisite amount of solvent in the viscometer and allowing 15 minutes to stabilize the temperature. The flow time measurements were taken using a digital stop watch at least three times for each concentration. The errors within the measurements were less than 0.2%. The density increment was measured for the three block polymer solution at different acid doping and correction of this was included in the calculated values of viscosity. Viscosity of the solvent and toluene were determined relative to the viscosity of water at 30°C.

### 3.2.3 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out with TA Instruments DSC 2010 calorimeter. We used gold coated pans to prevent the concentrated phosphoric acid to react with Aluminum. Samples were typically subjected to a heating and cooling protocol that consisted of

1. heating the sample to 60°C, 5min hold time
2. cooling to -60°C,
3. heating to 200°C, 10min hold time
4. cooling to -60°C, and
5. heating to 260°C at heating and cooling rates of 10°C/min.

The nitrogen flow rate for purging was set to 50 ml/min.
CHAPTER 4
RESULTS

4.1 Dynamic light Scattering

Characteristic relaxation times for each solution concentration at various scattering angles were recorded to measure the diffusion coefficients. Figures 6 (a-d) show plots of autocorrelation functions for 0.02g/mL solution of 33mole% PEO block polymer at different acid doping levels.

**Figure 6 a-d** Autocorrelation versus time graphs for 33% PEO block polymer
The autocorrelation functions graphs for all the acid dopings (except the 10mole% acid) show curves that resemble to sigmoid shaped curves. In actuality, the autocorrelation decay curves are exponential when plotted in linear scale. However, these graphs are plotted on a semi logarithm axes which give a sigmoid shape to the exponential curves. Therefore the sigmoid corresponds to a single exponential decay or distribution of single size particles. In the 10mole% doped acid solution, the autocorrelation function curve similarly resembles to a bimodal shaped curve on the semi logarithm scale. This corresponds to a distribution or a double exponential decay curves when plotted in linear scale or solution containing distribution of two distinct sizes of particles.

When plotting the autocorrelation function as a function of $Q^2t$ for the 33%PEO block polymer (see Figure 7 (a-d)), we clearly see that the autocorrelation graphs for the solution with NO ACID at various scattering angles collapses to a single curve, suggesting that particles in these solutions are simple diffusing particle. However, for the 20% and 50% acid doping, the curves are compressed but not collapsing perfectly to a single curve. Similarly, the 10% acid doping, various scattering angle curves also compress but do not collapse perfectly to a single bimodal distribution curve. This could possibly be because these solutions are in a semi-dilute region where interaction between the particles such as chain entanglement is significant.
Similar trends are observed for the curves in the 11%PEO block polymer system. The autocorrelation curves are sigmoid shaped for all acid doping (Figure 8a-d). When graphed against Q^2t, all the curves at different angles collapses to a single line (Figure 9a-b) suggesting the particles in these solution are simple diffusing particles.
Figure 8 a-d: Autocorrelation versus time graphs for 11% PEO block polymer.
Autocorrelation graphs for the 51% PEO block polymers were also similar in most respects, i.e., all the autocorrelation function decay curves show sigmoid shape decay curves and bimodal distribution curves for 10 mole% acid (see Figure 10 a-d). However, when plotting the graphs with $Q^2t$, the solution with NO ACID and 10 mole% acid do not collapse to a single line (Figure 11 a-b) and the 20 and 50 mole% acid (Figure 11c-d), the curves
show substantial collapsing after delay of $10^{13}$ s/cm². This suggests that in these solution, the particles are not simple diffusing particles.

---

**Figure 10 a-d** Autocorrelation versus time graphs for 51% PEO block polymer.
The graphs in Figure 12 -14 are plots of normalized intensity versus the inverse characteristic relaxation times (Gamma $\Gamma$ sec$^{-1}$) from the CONTIN algorithms analysis. The normalized intensity is the each intensity divided by the area under the curve from the CONTIN histograms.

In these graphs the transition of the copolymer chains of a molecularly dissolved state to an aggregated or micellized state as a function of concentration and the level of acid
doping is displayed. The size of the entities in solution is reflected by the position of the histogram peaks on the scale of inverse characteristic relaxation times, Gamma.

In all the three block polymers solutions with NO ACID, there is a single peak at all the solution concentrations (low to high), and the peaks are positioned at higher relaxation times (between 4-5 on Log scales) that correspond to a fast diffusion coefficient. In comparison to the solution with NO ACID, the solution of 20 and 50 mole% doped acid also shows single peaks at all concentrations (low to high). However, the peaks in these solutions are positioned at lower relaxation times (2-3 on log scale) which correspond to a slow diffusion coefficient. The change in position of the intensity peaks on the log scale indicate that there is a shift from a fast to slow diffusion coefficient in solution from NO ACID to solution with 20 and 50 percent acid. In other words, there is a significant increase in size of particles in these acid doped solutions relative to the solution with NO ACID. The change in size from NO ACID to high acid doping could reasonably be due to the transition of free chains to complete aggregation of free chains due to complexation of POE segments with the phosphoric acid.

In the solution of 10mole% acid in all the three block polymers, a single peak is observed at very low concentrations (0.002 to 0.003 g/mL) and is located at higher relaxation times (4-5 on Log scale) corresponding to a fast diffusion coefficient. At slightly higher concentrations (0.01g/mL), we notice an emergence of another peak at lower relaxation times and gradual diminishing of the peak at higher relaxation times. Such complementary formation of one peak and diminishing of another peak from lower to higher concentration could be an indication of the transition of the polymer free chains towards aggregation. At higher concentrations in this solution, two well formed peaks located at low and higher
relaxation times are observed; suggesting that in the 10mole% acid solution, there are two translational diffusion coefficients (fast and slow) for two distinct particle sizes, i.e. very small and large particle sizes.

One exception is for the 11% PEO block polymer solution with 20 and 50 mole% acid doping. In these solutions, even at higher acid doping, we still observe a fast relaxation peak, although the fraction of intensity from these peaks are relatively very small. This may be because of a relatively small segment of the Poly ethylene oxide of the block polymer.

Figure 12: 11%PEO block polymer (theta = 90)
Figure 13: 33%PEO block polymer (theta = 90)

Figure 14: 51%PEO block polymer (theta = 90)
The effective translation diffusion coefficient for each concentration was determined from the plot of inverse characteristic relaxation times $\Gamma$ versus scattering vector $Q^2$. Using the spectral line width equation, the effective diffusion coefficient, which is the slope (through the origin), is estimated. Figures 15 a-d displays plots of $\Gamma$ vs $Q^2$ for the 33 mole% block copolymers at varying levels of acid doping. In the case of a 10 mole% solution, two relaxation times are graphed on the same graph and two diffusion coefficients are estimated.

**Figure 15 a-d:** Effective diffusion coefficient (Inverse characteristics relaxation times verses Q square) for 33% PEO block polymer
The diffusion coefficient at infinite dilution is estimated at zero concentration or the vertical-intercept from the graph of diffusion coefficients at various concentrations as shown in figure 16 for the 33% PEO block polymers.

**Figure 16 a-d:** Characteristic diffusion coefficient at infinite dilution for all Acid concentration of 33% PEO block polymer.
Graphs for the Characteristic diffusion versus concentrations for the 11 and 51% PEO block polymer to measure the diffusion coefficient at infinite dilution is shown in the appendix i. The diffusion coefficients at infinite dilution were used to determine the hydrodynamic radius of the particles using the Stokes-Einstein equation. The size of the particles measured in the solution with NO ACID closely matched with the particles with the fast diffusion coefficient in the 10 mole% ACID doped solution. This confirms our understanding that the presence of two peaks in the 10 mole% solution is because of large particles due to the aggregation of polymer chains and the small particles that were due to free polymer chains. The hydrodynamic radius of the micelles are calculated using the Stokes-Einstein equation and are shown in the table below.

**Table 2: Hydrodynamic radius**

<table>
<thead>
<tr>
<th>PEO segments</th>
<th>NO Acid</th>
<th>10 mole% Acid</th>
<th>20 mole% Acid</th>
<th>50 mole% Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>11mole% 53K_b_3K</td>
<td>7.7±0.5nm</td>
<td>5.6±0.2nm</td>
<td>46.9±1.4nm</td>
<td>45.6±2.2nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44±3.6nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33mole% 58K_b_12K</td>
<td>6.2±0.3nm</td>
<td>7.8±0.4nm</td>
<td>79.7±3.3nm</td>
<td>56±1.2nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>242±28nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51mole% 53K_b_28K</td>
<td>8.1±0.9nm</td>
<td>6.1±0.6nm</td>
<td>84.4±2.2nm</td>
<td>61.2±0.9nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>449.5±14.5nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values for the hydrodynamic radius for the 10 mole% acid doped solution are huge compared to than the $R_H$ values of the 20 and 50% acid doped solution. This is certainly an exception observed for all the three block polymer series at this acid doping. It is possible
that the large values of $R_H$ may be because solution is in the semi dilute region instead of dilute region.

The overlap concentration $C^*$ that defines boundary between dilute and concentrated region is proportional to $M^{-0.764}$ for polymer molecules at theta condition in good solvents. Taking the $M$ value $\sim 80K$ for all the three block polymers, $C^*$ concentration of $\sim 0.0001778$ g/ml in the dilute region. Hence all the solution in the DLS experiments, including the smallest concentration of 0.001g/mL is in either semi dilute or concentrated region where the interaction between the neighboring particles significant significant. Hence the diffusion coefficient and the hydrodynamic radius calculated using of Stokes-Einstein equation may not be applicable. This could be the reason for a huge $R_H$ values for the 10 mole% acid doped solution.

4.2 Static Light Scattering

In Figures 17-19, the excess Rayleigh ratio for each block polymer solution is plotted as a function of solution concentrations for the copolymers containing 11, 33 and 51 mole % POE doped at varying levels with acid. For solutions doped with 10 mole% acid, in which DLS analysis indicated the presence of fast diffusing and slow diffusing entities, the excess Rayleigh ratio for the fast and slow diffusion entities are calculated by multiplying the total intensity with the normalized area under each peak from the CONTIN functions.
Figure 17 a-d: Excess Rayleigh ratio versus Concentration for 11% PEO block polymer
Figure 18 a-d: Excess Rayleigh ratio versus Concentration for 33% PEO block polymer.
These graphs in Figures 17, 18 and 19 for the three block copolymers clearly show that the excess Rayleigh scattering by solutions with NO ACID and the fast diffusing component in the 10 mole% doped acid solutions in each of these block copolymers are relatively the same. In other words, same Rayleigh scattering from these two solutions could
be the particles in these solutions have similar sizes (polymer free chains). Also, at very low concentration in 10 mole% acid doped solution, the excess Rayleigh ratio for the aggregation is almost zero, suggesting that there is no aggregation at very low concentration in the 10 mole% acid solution.

For the solution of 20 and 50 mole% doped acid solution in all the three block polymers, the Excess Rayleigh values are much higher than that of solution with NO ACID and 10 mole% ACID. High Rayleigh scattering in the 20 and 50% acid doping can be reasoned due to formation of larger particles or aggregation in the solution relative to the free copolymer molecules in solution with NO acid and 10% acid. Secondly, when comparing the scattering produced by the three block polymers for 20% and 50% acid doping, the excess Rayleigh scattering values increase accordingly with the PEO segment of the block copolymer. The Rayleigh scattering values (vertical axis) are highest for the 51% PEO block copolymer, followed by the 33% PEO block copolymer series and then lowest for 11% PEO block polymer series. The PEO content in the block copolymer determines the amount of acid it can hold in the core of the micelle. Therefore the larger PEO segment block copolymer will have a larger micelle core. The 51% PEO block copolymer have the highest Rayleigh scattering because it forms a larger micelle core than the 33 and 11% PEO block copolymer.

Another interesting observation is that the scattering in the 20% and 50% doped acid solution does not increase continuously relative to increasing solution concentration. The scattered intensity decreases at higher concentration, especially for the 50% acid doped solution after 0.01 g/mL for all the three block polymers. This is because of the interaction of the particles or aggregation at this higher concentration.
Because of the interaction between particles, the radius of gyration of the individual entities (macromolecules or aggregates of macromolecules) is perturbed at higher concentrations. The unperturbed radius of gyration is therefore better reflected in the plateau radius of gyration at lower concentrations. According to the Zimm expression, as discussed in the theory section of SLS, the radius of gyration is calculated by taking the square root of the slope over the vertical-intercept. Therefore both the slope and the vertical-intercept have to be a positive value to measure the radius of gyration. The graph in Figures 20 - 22, display plots of the inverse Rayleigh ratio (1/R₀) versus square of the scattering angle, Q², for the three block polymers doped at 20% and 50% acid at various concentration for measuring the radius of gyration. At low concentrations the plots give positive slopes and vertical-intercepts to measure the radius of gyration. However, at higher concentration (0.01g/mL and above), especially for the 50% acid either the slope or the vertical intercept are negative due to interaction of the particles at these concentration and therefore the radius of gyration cannot be calculated.
Figure 20 a and b: Inverse Rayleigh ratio versus $Q^2$ for 11% PEO block polymers (20% and 50% acid doped solution)

Figure 21 a and b: Inverse Rayleigh ratio versus $Q^2$ for 33% PEO block polymers (20% and 50% acid doped solution)

Figure 22 a and b: Inverse Rayleigh ratio versus $Q^2$ for 51% PEO block polymers (20% and 50% acid doped solution)
From the graphs of inverse Rayleigh ratio and $Q^2$, the slope and vertical intercepts were used to calculate the radius of gyration of the aggregates at different concentration. Comprehensive data for evaluation of hydrodynamic radii for all block polymer solutions is provided in Appendix i. The Table 3 summarizes the values of radius of gyration for all three block polymer at different concentrations.

Table 3: Radius of gyration

<table>
<thead>
<tr>
<th></th>
<th>10% Acid</th>
<th>20% Acid</th>
<th>50% Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>11% PEO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>53K_b_3K</strong></td>
<td>0.02g/mL Rg = 28nm</td>
<td>0.02g/mL Rg = 13nm</td>
<td>0.005g/mL Rg = 18nm</td>
</tr>
<tr>
<td></td>
<td>0.01g/mL Rg = 25nm</td>
<td>0.01g/mL Rg = 30nm</td>
<td>0.004g/mL Rg = 22nm</td>
</tr>
<tr>
<td></td>
<td>0.005g/mL Rg = ?</td>
<td>0.005g/mL Rg = 37nm</td>
<td>0.003g/mL Rg = 32nm</td>
</tr>
<tr>
<td></td>
<td>0.004g/mL Rg = 47nm</td>
<td>0.004g/mL Rg = 35nm</td>
<td>0.002g/mL Rg = 32nm</td>
</tr>
<tr>
<td></td>
<td>0.003g/mL Rg = 31nm</td>
<td>0.003g/mL Rg = 36nm</td>
<td>0.001g/mL Rg = 27nm</td>
</tr>
<tr>
<td></td>
<td>0.002g/mL Rg = 58nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>33% PEO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>58K_b_12K</strong></td>
<td>0.02g/mL Rg = 74nm</td>
<td>0.03g/mL Rg = 45nm</td>
<td>0.01g/mL Rg = 25nm</td>
</tr>
<tr>
<td></td>
<td>0.01g/mL Rg = ?</td>
<td>0.02g/mL Rg = 42nm</td>
<td>0.005g/mL Rg = 35nm</td>
</tr>
<tr>
<td></td>
<td>0.005g/mL Rg = ?</td>
<td>0.01g/mL Rg = 49nm</td>
<td>0.004g/mL Rg = 43nm</td>
</tr>
<tr>
<td></td>
<td>0.004g/mL Rg = 575nm</td>
<td>0.005g/mL Rg = 62nm</td>
<td>0.003g/mL Rg = 41nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.004g/mL Rg = 70nm</td>
<td>0.002g/mL Rg = 44nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.003g/mL Rg = 70nm</td>
<td>0.001g/mL Rg = 52nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002g/mL Rg = 89nm</td>
<td></td>
</tr>
<tr>
<td><strong>51% PEO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>53K_b_28K</strong></td>
<td>0.03g/mL Rg = 1460nm</td>
<td>0.03g/mL Rg = 70nm</td>
<td>0.01g/mL Rg = 35nm</td>
</tr>
<tr>
<td></td>
<td>0.02g/mL Rg = 265nm</td>
<td>0.02g/mL Rg = 84nm</td>
<td>0.005g/mL Rg = 50nm</td>
</tr>
<tr>
<td></td>
<td>0.01g/mL Rg = 409nm</td>
<td>0.01g/mL Rg = 88nm</td>
<td>0.004g/mL Rg = 53nm</td>
</tr>
<tr>
<td></td>
<td>0.005g/mL Rg = 205nm</td>
<td>0.005g/mL Rg = 97nm</td>
<td>0.003g/mL Rg = 55nm</td>
</tr>
<tr>
<td></td>
<td>0.004g/mL Rg = 353nm</td>
<td>0.004g/mL Rg = 122nm</td>
<td>0.002g/mL Rg = 59nm</td>
</tr>
<tr>
<td></td>
<td>0.003g/mL Rg = 133nm</td>
<td>0.003g/mL Rg = 144nm</td>
<td>0.001g/mL Rg = 61nm</td>
</tr>
<tr>
<td></td>
<td>0.001g/mL Rg = 409nm</td>
<td>0.002g/mL Rg = 196nm</td>
<td></td>
</tr>
</tbody>
</table>
The $R_g$ for molecularly dissolved polymer chains could not be measured because of limitations of the wavelength of the incident light used in our SLS experiment. Ideally, to measure the $R_g$'s of free chains, which are typically less than 10 nm, the wavelength of incident light should not be greater 200nm. Figures 23 a-c are graphs of radius of gyration versus concentration obtained from solutions of all the three block polymers doped with 20 mole % acid. From these graphs we see that the $R_g$ values tend to plateau at high and low concentrations. Unperturbed chain dimension are best reflected at the lower concentrations.

<table>
<thead>
<tr>
<th>Radius of gyration versus Concentration</th>
<th>Radius of gyration versus Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>11% PEO block polymer with 20% ACID</td>
<td>33% PEO block polymer with 20% ACID</td>
</tr>
<tr>
<td>$R_g = 46.9$nm</td>
<td>$R_g = 79.7$nm</td>
</tr>
</tbody>
</table>

a.) 11%PEO block polymer solution   b.) 33%PEO block polymer solution
c.) 51%PEO block polymer solution with 20% acid

**Figure 23 a-c:** Radius of gyration (nm) *versus* concentration g/mL for copolymer solutions doped with 20% acid

### 4.3 Viscometry

Results from the show that there is significant deviation from linearity in plots of specific viscosity *versus* concentration when the copolymer solutions are doped with phosphoric acid. Figure 24 a-c displays these graphs for all the three block copolymers in the undoped state and doped with 10, 20 and 50 mole % acid.
Figure 24a-c: Specific viscosity for 11%, 33% and 51% PEO block copolymer solutions

The plots of specific viscosity versus concentration for block copolymer solutions deviate from linearity at concentrations in excess of above 0.01 g/mL. The overlapping concentration C* which defines the dilute, semidilute and concentrated regions can be approximated as follows $C^* \sim M^{0.764}$, based on the molecular mass of the block copolymers.
(~80,000 g/mol), C*~0.000178g/mL in dilute region. Therefore even at the lowest concentration of 0.001g/mL where we see a linear increase of specific viscosity, the solution concentration is not in the dilute region, instead is in the semi dilute region where there is sufficient interaction between the particles such as chain entanglements.

The C* values can also be approximated using the intrinsic viscosity values. The semi-dilute region is reached when \(C^* \geq \frac{1}{[7]}\). In the semi-dilute region there is an onset interaction between copolymer molecules.

From the measured intrinsic viscosities, the \(C^* \geq 0.02g/mL\) would be in the semi-dilute regime. However, light scattering results in our solutions shows the semi-dilute regime occurred at concentrations less than 0.02g/mL concentration.

According to the Einstein model, nonlinearly is observed above certain volume fraction due to overcrowding or interaction between particles. This is consistent with the static light scattering results too where solution above 0.01g/mL, especially for the 50% acid doped solution we observed reduction in intensity due to the interaction between the particles.

On the other hand, the viscosity of the concentrations less than 0.005g/mL concentration are linearly increasing as expected at low volume fraction in the Einstein model. Values in this linear region were used to measure the intrinsic viscosity for each block copolymer series.

The viscosity for all three block polymer is higher at 50% acid doping compared to that of solution with NO ACID. The increase in viscosity is due to full micellization of block copolymer molecules at 50% acid doping as confirmed from the light scattering experiments.
The viscosity is a function of the volume fraction of the particles according to the Einstein model of viscosity. The increase in viscosity at 50% acid doping is because the volume fraction of the copolymer chains in aggregates is larger than copolymer chain itself in the solution with NO ACID.

However, for solution with NO Acid, 10% acid and 20% acid with respect to the three block polymer with different PEO composition remain inconclusive. The trend of changes in viscosities for the three block polymer in these acid doping are not consistent or not increasing for all the three block copolymer at increasing acid doping. Explanation for such trend is quite complex and the simple models such as Einstein model may not be sufficient to know the reasons.

The measurement for the intrinsic viscosities for each block polymer solution was done by taking the slope, in the linear or dilute region of the viscosity changes, as described in the theory section. Comprehensive data and graphs of viscosity are provided in Appendix ii. Table 4 summarizes the intrinsic viscosity for all three block polymer solutions in the acid free state and doped at 10, 20 and 50 mole %.

**Table 4: Intrinsic viscosity**

<table>
<thead>
<tr>
<th></th>
<th>NO ACID</th>
<th>10% Acid</th>
<th>20% Acid</th>
<th>50% Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>11% PEO 53K_b_3K</td>
<td>53.8 ± 0.5 mL/g</td>
<td>51.2 ± 0.2 mL/g</td>
<td>50.6 ± 0.7 mL/g</td>
<td>58.3 ± 0.8 mL/g</td>
</tr>
<tr>
<td>33% PEO 58K_b_12K</td>
<td>53.1 ± 1.6 mL/g</td>
<td>51.6 ± 0.3 mL/g</td>
<td>49.4 ± 0.5 mL/g</td>
<td>48.6 ± 0.5 mL/g</td>
</tr>
<tr>
<td>51% PEO 53K_b_28K</td>
<td>52.7 ± 0.5 mL/g</td>
<td>53.3 ± 0.4 mL/g</td>
<td>49.6 ± 0.4 mL/g</td>
<td>43 ± 0.4 mL/g</td>
</tr>
</tbody>
</table>
4.4 Differential Scanning Calorimetry

Phosphoric acid doped polymer solutions were cast on microscope slides and dried @50C. DSC scans for these films generally reflect that there is some kind of complexation of the phosphoric acid with the ethylene oxide molecules as confirmed from the light scattering experiments. This conclusion is inferred from the reduced intensity and area of the endotherms associated with the melting of crystalline poly(ethylene oxide) in the copolymers containing 33 and 51 mole % PEO and doped with 20 and 50 mole% phosphoric acid at as compared to that in the copolymers that were free of acid. Figures 25-27 show DSC scans for the three block polymers doped with 10, 20 and 50 mole % with phosphoric acid.

In the copolymer containing 11 mole% PEO, the size and area of the endotherm associated with the melting of crystalline poly(ethylene oxide) is minimal in both the undoped and acid-doped systems. The DSC thermograms also show significant depression of the glass transition of the poly (styrene) phase for the acid doped films (see Figure 25).

In the copolymers containing 33 and 51 mole % PEO, there is a clear inverse relationship between the level of acid doping and % crystallinity of the poly ethylene oxide phase. The literature teaches that phosphoric acid complexes strongly with poly ethylene oxide. Accordingly, it is expected that acid doping will inhibit crystallization. At acid doping levels of 20 and 50 mole%, the DSC thermograms of the copolymer containing 33 mole % PEO (figure 26) show a significant depression of the glass transition of the poly(styrene) phase. For the copolymer containing 51 mole % PEO the glass transition of the poly(styrene) phase is also depressed when doped with 50 mole% acid. When doped at 10 mole% acid, the DSC thermograms of the copolymers containing 33 and 51 mole % PEO both show and enhancement of the glass transition of the poly(styrene) phase. When doped at
20 mole % acid, a modest depression of the glass transition of the poly(styrene) phase is observed for the copolymer containing 51 mole % PEO.

A slight enhancement to depression of the glass transition of poly styrene at different acid doping in the DSC scans could be reasoned as plasticization of styrene molecules in the presence of acid. At smaller acid doping of 10 mole% the styrene molecules may be well separated with the ethylene oxide that slightly enhance the glass transition. At higher acid doping (20 and 50 mole%) the polystyrene is plasticized that results in compression of Tg.

![DSC scans for 11%PEO block polymer](image)

Figure 25: DSC scans for 11%PEO block polymer
Figure 26: DSC scans for 33%PEO block polymer

Figure 27: DSC scans for 51%PEO block polymer
The solutions of the block copolymer containing 33 mole % PEO were doped at 10, 20 and 50 mole % acid and stoichiometrically neutralized with one equivalent of potassium hydroxide. Films of these solutions were prepared by puddle casting on glass slides and dry at 50°C. Figure 28-30 display DSC scans for these neutralized composites.

Figure 28 shows DSC scans for the copolymer doped with 10 mole % acid and neutralized with KOH. In the initial heating scan, one sees a sharp endotherm at about 50°C which is attributed to the melting of a nanocrystalline PEO phase. This is followed by an apparent glass transition at ~75°C and a broad endotherm in the temperature range from 90-150°C that peaks at about 120°C. The glass transition at ~75°C is attributed to a depressed glass transition of a polystyrene phase plasticized by PEO chain segments. The broad endotherm from 90-150°C which might be attributed to the melting of a complex of poly(ethylene oxide) segments with K⁺ and H₂PO₄⁻ ions. The second heating scan shows an enhancement of melting of ethylene oxide and a well-formed glass transition of styrene around 100°C. The broad endotherm center between 90 and 150°C is gone; however, a new endotherm, centered between about 210 and 240 and peaking at about 225°C, has appeared. Handbooks report that crystalline KDP melts, with decomposition, at 256°C. This endotherm might therefore be attributed to the melting of KDP nanocrystals. The appearance of the crystalline endotherm at 225°C, the complementery enhancement of PEO melt peak and the disappearance of the broad endotherm at 90-150°C can be explained as arising from bifurcation of PEO and K⁺H₂PO₄⁻ after melting of this complex.
Figure 28: DSC scans for the neutralized 33%PEO block polymer doped with 10% acid

Figure 29 shows DSC scans for the copolymer doped with 20 mole % acid and neutralized with KOH. In this scan we see that the feature of the first heating scan in Figure 28 is repeated. There is a sharp endotherm at 50C that is the melting of the crystalline poly ethylene oxide nanophases in the material and a depressed glass transition of poly styrene around 60-70C. Also a broad endotherm between 110 to 180C that is attributed to the melting of a complex of poly(ethylene oxide) segments with K+ and H2PO4- ions is seen similar to the one in Figure 28. In the second heating scan, a well formed glass transition of polystyrene is observed at 100C. However a sharp endotherm of crystalline poly ethylene oxide is not enhanced and a new endotherm above 200C attributed to melting of KDP nanocrystal is
absent. The absence of endotherm for the melting of KDP material may be an indication that the KDP material in the composite film has not crystallized.

Figure 29: DSC scans for the neutralized 33%PEO block polymer doped with 20% acid

Figure 30 shows DSC scans for the copolymer doped with 50 mole% acid and neutralized with KOH. In this DSC, similar pattern to the film doped with 20% acid in figure 29 is repeated. However, in the first heating scan we see a large, sharp endotherm which may be due to the poly ethylene oxide molecules complexed with the KDP material. This endotherm is much larger than that is observed in Figure 28 and 29 and this may be because of the presence of larger amount of KDP material for the 50% acid doped and neutralized film.
Figure 30: DSC scans for the neutralized 33%PEO block polymer doped with 50% acid

3.2.4 Atomic Force Microscopy (AFM)

AFM micrographs were taken on ultra thin films, ≤ 200nm, which were obtained, as described in the Experimental Section, 3.1.5, by spin casting solutions on 2 x 2 glass slides. As was also described in the Experimental Section, 3.1.6, force modulation AFM mode was employed to scan the surface morphology of the films doped with the acid and the neutralized films. Phase contrast and topological images were simultaneously acquired thereby allowing PEO and PS phases to be distinguished.\textsuperscript{28} In addition crystallization of KDP within the film was observed. In the force modulation mode, the AFM tip experiences either a repulsive or attractive force depending on the hardness of the surface where the tip makes
contact with the material and changes its original position to form height and phase contrast images. In our films, the soft region usually corresponds to the polymer material and hard the inorganic crystals such as KDP crystals.

A set of 33% PEO block copolymer films were prepared for each synthesis steps to inspect the morphology changes in the material. Figure 31, is the AFM micrograph of 33% PEO block polymer. The phase contrast image shows nanosized structures or domains in the film that are blurred due to poor contrast of the image. Considering the volume ratio or mole% of PEO, the white spots or domains in the film are the ethylene oxide in the film with a continuous polystyrene matrix. Similar nanostructures in the AFM micrographs were observed by Russell Thomas and Spatz and coworkers on PS_b_PEO diblock copolymers films^29,29.

Figure 31: AFM micrograph, left is the height and right is phase contrast image for the 33%PEO block polymer film annealed@150C for 1 hrs.

Figure 32 is the AFM micrograph of 33% PEO block polymer doped with 20 mole% phosphoric acid. A well ordered distribution of spherical phases is observed in the film in
both the height and phase contrast images. These domains correspond to the complex of ethylene oxide bound with the phosphoric acid and the continuous of darker brown area corresponds to polystyrene matrix. The micrograph confirms formation of localized region formed in an ordered array. These domains are expected to act like a nanoreactor where the neutralization reaction would be localized when adding potassium hydroxide. Rieter G, Castelein and Sommer also were able to see similar nanometer sized arrays of poly ethylene oxide crystals through AFM\textsuperscript{30}.

![AFM micrograph](image)

**Figure 32:** AFM micrograph, left is the height and right is phase contrast image for the 33%PEO block polymer film doped with 20 mole% acid and annealed@150C for 1 hrs

Figure 33, is the AFM micrograph of neutralized film of 33% PEO block polymer that is doped with 20% acid and neutralized with KOH and then annealed@150°C for one hour. The micrographs show KDP particles that are randomly dispersed in the film and there is also variability in sizes of the crystals.

This micrograph also indicates that the crystallization of KDP is no longer confined within the PEO domains. One might speculate that at 150°C, a temperature well in excess of the T\textsubscript{g} of the PS matrix, that both the PS and PEO phases will be quite mobile. Moreover, the mobility of molten phases at 150°C allows for diffusion of K\textsuperscript{+} and H\textsubscript{2}PO\textsubscript{4}- ions between PEO
domains. Accordingly, unless nucleation occurs simultaneously with all PEO nanodomains, it will be likely that crystals nucleated early will grow, depleting ions in neighboring PEO domains. The ultimate result will be an inability to confine the crystallization process and substantial polydispersity in the sizes of KDP nanocrystals formed.

Figure 33: AFM micrograph, left is the height and right is phase contrast image for the 33%PEO block polymer neutralized film and annealed@150°C for 1 hrs

Figure 34 is the AFM micrograph of the same material in Figure 33, i.e. 33%PEO block copolymer doped with 20% acid and neutralized but, this film is annealed @ 180°C for 20 min. It can be seen that the heat treatment induces more crystallization of the KDP. Even though the scan is taken in a smaller area, KDP nanocrystals are clearly visible. The white spots are the KDP nanocrystals. That is the white regions in the height image correspond to topologies that correspond to solid particles or topologies in a smooth or flat surface. However, there is a polydispersity in sizes of these crystals and they are not in order or dispersed as expected.
CHAPTER 5
DISCUSSION OF RESULTS

5.1 Light scattering and viscometry

Results from the light scattering and viscometry clearly indicate that block copolymer micelles are formed when solutions of PS/PEO block copolymers in toluene/DME (80/20) vol/vol are doped with phosphoric acid. The aggregation of the copolymer chains is ostensibly a result of protonation of non-bonding electron pairs on ethylene oxide residues in PEO chain segments. In the dynamic light scattering experiments, aggregation of polymer chains was confirmed by the change in characteristic relaxation times or the diffusion coefficient of the particles in acid-free and acid-doped solutions. Diffusion rates of the particles in block copolymer solutions doped with 20 and 50 mole % phosphoric acid were “slow” as compared to those for acid-free copolymer solutions and were indicative of the predominance of micelles whose hydrodynamic radii ranged from about 40-80 nm. Diffusion
rates of particles in solutions containing no acid, were “fast” and were indicative of the presence of particles whose hydrodynamic radii would approximate those of molecularly dissolved copolymer molecules, i.e., 6-8 nm. In block copolymer solutions doped with 10 mole% H₃PO₄, micellization was concentration dependent and characteristic relaxation curves were indicative of solutions containing “fast” and “slow” diffusing species, with the fraction of slow diffusing entities increasing as the concentrations of the solution was increased. In the solutions of block copolymers containing 11 and 33 mole% PEO doped with 10 mole % H₃PO₄, the onset of micellization was observed at concentrations in excess of 0.003 g/ml. In solutions of the block copolymer containing 51 mole% PEO, and doped with 10 mole % H₃PO₄, a critical micelle concentration was not observed.

Our observations relative to the H₃PO₄ induced micellization of PS/PEO block copolymers in toluene/DME solutions are somewhat analogous with the observations of acid-induced micellization of the complexes of polystyrene-\textit{b}-poly(4-vinylpyridine) (PS-\textit{b}-P4VP) with formic acid (FA) in chloroform reported by Yao et al.\textsuperscript{31} These workers reported that for block copolymers in which the length ratio of the PS block to the P4VP block was 2/1 and at a copolymer concentration of the of 1.0 mg/mL, ‘regular aggregates’ of PS-\textit{b}-P4VP/FA were obtained when the mole ration of block copolymer/FA was larger than or equal to 1/5. However, when the mole ratio of block copolymer/FA was less that or equal to 1/2, micelles with a ‘low-density core’ were obtained.

Static light scattering results also supported micellization of the polymer chains when doped with acid. The scattered intensity or the excess Rayleigh ratio increased significantly when solutions were doped with phosphoric acid. The increase in scattering intensity as a function in concentration (see Figures 17c, 17d, 18c, 18d, 19c and 19d) was attributed the to
formation of large particles or aggregates in solution. On the other hand, solutions without any acid, i.e., solutions containing molecularly dissolved copolymer chains, exhibited a relatively low scattered intensity (see Figures 17a, 17b, 18a, 18b 19a and 19b). At higher concentrations, the scattering intensity of the acid doped solutions plateaued or declined. This saturation or reduction in scattered light intensity was attributed to interaction between micelles. Interaction between micelles was also evidenced in broadening of peaks in the intensity plots (Figure 13 and 14) of higher concentration solutions (0.02g/mL) doped with 50 mole % acid. In these solutions, the peaks are broader and lower in intensity relative to the peaks in the solutions doped with 20 mole % acid. The hydrodynamic radii presented in the DLS (Table 2), however, show that the size of the aggregates in solutions doped at 50 mole % acid are smaller than aggregates in solutions doped at 20 mole % acid.

SLS results also indicated that there is a significant correlation between the block length of the ethylene oxide segment and relative scattered intensity from the acid doped solution. Result shows that the scattered intensity is the highest for the block copolymer with the largest ethylene oxide (PEO) segment (51% PEO block polymer). The block length or the mole% of the ethylene oxide effectively determines the dimensions of the micelle core, moreover the amount of acid that can be bound to any given micelle will also be proportional to the oxyethylene content of the micelles. It is reasonable, therefore, to expect that the size of the micelle core will be directly correlated with the relative intensity of scattered light.

The viscometry results also go hand in hand with the light scattering results. The viscosity of the solution increases when the solution is doped with phosphoric acid (especially 50mol% acid). The increase in viscosity may be attributed due to formation of large particles or aggregation of polymer chains. Since the viscosity is a function of the
volume fraction of the particles, according to the Einstein model the increase in viscosity in fully micellized block copolymer solutions must because the volume occupied by copolymer chains in the aggregates structures is larger than that for freely dissolved copolymer chains. Furthermore, the intrinsic viscosity of the polymer solution changes upon adding various amounts of acid to the solution. This suggests that changes to the solution upon doping with acid could be due to changes in particles sizes or micellization of polymer chains. However, since the viscosity model is a function of the volume fraction of the particles, the data does not conclusively describe the transition of the micellization process at different amount of acid. In fact for some block polymers we see that the viscosity reduces upon adding acid at 10 and 20 mole% to the solution. Explanation for this trend is complex and cannot be reasoned through the simple viscosity models.

5.2 Differential Scanning Calorimetry

DSC scans for the pure copolymers of PS and PEO show a sharp peak for melting of the crystalline poly(ethylene oxide) around 60°C, and glass transition of polystyrene at about 100°C. The area under the melt endotherm peak of crystalline poly(ethylene oxide) scales with the amount of the ethylene oxide in the block copolymer. In Figures 25-27, one can see that the copolymer with greatest ethylene oxide content (51%PEO block copolymer) has the largest area under the melt peak of the poly(ethylene oxide) phase. DSC scans of the copolymer films doped with acid show a reduction in the area of the endothermic melt of poly(ethylene oxide). The intensity of this is peak is reduced somewhat in proportion to the amount of acid doped into the system. The crystallization of ethylene oxide is suppressed upon adding acid because the acid strongly binds with the ethylene oxide molecules through ion dipole forces. Copolymer films with short poly(ethylene oxide) chain segments (i.e.,
11%PEO block copolymer), do not crystallize well, accordingly one see less difference in the intensity of the crystalline melt peak of undoped and acid-doped films. In comparison, copolymers with longer poly(ethylene oxide) chain segments (33 and 51 mole% PEO), the crystallization of ethylene oxide is greatly reduced upon adding more acid.

Initial DSC scans for the neutralized films exhibit a suppression of the intensity of the poly(ethylene oxide) melt peak and a reduced glass transition temperature for the polystyrene phase. In addition, a broad endotherm is observed around 100-150°C which is attributed to a melting of a complex of the oxyethylene chain segments with K⁺ and H₂PO₄⁻ ions. In the second heating scan to 300°C, one sees an enhanced poly(ethylene oxide) melt peak. The endotherm attributed to the complex between oxyethylene chain segments K⁺ and H₂PO₄ ions has disappeared and a well-defined glass transition of a more pure poly(styrene) phase appears. Most importantly, a new endotherm which approximates the melt temperature of the bulk crystalline KDP is observed around 225°C. This endotherm has therefore been attributed to the melting of KDP nanocrystals. This endotherm is not observed in the DSC scans in Figure 29 and 30 for neutralized films cast from block copolymer compositions doped at 20 and 50 mole % acid, respectively. This may be because the KDP material in these films is not able to crystallize. Further work remains to develop optimal heat treatments, compositions and annealing condition for crystallization of the KDP.

5.3 Atomic Force Microscopy

The AFM micrographs of the acid doped film, Figure 32, showed a well-ordered two-dimensional array of spherical domains, micelle cores of acid-doped PEO in a PS continuum.

The AFM micrographs of the neutralized film (Figure 33 and 34) showed a randomly
ordered distribution nanosized particles which varied in size from about 20 to 200 nm. We speculate that these particles are nanocrystals of KDP. On cannot, however, unequivocally determine that these particles are crystalline or amorphous or even that they are KDP solely on the basis of what is seen in the AFM micrographs. The fact that a melt endotherm at \(~225^\circ\text{C}\) is often observed in neutralized films is the best indicator that these particles are nanocrystals of KDP. Given that these particles are nanocrystals of KDP, their polydispersity in size and random spacial distribution suggests that the crystallization of KDP, induced upon annealing, was not confined to the well-ordered micellar PEO domains observed in the AFM micrograph of polyethylene oxide doped with the acid. If the crystallization of KDP was restricted to the domains one would have expected to see a regularly ordered array of KDP nanoparticles which monodisperse in their size distribution. It is our belief that in the course of annealing at temperatures well above the glass transition of polystyrene, \(\text{K}^+\) and \(\text{H}_2\text{PO}_4^-\) ions are able to move between domains and nanocrystals nucleated early will be larger in size that those nucleated later. Moreover, \(\text{K}^+\) and \(\text{H}_2\text{PO}_4^-\) ions would be depleted in the domains surrounding nucleation sites. This overall process leads to a condition wherein crystallization would not be confined within the domains resulting in variability in size and aerial distribution of particles.

Another approach that can be taken would be to use microwave radiation which would selectively heat or supply energy to the KDP/PEO domain in the film without increasing the temperature of the polymer. The reason is that the polystyrene is a hydrocarbon or a nonpolar molecule that does not absorb the microwave energy. KDP and polyethylene oxide on the other hand polar molecules which will absorb microwave energy for crystallization. Using this approach, one might be able to maintain the temperature of the
PS phase below its glass transition while increasing the temperature of the K⁺H₂PO₄/PEO phase to induce of KDP. If the PS phase is of high viscosity migration of ions between PEO domains will be suppressed and crystallization of the KDP may be confined within the domains.

SUMMARY & CONCLUSIONS

Light scattering and viscometry were used to characterize the micellization of block copolymers of polystyrene and poly(ethylene oxide) induced by phosphoric acid doping of toluene/DME solutions. Results from both techniques, indicated that micellization of the copolymer molecule was induced upon doping with acid. The micellization process was a function of the acid doping and the block copolymer composition. Further analysis needs to be done to extract information such as micelle aggregation number and the shape of the micelle as a function of the relative level of acid doping and the block copolymer composition.

The DSC studies elucidated the characteristics and composition of nanophases formed in films cast from undoped, acid-doped and neutralized materials. DSC analysis provided the most conclusive evidence for crystallization of the KDP in films which were neutralized and annealed. AFM micrographs gave a visual picture of the domains structure in thin films cast from solutions of undoped, acid-doped and neutralized/annealed materials. Ordered arrays of spherical PEO domains were observed in undoped and acid doped materials. Micrographs of the neutralized/annealed films, however, showed randomly distributed nanoparticles that ranged in sized from 20 to 200 nm. While these particles are believed to be KDP
nanocrystals, it appears that it was not possible to confine the crystallization process within isolated PEO/K\(^+\)H\(_2\)PO\(_4\)^\(-\) domains.
REFERENCES:

1 Cleveland Crystals, Inc “Electro-Optic properties of KH₂PO₄ and isomorphs” www.clevelandcrystals.com/KDP.shtml


Kratochvill, P. *Determination of Molecular Parameters of Polymer by Light Scattering*. Institute of Macromolecular Chemistry, Academy of Science.

Provencher, S.W., and Glockner, J. *Biochemistry* 1981, 20, 1085-1094

Hiemenz C. P.; and Rajagopalan R. *Principle of Colloid and Surface Chemistry* Basil, New York pg.236.


Rieter G.; Castelein G.; and Sommer J. *Physics Review letters*, 2001, 87(22).


Appendix i:

**Effective Diffusion Coefficient versus Concentration**

IM4A030705 11% PEO with NO Acid

- **Fit 1: Linear**
  - Equation $Y = 6.56E-06 * X + 5.894E-07$

**Effective Fast Diffusion Coefficient versus Concentration**

IM4A032105 11% PEO with 10% acid

- **Fit 1: Linear**
  - Equation $Y = 3.692E-006 * X + 7.3622E-007$

**Effective Diffusion Coefficient versus Concentration**

IM4A030705 11% PEO with 20% Acid

- **Fit 1: Linear**
  - Equation $Y = -3.5134E-007 * X + 9.099186E-008$

**Effective Diffusion Coefficient versus Concentration**

IM4A032105 11% PEO with 50% acid

- **Fit 1: Linear**
  - Equation $Y = -9.099186E-008 * X + 3.5134E-007$

Characteristic diffusion coefficient at infinite dilution for all Acid concentration of 11% PEO block polymer.
Effective Diffusion Coefficient versus Concentration
IM4A030705 51% PEO with NO Acid

Fit 1: Linear Equation $Y = 6.3E-06 \times X + 5.124E-07$

Effective Diffusion Coefficient VS concentration 51% PEO with 10% acid

Effective Diffusion Coefficient VS concentration 51% PEO with 20% acid

Effective diffusion coefficient cm$^2$/sec versus Concentration 51% PEO with 50% acid

Fit 1: Linear Equation $Y = -1.4111E-006 \times X + 6.77895E-008$

Characteristic diffusion coefficient at infinite dilution for all Acid concentration of 11% PEO block polymer
Appendix ii:

Specific viscosity for the 11% PEO block copolymer
Specific viscosity for the 33% PEO block copolymer
Specific viscosity for the 51% PEO block copolymer